Dissociative recombination of organic molecular ions of relevance for interstellar clouds and Titan’s upper atmosphere
Dissociative recombination of organic molecular ions of relevance for interstellar clouds and Titan’s upper atmosphere

Erik Vigren
To my family
Abstract

This thesis presents experimental studies on the dissociative recombination (DR) of the organic molecular ions $\text{CD}_3\text{CND}^+$, $\text{CH}_2\text{CHCNH}^+$, $\text{CH}_3\text{CH}_2\text{CNH}^+$, $\text{CD}_3\text{CDO}^+$, $\text{CH}_3\text{CHO}^+$ and $\text{DCOOD}_2^+$. The experiments were all performed at the heavy ion storage ring CRYRING at the Manne Siegbahn Laboratory in Stockholm, Sweden. DR is the process in which a singly charged molecular cation captures a free electron, forming a highly excited intermediate molecule which then dissociates into exclusively neutral fragments. The process plays an important role as a plasma neutralizing mechanism in many cold, low density plasmas such as those encountered in planetary ionospheres and interstellar clouds. DR can also act as the final step in the gas-phase synthesis of different neutral molecules in such environments.

Our experimental findings indicate that nitriles that are lost by protonation in Titan’s upper atmosphere or in interstellar clouds to a large extent may be recycled by DR. Also, it appears that the DR of nitrile ions does not break the C-N bond, which supports the hypothesis that nitriles which are formed in Titan’s upper atmosphere do not degrade to recover $\text{N}_2$. For the studied acetaldehyde cations, $\text{CD}_3\text{CDO}^+$ and $\text{CH}_3\text{CHO}^+$, we observed a considerable isotopic effect in the cross section, with the lighter isotopologue being more reactive. In the DR of $\text{DCOOD}_2^+$ an upper limit of only 13% for the branching fraction of the $\text{DCOOD} + \text{D}$ channel was found. This finding has pronounced effects on the predicted abundance of formic acid in dark clouds.
List of publications

Included in thesis


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Publications not included in thesis


Contribution by author

I have participated in the CRYRING experiments on the dissociative recombination of CH$_2$CHCNH$^+$, CH$_3$CH$_2$CNH$^+$, DCOOD$_2^+$, CD$_3$CDO$^+$ and CH$_3$CHO$^+$. I also took part in the preparation for these experiments. I have been responsible for the data analysis to extract information on the dissociative recombination cross sections, thermal rate coefficients and branching fractions for the molecular ions mentioned above and also for CD$_3$CND$^+$. I wrote all papers included in the thesis. In 2007 I spent two weeks at Queen’s University in Belfast and was instructed by Professor Tom J. Millar and Catherine Walsh how to modify and run a gas-phase model of dark molecular clouds using the UMIST database for astrochemistry. I used this model in Paper II, V and VI to investigate the effects of our experimental results on the predicted abundances of various organic molecules in the dark cloud TMC-1.

Apart from the work presented in the thesis I have taken part in other CRYRING experiments on dissociative recombination reactions. I have also spent a total of six weeks with the group of Roland Wester at the University of Freiburg, Germany, participating in photodetachment experiments on carbon chain anions, which are of astrochemical relevance. Finally I have been involved in radio observations at Onsala Space Observatory, Sweden, with the aim to gain understanding of the synthesis of methanol in different astrophysical environments.
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Chapter 1

Introduction

In this chapter an introduction to interactions between singly charged molecular cations and free electrons is presented and different possible outcomes of such reactions are discussed. In particular, dissociative recombination is emphasized; the process in which the highly excited intermediate molecule formed by the electron capture dissociates into exclusively neutral fragments.

1.1 Interactions between molecular cations and free electrons

When a free electron ($e^-$) is captured by a singly charged molecular cation ($AB^+$) (see section 1.2.1) a highly excited neutral molecule ($AB^*$) is formed with various possibilities to dispel this excess energy. If the electron is reemitted ($AB^+ + e^- \rightarrow AB^* \rightarrow AB^+ + e^-$) the process is called autoionization or scattering. Depending on whether the internal energy of the ion is increased, stays constant, or is decreased by the process, one distinguishes between inelastic, elastic and super-elastic scattering, respectively. Relaxation by emission of one or more photons, so called radiative recombination ($AB^+ + e^- \rightarrow AB^* \rightarrow AB + h\nu$) is another way for the intermediate molecule to dispel its excess energy. In dense environments there is also the possibility of stabilization via collisions with a third body ($AB^+ + e^- \rightarrow AB^* + M \rightarrow AB + M^*$).

Another way for $AB^*$ to relax is to dissociate into various fragments with a neutral net charge. The excess energy is used to break chemical bonds and the remainder goes into internal and/or translational energy of the fragments. With neutral products the process is called dissociative recombination ($AB^+ + e^- \rightarrow AB^* \rightarrow A + B$). Other processes, such as dissociative excitation ($AB^+ + e^- \rightarrow AB^* \rightarrow A^+ + B + e^-$) or ion pair formation ($AB^+ + e^- \rightarrow AB^* \rightarrow A^+ + B^-$) are typically highly endoergic and thus largely irrelevant for e.g. the chemistry in the interstellar medium.

