Deoxyribose

The DNA backbone is built up from 2-Deoxy-D-Ribose molecules linked together by phosphate groups. Radiation damage studies on deoxyribose molecules in condensed phase have been performed by soft X-rays and low energy ions. So far only the response of gas phase deoxyribose to electrons has been studied. In this chapter, an in-depth study of the interactions of keV \( \text{H}^+ \) and \( \text{He}^{2+} \) ions with isolated deoxyribose is presented. The deoxyribose molecule is identified as the weakest DNA compound with respect to keV ion impact. Extensive statistical fragmentation of the molecules is observed. The fragment distribution follows a power law dependence \( M^{-\tau} \), whose exponent \( \tau \) can be used to characterize and quantify the molecular damage.

based on:

Quantification of ion-induced molecular fragmentation of isolated 2-deoxy-D-ribose molecules.
F. Alvarado, S. Bari, R. Hoekstra, and T. Schlathölter.
The deoxyribose molecule (dR) is a five–carbon monosaccharide with molecular formula C$_5$H$_{10}$O$_4$. Fig. 6.1 shows an optimized geometrical structure of the 2-deoxy-D-ribose molecule in its furanose isomeric form, as found in DNA. In the DNA backbone, a nucleobase takes the place of the OH group at the C–1 position and the C–3-hydroxyl group is joined to the C–5-hydroxyl of the adjacent dR molecule by a phosphate linking group.

The sugar’s furanose ring is puckered rather than planar. It may have either one non-coplanar atom or two atoms displaced from the plane of the other three [109]. In comparison with the aromatic nucleobases, the non-aromatic furanose molecule has a less symmetrically distributed HOMO and the atoms within the ring do not form double bonds. In the nucleobases the double bonds within the ring can stabilize the molecule against external electrostatic influences [110]. In fig. 6.3 molecular structures and the HOMO’s for deoxyribose and the nucleobase adenine are presented. The planar structure of the nucleobase as compared to the puckered ring of the deoxyribose is obvious. The figures also show the highly symmetric distribution of the HOMO for the adenine whereas for the deoxyribose, the distribution is irregular.

Molecular fragmentation of deoxyribose has been studied in the condensed phase using soft X-rays [111,112] and low energy ions (10–100 eV Ar$^+$) [113]. The molecule was shown to be very fragile in comparison with nucleobases. Studies of low energy (5-20 eV) electron damage to condensed phase deoxyribose analogues showed that not only ring CH bond cleavage can occur but also dissociation of exocyclic OH and CH bonds [114]. However, in condensed phase experiments the action of direct and indirect effects on the molecule under study is always observed. Only gas phase experiments can isolate the primary processes. The response of gas phase deoxyribose has been studied only upon dissociative electron attachment, yet [110].

In this chapter, the fragmentation of gas phase deoxyribose molecules after irradiation with keV H$^+$ and He$^q+$ projectile ions will be discussed in detail. It will be shown that the molecular response is dominated by statistical fragmentation and that the fragment distribution can be described by a power law with exponent $\tau$. This exponent can be used to quantify the damage. At the end of the chapter, it will be shown that this characteristic exponent is directly related to the energy deposited by the projectile on the molecular target.
6.2. Fragment formation dependence on temperature

Three TOF spectra of dR fragments after bombardment with 7 keV He$^{2+}$ ions at different oven temperatures $T=70, 80$ and $95^\circ$C are shown in fig. 6.2. The spectra are normalized to the total integral yield. Obviously the overall fragmentation pattern does not change in this range of temperatures. The major differences are i) the intensity increase of the peak around $13 \mu s$ assigned to $m/z = 18$ (H$_2$O$^+$) and ii) the intensity decrease of the peak at $22 \mu s$ assigned to $m/z = 44$ (possibly partly CO$_2^+$).

The peak labelled O$_2^+$ can help to understand the difference. A doubly charged atomic fragment ion, such as O$_2^+$, is usually not produced in He$^{2+}$ collisions with larger molecules. It is thus not very likely that O$_2^+$ stems from dR. Probably, this fragment comes from collisions with residual gas, namely H$_2$O or CO$_2$. It is known that after interactions of He$^{2+}$ with neutral water the fragment products are H$^+$, O$^+$, OH$^+$ and O$^{2+}$. At 7 keV projectile energy the ratio O$^{2+}$/H$_2$O$^+$ resulting from these collisions is around 10% (see chapter 4). In fig. 6.2, the ratio O$^{2+}$/H$_2$O$^+$ is only 5% for all oven temperatures. This implies that more than half of the H$_2$O$^+$ observed comes from dR itself and the rest corresponds to residual gas, probably originating from contaminations in the dR powder which is highly hygroscopic.

