Ion induced radiation damage on the molecular level
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CHAPTER 2

Experiment

The bulk of the experimental results presented and discussed in this thesis were obtained at the KVI in Groningen, using the CHEOPS setup. In this chapter the ion-source used to produce the projectile ions will be briefly discussed. A complete description of the technical details of the experimental setup will be given. Then, the modifications made in order to perform the experiments with neutral projectiles will be addressed. The data analysis procedures will also be described in detail. The experiments on energy deposition (chapter 6) were performed at LASIM (Lyon). The data presented in chapter 7 were measured at CIRIL (Caen). A brief description of the setups used in Lyon and Caen will close this chapter.
Figure 2.1: Sketch of the Electron Cyclotron Resonance Ion Source (ECRIS) at KVI, Groningen.

2.1. ECRIS and beam transport

The projectile ions used for our studies employing the CHEOPS setup are extracted from a 14 GHz Electron Cyclotron Resonance Ion Source (ECRIS). A sketch of the ion source at the disposal of the KVI-Atomic Physics group is shown in fig. 2.1. The principle of operation of an ECRIS is the following: In the plasma chamber, electrons gyrate around magnetic field lines according to their cyclotron frequency $\omega_c = \frac{eB}{m_e}$. If microwave radiation of the same frequency propagates into that region, the electrons are resonantly accelerated or decelerated. Plasma electrons can pass the resonance region very often, gain high energies and ionize plasma atoms and ions into high charge states via sequential electron impact ionization. The plasma electrons are confined in a superposition of an axial magnetic field component (produced by the injection and extraction solenoids) and the radial magnetic field due to the permanent hexapole magnet. This configuration is called a minimum-B-structure.

The magnetic confinement, however, is not perfect and electrons can leave the plasma. The ions are extracted from the plasma using a puller lens that can be negatively biased for more efficient extraction. The key parameters for getting a stable and optimized ion output, are the gas pressure, RF power (0.1-0.5 kW) and the current of the solenoid coil on the extraction side (700-1000 A). The injection solenoid’s current is usually set to the maximum value of the supply: 1000 A.

The source can be floated on potentials up to 25 kV. The ion kinetic energies depend on the charge state $q$ of the projectile. Typical energies used range from $2 \times q$ to $25 \times q$ keV. For our studies, H$^+$, He$^{q+}$, C$^{q+}$ and O$^{5+}$ projectile ions are mainly used. For highly charged projectiles ($q > 3$), the source is most conveniently run with a support gas.

Ions with the desired $m/q$ ratio are selected by deflection in a 110° magnet. The beam current is measured just after the 110° magnet by a movable faraday cup. The beam currents usually range from a few hundred nA to 100 µA, depending on the element and charge state. In order to avoid overlap with other ions of similar mass–over–charge ratio present in the plasma, particularly for highly charged ions isotopically pure gases are often used.
2.2 Experimental setup

2.2.1. General features

Fig. 2.2 displays a sketch of the experimental setup CHEOPS. After optimization of the beam current, the ion beam can be chopped right in front of the first diaphragm (D1) by means of a set of chopper–sweeper plates in order to produce ns beam bunches. After chopping, the bunch of ions crosses a set of focusing lenses used only for small corrections on very low energy beams. The diameter of the ion bunch is restricted by two 1-mm diaphragms (D1 and D2) fixed 205 mm apart.
The targets are produced in two ways: they are either evaporated from a small oven with a 1 mm nozzle or they effuse into the setup via a 1 mm injection needle controlled by a high-precision valve. More details on target production will be given in the next subsection. In both cases the exits of the 1 mm capillaries are placed at a distance of \( \approx 20 \) mm away from the collision center. The base pressure is always below \( 2 \times 10^{-8} \) mbar. In order to keep the collision chamber free from residual gas, a stainless steel plate mounted close to the collision region and kept at liquid nitrogen temperature serves as a cryo-trap. For the experiments to be discussed in chapter 4, the pressure inside the collision chamber stayed below \( 1 \times 10^{-6} \) mbar during measurements. For the rest of the experiments with evaporated gaseous molecules, the pressure close to the collision chamber stayed below \( 5 \times 10^{-7} \) mbar during the experiments.