1.2 Dissociative recombination

Dissociative recombination (DR) is the gas-phase process described by the following simplified formula

$$AB^+ + e^- \rightarrow AB^* \rightarrow A + B$$ (1.1)

As will be seen later DR plays an important role in the chemistry of e.g. interstellar clouds and when incorporated in astrochemical models it is necessary to have insight into the thermal
rate coefficients and the branching fractions of the reaction. DR is a binary reaction, thus associated with a second order rate coefficient. The loss rate in the concentration of the molecular ion, \( i \), due to DR in a plasma is proportional to the concentration of \( i \) and the free electron concentration, \( n_e \)

\[
\frac{dn_i}{dt} = -k_{DR} n_i n_e
\]  

(1.2)

The temperature dependent proportionality constant \( k_{DR} \) is the thermal rate coefficient (unit of \( \text{cm}^3\text{s}^{-1} \)) also defined as the expectation value of the product of the relative velocity between the reactants and the cross section, \( \sigma \), for DR

\[
k_{DR} = \langle v_{rel}\sigma \rangle
\]  

(1.3)

For polyatomic molecules ABC\(^+\) the highly excited intermediate molecule can dissociate into different sets of fragments, e.g.

\[
\text{ABC}^+ + e^- \rightarrow \text{ABC}^* \rightarrow \text{AB} + \text{C} \text{ or A + BC or A + B + C}
\]  

(1.4)

For astrochemical models it is important to know the branching fractions of the different possible product channels. The main focus of this thesis is the experimental determination of the thermal rate coefficients and branching fractions for the DR of a selection of organic molecular ions.

### 1.2.1 Mechanisms of dissociative recombination

DR was first drawn attention to in 1931 as it was suggested as a depletion mechanism for \( \text{O}_2^+ \) in the Earth’s ionosphere, leading to the observed green light aurora [1, 2]. In early attempts to describe the ionization balance of the ionosphere the DR reaction was, however, thought of as being too slow a process to play a significant role and electrons were instead assumed to be removed primarily by attachment to neutrals followed by recombination of negative and positive ions [3]. In 1949 it was experimentally proven in a stationary afterglow measurement that electron recombination indeed can be an efficient reaction for molecular ions, proceeding with much larger rate coefficients than predicted theoretically for radiative recombination [4]. That finding stimulated theoreticians to formulate theories regarding DR and two major pathways for the reaction, the so-called direct and indirect mechanisms, were formulated. In the direct DR process, proposed by Bates in 1950 [5], the free electron is captured into a molecular orbital with the released energy being simultaneously transferred into excitation of a bound electron forming a doubly excited repulsive neutral state. Autoionization can occur until the internuclear distance passes the crossing point between the repulsive curve and the ground state of the molecular ion. Thereafter the molecule cannot autoionize and will dissociate. In the indirect DR process, independently proposed by Bardsley [6] and Chen & Mittleman in 1967 [7], the electron is captured into a ro-vibrationally excited Rydberg state,
i.e. the nuclear core is excited. Subsequently, by a radiationless transition, the doubly excited repulsive state is reached from which the molecule can dissociate. The potential curves for these two mechanisms are shown in Figure 1.1.

![Diagram of potential energy curves](image)

**Figure 1.1** The direct and indirect DR mechanisms for a diatomic molecular ion AB^+. In the direct DR process (1) the ion captures an electron into a doubly excited repulsive state of the neutral, AB**, through which dissociation into A and B can occur. In the indirect process (2) the dissociation also occurs from AB** but in this mechanism the electron is initially captured into a ro-vibrationally excited Rydberg state, AB*(Rydberg).

### 1.2.2 Role of dissociative recombination in some natural plasmas

Among the molecular cation-electron interactions mentioned in section (1.1) DR is in fact the most important process in environments such as interstellar clouds, planetary ionospheres and cometary comae. These are typically associated with low temperatures (10 to a few 100 K) and low particle concentrations ($10^2$-$10^{10}$ cm$^{-3}$) thereby implying low collision energies and the absence of three-body reactions. The low collision energies prevent the highly excited intermediate molecule formed by the electron capture from dissociating into any other charged fragments than the initial reactants. Rate coefficients for the DR of molecular ions are typically $10^{-7}$-$10^{-6}$ cm$^3$ s$^{-1}$ at 300 K and higher at lower temperatures while radiative recombination reactions have rate coefficients in the vicinity of $10^{-12}$ cm$^3$ s$^{-1}$ [2].

Autoionization competes with DR but is not a process that needs to be considered in astrochemical models since the chemical products of the reaction are the same as the initial reactants.

One important role of DR in planetary ionospheres and interstellar clouds is that it acts as a plasma neutralizing mechanism. Furthermore, DR can serve as a final step in the gas-phase synthesis of different molecules in such environments. It should also be noted that DR plays a role for the chemistry occurring in man-made plasmas in e.g. combustion processes [8].
1.3 General motivations and outline of thesis

Theoretical investigations of the DR process have essentially been limited to smaller ions than those considered in this thesis, and at present there exists no theory with a general predictive power on the DR branching fractions. An earlier hypothesis implying that DR proceeds through the channel involving minimum rearrangement of valence bonds [9] has been disproved by numerous experiments. For example it was shown in the DR of C$_2$D$_5^+$ that 13% of the reactions occur via a four-body breakup, and in the DR of protonated methanol (CH$_3$OH$_2^+$) only a few percent of the reactions lead to methanol [10, 11]. Moreover, in the DR of the ozone cation, O$_3^+$, as much as 94% of the reactions involved the three-body breakup [12]. These results prove the prediction of branching ratios by chemical intuition to be associated with a certain amount of doubt and highlight the need for experimental investigations into astrophysically relevant DR processes.

