Dynamics in the Dissociative Recombination of Small Polyatomic Molecular Ions

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Abstract

Dissociative recombination (DR) is a process in which a positive molecular ion recombines with an electron and subsequently dissociates into neutral fragments. Among the different types of molecular ion-electron reactions DR deserves particular attention due to the important role it plays in low-temperature and low-density plasmas. Despite the apparent simplicity of the DR reaction, its investigation has proven to be a difficult task from both experimental and theoretical perspectives. In order to shed more light upon this process the storage ring technique has been introduced and utilised extensively for the last few decades. This thesis is devoted to experimental studies into the DR reaction at the storage ring CRYRING. The DR reaction has been investigated for the following molecular ions: Na\(^+\)(D\(_2\)O), PD\(_2\)^+, O\(_3^+\), N\(_3^+\), H\(_2^+\), D\(_2\)H\(^+\), OPCl\(^+\), OPCl\(_2^+\) and H\(_3\)O\(^+\), with the aim to ascertain rotational state effects, to find patterns in the branching products of similar molecular ions, to investigate isotope effects and to study in detail the dynamics involved in the three-body break-up channel.
List of publications

I Dissociative recombination study of Na\(^+\)(D\(_2\)O) in a storage ring.

II Dissociative recombination study of PD\(_2^+\) at CRYRING: absolute cross-section, chemical branching ratios and three-body fragmentation dynamics.
Molecular Physics 103, 2735 (2005).

III Three-body breakup in the dissociative recombination of the covalent triatomic molecular ion O\(_3^+\).

IV Dissociative recombination dynamics of the ozone cation.

V Dissociative recombination study of N\(_3^+\): cross section and branching fraction measurements.
V. Zhaunerchyk, W. D. Geppert, E. Vigren, M. Hamberg, M. Danielsson, M. Larsson, R. D. Thomas, M. Kaminska, and F. Österdahl,

VI Rotational state effects in the dissociative recombination of H\(_2^+\).

VII Dissociative recombination of D\(_2\)H\(^+\): comparison between recent storage-ring results and theoretical calculations.
V. Zhaunerchyk, R. D. Thomas, W. D. Geppert, M. Hamberg, M. Kaminska, E. Vigren, and M. Larsson,

VIII Dissociative recombination of OPCl\(^+\) and OPCl\(_2^+\): pushing the upper mass limit at CRYRING.
IX Dissociative recombination of BH$_2^+$: the dominance of two-body break-up and an understanding of the fragmentation.
V. Zhaunerchyk, E. Vigren, W. D. Geppert, M. Hamberg, M. Danielsson, M. Kaminska, M. Larsson, and R. D. Thomas,
submitted to Physical Review A.

X Investigation of the three-body break-up in the dissociative recombination of the H$_3$O$^+$ ion.
V. Zhaunerchyk, W. D. Geppert, E. Vigren, M. Hamberg, M. Kaminska, M. Larsson, R. D. Thomas, E. Bahati and C. R. Vane,
manuscript
Publications not included in the thesis

XI Dissociative recombination cross section and branching ratios of protonated dimethyl disulfide and N-methylacetamide.

XII Dissociative recombination of $S^{18}O_2^+$: Evidence for three-body break-up.

XIII Dissociative recombination of nitrile ions: DCCCN$^+$ and DCCCND$^+$.

XIV Dissociative recombination branching ratios and their influence on interstellar clouds.

XV The effect on bonding on the fragmentations of small systems.

XVI Branching ratios and absolute cross sections of the dissociative recombination of $N_2O^+$.

XVII Rate constants and branching ratios for the dissociative recombination of $CO_2^+$. 

XVIII Investigating the breakup dynamics of dihydrogen sulfide ions recombining with electrons.

XIX Dissociative recombination of the thioformyl (HCS+) and carbonyl sulfide (OCS+) cations.

XX The dissociative recombination of fluorocarbon ions II: CF+.

XXI The dissociative recombination of fluorocarbon ions III: CF2+ and CF3+.

XXII Experimental determination of dissociative recombination reaction pathways and absolute reaction cross-sections of CH2OH+, CD2OD+ and CD3OD2+.

XXIII Dissociative Recombination of the deuterated acetadehyde ion, CD3CDO+: product branching fractions, absolute cross sections and thermal rate coefficient.
E. Vigren, M. Kaminska, M. Hamberg, V. Zhaunerchyk, R. D. Thomas, J.
Semaniak, M. Danielsson, M. Larsson, and W. D. Geppert,
Physical Chemistry Chemical Physics 9, 2856 (2007).
Contributions by the author

This thesis is based on the ten papers to which I have given the most significant contributions. All the papers are based on experiments in which I have very actively participated. In all these papers the data analysis has been performed by myself except the cross section evaluation in Paper I and the \textit{ab initio} calculations performed in Paper VIII. I have been responsible for writing all of the papers included here with the sole exception of Paper VI where a significant amount was written by Wim J. van der Zande.
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Chapter 1

Introduction

1.1 General description of the reaction

Dissociative recombination (DR) is the name given to the reaction in which a molecular cation recombines with an electron forming a highly excited neutral state which then subsequently releases its excess energy through fragmentation into neutral products. For the simplest case of a diatomic molecular ion the reaction can be written as

\[ XY^+ + e \rightarrow XY^* \rightarrow X + Y. \]  \hspace{1cm} (1.1)

DR is a very fast process occurring on a time scale comparable to that of autoionisation \((10^{-15} \text{ s})\). Radiative recombination, which results in non-dissociated molecule stabilising by means of photon emission

\[ XY^+ + e \rightarrow XY^* \rightarrow XY + h\nu \]  \hspace{1cm} (1.2)

is relatively slow and, therefore, does not compete with the two former processes.

The term autoionisation is a collective name for the following reactions

\[ XY^+ + e(E) \rightarrow XY^* \rightarrow XY^+ + e(E'), \]  \hspace{1cm} (1.3)

where \( E \) and \( E' \) are used to denote the electron energy before and after the interaction, respectively. The processes are called elastic, inelastic, and super-elastic when \( E=E' \), \( E>E' \) and \( E<E' \), respectively. An inelastic collision leads to internal excitation of the molecular ion while a super-elastic collision leaves the molecular ion internally de-excited.

Since in DR the electron is captured into a neutral state which has an excess energy comparable to the energy required to ionise the neutral molecule from its ground state, the reaction is highly exothermic and, in the DR of a polyatomic molecular ion, can lead to the rupture of multiple bonds. For example, in the case of a triatomic molecular ion, the reaction could proceed through the
following channels

\[
\text{XYZ}^+ + e \rightarrow \begin{cases} 
\text{XY} + \text{Z} \\
\text{X} + \text{YZ} \\
\text{XZ} + \text{Y} \\
\text{X} + \text{Y} + \text{Z}
\end{cases}
\]  

(1.4)

Knowledge of the branching fractions is crucial for modelling astrophysical environments and other plasmas. The reaction energy is also available for use in processes other than breaking chemical bonds, e.g. as kinetic and/or internal energy of the fragments. Translationally hot fragments can lead to local heating of the plasma or, in some cases, the products gain sufficient kinetic energy to escape the planet’s gravitational pull. Information about the internal state distribution is also of great interest, e.g. most excited states are more reactive than the ground state species and, furthermore, excited products can relax by emitting light, a process which is known as airglow in planetary atmospheres. Moreover, some of the molecular fragments are internally excited enough to fragment further and, in such situations, the internal excitation of the products has a direct impact on the final branching fractions.

1.2 Historical overview

The DR reaction first attracted attention in 1931 when it was proposed to be a depletion mechanism for ionised oxygen molecules in the terrestrial ionosphere, subsequently leading to the observed aurora and night airglow [1]. The main obstacle for such an assertion at that time was the fact that the electron mass is at least three orders of magnitude smaller than the mass of a molecular ion and it was not believed possible that the light electron could cause bond ruptures in the much more massive ion. In an attempt to explain the destruction of the positive ions in the terrestrial ionosphere, their recombination with negative ions, which were known to be formed by electron attachment to neutral molecules in the lower layers of the atmosphere [2], was suggested as the most dominant neutralising mechanism and DR was regarded to be too slow a process. However, pioneering experiments in the field of electron-ion recombination showed exactly the opposite. In 1949 Biondi and Brown studying ambipolar diffusion using a microwave afterglow technique found the rate coefficient for electron-ion recombination in He to be unexpectedly large [3]. In a subsequent experiment they revealed that the recombination reaction for diatomic gases were even more violent than for monatomic gases [4]. Such a puzzle required a theory capable of explaining the experimentally obtained results, and the earliest theoretical treatment was reported one year later by Bates [5].

In this seminal one page paper Bates suggested that the electron did not directly break the molecular bonds, as it had been believed before, but its energy is transferred entirely into the energy of the target electrons [5], i.e. the electron is captured into a molecular orbital and the released energy goes into excitation of a bound electron such that a doubly-excited neutral state is formed which has a repulsive potential energy curve (Fig. 1.1). This state is unstable
and has a tendency to eject an electron back into the continuum. Conversely,

![Diagram of DR mechanisms](image)

Figure 1.1: Schematic presentation of the direct and indirect DR mechanisms.

since the potential is repulsive in the bonding coordinate, the molecule begins to stretch. As soon as the internuclear distance passes the crossing point between the repulsive curve and the ground state of the molecular ion, \( r_{\text{crit}} \), autoionisation is no longer possible and the molecule must fragment. This description of the DR reaction is called the direct mechanism. The direct mechanism is a resonant process. However, due to the nuclear motion, it can occur over a wide range of interaction energies. Mitchell, based on the Wigner threshold law [6], showed that the cross section of a DR reaction proceeding through the direct mechanism can be expressed by [7]

\[
\sigma = \frac{\Gamma \times FC \times S}{E}, \tag{1.5}
\]

where \( \Gamma \) is the capture width, which expresses the strength of the capture process, \( FC \) is the Franck-Condon factor between the ion ground state and the doubly-excited dissociative state, \( S \) is the survival factor describing the probability of dissociation over autoionisation, and \( E \) is interaction energy. It follows from Eq. 1.5 that the cross section of the direct mechanism is inversely proportional to \( E \).

By the 1960s the microwave afterglow technique had been extensively utilised for investigations into the DR reaction for diatomic molecular ions [3, 4, 8, 9].
The results generally supported Bates’ predictions regarding the value of the DR rate coefficient to be around $10^{-7}$ cm$^3$s$^{-1}$ at room temperature. However, the Bates model was not able to explain the temperature dependence of the rate coefficient. Based on the suggestion of Stabler [10], Bardsley proposed a second competing DR scheme called the indirect mechanism [11]. Here, in the indirect mechanism, the electron is captured into a vibrationally excited Rydberg state in a breakdown of the Born-Oppenheimer approximation, i.e. the electron is captured into a Rydberg orbital and the energy released is transferred into the vibrational motion of the molecule. Such a state is also unstable having a tendency to autoionise or predissociate by the doubly-excited neutral state (Fig. 1.1). Bardsley concluded that the temperature dependence of DR proceeding through the direct mechanism is $T^{-0.5}$, while for the indirect mechanism it can be as steep as $T^{-1.5}$. Such predictions enabled the experimental observations to be theoretically explained.

In addition to the stationary afterglow technique, other experimental methods were also being used for studying DR and these are briefly discussed here. Among the earliest methods for studying electron-ion recombination reactions were combustion measurements [12, 13]. The decay of ionised species was measured with a Langmuir probe as a function of distance through the flame front. Converting distance to time, and assuming that the ion and electron concentrations are equal, $n_+ = n_-$, the ion concentration can be expressed as

$$\frac{1}{n_+(t)} = \alpha t + \frac{1}{n_0},$$

where $\alpha$ is the reaction rate coefficient, which is given by the slope of the function $1/n_+$ versus $t$. Using this technique, the authors reported DR rate coefficients to be of the order of $10^{-7}$ cm$^3$s$^{-1}$ and concluded that DR is the predominant process in the flame.

In 1966 the development of the shock-heated afterglow plasma was reported which later underwent some improvements [14, 15, 16, 17, 18, 19]. The principle behind such a technique is the propagation of a shock wave through an afterglow plasma ignited by an rf discharge. On passage of the shock front the plasma is compressed and heated, with a pressure change from a few Torr to 10-120 Torr which corresponds to the propagation of shock waves in the range 1-6 Mach. The gas temperature is varied by the shock Mach number and can be as high as few thousand K. The electron temperature can be elevated above the gas temperature by using a microwave field director. The advantage of such an apparatus is the possibility to study the DR reaction for different values of both ion and electron temperatures with a near Maxwellian electron distribution.

In the same year that the shock-heated apparatus was first reported the charge-collection technique appeared [20]. In this method ions are produced by chemi-ionisation [21] between two parallel-plate electrodes. Initially the ions are removed by a voltage pulse applied between the electrodes. By applying an additional pulse after a certain delay the ion number density can be determined by measuring the transient current flowing from the negative electrode. The DR
rate coefficient can be obtained from the dependence of the ion density versus the delay time.

Ion-trapping methods have also been used successfully, and one example is a study into the DR of $\text{H}_3\text{O}^+$ which enabled the cross section to be obtained versus interaction energy over the range 0.06 to 1.15 eV [22]. The main advantage of this technique is the possibility to store the ions in isolation for up to 300 s which gives time for the relaxation of internally excited states to that of the surroundings. The rate coefficient can then be obtained by integrating the cross section over an isotropic Maxwellian distribution.

Spectroscopic techniques were introduced by Amano in 1988 [23, 24]. The ions are produced in a cooled hollow cathode by applying a discharge. The frequency of the infrared laser is tuned to a particular rovibrational transition. The laser beam is directed into the hollow cathode and the change in the absorption spectrum versus time is related to the depletion of the probed state primarily due to the DR reaction. The advantage of this method is the possibility to study the recombination of a particular rovibrational state. However, the main disadvantage is a depletion of ions by radiative recombination processes interfering with the measurements [25].

The development of the Flowing Afterglow Langmuir Probe (FALP) [26] and Merged Electron-Ion Beam Experiment (MEIBE) machines [27], which are very different in design and operation, significantly accelerated progress in the research of the DR reaction. At the heart of the FALP apparatus is a flow tube in which a constant flow of gas is created by means of a roots pump. Upstream the plasma is created from a carrier gas, usually He, by a microwave discharge. Just prior to the measurement region, argon gas is introduced to convert the He plasma into an $\text{Ar}^+$ dominated plasma. The electron recombination for $\text{Ar}^+$ is very slow and cannot lead to a significant loss of electrons. Further downstream, in the interaction region, the reactant gas or gas mixtures are introduced and, via ion-molecular reactions, the molecular ion species to be studied are generated. Neglecting ambipolar diffusion the DR reaction of these molecular ions with the electrons is the dominant electron loss process. By measuring the electron density along the flow by a movable Langmuir probe the DR rate coefficient can be obtained from the dependence of $n_e$ versus the distance along the flow tube, $z$, i.e.

$$\frac{1}{n_e(z_1)} - \frac{1}{n_e(z_2)} = \frac{\alpha}{\nu}(z_2 - z_1),$$

where $\nu$ is the plasma flow velocity. Subsequent improvements to the basic FALP design include the introduction of a movable mass spectrometer enabling the investigation of the DR reaction of a specific ion even if this ion is only present in a minute amount [28, 29]. The advantage of the FALP apparatus is that the plasma production and interaction regions are separated and due to the relatively high pressure (Torr) the hot electrons are collisionally cooled very quickly such that $T_e$=T_i is obtained. Another advantage is the possibility to study internal state product distributions using either laser induced fluorescence detection [30, 31, 32] or direct emission of the excited states [33].
The MEIBE technique was introduced in 1977 by Auerbach et al. and is based on a single-pass electron-ion merged-beam concept [27]. After production in the source the ions are then accelerated by Van de Graaff accelerator and injected into a collision chamber, where they are merged with an electron beam over a short distance. The neutral fragments produced in the DR reaction are detected by a surface-barrier detector. Using this merged-beams approach, by varying the electron energy in the laboratory frame a wide range of interaction energies can be achieved. This then allowed, for the first time, highly accurate DR measurements to be performed and the energy resolution of the interacting beams was reported to be as good as 7 meV at low interaction energies [34]. Through the introduction of a trap RF ion source to create internally cold ions it was possible to investigate the DR of relatively pure beams of H$_2^+$, i.e. only a few internal states were populated [35]. This approach allowed to observe previously unseen structures in the cross section which enabled these features to be assigned to the indirect mechanism and gave greater insight into the DR reaction [34, 36].

In the DR of polyatomic molecular ions different sets of neutral fragments, called channels, can be created (Eq. 1.4). Several attempts have been reported to develop models able to predict the branching fractions from the DR of polyatomic molecules. The earliest model was developed by Herbst [37, 38]. In this model the probability that a specific channel is populated is proportional to the number of quantum states existing in the channel. This implies that more exothermic channels are more probable. The model also predicts that different channels are possible but, generally, that channels which involve two-body break-up dominate over those which break multiple bonds. A second, predissociative, model was introduced by Green and Herbst in 1979 [39]. This model was mostly utilised for hydrogen containing ions and predicts that H-heavy atom (H-X) bond rupture is preferential. This assertion is based on the lightness of the hydrogen atom, i.e. after the electron capture the molecule moves to dissociation along the potential surface and the fragmentation time will be the smallest for H-heavy atom break-up due to the high mobility of the hydrogen atom and that autoionisation will be less probable than for other bond ruptures. The valence bond approach was developed by Bates [40, 41]. This model predicts that, in general, the channel involving the least rearrangement of valence bonds is most favoured. For example, for small polyatomic ions, e.g. CH$_4^+$, CH$_3^+$, H$_2$O$^+$, etc. the loss of a single hydrogen atom will dominate. The fragmentation of CH$_4^+$ and CH$_3^+$ was explained in the following way: since C$^+$ has a valence of three the molecular structures should be represented as CH$_3^+$-H and CH$_3^+$-H$_2$, respectively, where H and H$_2$ are bound to the CH$_3^+$ by the ion-induced dipole attraction. As a result of this the incoming electron recombines with CH$_3^+$ and the dipole attraction simultaneously disappears, i.e. 

$$\text{CH}_4^+ + e \rightarrow \text{CH}_2 + \text{H} + \text{H},$$

$$\text{CH}_3^+ + e \rightarrow \text{CH}_2 + \text{H} + \text{H}_2.$$  

(1.8)

The following fragmentation pathways are also possible, though would be much
less populated
\[
\text{CH}_4^+ + e \rightarrow \text{CH}_3 + \text{H},
\]
\[
\text{CH}_5^+ + e \rightarrow \text{CH}_4 + \text{H}.
\]

Millar et al. extended Bates’ approach and concluded that since the probability of a bond rupture is proportional to the charge surrounding the bond, for polyatomic molecular ions in which the charge can be delocalised a wide variety of fragments is possible [42]. They performed accurate calculations of the charge distribution in the complex ions relevant for astrophysical environments, which led them to revise the gas-phase models of dense interstellar clouds. A statistical model developed by Strasser et al. [43] predicts the same energy dependent branching fractions in the DR of \( \text{H}_3^+ \) as was measured by Datz et al. [44]. In particular, it was predicted that at \( \approx 0 \) eV interaction energy 52% of the \( \text{H}_2 \) molecules have sufficient energy to fragment further. However, the imaging results showed negligible formation of the \( \text{H}^+\text{H}^+\text{H} \) channel arising from sequential break-up [45], i.e.
\[
\text{H}_3^+ + e \rightarrow \text{H}_2^+ + \text{H} \rightarrow \text{H} + \text{H} + \text{H}.
\]

This model is based on the two statistical assumptions of random fragment energy distribution and a purely statistical population of the relevant electronic states. Such assumptions are very approximate since the presence of favourable curve crossings as well as Franck-Condon overlap are not taken into account. As a result of this, such models are not able to explain the rotational state effect in the branching which was observed experimentally [46]. The inability of the models to generally describe fragmentation behaviour requires experimental techniques which are capable of measuring the branching fractions, and such measurements have become feasible through the use of the storage rings.

1.3 Storage ring approach

The overwhelming impetus behind experimental research into the DR reaction has been due to the introduction of the storage rings into this field, which overcame imperfections of earlier experimental approaches. The initial idea to use storage rings for investigation into the DR reaction was proposed by Datz and Larsson [47]. They utilised the CRYRING facility at the Manne Siegbahn Laboratory, Stockholm, and concluded: 1) due to the ultrahigh vacuum in the ring \( 10^{-11} \) Torr and the possibility to reach high beam energies (25 MeV for \( \text{HeH}^+ \)), the storage time can be as long as 50 s which is much longer than the radiative lifetimes of internally excited \( \text{HeH}^+ \) states, i.e. the storage ring enables the DR reaction to be studied for internally relaxed molecular ions, 2) due to the relatively low cross section for the interaction between \( \text{HeH}^+ \) and the residual gas (mostly \( \text{H}_2 \)) at the beam energy of 25 MeV, the DR count rate dominates over background. These two very important conclusions ignited deeper investigation into the DR reaction at new unprecedented levels. Inspired by the
seminal paper of Datz and Larsson, in 1993 three independent experiments were carried out at three different storage rings: TARN II (Japan), TSR (Germany) and CRYRING (Stockholm). The results completely supported the suggestion of Datz and Larsson and the results were published in a single Physical Review Letters volume [48, 49, 50].

Today storage rings represent the most powerful tools for studying the DR reaction. Since the first experiment in 1992 up to the present day storage rings have undergone improvements which have significantly increased the accuracy of the experimental results. The storage ring approach is based on the concept of merged beams suggested by Auerbach et al. in 1977 and successfully implemented at the MEIBE apparatus [27]. However, while the MEIBE is a single pass apparatus, in the storage rings the beams interact continuously. This enables a high DR count rate to be achieved, usually kept below 10 kHz, making data acquisition relatively fast while, for instance, the acquisition time for several spectra obtained from the MEIBE was as long as a week. The nominal energy resolution at storage rings is $\approx 0.1$ eV, which is determined by the temperature distribution of the electrons emitted from the cathode. The method of adiabatic expansion of the electron beam allows a reduction of the thermal spread of the electrons which leads to even better interaction energy resolution. Such a method was implemented for the first time at CRYRING in 1993 and, as a result of this, the transverse temperature was reduced to 10 meV [51, 52]. Subsequently this technique was also applied at the TSR and TARN II storage rings [53, 54]. Implementing superconducting magnets at both the CRYRING and TARN II storage rings the adiabatic expansion was achieved to be 100 times which leads to electron energy spread of 1 meV [55, 56]. Quite recently, at the TSR, a photocathode was installed in the electron target which makes it possible to increase the resolution down to 0.5 meV [57].

The question on the fragmentation of the molecule in the DR reaction was controversial for decades and sometimes the branching fractions were just guessed. Datz et al. extended the idea of Mitchell et al. [58] and implemented the translucent grid at the CRYRING storage ring which enabled the authors to measure the branching fractions for $\text{H}_2^+$ with high accuracy and the result showed that the full fragmentation channel dominated the reaction products [44]. One year later using the same technique the branching fractions were measured for the hydronium ion, $\text{H}_3\text{O}^+$, at the ASTRID storage ring [59]. These results showed the dominance of the OH+H+H product channel. The existing models at the time could not support the observations from these storage rings experiments, which required the model results to be revised. To date, the DR fragmentation has been extensively investigated at the ASTRID and CRYRING storage rings and some patterns have been found which will be discussed in more detail in the Results and Discussion chapter.

The relatively high exothermicity of the DR reaction can lead to both translationally hot and internally excited DR products. Knowledge about internal states is very important, and the imaging detector (ID) was developed and implemented at the storage rings to investigate the internal state distributions. This approach was used for first time at the TSR for studying the DR of $\text{HD}^+$
Subsequently, it was also implemented at the ASTRID, TARN II and CRYRING storage rings [61, 62, 63]. The earlier experiments concerned the internal excitation of the atomic fragments from the DR of diatomic molecules. Later the possibility to utilise such detectors for three-body break-up in the DR of polyatomic ions was first demonstrated by Datz et al. at CRYRING [64]. To date, the dynamics of the three-body fragmentation channel in DR has been investigated for H$^+$ and its isotopologues, CH$^+_2$, NH$^+_2$, H$_2$O$^+$, PD$_2^+$, SD$_2^+$, O$_3^+$, H$_3$O$^+$, (NO)$_2^+$, CH$_5^+$ and D$_5$O$^+_2$ [45, 64, 65, 66, 67, 68, 69, 70, 71], [Papers II, III, IV, X]. Initially the imaging detectors were designed to operate as purely two-dimensional (2D) detectors. The ID underwent improvements and was redesigned to be 3D which resulted in better identification of the DR product distributions [72, 73, 74]. The possibility to perform both highly accurate cross section measurements as well as investigate the DR fragmentation and internal state product distributions makes the storage ring a unique tool for detailed studies of the DR reaction.

Despite the unique information obtained from the storage rings on the DR reaction, the technique has its imperfections. One of the major drawbacks is that using magnetic confinement of the ions limits the mass range of the ions that can be stored. As a result of this, the low beam energy of heavier ions places constraints on: 1) the unique identification of the DR products, 2) the storage time of the ion beam, 3) the ability to confine a stable and dense electron beam to velocity match with the ions, and 4) the efficiency of the electron cooling. Another disadvantage of the storage rings is an ability to run only at the temperature of 300 K, i.e. for molecular ions with dipole moments a DR study of a single quantum state is in principle not feasible.