After the interaction of the ion beam with the gaseous target, the charged fragments are extracted from the collision region by means of a static electric field (600 V cm\(^{-1}\) in most cases or 100 V cm\(^{-1}\) for low extraction experiments). The field is provided by opposite voltages on two stainless steel discs of 60 mm diameter, mounted 10 mm apart. When using sublimated targets, the plates are resistively heated to 100°C during measurements in order to prevent coverage with an insulating molecular layer. Due to the electric field, positively charged collision products generated in the collision region are extracted through a diaphragm and a lens system into a reflectron time–of–flight (TOF) spectrometer, to be discussed in detail in section 2.2.4. The extraction diaphragm can be varied in size, most measurements are performed using a 5 mm diaphragm. The time projectile ions spend in front of the diaphragm is usually of the order of a few ns. A typical value for 10 keV He\(^{2+}\) is \( \sim 1.5 \) ns/mm.

The ions are detected by a 5 cm diameter Microchannel plate (MCP) detector. The detection efficiency of the MCP is of the order of 55% (close to the detector optimum). The MCP is connected to standard electronic components (preamplifier–amplifier–discriminator) that amplify and filter the signal. The signal is then fed into a multi–hit time-to–digital converter (TDC, FAST 7888, 1 ns resolution) in order to measure the time-of-flight (TOF) of one or more collision products from each collision event in coincidence. The TDC is triggered by the DDG using the signal delayed with respect to the chopper pulse as shown in fig. 2.3. This is known as the start signal. Our data acquisition system can be used in single–stop mode as well as in multiple–stop mode, \textit{i.e.} two or more charged fragments stemming from the same collision event are detected.

### 2.2.2. Chopping schemes

Depending on the target density and the beam current, and also the type of experiment (single– or multiple–stop measurements) two different chopping schemes are used. The time structures of both chopping modes are shown in fig. 2.3:

1. One of the chopper plates (pl1) is kept at a constant voltage and block pulses of higher amplitude are applied to the other one (pl2), so that when the voltages on both plates equal, the ion beam can pass through the diaphragm. This way ion beam pulses with less than 10 ns duration are produced. Such short pulses are a requirement for good mass resolution of the system. The falling edge of the square pulses is wider than the rising edge. Therefore it is discarded.

2. One of the chopper plates (pl1) is grounded or at a fixed potential and very sharp block pulses with the same voltage amplitude as on pl1 are applied to the second plate (pl2).
In this scheme the beam will again pass only when the voltages on both plates are equal. The duration of the pulses can be as short as typically 30 ns. Longer pulse duration is useful when good mass resolution is not critical for the experiment.

The constant voltages are supplied by a standard 300 V power supply while the pulsed voltages are generated by a Digital Delay Generator (DDG) driven HV–pulser with a minimum pulse duration of 30 ns. The trigger for the TOF measurement is also generated by the DDG. Typical values for chopping using the first scheme are the following:

1) for measurements on small molecules such as water (high target density): constant \( V = 90 \, V \), pulsed voltage amplitude \( 250 \, V \), period \( 26 \, \mu s \), pulse width \( 13 \, \mu s \);  
2) for biomolecules (adenine and deoxyribose for example): constant \( V = 90 \, V \), pulsed voltage \( 200 \, V \), period \( 86 \, \mu s \), pulse width \( 43 \, \mu s \).