The thesis is mainly devoted to experimental studies on the DR of the molecular ions CD$_3$CND$^+$ (Paper I), CH$_2$CHCNH$^+$ (Paper II), CH$_3$CH$_2$CNH$^+$ (Paper III), CD$_3$CDO$^+$ (Paper IV), CH$_3$CHO$^+$ (Paper V) and DCOOD$_2^+$ (Paper VI). The experiments were all conducted at the heavy ion storage ring CRYRING in Stockholm.

Most of the experiments were followed up by chemical modelling in order to see the effects of our results on the predicted abundances of various organic molecules in dark molecular clouds. Some of the results are also expected to add further insight into the chemistry of environments such as hot cores, cometary comae and in particular the upper atmosphere of Titan, the largest satellite of Saturn.

The outline of the thesis is as follows. In chapter 2 a brief overview is given on the chemistry of different types of interstellar clouds and the atmosphere of Titan. Chapter 3 and 4 present the experimental approach and data evaluation, respectively. Chapter 5 describes the chemical model that has been used to simulate the chemistry of dark clouds. Finally, in chapter 6, motivations for the individual studies are given as well as a summary of the obtained results and discussions on their influence on models of dark clouds and/or Titan’s upper atmosphere.
Chapter 2

Interstellar clouds and Titan’s atmosphere

In this chapter a brief overview is given of the chemistry in different types of interstellar clouds. Dark interstellar clouds are the birth-sites of new stars that possibly can be surrounded by planetary systems. We also briefly discuss atmospheres in the solar system and focus in particular on the atmosphere of Titan.

2.1 Interstellar clouds

The interstellar medium (ISM), the region between stars in a galaxy, is far from empty but consists of gas and dust grains, mainly distributed in very large regions known as interstellar clouds. The denser clouds act as sites for formation of new stars; possibly surrounded by planetary systems. Hydrogen and helium are the major elemental constituents, but the ISM consists also of heavier elements that have been produced during the lifetimes and final stages of earlier stars [13, 14].

One of the main goals within astrochemistry is to gain an understanding of the chemistry of interstellar clouds and observations are a key part in this study. Not only do they reveal their chemical composition but also provide necessary information to enable the extraction of physical parameters such as gas-temperatures and number densities [13]. Knowing the abundances of different molecules in a region in the ISM naturally leads to the question of how these molecules may have been formed. The underlying reasons differ between the various types of clouds, just as the chemical compositions also vary. Astrochemical models are run in order to simulate the chemical evolution of interstellar clouds. Such models, described further in chapter 5, consist of networks of chemical reactions in which constituents are linked to each other by reactions with associated rate coefficients. This highlights the need for detailed investigations, either experimental or theoretical, into chemical reactions of relevance for interstellar chemistry.

More than 150 molecules [15], many of which are organic, have hitherto been observed in interstellar and circumstellar environments. The actual number of different molecules in these media is probably much higher. Many molecules existing in the ISM are difficult to produce in laboratories and their spectral signatures largely unknown. Molecules can also be fairly complex and possess many ways to internally relax. This implies that the emissions from these species can be spread over so many lines that no single line becomes strong enough for a firm detection.
2.1.1 Diffuse clouds

Diffuse clouds (diameters often tens of light years) are associated with particle densities of about 10-100 cm$^{-3}$ and temperatures in the region of 30-100 K [13, 14, 16]. The chemistry is dominated by atomic hydrogen (diffuse molecular clouds can have as much hydrogen in molecular form) and helium. Due to the low particle density the grains in diffuse clouds do not effectively block out the interstellar UV-field (from stars). This not only implies that the chemistry can be probed by a wide range of observational techniques [13], it has also important in situ consequences. Virtually all carbon is ionized, thus C$^+$ becomes the main sink for carbon. It is expected that the concentration of this ion closely resembles the concentration of free electrons [16], such that diffuse clouds have a fractional ionization of $\sim 10^{-4}$. Other major constituents such as H, He, H$_2$, O and N cannot be ionized by stellar UV radiation because it does not extend to high enough energies, terminating at 13.6 eV, the ionization potential of atomic hydrogen [13, 17]. Species with higher ionization potentials can, on the other hand, be ionized by cosmic ray particles (thought to originate from supernovae), which can trigger some ion-neutral chemistry. Molecules that are produced in diffuse clouds are subjected to the UV-field and are expected to photodissociate relatively fast. Nevertheless, simple diatomic molecules have been observed in these media, such as CN, CH and CH$^+$ as well as a few more complex molecules including formaldehyde (H$_2$CO) and hydrogen cyanide (HCN) [16].

The grains, produced in the final stages of the life of a star, play an important role in the chemistry despite the fact that they are estimated to account for only about 1% of the mass of diffuse clouds [13, 16, 18]. It is primarily on their surfaces that the formation of H$_2$ molecules occurs through the reaction H + H$\rightarrow$ H$_2$ [13, 16]. In the gas phase this reaction is inefficient, as the hydrogen atoms come together an unstable excited molecule forms which is much more likely to dissociate back to the reactants than to relax through photon emission. On grains reaction energy can be taken up by the grain itself allowing for a kind of third body relaxation mechanism of the H$_2$ molecule [18].