The residual CO$_2^+$ yield follows the opposite trend than the H$_2$O$^+$ yield: it decreases with $T$. The peak is relatively strong at low $T$ (panel (a) in fig. 6.2) where the vapor pressure of the deoxyribose is low. At higher $T$, the dR vapor pressure is higher so the relative intensity of CO$_2^+$ decreases and the fragment coming from dR at the same mass (C$_2$H$_4$O$^+$) starts to be important. This can be confirmed by again looking at the change of the O$_2^+$ from panel (a) to (b), there the H$_2$O$^+$ is more or less constant. The O$^{2+}$ formed from the CO$_2^+$ decreases as the residual gas gets less important, but the H$_2$O$^+$ contribution stays high. Note that a similar increase of the H$_2$O$^+$ peak with temperature was observed by Ptasińska et al. [110] after 70 eV electron impact and higher dR temperatures up to 110$^\circ$C. There, the formation of H$_2$O$^+$ was attributed to deoxyribose fragmentation only.

In fig. 6.2, there is also a slight increase in the peak at $17 \mu s$, assigned to $m/z = 29$ (CHO$^+$). As the residual gas is less important, the fragments originating from the collisions with the deoxyribose itself start to be more important. Then, already at $80^\circ$C the CHO$^+$ peak becomes the second strongest fragment after the H$_2$O$^+$. The intensity change in the other peaks is negligible.

The oven temperature of 95$^\circ$C used in our experiments ensures sufficient signal–to–noise ratio without noticeable thermal modifications. Fragment ions with very low relative intensity can thus be clearly distinguished from the background. A negligible contribution of thermal fragmentation of deoxyribose, however, cannot be rule out. Since ion-induced fragmentation turns out to be a rather violent process, this contribution can be neglected.

6.3. Comparison with nucleobases

In fig. 6.3 mass spectra for 5 keV/amu He$^+$ induced ionization/fragmentation of the nucleobase adenine C$_5$H$_5$N$_5$ (a) and deoxyribose C$_5$H$_{10}$O$_4$ (b) are compared. Striking differences are obvious. The most remarkable difference is the intensity of the surviving parent molecules. For adenine a very strong parent molecule peak is observed. For deoxyribose, on
Figure 6.2: TOF spectra of dR fragments after collisions with 7 keV He$^{2+}$ for different T. Panel (a) shows a spectrum with dR molecules from an oven at 70°C, panel (b) from an oven at 80°C and panel (c) from an oven at 95°C.
Figure 6.3: Mass spectra of adenine (a) and deoxyribose (b) fragments after collisions with 5 keV/amu He$^+$ ions. As an inset in each graph the structure of the correspondent molecule together with the respective HOMO is shown.
the other hand, the parent peak is negligible (for some projectile energies even zero). The spectrum shown in panel (a) is typical for nucleobases; similar characteristics were observed for uracil [31] and for thymine [27] after irradiation with carbon ions in different charge states.

The stability of adenine as compared to dR manifests itself in the appearance energies (AE) of different fragments. For example, for group 8 from fig. 6.3 in the case of adenine 3.34 eV are needed in addition to the ionization energy (8.20 eV) to form the fragment at \( m/z = 108 \), according to photoionization studies [101]. In the case of deoxyribose, for the same group only 0.3 eV excess energy is needed in order to form the fragment at \( m/z = 116 \) [110]. According to electron impact studies on appearance energies, some fragment cations are even formed at energies below the dR IP (10.51 eV) [110].

In general, the nucleobase spectra are very structured with clearly defined groups of peaks. These groups –numbered from 1 to 8 in figure 6.3(a)– are due to fragments with different numbers of “heavy” atoms (carbon and nitrogen for adenine) and a variable number of hydrogen atoms. It is important to notice that not all groups are present. For example, in adenine fragmentation, a group containing 9 heavy atoms (the parent molecule missing only one nitrogen or one carbon) was not observed. Furthermore, the fragmentation patterns for adenine and other nucleobases follow a bimodal distribution with decreasing intensities down to a minimum (around group 7 for adenine) and increasing again up to the parent molecule. In chapter 5, these characteristics are discussed in greater detail.