The signal of the trigger can be a standard TTL pulse or a square pulse of \( 7.5 \, V \) amplitude. The trigger signal has a width of \( 1 \, \mu s \) and it is delayed with respect to the chopping signal depending on the projectile velocity, to account for the flight time of the projectile ions from the chopper plates to the collision chamber. For example for \( 12 \, keV \, He^+ \) the delay needed is \( 2 \, \mu s \), whereas for \( 6 \, keV \, He^+ \) the delay is \( 3.5 \, \mu s \). In order to increase the acquisition frequency when using the first chopping scheme, a second pulse can be applied to the sweeper plates (just after the chopper plates) in order to block the ion bunch generated by the falling edge of the chopper pulse and then decrease the period. When going from the first chopping scheme to the second one, the rate can be increased from \( \sim 40 \, kHz \) to \( \sim 76 \, kHz \).
2.2.3. Gas phase targets

H₂O molecules

Water molecules enter the setup through a 1 mm needle placed at a distance of ≈ 20 mm from the collision center. The flux is controlled by a high precision valve. The distilled water used as target is stored in the liquid phase in a container in which it can be purified by repeated freezing-pumping-liquifying cycles. From the negligible contribution of residual gas species to the obtained mass spectra, it can be concluded that the target purity was at least 99.9%.

Nucleobases

The nucleobases with purity ≥ 99% are purchased from Sigma-Aldrich and used without further purification. Isolated nucleobase targets are produced by evaporation from the purchased powder sample in a resistively heated oven. Oven temperatures of 180°C for uracil (C₄H₄N₂O₂), 170°C for thymine (C₅H₆N₂O₂) 150°C for adenine (C₅H₅N₅) and 160°C for cytosine (C₄H₅N₃O) ensure sufficient target densities without thermal fragmentation of the molecules. The molecular vapor escapes from the oven through a 1 mm nozzle. The nozzle can be varied in length and diameter to avoid clogging. In all experiments, no signs of polymerization or thermal fragmentation of any of the nucleobases are observed in the range of temperatures used. For cluster production the oven is located inside a nitrogen cooled atmosphere and the oven temperatures used are around 200°C.

2-Deoxy-D-Ribose

2-Deoxy-D-ribose (C₅H₁₀O₄, purity ≥ 99%) by FLUKA is purchased from Sigma-Aldrich and employed without further purification. The powder is evaporated from a stainless steel oven with a nozzle of 1 mm diameter kept at 95°C. The temperature for sublimation of the deoxyribose (dR) from the oven is chosen such that the signal-to-noise ratio is optimal. This is particularly important for a precise quantification of the weaker peaks in the spectrum, such as the parent molecular ion (C₅H₁₀O₄⁺). The temperature, therefore, is chosen just above the melting point of deoxyribose (∼ 85°C), but below the threshold for polymerization into long molecular chains. No clusters or cluster-fragments bigger than the parent molecule are observed. Details on the temperature dependence of the spectra will be given in chapter 6.

2.2.4. The reflectron TOF

Time-of-flight (TOF) spectrometry techniques have been used since the beginning of the last century to measure the mass-to-charge ratio of ionic systems (for a review see [34]). The basic idea of TOF spectrometry is that monoenergetic ions with different m/q ratios have different velocities but follow identical trajectories. This implies that they need different times to traverse a given path in the instrument. One of the major limitations to improve the resolution of linear TOF was the energy spread and initial velocity of the ions. A major step in the improvement of the resolution in TOF systems was, therefore, the reflection of the ions by means of an electrostatic mirror: the advent of the so-called reflectron type TOF
systems with first results published already in 1973 [35]. The idea of the first reflectrons was to compensate the initial energy spread of the ions. Due to the fact that the collision center is not point like but occupies a certain volume, two identical ions can have different TOF when their starting positions are different. The principle of operation of reflectron TOF spectrometers is to compensate for different starting positions with an electrostatic mirror at the end of the flight-tube. The principle can be understood as follows: consider two identical ions starting at different points in the extraction field. At the end of the extraction region, the ions will have different velocities due to the different starting potentials. The ion which was further from the spectrometer will be accelerated more and will reach the reflection region first. It will go deeper inside the mirror because of its higher kinetic energy whereas the other one starting closer to the spectrometer will have a lower energy and will leave the mirror before. During the second drift stage the faster ions catch up with the slower ones. With the correct acceleration lenses and mirror settings, time–focused ions with the same mass per charge ratio but starting at different positions in the collision region will be obtained. Thus, the resolution of the system is improved and it increases proportionally to the drift length.