### 1.4 DR in astrophysical environments

Interstellar space is not empty and not homogenous. Depending on the particle concentration, temperature, and constituents the high density interstellar regions are divided into diffuse and dense clouds. Diffuse clouds are so named due to the relatively low particle density ($10^{-10}$ cm$^{-3}$, T=50-100 K) which allows both cosmic rays and stellar UV to penetrate deep into the cloud’s interior providing both a source of ionisation and as a probe of their composition, where the background radiation serves as a “lamp” for spectroscopic measurements [75]. In contrast, the dense clouds have significantly higher particle densities ($10^4$ cm$^{-3}$, T=10 K) and, therefore, the only source of ionisation in these clouds are cosmic rays. These clouds have high opacity in the UV region and are seen as dark areas in the night sky [76]. Due to the relatively low density the particles in diffuse clouds are mostly atoms, though several diatomic molecules have been detected, but to a much lesser extent, and only molecular hydrogen has a density comparable to that of atomic hydrogen [77]. In such clouds the fractional ionisation is about $10^{-4}$ and corresponds mostly to C$^+$, while, for instance, the molecular ion of CH$^+$ is less abundant by a factor of $10^{-7}$ [77]. The situation is reversed in the dense clouds where, due to the high concentration of particles,
the ongoing chemistry can lead to formation of relatively large molecules. Since neutral-neutral reactions usually possess activation barriers, the most important processes are those which involve ions. Indeed, such reactions, i.e. ion-neutral and electron-ion interactions, are usually barrierless and so quite efficient at low temperatures. The chemistry occurring in dense clouds is rather complicated, involving thousands of reactions [78], and so I will confine myself to the most important reactions relevant to the present thesis.

In 1961 Martin et al. suggested that H$_3^+$ could play a significant role in the interstellar media [79]. 35 years later it was indeed detected in dense clouds [80] and later in diffuse clouds [81]. The formation of H$_3^+$ proceeds through the following chain of reactions [75]

$$\text{H}_2 \overset{CR}{\rightarrow} \text{H}_2^+ \quad (a),$$

$$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \quad (b),$$

where $CR$ represents a cosmic ray. Since H$_3^+$ does not react with H$_2$ under two-body conditions, it is either destroyed by DR or donates a proton to other atoms and/or molecules to form more complex molecules, so igniting a network of chemical reactions. The high reactivity of H$_3^+$ is due to the relatively low proton affinity of H$_2$. In dense interstellar clouds H$_3^+$ can react with oxygen atom and through the following sequence of reactions protonated water can be formed [75]:

$$\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2,$$

$$\text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ + \text{H},$$

$$\text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{H}. \quad (1.12)$$

The closed shell hydronium ion does not react further with the abundant H$_2$ but readily undergoes DR. The product distribution for this reaction is crucial for understanding the abundances of the oxygen containing molecules, i.e. if the OH+H+H channel is the most dominant then O$_2$ is the main repository of oxygen forming through the following reaction

$$\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}. \quad (1.13)$$

Conversely, if the H$_2$O+H channel dominates then water is the predominant sink for oxygen in the dense clouds [82]. It is noted that the search for interstellar O$_2$ from the ground was unsuccessful and only quite recently it has been detected by Odin satellite with the abundance of 5·10$^{-8}$ relative to H$_2$ [83]. Although the DR rate coefficient for H$_3$O$^+$ has been well established by the majority of experiments [22, 31, 84, 85], it was controversial which channel dominated in the fragmentation until quite recently when experiments at both CRYRING and ASTRID showed similar results and revealed that the OH+H+H channel occurs in $\approx$65 % of the DR events [85, 86].
In a similar fashion, atomic carbon interacts with $H_3^+$ and subsequently with $H_2$ producing $CH_5^+$ [75]

\[
H_3^+ + C \rightarrow CH^+ + H_2, \\
CH^+ + H_2 \rightarrow CH_2^+ + H, \\
CH_2^+ + H_2 \rightarrow CH_3^+ + H, \\
CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu.
\]

(1.14)

This ion also undergoes very efficient reaction with electrons. However, unlike the consensus achieved for the DR of $H_3O^+$, the various experimental studies have not yet converged on the value for the DR reaction rate. FALP measurement showed the rate coefficient at 300 K to be higher than $9 \times 10^{-7}$ cm$^3$s$^{-1}$ [84, 87], while results from CRYRING report it to be $2.8 \times 10^{-7}$ cm$^3$s$^{-1}$ [88].

Due to the relatively less versatile chemistry occurring in diffuse interstellar clouds, $H_3^+$ is predominantly destroyed by DR and, since the fractional ionisation in such regions ($10^{-4}$) is higher than that in dense clouds ($10^{-8}$-$10^{-9}$) [89], $H_3^+$ would be less abundant. However, the detection of $H_3^+$ with an abundance comparable to that in dense clouds was totally unexpected [81]. One of the possible reasons suggested for this observation was either that the cosmic-ray ionization rate in diffuse clouds is higher than previously thought or that the DR of $H_3^+$ is relatively slow [90]. The experimental values of the rate coefficient at that time were established to be $\approx 1.1 \times 10^{-7}$ cm$^3$s$^{-1}$ [91, 92]. However, Larsson et al. showed that the DR rate coefficient is also dependent on the rotational population, something which had not been expected to play a significant role due to the relatively small amounts of internal energy involved in such motion - as compared with vibrational energy [93], i.e. it could be that at interstellar clouds conditions the rate is quite slow, while at experimental conditions (>300 K) it is high. McCall et al. designed a supersonic expansion ion source to produce rotationally cold ions (20-60 K) and using such a source in the CRYRING storage ring, reported a DR rate constant which was only 40 % lower than for hot ions [46, 94]. Such a relatively high value led them to conclude that the ionisation rate in diffuse clouds is $10^{-15}$ s$^{-1}$ [94], while before it was believed to be $\approx 10^{-17}$ s$^{-1}$ [95]. It was suggested that there are large flux of low energy cosmic rays which do not have enough energy to penetrate the dense clouds but sufficient for diffuse clouds. However, this very important discovery is difficult to reconcile with the model predictions [77].

There has also been special interest in chemistry of deuterated molecules due to the large variety of such compounds detected in the interstellar medium [96]. The cosmic atomic ratio of $n[H]/n[D]$ is $10^5$, while the same ratio for molecular species is observed to be much lower [96]. This is explained by the fact that in chemical reactions the formation of deuterated species is more favourable, since they are energetically more preferred due to the lower zero point vibrational energy. Furthermore, some dense clouds undergo further development. Due to
gravity the clouds collapse into denser cores which can be as cold as 5 K and as
dense as $10^6$ cm$^{-3}$. Such a stage is known as a pre-stellar core. Due to the low
temperature, gas phase species (CO, O, H$_2$O etc.) are expected to accrete on
the dust grains and HD, which is the main repository for deuterons, is expected
to efficiently react to form H$_2$D$^+$, D$_2$H$^+$ and D$_3^+$:

$$H_3^+ + \text{HD} \rightarrow H_2D^+ + H_2,$$

$$H_2D^+ + \text{HD} \rightarrow D_2H^+ + H_2,$$  \hspace{1cm} (1.15)

$$D_2H^+ + H_2 \rightarrow D_3^+ + H_2.$$

Recent model calculations and observations have shown that in the pre-stellar
cores the abundance of H$_2$D$^+$ is comparable to that of D$_2$H$^+$\cite{97, 98}. The fact
that D$_3^+$ does not react further with HD implies that D$_3^+$ is more abundant than
H$_3^+$ in pre-stellar cores.\cite{98}.

1.5 DR in the terrestrial atmosphere

Due to the UV component of the sun’s radiation, ions are prevalent in the upper
layer of the terrestrial atmosphere known as the ionosphere. The ionosphere
plays a significant role in modern life since it ensures communication by radio
waves. Dependent on the local composition the ionosphere is divided into the
F, E and D layers. The highest layer, F, lies approximately 150 km above the
Earth’s surface. In this region, due to the relatively intense external radiation,
particles here are predominantly atomic ions, dominated by O$^+$ and N$^+$. In
the E layer (100-150 km), the decreased amount of ionising radiation, due to
absorption by particles in the F layer and the higher pressure, the NO$^+$ and
O$^+_2$ are the dominant molecular ions. It is believed that upon ionisation, the
most abundant molecule, nitrogen, N$_2$, reacts quickly to form oxygen containing
molecular ions\cite{99}, i.e.

$$N_2^+ + \text{O} \rightarrow \text{N} + \text{NO}^+, \hspace{1cm} (1.16)$$

$$N_2^+ + \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2^+.$$  

Due to the relatively high electron concentration ($10^3$-$10^5$ cm$^{-3}$), the value
varies between the day- and night-time, the DR reaction efficiently destroys
these molecular ions\cite{100, 101}. The D region (60-100 km) involves very rich
molecular-ion chemistry. Due to the low temperature and relatively high pres-
sure, cluster ions dominate in this region, the most relevant of these being
H$^+(\text{H}_2\text{O})_n$\cite{99, 102}. The formation of some type of cluster ions is only possi-
ble in ternary reactions that cannot occur at higher altitudes due to the lower
number density\cite{103}, e.g.

$$\text{O}_2^+ + \text{O}_2 + M \rightarrow \text{O}_4^+ + M.$$  \hspace{1cm} (1.17)
Experimental investigations have shown that clusters react very efficiently through DR with a rate coefficient $> 10^{-6}$ cm$^3$s$^{-1}$ [104, 105, 106, 107, 108]. Such unusually large rate coefficients was referred to as super-dissociative recombination [109]. In an attempt to explain the DR rate of H$^+$(H$_2$O)$_2$, Bates suggested that the reaction involves a single electron transition [109], i.e.

$$\text{H}^+(\text{H}_2\text{O})_2 + e \rightarrow \text{H}(\text{H}_2\text{O})_2 \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O}. \quad (1.18)$$

Indeed, as reported by Någård et al. at CRYRING, this channel almost exclusively dominates the DR of H$^+(\text{H}_2\text{O})_2$ [105].

In the region below 70-80 km, the number density of molecules is sufficiently larger such that electrons preferentially attach to neutral species to form negative ions. At these altitudes the DR reaction is no longer competitive and the positive ions are neutralised by mutual neutralisation [99].

Despite the relatively low abundance of ozone in the stratosphere it plays a crucial role in the absorption of energetic UV radiation (230-290 nm), otherwise life in its present form would not be possible on the Earth. The formation and destruction of ozone is governed by the following reactions

$$\text{O}_2 + h\nu \rightarrow \text{O} + \text{O},$$

$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}, \quad (1.19)$$

$$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}.$$

However, theoretical calculations underestimate the ozone concentration and are incapable of explaining the observed values and the discrepancy is even more significant for higher altitudes (> 70km) [111]. This problem is known in the literature as the “ozone deficit” and has led to a search for new sources of ozone and some solutions have been suggested [112, 113, 114, 115]. However, the ion chemistry of ozone has not been taken into account, even though ozone is also present in the lower layers of the ionosphere. In such regions ozone can be ionised [116], or, alternately, the cation can be formed through ion-neutral reactions [117], and very efficiently reacts with electrons.

At altitudes of about 100 km, due to the relatively low pressure, internally excited atoms and molecules are not efficiently collisionally quenched, and, therefore, excess energy is removed radiatively. Such emission is called airglow. The DR of the ionised oxygen molecule can create atomic fragments in different excited states, for examples O($^1S$) and O($^1D$) [118]. The spin-forbidden transition O($^1D$)→O($^3P_{1,2}$) with a decay time of $\approx$100 s is a source of red emission at 636.4 and 630.0 nm, respectively, while the transition O($^1S$)→O($^1D$) emits green light ($\tau \approx$1 s, 557.7 nm). Furthermore, the ozone cation can also fragment through the DR reaction to produce O($^1D$).

At altitudes of about 85-100 km there is a Na-belt with a peak concentration at 93 km [119]. It is believed that such a belt is present due to the meteor ablation. By means of the solar radiation sodium atoms can be either excited to $^2\text{P}$ state subsequently emitting yellow light, Na($^2P_{1/2,3/2}$)→Na($^2S$) ($\tau \approx$12
ns, 589.6 and 589.0 nm) or ionised. The latter, \( \text{Na}^+ \), can be efficiently clustered to water and then neutralised back to Na by DR, i.e

\[
\text{Na}^+ + \text{H}_2\text{O} + M \rightarrow \text{Na}^+ (\text{H}_2\text{O}) + M,
\]

\[
\text{Na}^+ (\text{H}_2\text{O}) + e \rightarrow \text{Na} + \text{H}_2\text{O}.
\]

This chain of reactions was suggested to be one of the routes for the formation of the sporadic Na layers, an abrupt increase of Na density at the altitudes between 90 and 150 km and which can last from few minutes to several hours [120, 121].
Chapter 2

Experimental set-up

2.1 CRYRING overview

The experimental investigation of the DR reactions reported here has been performed at the storage ring CRYRING located in Manne Siegbahn Laboratory, Stockholm. The ring functions as a synchrotron [122] and its name arises from an abbreviation of CRYogenic ion source at the storage RING. CRYRING was originally designed and developed for atomic physics experiments [123], but following the suggestion of Datz and Larsson its use was extended to molecular physics [47]. The ring itself is nearly circular with a circumference of 51.63 m and consists of twelve straight sections separated by dipole magnets to confine the beam. Every second section is equipped with focusing elements and others are used for experimental purposes, the most relevant of which contains an electron cooler. The ion-source platform used exclusively for creating the ions investigated in this thesis is the high-voltage MINIS platform, which can be equipped with a variety of ion sources, e.g. Nielsen, JIMIS and supersonic expansion ion sources, and these are explained in the next section. After the production the ions are mass analysed by a bending magnet located after the MINIS platform.

Figure 2.1: The storage ring CRYRING.
On the way to the ring the ions pass through the radio-frequency quadrupole (RFQ) which is used to pre-accelerate those ions which have charge-to-mass ratio of \( \geq 0.25 \) to an energy of 300 keV/amu. The acceptance energy of the RFQ is 10 keV/amu. As such, for heavier molecular ions for which RFQ cannot be used the MINIS platform voltage is usually 40 kV. After injection the ion beam is accelerated by a radio-frequency driven drift tube \([124]\) to the final beam energy, a value that is limited by the magnetic rigidity of the ring, \( B \cdot \rho \), as

\[
E_i = 48.25 \times \frac{q^2 (B \cdot \rho)^2}{M},
\]

where \( q \) is the ion charge state, \( M \) is the ion mass in amu units, \( B \) is the magnetic field in the dipole magnets \((B_{\text{max}}=1.2 \, \text{T})\) and \( \rho = 1.2 \, \text{m} \) is the bending radius. Prior to the experiment, and after full acceleration, the ion beam is usually stored for several seconds to ensure radiative decay of the active modes. During this time the electron cooler also provides a reduction in the phase-space occupied by the ions due to the Coulomb interaction of the ions with the cold continuously renewed electron beam. However, for heavy molecular ions, electron cooling is not efficient and would require a storage time which is much longer than the life time of the ion beam. For such molecular ions the electron cooler serves only as an electron target. The neutral fragments arising both from the DR reaction and background interactions leave the ring tangentially along the so-called zero-degree arm, which is equipped with various detection systems. A more detailed description of the most relevant parts of the ring follows.

### 2.2 Ion sources

#### 2.2.1 Nielsen ion source

A Nielsen type ion source has been used to produce the majority of the molecular ions studied in this thesis. This is a traditional hot filament ion source which was developed in 1957 \([125]\). The tantalum filament is heated up by the passage of electrical current such that it emits electrons. The filament temperature, depending on the current, can be as high as a few thousand K. Due to an applied electrical field the emitted electrons are accelerated to energies as high as a few hundred eV. Since the impact ionisation cross sections for molecules usually has a maximum at \( \approx 100 \, \text{eV} \), electrons efficiently ionise any vapour or gas introduced into the source chamber. A magnetic field \((10-30 \, \text{mT})\) is used to confine the plasma to the central part of the source chamber, which increases the ionisation efficiency. In some cases noble gases are also introduced into the source to ensure Penning ionisation for those molecules that have a lower ionisation energy than the buffer gas. This ion source is capable of producing high ion currents. However, it has disadvantages. 1) Due to the hot filament and relatively high electron energy, the ions that are produced are internally excited. For molecular ions with dipole moments, relaxation of the excited
states can be achieved by storing them in the ring for a few seconds. However, for molecular ions that have no dipole moment the quenching time can be very long, which requires the use of other kind of sources. 2) Oxygen containing molecules put constraints on the filament lifetime due to their corrosive nature - sputtering through oxidation. In such cases, the Nielsen type ion source can be also operated in high-voltage mode, i.e. the plasma is ignited by a short discharge pulse and filament is not used. This mode of operation was used to produce the ozone ion beam.

2.2.2 JIMIS ion source

The JIMIS ion source has been developed in order to solve the first of the disadvantages of the Nielsen type ion source just listed, i.e. to produce vibrationally cold ions. The plasma in such a source is ignited by a high-voltage discharge pulse of a few tens of ms across the gas present in the hollow cathode. Due to the relatively high pressure the ions are expected to collisionally thermalise. In order to keep the plasma cold, the ion source is cooled by water flowing through the hollow cathode. The first time that JIMIS was used at CRYRING was to create N$_2^+$. However, analysis of the reaction products revealed that complete vibrational relaxation of the parent ion was not totally achieved [126]. On the other hand, success was reported for O$_2^+$, which also has a zero dipole moment, and the ions extracted from the source were only in the vibrational ground state [118]. Despite its effectiveness in vibrational quenching, JIMIS produces rotationally excited ions and for H$_3$O$^+$ the rotational temperature was estimated to be about 2000 K [Paper X].

2.2.3 Supersonic expansion ion source

A supersonic expansion ion source has been used to produce rotationally cold H$_2^+$ ions with a rotational population described by a temperature of 20-60 K, a value that has been measured spectroscopically for H$_3^+$ ions [46]. The source involves expansion of a gas through a small nozzle (500 µm) from a region of high pressure (≈2 Torr) into vacuum (≈10$^{-6}$ Torr). A solenoid valve which is used to drive a poppet into and out of the nozzle - to allow sealing of the nozzle and pumping down - is used to create the gas pulse and the subsequent supersonic flow. The gas pulse length is ≈400 µs and upon expansion the gas is ionised by a DC voltage of >400 V. A grounded skimmer is used downstream in order to avoid off-axis flow as well as to reduce arcing - due to the high gas number density - between the ion source and extraction potential which is 20 kV for H$_2^+$ and 30 kV for H$_3^+$, respectively, values determined for acceptance into the RFQ pre-accelerator. This type of source is very efficient in cooling rotational motion while this is not the case for vibrational motion. For more detailed description of the supersonic jet see ref. [127].
2.3 Electron cooler and cooling effect

One of the straight sections of CRYRING contains an electron cooler, in which the ion beam is merged with a continuously renewed monoenergetic electron beam over a length of 0.85 m.

2.3.1 General description

![Figure 2.2: The CRYRING electron cooler.](image)

The electron cooler consists of an electron gun, a reservoir with liquid helium, a superconducting magnet, toroidal magnets, a guiding solenoid, and an electron collector (Fig. 2.2). The toroidal magnets are used to bend the electron beam into and out of the interaction region. The electron beam is produced by an electron gun cathode, which is 4 mm in diameter and situated in a strong magnetic field of about 3 T. Such a high magnetic field is achieved by the superconducting solenoid surrounding the electron gun, and which is continuously cooled by liquid helium. The velocity spread of the electrons immediately after emission from the cathode is determined by the cathode temperature \((kT_c \approx 0.1\) eV) and, therefore, the velocity distribution can be described in the lab frame by a Maxwellian distribution

\[
f(v) = \left(\frac{m_e}{2\pi kT_c}\right)^{3/2} \exp\left(\frac{m_e(v - v_e)^2}{2kT_c}\right),
\]

(2.2)
where $v_e$ is the electron velocity determined by the value of cathode voltage $U$, as

$$v_e = \sqrt{2Ue \over m_e}. \tag{2.3}$$

The magnetic field created by the guided solenoid in the interaction region is 0.03 T, while the electrons are produced in a field of 3 T. The reason behind such a steep drop in the magnetic field is to adiabatically expand the electron beam. The ratio of $kT_e/B$ has to remain constant [67], and so this adiabatic expansion results in a 100 times reduction of the electron velocity spread in the transverse direction to a value of about 2 meV. Due to the acceleration of the electrons by the cathode voltage, the longitudinal spread significantly shrinks. However, this spread is lower than the average potential interaction energy between the electrons and, therefore, the spread is mostly determined by “longitudinal-longitudinal” relaxation between electrons

$$kT_\parallel = {e^2 n_e^{1/3} \over 4\pi\epsilon_0}. \tag{2.4}$$

It was shown that such relaxation happens on the time scale comparable to the electron plasma frequency [128]. Another contribution to the longitudinal spread arises from the so-called “transverse-longitudinal” relaxation, i.e. since $kT_e|| < < kT_e\perp$ heat can be transferred from transverse to longitudinal component. It has been shown that such process is dependent on the strength of the guiding magnetic field and is more pronounced at smaller values. As a result of this, at 0.03 T such relaxation is insignificant [128]. Due to the different temperatures components of $kT_e|| = 0.1$ meV and $kT_e\perp = 2$ meV, the electron velocity distribution is now best described by an anisotropic Maxwellian distribution and for the case when electron and ion beams have the same average velocities, the distribution can be expressed by

$$f(v) = {m_e \over 2\pi kT_e\perp} \left( {m_e \over 2\pi kT_e||} \right)^{3/2} \exp \left( -{m_e v_\perp^2 \over 2kT_e\perp} - {m_e v_\parallel^2 \over 2kT_e||} \right). \tag{2.5}$$

### 2.3.2 Electron cooling

The term “electron cooler” derives from the effect of a reduction of the phase space occupied by the ions by means of their interaction with the cold electron beam. Such an effect, known as electron cooling, was first demonstrated in Novosibirsk, in the former Soviet Union [129, 130]. In 1990 Poth gave detailed explanation of this process in his review article [131]. The force underlying the electron cooling effect is the Coulomb attraction between the electrons and ions. The energy gained by the electron during the collision with the ion is [132]

$$\Delta E_{i\rightarrow e} = {2Z^2e^4 \over (4\pi\epsilon_0)^2 m_e e^2 b^2}. \tag{2.6}$$
where $b$ is the impact parameter, $Z$ is the charge state and $v$ is the relative electron-ion velocity. The ion energy loss per unit length can be found by integrating over all possible impact parameters

$$\frac{dE}{dx} = -2\pi \int_{b_{\text{min}}}^{b_{\text{max}}} \Delta E_{i\rightarrow e}(b)n_e b db = -F_0 \frac{e^2}{v^2} \ln \left(\frac{b_{\text{max}}}{b_{\text{min}}}\right),$$

(2.7)

where

$$F_0 = \frac{4\pi Z^2 e^4 n_e}{(4\pi\epsilon_0)^2 m_e c^2},$$

(2.8)

and $n_e$ is the electron density. The value of $b_{\text{min}}$ is found from the relation $(\Delta p)_{\text{max}} = 2m_e v$ to be

$$b_{\text{min}} = \frac{Zr_c c^2}{v^2},$$

(2.9)

where $r_c$ is the classical electron radius

$$r_c = \frac{e^2}{4\pi\epsilon_0 m_e c^2}.$$  

(2.10)

In order for energy to be transferred from an ion to electrons, the interaction time, $\approx b/v$, should be shorter than the electron oscillation period, $1/w_{pe}$, where $w_{pe}$ is the electron plasma frequency

$$w_{pe} = \sqrt{4\pi n_e r_c c^2},$$

(2.11)

which allows to determine $b_{\text{max}}$ as

$$b_{\text{max}} = \frac{v}{w_p}.$$

(2.12)

The value of $L_c = \ln(b_{\text{max}}/b_{\text{min}})$ is called the Coulomb integral and was shown to be $\approx 10$ [131]. Taking into account the electron thermal distribution in the electron cooler (Eq. 2.5), the cooling force can be expressed as

$$\mathbf{F}(v) = -F_0 e^2 \int L_c(v) f(v) \frac{v}{|v|^3} dv.$$  

(2.13)

It follows from Eq. 2.13 that the cooling force is inversely proportional to the interaction energy and reaches its maximum value when the average ion and electron velocities are equal. The case $v_i = v_e$ is referred to as the cooling condition. Eq. 2.13 has been derived without taking into account the weak solenoid magnetic field used in the electron cooler to prevent the electron beam from blowing up due to the electron-electron repulsion. However, it has been shown that this assumption is quite reliable and Eq. 2.13 adequately describes the measured drug force [133].
2.4 Detection systems

Since the neutral fragments arising from DR are not affected by the dipole magnet placed after the electron cooler they are separated from the ion beam and proceed along a straight line where they can then be detected. The detection of the DR products is accomplished in the so called 0\(^\circ\) (zero degree) arm located directly after the bending magnet and the electron cooler. Depending on experimental aim two principally different kinds of detection systems have been used; an energy-sensitive ion-implanted silicon detector (IISD) and a position-sensitive imaging detector (ID). The IISD is used for investigating the DR rate and the branching fractions, while the ID is used to study the internal excitation and dynamics of the DR products.

2.4.1 Energy-sensitive ion-implanted silicon detector

The silicon detector is used to analyse the energy of the DR products. It is an ion-implanted silicon crystal detector which has a very thin B-implanted entrance of ≈500 Å and functions as a \(p-n\) junction. A reverse bias voltage is applied (50 V) such that a depletion layer is created which is ≈500 \(\mu\)m thick. When a fast particle enters into this active volume, its energy is used to create electron-hole pairs. Since the ion-implanted entrance is very thin, the energy loss in this region is expected to be small, and so the majority of the particle’s kinetic energy is deposited into this active region. The higher the energy of the incoming particle the more electron-holes pairs that are created. A charge-sensitive preamplifier is used to create an output signal, which is then further amplified and shaped. The output pulse, which is typically ≈\(\mu\)s long and <10 V in amplitude, is therefore proportional to the energy of the incoming particle. The pulse length can be assumed to be the dead time of the detector. The amplified signal can be read out either by a multi-channel scaler (MCS) via a single channel analyser (SCA) or by a multi-channel analyser (MCA). The MCS records the number of counts within a short dwell time. The MCA is used to record the pulse-height spectrum showing the number of counts versus the particle energy.