For targets like nucleobases and \( C_{60} \), the formation of stable parent molecular cations is usually assigned to resonant electron capture into the unoccupied states of the projectile, a process that depends on the projectile electronic structure. Resonant electron capture processes are considered comparably gentle, i.e. the transfer is not accompanied by strong excitation of the target. In collisions with keV ions, resonant electron capture mainly involves electrons from the highest occupied molecular orbitals of the target molecule. In contrast, the formation of small fragments (with low masses) is associated with more violent close collisions involving mainly direct ionization and vibrational excitation. These collisions can involve virtually any target electron. The transferred energy mainly stems from kinetic energy of the projectile ion [90, 102]. In fig. 6.3 the HOMO of the nucleobase adenine and the one of the dR molecule are shown.

In contrast to the nucleobase case, dR shows a very small parent ion peak. No groups are missing and the overall peak intensities monotonically decrease with \( m/z \). These characteristics hold for all projectiles under study as obvious from fig. 6.4, which shows mass spectra of the dR fragmentation, obtained from collisions with \( H^+ \), \( He^+ \) and \( He^{2+} \) of equal velocity. The spectra resemble the mass spectrum for 70 eV electron impact from the NIST database [115]. The ratio between the large fragments (\( m \geq 65 \)) and small fragments (\( m \leq 62 \)) changes with projectile, being three times smaller for \( He^+ \) than for \( H^+ \) and \( He^{2+} \).

In fig. 6.5, the vertical IP of dR is compared to the electronic structure of the projectiles, as done in fig. 5.9 for the adenine molecule. Obviously, for \( He^+ \) resonant capture from the dR HOMO is energetically ruled out, inhibiting the most gentle electron removal mechanism. This explains the more severe fragmentation for \( He^+ \) than for \( H^+ \) and \( He^{2+} \) for which resonant or quasi-resonant capture is possible. Only for \( He^+ \), part of the potential energy of the projectile has to be transferred to the dR molecule. For \( He^+ \), we thus only look at events of high energy deposition: direct ionization or electron capture accompanied by potential energy
Figure 6.4: Mass spectra of deoxyribose fragments after collisions with 5 keV/amu projectiles. Panel (a), (b) and (c) show spectra obtained after collisions with $H^+$, $He^+$ and $He^{2+}$. The marked peaks are discussed in detail in the text.
Figure 6.5: Relevant energy levels of the different projectiles in comparison with the vertical ionization energy of deoxyribose. The dashed rectangle contains the levels where electron resonant capture is possible.

transfer of the order of $\sim 15$ eV. For $\text{He}^{2+}$ and $\text{H}^+$, on the other hand, resonant capture into excited states leave most of the projectile potential energy on the projectile ion.

In general, some obvious differences between the spectra for different projectile impact as shown in fig. 6.4 are:

- The peaks of $\text{C}_n^+$ with $n=1, 2$ and $3$ and of $\text{C}_n\text{H}_m^+$ with $m=1, 2$ and $3$ for $\text{H}^+$ (a) are very low compared to the same peaks in $\text{He}^+$ (b) and $\text{He}^{2+}$ (c). This was observed for all investigated ion velocities. This implies that on average the energy deposited to the dR molecules is less for protons than for $\text{He}^+$ and $\text{He}^{2+}$ ions. This might be attributed to the lower electronic stopping of $\text{H}^+$ in this projectile energy range [116].

- In the shaded area of fig. 6.4, ranging from $m/z = 46$ to $m/z = 55$, the intensity of the peaks changes with projectile, being highest for $\text{He}^+$.  

- For $\text{H}^+$ (a) and $\text{He}^{2+}$ (c) the fragments $\text{C}_5\text{H}_5\text{O}^+$ at $m/z = 81$ and $\text{C}_5\text{H}_9\text{O}_3^+$ at $m/z = 117$ are observed. For $\text{He}^+$ (b) these fragments are negligible.