Our TOF spectrometer consists of a set of extraction lenses (L1 to L4 in fig. 2.4) which ends with an extraction tube lens (L5). A pair of deflecting plates just after the extraction tube direct the beam towards the mirror. The drift tube is 80 cm long and just before the mirror it is closed by a high transmission grid\(^1\)(G1). Another grid is placed just at the entrance of the mirror (G2) and a third one is between the drift region and the detector (G3). The grids are used to ensure a homogeneous transition between the drift region and the mirror (G1 and G2) or the detector (G3). The electrostatic mirror compresses and reflects the ion bunch into the direction of the 5 cm diameter MCP detector. The optimization of the voltages needed for each lens and the mirror is made by maximizing the count rate of the molecular fragments under study but trying to keep an optimum peak width and shape for the parent

\(^1\)The high transmission grids used in CHEOPS are electroformed copper meshes with 118 wires per inch and 12.5 micron wire diameter (Goodfellow) which implies 88% open area.
ions, i.e. a trade-off between ion beam focusing (reflected in the count rate) and time resolution (reflected in the peak width).

The potential array of our TOF reflectron together with the extraction system and the corresponding mirror section is shown to scale in fig. 2.4. The potential array was generated by using the SIMION software package [36]. Ions are propagated under the influence of the static E field of the whole TOF system. The displayed ion trajectory in a) corresponds to a singly charged ion with mass 135 starting from the center of the collision region. Below the sketch, a graph of the electrostatic potentials vs. distance is shown. The values of the potentials used in the figure and for the simulation correspond to typical values used during the experiments.

Our TOF spectrometer has a maximum resolution of $m/\Delta m \sim 1500$ at 720 amu [37]. For an ion, the overall efficiency of the spectrometer (considering only the transmission grids and the detector efficiency) is around 30%. For multiple stop measurements the transmission is lowered accordingly (for two-stops: 9% and for three-stops: <3%). It is important to note here that 30% is an upper limit since losses in the lenses and mirror are not considered. This makes the recording of data from two-stop measurements (coincidence experiments) very time consuming and extremely challenging (since the experimental conditions have to keep constant for very long times).

2.3. Producing neutral projectiles

For the experiments with neutral projectiles, the ion beam is neutralized in a gas–filled cell. The original design of the gas cell can be found in [38]. The projectiles are neutralized by charge transfer processes in collisions with the buffer gas. The buffer gases used are H$_2$ to neutralize H$^+$, He for He$^+$ and Kr for C$^+$. The gases are chosen such that the neutralization efficiency is high enough to ensure sufficient beam intensity and that the mass of buffer gas atoms effusing into the collision chamber does not overlap with a biomolecular fragment mass. The only case where this is not fully achieved is for the Kr buffer gas because some of its isotopes overlap with important peaks in the spectra. But since the natural isotope distribution of Kr is known, the contributions of specific Kr isotopes can be corrected for. To avoid significant pressure rise in the collision chamber the neutralization cell is closed by two diaphragms of 4 mm and 2 mm diameter and it is differentially pumped by an additional turbo pump.

Fig. 2.5 displays a schematic of the modified CHEOPS experimental setup. For the experiments with neutral projectiles, the ion beam is chopped in front of the bending magnet, by two plates placed in the main beam line. Then the beam is deflected by a 45° magnet. After traversing the first new diaphragm (ND1, $\phi=4$ mm), it enters the neutralization chamber. There, the ion beam can be neutralized when the gas cell is filled with buffer gas. The early chopping of the beam is necessary to ensure a low signal–to–noise ratio: in the conventional scheme, neutralization gas leaks into the chopper leading to neutralization before the chopper and therefore a high flat background.