The resolution of the signal is usually determined by its full width at half maximum (FWHM). The lower limit of the energy resolution is established by the electronic noise, which is independent of the particle energy and mass. The noise is determined by many factors, the most important of which are the detector leakage current and the noise generated from the preamplifier. However, the energy resolution depends also on statistical effects. The contribution from this factor can be expressed as

\[
\Delta E = 2.35\sqrt{wEF}, \tag{2.14}
\]

where the factor of 2.35 relates the difference between the standard deviation and the FWHM, \(w\) is the average energy required to produce one electron-hole pair (3.62 eV), \(E\) is the energy of the incoming particle and \(F\) is the Fano factor showing the deflection of a number of created electron-hole pairs from
When the Poisson statistics is applied then $F$ is equal to 1. It has been shown that in most cases the Fano factor can be assumed to be 0.1. Since $w$ is equal to 3.62 eV at room temperature, Eq. 2.14 can be written in eV units as

$$\Delta E = 1.41\sqrt{E},$$

(2.15)

The overall resolution of the signal, $\Delta E_s$, is determined by the noise, $\Delta N$, and statistical contributions, $\Delta E$, via the quadratic sum

$$\Delta E_s = \sqrt{(\Delta N)^2 + (\Delta E)^2},$$

(2.16)

For example, in the DR of $O^+_3$ the atomic oxygen products have $\approx 650$ keV kinetic energy, and the energy resolution due to the statistical effect should be 1.1 keV. However, the energy resolution was observed to be $\approx 100$ keV, meaning that it is the electrical noise which determines the detector energy resolution. Due to the relatively high electrical noise, fragments which either differ little in kinetic energy or have little kinetic energy themselves cannot be resolved. When the DR fragment is a molecule, then the resolution of the corresponding signal is summed in quadrature over the resolutions of the constituting atoms.

In the present study two ion-implanted silicon detectors with active areas of 900 and 3000 mm$^2$ have been used which are located $\approx 4$ m from the middle of the electron cooler. The larger detector is used when a higher fragment collection efficiency is required, but, on the other hand, due to the higher leakage current and higher junction capacitance, this detector generates more noise and therefore has lower energy resolution.

### 2.4.2 Position-sensitive imaging detector

The imaging detector used in the present study consists of a stack of three micro-channel plates (MCPs), a phosphor screen (PS, $\varnothing 77$ mm) and a CCD camera which has a photosensitive chip of $64 \times 64$ pixels with a size of $1.024 \times 1.024$ mm$^2$ (Fig. 2.3). The MCPs and PS are mounted in the internal vacuum ($<10^{-8}$ Torr) at the end station of the $0^\text{th}$ arm at a distance of $\approx 7$ m from the middle of the electron cooler. When a fast neutral fragment arising from the DR reaction hits the first MCP it gives rise to a cascade of secondary electrons ($\approx 10^3 e$) which is then amplified by the second and the third MCPs. The electron cloud emerging from the third MCP ($\approx 10^8 e$) induces a flash on the phosphor screen which is then detected by the CCD camera. The highest speed at which the CCD camera can operate is $\approx 2.6$ kHz and such mode of operation is called free-running mode. However, at such high speed the ID is more prone to monitor non-DR events. In order to eliminate spurious signals arising from false-coincidence events, thermal electrons on CCD and dark counts on the PS ($\approx 25$ Hz) the imaging detector operates in a “switch-off” mode. This mode of operation is accomplished by means of a fast image intensifier (II), which functions as a “shutter” for the CCD camera. The II consists of a photo cathode, an MCP and a phosphor screen ($\varnothing 25$mm). The image of the PS is projected on the II by means of two lenses (120 and 100 mm focal distances) and the image from the II is further...
CHAPTER 2. EXPERIMENTAL SET-UP

Figure 2.3: Position-sensitive imaging detector.

projected on the photosensitive chip of the CCD camera by a camera lens with focal distance of 50 mm. In order to ensure all particles from the same DR event to be detected, the II is switched off 200 ns after the first particle have been detected by a photomultiplier tube (PMT). The PMT is connected to the detecting system via a constant fraction discriminator (CFD) in order to create a NIM output pulse. The information stored in the CCD camera is read out by a frame grabber card, mounted in a personal computer, 40 \( \mu \text{s} \) after the detection of the first particle. Then a spot finding routine determines the position of the flash on the CCD chip. A veto signal blocks the PMT from false triggering until the frame grabber reads out the CCD frame. The veto signal determines the operation speed of the imaging detector, which constitutes typically about 500 Hz. The detection efficiency for one fragment was determined to be 0.6, which is mostly due to the open area ratio on of the MCPs [134]. Such an ID operates as a two-dimensional detector. The 3D detection system, providing additionally the time information, has also been introduced [73]. Since DR happens randomly at any point of the electron cooler and at any time, it is not possible to measure directly the time-of-flight of the fragments and, instead, the relative arrival times between the products arising from the same DR event are recorded. Due to the relatively low time resolution, the 3D measurements provide a little additional information in comparison with 2D for investigation of the three-body break-up and the data acquisition time is much longer [66]. As such, 3D imaging has not been performed in the present study.
Chapter 3

Data evaluation

3.1 Interaction energy

In the general case the interaction energy between an electron and ion is presented as a sum of their kinetic energies in the centre-of-mass (c.m.) frame which is determined by

\[ E_{cm} = \frac{\mu v^2}{2}, \]  (3.1)

where \( \mu \) is the reduced mass of the particles

\[ \mu = \frac{m_e M_i}{m_e + M_i}, \]  (3.2)

and \( v \) is their relative velocity. Since \( M_i \gg m_e \), the reduced mass equals the electron mass and the c.m. is located on the ion. As such, \( E_{cm} \) can be viewed as the kinetic energy of the electron moving in the ion frame. When the velocities of the electron and the ion are collinear then

\[ \sqrt{E_{cm}} = \left| \sqrt{\frac{m_e v_e^2}{2}} - \sqrt{\frac{m_i v_i^2}{2}} \right|. \]  (3.3)

This expression for the interaction energy in eV units can be directly expressed via experimental quantities as

\[ \sqrt{E_d} = \left| \sqrt{U} - \sqrt{U_{cool}} \right|, \]  (3.4)

where \( U \) is the electron cooler cathode voltage and “cool” stands for the case when \( v_e = v_i \). Eq. 3.4 implies that in order to vary the interaction energy at CRYRING the cathode voltage is detuned away from the value corresponding to the cooling conditions, therefore such interaction energy is called detuning. Since the electron and ion energies in the lab frame are much higher than their
spread in energy, $E_{i,e} \gg \Delta E_{i,e}$, such spreads do not influence on the value of $E_d$. As a result of this, the detuning velocity,

$$v_d = \sqrt{\frac{2E_d}{m_e}}, \quad (3.5)$$

corresponds to the relative electron-ion velocity when the energy spreads are not taken into account. Since the ion and electron beams are collinear, $v_d$ can be viewed as the difference between the beam velocities in the longitudinal direction. When $v_d \neq 0$, the electron distribution in the ion (or c.m.) frame can be written as

$$f(v, v_d) = \frac{m_e}{2\pi kT_{e,\perp}} \left( \frac{m_e}{2\pi kT_{e,||}} \right)^{\frac{1}{2}} \exp \left( -\frac{m_e v_\perp^2}{2kT_{e,\perp}} - \frac{m_e (v_|| - v_d)^2}{2kT_{e,||}} \right). \quad (3.6)$$

From Eq. 3.6 it follows that the Maxwellian distribution corresponds to a particular value of $E_d$ and only when the thermal spread is negligible the detuning energy is equal to $E_{cm}$. The deviation of $E_d$ from $E_{cm}$ can be estimated as

$$\Delta E = E_{cm} - E_d. \quad (3.7)$$

If $v_||$ and $v_\perp$ are components of the electron velocities determined by the longitudinal and transverse thermal energy spreads, then

$$E_{cm} = \frac{m_e (v_|| \pm v_d)^2}{2} + \frac{m_e v_\perp^2}{2}. \quad (3.8)$$

Taking into account that $\frac{1}{2}kT$ corresponds to one translational degree of freedom, Eq. 3.7 and Eq. 3.8 can be expressed by

$$\Delta E = \frac{1}{2}kT_|| + kT_\perp \pm \sqrt{2E_d kT_||}. \quad (3.9)$$

At small interaction energies the difference is predominantly determined by the transverse electron temperature, since $kT_|| \ll kT_\perp$, while for higher energies the longitudinal temperature starts to play a role.

### 3.2 Cross section and rate coefficient

If we have a flux of particles $nv$ and there is an obstacle in the path with a geometrical cross section of $\sigma$, then the number of particles encountering this obstacle per unit time is

$$\frac{dN}{dt} = \sigma nv. \quad (3.10)$$

In the example of the DR reaction, this can be viewed simply that there is a flux of electrons, $n_e v$, which encounter $N_i$ identical molecular ions, such that $v$ is the electron velocity in the ion frame, then the DR count rate, $dN/dt$, is proportional to the “cross section of the ion” as $\sigma n_e v N_i$, i.e. the larger the
cross section, the DR count rate is higher. However, the cross section in this case should not be regarded literally as a geometrical size of the ion, but should be understood as a probability of the DR reaction to occur, despite the fact that it is described by units of area.

Another important parameter describing the speed of reaction is the rate coefficient, $\alpha$, which is a constant of proportionality in the rate equation

$$\frac{dn_i}{dt} = -\alpha n_e n_i,$$  \hspace{1cm} (3.11)

where $n_i$ is the ion concentration. Taking into account that

$$\frac{dN_i}{dt} = -\frac{dN}{dt},$$  \hspace{1cm} (3.12)

then according to Eq. 3.10 and Eq. 3.11 the relation between the reaction cross section and rate coefficient is

$$\alpha = \sigma v.$$  \hspace{1cm} (3.13)

Due to the thermal spread of the electrons in the electron cooler, the measured rate coefficient is a velocity weighted cross section averaged over the anisotropic Maxwellian distribution (Eq. 3.6)

$$\alpha = \langle v \sigma \rangle = \int v \sigma f(v, v_d) d^3v, \hspace{0.5cm} d^3v = 2\pi v_\perp dv_\perp dv_{||}. \hspace{1cm} (3.14)$$

The electron density and number of ions in the interaction region can be expressed via measured quantities as

$$n_e = \frac{I_e}{e v_e \pi r_e^2}, \hspace{0.5cm} N_i = \frac{I_i l}{e v_i}, \hspace{1cm} (3.15)$$

where $I_i$ and $I_e$ are the ion and electron currents, respectively, $v_i$ and $v_e$ are ion and electron velocities in the lab frame, $r_e$ is the electron beam radius and $l$ is the length of the interaction region. Then the rate coefficient can be calculated as

$$\alpha = \langle v \sigma \rangle = \frac{dN}{dt} \frac{1}{n_e N_i v} = \frac{dN}{dt} \frac{v_e v_i e^2 \pi r_e^2}{I_e I_i} l. \hspace{1cm} (3.16)$$

If it is assumed that $kT_{e||}=0$ and cross section is described by

$$\sigma = \frac{C}{E},$$  \hspace{1cm} (3.17)

then the rate coefficient (Eq. 3.14) can be evaluated analytically as

$$\alpha(E_d) = \sqrt{\frac{2\pi}{m_e kT_{e\perp}}} C \exp \frac{E_d}{kT_{e\perp}} \text{erfc} \sqrt{\frac{E_d}{kT_{e\perp}}}. \hspace{1cm} (3.18)$$
In order to measure the DR count rate as a function of interaction energy the electron cooler cathode voltage ramp method is used. Here, the voltage on the electron gun cathode is changed linearly, usually from a value corresponding to when the electrons are faster than the ions, and then the voltage is decreased until the electrons are slower than the ions (Fig. 3.1(a)). Such a method makes data acquisition relatively fast and data are acquired over a broad range of interaction energies within one cycle. The DR count rate is continuously monitored by an MCS card with a short dwell time (≈ms). At the voltage when the beam energies are equal, the count rate reaches its maximum value, which can be used as a tool for a search of the cooling conditions (Fig. 3.1(b)). The rate coefficient is evaluated from the measured count rate using Eq. 3.16. The electron velocity is determined by the value of the cathode voltage (Eq. 2.3) and the electron current is measured at the electron cooler collector after the electrons have been guided out of the interaction region. The ion velocity is calculated from the ion beam frequency, \( f_i \), and the circumference of CRYRING, \( L=51.63 \) m, as

\[
v_i = f_i \cdot L.
\]
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The absolute current measurement is made by an AC transformer at the end of the ion beam acceleration when the beam is still bunched. The destruction of the ion beam, due to its interaction with residual gas in the ring and the DR reaction, is monitored by an MCP detector placed at the end of one of the straight sections of the ring. The count rate of neutral fragments recorded by the MCP detector is

$$\left( \frac{dN}{dt} \right)_{bg} = const \times \exp \left( -\frac{t}{\tau} \right),$$

(3.20)

and

$$\frac{1}{\tau} = \frac{1}{\tau_{rg}} + \frac{1}{\tau_{DR}},$$

(3.21)

where $\tau_{rg}$ is the beam lifetime determined only by the beam interaction with the residual gas and

$$\frac{1}{\tau_{DR}} = \alpha n_e \frac{l}{L}.$$  

(3.22)

Since the ion current is proportional to the beam destruction rate, the latter can be used as a measure of the relative ion current, an absolute value that can be obtained by normalisation to the transformer value. This technique allows the absolute ion current to be measured during the whole cycle. Since the electron beam is 100 times adiabatically expanded, the electron beam radius is one order of magnitude larger than the cathode radius, i.e. $r_e=2$ cm.

3.2.2 Corrections

Due to experimental constraints the direct measurements of the rate coefficient does not lead to the absolute values and in order to retrieve them some corrections to the measured data have to be made.

Background correction

Despite the ultra-high vacuum in the ring, neutral fragments can also be formed in the electron cooler due to interaction of the ions with the residual gas. One such type of interaction is charge transfer from a residual gas particle to the ion which gives rise to the neutral fragments with the same overall mass as that of the ion. As such, these events contribute to the measured count rate. It was shown that at 1 eV interaction energy the DR rate coefficient is vanishingly small and the count rate is predominantly due to these non-DR events [70]. The background signal measured by the MCP detector is normalised to the count rates taken at $>1$ eV interaction energy and subtracted from the total spectrum obtained during the ramp (Fig. 3.1(b)). This correction is more important for heavier ions, since they have lower beam energies and therefore higher probability to interact with the residual gas.
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Space-charge correction

Due to the repulsive force between electrons, a magnetic field is used in the electron cooler to prevent the electron beam from blowing up and also to create the homogeneous cylindrical shape of the beam. Furthermore, the electrons, being charged particles, create a potential, i.e. the electrons move in the self induced electrical field which has a tendency to decelerate them. Using Gauss’ law, which states that the electric flux outside a closed surface equals to the charge enclosed by this surface divided by the permittivity, \( \epsilon_0 \), the electron induced electrical field can be calculated inside and outside the electron beam. Assuming that the charge is uniformly distributed with density of \( \rho_e \), due to the cylindrical nature of the interaction region the induced field inside the beam depends only on the distance from the beam axis, \( r \), as

\[
E(r) = \frac{\rho_e}{2\epsilon_0} r, \quad r < r_e. \tag{3.23}
\]

Since the ion beam is confined in a grounded pipe with radius of \( r_b=5 \text{ cm} \), according to Gauss’ law the electrical field outside the beam is

\[
E(r) = \frac{\rho_e}{2\epsilon_0} \frac{r_e^2}{r}, \quad r_e > r > r_b. \tag{3.24}
\]

The space charge potential can be found by integrating over the electrical field as

\[
U_{sp}(r) = \frac{\rho_e r_e^2}{4\epsilon_0} \left( 1 + 2\ln \left( \frac{r_b}{r_e} \right) - \left( \frac{r}{r_e} \right)^2 \right). \tag{3.25}
\]

The absolute value of the space charge potential has the highest value in the middle of the electron beam and decreases radially. Assuming efficient electron cooling, the position of the ion beam inside the electron beam is close to \( r\approx0 \) and, as such, the true electron energy in eV units can be found as

\[
E_e = U_{cath} - \frac{I_e m_e v_e^2}{v_e e^2} \left( 1 + 2 \ln \left( \frac{r_b}{r_e} \right) \right). \tag{3.26}
\]

However, due to the presence of the residual gas in the electron cooler which is mostly \( \text{H}_2 \), the space charge potential can be partly compensated due to the trapped positive ions, i.e. the electrons have enough energy to ionise residual gas molecules and due to the attraction force such ionised species can be trapped inside the electron beam. Such effects can be taken into account by

\[
U_{sp} = (1 - A\sigma(v_e)) \frac{I_e m_e v_e c^2}{v_e e^2} \left( 1 + 2 \ln \left( \frac{r_b}{r_e} \right) \right), \tag{3.27}
\]

where \( A \) is a scaling parameter and \( \sigma(v_e) \) is the electron-impact ionization cross section for molecular hydrogen. The parameter \( A \) can be determined from cooling conditions when \( v_i=v_e \), i.e.

\[
A = \frac{1}{\sigma(f_i L)} \left[ 1 - \sqrt{\frac{U_{cool}}{U_{true(cool)}}} \right], \tag{3.28}
\]
Figure 3.2: a) The electron cooler cathode voltage ramp. b) The change in the ion beam energy of $\text{H}_2^+$ during the ramp. Initial ion beam energy is 8 MeV and $I_e=30$ mA.

where
\[
const = \frac{I_e r_c m_e c^2}{\sqrt{2} m_e e^2} \left( 1 + 2 \ln \left( \frac{r_b}{r_e} \right) \right),
\]  
(3.29)

and
\[
U_{\text{true(cool)}} = \frac{m_e (f_i L)^2}{2e}.
\]  
(3.30)

Space-charge correction has impact on both the interaction energy scale and on the value of the measured rate coefficient.

**Drag force correction**

Due to the attraction force between the positive ion beam and the negative electron beam, the ion beam has a tendency to be attracted towards the electron beam when $v_d \neq 0$. This effect is known as beam dragging. During the cathode voltage ramp, if the drag force is quite substantial the interaction energy scale is shifted. As a result of this, for a structured cross section, the positions of the resonances are changed. Following the suggestion given in ref. [135] the ion velocity change during the ramp can be found from the second Newton Law as

\[
\frac{dv_i}{dt} = \eta \frac{l}{M_i L} F_{||}(t),
\]  
(3.31)
where $F_{||}$ is the longitudinal component of the cooling force (Eq. 2.13). $\eta$ is a scaling parameter which is introduced to take into consideration uncertainties in the electron temperature and the interaction length. However, in most cases it is assumed to be $\approx 1$. The dragging effect is dependent on many parameters such as the electron density, the electron beam temperature, the detuning velocity between the beams and the ion mass. The result of calculation of the ion beam velocity during the ramp in the DR of $H_2^+$ is shown in Fig. 3.2. The calculations indicate that during the ramp the ion beam can gain up to 4.6 keV.

![figure showing change of interaction energy](image)

Figure 3.3: Change of the interaction energy due to the dragging of the ion beam for two cases when the electrons are faster than the ions (a) and vice versa (b).

During the interaction energy scan the $E_d$ is changed both due to the variation in the electron and ion beam energies caused by the cathode voltage ramp and by the drag force, respectively. The variation arising solely from the drag force is

$$
\frac{dE_d}{dt} = \begin{cases} 
- \frac{m_e}{M_i} \sqrt{\frac{E_d}{E_i}} \frac{dE_i}{dt}, & v_e > v_i, \\
\sqrt{\frac{m_e}{M_i}} \frac{E_d}{E_i} \frac{dE_i}{dt}, & v_e < v_i.
\end{cases}
$$

(3.32)

From Fig. 3.3 it follows that the drag force acts in the direction to minimise the interaction energy ($dE_d/dt < 0$), i.e. to make the electron and ion beam velocities equal, and the drag (cooling) force is strongest at energies comparable to the electron thermal spread ($\approx 2$ meV). The $dE_d/dt$ dependence implies that the drag force correction is only significant for sub-meV interaction energy range. For other heavier ions studied in the thesis, this correction is even less important.
This effect is more significant for highly charged atoms, since the ion beam energy is high which leads to higher electron densities, and the force itself is proportional to charge state.

**Toroidal correction**

Due to the fact that the electrons are deflected into and out of the interaction region in the electron cooler by the toroidal magnets the electron and ion velocities are not collinear over a distance of $2 \times 25.5$ cm and DR in these regions occurs at higher interaction energies. The difference between the collision energy in the straight section of the electron cooler, $E_d$, and in the bending regions, $E(x)$, can be expressed as

$$E(x) = E_d + m_e v_e v_i (1 - \cos \theta(x)),$$

where $\theta(x)$ is the angle between the ion and electron velocity vectors versus the position in the toroidal region in cm units which has been measured according to the direction of the guided magnetic field to be

$$\theta(x) [\text{rad}] = 0.75638 \left(1 - \frac{1}{1 + \left(\frac{x}{51.3776}\right)^{2.3527}}\right).$$

The toroidal regions contribute to the measured rate coefficient from the DR events occurring at higher interaction energies and the contribution can be taken into account as

$$\frac{dN}{dt} = S n_i n_e \left[ \alpha(E_d)l + 2 \int_0^{25.5} \alpha(E(x))dx \right],$$

where $n_i$ and $n_e$ are the ion and electron densities, $S$ is the overlap between the beams and $l$ is the length of the straight part of the interaction region. The rate coefficient can then be found via an iterative procedure as

$$\alpha_n = \alpha_0 - \frac{2}{l} \int_0^{25.5} \alpha_{n-1}(E(x))dx,$$

where $\alpha_0$ is the measured rate coefficient.

**Electron energy spread correction**

The thermal energy spread of the electrons affects the values of the measured rate coefficient at interaction energies comparable to this spread. As such, the measured rate coefficient is usually called the effective rate, $\alpha_{eff}$, and is then related to the absolute rate coefficient, $\alpha_{abs}$ through Eq. 3.14, where $\nu\sigma=\alpha_{abs}$. Since $\alpha_{abs}$ is the integrated function in the two-dimensional integral, its extraction is not straightforward. In order to make it feasible, the assumption
of $kT_e || = 0$ is made which is quite reliable since $kT_e || < kT_e \perp$ and the behaviour of $\alpha_{eff}$ for small $E_d$ is mostly determined by the larger transverse energy spread. With such an assumption the c.m. energy is determined by

$$E_{cm} = E_d + E_\perp,$$  \hspace{1cm} (3.37)

where $E_\perp$ is the transverse energy spread. Eq. 3.14 is then written as

$$\alpha_{eff}(E_d) = \frac{1}{kT_e \perp} \int_0^\infty \alpha_{abs}(E_d + E_\perp) \exp \left( -\frac{E_\perp}{kT_e \perp} \right) dE_\perp =$$

$$[E_{cm} = E_d + E_\perp] = \frac{1}{kT_e \perp} \int_{E_d}^\infty \alpha_{abs}(E_{cm}) \exp \left( -\frac{E_{cm} - E_d}{kT_e \perp} \right) dE_{cm} =$$  \hspace{1cm} (3.38)

$$\frac{1}{kT_e \perp} \int_0^\infty \alpha_{abs}(E_{cm} + E_d) \exp \left( -\frac{E_{cm}}{kT_e \perp} \right) dE_{cm}.$$  

The latter equation is performed in the form of correlation integral

$$g \circ f = \int g(E_{cm} + E_d)f(E_{cm})dE_{cm},$$  \hspace{1cm} (3.39)

where $g$ is the measured rate coefficient and the second function is

$$f = \begin{cases} 
0, & E_{cm} < 0 \\
\frac{1}{kT_e \perp} \exp \left( -\frac{E_{cm}}{kT_e \perp} \right), & E_{cm} > 0 \end{cases}$$  \hspace{1cm} (3.40)

The correlation theorem states that the Fourier transform of a correlation integral is equal to the product of the complex conjugate of the Fourier transform of function $f$ and the Fourier transform of the second function. Therefore, the $\alpha_{abs}$ can be retrieved as

$$\alpha_{abs} = F^{-1} \left( \frac{F(\alpha_{eff})}{F^\ast(f)} \right),$$  \hspace{1cm} (3.41)

where $F$ and $F^{-1}$ are Fourier and inverse Fourier transforms, respectively. Such a deconvolution procedure results in the absolute rate coefficient versus $E_{cm}$. The absolute cross section is obtained from the ratio of $\alpha_{abs}$ and $v_{cm}$. The disadvantage of this approach is that it is very sensitive to spreads in the measured data, and if the statistics are relatively poor this method can retrieve artificial structures. On the other hand, in order to reduce statistical dispersion in the measured data, the assumption can be made that the rate coefficient is a smooth function of the interaction energy which enables a statistically averaging procedure to be used.
Another method of finding the absolute cross sections can also be applied. It is reasonable to assume that the cross section can be described by

\[ \sigma = \frac{C}{E^n}. \]  

(3.42)

Indeed, it has been observed that Eq. 3.42 adequately describes cross sections for many polyatomic molecular ions. However, for simpler molecular ions such as \( \text{H}_2^+, \text{HeH}^+ \) and \( \text{H}_3^+ \) this assumption is not valid since the cross sections have been observed to be more complicated than can be simply described by a power law [46, 136, 137], [Paper VI]. In order to find \( C \) and \( n \) coefficients, the cross section can be folded as \( \int \sigma v f(v, v_d) dv \) until the best match to the measured rate coefficient is found (Fig. 3.5).