2.1.2 Dark clouds

Dark clouds (also referred to as cold molecular or dense clouds) have number densities of about $10^4$ cm$^{-3}$ or higher and temperatures between $\sim$10 and 50 K [13, 16]. Their sizes vary but diameters of approximately a light year are rather common. These clouds are formed by gravitational contraction of diffuser media. Dark clouds owe their name to their appearance as holes in the night sky. Their densities are sufficient to block the light in the visible and UV range from background stars, while light at longer wavelengths can penetrate them. Figure 2.1 shows the dark cloud Barnard 68 (a so-called bok-globule) seen in visible and infrared. The hydrogen in dark clouds is almost exclusively in molecular form. The self-shielding against external UV-radiation results in a lower fractional ionization ($\sim 10^{-8}$ - $10^{-7}$) than in diffuse clouds and the main carrier of carbon in these regions is CO [13, 19]. In the absence of external UV radiation and with lower fractional abundance of free electrons than in diffuse clouds ion-neutral chemistry can produce a rich variety of molecules [13, 16, 19].
The chemistry in these regions is mainly initiated by the ionization of H$_2$ by cosmic ray particles leading to H$_2^+$, which reacts with H$_2$ forming H$_3^+$ [20]. H$_3^+$ ions serve as proton donors to species with higher proton affinities than H$_2$. As an example the main gas-phase synthesis of water is associated with the reaction sequence

\[
H_3^+ + O \rightarrow OH^+ + H_2 \\
OH^+ + H_2 \rightarrow H_2O^+ + H \\
H_2O^+ + H_2 \rightarrow H_3O^+ + H \\
H_3O^+ + e^- \rightarrow H_2O + H
\]

The feasibility of all of these reactions and their rate coefficients have been demonstrated and determined experimentally [21-24]. As for the DR of H$_3$O$^+$ the channel leading to H$_2$O has been shown to have a branching fraction of $\sim$18%, while the channel leading to OH + H + H dominates ($\sim$67%) [24].

One of the most extensively studied dark clouds is TMC-1, a dense starless region within the Taurus Molecular Cloud, located towards the Taurus constellation at a distance of $\sim$400 light years from our solar system. More than 50 molecules (mainly organic ones) have been observed in this cloud and its physical parameters are reasonably well established [25, 26].

2.1.3 Hot cores

Hot cores, or hot molecular cores, are found in the vicinity of young and massive stellar objects formed through the gravitational contraction of dark clouds. The gas density and temperature vary with the distance to the star(s) but are typically given as $\sim$10$^6$-$10^8$ cm$^{-3}$ and 100-300 K, respectively [13]. Hot cores have rich chemistries characterized by high fractional abundances of saturated molecules such as water, ammonia and methanol. These molecules are believed to be products of chemistry occurring both in the gas-phase and on grains. During the collapse of dark clouds, gas-phase species freeze out on interstellar grains where
they can serve as reagents in grain-surface reactions. As the temperature increases through the conversion of potential energy into kinetic energy in the collapsing cloud and through the photon emission of emerging stars, these molecules desorb from the grains into the gas-phase where they can be further processed [13, 27].

2.1.4 Star and planetary system formation

The collapse of a molecular cloud can lead to a central temperature that is high enough for fusion processes to start and for a star to be born. Typically, interstellar clouds have a very small rotational velocity and during contraction the ensemble of material starts to rotate faster and faster according to the law of conservation of angular momentum. This results in the development of a disk centered about the young star (in this description it is assumed that one solar mass star develops) which continues to accrete (and blow away) surrounding material [28, 29]. Models, which partly rely on ion chemistry including DR reactions, have been run with the aim to simulate the chemistry in disks around young stellar objects [30, 31]. One ultimate goal of such models is to aid understanding and to enable the prediction of chemical properties of planets formed at different radii from a star [30]. The disks have a 2-D layered structure controlled by the irradiation from the star such that the chemistry is dependent on both the distance to the star as well as the height above the midplane of the disk [30].

Gradually the dust particles in the disk coagulate to form planetesimals and eventually planets. Small objects in close vicinity to the star cannot keep volatile species such as hydrogen and helium. Planetesimals further out in the system, beyond the so-called snow line, can use (water rich) ice in their build-up processes and accumulate volatiles to increase their mass and gravity [28], which enables them to attract even more gas. This explains why the inner planets (Mercury, Venus, Earth and Mars) in our solar system are rocky while the outer ones (Jupiter, Saturn, Uranus and Neptune) are gas giants.