After the neutralization the beam is unaffected by electrostatic deflection and continues its original trajectory through the two 1mm-diaphragms into the direction of the collision chamber. Before the second new diaphragm (ND2, $\phi=2$ mm) a set of plates deflects the
remaining charged particles. To measure the neutralization efficiency, the beam current is precisely monitored on the end FC while letting the buffer gas in. The decrease in the beam current represents the percentage of neutralized beam. Neutralization efficiencies of a maximum of 10% are achieved for He projectiles. In order to ensure no influence from the charged particles the counting system is started and the voltage on the deflection plates is increased until the signal is gone. This is done before letting the buffer gas in.

The count rate of the TOF measurements was maximum for 14 keV He\(^0\) projectiles. It was about 15 counts/s. This quantity is only 4% of the fragment count rate after interactions with the ion beam at the same energy (He\(^+\)). For C\(^0\) projectiles, the count rate was around 1-2 counts/s (only 1% from the count rate with C\(^+\)). For H\(^0\) projectiles, the fragment rate was only 1-2 counts/s when for H\(^+\) it was more than 1000 events/s ($\ll 1\%$). This makes the measurements with neutral projectiles time consuming and rules out the possibility of measuring multiple-stop signals with enough statistics. The chopping scheme used in the experiments with neutrals was the second one in order to increase the number of ion/neutral bunches per second.

### 2.4. Data analysis

The obtained data can be classified according to the number of charged collision products detected per projectile pulse. Category one (first-stop) contains only the TOF of the first detected product ion, whereas category two (multiple-stop) contains the TOF of two or more detected product ions, i.e. the coincidence information. Usually, the setup is run at chopper frequencies of $>10$ kHz and the count rate for first stops is of the order of 100 Hz. Random coincidences thus contribute only weakly.

An example of a TOF first-stop spectrum for adenine molecules after collision with He\(^+\) projectiles is given in fig. 2.6. This spectrum collects all the events produced by single, double or multiple ionization. As can be seen, the smaller fragments such as H\(^+\) and C\(^+\) arrive at
earlier times to the detector, i.e. their times of flight are short. Typical TOF of the singly charged parent molecules under study is around 40 µs. The lighter/faster fragments appear on the left and the heavier/slower ones on the right.

Fig. 2.7 shows an example of a coincidence plot for adenine molecules after collisions with He\(^{2+}\) projectiles. The first fragment giving the first stop is plotted on the X-axis and the second fragment stemming from the same process gives the second TOF in the Y-axis. Islands can be observed that correspond to pairs of fragments. Some of the fragment pairs are marked in the figure as an example.

The time of flight of ions travelling under the influence of electrostatic potentials is always proportional to the square root of the mass per charge of the ion travelling plus a constant that defines the zero time in the TOF spectrum. So it is straightforward to convert time of flight to \(m/q\).

### 2.4.1. Information from first–stop spectra

From the first–stop TOF spectrum of a molecule, different information can be obtained: preferential fragmentation paths, relative fragmentation cross sections, relative stability of the molecular fragments, etc. In order to obtain precise information from a spectrum, the procedure before analyzing the data is as follows, first a background level is subtracted. In our measurements with charged projectiles, background is usually not an issue but for the neutral projectiles the background substraction is an important step in view of the long counting time. The uncertainty in the quantities obtained from the first–stop spectrum is related to the number of counts, so the square–root rule is used to estimate relative error bars.

Information on single ionization events is only contained in the first–stop data. However, the first–stop data also contain contributions from multiple ionization processes. Single ionization events can be separated for cases where information on multiple ionization events can be extracted from a multiple–stop measurement. As an example, the procedure to separate...
2.4 Data analysis

Figure 2.7: TOF coincidence spectra of adenine molecules after collisions with 20 keV He$^{2+}$ projectiles. Some of the pairs of ionic fragments are marked as an example.