### 3.3 Thermal rate coefficient

For some applications the thermal rate coefficient is required. In order to obtain this, the derived absolute cross section is folded with an isotropic Maxwellian distribution as

\[ \alpha(T_e) = \left( \frac{m_e}{2\pi k T_e} \right)^{\frac{3}{2}} \int v \sigma(v) \exp\left( -\frac{m_e v^2}{2k T_e} \right) 4\pi v^2 dv. \]  

(3.43)
Figure 3.5: The measured rate coefficient for DR of $\text{N}_3^+$ is shown by solid squares with statistical error bars. The power function is folded according to Eq. 3.14 is depicted by the solid line.

The latter equation is more often expressed as

$$\alpha(T_e) = \frac{8\pi m_e}{(2\pi m_e kT_e)^{\frac{3}{2}}} \int E\sigma(E) \exp \left( -\frac{E}{kT_e} \right) dE.$$ (3.44)

However, direct application of the obtained result in some cases is not appropriate. For steady-state plasmas in which the equilibrium has been achieved, e.g. interstellar space, the ion temperature equals the electron temperature, while the present results imply the dependency only on the electron temperature. For molecular ions with dipole moment it is reasonable to assume that molecular ion beam is in equilibrium with the black-body radiation at 300 K, which mostly effects only the rotational distribution. However, for molecular ions with no dipole moment, the ion temperature is usually determined by the conditions in the ion source, i.e. due to the “transparency” of ions to the ambient thermal radiation the ions internal population is not varied during the measurement. However, as it was demonstrated at TSR, the ion temperature can be manipulated by the conditions in the electron cooler [138]. In such cases, the ions are merged with very cold electron beam and such interaction can change the ion temperature.

If the measured cross section can be described by the expression presented
in Eq. 3.42, then Eq. 3.44 can be evaluated analytically as

$$\alpha(T_e) = Ce^n \sqrt{\frac{8}{\pi m_e}} \Gamma(2-n)(kT_e)^{\frac{1}{2}-n},$$

(3.45)

where $\Gamma$ is the gamma-function.

### 3.4 Branching fractions

From the DR reaction of polyatomic molecular ions different sets of neutral products can be produced. In order to be able to measure the branching fractions a grid technique is applied at CRYRING [44, 85]. The need for such a technique is motivated by the fact that the IISD is not fast enough to detect individually each of the fragments arising from the same channel. The grid which is a 50 $\mu$m thick stainless steel foil with a transmission of $t = 0.297 \pm 0.015$ ($3\sigma$ level confidence) is mounted in front of the IISD. The intensities of the measured products can then be related to the branching fractions through the grid transmission. As an example, consider the DR of $XY_2^+$ with the following open channels

$$XY_2^+ + e \rightarrow \begin{cases} X + Y + Y & (\alpha) \\ X + Y_2 & (\beta) \\ XY + Y & (\gamma) \end{cases}.$$  

(3.46)

Each fragment has a probability of either $t$ to be detected or $(1-t)$ to be stopped by the grid. Similarly, for two-body break-up, the probabilities of $t^2$, $t(1-t)$ and $(1-t)^2$ correspond to the cases when both fragments are detected, when one of the fragments is detected and another is stopped, and when both are stopped, respectively. As such, the intensities of each combination of the fragments can be related to the channel intensities through a set of linear equations

$$\begin{bmatrix} P_X \\ P_Y \\ P_{X+Y} \\ P_{Y+Y} \end{bmatrix} = \begin{bmatrix} t(1-t)^2 & t(1-t) & 0 \\ 2t(1-t)^2 & 0 & t(1-t) \\ 2t^2(1-t) & 0 & t(1-t) \\ t^2(1-t) & t(1-t) & 0 \end{bmatrix} \times \begin{bmatrix} N_\alpha \\ N_\beta \\ N_\gamma \end{bmatrix},$$

(3.47)

where $P$ and $N$ are used to denote the number of counts of the detected fragments and channel intensities, respectively. The intensities of the fragments are monitored by the MCA recording the pulse-height spectrum in which the fragments are identified according to their energies, i.e. the heavier fragment, the more energy it has

$$E_n = \frac{m_n}{M_i} E_i,$$

(3.48)

where $m_n$ and $E_n$ are mass of the fragments passed through the grid and their total kinetic energy, respectively. A typical pulse-height spectrum taken at $\approx 0$ eV interaction energy in the DR of $D_2H^+$ is shown in Fig. 3.6(a). However, the background events originating from interaction of the ion beam with the
residual gas in the ring can also contribute to the spectrum. In order to take into account such contributions a spectrum is also recorded at 1 eV interaction energy (Fig. 3.6(b)) since the DR rate at such energy is vanishingly small and the signals are dominated by the background events [70]. Since the ion beam intensity is proportional to the beam destruction rate, two spectra can be normalised according to the total number of background events recorded by the MCP detector during the whole time of measurements. The pure DR spectrum is then obtained by subtracting the background pulse-height spectrum from the spectrum recorded at \( \approx 0 \) eV interaction energy (Fig. 3.6(c)). Finally the branching fractions are determined by normalisation of the channel intensities

\[
N_{\alpha,\beta,\gamma} = \frac{N_{\alpha,\beta,\gamma}}{N_{\alpha} + N_{\beta} + N_{\gamma}}.
\]

In some cases, and this is the case for \( \text{D}_2\text{H}^+ \), the system of equations can be over determined. In this situation the solution can be found by a least-square fit or by combining some of the equations.

Due to the geometrical size of the detector, some energetic fragments can miss the detector and are not detected. For instance, if the Y fragments produced in the \( \text{XY}+\text{Y} \) channel miss the detector with a probability of \( M \), Eq. 3.47
is transformed into
\[
\begin{bmatrix}
P_X \\
P_Y \\
P_{X+Y} \\
P_{Y+Y}
\end{bmatrix} =
\begin{bmatrix}
t(1-t)^2 & t(1-t) & 0 \\
2t(1-t)^2 & 0 & t(1-t)(1-M) \\
2t^2(1-t) & 0 & t(1-t) + t^2M \\
t^2(1-t) & t(1-t) & 0 \\
t^2 & t^2(1-M) & 
\end{bmatrix}
\begin{bmatrix}
P_X \\
P_Y \\
P_{X+Y} \\
P_{Y+Y}
\end{bmatrix}
\times
\begin{bmatrix}
N_\alpha \\
N_\beta \\
N_\gamma
\end{bmatrix},
\]
(3.50)

If such a loss factor cannot be found, in the over determined system of the equations it can be regarded as an additional unknown value.

Due to the limitations in the resolution of the detector, in some cases the peaks in the pulse-height spectrum corresponding to the close masses are not resolved. The peaks can in some cases be identified using fitting procedures assuming a Gaussian shape of the signals arising from the detector [139, 140]. In other cases, isotope substitution can be used instead leading to an increase in the separation of the peaks due to the increased mass difference. Usually, there is no isotope effect in the branching fraction values, though some observations have been reported [141, 142]. Another constraint for the branching measurement arises from an electrical noise generated in the detector, which in some cases does not allow low energy fragments to be detected.

### 3.5 Evaluation of imaging data

#### 3.5.1 Two-body break-up

![Diagram of two-body break-up](image)

Figure 3.7: The separation between the fragments on the ID arising from the two-body break-up with KER₂ > KER₁.

Due to the two-dimensionality of the ID and the random orientation of the
molecular axis in the space, a whole range of the projected distances between the fragments on the MCPs, \( R \), corresponds to a particular two-body channel. The value of \( R \) is determined only by the angle between the beam and molecular axes (Fig. 3.7)

\[
R = R_{\text{max}} \sin \theta, \quad (3.51)
\]

where

\[
R_{\text{max}} = \sqrt{\frac{\text{KER} M_i}{E_i \mu}} D, \quad (3.52)
\]

where \( \text{KER} \) is the kinetic energy released, \( E_i \) is the beam energy, \( M_i \) is the ion mass, \( \mu \) is the reduced mass of the fragments and \( D \) is the distance from the middle of interaction region to the MCPs. In the general case the distance distribution can be written as

\[
w(R) = P(\cos \theta) \sin \theta \frac{d\theta}{dR}. \quad (3.53)
\]

An isotropic distribution, i.e. when \( P(\cos \theta)=1 \), is found to be

\[
w(R) = \frac{R}{R_{\text{max}}^2 \sqrt{1 - \left( \frac{R}{R_{\text{max}}} \right)^2}}. \quad (3.54)
\]

It is also necessary to take into account the electron cooler length, since DR can occur at any point of the interaction region, i.e.

\[
w(d) = \frac{1}{7} \int_{D-l/2}^{D+l/2} \frac{R}{R_{\text{max}}^2 \sqrt{1 - \left( \frac{R}{R_{\text{max}}} \right)^2}} dD =
\]

\[
\frac{1}{R_{\text{max}1} - R_{\text{max}2}} \left( \arcsin \left( \frac{R}{R_{\text{max}1}} \right) - \arcsin \left( \frac{R}{R_{\text{max}2}} \right) \right), \quad (3.55)
\]

where \( R_{\text{max}1} \) and \( R_{\text{max}2} \) are found from Eq. 3.52 where \( D \) is replaced by \( D-l/2 \) and \( D+l/2 \). The obtained distribution (Eq. 3.55) has been derived assuming that the molecule has no preferred directions to dissociate, which is usually observed to be the case for the DR reaction occurring at \( \approx 0 \) eV interaction energy. However, for non-zero collisions, the break-up can show anisotropic behaviour. In this case \( P(\cos \theta) \) is no longer constant and, due to the axial symmetry of the interaction region, this function can be expanded in terms of Legendre polynomials, \( p_k \),

\[
P(\cos \theta) = \sum_{k=0}^{\infty} a_k p_k(\cos \theta), \quad (3.56)
\]

where

\[
p_k(x) = \frac{1}{2^k k!} \frac{d^k}{dx^k} (x^2 - 1)^k. \quad (3.57)
\]
Taking into account the first three terms only the angular distribution can be written as
\begin{equation}
P(\cos \theta) = 1 + \frac{a_2}{2} (3 \cos^2 \theta - 1).
\end{equation}

If \(a_2=0\) then the resulting distribution is isotropic. Since \(P(\cos \theta) \geq 0\), the parameter \(a_2\) can vary from -1 to 2. The extreme cases correspond to
\begin{equation}
P(\cos \theta) = \begin{cases} 
3 \sin^2 \theta, & a_2 = -1, \quad \text{(a)}, \\
3 \cos^2 \theta, & a_2 = 2 \quad \text{(b)}. 
\end{cases}
\end{equation}

Eq. 3.59(a) implies that dissociation predominantly occurs in the detector plane, since \(\sin^2 \theta\) has a peak at \(\pi/2\). Similarly, Eq. 3.59(b) corresponds to perpendicular dissociation with respect to the detector surface (Fig. 3.8).

### 3.5.2 Homonuclear three-body break-up

In contrast to two-body break-up, a description of three-body break-up is more complicated. To the best of the author’s knowledge analytic functions describing the distance distributions arising from three-body break-up do not exist. A
Monte-Carlo simulation has been developed in order to simulate the break-up. In the general case, three velocity vectors of the fragments can be determined in one plane as shown in Fig. 3.9(a). The components of the momenta can be defined by means of the conservation laws of energy and momentum

\[ m_1 v_1^2 + m_2 v_2^2 + m_3 v_3^2 = 2K_E R, \]

\[ OX : \quad m_1 v_1 + m_2 v_2 \cos \alpha + m_3 v_3 \cos \beta = 0, \quad (3.60) \]

\[ OY : \quad m_2 v_2 \sin \alpha - m_3 v_3 \sin \beta = 0. \]

Due to the conservation laws, only two parameters are required to uniquely determine the six components. For description of homonuclear three-body break-up Müllner and Cosby chose these parameters to be the fractions of the kinetic energies received by two of the fragments upon break-up [143]

\[ E_1 = a \cdot K_E R, \quad E_2 = b \cdot K_E R, \quad E_3 = (1 - a - b) \cdot K_E R, \]

\[ a \leq b \leq 1 - a - b. \quad (3.61) \]

The momenta vectors can then be defined as

\[ u_1 = (u_{1x}, 0, 0), \]
\[ u_2 = (u_{2x}, u_y, 0), \]
\[ u_3 = (-u_{1x} + u_{2x}), -u_y, 0), \quad (3.62) \]
where
\[ u_{1x} = u_0 \sqrt{a}, \]
\[ u_{2x} = u_0 \frac{0.5 - a - b}{\sqrt{a}}, \]
\[ u_y = u_0 \left( b - \frac{(0.5 - a - b)^2}{a} \right)^{\frac{1}{2}}, \]
\[ u_0 = \sqrt{2KER \cdot m}. \]

Due to the conservation law of momentum the values of parameters \( a \) and \( b \) are restricted according to the following expressions
\[ 0 \leq a \leq \frac{1}{3}, \]
\[ \frac{1}{2}(1 - a - \sqrt{2a - 3a^2}) \leq b \leq \frac{1}{2}(1 - a). \]

Since the vectors are defined in the plane, its orientation in the space can be

Figure 3.10: The experimentally measured \( TD \) distribution in the DR of \( O_3^+ \) is shown by solid squares. The dashed curves are Monte-Carlo simulated distributions. The overall fit is shown by the solid curve.

performed by means of Euler angles \((\phi, \theta, \psi)\) (Fig. 3.9(b)). Such a transformation
is accomplished in three steps: 1) the rotation of the (X,Y) plane by the angle \( \phi \) about the Z axis; 2) the rotation of the new obtained (x,z) plane by the angle \( \theta \) about the new y axis; 3) the rotation of the new obtained (x,y) plane by angle \( \psi \) about the z axis. The total transformation by Euler angles is performed in matrix form as

\[
S = \begin{pmatrix}
    \cos \phi & \sin \phi & 0 \\
    -\sin \phi & \cos \phi & 0 \\
    0 & 0 & 1
\end{pmatrix}
\times \begin{pmatrix}
    \cos \theta & 0 & -\sin \theta \\
    0 & 1 & 0 \\
    \sin \theta & 0 & \cos \theta
\end{pmatrix}
\times \begin{pmatrix}
    \cos \phi & \sin \phi & 0 \\
    -\sin \phi & \cos \phi & 0 \\
    0 & 0 & 1
\end{pmatrix}.
\]  

(3.65)

If the DR reaction occurs at \( \approx 0 \) eV interaction energy, it is reasonable to assume

that there is no preferred dissociation direction, i.e. Euler angles are uniformly distributed. In order to correctly distribute angle \( \theta \), \( \cos \theta \) must be random in the range between -1 to 1. Finally, it is assumed that DR occurs randomly at any point in the interaction region, i.e. time between the DR event and its detection is

\[
t = \frac{D}{\sqrt{2}\frac{E_i}{M_i}},
\]  

(3.66)

Where \( D \) can take any value in the interval \((7.0-l/2, 7.0+l/2)\).

The distance distribution of the three-body break-up can be represented via the so-called total displacement, \( TD \), the square of which is proportional to the total kinetic energy released in the detector plane and determined as

\[
TD = \sqrt{\sum d_i^2},
\]  

(3.67)

where \( d_i \) denotes a displacement of the fragments in the c.m. frame. Monte-Carlo simulated \( TD \) distributions are shown in Fig. 3.10 by dashed curves.

Figure 3.11: a) The relation between break-up geometries and values of parameters \( a \) and \( b \). b) The Dalitz plot for \( X_3 \) molecule.
If the three-body break-up involves different channels, in order to find their intensities, the Monte-Carlo TD distributions are generated for each channel which are then fit to the experimentally measured distribution and the scaling parameters determines the branching fractions (Fig. 3.10).

It is noted that certain values of $a$ and $b$ corresponds to unique break-up geometry (Fig. 3.11(a)). Another method of relation between fragments energies and break-up geometries was suggested by Dalitz in 1953 [144]. In the equilateral triangle the sum of altitudes from any point inside the triangle to three sides equals to the length of any of the altitudes (see Fig. 3.12), i.e.

$$BD = PL + PM + PN.$$  (3.68)

As such, conservation law of energy can be represented by such triangle, where any point determines the energy of the fragments received upon break-up. In this case the coordinates of the point P can be expressed through the values of $E_1$, $E_2$ and $E_3$ as

$$P(x) = \eta_1 = \frac{E_2 - E_1}{\sqrt{3} \times KER},$$

$$P(y) = \eta_2 = \frac{E_3 - \frac{1}{3}}{KER}.$$

(3.69)
BD is chosen quite arbitrarily to have unit length. Taking into account the conservation law of momentum it is possible to show that

$$\eta_1^2 + \eta_2^2 \leq \left(\frac{1}{3}\right)^2.$$ \hspace{1cm} (3.70)

This implies that due to the conservation law of energy and due to the conservation law of momentum the Dalitz coordinates are restricted by triangle with $2/\sqrt{3}$ side and by circle with radius of 1/3, respectively (Fig. 3.12). Dalitz plot initially was developed for description of nuclear three-body decays, but subsequently was also applied in molecular physics [145, 146, 147, 148, 149]. The possibility to utilise such representation for four-body break-up has also been demonstrated [150]. The Dalitz plot presented in Fig. 3.11(b) has been obtained through interchange of the fragments due to the symmetry of X$^3_3$ break-up.

### 3.5.3 XY$_2$ break-up

In the case of XY$_2$ break-up $TD$ calculated as

$$TD = \left(\frac{m_X}{m_Y} d_X^2 + d_Y^2 \right)^{1/2},$$ \hspace{1cm} (3.71)

where $d$ is the fragment displacement from the c.m. The latter equation implies that the X fragment must be identified. In assigning the fragments several approaches can be applied. 1) If the beam position on the ID is well defined, then the heavier fragment (X or Y) can be identified to be that with the smallest displacement from the c.m. (the beam position). This method requires the ion beam to be very narrow, since its size is related to the spread of the c.m. position, i.e. the broader the beam, the less accurate this method will be. 2) As it was suggested by Datz et al. [64] that the fragments can be assigned according to their energy in the lab frame. For instance, for XH$^+$ ions a 2.5 $\mu$m Al foil is mounted in front of the first MCP and if the ion beam is accelerated to the energy of 250 keV/amu, only the heavy X fragment, having the higher energy, can pass through the foil, while the H atoms are stopped [64, 66, 67]. This method is quite reliable and allows almost 100% correct identification of the particles. However, one of the important disadvantages is that the channels with low values of $KER$ cannot be detected since the H atoms do not have enough transverse energy to avoid the foil and so the three particles from a DR event are never registered. For molecular ions which cannot be accelerated to such high energies, a foil of another material can be used. For example, in studying PD$^+_2$ and SD$^+_2$ a carbon foil has been used instead. However, the implementation of such foil deteriorates the quality of MCP most likely due to sputtering of carbon onto the plates thus reducing their ability to generate secondary electrons [70], [Paper II]. 3) If $m_Y >> m_X$ then in the break-up triangle composed from the fragments the smallest distance corresponds to $d_Y - d_Y$ [71]. The advantage of this method that the accuracy does not depend on the ion beam profile, though
it does not allow 100 % correct fragment identification, e.g. it fails for linear
Y-X-Y break-up.

The approach of Müller and Cosby can be extended to the XY$_2$ break-up
[143]. In this case parameter $a$ is the energy received by the X fragment and
the parameters are distributed as

$$0 \leq a \leq \frac{2m_Y}{2m_Y + m_X},$$

$$\frac{1}{2} \left[ (1 - a) - \frac{1}{m_Y} \sqrt{am_X (2m_Y - a(2m_Y + m_X))} \right] \leq b \leq \frac{1}{2} (1 - a).$$

The momenta components are defined according to Eq. (3.63) where

$$u_{1x} = \sqrt{2am_X KER},$$

$$u_{2x} = \sqrt{2m_X KER} \left( \frac{m_Y - a(m_X + m_Y) - 2bm_Y}{2m_X \sqrt{a}} \right),$$

$$u_y = \sqrt{2m_X KER} \left[ b - \left( \frac{m_Y - a(m_X + m_Y) - 2bm_Y}{2 \sqrt{am_X m_Y}} \right)^2 \right]^{\frac{1}{2}},$$

and $u_1$ is the momentum of the X fragment. For such break-up, the Dalitz
coordinates are determined as

$$\eta_1 = \frac{m_Y (E_{Y_2} - E_{Y_1})}{3 \times KER},$$

$$\eta_2 = \frac{\left( 1 + \frac{m_X}{m_Y} \right) E_X - E_{Y_2} - E_{Y_1}}{3 \times KER}.$$

The relation between Dalitz coordinates and momenta of the fragments received
upon break-up for NH$_2$ molecule are shown in Fig. 3.13(a).

Thomas et al. instead of energy fractions used parameters $\rho$ and $\chi$ for de-
scription of XY$_2$ break-up, which denote the Y fragments energy ratio ($\rho=E(Y_1)/E(Y_2)$,
$E(Y_1)\leq E(Y_2)$) and angle between the Y fragments in the c.m. frame [66]. In
such approach the momentum components are defined as

$$u(Y_1) = (u, 0, 0),$$

$$u(Y_2) = (u\sqrt{\rho} \cos \chi, \sqrt{\rho} \sin \chi, 0),$$

$$u(X) = (- (1 + \sqrt{\rho} \cos \chi), -u\sqrt{\rho} \sin \chi, 0),$$

where

$$u = \left[ \frac{2m_Y KER}{(1 + \rho) + (m_Y / m_X)(1 + \rho + 2\sqrt{\rho} \cos \chi)} \right]^{\frac{1}{2}}.$$
Figure 3.13: a) The relation between Dalitz coordinates and NH$_2$ break-up geometries, where the N atom is shown by black circles. b), c) The experimentally measured and retrieved Dalitz plots for N($^4$S)+H($^2$S)+H($^2$S) channel. d) The preferred geometries for N($^2$D)+H($^2$S)+H($^2$S) channel.
Figure 3.14: a) The angle calculated in the c.m. frame between the Y fragments in the detector plane by means of the Müller and Cosby, and the Thomas et al. approaches when the involved parameters are randomly distributed are presented by the black and gray curves, respectively. b) Dalitz plot calculated in the detector plane when all break-up geometries are equally distributed in the molecular frame.

geometries, while it is not a case for the method used by Thomas et al. The difference between two approaches can be obviously seen, for instance, from Monte-Carlo simulated $\cos \chi$ distributions measured in the detector plane (Fig. 3.14(a)), i.e. the Thomas et al. approach overestimates geometries with bent angles, an effect which has been pointed out by Petrignani et al. [68], and which requires a further normalisation step. In principle, Müller and Cosby approach can be extended for any type of three-body break-up, i.e. for any XYZ molecule, however, in the present thesis only $X_3$ and $XY_2$ molecules have been investigated.

3.5.4 Investigation of the break-up dynamics

In order to investigate the parameter distributions describing the three-body break-up dynamics the Monte-Carlo simulation must be utilised in order to take into account the response of the two-dimensional detector. The Monte-Carlo simulation is run for the case when all break-up geometries are equally probable in the detector plane which then shows how the 2D detector responds. For example, $\cos \chi$-distribution and transverse Dalitz plot ($Q_1, Q_2$) constructed by means of the Monte-Carlo simulation clearly indicate that bent and linear break-up are overestimated in the detector plane (Fig. 3.14), since any break-up geometry in the molecular plane contributes to such geometries in the detector plane. The straightforward method to obtain the preferred parameters values is to divide the experimentally obtained distribution by that obtained from the Monte-Carlo simulation in the detector plane [66, 67]. A similar method is also
used to retrieve the actual Dalitz plot \([45, 65]\) (Fig. 3.13). The Dalitz plot method is more suitable for investigation into the break-up dynamics, since it allows simultaneous two Dalitz coordinates to be retrieved, while the parameters \((\rho, \chi)\) or \((a, b)\) are retrieved independently. Such a “deconvolution” procedure enables an insight into the preferred or avoided parameter values. For a more detailed reconstruction of 3D data from 2D other methods must be applied. One of them involves Monte-Carlo image reconstruction technique \([65]\). However, as it was subsequently highlighted, the 2D data must be statistically excellent \([69]\), something which is often constrained by experimental conditions.

Figure 3.15: Presentation of momenta vectors of the fragments after sequential \(XY_2\) break-up for the case when intermediate \(XY\) molecule is formed.