Comets, having spent their existence at far distances from the sun, are probably the most pristine bodies in the solar system. They have been claimed to carry almost unaltered material from the protoplanetary disk and possibly also from the molecular cloud that pre-dated the sun. Studies of comets can therefore provide insights, and have indeed done so, into the very early solar system history [32-34]. Comets contain minerals and ice composed primarily of H$_2$O, CO and CO$_2$, but other molecules have also been discovered, including e.g. HCN, H$_2$CO, CH$_3$OH, CH$_3$CN, HCOOH and CH$_3$CHO [33]. Chemical modelling, involving e.g. radical-radical reactions, ion-neutral reactions and DR, is an important aspect also in the study of comets providing clues to whether specific molecules observed in the cometary comae are parent molecules (sublimated from the cometary surface) or daughter molecules (synthesized via gas-phase reactions in the coma) [33]. During the turbulent early phases in the formation of the solar system there is evidence, for example provided by studies of craters on the moon, that the Earth was heavily bombarded by comets; the so called late heavy bombardment ended about 3.8 billion years ago. It has been suggested that these impacts possibly delivered large amounts of water and bio-molecular precursors to the Earth [34, 35].
The planets in the solar system have atmospheres of different compositions [28]. Mercury, due to its low mass and close mean distance to the sun, has practically no atmosphere (surface pressure of $\sim 10^{-15}$ atm). Its closest neighbor, Venus, has a very dense atmosphere with a surface pressure of 90 atm and is dominated by CO$_2$ (96%), N$_2$ (3.5%) and sulphur compounds. The Earth’s atmosphere is mainly composed of N$_2$ (78%) and O$_2$ (21%). Mars has a thin atmosphere (a surface pressure of 0.007 atm) which is composed primarily of CO$_2$ (95%) with residual N$_2$, O$_2$ and Ar.

The atmospheres, or outer parts, of the gaseous planets Jupiter, Saturn, Uranus and Neptune are all dominated by H$_2$ and He but do contain traces of other species. To obtain an understanding of the bulk chemical composition of planetary atmospheres, in particular those of the inner planets, requires input from a wide range of scientific fields and the reasons for the planets having different atmospheres will not be further discussed here.

Among all the satellites orbiting planets in our solar system only one has a substantial atmosphere, the Saturnian moon Titan. The investigation on the DR of protonated nitriles (Paper I-III) was partly motivated by recent observations in Titan’s upper atmosphere. Therefore, we present in the next section a brief overview on the chemistry of Titan’s atmosphere.

### 2.3 Chemistry of Titan’s atmosphere

Titan is the largest satellite of Saturn and the second largest moon in the solar system after Jupiter’s Ganymede. As noted it is the only satellite within the solar system carrying a dense atmosphere with a surface pressure of $\sim 1.5$ atm [36]. Some other important figures relating to Titan are given in Table 2.1. Titan generates no magnetic field of its own, but is, however, mostly within the magnetosphere of Saturn, and thus shielded from the solar wind.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean distance to the sun</td>
<td>$1.4 \cdot 10^7$ km (9.54 AU)</td>
</tr>
<tr>
<td>Mean distance to Saturn</td>
<td>$1.2 \cdot 10^8$ km (~20 Saturn radii)</td>
</tr>
<tr>
<td>Mass</td>
<td>$1.35 \cdot 10^{23}$ (5.97 \cdot 10^{24}$ kg</td>
</tr>
<tr>
<td>Mean radius</td>
<td>2576 ${6371}$ km</td>
</tr>
<tr>
<td>Mean surface temperature</td>
<td>93 ${287}$ K</td>
</tr>
<tr>
<td>Mean density</td>
<td>1.88 ${5.5}$ g cm$^{-3}$</td>
</tr>
<tr>
<td>Rotation about axis, Saturn, and the sun</td>
<td>16 days, 16 days, 30 years</td>
</tr>
<tr>
<td>Acceleration constant</td>
<td>1.35 ${9.81}$ m s$^{-2}$</td>
</tr>
<tr>
<td>Solar constant</td>
<td>15 ${1370}$ Wm$^{-2}$</td>
</tr>
</tbody>
</table>
2.3.1 Major constituents of Titan’s atmosphere

Titan was first suggested to possess an atmosphere in 1908 by Comas Solá. He noted in an optical observation that the edges of Titan appeared fuzzy which was indicative of an atmosphere absorbing light from the sun [37]. A major discovery was reported in 1944 by Kuiper. Sunlight reflected on Titan showed absorption features corresponding to transitions in methane [38]. In fact Kuiper appointed that this finding should be regarded as the first proof of Titan having an atmosphere and wrote “It is difficult to see how ordinary visual observations could have ascertained the presence of an atmosphere on bodies less than 1´´ in diameter; in fact, such a thing would seem impossible.” It was not until the Voyager I mission, during which an UV spectrometer was used to probe the chemistry, that it was firmly established that the major constituent of Titan’s atmosphere, as of Earth’s, is nitrogen [39]. Subsequent observations and space missions, including the NASA/ESA Cassini/Huygens mission (Cassini is still operating) have improved the understanding of Titan and its atmospheric chemistry [40]. Mole fractions (altitude dependent) of the most abundant molecules in Titan’s atmosphere are 95-98% for N₂, a few percent for CH₄, and a few tenths of percent for H₂. The mole fractions of more complex hydrocarbons (e.g. C₂H₂, C₂H₄, C₄H₂) and nitriles (e.g. HCN, CH₃CN) are more sensitive to altitude [41], but in the upper atmosphere expected to be present on levels ranging from 0.1-1000 ppm [42].

2.3.2 Complex organic molecules in Titan’s atmosphere

Despite being minor constituents of Titan’s atmosphere the more complex hydrocarbons and nitriles have received substantial attention [42, 43]. These compounds are formed after the destruction of the major components by UV- and particle irradiation, and act as intermediates in the formation of the haze (aerosols) that envelopes Titan, giving the moon its brown/orange appearance [43-45] (see Figure 2.2).