Figure 2.8: TOF spectra for H$^+$ fragments produced in collision of 6 keV He$^{2+}$ with water. Dotted line: total first-stop data; dashed lines: multiple ionization spectra taken from double stop data; solid line: resulting single ionization spectrum after substraction of multiple ionization spectra.
both contributions (from single and multiple ionization events) for a simple target system like water is sketched in fig. 2.8. The H$^+$ fragment peak in the first–stop spectrum contains contributions from multiple ionization processes. The respective spectra taken from the coincidence experiments are scaled to fit to the first–stop spectrum and then subtracted. This way an anti-coincidence spectrum, \textit{i.e.} the H$^+$ TOF spectrum from single ionization processes only, is obtained.

Furthermore as can be seen from fig. 2.7, albeit very weak, random coincidences are usually present in the coincidences plot. In order to account for them, the TOF spectrum obtained in the single ionization events is used. Its autocorrelation distribution is scaled to a known false coincidence island (for example H$^+$–ade$^+$) and subtracted from the coincidence data.

### 2.4.2. Extraction of the kinetic energies for different fragments

When two charged particles start from the same position within an electric field with an initial velocity $v_0 = 0$, they will follow exactly the same trajectory. However when they have an initial $v_0 \neq 0$, their trajectories will be slightly different and also their times of flight. The last situation is sketched in 2 dimensions in fig. 2.9 for the two limit cases: fragmentation of molecules oriented a) parallel and b) perpendicular to the applied electric field. The situation sketched in a) implies 100% transmission whereas the situation in b) illustrates a case where transmission is zero, \textit{i.e.} the fragments do not go through to the spectrometer. In reality, the molecules are oriented in any direction, but fragments originating from molecular orientations with large angles to the electric field get intercepted by the extraction plate. The transmission will be discussed further on. Let us consider only the situation sketched in a): one of the two positively charged fragments will go initially backward and the other will go forward due to their mutual Coulomb interaction. In the case of identical particles, their initial velocities $v_0$ and $-v_0$ only differ in sign. This will lead to a difference in the observed time of flights of the initially backward and the forward emitted fragments. In the single–stop TOF spectrum peak...
splitting is observed for very low extraction voltages and in the two-dimensional plots formation of separated islands is the result. The difference in time (Δt) can be used to calculate the kinetic energy released during the fragmentation.

The relation between the difference in time (Δt) and the kinetic energy of each recoil ion \(U_r\) can be written as follows:

\[
\Delta t = \frac{\sqrt{8mU_r}}{qE}
\]  

(2.1)

where \(q\) is the charge state of the fragment, \(m\) is its mass and \(E\) is the extraction field.

As an example of how to obtain kinetic energy releases for different types of islands, i.e. different fragmentation channels, coincidence data for fragmentation of the water molecule, the simplest molecule studied in this thesis, are used. In fig. 2.10 coincidence data for collisions of He\(^{2+}\) with water molecules is visualized in 2-D plots of the TOF of the faster fragment ion (TOF1) vs the TOF of the slower fragment ion (TOF2). The number of ions

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**Figure 2.10:** Coincidence plots for different fragment ion pairs stemming from water multiple ionization after collisions with 16 keV He\(^{2+}\) ions.
within a given bin is gray scale coded. Three different regions of interest corresponding to the fragment ion pairs a) H$^+$–OH$^+$, b) H$^+$–O$^+$ and c) H$^+$–O$_2^+$ are shown. For each ion pair, two islands are observed. As mentioned before, kinetic energy released in the dissociation event leads to an initial momentum of the fragment ions. If the momentum vector is parallel to the spectrometer axis, the fragment ions can pass the diaphragm and enter the reflectron. Thus, identical fragment ions with a positive (forward) or negative (backward) initial velocity $v_0$ along the spectrometer axis are detected at different TOF. In fig. 2.10, the left islands correspond to the lighter fragment emitted forward (H$^+_f$) and the heavy fragment emitted backward (OH$^+_b$, O$_b^+$ and O$_b^{2+}$). The right islands correspond to the light ion emitted backward (H$^+_b$) and the heavy fragment emitted forward (OH$^+_f$, O$_f^+$ and O$_f^{2+}$). This coincidence spectrum was obtained with a low (100 V cm$^{-1}$) extraction field, in order to separate the islands clearly. By simply looking at the shape and orientation of the islands in the 2D-plot, already some information about the fragmentation process can be obtained. In a two–body breakup process (e.g. H$^+$–OH$^+$) the complete kinetics of the fragmentation process can be obtained from the coincidence data. Due to conservation of momentum, the slope of a line drawn through both islands is $-1$ (see fig. 2.10a).