In the general case the evolution of the three-body break-up for \(XY_2^+\) ion can be expressed in the following way

\[
XY_2^+ + e \rightarrow XY_2^* \overset{\tau_2}{\rightarrow} \left\{ \begin{array}{l} XY^* + Y \\ X + Y^*_2 \end{array} \right\} \overset{\tau_3}{\rightarrow} X + Y + Y. \tag{3.77}
\]

Using the terminology of Maul and Gericke, if \(\Delta \tau = \tau_2 - \tau_1\) is longer than a rotational period of the intermediate \(XY\) or \(Y_2\) molecule the break-up is defined as “sequential”, and if it is shorter as “concerted” \([151]\). A sequential break-up implies that fragment which is released first does not have influence on the subsequent bond cleavage since it has travelled a sufficient distance away from the un-fragmented molecule during one rotational period such that energy exchange is no longer possible. The two bond ruptures are then independent. For a description of the sequential break-up a model of a free rotator can be
used [152] (Fig. 3.15). In such a model the momenta are defined as

\[ p_{Y_1} = (-p, 0), \]

\[ p_{Y_2} = \left( \frac{m(Y)}{m(X)}p + \Delta p \cos \theta, \Delta p \sin \theta \right), \]

\[ p_X = \left( \frac{m(X)}{m(Y)}p - \Delta p \cos \theta, -\Delta p \sin \theta \right). \]

If \( KER \) is the kinetic energy released upon the first bond rupture and \( \Delta E \) is the difference between internal energy of the intermediate XY molecule and its dissociation energy, \( p \) and \( \Delta p \) are found by

\[ p = \sqrt{\frac{2m(Y)m(X)}{m(Y) + m(X)} KER}, \]

\[ \Delta p = \sqrt{\frac{2m(Y)m(X)}{m(Y) + m(X)} \Delta E}. \]

In the simplest case, \( \Delta E=0 \), the intermediate XY molecule contains excess energy comparable to the dissociation limit, which implies that the parameter \( \rho \approx \frac{m_Y}{m_{XY}} \). Using the free rotator model and assuming that the angle \( \theta \) is randomly distributed, a Dalitz plot describing the sequential break-up can be constructed (Fig 3.16). The concerted mechanism is defined as synchronous if \( \Delta \tau=0 \), otherwise it is termed asynchronous. The synchronous mechanism implies simultaneous cleavage of the two X-Y bonds, i.e. it corresponds to \( \rho=1 \) or \( \eta_1=0 \) for the Dalitz plot. The situation is more complicated for an identification of asynchronous concerted break-up, since it can involve very broad energy distributions.
Chapter 4

Results and discussion

4.1 Paper I

The DR reaction of Na$^+$($H_2O$) has been investigated using the storage ring CRYRING. Due to experimental constraints the heavier isotopologue Na$^+$(D$_2$O) has been used. It is expected that the isotope effect is insignificant for the fragmentation of the molecule, though the lighter isotopologue is usually characterised by higher DR rate coefficient [85]. This investigation has been motivated by two reasons: the importance for reentry vehicles and for the terrestrial atmosphere. When a supersonic vehicle moves in the atmosphere, a shock wave is created which leads to the compression and heating of the air. The easily ionisable alkali metals are emitted from the hot surface forming a plasma layer around the vehicle. Such a plasma can have a negative effect, disturbing radio-communication between the vehicle and the ground. Therefore, the study into neutralisation processes of a Na-dominated plasma is important. Furthermore, a natural Na-plasma is present in the terrestrial ionosphere in the D-region, where a 10 km half-width Na-belt is located at an altitude of 93 km [119]. As it is discussed in Chapter 1.5 this belt gives rise to a yellow airglow. The Na-layer is believed to be present due to meteor oblation. A sudden abrupt increase of sodium density by one order of magnitude over the background level is known as a sporadic layer [120, 121]. The mechanism which is responsible for the formation of such layers is likely neutralisation of sodium reservoir ions, which can proceed through the following pathways: radiative recombination

$$Na^+ + e \rightarrow Na + h\nu, \quad (4.1)$$

or three-body recombination

$$Na^+ + e + M \rightarrow Na + M, \quad (4.2)$$
or

$$Na^+ + X + M \rightarrow Na^+X + M \quad (a),$$

$$Na^+X + e \rightarrow Na + X \quad (b). \quad (4.3)$$
It is believed that neutralisation through the latter pathway (Eq. 4.3) dominates over the other two [120]. It is expected that \( \text{Na}^+ (\text{H}_2\text{O}) \) clusters are more abundant than \( \text{Na}^+ \cdot \text{N}_2 \) and \( \text{Na}^+ \cdot \text{O}_2 \) due to the stronger binding energy [153, 154]. Even if \( \text{Na}^+ \cdot \text{N}_2 \) is formed it undergoes quick ligand switching into the more stable \( \text{Na}^+ (\text{H}_2\text{O}) \) and \( \text{Na}^+ (\text{CO}_2) \) and the latter can also efficiently interconvert into \( \text{Na}^+ (\text{H}_2\text{O}) \) [121]. The rate expressions for Eq. 4.3(a) and Eq. 4.3(b) can be expressed by

\[
\frac{d[\text{Na}^+]}{dt} = -k_f[\text{Na}^+][\text{H}_2\text{O}][M] + k_r[\text{Na}^+ (\text{H}_2\text{O})][M] \quad \text{(a)},
\]

\[
\frac{d[\text{Na}^+ (\text{H}_2\text{O})]}{dt} = k_f[\text{Na}^+][\text{H}_2\text{O}][M] - k_r[\text{Na}^+ (\text{H}_2\text{O})][M] - \alpha[\text{Na}^+ (\text{H}_2\text{O})]n_e \quad \text{(b)},
\]

where \( k_f \) and \( k_r \) are the forward and reverse rate coefficients for Eq. 4.3(a), respectively, \( \alpha \) is the DR rate coefficient for the reaction described in Eq. 4.3(b). Applying the steady-state approximation for the intermediate \( \text{Na}^+ (\text{H}_2\text{O}) \), i.e.

\[
\frac{d[\text{Na}^+ (\text{H}_2\text{O})]}{dt} = 0,
\]

the system of equations (Eq. 4.4) can be simplified to

\[
\frac{d[\text{Na}^+]}{dt} = - \frac{k_f[\text{H}_2\text{O}][M]n_e[\text{Na}^+]}{k_r[M] + \alpha n_e} \quad \text{(4.6)}.
\]

Two limiting cases can be regarded, i.e. when \( \alpha n_e > k_r[M] \) (a) and vice versa (b). For the limiting case (a) the rate expression for \( \text{Na}^+ \) can be written as

\[
\frac{d[\text{Na}^+]}{dt} = -k_f[\text{H}_2\text{O}][M][\text{Na}^+]. \quad \text{(4.7)}
\]

In this case the rate is limited by the clustering process, i.e. as soon as the cluster forms, it immediately recombines with an electron. Conversely, for case (b) the rate is

\[
\frac{d[\text{Na}^+]}{dt} = -K_{eq}\alpha[\text{H}_2\text{O}]n_e[\text{Na}^+], \quad \text{(4.8)}
\]

where \( K_{eq} \) is the equilibrium constant for Eq. 4.3(a). The rate for forward reaction in Eq. 4.3(a) can be adequately described as [155]

\[
k_f = 9.5 \times 10^{-30} \left( \frac{300}{T} \right)^{1.5} \text{cm}^6\text{s}^{-1}. \quad \text{(4.9)}
\]

The rate coefficient for the DR of \( \text{Na}^+ (\text{D}_2\text{O}) \) is reported here to be

\[
\alpha = (2.3 \pm 0.32) \times 10^{-7} \left( \frac{300}{T} \right)^{-0.95 \pm 0.01} \text{cm}^3\text{s}^{-1}. \quad \text{(4.10)}
\]
\[
\begin{array}{|c|c|c|}
\hline
\text{Cluster} & \alpha_{\text{DR}}(300 \text{ K}) & N \\
\hline
\text{Na}^+(D_2O) & 0.23\pm0.032 & 2 \\
D^+(D_2O)_2 & \approx 1.5 & 3 \\
H^+(NH_3)_2 & 1.07\pm0.04 & 3 \\
D^+(ND_2)_2 & 2.31\pm0.09 & 3 \\
H^+(H_2O)_3 & 2.48\pm0.05 & 4 \\
H^+(H_2O)_4 & 0.55\pm0.035 & 5 \\
H^+(H_2O)_5 & 3.8\pm0.61 & 6 \\
H^+(H_2O)_6 & 2.25\pm0.44 & 7 \\
\hline
\end{array}
\]

Table 4.1: Comparison between different studied cluster ions. The rate coefficient is expressed in \(10^{-6} \text{ cm}^3\text{s}^{-1}\) units. \(N\) is used to denote the number of fragments in the dominant channel, which involves ruptures of all cluster bonds, with the branching fraction of \(n\).

Taking into account atmospheric conditions at an altitude of 85 km near the Na-belt, i.e. \(n_e=10^3-10^5 \text{ cm}^{-3}\), \([M]=1.7\cdot10^{14} \text{ cm}^{-3}\), \([H_2O]=4\cdot10^{-6}[M]\) and \(T=180\ \text{K}\) [156], it is found that under such conditions the reaction is limited by the clustering rate. This implies that neutralisation of Na\(^+\) ions in the terrestrial ionosphere through formation of intermediate Na\(^+\)(H\(_2\)O) can be adequately described by Eq. 4.7 for altitudes of \(\approx 85\ \text{km}\) and higher.

The branching fraction analysis for the DR of Na\(^+\)(D\(_2\)O) reveals the following results at \(\approx 0\ \text{eV}\) interaction energy:

\[
\begin{align*}
n(\text{NaOD}+D) &= 0.05 \pm 0.01, \\
n(\text{NaO}+D_2) &= 0.03 \pm 0.01, \\
n(\text{NaD}+OD) &= 0, \\
n(\text{Na}+D_2O) &= 0.92 \pm 0.03.
\end{align*}
\] (4.11)

This result implies that cleavage of the weakest cluster bond is by far the most dominant. Among the channels involving the rupture of covalent bonds the most important is that with the least rearrangement of the covalent bonds, i.e. channel probabilities decrease in the order of \(N(\text{NaOD}+D) > N(\text{NaO}+D_2) > N(\text{NaD}+OD)\). Such branching fractions can be expected and are similar to those observed previously, i.e. 1) for the clusters of H\(^+\)(H\(_2\)O)\(_n\) \((n=2-6)\) and H\(^+\)(NH\(_3\))\(_n\) \((n=2-3)\) the cleavages of cluster bonds dominate by far the fragmentation and the breaking of covalent bonds are much less important (Table 4.1). 2) For molecular ions of the type XH\(_2^+\) (X=B, C, N, O and P) the break-up of XH\(^+\)H dominates over X+H\(_2\) (Table 4.2, Paper IX). 3) The absence of the NaD+OD channel confirms the very short timescale over which the DR reaction occurs, i.e. it is very unlikely that D fragment would have sufficient time to migrate by \(\approx 3\text{Å}\) to create a Na-D bond.

The obtained rate coefficient is significantly lower than those obtained for other clusters, e.g. for clusters the rate coefficient was measured to be \(>10^{-6} \text{ cm}^3\text{s}^{-1}\) at room temperature (Table 4.1). It could be the case, for example, when an isotope effect in the rate coefficient is very significant, i.e. the lighter
CHAPTER 4. RESULTS AND DISCUSSION

Na⁺(H₂O) would dissociate much faster. On the other hand, the DR reaction for other studied clusters is dominated by the multiple fragmentation, which is the exact opposite for the case of Na⁺(H₂O). Indeed, such a tendency is obviously seen from Table 4.1. Moreover, it is interesting to note that the rate coefficient for diatomic molecules usually does not exceed 3·10⁻⁷ cm³s⁻¹ [118, 126, 157, 158, 159].

### 4.2 Paper II

The investigation of the fragmentation behaviour of XH⁺₂ type ions revealed the predominance for full fragmentation (Table 4.2). Such behaviour is still not understood and in order to resolve this problem the three-body channel has been investigated in detail with the imaging detector. The pioneering investigation of the three-body break-up channel in the DR reaction was performed at CRYRING in 2000 for H₂O⁺ by Datz et al. [64]. In order to identify the O fragment a 2.5 µm thick Al foil, 5 mm in diameter, was mounted in front of the stack of MCPs. The beam energy used was 250 keV/amu and, as such, only the oxygen atom could pass through the foil while the H atoms were stopped. A subsequent paper reported a more detailed discussion of the obtained results [66]. One year later a similar experiment was performed at the TSR storage ring for H₃⁺ [45, 65]. In both experiments a 2D imaging detector was used and a Monte-Carlo simulation was applied to take into consideration a response of the 2D detector [66, 143]. Both experiment revealed that molecular geometry is changed significantly upon break-up: the rupture of the bonds in the water molecule occurs with high level of randomisation and break-up prefers open and closed geometries, while for H₃⁺ the break-up predominantly occurs at open geometry when two hydrogen atoms receives the same amount of energy, i.e. synchronous concerted mechanism.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>X+Y+Y</th>
<th>XY+Y</th>
<th>X+Y₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃⁺ [44]</td>
<td>0.77±0.02</td>
<td>-</td>
<td>0.23±0.02</td>
</tr>
<tr>
<td>H₃⁺(Trot≈30 K) [46]</td>
<td>0.64±0.05</td>
<td>-</td>
<td>0.36±0.05</td>
</tr>
<tr>
<td>H₂D⁺ [160]</td>
<td>0.73</td>
<td>0.20</td>
<td>0.07</td>
</tr>
<tr>
<td>D₂H⁺ [Paper VII]</td>
<td>0.765±0.022</td>
<td>0.135±0.015</td>
<td>0.10±0.007</td>
</tr>
<tr>
<td>CH⁺ [161]</td>
<td>0.63±0.06</td>
<td>0.25±0.04</td>
<td>0.12±0.02</td>
</tr>
<tr>
<td>NH⁺ [162]</td>
<td>0.66±0.01</td>
<td>0.34±0.02</td>
<td>0.00±0.02</td>
</tr>
<tr>
<td>NH₂⁺ [67]</td>
<td>0.57±0.08</td>
<td>0.39±0.05</td>
<td>0.04±0.03</td>
</tr>
<tr>
<td>H₂O⁺ [163]</td>
<td>0.68±0.20</td>
<td>0.22±0.10</td>
<td>0.10±0.10</td>
</tr>
<tr>
<td>H₂O⁺ [164]</td>
<td>0.57±0.06</td>
<td>0.30±0.05</td>
<td>0.13±0.03</td>
</tr>
<tr>
<td>H₂O⁺ [165]</td>
<td>0.71±0.05</td>
<td>0.20±0.04</td>
<td>0.09±0.06</td>
</tr>
<tr>
<td>PD₂⁺</td>
<td>0.78±0.07</td>
<td>0.14±0.05</td>
<td>0.08±0.02</td>
</tr>
</tbody>
</table>

Table 4.2: The branching fractions in the DR reaction for XY⁺₂ ions (Y=H or D) measured at ≈0 eV interaction energy.

Na⁺(H₂O) would dissociate much faster. On the other hand, the DR reaction for other studied clusters is dominated by the multiple fragmentation, which is the exact opposite for the case of Na⁺(H₂O). Indeed, such a tendency is obviously seen from Table 4.1. Moreover, it is interesting to note that the rate coefficient for diatomic molecules usually does not exceed 3·10⁻⁷ cm³s⁻¹ [118, 126, 157, 158, 159].
Subsequently at CRYRING two other similar molecular ions, NH$_2^+$ and CH$_2^+$, were investigated in the same fashion as H$_2$O$^+$ [67]. Similarly, fragmentation of NH$_2^+$ occurs preferentially at both open and closed angles, but with smaller level of randomisation, i.e. $\rho$ can take any random value in the range between 0.4 and 1. In particular, it was suggested that open geometry could be partly due to the very low barrier to linearity which is $\approx$25 meV, i.e. the stored NH$_2^+$ could have enough internal energy to reach a linear geometry. Since the parent ion is linear, preference for closed angles indicates very strong bending motion of the intermediate NH$_2^*$ which could favour the formation of N+H$_2$. However, Vikor et al. reported this channel not to be formed [162]. Subsequently, Thomas et al. remeasured this channel and found it to constitute 0.04$\pm$0.03 [67]. In contrast to H$_2$O$^+$ and NH$_2^+$, CH$_2^+$ predominantly dissociates with an open geometry and the parameter $\rho$ is randomly distributed in the range between 0.2 and 1 [67]. The three-body break-up of CH$_2^+$ was studied at the TSR storage ring as well but with 3D imaging [74]. In particular, it was reported that the ratio of C(3P):C(1D) was $\approx$70:30, whilst Thomas et al. reported that two states are evenly populated [67]. One source of the discrepancy could be related to the technique used for identification of the C fragments. Nevo et al. assumed that the closest flash to the position of the c.m. corresponds to C fragment [74]. However, this approach requires the ion beam of very good quality. As such, for the channels with lower $K E R$ the error in the product assignment is higher. It is unlikely that the discrepancy could be due to the foil technique applied by Thomas et al. since such an effect was taken into consideration in the data analysis. Nevo et al. and Thomas et al. used two different approaches to investigate the fragmentation dynamics, i.e. Dalitz plot method and by means of parameters $\rho$ and $\chi$ described in section 3.5.3. Dalitz plot obtained by Nevo et al. for C(3P)+H+H channel showed that most of the dissociation events are in the range of $-0.2 \leq \eta_1 \leq 0.2$ and $-1/3 \leq \eta_2 \leq -0.2$ and this allows $\rho$ to vary only in the range between 0.2 and 1 and cos $\chi$ $<$-0.6, a result which was reported by Thomas et al. However, it is noted that Dalitz plot method is more useful since allows more insight into the nuances of the break-up dynamics to be obtained. Thomas et al. based on the results obtained for H$_2$O$^+$, CH$_2^+$ and NH$_2^+$, pointed out that for more bent molecular ions more randomisation is observed in the energy sharing between the hydrogen fragments.

The next step in the investigation into XH$_2^+$ type ions was an extension to heavier species such as SD$_2^+$ and PD$_2^+$ [70]. However, in contrast to the lighter ions previously studied, XH$_2^+$ (X=C, N and O), it was not possible to accelerate the heavier ions to the beam energy of 250 keV/amu. Instead, a carbon foil of 265 $\mu$g/cm$^2$ was utilised to identify the phosphor or sulphur fragment. Due to the slowness of the ion beams the light hydrogen in the three-body channel could miss the detector. In order to avoid this, the heavier fully deuterated isotopologues were used. However, due to other isotopic issues, measurement of the branching fractions was not possible for $^{32}$SD$_2^+$, although it did not present a serious problem for imaging experiment since the isobaric $^{34}$SD$^+$ gives rise only two fragments. The investigation of the three-body dynamics of SD$_2^+$ is of great interest, since its photodissociation was studied previously with Lyman-$\alpha$
photons which is very close to ionisation energy of SD₂ [166]. In particular, it was found that a high kinetic energy D fragment arose from the break-up involving the long lived SD(A²Σ⁺) state, with the lifetime of ns, and low kinetic energy fragments were assigned to direct dissociation to S¹(¹D)+D+D or fast predissociation of SD(A²Σ⁺) occurring on the ps scale. Indeed, the vibrational ground state of SD(A²Σ⁺) is long lived due to the poor overlap with the repulsive curves, while for vibrationally excited states such an overlap is significantly increased making predissociation faster by several orders of magnitude [167]. Hellberg et al. used a D fragment displacement distribution and showed that, in contrast to H₂O⁺ and PD₂⁺, the total randomisation of the kinetic energy received by the fragments cannot reproduce the obtained distribution. A reliable fit could be obtained if 60 % of the three-body events are described by a totally random ρ and the remaining 40 % by ρ<0.7 with values of 0.3−0.5 dominating. It was concluded that such energy sharing could be evidence for a sequential break-up proceeding through predissociative SD(A²Σ⁺). Similar to SD₂⁺, trajectory calculations performed for the isovalent H₂O⁺ system started from the point close to the ionisation energy of the ground state revealed OH(A²Σ⁺)+H products to be dominant such that intermediate molecule can dissociate further leading to the enhancement of the three-body O(³P)+H+H channel [66]. However, the imaging experiment on the DR of H₂O⁺, in contrast to SD₂⁺, did not show obvious evidence for sequential break-up [66].

The molecular angle on dissociation were investigated for the first two channels of SD₂⁺ and PD₂⁺ and a preference for both closed and open geometries were found. A similar angular distribution was obtained for the ground state products formed in the DR of NH₂⁺ and H₂O⁺. In contrast to NH₂⁺, the predominance for the open angles for H₂O⁺, SD₂⁺ and PD₂⁺ cannot be related to the linear geometry of the parent ions, since the parent molecular ions are bent.
with intramolecular angles of 108°, 93° and 93°, respectively, and have barriers to linearity in eV range.

Van der Zande demonstrated that a purely statistical model, taking into consideration only the spin multiplicity and orbital angular momentum degeneracy of the atomic fragments formed in the DR reaction, applied to the DR of CO+, NO+, O2+ and N2+ could well describe the experimental values [168] (Model I). Hellberg et al. showed the predictive power of such a model for the DR of NO+ for different interaction energies [101]. Thomas et al. showed that the competition among the O(3P)+H+H and O(1D)+H+H channels arising from the DR of water ion could be predicted by statistical model as well if the total channel degeneracy is multiplied by the square root from the KER value, which was explained that such a factor is proportional to the number of translational degrees of freedom [66] (Model II). Although the statistical approaches quite well reproduce the experimental measurements (see Table 4.3), it could be just fortuitous since any dynamics occurring on the potential energy surfaces is not taken into account.

All of the investigations into the DR of triatomic dihydride ions has revealed some similarities for this series of ions: 1) there is a tendency to predominantly dissociate through the three-body channel. 2) The X+H2 channel has been observed to constitute ≈ 10%, which implies very strong bending motion in the molecule after the electron capture. Such reactivity has not been observed in heavier triatomic molecules. 3) The reaction rate coefficients are in the range \((5.8±2.0)\times10^{-7}\) cm³s⁻¹ with the exception of H3+ which is known not to have favourable curve crossing (Table 4.4). 4) The final product state distribution in most cases can be described by simple purely statistical model, which could be fortuitous. 5) The kinetic energy is randomly distributed between the fragments for H2O+ and PD2+, nearly random for CH2+ and to a lesser extent for NH2+, while for SD2+ the kinetic energy sharing could be partly determined by predissociation via SD(A2Σ⁺) state. In contrast to these molecules, H3+ dissociates with a linear geometry and with equal energy sharing between two of the fragments. 6) All of the studied XH+n ions show an obvious propensity to dissociate from a linear geometry and some also dissociate from states with closed geometry. The next ion in this series has been chosen to be BH2+ which is known to have a linear geometry in the ground state and the relatively low exothermicity of the three-body channel which prevents electronic excitation of the fragments, something which is different to the majority of the other XH+n ions which have been studied. The results of this investigation are presented in Paper IX.
4.3 Papers III, IV

The atmosphere prevents the penetration of biologically dangerous solar UV-radiation to the Earth’s surface. For example, radiation below 240 nm is absorbed by the abundant O$_2$ and, despite its minute amount, another oxygen containing molecule, ozone, absorbs UV in the range 240 to 290 nm. The peak concentration of O$_3$ occurs at an altitude of 35 km and constitutes about 10 p.p.m. A great deal of attention has been paid to neutral O$_3$, while its ionised species has received much less attention. Due to the important roles that both ozone and the DR reaction play in the terrestrial atmosphere, an investigation into the DR of O$_3^+$ is of great interest.

The measured effective reaction rate coefficient is shown in Fig. 4.1 by the solid squares. It is noted that rate coefficient from 0.1 meV to 0.3 eV is well described by a single power function of

$$\alpha(E_d) = \frac{1.43 \cdot 10^{-15}}{E_d^{1.05}} \sqrt{\frac{2E_d}{m_e}},$$  

(4.12)

Figure 4.1: The measured rate coefficient for the DR of O$_3^+$ is shown by the solid squares with statistical error bars. The solid line is Eq. 4.12. The dotted and dashed curves present Eq. 4.12 folded with Maxwellian distribution assuming that $kT_{e\perp} = 2$ and 0.15 meV, respectively.

despite the fact that the slope should change at energies below meV due to the influence of the electron temperature ($kT_{e\perp} = 2$ meV). In order to investigate...
the influence of the electron energy spread, Eq. 4.12 has been folded with a Maxwellian distribution according to Eq. 3.14 (Fig. 4.1, dotted curve). The result implies that the absolute rate coefficient at energies below 5 meV cannot be described by Eq. 4.12. It is interesting to note that if the transverse electron temperature is fixed to 0.15 meV, quite reasonable agreement between the measured and folded rate coefficients is obtained (Fig. 4.1, dashed curve). However, such a low temperature is not realistic, since its value has been accurately derived from the shape of dielectronic recombination resonances and was found to be 2 meV. Quite good agreement with the measured rate coefficient can be obtained if the absolute rate coefficient is described by

\[
\alpha(E_{cm}) = \left( \frac{2.77 \times 10^{-17}}{E_{cm}^{1.58}} + \frac{1.43 \times 10^{-15}}{E_{cm}^{1.05}} \right) \sqrt{\frac{2E_{cm}e}{m_e}}.
\]

Indeed, the term with the \(1/E_{cm}^{1.58}\) dependence determines the behaviour of the rate coefficient at energies below 1 meV, i.e. there is a rate coefficient enhancement at very low interaction energies. A similar effect of an enhancement of the reaction rate at very low interaction energies was firstly reported in 1995 for the radiative recombination of Ne\(^{10+}\). In this case dielectronic recombination is not possible since it is a bare ion and, therefore, low energy resonances could not give rise to an enhancement [169]. As such, it was concluded that this effect is an artifact of the storage ring. The observed enhancement was suggested to be due to 1) the much lower transverse electron temperature, 2) a local electron density enhancement, 3) field effects or 4) three-body recombination processes. Subsequently this effect was observed at the TSR experiments [170]. In particular, it was shown by the TSR group that the enhancement is dependent on both the longitudinal and transverse components of the electron temperature as well as the charge state of the ion. Quite recently a model capable of explaining this effect has been reported [171, 172, 173, 174]. The main idea of this model is that the enhancement is due to field induced recombination (FIR) in the toroidal regions of the electron cooler. When the ion beam enters the toroidal region it experiences a transverse magnetic field which gives rise to a motional electric field. Such a field has a tendency to reduce the electrical potential inside the ion which gives rise to FIR. Due to the relatively weak electrical field only very highly excited Rydberg states can be formed. As soon as the Rydberg atom leaves the toroidal region, autoionisation is no longer possible and the electron is captured. After passing through the straight section of the cooler the Rydberg atom can be very efficiently ionised in the second toroidal region in a reverse process to FIR, i.e. field induced ionisation. In order to prevent this, the Rydberg atom has to stabilise through photon emission, a process which is very slow for highly excited Rydberg states. Nevertheless, it has been shown that despite the long lifetime of such Rydberg states they efficiently contribute to the signals arising from radiative recombination. In contrast to atoms, molecular Rydberg states are very efficiently stabilised through fragmentation, a process which occurs on a time scale much shorter than radiative stabilisation. It is noted out that FIR can be regarded to occur at negative interaction
energies since the electron is captured into a Rydberg state which lies below the ion ground state, i.e. only a singly excited state can be formed. It is assumed that FIR is much more efficient than DR since for FIR there is no competition with autoionisation. In this case all of the neutral Rydberg states which are formed will dissociate, while the efficiency of the DR reaction is related to the competing reverse process of autoionisation. The explanation of why the enhancement occurs only at small interaction energies is given by the fact that the probability to form a Rydberg state is higher at smaller values of $E_{cm}$, and when $E_{cm}$ is quite high the formation of a bound state ($E < 0$) is not possible. However, it must be noted that the enhancement of the DR rate coefficient can also be due to the presence of low energy resonances in the cross section. In order to answer this question high quality theoretical calculations are necessary, which exist only for few cases. In particular, Curik and Greene performed such calculations [175] to explain the experimental measurements by Krohn et al. for the DR of LiH$^+$ [176]. Indeed, the agreement is perfect apart from very low interaction energies where the enhancement effect is expected to be significant which could explain the discrepancy. If such an effect is indeed realistic for molecular ion-electron recombination, then FIR is capable of explaining the absence of the $1/E$ dependency which is predicted theoretically to occur at very small interaction energies [6].