- The group of peaks at $m/z = 97 – 99$ (dashed circled) is present for $\text{H}^+$ projectile (a) and $\text{He}^{2+}$ projectile (c) but absent or very weak for $\text{He}^+$ (b). This is valid for the whole energy range under study.

Another characteristic specific for $\text{He}^{2+}$ projectiles that is not seen in fig. 6.4 is the appearance of fragments at $m/z = 65$ (not observed for films [26] and very weak in electron
Table 6.1: Ratios of the yields of the fragments at \( m/z = 18 \) (\( \text{H}_2\text{O}^+ \)), 19 (\( \text{H}_3\text{O}^+ \)) and 20 (\( \text{H}_2\text{^{18}O}^+ \)) for different projectile ions.

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}^+ )</th>
<th>( \text{He}^+ )</th>
<th>( \text{He}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ratio 19/18</td>
<td>2.8</td>
<td>8.4</td>
<td>2.5</td>
</tr>
<tr>
<td>ratio 20/18</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

studies [110, 115]) and at \( m/z = 104 \) (\( \text{C}_4\text{H}_8\text{O}^+ \)). Both fragments are formed in collisions of \( \text{He}^{2+} \) at most energies but not at the one shown in the fig. 6.4. These fragments are absent for singly charged projectiles at any energy.

The relative change in peak intensity with projectile (stronger for \( \text{He}^+ \) than for \( \text{H}^+ \) and \( \text{He}^{2+} \)) implies that fragments, such as the ones at \( m/z = 46 - 55 \), originate from scission of rather strong bonds. This process is only possible after high energy deposition and thus more prominent for \( \text{He}^+ \) projectiles. Meanwhile, fragments formed in more gentle collisions (for example the ones in the dashed circle) are not stable after high energy depositions in the molecule and are not observed for \( \text{He}^+ \) projectiles.

A very strong peak at \( m/z = 19 \) is observed in the spectra in fig. 6.4. In the results on low ion bombardment on condensed phase [26, 113], this fragment was observed clearly and was attributed to \( \text{H}_3\text{O}^+ \). This fragment has not been observed in our studies on nucleobases. According to the isotopic studies of Bald et al. in the condensed phase, this fragment is a clear evidence of H abstraction or proton transfer from the parent or adjacent dR molecules. Two possible mechanisms are proposed to explain the formation of \( \text{H}_3\text{O}^+ \) fragments in condensed phase: i) formation of a very reactive (\( \text{OH}^+ \)) which removes two other hydrogen atoms from adjacent sites and ii) intramolecular proton transfer forming an \( \text{OH}^+ \) which will pick up another H. The presence of the \( \text{H}_2\text{O}^+ \) peak in our spectra shows that in the gas phase it is possible to generate such fragments directly from the dR fragmentation without the action of the reactive radicals that form in the condensed phase. The ratios between the yields of the fragments at \( m/z = 19 \) (\( \text{H}_3\text{O}^+ \)) and \( m/z = 18 \) (\( \text{H}_2\text{O}^+ \)) is shown in table 6.1 for different projectiles. It gives a clear indication that the appearance of \( m/z = 19 \) peak is not an isotope effect: the natural abundance of deuterium (\( ^2\text{H} \)) is 0.01% and the natural isotopic abundance of \( ^17\text{O} \) is 0.04%. For comparison, the ratios of the yield at \( m/z = 20 \) compared to the yield at \( m/z = 18 \) are also shown for the different projectile ions. The peak at \( m/z = 20 \) can be unambiguously assigned to \( \text{H}_2\text{^{18}O}^+ \) because the ratios for all projectile ions are the same and correspond to the natural abundance of isotopic \( ^{18}\text{O} \) (0.20%).

6.4. Quantification of the damage

For nucleobases the surviving molecular ions represent an appreciable fraction of the total yield so that relative fragmentation cross sections can be obtained and relative yields for the different groups of fragments can be evaluated [31]. For deoxyribose the yield of surviving parent molecules is usually less than 0.01% and the fragmentation yields are thus always
Figure 6.6: Peak integrals of a deoxyribose spectrum with their corresponding statistical error on a double-log scale. The apparent fit of the points (dashed line) gives the trend of the fragmentation and a value for the characteristic exponent $\tau$. The labels are discussed in the text.

very close to 100%. We hence have to find another parameter (equivalent to the relative fragmentation cross sections) to quantify the damage inflicted upon deoxyribose molecules by the different projectiles.