It does not always occur that the molecule dissociates in exactly two charged fragments. The molecule can also dissociate emitting neutral fragments or more than two ionic fragments. Neutral fragments can not be accelerated by an electric field, which may be overcome by using post-ionization techniques. In our system this is not possible and our studies are limited to cases where at least two charged fragments are emitted. Nevertheless, information on the fragmentation process can be also obtained when neutral fragments are emitted. If for example a third undetected (neutral or ionic) fragment is formed, the line deviates from the -1 slope since momentum is carried by the third body (see fig. 2.10b and c)).

From the projection of the coincidence data to TOF1 or TOF2 (see fig. 2.10) the kinetic energy distributions for the respective ion recoil ($U_r$) can be calculated. The time reference is determined by the requirement that the energy–release spectra from forward and backward emission have to agree. For a two–body breakup $U_r$ is called $U_{KER}$ since the total kinetic energy released during the process can be calculated from the difference in time between the forward and backward emitted fragments.

### 2.4.3. Correction for transmission

Due to the diaphragm on the extraction plate (E2 in fig. 2.4), the product ions from a collision are extracted from the collision center into the spectrometer with certain probability. The probability depends on: the diaphragm radius ($r_d$) and the extraction field $E$ as well as the fragment ion parameters: kinetic energy, mass and charge state. This transmission can be calculated under the assumption that the emitted fragments have an isotropic distribution. In fig. 2.11 a sketch of the model used for calculating the transmission is shown for five different times $t_1$ to $t_5$. For $t_3$ the sphere coordinates are given. The model is based on the translation of an expanding sphere (represented as circles). The sphere radius expands according to the initial velocity of the ion $v_0$ and its center displaces due to the extraction field $E$. The initial
velocity of the ion is given by

\[ v_0 = \sqrt{\frac{2U_r}{m}} \]  \hspace{1cm} (2.2)

and its acceleration is given by

\[ a = \frac{qE}{m} \]  \hspace{1cm} (2.3)

From these equations the time \( t_3 \) at which the ions emitted forward intersect the diaphragm, and the time \( t_5 \) at which the ions emitted backward intersect the diaphragm can be obtained. The particles passing the diaphragm are assumed to be detected, leading to the forward or backward peak, respectively. The transmission of the forward emitted ions \( k \) can be calculated as:

\[ k = 1 - \cos \varphi \]  \hspace{1cm} (2.4)

where

\[ \varphi = \arcsin \frac{r_d}{v_0 t_5} \]  \hspace{1cm} (2.5)

The obtained kinetic energy distributions then have to be corrected for transmission through the extraction diaphragm using the correction functions \( 1/k \). The transmission of the backward emitted ions is smaller than for the forward emitted ions. The maximum transmission for our systems is obtained for high extraction fields, large diaphragm diameter and low initial kinetic energies. Projectile ions are too energetic to be extracted.
2.5. Experiments performed in other facilities outside KVI

The experiments on quantification of energy deposition (chapter 6) and on cluster formation (chapter 7) were performed in other experimental facilities outside KVI. In both cases, key experimental features are similar to the KVI experiments. Here, only a brief description of the Lyon and Caen setups, focusing on the additional features will be given.