Figure 2.2 Titan is enveloped by haze (aerosols) that covers the surface in the visible region. (NASA/courtesy of nasaimages.org)
Experiments on Titan aerosols (by instruments on the \textit{Huygens} probe) and laboratory produced analogs (tholins) have shown that they presumably are nitrogen rich [46-48]. Biomolecules such as amino acids can be produced by acid or basic hydrolysis of tholins [49-51]. These findings have raised the question of whether life can exist or could have been present once on Titan. It has also been debated that the early Earth could have had an atmosphere fairly similar to that presently existing on Titan, and it has been discussed that the synthesis of complex organic molecules in the atmosphere, and their further processing upon precipitation and contact with liquid water, may have played a role in the early evolution and even the origin of life on Earth [49, 50, 52]; although it is important to note that the question of the origin of life is far more complex than producing a few of its basic building blocks.

It has been suggested that the formation of nitriles mainly occurs in Titan’s upper atmosphere, \textasciitilde 1000 km above the surface, where the extreme UV-radiation and energetic electrons from Saturn’s magnetosphere can penetrate and break the strong triple bond of \( \text{N}_2 \) [53]. Nitrogen atoms in the ground state can react with hydrocarbon radicals to form C-N bonds, while excited nitrogen atoms and nitrogen ions also can react with the abundant methane and other hydrocarbons to create such bonds [54, 55]. Indeed a collection of instruments on the \textit{Cassini} spacecraft have recorded evidence for a rich abundance of very heavy molecular ions (both positive and negative) in Titan’s upper atmosphere, suggesting that this environment is not only an important factory for nitriles but also for the aerosols of Titan [56-58]. It has in fact been argued that determination of the upper atmosphere composition is necessary for an understanding of the nitrogen chemistry at all altitudes of Titan’s atmosphere [59].

\section*{2.3.3 Chemistry in Titan’s upper atmosphere}

In an attempt to reveal the chemical composition of Titan’s upper atmosphere, in particular to estimate the abundances of trace molecules, Vuitton et al. [59] used an ion-chemistry steady state model and data recorded by the Ion Neutral Mass Spectrometer (INMS) on the \textit{Cassini} spacecraft during the T5 flyby. We will refer to this work as V07 throughout this section. Other models have been run for Titan’s atmospheric chemistry including fully coupled ones [54, 60, 61]. The model by Krasnopolsky from 2009 is among the most ambitious, accounting for chemical reactions, different ionization mechanisms, haze formation, precipitation to the surface, atmospheric escape and diffusion [54]. This model also accounts for different temperatures and pressures at different altitudes.

V07 focused on Titan’s upper atmosphere, at an altitude of \textasciitilde 1100 km \( (T_{\text{gas}} \sim 180-200 \text{ K}, \text{ particle density} \sim 1-2 \cdot 10^9 \text{ cm}^{-3} ) \). The T5 flyby was conducted on April 16 2005 at a latitude 74º N with a closest approach of 1027 km above the surface. It occurred at the night side of Titan implying that the effects of UV-irradiation did not need to be accounted for in the model.

It is noted in V07 that the expected half-life for a molecule to undergo a chemical reaction in Titan’s upper atmosphere is significantly shorter than the expected half-life for it to be ionized or dissociated by energetic electrons. Therefore, the ionization (or dissociation) caused by energetic electrons is, in V07, only considered for the main chemical constituents \text{N}_2 and \text{CH}_4. The relative production rates of \text{N}_2^+, \text{N}^+, \text{CH}_n^+ (n=0,1,2,3,4) are calculated
adopting a CH$_4$ mole fraction of 3% [62], a mean electron energy of 100 eV [63], and electron impact ionization cross sections for N$_2$ and CH$_4$ taken from experimental studies [64, 65]. A net ionization rate of 1 cm$^3$s$^{-1}$ is used as it results in a good agreement between the model and the ion density as measured by the INMS.

All the chemical reactions considered in V07 include a cation as one of the reactants. Rate coefficients and branching fractions for ion-neutral reactions are retrieved from the literature and for unmeasured reactions a probable channel is assigned and a rate coefficient of $3 \cdot 10^{-9}$ cm$^3$s$^{-1}$ is adopted. DR is the only plasma neutralizing mechanism considered in the model. An electron temperature of 718 K is used in accordance with in situ measurements by the Langmuir probe on the Cassini spacecraft. DR reactions that only have been investigated at 300 K are assumed to have a temperature dependence of $T^{-0.7}$, while DR reactions that have not been measured at all are assigned with thermal rate coefficients of $3.8 \cdot 10^{-7}$ cm$^3$s$^{-1}$ (at 718 K). Since a steady state approach is used the branching fractions of the DR reactions are not of importance for this particular model. The idea behind the model is to obtain neutral densities that give steady state abundances of ions that are in as good agreement with the INMS measurement as possible.

For each ion $i$ the production rate $P_i$ is given by

$$P_i = \sum_n \xi_n N_n + \sum_{jn} f_{jn} k_{jn} N_j N_n$$

(2.5)

where $N_j$ and $N_n$ (cm$^{-3}$) are the densities of other ion species $j$ and neutral species $n$, $\xi_n$ (s$^{-1}$) is the ionization rate of the neutral species $n$ leading to $i$, $f_{jn}$ is the branching fraction of the channel leading to $i$ and $k_{jn}$ (cm$^3$s$^{-1}$) is the ion-neutral rate coefficient for the reaction between $j$ and $n$. The loss rate of $i$, $L_i$, is given by

$$L_i = k_i N_e N_i + \sum_n k_{in} N_i N_n$$

(2.6)

where $N_e$, $N_i$ and $N_n$ (cm$^{-3}$) are the densities of electrons, the ion $i$, and neutral species $n$. $k_i$ (cm$^3$s$^{-1}$) is the thermal rate coefficient for the DR of $i$, and $k_{in}$ is the ion-neutral rate coefficient for the reaction between $i$ and $n$. Some neutral abundances (those of H, N, NH, N$_2$, CH$_4$, H$_2$, C$_2$H$_2$, C$_2$H$_6$, C$_3$H$_4$, C$_3$H$_6$) constrained from measurements or earlier fully coupled models, are held fixed in the analysis while the abundances of other neutral molecules are tuned until the steady state model best reproduces the ion-densities as measured by the INMS.