A more detailed analysis of the fragmentation patterns discussed in fig. 6.4 can be done by evaluating the relative yield for each $m/z$ (see fig. 6.6). Every point represents the relative yield of the respective fragment with the corresponding statistical error. The line shown is an apparent power law fit $^1$ to the data points. Deviations from the fit are not statistical but an inherent property of the molecular fragmentation. They reflect fragment stabilities, ionization energies, bond strengths within the molecule, etc. The deviations will be discussed in detail later in this section.

Numerous studies in a variety of fields have already shown that a fragment mass distribution following a power law $n(M) \sim M^{-\tau}$ ($n$: number of fragments, $M$: fragment mass, $\tau$: characteristic exponent) is a signature of statistical fragmentation processes. Examples are the fragmentation of nuclei [117], size distributions of asteroids [118], fragmentation of solid and liquid matter [119] or sputtering of clusters [120]. The power law-like behavior is often

$^1$The apparent fit is used by Origin software to fit exponential decaying data with a straight line fit when the data are plotted on a log scale. The larger positive/negative errors are used as weight.
6.4 Quantification of the damage

Table 6.2: Appearance energy of cations produced by electron impact of neutral deoxyribose [110].

<table>
<thead>
<tr>
<th>Cation</th>
<th>Mass (Da)</th>
<th>AE value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3^+$</td>
<td>15</td>
<td>13.31±0.50</td>
</tr>
<tr>
<td>CHO$^+$</td>
<td>29</td>
<td>12.18±0.49</td>
</tr>
<tr>
<td>CH$_3$O$^+$</td>
<td>31</td>
<td>12.36±0.14</td>
</tr>
<tr>
<td>C$_3$H$_3^+$</td>
<td>39</td>
<td>13.01±0.42</td>
</tr>
<tr>
<td>C$_2$H$_4$O$^+$</td>
<td>44</td>
<td>12.50±0.02</td>
</tr>
<tr>
<td>C$_3$H$_5$O$^+$</td>
<td>57</td>
<td>11.63±0.06</td>
</tr>
<tr>
<td>C$_2$H$_4$O$_2^+$</td>
<td>60</td>
<td>11.28±0.16</td>
</tr>
<tr>
<td>C$_4$H$_6$O$^+$</td>
<td>70</td>
<td>10.67±0.03</td>
</tr>
<tr>
<td>C$_4$H$_9$O$^+$</td>
<td>73</td>
<td>10.74±0.03</td>
</tr>
<tr>
<td>C$_5$H$_5$O$^+$</td>
<td>81</td>
<td>11.72±0.50</td>
</tr>
<tr>
<td>C$_4$H$_6$O$_2^+$</td>
<td>86</td>
<td>11.41±0.02</td>
</tr>
<tr>
<td>C$_5$H$_6$O$_2^+$</td>
<td>98</td>
<td>10.12±0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.36±0.15</td>
</tr>
<tr>
<td>C$_4$H$_7$O$_3^+$</td>
<td>103</td>
<td>11.25±0.08</td>
</tr>
<tr>
<td>C$_5$H$_8$O$_3^+$</td>
<td>116</td>
<td>10.82±0.05</td>
</tr>
<tr>
<td>C$_5$H$_10$O$_4^+$</td>
<td>134</td>
<td>10.51±0.11</td>
</tr>
</tbody>
</table>

linked to critical phenomena, for instance at the liquid-gas phase transition. However, other fragmentation processes, such as weathering, can exhibit a power-law behavior as well [121]. Almost independent on the nature of the system, exponents of the order of $\tau \approx 2$ are found.