2.5.1. Collision induced dissociation under energy control at LASIM

The H$^+$ ion beams (2-10 keV) used in our studies are delivered by a 10 GHz electron cyclotron resonance ion source (Nanogan III). After collimation the ion beam enters the interaction chamber through a 500 $\mu$m diameter hole and crosses an effusive jet of biomolecules created by evaporation in an oven at temperatures below 90$^\circ$C. Under these conditions, the background vacuum inside the chamber is below $1 \times 10^{-8}$ mbar. After the interaction, the outgoing projectile is charge and energy selected by an electrostatic analyzer and detected by a channeltron electron multiplier with an efficiency of about 100% in the energy range considered in this work. For our studies, the selected projectile was H$^-$. The ejected electrons and charged fragments are extracted from the interaction region by a 250 V cm$^{-1}$ transverse electric field. After extraction, the electrons are accelerated by a 17-20 kV potential towards a semi-conductor detector (PIPS). The signal delivered by the PIPS is proportional to the energy deposition into the detector and thus to the number of electrons that hit the detector. The recoil ions are analyzed by time of flight spectroscopy and detected by two multi-channel plates followed by a multianode composed of 121 pixels. The signals delivered by the multianode detector are sent to four multi-hit time-to-digital converters (TDC 3377 Lecroy). For singly charged ions the detection efficiency has been estimated to be 75%. Multi–coincidence measurements between a charge selected projectile, the electrons and the recoil ions are performed in event-by-event mode data acquisition.
For fragmentation processes the initial charge of the deoxyribose parent \((C_5H_{10}O_4)^{r+}\) is determined using the electron number conservation law \(r = n + s\) where \(s\) refers to the number of electrons stabilized by the outgoing projectile (e.g. \(s = 2\) for \(H^+ \rightarrow H^-\) collisions) and \(n\) is the number of ejected electrons. More information about the experimental setup at LASIM can be found in [33, 39].

### 2.5.2. The cluster source at CIRIL/GANIL

The keV multiply charged ions employed for the cluster studies are extracted from the electron cyclotron resonance ion source at CIRIL/GANIL in Caen. Bending magnets are used for \(m/q\) separation of the projectile ion beam before it is collimated and guided into the collision chamber.

Neutral nucleobase clusters are produced in a cluster aggregation source [40, 41]. The original design contains one oven with two parts (the crucible and the lid) which can be heated separately. For the experiments with mixed clusters, the oven is replaced by two crucibles. Nucleobase powder is evaporated in the oven(s) at temperatures around 200°C. The evaporated material diffuses out of the oven(s) and passes through a heat shield into a cold helium stream at a few mbar pressure. The gas mixture enters a condensation channel which is cooled continuously with liquid nitrogen. Formation of clusters occurs in this region due to supersaturation of the vapor (see fig. 2.13). The main parameters controlling the cluster formation are the oven temperature (the vapor pressure of the material) and the carrier gas pressure. Our experiments are carried out at a constant He-flow of 280 ml/min and oven temperatures are only varied within a range where no thermal fragmentation is expected.

The formed neutral clusters pass several differential pumping stages separated by skimmers before interacting with the beam of multiply charged ions. Similar to the experiment on isolated biomolecules, charged reaction products are extracted from the interaction zone perpendicular to the two beams. In this experiment, the ion beam as well as the extraction voltage are pulsed. The charged collision products are analyzed with a linear Wiley-McLaren time-of-flight mass spectrometer. It consists of an ionization and acceleration region, a field-
free drift region and a detector. The particles are post-accelerated towards a conversion plate kept at voltages up to 25 kV in order to obtain a constant detection efficiency (close to 1) for the heavier (cluster-)ions. The electrons emitted from the conversion plate are focused on a channel plate. The resulting signals are then registered with a multihit TDC on an event-by-event basis. The transmission and detection efficiency of the spectrometer are close to 100%.