Through their model calculation Vuitton et al. [59] estimated the mole fraction (ranging from $10^{-7}$ to $10^{-3}$) of 19 neutral molecules in Titan’s upper atmosphere. It is pointed out that the INMS measurements represent a snapshot of this environment at a particular altitude, latitude, and local time. The uncertainties in the results are discussed and the major contributions are from the uncertainties in the measured ion densities, in the ionization rate, and in the employed list of reactions and rate coefficients. The mole fractions determined for the species C$_2$H$_4$ ($10^{-3}$), C$_4$H$_2$ ($10^{-5}$), NH$_3$ ($7 \cdot 10^{-6}$), HCN ($2 \cdot 10^{-4}$), HC$_3$N ($4 \cdot 10^{-5}$), CH$_3$CN (3 $\cdot 10^{-6}$), and C$_2$H$_2$CN ($10^{-5}$) are stated to be uncertain by a factor of 2-3 [59].

It is noteworthy that subsequent to the publication by Vuitton et al. [59], efforts have been made to estimate the abundances of minor neutral molecules directly from measurements conducted in the closed source neutral mode of the INMS [66, 67]. Cui et al. [66] compared
their results obtained for the T5 flyby with the results in V07 and noted that the agreement was satisfying (within a factor of 4) for C₄H₂, CH₂CHCN and HC₃N. The only exception, where the agreement was not good, in their presented comparison, was for the abundance of CH₃CN which Cui et al. assigned a mole fraction of \((2.8\pm0.5) \cdot 10^{-5}\), about an order of magnitude higher than calculated in V07.

The understanding of the chemistry of Titan’s upper atmosphere is still improving thanks to the Cassini mission. This happens not only through data from new flybys, but also by the efforts made to better understand how to interpret recorded data. Two (almost) independent methods exist to determine the neutral composition of Titan’s upper atmosphere based on measurements by the INMS. The methods can be used for numerous Titan flybys already conducted and for flybys to come. With better insight into the relevant ion-chemistry and into the interpretation of INMS data the two methods might eventually give consistent results.
In this chapter information about the experiments on the DR of CD$_3$CND$^+$, CH$_2$CHC$^+$, CH$_3$CH$_2$CNH$^+$, CD$_3$CDO$^+$, CH$_3$CHO$^+$ and DCOOD$_2^+$ is presented. After the presentation of the utilized experimental approach, short descriptions with references are given for a few other methods by which DR reactions are studied.

3.1 Experimental overview (CRYRING)

The DR experiments described in this thesis were all performed at the heavy ion storage ring, CRYRING, at the Manne Siegbahn Laboratory in Stockholm, Sweden. A schematic of the apparatus is shown in Figure 3.1. The ring has a circumference of 51.6 m and consists of twelve straight sections joined by bending magnets. Every second straight section is equipped with focusing magnets used to define the orbit of the circulating ions while the other sections are used for experimental purposes. An important aspect with CRYRING is its ultra high vacuum (~100 pPa) [68], which reduces the number of reactions between the stored ions and residual gas molecules thereby increasing the life-time of the ions stored in the ring. The ions considered in this thesis had half-lives exceeding a second.

An experimental cycle, with a duration of ~6-10 s, consists of ion production in an ion source mounted on a high voltage platform (MINIS), injection of the ions into the ring, acceleration by a radio frequency cavity system up to the highest possible kinetic energy (limited by the magnetic rigidity of CRYRING), storage of the accelerated ion beam for a few seconds (to give time for internal relaxation), and data acquisition. To achieve good statistics the experimental cycle is typically repeated ~1000 times.

![Figure 3.1 A schematic of the heavy ion storage ring CRYRING.](image)
An important part of the ring, described further in section 3.1.3, is the so-called electron cooler in which the ion beam is merged with a parallel beam of electrons. The continuously renewed electrons have a low thermal energy spread and their velocities can be controlled by tuning the cathode voltage of the electron cooler. During the storage of the ions, the electron beam velocity is tuned to match the velocity of the ions. By Coulombic attraction heat is transferred to the cold electrons from the warmer ions which reduce their momentum spread. For heavy ions this cooling effect is not so important. The main purpose of the electrons is to serve as a DR reaction target for the ions. Neutral fragments produced in the DR reactions are unaffected by the bending magnet located just after the electron cooler and so leave the ring tangentially for detection. The detector used in these experiments is an energy sensitive ion implanted silicon detectors (IISD) mounted at ~4 m from the centre of the interaction region.