During the last decade, statistical fragmentation has also been observed for atomic clusters, for instance in H$_n^+$ collisions with atoms [122] or in ion–fullerene collisions [123]. For these systems, which come closest to the case of a polyatomic molecule studied here, a general requirement for statistical fragmentation is a rather hot intermediate system. The excitation energy has to clearly exceed the binding energy of the system. Within a cluster, the energy is then quickly distributed over all available electronic and vibrational degrees of freedom. This can lead to evaporation of fragments (a sequential process governed by rate constants) or to multifragmentation, if the excitation energy is sufficient. Multifragmentation is an entropy-driven process during which the system tries to reach a distribution of products that occupies the maximum volume in accessible phase-space. The fragment distribution is thus dominated by smaller fragments. This is exactly what we observe in the fragmentation of deoxyribose (fig. 6.6). The power law fit in fig. 6.6 for dR fragmentation yields an exponent $\tau = 2.0$ for 20 keV He$^+$ impact.
Fragments with yields exceeding the power law fit could be either due to high stability or low IP. In their electron impact ionization experiments, Ptasińska et al. [110] have observed that indeed almost all these fragments (marked by a framed label in fig. 6.6) have low appearance energies between 10 and 14 eV (the energies are given in table 6.2). The fragments below the fit therefore probably correspond to high appearance energies or are very unstable. Note that in order to obtain the parameter $\tau$, the contribution of $\text{H}_2\text{O}^+$ and its fragments was neglected because of potential contributions from background $\text{H}_2\text{O}$.

By fitting a power law to all the measured fragmentation spectra, the characteristic exponent $\tau$ can be obtained for $\text{H}^+$, $\text{He}^+$ and $\text{He}^{2+}$ colliding with deoxyribose over the whole velocity range under study. The results are displayed in fig. 6.7. Obviously, lowest exponents that increase linearly with $v$ are observed for $\text{H}^+$. For $\text{He}^{2+}$ projectiles, higher values are found and the exponents increase linearly with $v$, as well. For $\text{He}^+$ projectiles, on the other hand, largest characteristic exponents are observed which exhibit a linear decrease with $v$. The explanation for this behavior has already been outlined in the discussion of fig. 6.4 (and in [31] for collisions of $\text{C}^q^+$ with uracil): Whereas $\text{H}^+$ and $\text{He}^{2+}$ can resonantly capture an electron from the deoxyribose HOMOs, this is energetically ruled out for $\text{He}^+$ projectiles. In the later case, the measured fragment ions almost exclusively originate from collisional ionization processes at small impact parameters. The violent nature of the ionization process is reflected in the mass spectrum by a fragmentation spectrum characterized by a high $\tau$.

In most ion-molecule collision systems, if energetically possible, resonant electron transfer from the highest molecular orbitals is usually the channel with the largest cross section ($\text{H}^+$, $\text{He}^{2+}$). For $\text{He}^+$, where resonant capture from the HOMOs is ruled out, different scenarios are possible. Non resonant capture from HOMOs would lead to excess energy sufficient for release of an additional electron from the dR. Electron capture from lower lying states is also possible, leaving the molecule in a strongly excited state. Both scenarios could explain the observation of much stronger fragmentation for $\text{He}^+$ and its high characteristic exponent.

Figure 6.7: Values of the characteristic exponent $\tau$ for deoxyribose spectra after collisions with different projectiles at different kinetic energies.
6.5 Energy loss of the projectile ion

The increase in fragmentation when going from \( \text{H}^+ \) to \( \text{He}^{2+} \) can be explained by the fact that a doubly charged projectile usually induces more double ionization than a singly charged one. Double ionization in turn will lead to much more severe fragmentation than single ionization.

The velocity dependence of the characteristic exponents can be easily explained within the same framework. In case resonant electron capture is possible (\( \text{H}^+ \), \( \text{He}^{2+} \)) the projectiles can still induce collisional excitation of the electronic system of the target molecule. This process is usually called electronic stopping of the projectile. For ion-fullerene collisions at \( v=0.1 \) – 1 a.u., it has been shown that electronic stopping depends strongly on the impact parameter but generally scales and increases with \( v \) [102, 116]. If ion-deoxyribose collisions follow a similar trend, the energy deposited into the target molecule by a given projectile increases with \( v \) and therefore the characteristic exponent increases as well. In case resonant capture is ruled out (\( \text{He}^+ \)) only small impact parameters are involved. At small impact parameter electronic stopping is highest because the projectile traverses a high electron density.

However, with increasing \( v \) non–resonant processes become possible. This facilitates electron capture into excited projectile states [124–126]. Gentle electron capture at larger impact parameters thus becomes increasingly important with increasing \( v \). This is reflected in a characteristic exponent decreasing with \( v \) (see fig. 6.7).