The following channels are energetically available in the DR of O$_3^+$

$$O_3^+ + e \rightarrow \begin{cases} O_2 + O + 11.43 \text{ eV} \ (\alpha) \\ O + O + O + 6.27 \text{ eV} \ (\beta) \end{cases},$$

(4.14)

where the quoted $KER$ values indicates that the interaction occurs at $\approx 0$ eV interaction energy and that parent ion and all the fragments are formed in their ground state. The channels are considerably exothermic which is due to the relatively weak intramolecular bonds in the ozone molecule. Using the grid technique described in Chapter 3.4 the branching fractions for the channels $\alpha$ and $\beta$ have been derived to be 0.06$\pm$0.03 and 0.94$\pm$0.03, respectively. The big IISD with an active area of 3000 mm$^2$ has been used in order to eliminate losses of O fragments arising from the channel $\alpha$ due to the relatively high exohermicity of this channel. The result is of great interest, since it is the first observation for a DR reaction which leads to an almost total fragmentation of a polyatomic molecular ion. It is noted that evidence for four-body break-up has been reported by Geppert et al. in the DR of C$_2$D$_3^+$ though it is not the dominant channel [177]. Moreover, a high degree of fragmentation has been observed for the cluster ions D$^+(D_2O)_2$, X$^+(NX_3)_2$ (X=H and D), and H$^+(H_2O)_n$ ($n=3-6$) (Table 4.1). However, these results could be expected since fragmentation involves only the rupture of the cluster bonds, while in the case of O$_3^+$ the complete cleavage of covalent bonds occurs. The possible explanation for such a phenomenon is given in the next section (Paper V), where comparative analysis is undertaken for O$_3^+$ and N$_3^+$. It is also interesting to note that in photodissociation of the neutral O$_3$ by a 193 nm photon only 2% of events involve complete fragmentation [178], while at a shorter wavelength of 157.6 nm the two channels, O$_2$+O and O+O+O, were observed to be comparable [179], i.e.
### Table 4.5: Calculated values of the electronic branching fractions of the available three-body fragmentation channels. The quoted error bars originate from both the statistical uncertainties of the individual channel intensities and the uncertainty in conversion from CCD camera pixel size to mm.

<table>
<thead>
<tr>
<th>channel</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\beta_3$</th>
<th>$\beta_4$</th>
<th>$\beta_5$</th>
<th>$\beta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fraction</td>
<td>0.28±0.03</td>
<td>0.5±0.03</td>
<td>0.21±0.02</td>
<td>0±0.01</td>
<td>0.01±0.05</td>
<td>0±0.01</td>
</tr>
</tbody>
</table>

when more energy is available in the reaction the importance of the three-body channel grows. Indeed, the present result implies exclusiveness of the O+O+O break-up when 6.27 eV is available for this channel. A similar phenomenon was observed for SH$_2$ when photodissociation by 157.6 nm photons showed the predominance for SH(X$^2\Pi$)+H break-up [180], and when the photon energy was raised to 121.6 nm (Lyman-\(\alpha\)), which is close to the ionisation energy of SH$_2$, full fragmentation was observed to dominate [166]. Furthermore, the photodissociation of water with Lyman-\(\alpha\) photon showed the dominating tendency for OH(X$^2\Pi$)+H channel [181]. On the other hand, trajectory calculations started with 12.6 eV excitation energy predicted the enhancement of the O(3P)+H+H channel [66] and, indeed, DR of the H$_2$O$^+$ dominates by the full fragmentation break-up. However, the comparison between the DR reaction and photodissociation should not be taken too far, since selection rules for photodissociation implies that photon excitation from the ground O$_3$ can only lead to the singlet states, while both singlet and triplet states are allowed in DR.

Due to the predominance of the three-body break-up channel, it is of particular interest to investigate this channel in more detail. The ID has been utilised to achieve this. The advantage in this investigation is that all the fragments are identical, i.e. homonuclear break-up and, therefore, there is no need for additional techniques to identify the fragments. Furthermore, all CCD frames containing three flashes have been accepted for analysis. The starting point is to investigate the competition occurring between the different excited fragments which can be formed in this channel:

$$O_3^+ + e \rightarrow \begin{cases} O(3\mathrm{P}) + O(3\mathrm{P}) + O(3\mathrm{P}) + 6.27 \text{ eV} (\beta_1) \\ O(3\mathrm{P}) + O(3\mathrm{P}) + O(1\mathrm{D}) + 4.30 \text{ eV} (\beta_2) \\ O(3\mathrm{P}) + O(1\mathrm{D}) + O(1\mathrm{D}) + 2.33 \text{ eV} (\beta_3) \\ O(3\mathrm{P}) + O(3\mathrm{P}) + O(1\mathrm{S}) + 2.08 \text{ eV} (\beta_4) \\ O(1\mathrm{D}) + O(1\mathrm{D}) + O(1\mathrm{D}) + 0.36 \text{ eV} (\beta_5) \\ O(3\mathrm{P}) + O(1\mathrm{D}) + O(1\mathrm{S}) + 0.11 \text{ eV} (\beta_6) \end{cases}$$

A Monte-Carlo simulation based on the approach of Müller and Cosby has been run, assuming all parameters to be equally distributed, to generate a TD distribution for each channel ($\beta_1$–$\beta_6$) which have then been scaled to the measured distribution (Fig. 3.10). The results of such procedure is given in Table 4.5. It is noted that the simulated TD distributions have been generated without taking into account any internal excitation of the parent O$_3$ ions, which implies that the few seconds which were used to store the ion beam prior to the
measurement was sufficient to allow time for the ions to spontaneously relax through photon emission. In this case it is expected that ions were all in their vibrational ground state, while their rotational distribution is characterised by the ambient temperature of 300 K. The results indicate that oxygen fragments are predominantly formed in the $^3P$ and $^1D$ states, while formation in the $^1S$ state is highly unfavoured. It is interesting to note that the formation of this electronic state in the DR of other oxygen-containing compounds, e.g. O$_2^+$, NO$^+$ and CO$^+$, is also observed to be unfavourable [101, 118, 157]. Van der Zande and Hellberg et al. explained the product distribution for O$_2^+$, CO$^+$ and NO$^+$ with a simple statistical model [101, 168], i.e. the unfavourable formation of O($^1S$) is related to the statistical degeneracy of this state which is unity, i.e. the smallest possible. However, such a model is oversimplified since it considers only the final states and does not take into account the intermediate dynamics occurring on the way from formation of the highly excited state to fragmentation, as noted earlier. Moreover, none of these models are able to explain the branching fractions reported here since they all predict that the $\beta_1$ channel should be dominant. Herbst and Lee explained the dominance of the three-body break-up by the further fragmentation of internally excited fragments arising from a parent two-body break-up [182]. In order to verify such a general explanation the break-up dynamics needs to be investigated.

The Dalitz plot method has been applied to establish the preferred geometries upon break-up. The starting point is to investigate the $\beta_1$ channel in which all of the fragments are formed in their electronic ground state. It is accomplished by investigating the events with $TD >18.5$ mm since in this region the fragments can only arise from the $\beta_1$ channel (Fig. 3.10). The Dalitz plot constructed by the Monte-Carlo simulation is shown in Fig. 4.2(a). The break-up involves linear open geometries such that the two “outside” O atoms share the $KER$ almost equally and the central oxygen atom receives only a minute amount of it. Such a break-up proceeds via a synchronous concerted mechanism, i.e. the intermediate highly excited O$_2^*$ stays intact for a sufficient time to rearrange itself from its initially bent geometry to linear and afterwards synchronous rupture of two bonds occurs. It is interesting to note that photodissociation of neutral ozone leads also to synchronous break-up occurring almost at linear geometry [178]. For investigation of the $\beta_2$ channel the events with $TD$ values from 14 to 16 mm for which this channel dominates (Fig. 3.10) and, since the contribution of the $\beta_1$ and $\beta_2$ channels is known in this region, the contribution from the $\beta_1$ channel can be eliminated, allowing the construction of a Dalitz plot for events arising predominantly from the $\beta_2$ channel (Fig. 4.2(b)). The Dalitz plots imply that dynamics involved in the fragmentation of the two channels is similar. In a similar fashion a Dalitz plot can be constructed for the $\beta_3$ channel (Fig. 4.2(c)) using events with $TD$ values from 7.5 to 11.5 mm (Fig. 3.10). The results show three groups of preferred break-up geometries which is due to the total symmetry of the parent molecule. The coordinate $Q_2$ depends only on the energy of one of the fragments, i.e. $E_3 \approx 0.6 KER$ for all possible break-up geometries. This implies that a sequential break-up is involved in the fragmentation, i.e. upon the breaking of the first bond to form O+O$_2$ the oxygen
Figure 4.2: a), b), c) Reconstructed with Monte-Carlo simulation Dalitz plot for $\beta_1$, $\beta_2$ and $\beta_3$ channels, respectively. d) The result of free-rotator model for purely sequential break-up.

atom receives almost $0.6\, KER$ and the intermediate $O_2^*$ contains enough internal energy close to the dissociation limit for further fragmentation. According to Maul and Griecke the molecule should stay intact for a time period longer than a rotational period such that the subsequent break-up of $O_2^*$ occurs completely independently from the free oxygen atom [151]. The free rotator model [152] describing the sequential break-up results in the Dalitz plot presented in Fig. 4.2(d). This observation agrees with the suggestion of Herbst and Lee that two-body break-up subsequently gives rise to further fragmentation [182]. However, this cannot totally explain the predominance of the three-body break-up since channel $\beta_3$ occurs for only 21% of the total three-body events.

4.4 Paper V

For the DR of $N_2^+$, measurements of the electron-ion neutralisation have been reported for different values of the nitrogen pressure and it was found that the neutralisation rate is enhanced for higher pressures (Table 4.6). At small
Table 4.6: The rate coefficient for electron-ion recombination in N-dominated plasma versus different ambient pressures. The rate coefficient is shown in $10^{-7}$ cm$^3$s$^{-1}$ units. The value presented in the last column was measured for N$^+_3$ and was found to decrease with increase of the pressure to 1315 Torr. $^a$Ref. [183], $^b$Ref. [184], $^c$Ref. [185], $^d$Ref. [186].

pressures the rate coefficient is relatively low [183], since at such conditions N$^+_2$ ions dominate, and the DR rate coefficient measured at CRYRING was reported to be $1.75 \times 10^{-7}$ cm$^3$s$^{-1}$ at 300 K [126]. When the pressure is raised more complex ion are formed, e.g. N$^+_3$ and N$^+_4$, which leads to the observed enhancement of the DR rate [183, 184, 185]. Indeed, the DR rate coefficient for cluster ions is in many cases higher than $>10^{-6}$ cm$^3$s$^{-1}$ (Table 4.1). However, it must be pointed out that at higher pressures other processes than DR can also be responsible for neutralisation of the ions. For example, the efficiency of the three-body recombination process is known to increase with increasing pressure. On the other hand, diffusion controlled recombination decreases with increasing pressure [186]. The neutralisation rate coefficient for N$^+_3$ was reported to decrease for pressures higher than 1 atm [186]. In order to investigate the importance of non-DR processes at high pressure, measurement of the DR rate for N$^+_3$ in ultrahigh vacuum would be instructive, since under such conditions only the DR reaction can lead to ion neutralisation. Moreover, the DR reaction studied for homonuclear H$^+_3$ and O$^+_3$ ions have shown some similarities, e.g. 1) the branching for both ions is dominated by the full fragmentation with almost 100 % of all bond ruptures in O$^+_3$; 2) the imaging experiments have revealed a propensity to fragment through three-body synchronous concerted mechanism [45, 64], [Paper III, IV]. As such, DR investigation of other homonuclear ions, e.g. N$^+_3$, would provide more insight into the DR of this series of ions.

The DR cross section for N$^+_3$ was measured at CRYRING by applying the cathode voltage ramp method and was found to be best described by the following analytic expressions (Fig. 3.5)

$$
\sigma(E_{cm}) = \begin{cases} 
6.53 \times 10^{-16}, & E_{cm} < 65 \text{ meV}, \\
\frac{E_{cm}^{1.198}}{2.28 \times 10^{-16}}, & E_{cm} > 65 \text{ meV}.
\end{cases}
$$

(4.16)

The slope of the rate coefficient changes for energies above 65 meV which is assumed to be due to the opening of new autoionisation channels into the excited states of the bending vibration [187]. The folding of Eq. 4.16 with an isotropic Maxwellian distribution yields the rate coefficient at 300 K to be $6.47 \times 10^{-7}$ cm$^3$s$^{-1}$, which is quite similar to that observed for O$^+_3$. It is interesting to note that these two ions have a similar size, i.e. consist of three atoms with close masses. It seems to be likely that for more complex ions the DR reaction is
CHAPTER 4. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th></th>
<th>X₂⁺</th>
<th>X₃⁺</th>
<th>X₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=O</td>
<td>2.4°</td>
<td>1.75°</td>
<td>7.37</td>
</tr>
<tr>
<td>X=N</td>
<td>6.47</td>
<td>42°</td>
<td>14°</td>
</tr>
</tbody>
</table>

Table 4.7: Rate coefficient are presented in 10⁻⁷ cm³s⁻¹ units. 

aRef. [118]. bRef. [126]. cRef. [104]. dRef. [188].

faster, and this is indeed a case for nitrogen and oxygen compounds (Table 4.7).

Similar dependence can also be seen for other series of ions, e.g. $\alpha$(OH⁺) < $\alpha$(H₂O⁺) < $\alpha$(H₃O⁺) [85, 165, 189].

Similar to the case of O₃⁺ all possible channels are energetically available in the DR of N₃⁺:

$$N₃⁺ + e \rightarrow \begin{cases} N₂ + N + 10.5 \text{ eV (}\alpha\text{)} \\ N + N + N + 0.7 \text{ eV (}\beta\text{)} \end{cases}$$

(4.17)

The branching fractions for the DR of N₃⁺ have been measured at ≈0 eV interaction energy and have been found to be

$$n_\alpha = 0.92 \pm 0.03,$$

$$n_\beta = 0.08 \pm 0.03.$$  

(4.18)

The expected similarities in the branching behaviour for X₃⁺ is not found, since N₃⁺ and O₃⁺ show completely opposite tendencies. It is well known that the azide radical is quite strongly bound and the lowest dissociation limit $N^+(3P)+N₂(X¹Σ_g^+)$ lies 3.53 eV above the ion ground state [190], while the dissociation energy of O₃⁺ into (O₂⁺(X²Π_g)+O(3P)) is only 0.6 eV [191]. Based on this it could be concluded that in the DR reaction the cleavage of weaker bonds are more likely. Indeed, from the data listed in Table 4.1, the rupture of all cluster bonds is by far the dominant process. Since N₃⁺ is bound much more strongly than O₃⁺, the three-body break-up channel is much more energetic in the case of the ozone cation. As a result of this, for ozone, six three-body channels are energetically available and three of them are significantly populated (Table 4.5), while the N atoms arising from β channel (Eq. 4.17) are always formed in their ground state. The purely statistical model developed by Herbst predicts that the channel probability is related to the number of quantum states [37, 38]. Comparing these two molecular ions, it can be concluded that the value of KER in the X+X+X channel reflects both the strength of intermolecular bonds and the number of possible pathways through which the reaction can proceed along this channel. Vikor et al. suggested that the population of the three-body channel depended on the KER [162] and, indeed, this agrees with current observations. Despite the fact that in H+H+H channel arising from the DR of H₃⁺ the fragments can only be formed in the ground states due to the relatively high excitation energy of the hydrogen atom, the suggestion of Vikor et al. can be applied to these three ions: N₃⁺ - 0.08±0.03 (0.7 eV), H₃⁺ - 0.75 (4.8 eV) and O₃⁺ - 0.94±0.03 (6.27 eV). The validity of such dependency is valid for XH₂⁺ ions as well (Paper IX). It must be pointed out
that from a structural point of view these ions are very different: \( \text{N}^+_3(D_{\infty h}) \), \( \text{H}^+_3(D_3h) \) and \( \text{O}^+_3(C_{2v}) \). In particular, it would be interesting to investigate the dynamics of the \( \text{N}+\text{N}+\text{N} \) channel if it involves synchronous bond rupture as in the case of \( \text{H}^+_3 \) and \( \text{O}^+_3 \). However, due to the relatively low populations of this channel it is experimentally complicated.

\subsection*{4.5 Paper VI}

Due to its simplicity \( \text{H}^+_2 \) was among the first molecular ions for which the DR reaction was investigated both experimentally and theoretically. The earlier existing technique such as plasma afterglow were not suitable for studying the DR of this ion, since \( \text{H}^+_2 \) quickly interconverts to \( \text{H}^+_3 \) (Eq. 1.11(b)). The fundamentally different approach of electron-ion beam interaction was developed in order to avoid this problem. The advantage of the beam apparatus is that it totally eliminates unwanted chemical and three-body processes. The first experiment reporting the cross section involved an inclined beams technique in which two beams are interacted at an angle of \( 10^\circ \) [192]. In order to improve the interaction energy resolution the merged beam machine (MEIBE) was introduced [27, 193]. Both experiments agreed regarding the order and the shape of the cross section. In particular, it was shown that the cross section drops with a nearly \( 1/E \) dependence which was attributed to the direct DR mechanism. Moreover, due to the better energy resolution, some dips were observed in the MEIBE experiment, which were assigned as being due to the DR reaction proceeding through intermediate Rydberg states. McGowan \textit{et al.} showed that for such Rydberg states autoionisation competes with predissociation and at higher energies with resonant ion-pair formation, \( \text{H}^+ \text{H}^+ [193] \). However, due to the methods of the ion creation, the two experiments involve the reaction of all possible vibrationally excited states of the parent \( \text{H}^+_2 \) ions. In this case the fine structure due to the indirect mechanism is smeared out. In order to reduce the vibration excitation an RF discharge ion source was applied which gave rise to a significant increase in the population of \( v=0, 1 \) and \( 2 \). Indeed, the cross section was observed to be more structured and to be decreased by a factor of 2.65 than that measured when all \( v \) were involved [27, 193]. This implied that the rate coefficient for vibrationally relaxed ions is lower. Such an effect is now well established. Guberman performed accurate calculation of the doubly-excited states for \( \text{H}_2 \) and showed that there are two groups of the doubly-excited states, the so called \( Q_1 \) and \( Q_2 \) series, which asymptotically lead to \( \text{H}(1s)+\text{H}(nl) \) and \( \text{H}(2l)+\text{H}(nl) \), respectively [194]. In particular, the lowest lying state in the \( Q_1 \) series, \( \Sigma^+_g(2p\sigma_u)^2 \), is responsible for the DR fragmentation at low interaction energies (Fig. 4.3). This state has a poor overlap with the \( v=0 \) ground state of \( \text{H}^+_2 \) and, therefore, it is expected that the cross section for \( v=0 \) is significantly smaller than for \( v>0 \). Furthermore, the rate is anticipated to increase for \( v\geq5 \) since other dissociative states open up.

One of the earliest theoretical treatments of the DR of \( \text{H}^+_2 \) was performed by Giusti-Suzor \textit{et al.} using MQDT theory [195]. Indeed, they revealed the
cross section enhancement for $v=1$. Moreover, the contribution from the indirect DR mechanism appeared as window resonances where the cross section is reduced, i.e. destructive interference. Such phenomenon was explained due to the relatively weak coupling between the electronic states and the vibrational motion. Nakashima et al. also used an MQDT approach for $\text{H}_2^+$, HD$^+_2$, and D$^+_2$, and reported the thermal rate coefficient for the first five vibrational states and revealed them to be dependent on $v$ such that $\alpha(v = 0) \ll \alpha(v = 1)$ for all three molecules [196]. Moreover, they supported destructive interference due to the indirect mechanism. Hickman applied configuration interaction method and showed that the indirect mechanism could lead to constructive interference [197].

The experimental identification of the direct mechanism requires apparatus with a very high intrinsic energy resolution and, furthermore, only one vibrational state must be populated, otherwise the fine structure due to the indirect mechanism are washed out. Such an investigation was hindered by the fact that $\text{H}_2^+$ cannot efficiently transfer its internal energy by spontaneous photon emission and such radiative decay can be as long as $10^6$ s. Alternatively, an RF trap ion source was introduced which enabled the ions to be confined for few ms before extraction. Furthermore, it was shown that by using a mixture of H$_2$ gas together with Ne or He only a few vibrational states was created through
the following reactions [35]

\[ \text{H}_2^+(v \geq 3) + \text{He} \rightarrow \text{HeH}^+ + \text{H} \quad (a), \]

\[ \text{H}_2^+(v \geq 2) + \text{Ne} \rightarrow \text{NeH}^+ + \text{H} \quad (b). \]

Without such collisions, the infra-red inactive H\(_2^+\) ions would not cool. The purity of the ion beam was verified by collision induced dissociation of H\(_2^+\) on He atoms which is known to have threshold which decreases with vibration quantum number, \(v\). This enabled Hus \textit{et al.} using a MEIBE machine together with an RF ion source to observe for the first time dips in the cross section with a change of about one order of magnitude [36]. The resolution was reported to be 20 meV at 0.1 eV and 40 meV at 1.0 eV. Subsequently the resolution of the MEIBE machine was improved to be 7 meV at 20 meV and 15 meV at 0.1 eV which enabled Van der Donk \textit{et al.} to observe more structured cross section [34]. Moreover, MQDT calculations reported by the same authors for \(v=0\) was surprisingly in excellent agreement with the measurements regarding the position of the dips and the order of the cross section [34]. It was concluded that only a single vibrational state (\(v=0\)) was achieved. However, as was pointed out by the authors, the rotational distribution of the H\(_2^+\) should be thermal. At that time it was believed that due to both the slowness of the rotational motion and the small energy gap the molecular rotation could not influence the DR rate. However, Takagi raised this question in 1993 and by means of an MQDT approach predicted a significant rotational effect [198]. In particular, it was shown that if the rotational temperature is 145 K, the resonances in the cross section are washed out. Takagi's calculation implies that van der Donk \textit{et al.} measurement is reliable if only few rotational quantum numbers were populated, which is doubtful.