Itoh et al. [127] showed that for collisions of MeV Si\( q^+ \) ions with \( \text{C}_6\text{O} \) the characteristic exponent can be used to quantify the exact amount of electronic stopping deposited into the target at a given projectile velocity. For ion-fullerene collisions \( \tau \) appears to follow a simple exponential dependence on the deposited energy. In the next section the relation between characteristic exponent and deposited energy will be explored for the double electron capture channel in \( \text{H}^+\text{-dR} \) collisions.

### 6.5. Energy loss of the projectile ion

In order to experimentally access the total internal energies of deoxyribose cations produced in ionizing collisions with keV projectiles, several requirements have to be fulfilled:

1) The kinetic energy of the outgoing projectile has to be measured in coincidence with the fragments formed.
2) The projectile needs to be charged after the collision.
3) The outgoing projectile should be in the ground state since excitation energies cannot be measured.

As outgoing projectiles, negative ions such as \( \text{H}^- \) are perfectly suited, since they have only one stable state. With the experimental setup at LASIM, the first requirement is fulfilled. In this setup, the detection of projectile–recoil ions in coincidence is possible. The process chosen is double electron capture from deoxyribose by \( \text{H}^+ \) projectiles:

\[
\text{H}^+ + \text{dR} \rightarrow \text{H}^- + \text{dR}^{2+*} \tag{6.1}
\]

The cases under study in this section are a subset of the data presented in the previous sections. Here, only double electron capture from the molecular target is considered. The non–coincident spectra included single and multiple electron capture plus ionization and excitation events. Therefore this data will be called “inclusive”.
From conservation of energy for the processes studied here, it follows that the energy lost by the projectile and the energy gained by the molecular target are equal under the following assumptions: a) the double ionization of the molecule is a Franck–Condon transition since the proton–molecule interaction occurs on a fs timescale. b) momentum transfer to the molecule can be neglected for this system. Then the excitation energy of the dR fragments or, in other words, the energy deposited into the target can be written as follows:

\[ E_{\text{exc}} = \Delta E - [I_1 + I_2 - EA_H - I_H] \]  

(6.2)

where \( \Delta E \) is the measured projectile kinetic energy loss, \( I_1 \) and \( I_2 \) are the first and second vertical ionization energies of deoxyribose, \( EA_H = 0.754 \text{ eV} \) is the electron affinity of the H atom and \( I_H = 13.6 \text{ eV} \) is the ionization energy of the H atom. The first vertical ionization energy of deoxyribose has been determined experimentally as \( I_1^{\text{exp}} = 10.51 \text{ eV} \) \[110\]. The second deoxyribose vertical ionization energy cannot be obtained experimentally since no stable deoxyribose dication has been observed, yet. Therefore, both vertical ionization energies were quantum-chemically calculated with the GAUSSIAN-03 package \[49\] following the recipe described by Cauet et al. \[128\]. The geometry of 2-deoxy-D-ribose was first optimized using DFT at the B3LYP level with a large 6-311+g(3df,3pd) basis set. The ionization energies have then been calculated using MP2 theory with a smaller 6-311+g(d,p) basis set. \( I_1^{\text{theor}} = 10.4 \text{ eV} \) is found to be in good agreement with the experimental value. For the second ionization energy we obtain \( I_2^{\text{theor}} = 13.9 \text{ eV} \). The deposited energy is thus:

\[ E_{\text{exc}} = \Delta E - [I_1^{\text{exp}} + I_2^{\text{theor}} - EA_H - I_H] = \Delta E - \delta \]  

(6.3)

with \( \delta = 10.05 \text{ eV} \).

In fig. 6.8 the mass spectrum of the fragments formed after collisions of 3 keV H\(^+\) projectile ions with dR and double capture events only is shown. For comparison and identification of the peaks an “inclusive” \(m/q\) spectrum is shown in gray. The “inclusive” mass spectrum includes the fragments stemming not only from dR\(^{2+}\) fragmentation but also from deoxyribose single and multiple ionization as well as excitation and decay of the excited molecule. It can be seen that for the double capture spectrum due to the poor mass resolution the peaks are very broad and they can contain several fragments. These peaks are labeled according to the \(m/q\) of their maximum. The average energy deposited for the projectile to form each of the fragments is shown in the upper panel of fig. 6.8. The dashed line in the upper panel represents the average energy deposited by the projectile.