Larsson \textit{et al.} investigated the DR reaction of D\(_2^+\) at the storage ring CRYRING and reported that the rate coefficients measured after storing the ion beam for 9.5 s is higher than that obtained after 22.5 s [199]. A plausible explanation for this observation was that the vibrational population of the stored D\(_2^+\) ions varied and, since the rate for \(v>0\) is higher, it implied that population of the vibrational ground state (\(v=0\)) increased. Such de-excitation could not be due to spontaneous photon emission, since it is expected to be much longer that the storage time. Larsson \textit{et al.} suggested that interaction with the residual gas was responsible for vibrational quenching [199]. Such a conclusion is supported by the fact that despite the ultrahigh vacuum in the ring (10\(^{-11}\) Torr) the lifetime of the ion beam is predominantly determined by collisions with the residual gas. Using a similar approach van der Zande \textit{et al.} observed that the rate coefficient measured at \(\approx 0\) eV interaction energy after storing the H\(_2^+\) beam for 40 s did not change and the asymptotical value of the rate coefficient is similar to than obtained for HD\(^+\) [200]. Such de-excitation could be due to super-elastic collisions (SEC). However, adopting the values for the SEC rate coefficients calculated by Sapral and Tennyson [201], van der Zande \textit{et al.} showed that such a de-excitation mechanism could not explain
the experimental observations [200]. It was concluded that the DR reaction itself leads to $H_2^+(v=0)$, since the rate for $v>0$ is much higher than that for the vibrational ground state, i.e. vibrationally excited states are depleted by the DR reactions faster. Furthermore, the product state distribution was also investigated and it was reported that the hydrogen fragments are never formed in their ground state [200]. An experiment performed by Tanabe et al. using the TARN II storage ring shed more light on the de-excitation mechanism [202]. Measurement of the rate coefficient for $H_2^+$ at $\approx 0$ eV interaction energy versus storage time were measured twice, such that in the second case the electron cooler was switched off for 10 s prior to the measurements. This delay did not cause any change in the rate coefficient, which enabled Tanabe et al. to conclude that residual gas cannot change the vibrational population [202]. Furthermore, the authors provided strong evidence that the de-excitation was due to the SEC process. Krohn devoted a great deal of attention to a quantified investigation of the SEC process [203]. The measurements were performed using the TSR storage ring in combination with Coulomb-Explosion Imaging (CEI). Such a technique involves a very thin foil ($\approx 100$ Å). When an $H_2^+$ ion passes through the foil the binding electron is stripped away on a time scale of $\approx 10^{-17}$ s, while the vibration period is $\approx 10^{-14}$ s. As such, the position of two protons still reflects the ionic vibrational motion. The Coulomb energy at a distance $\approx 1 \mu$m is entirely transferred into the kinetic energy of the fragments which is sufficient for the protons to be separated from a distance of $\approx 1$ Å to few cm after several metres of flight, which can then be measured by an ID. Based on the calculations of Sapral and Tennyson, Krohn et al. included only SEC transition when $\Delta v=1$ [204]. Subsequent and more accurate measurement were performed in combination with direct detection of the DR products by the ID. This enabled Krohn to derive the rate coefficients for both the DR and SEC processes [203] and the results showed that the SEC process is more efficient than the DR reaction. Furthermore, as it was expected, Krohn’s measurement showed the rate coefficient to be the smallest for $v=0$ and increases for $v>0$ and with a second enhancement occurring for $v\geq 5$. Moreover, the SEC rate coefficients are also larger for higher $v$. Such results are only reported in the PhD thesis of Sven Krohn and to the best of the author’s knowledge have never been published. Ngassam et al. recently reported theoretical calculations for both the DR and SEC rate coefficients [205]. The calculations generally supported the DR rate coefficient, while the SEC value is too low to reproduce the experimental observations.

In order to shed more light on the DR of this apparently simple $H_2^+$ ion, which has proven to be a difficult task at both experimental and theoretical levels, the DR reaction of the $H_2^+$ has been investigated at CRYRING at the ion beam energy of 8 MeV with the aim of ascertaining the rotational state effect. Normal hydrogen is divided into para($I=0$)- and ortho($I=1$)-hydrogen, where $I$ is used to denote the total nuclear spin. Due to reasons of symmetry para-hydrogen can occupy only even rotational states, i.e. $J=0,2,4...$, while ortho- only odd. Due to the nuclear spin statistics under normal conditions ortho- is three times more abundant than para-hydrogen. The rotational ef-
fect was investigated by separate measurements of para- and normal-H$_2^+$. The para-gas was produced off-line and was checked to have purity of 99%. In order to significantly reduce rotational motion of the H$_2^+$ ions, the supersonic ion source was utilised which is known to produce ions with rotational temperature of $\approx 30$ K [46]. This temperature implies that para-H$_2^+$ can only occupy one rotational state, $J=0$, while for normal-H$_2^+$ $J=0$ and $J=1$ constitute 25% and 75%, respectively. However, this source is not sufficient to eliminate vibrational population of the ions. Similar to experiments of van der Donk et al. Ne gas was mixed with H$_2$ gas in ratio of 9/1 [34]. It was expected that such ratio and relatively high pressure of the expanded gas would provide sufficient number of collisions promoting reaction described in Eq. 4.19(b). However, it was not observed in the present study that such a method would ensure the production of only $v=0$ and 1. On the other hand, SEC has proven to be sufficiently efficient which enabled us to significantly increase $v=0$ after storing the ion beam for 17 s. The rate coefficients were measured for both para- and normal-H$_2^+$ after storing the beam for 3, 8, 13 and 17 s (Fig. 4.4). Our results are consistent with previous observations that the rate coefficient is the smallest for $v=0$. It is also observed that the rate coefficient measured after a longer storage time is more structured and this is explained by the fact that for high values of $v$ the DR reaction is predominantly driven by the direct mechanism while for $v=0$, due to

![Figure 4.4](image-url)

Figure 4.4: The measured DR cross section for para- and normal-H$_2^+$, dashed and solid curves, respectively, at storage time of 3 s (a), 8 s (b), 13 s (c) and 17 s (d). In order to avoid logarithmical scaling the cross section is multiplied by $E_d$. The ion beam energy is 8 MeV.
to the small Franck-Condon factor, the indirect mechanism is significant and which leads to resonances. It is anticipated that features measured for para-H$_2^+$ are predominantly due to a single quantum state, $v=0$ and $J=0$, while for normal-H$_2^+$ two quantum states are involved, i.e. 25% of $v=0$ and $J=0$ and 75% of $v=0$ and $J=1$. The observed resonances at $\approx 2$ and 20 mev are ortho-features, while the resonance at $\approx 6$ meV is a para-feature (Fig. 4.4(a)). Our measurement completely supports Takagi’s calculations predicting significant rotational state effects in the DR reaction of H$_2^+$ [198]. The cross sections reported here disagree with the measurements reported from the MEIBE machine by Hus et al. and van der Donk et al. [34, 36]. Our measurements imply that the indirect mechanism gives rise to the enhancement of the rate coefficient due to the indirect mechanism, an effect predicted by Hickman [197], while the MEIBE experiments showed obvious destructive interference. It is worth noting that the reported resolution of 7 meV from MEIBE experiment would not allow to observe unresolved structures in the storage ring experiment since the resolution at CRYRING is 2 meV. The latest calculations performed by Takagi support our observation regarding the shape of the resonances though disagrees with their positions. It is interesting to note that the positions of the window resonances reported here for normal-H$_2^+$ occupying predominantly two rotational states are similar to those observed by van der Donk et al. [34], despite the fact they conclude the opposite reasons, i.e. constructive and destructive interferences, respectively, which of course could be fortuitous. It is pointed out that quite recently a laser-ion source has been developed and implemented at the TSR storage ring which has enabled Ruette et al. to produce H$_2^+$ in particular rovibrational states and the DR measurement of such states have also revealed the rotational state effect [206].

A similar experiment was carried out at CRYRING at a higher beam energy of 15 MeV. The higher energy was chosen to increase the electron density providing faster beam relaxation due to the SEC. Unfortunately, a source of ion beam reheating was observed. This effect is seen from distance spectra distribution taken at 30-35 s and 45-60 s which indicates that the ion beam population does not change. Fig. 4.5(a,b) does not reflect the actual ion beam population, but shows relative contribution to the distance spectra from the vibrational state $v$, $k_v$,

$$k_v = \frac{p_v \alpha_v}{\sum p_v \alpha_v},$$

where $p_v$ is the relative population of the $v$ vibrational state with a DR rate coefficient of $\alpha_v$. The discrepancy between the experimentally measured distance distribution and the analytic functions (Eq. 3.55) is assumed to be because of relatively poor detection efficiency at very small distances (<2 mm), an effect reported earlier for NO$^+$ [101]. However, anisotropic behaviour cannot be ruled out. An experiment performed at TARN II storage ring showed a similar effect when contributions to the distance spectra from $v=0-3$ was obtained between 25-28 s of storing the ion beam to be 0.73, 0.13, 0.11 and 0.03, respectively, and was found to be the same after 35-38 s of storing [63], while the results reported here are 0.44, 0.38, 0.1 and 0.08, respectively (Fig. 4.5(a,b)). An experiment
performed at TSR showed much higher purity of the ion beam with the $k_0$ and $k_1$ to be $\approx 0.9$ and 0.1, respectively [203]. Evidence for reheating at 15 MeV can be deduced from the raw MCS spectrums taken after 13 s of beam storing, at 8 MeV beam energy the structures are already observed, while it is not a case for ion beam of 15 MeV (Fig. 4.6). The source of reheating is not completely identified, but could be due to residual gas collisions or interactions in the toroidal region. However, Tanabe et al. provided strong evidence for the absence of residual gas heating [202]. A similar effect was observed by Lammich et al. at the TSR storage ring for the time-dependent rate coefficient for $\text{H}_3^+$ [207]. At some point of the storage the electron beam was switched off and it was observed that the rate coefficient increased which could not be due to 300 K black-body radiation since $\text{H}_3^+$ belongs to $D_{3h}$ symmetry. The TSR group could not identify the source of reheating either.

Using both measured product state distribution and rate coefficient versus different storage time (Fig. 4.5(c,d,e)), the absolute values of the DR rate
CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.6: The MCS spectra recorded for the DR reaction of para-H$^+_2$ ions produced by the supersonic expansion ion source with the beam energies of 8 MeV (a) and 15 MeV (b).

Table 4.8: The absolute DR rate coefficients for the first four vibrational states of para- and normal-hydrogen obtained at $\approx 0$ eV interaction energy (all rate coefficients are written in $1 \times 10^{-8}$ cm$^3$s$^{-1}$ units) as well as the results reported from TSR experiment for normal-H$^+_2$ by Krohn.

<table>
<thead>
<tr>
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<th>$\nu=0$</th>
<th>$\nu=1$</th>
<th>$\nu=2$</th>
<th>$\nu=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>para-H$^+_2$</td>
<td>2.7</td>
<td>6.04 ± 1.22</td>
<td>3.64 ± 0.87</td>
<td>3.73 ± 0.96</td>
</tr>
<tr>
<td>normal-H$^+_2$</td>
<td>1.42</td>
<td>11.5 ± 2.76</td>
<td>13.7</td>
<td>1.63 ± 0.56</td>
</tr>
<tr>
<td>Ref. [203]</td>
<td>1.87±0.15</td>
<td>18.7 ± 11.2</td>
<td>15.3±9.5</td>
<td>18.0 ± 11.5</td>
</tr>
</tbody>
</table>

The result of this procedure for para- and normal-H$^+_2$ is shown in Table 4.8 together with the values reported by Krohn [203]. The vibrational rate coefficient values measured at both the CRYRING and TSR storage rings agrees well for $\nu=0$–2. However, it must be pointed out that due to the different transverse electron temperatures which are 2 and 12 meV at CRYRING and TSR, respectively, the values of $\alpha_\nu$ should differ by at least 2.4. The reason for such a discrepancy is not clear. Nevertheless, Takagi reported the significant dependence of $\alpha_\nu$ on rotational quantum number as well [198]. The results reported here implies rotational temperature of 30 K, which is proven by the spectra shown in Fig. 4.5(a,b), while Krohn used a temperature of 600 K to describe the distance distribution. The result for $\alpha_\nu$ for para- and normal-H$^+_2$ implies that the rate coefficients at different vibrational states depends on the rotational population, an effect reported by Takagi [198]. Such an effect should
be unexpected since the rotational gap of $\approx 10$ meV is much lower than that for vibrational levels of $\approx 0.25$ eV. As such, it could be concluded that the difference is due to the indirect mechanism, i.e. low energy resonances determines the rate coefficient values at $\approx 0$ eV interaction energy. The relative vibrationally dependent rate coefficients reported here for normal-H$_3^+$ are similar to those reported by Takagi (Fig. 4.5(f)), which show an increase at $v=1$ and then drop at $v=3$ [198]. The method applied here of deriving vibrational rate coefficient values (Eq. 4.21) is more convenient than that used by Krohn [203], since the implementation of the CEI can be avoided and, instead, absolute rate coefficients are measured which is more straightforward.

4.6 Paper VII

In a cold hydrogen containing plasma H$_3^+$ is the most dominant molecular ion. Due to the relatively low proton affinity H$_3^+$ serves as a proton donor for other molecules leading to the formation of more complex species. The idea that H$_3^+$ exists in interstellar space was put forward by Martin et al. in 1961 [79]. Indeed, 35 years later this was verified by spectroscopic observations [80]. In less dense clouds, i.e. diffuse clouds, the detection of H$_3^+$ was reported with a number density similar to that in dense clouds which was totally unexpected [81]. This was explained by two possible reasons: either the ionisation rate in diffuse clouds is much higher than previously thought or the DR of H$_3^+$ is a very slow reaction [90]. The latter was quite unclear at this time since different experimental techniques reported DR rate coefficients at 300 K which varied from $10^{-11}$ to $10^{-7}$ cm$^3$s$^{-1}$. Such a controversial topic was reported in several review articles [208, 209]. One possible explanation was that the rate coefficient is a strong function of internal state distribution. To investigate this effect experimentally was complicated since H$_3^+$ does not have a dipole moment due to the molecular symmetry and, as such, spontaneous relaxation of the excited states is very slow process. Two completely different approaches to solve this issue have been suggested. McCall et al. designed a supersonic expansion ion source which was spectroscopically characterised and produces ions at rotational temperature of 20-60 K [46, 94]. Implementation of such an ion source at CRYRING enabled McCall et al. to conclude that for rotationally relaxed ions the rate coefficient is only $\approx 40\%$ lower than that measured for rotationally hot ions [91, 92]. Independently, at the TSR storage ring, an ion trap with buffer gas was used to reduce the internal excitation of the ions [210]. The results from both storage rings completely agree with respect to the shape of the energy dependent rate coefficient, though absolute ion current measurement at TSR experiment was not feasible due the to relatively small number of ions. The most recent theoretical calculations performed by Kokouline and Greene agrees with the storage ring measurements [211, 212]. However, the theoretical rate coefficient is more structured, which could be explained only by the rotational temperature of 1000 K [213]. Such a high theoretically predicted rotational temperature questions the results of McCall et al. [46, 94]. However, it seems unrealistic for the ions to
change their rotational temperature from 20-60 K to 1000 K. Moreover, McCall et al. investigated effects of possible heating in the storage ring, e.g. residual gas or toroidal regions of the electron cooler, and verified it to be insignificant [46].

Another controversial topic concerning this molecular ion was its fragmentation. The simple empirical model of Bates implies the least rearrangement of valence bonds, i.e. channel \( \text{H}_2 + \text{H} \) must dominate [40, 41]. However, pioneering experiment performed by Mitchell et al. involving the grid technique at the MEIBE machine showed that the H+H+H channel is dominant and that fragmentation in \( \approx 10 \% \) involves formation of long-lived excited Rydberg states [58]. A similar grid approach was firstly utilised by Datz et al. at CRYRING [44]. The grid was translucent which enabled the DR and non-DR signals to be separated. The results showed that in 77 \% the molecule fragmented through the H+H+H channel. Moreover, the absence of long-lived neutral Rydberg states was verified. Subsequently, Larsson et al. reported the rate coefficient measurements for the heavier isotopologue of D\(_2^+\) [214]. The measurements were performed in the presence of a transverse magnetic field in the electron cooler which would lead to ionisation of the excited Rydberg states by means of a motionally induced electrical field. However, no dependence on the magnetic field was observed which again verified the unfavourable formation of H\(_3^+\). McCall et al. investigated the fragmentation of rotationally relaxed H\(_3^+\) and found that fragmentation through the H\(_2+\)H channel is slightly more favoured for rotationally cold ions [46]. The purely statistical model developed by Strasser et al. predicted the same energy dependent branching fractions as those measured by Datz et al. [43, 44]. However, the model is not capable of explaining the influence of the ion rotational temperature, an effect reported by McCall et al. [46]. Using the imaging detector at TSR storage ring Strasser et al. investigated the break-up dynamics of the full fragmentation channel [45, 65]. It was observed that the molecule has a tendency to significantly rearrange the geometry upon break-up from equilateral to open liner. In this case fragmentation proceeds through synchronous concerted mechanism in which cleavage of two bonds occurs synchronously. Moreover, Strasser et al. showed that ions produced by a discharge ion source had rotational temperature of 0.3 eV which is retained even after 40 s of storage [65].

Detection of many deuterated compounds in the interstellar medium has raised interest in the DR of heavier H\(_3^+\) isotopologues (Chapter 1.5). The DR reaction of H\(_2\)D\(^+\) was studied at both the CRYRING and TSR storage rings [69, 160]. The CRYRING experiment investigated both the reaction rate coefficient and branching fractions. In particular, it was established that similar to H\(_3^+\), the fragmentation of H\(_2\)D\(^+\) predominantly proceeds through the three-body channel, while the obtained ratio of [HD]/[H\(_2\)] = 1.2 in the two-body channel implies that from a purely statistical point of view the formation of HD is more favourable than H\(_2\) [160]. The imaging experiment performed at TSR storage ring for both H\(_2\)D\(^+\) and D\(_2\)H\(^+\) revealed that, similar to H\(_3^+\), the molecules dissociate from a linear geometry, H-D-H and H-D-D, respectively [69]. Moreover, analysis of the distance spectra enabled Strasser et al. to conclude that the
rotational temperature of the stored ions was below 70 meV, while for H\textsuperscript{3+} and D\textsuperscript{3+} the value was reported to be 0.23 eV [69]. This result is expected since for H\textsubscript{2}D\textsuperscript{+} and D\textsubscript{2}H\textsuperscript{+}, belonging to the C\textsubscript{2v} symmetry, relaxation by spontaneous photon emission is feasible. Lammich \textit{et al.} investigated the DR rate coefficient for D\textsubscript{2}H\textsuperscript{+} at \(\approx\)0 eV versus different storage times in the ring and reported that the reaction rate decreased with time and, furthermore, it depended on the density of the electron beam [138]. Plausible explanation was that rotationally excited D\textsubscript{2}H\textsuperscript{+} ions react faster than relaxed, an effect reported by McCall \textit{et al} for H\textsuperscript{3+} [46]. The electron cooler served as an electron bath which had very low temperature of \(kT_e\parallel=12\) meV. As such, this region in the ring provides very cold environment enabling spontaneous emission to much lower excited states. On the other hand, super-elastic collisions are known to be more efficient for lower interaction energies which could also lead to de-excitation of the ion beam.

As mentioned earlier, the rate coefficient measured for H\textsuperscript{3+} generally agrees with the calculations, though the theory overestimates the rotational temperature of the ions. Calculations also predicted the predominance of the H+H+H fragmentation channel. The rate coefficient measured for D\textsuperscript{3+} by Larsson \textit{et al.} also agrees with theoretical calculations [214]. Subsequently, Kokouline and Greene extended their theory to the isotopologues with C\textsubscript{2v} symmetry, i.e. H\textsubscript{2}D\textsuperscript{+} and D\textsubscript{2}H\textsuperscript{+} [215, 216]. Both theory and experiment are in agreement for the rate coefficient of H\textsubscript{2}D\textsuperscript{+}, while similar calculations underestimated the rate coefficient for D\textsubscript{2}H\textsuperscript{+} which differs by a factor of 2-5 from that measured by Lammich \textit{et al.} Such a situation questions the validity of either the theoretical calculations or the storage ring measurements [138]. In order to shed more light on the DR reaction for D\textsubscript{2}H\textsuperscript{+}, it has been investigated at the CRYRING storage ring.

The measurements of the rate coefficient were performed over an interaction energy range from \(\approx\)0 eV to 50 eV after storing the ion beam for 5 and 23 s. In order to increase the beam lifetime in the latter case the electron beam was switched off in order to prevent destruction of the beam by the DR reaction, i.e. relaxation of the ion beam was possible only due to the spontaneous photon emission but neither super-elastic collisions nor DR reaction itself. The measured rate coefficient is shown in Fig. 4.7 by the solid line. In order to make a direct comparison with the theory, the calculated rate coefficient needs to be folded with an electron Maxwellian distribution in the electron cooler and the ion rotational temperature must also be taken into consideration. Based on the estimated value by Strasser \textit{et al.} [69] the rotational temperature was chosen to be 600 K (Fig. 4.7, dashed curve). There is no agreement between the CRYRING measurements and the theoretical calculations and the discrepancy at very small interaction energies is one order of magnitude. The theoretical rate coefficient contains some resonances, while the experimentally measured dependence is smoother. It could be similar to the case for H\textsuperscript{3+}, when theory overestimated experimental rotational temperature which would mean that rotational temperature of D\textsubscript{2}H\textsuperscript{+} ions in the storage ring was higher than 600 K which disagrees with the observations of Strasser \textit{et al.} [69]. The rate coefficient measured by Lammich \textit{et al.} at the TSR storage ring agrees with that measured.
at CRYRING for interaction energies above 0.1 eV (Fig. 4.7). However, direct comparison at smaller energies is not possible due to the different transverse electron temperatures at the two storage rings which are 2 and 12 meV, respectively. In order to retrieve the absolute rate coefficient the deconvolution procedure was applied (Eq. 3.41). Both experimental rate coefficients are in good agreement (Fig. 4.8(a)). However, the value reported from CRYRING measured after storing the ions for 5 s is somewhat higher which is due to the different ion beam storage times before the data acquisition. Indeed, Lammich et al. reported for D$_2$H$^+$ that longer storage time provides internal de-excitation and rotationally warm ions react faster than cold. The rate coefficient measured at CRYRING after storing the beam for 23 s is in excellent agreement with the TSR measurements (Fig. 4.8(b)). This indicates that similar rotational temperatures were reached in the two storage rings. Comparing experimentally determined rate coefficients for H$_3^+$ and its isotopologues (Table 4.9), it could be concluded that an isotope effect implies that heavier isotopologue reacts slower with an exception of D$_2$H$^+$.

The branching fractions were measured at $\approx$0 eV interaction energy and
CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.8: The cross section for DR of D$_2$H$^+$ measured at TSR storage ring is shown by the gray curve. Measurements performed at CRYRING after the storing the ion beam for 5 (a) and 23 s (b) are shown by the black curves.

quoted at 1σ confidence level

\[
\begin{align*}
    n(D+D+H) &= 76.5 \pm 2.2, \\
    n(D_2 + H) &= 10.0 \pm 0.7, \\
    n(DH+D) &= 13.5 \pm 1.5. 
\end{align*}
\] (4.22)

As expected the D+D+H channel is most dominant occurring in 76% of all DR events, i.e. the same fraction of the three-body break-up was obtained for rotationally hot H$_3^+$ and H$_2$D$^+$ [44, 160]. If the fragmentation depends on the rotational temperature, then this result implies that the D$_2$H$^+$ ions were rotationally warm, since for rotationally cold H$_3^+$ McCall et al. reported this channel to be 66% [46]. In a similar fashion to H$_3^+$ and its isotopologues, an isotope effect was not observed for H$_2$O$^+$ and D$_3$O$^+$, and H$_2$O$^+$, HDO$^+$ and D$_2$O$^+$ [85, 86, 164], though for some ions such an effect was reported to be prominent [141, 142]. Purely statistically the DH+D channel is two times more favourable than D$_2$+H channel. However, the measured values show \(|D_2|/|HD|=1.48\pm0.22\) which implies that the formation of the heavier isotopologue is more preferred. Moreover, a similar effect was reported for H$_2$D$^+$ where \(|HD|/2|H_2|=1.20\pm0.05\) [160]. Indeed, if the DR reaction proceeds in the direction to minimise the energy, then formation of heavier isotopologues are favourable due to the dependence of the zero point vibrational energy on the mass.


<table>
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<tr>
<th>Isotopologue</th>
<th>Storage Ring</th>
<th>$\alpha$(300 K)</th>
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</thead>
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<tr>
<td>$\text{H}_3^+$ [91]</td>
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</tr>
<tr>
<td>$\text{H}_3^+$ [92]</td>
<td>ASTRID</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>$\text{H}_3^+$ [46]</td>
<td>CRYRING</td>
<td>0.68$^a$</td>
</tr>
<tr>
<td>$\text{D}_2\text{H}^+$[217]</td>
<td>CRYRING</td>
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</tr>
<tr>
<td>$\text{D}_2\text{H}^+$[138]</td>
<td>TSR</td>
<td>$\approx 1.1^c(\approx 0.9^c)$</td>
</tr>
<tr>
<td>$\text{D}_3^+$[214]</td>
<td>CRYRING</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 4.9: Rate coefficients for DR of $\text{H}_3^+$ and isotopologues in units of $10^{-7}$ cm$^3$s$^{-1}$. $^a$ $\text{H}_3^+ (T_{\text{rot}})$=30 K. $^b,c$ Measurements performed after beam storing for 5 and 23 s, respectively.

### 4.7 Paper VIII

Free electrons released with the exhaust of aircraft engines have undesired effects on radio communication. It was suggested that a possible way of removing electrons could be through their attachment to neutral species to form anions. Phosphoryl chloride, OPCl$_3$, was expected to be a very efficient electron scavenger due to the high electronegativity of chlorine and, furthermore, the P-Cl bond is weaker than the O-P bond and, therefore, could favour the cleavage of the former bond. However, experimental investigations revealed PO$_2^-$ and PO$_3^-$ to be the primary terminal anions [218]. In order to understand the transition from OPCl$_3$ to the latter anions, ion-molecular chemistry of the phosphorus oxychloride compounds was studied with flow tube instruments [219, 220, 221, 222, 223]. In particular it was found that the most dominant products from the interaction of PO$_2^-$Cl$_2^-$ with O$_2$ and O$_3$ are PO$_3^-$ and PO$_4^-$ [221]. On the other hand, free electrons can also interact with cation forming neutral fragment. Indeed, it was shown that the DR reaction can enhance the combustion process since it can form very reactive radicals [224]. This has lead us to investigate the DR reaction of two phosphorus oxychloride compounds, OPCl$_3^+$ and OPCl$_5^+$. 

Prior to the experiment, it was expected that the heavy nature of the ions would put constraints on the quality of the generated data. The heaviest molecular ion studied to date at CRYRING is $\text{H}^+ (\text{H}_2\text{O})_{26}$ [108], while OPCl$_5^+$ is 8 amu heavier. The first issue encountered was the spread of the ion beams. For both very heavy ions electron cooling was not feasible since this would require a time much longer that the storage time of the ion beams. For the relatively lighter ion, OPCl$_3^+$, the small IISD with an active area of 900 mm$^2$ was used in order to gain energy resolution but, due to the combination of the slowness of the beam and an insufficient electron cooling, 16 % of the DR events missed the detector. However, this does not present a serious problem, since it can be accounted for in the analysis of both the branching fractions and the cross section measurements. For OPCl$_5^+$ the ion beam spread was even more substantial and the detector with larger area (3000 mm$^2$) was needed. However, due to the larger geometrical size this detector generates more electrical noise which prevented
measurement of the branching fractions. Moreover, the signals generated by
the DR products were close to the noise level which also made it impossible
to quantify the amount of losses. As such, the rate coefficient measurement
represents a lower limit to the real values. Another issue was related to the
very low energies of the electron beams, which resulted in instability of the
electron beam. This limited the range of the interaction energies, specially for
the relatively slow \( \text{OPCl}_2^+ \) it was found that the cross section could be reliable
only for interaction energies \( > 6 \text{ meV} \). Nevertheless, it was assumed that the
cross section is described by simple power low, which was indeed observed for
many heavy polyatomic ions, which enabled extrapolation for smaller energies.
Consequently, using Eq. 3.45 the thermal rate coefficients were derived to be:

\[
\alpha(\text{OPCl}^+) = 7.62 \cdot 10^{-7} \left( \frac{T_e}{300} \right)^{-0.89} \text{ cm}^3\text{s}^{-1},
\]

\[
\alpha(\text{OPCl}_2^+) > 1.2 \cdot 10^{-6} \left( \frac{T_e}{300} \right)^{-1.22} \text{ cm}^3\text{s}^{-1}. \tag{4.23}
\]

The rate coefficient at 300 K for \( \text{OPCl}^+ \) is similar to the rates obtained for \( \text{N}_3^+ \)
and \( \text{O}_3^+ \), while the value for \( \text{OPCl}_2^+ \) is higher. It could be due to the size effect in
the rate coefficient, an evidence of which is obviously seen from Table 4.7. The
value higher than \( 10^{-6} \text{ cm}^3\text{s}^{-1} \) have previously seen for other ions containing
heavy ions \([225, 226, 227]\), which might indicate that despite ion beam spread
issue, the majority of the products were nevertheless detected.

The measurements of the branching fractions were only feasible for lighter
\( \text{OPCl}^+ \). The data clearly indicate that a mass difference of 6 amu is not sufficient
to resolve the P and Cl peaks (Fig. 4.9), and even when the mass difference
is 16 amu the peaks are blended together and only the shoulder indicates the
presence of two peaks. In order to establish the intensities of the peaks it was
assumed that the peak shape is well described by a Gaussian. Furthermore,
due to the inability to resolve P and Cl, it was assumed that the overall peak
can also be described by a single Gaussian. Further issues related to the low
detector resolution is the inability to resolve branching into the OP+Cl and
P+ClO channels. As such, the branching fractions are

\[
n(O+P+Cl) = 0.16 \pm 0.07, \\
n(O+PCl) = 0.16 \pm 0.03, \\
n(\text{OP}+\text{Cl}) + n(\text{P}+\text{ClO}) = 0.68 \pm 0.05. \tag{4.24}
\]

However, some information on the likelihood on the production of \( \text{P}+\text{Cl} \) can
be obtained. From structure calculations on \( \text{OPCl}^+ \) the intermolecular angle
is \( 101.5^0 \) and it is unlikely that during the time after the attachment of the
electron these two atoms, O and Cl, can combine, i.e. \( n(\text{P}+\text{ClO}) \) is assumed to
be zero. Such a conclusion is supported by the branching results for other heavy
atom systems, \( \text{SO}_2^+ \), \( \text{CO}_2^+ \), and \( \text{OCS}^+ \), in which the rearrangement channel
forming \( \text{O}_2 \) and \( \text{OS} \), respectively were not observed \([228, 229, 230]\). However,
such a channel is populated in the DR of \( \text{XH}_2^+ \) ions and plausible explanation
for such phenomena is relatively high mobility of the hydrogen atoms (Table 4.2). It is interesting to note that more exothermic diatomic channel, OP+Cl, is more abundant than O+PCl, an effect which is pointed out in Paper V. The population of three-body channel is relatively low which is consistent with other studied heavier ions in which this channel is exothermic, SO$_2^+$, N$_2$O$^+$ [229, 231] and N$_3^+$, with a sole exception so far of O$_3^+$.

The experiment is quite instructive in the sense of investigating what is possible in both the branching fractions and rate measurements for very heavy molecular ions. An alternative way to study such heavy compounds is to utilise electrostatic storage ring which due to the electrostatic nature do not have mass limitations, though the requirement to have a merged electron and ion beam for 0 eV collisions is still a serious limitation.

### 4.8 Paper IX

This paper is the latest extension in the ongoing investigation of XH$_2^+$ type ions to BH$_2^+$. The motivation for the study of this series of ions is underlined in Paper II. The ground state of the neutral BH$_2$ molecule, $^2A_1$, has a geometry $\angle$HBH$= 129^\circ$ and $r_{BH}=1.2$ Å, and its electronic configuration in $C_{2v}$ symmetry
is described as \((1a_1)^2(2a_1)^2(1b_2)^23a_1\). The \(3a_1\) orbital is bonding and removal of an electron from this orbital leads to the ground state of BH\(^{+}\), \(1\Sigma^+_g\), which is linear and characterised by an electronic configuration of \((1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2\).

The rate coefficient has been measured in the normal fashion, i.e. implementing the cathode voltage ramp method (Fig. 4.10). The rate coefficient in the range between 1 meV and 0.3 eV is adequately describes by

\[
\alpha(E_d) = \begin{cases} 
6.99 \times 10^{-16} \frac{2E_d e}{m_e}, & E_d < 0.12 \text{ eV} \\
1.02 \times 10^{-16} \frac{2E_d e}{E_d^{1.92} m_e}, & E_d > 0.12 \text{ eV}.
\end{cases}
\] (4.25)

The slope of the cross section changes above 0.12 eV which is assumed to be due to the opening of a new autoionisation channel into vibrationally excited states of BH\(^{+}\). Indeed, the excitation into the bending motion of BH\(^{+}\) is 1045 cm\(^{-1}\) (0.13 eV) [232]. In a similar way to the case of O\(_2^+\) (Paper III, IV), the effective rate coefficient obtained by folding Eq. 4.25 with the Maxwellian distribution of the electrons in the electron cooler can only adequately describe the measured values if \(kT_{e\perp}=0.2\) meV. On the other hand, the reliable agreement can be
Table 4.10: \( n \) is used to denote the fraction of X+H+H channel. Rate coefficients are presented in units of \( 10^{-7} \) cm\(^3\)s\(^{-1} \) at 300 K.

The increase of the rate coefficient below 1 meV could be due to the enhancement effect discussed in detail in Papers III, IV. However, the absence of theoretical calculations for the DR of BH\(_2^+\) does not allow us to draw a final conclusion if this increase is due to the enhancement effect [169], or due to low energy resonances.

It is interesting to note that the DR of both O\(_3^+\) and BH\(_2^+\) are characterised by \( \approx 1/E \) dependence for energies above 1 meV, which is predicted by theory [6], while for the lower energies the both cross sections are described by \( 1/E_{cm}^{1.58} \) dependence.

At \( \approx 0 \) eV all channels are energetically available in the DR of BH\(_2^+\):

\[
\text{BH}_2^+ + e \rightarrow \begin{cases} \text{BH} + \text{H} + 5.03 \text{ eV (\( \alpha \))} \\ \text{B} + \text{H}_2 + 6.08 \text{ eV (\( \beta \))} \\ \text{B} + \text{H} + \text{H} + 1.56 \text{ eV (\( \gamma \))} \end{cases}
\]

where the quoted energies implies the formation of all the fragments in their ground states. The analysis revealed the following results:

\[
\begin{align*}
n_{\alpha} &= 0.56 \pm 0.03, \\
n_{\beta} &= 0.09 \pm 0.0, \\
n_{\gamma} &= 0.35 \pm 0.05.
\end{align*}
\]

This result is completely opposite to those obtained for other XH\(_2^+\) (X=H, D, C, N, O and P) ions which predominantly fragment through the X+H+H channel (Table 4.2). First of all, it would be instructive to compare the KER value of the X+H+H channel for other XH\(_2^+\) ions. The dependency implies that the observed fraction of the B+H+H channel could be due to the relatively low
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exothermicity (Table 4.10), an effect which was suggested by Vikor et al [162]. The surplus energy directly reflects how strongly the molecule is bound, i.e. if the stronger bond is ruptured then less kinetic energy is available. This implies that the probability of the bond rupture is related to its strength, i.e. the cleavage of weaker bonds is more likely. A similar dependency is observed for X+ ions (Paper V). Moreover, the probability of the XH+H+H channel arising from the DR of XH+ + increases with KER: CH+ + 0.16±0.15 (0.7 eV), H3O+ - 0.67±0.06 (1.3 eV) and SD+ - 0.58±0.11 (2.3 eV) [85, 163, 233]. The relatively low KER of the B+H+H channel prevents electronic excitation of the boron atom, while for the other ions studied, CH2+, NH2+, H2O+ and PD2+, excitation of the heavier fragment is allowed and the total fragmentation is dominated by the three-body break-up (Table 4.2, Table 4.3). Indeed, the purely statistical model developed by Herbst implies that the channel probability is proportional to the number of the states available in this channel [37, 38]. Herbst and Lee explained the dominance of the three-body break-up to be due to the second fragmentation of the internally excited fragments originating initially from the two-body break-up [182]. Such an explanation fails for the present series of ions since no evidence for sequential break-up has been observed. The channel involving rearrangement of the valence bonds, B+H2, is also populated despite the fact that the parent ion is linear, while the relatively low population of the N+H2 channel arising from the DR of NH2+ [67, 162] was related to the linearity of the molecule.

It is interesting to note the rate coefficient for BH+2 is smaller than those obtained for other XH+2 ions (Table 4.10) with the sole exception of H3+ which is known not to have favourable curve crossing. It seems that when molecule undergoes higher level of fragmentation the rate coefficient is increased. It is also interesting to note that the DR of BH+2 is less exothermic in all of the channels than for H2O+, CH2+ and PD2+ which implies that when the DR is more energetic, the DR reaction is faster.

4.9 Paper X

The hydronium, H3O+, is one of the most important molecular ion in interstellar molecular clouds. Since it is a closed shell species, it does not react with abundant H2 but is very efficiently neutralised by an electron. The knowledge of the product distribution in this reaction is crucial for understanding into the oxygen composition of these clouds (Chapter 1.4). The DR reaction can proceed through the following channels:

\[ \text{H}_3\text{O}^+ + e^- \rightarrow \begin{cases} \text{H}_2\text{O} + \text{H} & (\alpha) \\ \text{OH} + \text{H}_2 & (\beta) \\ \text{OH} + \text{H} + \text{H} & (\gamma) \\ \text{O} + \text{H}_2 + \text{H} & (\delta) \end{cases} \] (4.29)

The first results concerning the branching were reported by Herbst in 1978 [37]. He applied a purely statistical model (Chapter 1.2) and ascertained that chan-
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<table>
<thead>
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<th>Approach</th>
<th>( \text{H}_2\text{O} + \text{H} )</th>
<th>( \text{OH} + \text{H}_2 )</th>
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<th>( \text{O} + \text{H}_2 + \text{H} )</th>
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<td>0.11±0.05</td>
<td>0.67±0.06</td>
<td>0.04±0.06</td>
</tr>
</tbody>
</table>

Table 4.11: Measured branching fractions in the DR of \( \text{H}_3\text{O}^+ \).

nel \( \beta \) should occur in 80% of all dissociation events. Conversely, Bates’ empirical model predicted the channel producing the water molecule to be dominant [40, 41]. The first experiments reporting the complete branching fractions were performed in 1996 at a FALP machine and the ASTRID storage ring [59, 234]. The results from the FALP experiment showed channels \( \beta, \gamma \) and \( \delta \) to be almost equally populated with channel \( \alpha \) being minor. The experiment at ASTRID utilised a similar grid technique to that implemented at CRYRING in 1995 by Datz et al. [44]. The results from the ASTRID measurements were significantly different to those from the FALP. Subsequent improvements to the quality of the detection system at ASTRID gave better precision in the measurements [86]. CRYRING experiment performed by Neau et al. for the DR of \( \text{H}_3\text{O}^+ \) and the heavier isotopologue \( \text{D}_3\text{O}^+ \) completely supported the ASTRID results [85]. In particular, the expected absence of the isotope effect for branching was verified [85, 86]. The different measurements of the branching fractions are summarised in Table 4.11. Use of laser induced fluorescence detection at the FALP machine enabled the total yield of the OH fragments to be measured. Two independent experiments ascertained that OH radicals are produced in 65% of all events and that formation of OH in its vibrational ground state dominates [31, 32]. These results support FALP experiment performed by Williams et al. for complete branching measurement where \( n_\beta + n_\gamma = 0.65 \) [234]. In an attempt to understand the branching behaviour some theoretical calculations were carried out. In particular, Ketvirtis and Simons suggested that the favourable formation of the OH+H+H channel is due to secondary fragmentation of \( \text{H}_2\text{O} \) and \( \text{H}_2 \) arising from \( \alpha \) and \( \beta \) channels, respectively [235]. \textit{Ab initio} trajectory calculations involving five state of neutral \( \text{H}_3\text{O} \) starting from the second Rydberg state verified predominance of \( \gamma \) channel and predicted that ejection of both H fragments occurs on the femtosecond scale which implies that sequential break-up is highly unfavoured since, in this case, the intermediate predissociative molecules are expected to be in-touch longer than \( 10^{-11} \) s [236]. In the present paper, the investigation into the DR reaction of \( \text{H}_3\text{O}^+ \) at CRYRING is extended with the aim of determining the break-up dynamics of the OH+H+H channel and vibrational population of the OH fragments, i.e.

\[
\text{H}_3\text{O}^+ + e \rightarrow \begin{cases} \text{OH}(v = 0, J = 0) + \text{H} + \text{H} + 1.3 \text{ eV} \ (\gamma_1) \\ \text{OH}(v = 1, J = 0) + \text{H} + \text{H} + 0.86 \text{ eV} \ (\gamma_2) \\ \text{OH}(v = 2, J = 0) + \text{H} + \text{H} + 1.44 \text{ eV} \ (\gamma_3) \\ \text{OH}(v = 3, J = 0) + \text{H} + \text{H} + 0.04 \text{ eV} \ (\gamma_4) \end{cases}
\] (4.30)
Figure 4.11: a) Estimated distribution of the kinetic energy released in the OH+H+H channel arising from the DR of H$_3$O$^+$. b) Experimentally measured and Monte-Carlo simulated TD distributions are shown by the solid squares and dashed curves, respectively. The overall fit is presented by the solid curve.

The experiment has been performed in a fashion similar to that employed in the studies of XH$_2^+$ ions, e.g. H$_2$O$^+$, CH$_3^+$, NH$_2^+$, PD$_2^+$ and PD$_3^+$ (Paper II). An Al foil 2.5 $\mu$m thick has been used to identify the flash on the PS belonging to the OH fragment. Due to the geometrical size of the foil, which is 5 mm in diameter, the information about $\gamma_4$ channel cannot be defined since the hydrogen atoms do not have enough translational energy to avoid the foil. In contrast to previously measured ions, the data analysis for the OH+H+H channel is expected to be more complicated, since 1) the $\gamma_1$-$\gamma_4$ channels should be resolved with the KER difference of $\approx$0.4 eV, while channels for previous molecular ions were separated at least by 1.5 eV; 2) the OH fragment can contain extra internal energy for rotational motion. In order to approximately estimate the KER distribution in the OH+H+H channel, the experimentally measured TD distribution has been analysed in the following fashion: quite arbitrary TD distributions have been generated by means of the Monte-Carlo simulation for KER values in the range from 0.1 eV to 1.9 eV with a step of 0.1 eV which have been then fitted to the experimental distribution and the scaling coefficient have defined the KER distribution (Fig. 4.11(a)). The contribution at energy of 1.9 eV is assumed to be spurious and to originate from non-DR events, such as dark counts on the PS, thermal electrons on the CCD camera and false-coincidence events. The contribution at energy of 1.5 eV can only arise from internal excitation of the parent H$_3$O$^+$ ions. It is unlikely that ions were vibrationally excited since all of the modes are infra-red active and 4 $s$ is expected to be long enough to spontaneously emit infra-red photons. As such, the ions were presumably rotationally hot. The ground state of H$_3$O$^+$ belongs to $C_{3v}$ symmetry therefore posses a dipole moment of 0.6738 $e$ a$_0$ [237]. However, the ground state has very low barrier to inversion of 90 meV to the $D_{3h}$ symmetry [238]. Indeed, the ions contained $\approx$0.2 eV internal energy which was enough to reach equilateral sym-
metry. It is interesting to note that $H_3^+$ produced by a similar ion source to that used here were reported by the TSR group based on the imaging data to retain the rotational energy of 0.3 eV for time longer than 40 s [65]. The reactions involved to produce $H_3O^+$ and $H_3^+$ are similar, i.e. protonation of water and $H_2$, respectively, therefore it is not surprising that in both cases the molecular ions are rotationally hot. The obtained vast $KER$ distribution implies that OH fragments were produced rotationally excited. In order to perform more qualified analysis of the vibrational branching fractions the rotational distributions have been assumed to be adequately described by pure thermal distributions. Since $H_3O^+$ is a symmetric top molecule the population of a particular rotational state described by $J$ and $K$ quantum numbers is

$$N(K, J) \propto g \cdot \exp \left( -\frac{E(K, J)}{kT} \right),$$

(4.31)

where $g$ is degeneracy which is $2J+1$ for $K=0$ and $2(2J+1)$ for $K>0$. A Monte-Carlo simulation considering the rotational distributions of both the parent $H_3O^+$ ions and the OH fragments has been employed to generate $TD$ distributions for $\gamma_1$-$\gamma_3$ channels which have enabled the fractions for these channels to be deduced: $0.15\pm0.12$, $0.63\pm0.08$ and $0.22\pm0.12$, respectively (Fig. 4.11(b)). The relatively large error bars is due to the uncertainties in the rotational temperatures values of $T_{H_3O^+}=1980\pm630$ K and $T_{OH}=1770\pm790$ K. The fact that two rotational temperatures are similar might indicate that energy stored in the parent ions efficiently transfers into the OH fragments.

The predominant formation of OH($v=1$) disagrees with two independent FALP experiments reporting OH($v=0$) as being the main route [31, 32], while \textit{ab initio} trajectory calculations clearly indicates the broad vibrational energy distribution [236]. This could be due to the principle different natures of two experiments. The experiments in the storage rings are carried out under ultra-high vacuum conditions while the flow tubes operate at a pressure of $\approx$Torr allowing high number of collisions such that plasma is expected to thermalise ($T_e=T_i$), i.e. in the FALP experiment the DR reaction occurs over a wide range of interaction energies described by an ambient temperature, while the present study has been performed for $T_e=15$ K and $T_i=2000$ K. On the other hand, in the FALP experiment the thermalisation of the DR products can also occur. Indeed, the rotational states of the OH fragments were observed to be totally thermalised to 290±40 K [31]. It was assumed that vibrational thermalisation is much slower. Indeed, if the fragments collide only with Ar, which is the main constituent of the plasma, then the rate coefficient for the reaction

$$Ar + OH(v \neq 0) \to Ar^* + OH(v = 0),$$

(4.32)

is $<10^{-14}$ cm$^3$s$^{-1}$ which is very low [239]. On the other hand, NO gas was introduced into the flow tube to substantially increase OH($v=0$) through the reaction

$$NO + OH(v \neq 0) \to NO^* + OH(v = 0),$$

(4.33)
which has rate constant of \(6 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}\) [30]. Such technique allows determination of fraction of OH(\(v \neq 0\)) by varying NO concentration [30, 84]. It is interesting to note that the reaction

\[
\text{H}_2\text{O} + \text{OH}(v \neq 0) \rightarrow \text{H}_2\text{O}^* + \text{OH}(v = 0),
\]

has a rate constant of \(\approx 2 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}\) [239] and water was used in the experiment as a precursor for the H\(_3\)O\(^+\) ions. One other aspect worth mentioning is that the interaction and detection region in the flow tube are separated and the time needed for the products to be detected is \(\approx 4 \text{ ms}\). However, radiative time for \(\tau(v = 1 - 15) = 93 - 8 \text{ ms}\) [30].

Unfortunately, little information is available on the vibrational population of the molecular DR products. Strasser et al. at TSR storage ring using the ID measured the vibrational population of the H\(_2\) fragments arising from the DR of H\(_3\)O\(^+\) [65]. The measurements showed quite broad vibrational distribution. Subsequently Strasser et al. developed a purely statistical model which enabled the observed distribution to be explained [43]. Furthermore, calculations performed for the DR NH\(_4\)\(^+\) predicted that the NH\(_3\) fragment is formed highly vibrationally excited and can store as much as 4.0 eV from the 5.1 eV available energy [141]. As a result of this, 20\% of the formed NH\(_3\) can fragment further into NH\(_2\)+H which is supported by experimental observations. Petrignani et al. investigated three-body break-up of NO+N+O arising from the DR of weakly-bound dimer, NO·NO\(^+\), and found that NO formed vibrationally excited as well [68]. Both of the heavy water molecules, D\(_2\)O, originating from the almost exclusive three-body break-up of D\(_5\)O\(^+\) store \(\approx 4.0 \text{ eV vibronic energy}\) [71]. This limited amount of information clearly indicates that vibrational excitation of the DR products is quite possible and in some cases can even lead to further fragmentation.

The dynamics of the OH+H+H fragmentation channel has also been investigated. By means of the Monte-Carlo simulation the distributions of angles measured in the c.m. frame between the H fragments (\(\chi\)), their energy ratio (\(\rho\)) and the fraction of the energy received by OH fragment upon break-up (\(E_{\text{OH}}/\text{KER}\)) are shown in Fig. 4.12. As mentioned earlier in Chapter 3.5.3 the parameters \(\rho\) and \(\chi\) can uniquely describe the break-up geometries. The \(\rho\) distribution for H\(_3\)O\(^+\) is similar to those obtained for H\(_2\)O\(^+\), CH\(_4\)+, NH\(_2\)+, PD\(_2\)+ and SD\(_2\)+ ions in which the energy between hydrogen atom is randomly (or partly randomly) distributed (Paper II). It is surprising that angular distribution is randomly distributed, while for a similar channel of X+H+H arising from the DR reaction of H\(_3\)\(^+\), H\(_2\)O\(^+\), CH\(_2\)+, NH\(_2\)+, PD\(_2\)+ and SD\(_2\)+ ions propensity to dissociate at bent and/or open angles has been observed (Paper II). Of course, it could be due to the increase in rotational states of the parent H\(_3\)O\(^+\) ions, i.e. more states are involved so less features are observed in the distribution. However, H\(_3\)\(^+\) were rotationally hot (\(kT \approx 0.3 \text{ eV}\)), while the molecule preferentially dissociate through synchronous concerted mechanism [65]. The obtained distribution allows to obtain insight into the mechanism responsible for the fragmentation. In the case of a sequential break-up involving intermediate H\(_2\)O(X\(^2\)A\(_1\)) as suggested by Krevits and Simonson [235], the free hydrogen
atoms receives \( \approx 95\% \) of the \( KER \) and the second bond rupture occurs quite late for the second hydrogen atom to receive some part of this energy, i.e. such a mechanism would manifest itself in the peak around 0.05 in the \( \rho \) distribution. On the other hand, if the break-up sequence involves \( \text{OH}(X^2\Pi) \) and \( \text{H}_2 \), then due to similar reasons the energy of the \( \text{OH} \) should be a certain value determined by the position of the predissociative state of the intermediate \( \text{H}_2 \). Both \( \rho \) and \( E_{\text{OH}} \) distributions imply that a sequential mechanism is unlikely to be responsible for the fragmentation (Fig. 4.12(b,f)). A synchronous concerted break-up is when \( E_{H_1} = E_{H_2} \), i.e. simultaneous rupture of two OH-H bonds and which corresponds to \( \rho \) being equal 1. The derived \( \rho \) distribution does not support such a mechanism. As such, it is reasonable to conclude that three-body fragmentation proceeds through an asynchronous concerted mechanism, i.e. on the time scale shorter than a rotational period of the molecule. Larsson and Thomas have assigned random distribution of \( \rho \) to this mechanism [240].

In order to be able to investigate the influence of the rotational population of parent \( \text{H}_3\text{O}^+ \) on both the product distribution and break-up dynamics, the ions should be produced at much lower energy. For instance, supersonic ion source would facilitate investigation into this effect. The next ion from this series (\( \text{XH}_3^+ \)) to be studied enabling more insight into fragmentation behaviour.

Figure 4.12: The experimentally measured and Monte-Carlo simulated distributions of kinetic energy ratio between hydrogen atoms, \( \rho \), (a), angle measured between hydrogen atom in the c.m. of frame, \( \chi \), (c), and fraction of the energy received by the OH fragments upon break-up (e) are shown by the solid squares and solid curves. The parameter distributions retrieved by the Monte-Carlo simulation are shown in (b), (d) and (f).
could be $\text{SH}_3^+$, since it is known to fragment predominantly through $\text{SH}+\text{H}+\text{H}$ break-up [233]. However, to make such measurement feasible at CRYRING the heavier isotopologue of $\text{SD}_3^+$ has to be used instead in order to reduce the H fragments loss fraction. A similar study has already been undertaken for the deuterated $\text{SD}_2^+$ [70].
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Yours Sincerely,

Vitali
Bibliography