In fig. 6.9 a mass spectrum of the fragments produced after dR\(^{2+}\) dissociation following impact of 7 keV H\(^+\) is shown. The fragments are labelled according to the intensity of the maximum peak. In the upper panel, the energy deposited by the projectile to form each of the fragments is shown. The main difference to the spectrum shown in fig. 6.8 are the intensities of some of the peaks. For example the group of peaks assigned to CHO\(^+\) becomes stronger. Also, a small shoulder next to CH\(_3\)\(^+\) is clearly visible and it can be assigned to CH\(_2\)\(^+\). The average energy needed to form the fragments is on average higher. The dashed line for 3 keV projectile ions has an average value of 4.9 eV while the one for 7 keV projectiles has an average value of 9.7 eV. Circa 4 eV difference.

Fig. 6.10 shows the relation between the average excitation energy deposited by each projectile into the molecular target and the characteristic exponent \( \tau \) previously obtained for
6.5 Energy loss of the projectile ion

Figure 6.8: Mass spectra of deoxyribose molecules after collisions with 3 keV $H^+$ projectiles. The solid line represents the fragments formed after the fragmentation of $dR^2+$. The dashed line corresponds to the inclusive spectrum and is used for peak assignment. In the upper panel the energy deposited by the projectile $E_{exc}$ for each major fragment is shown.

Figure 6.9: Mass spectra of deoxyribose molecules after collisions with 7 keV $H^+$ projectiles. The fragments observed are formed after the fragmentation of $dR^2+$. In the upper panel the energy deposited by the projectile for each fragment is shown.
Figure 6.10: Relation between the excitation energy deposited by the H\(^+\) projectiles into the dR target and the characteristic exponent \(\tau\)

3 and 7 keV H\(^+\) projectiles. A linear fit was made in order to indicate that as the exponent becomes larger, the energy deposited is higher as well. In the results from Itoh et al. [127], an exponential relation was found between the calculated energy deposition and the experimentally determined exponent for the collision system MeV Si\(^q^+\) in C\(_{60}\). Extraordinary high energy depositions of the order of thousands of eV are already expected for exponents between 1 and 2. In our case, the energy depositions expected are much lower, partly due to lower projectile energies. With only two data points, it is impossible to establish a mathematical relation between the two variables. Following Itoh et al., if an exponential relationship is assumed, an extrapolation to exponents like the ones observed for He\(^+\) (maximum 2.8 from fig. 6.7) will give energy depositions of the order of 140 eV. This is not very likely for our collision system. On the other hand, if a linear relationship is assumed, an extrapolation to \(\tau = 2.8\) will give an energy deposition of 28 eV. From fig. 6.5 and the discussion related to it, energy depositions 1–15 eV higher than for H\(^+\) are expected for He\(^+\) due to its electronic structure. This order of magnitude looks more reasonable than the one stemming from an exponential fit. There is no doubt that more data points are needed to determine the exact relation between the average energy deposited and the characteristic exponent.

6.6. Conclusions

The ionization and fragmentation of gas-phase deoxyribose molecules by keV H\(^+\), He\(^+\) and He\(^{2+}\) impact over a wide range of velocities was studied. Virtually complete disintegration of the molecule is observed invariably. The fragment distribution is found to follow a power law: a fingerprint of statistical fragmentation. Deviations from the power law trend can be explained by the different appearance energies of the fragments reported by Ptasińska et al. [110]. The characteristic exponent of the power law fit is obtained for each collision
system as a function of projectile velocity. For $\text{H}^+$ and $\text{He}^{2+}$, low exponents are observed which linearly increase with projectile $v$. For $\text{He}^+$, the characteristic exponent is larger and decreases with $v$. These findings can be explained in the framework of charge exchange and electronic stopping. The characteristic exponent is found to be a suitable parameter for quantitative studies of dR fragmentation. Most probable, it is also applicable to other fragile molecules.

For the first time, the energy deposited by $\text{H}^+$ projectiles into the molecular target was studied for two different projectile energies for double capture leading to doubly charged dR molecules. An increase in the deposited energy with increasing exponent $\tau$ is observed. For a quantitative interpretation of the characteristic exponent on the energy deposition theoretical studies on this collision system would be beneficial.