3.1.1 Ion production and acceleration

The ions, discussed in this thesis, were produced using a hollow cathode discharge ion source called JIMIS (JIM Peterson Ion Source, [69]) from the precursor compounds listed in Table 3.1. JIMIS operates under relatively high pressure and was originally designed to create beams of molecular ions with no permanent dipole moment (e.g. N$_2^+$, O$_2^+$). These ions would not decay down to the vibrational ground state with storage and had to be created in the ground state before injection. In JIMIS this is achieved through collisional quenching [69].

By injecting gases into the source chamber and by creating a ~1-2 kV discharge for ~50 ms, ionizations occur with subsequent ion-neutral reactions forming different ions. The ions are extracted, then accelerated by a high voltage (40 kV) and mass selected by a bending magnet. By the use of a Faraday cup it is possible to study the production of ions with different mass-to-charge ratios in the source. After injection into the ring, the ions are further accelerated by a radio frequency cavity. An alternating electric field collects the ions into bunches and accelerates them each time they pass through the cavity. Simultaneously the strength of the bending magnets in the ring is increased, i.e. CRYRING functions as a synchrotron. After the acceleration stops, the ions de-bunch and a continuous beam of ions then circulates in the ring [70]. Singly charged ions are typically accelerated to $96m_{ion}$ MeV, where $m_{ion}$ is the ion mass in atomic mass units. This relation, resulting from the circumference of CRYRING and the strength of the bending magnets, gives the highest possible kinetic energy for singly charged ions with mass $m_{ion}$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$CND$^+$</td>
<td>CD$_3$CN</td>
<td>D$_2$</td>
</tr>
<tr>
<td>CH$_2$CHCNH$^+$</td>
<td>CH$_2$CHCN</td>
<td>H$_2$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CNH$^+$</td>
<td>CH$_3$CH$_2$CN</td>
<td>H$_2$</td>
</tr>
<tr>
<td>CD$_2$CDO$^+$</td>
<td>CD$_2$CDO</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHO$^+$</td>
<td>CH$_3$CHO</td>
<td></td>
</tr>
<tr>
<td>DCOOD$_2^+$</td>
<td>DCOOD</td>
<td>D$_2$</td>
</tr>
</tbody>
</table>
3.1.2 Rest gas collisions and ion current measurement

Reactions between the ions and the residual gas molecules present in the ring are monitored by means of a micro-channel plate (MCP) detector located in one of the straight sections of the ring. The output signals from the MCP are monitored by a multi channel scaler (MCS) thus recording number of background reactions versus time. This type of spectrum is also used to obtain information about the ion current. Under the assumption of a constant rest gas pressure, the intensity of the recorded background reactions is proportional to the absolute ion current. A measurement of the absolute ion current is performed at the end of the acceleration phase by a capacitive pick up which is calibrated to an AC transformer. Details concerning these measurements are given in [71]. At the end of the acceleration phase the proportionality between the absolute ion current and the MCP signal from the background reactions is established. For each ion considered in this thesis the decay of the ion beam intensity could be described by a first order exponential decay, which indicated the feasibility of this approach. The ion currents at the beginning of data recording from DR reactions were in the region of ~1 nA for all ions studied in this thesis.

3.1.3 Electron cooler

The electron cooler (see Figure 3.2) provides a beam of electrons with a narrow energy spread that are merged with the ion beam in one of the straight sections of the ring.

The electron beam is generated by an electron gun cathode with a 2 mm radius positioned in a strong magnetic field of 3 T. This high magnetic field is achieved by a superconducting solenoid which is cooled by liquid helium. The temperature of the cathode is about 1200 K, giving an initial ~100 meV isotropic energy spread of the electrons immediately after they are emitted. The electron beam is bent into the straight section by a toroidal magnet, travels co-linearly with the ion beam for 85 cm, after which it is demerged by a second toroidal magnet.

Figure 3.2 The electron cooler at CRYRING
The electrons are then collected and the electron current is measured by a multimeter. For the experiments presented in the thesis typical electron currents of a few 100 μA were measured. The longitudinal electron energy spread, $k_B T_\parallel$, is decreased by the acceleration of the electrons and by electron-electron interactions. In the interaction region it has been estimated that $k_B T_\parallel \approx 0.1$ meV [72]. A guided solenoid, which creates a magnetic field of 0.03 T, is present in the interaction region. Due to the fact that the ratio $k_B T_\perp / B$ remains constant [72] the drop in magnetic field strength from 3 to 0.03 T causes the transverse component of the electron velocity spread to decrease by a factor of 100, which results in a transversal energy spread of $k_B T_\perp \approx 1-3$ meV for the electrons in the interaction region [72]. The decreased magnetic field strength also causes the geometrical cross section of the electron beam to increase by a factor of 100 [73], i.e. the electron beam radius increases by a factor of 10 to 2 cm.

3.1.4 Detection of products

The IISD (see Figure 3.3), used for product detection, has a thin (~50 nm) boron implanted entrance. A reverse bias voltage of 50 V is applied over the detector and a comparatively wide (~500 µm) depletion layer is created. When a fragment hits the IISD essentially all of its kinetic energy is lost within the depletion layer through the creation of electron-hole pairs in the silicon crystal. A current then flows through the detector and a charge sensitive preamplifier is used to create an output signal, which is further linearly amplified and shaped. The number of electron hole pairs created, and so the height of the output pulse, is proportional to the kinetic energy of the impinging fragment. The extra kinetic energy released in the DR reactions, typically a few eV, is small compared to the kinetic energy of the ions (a few MeV) that circulate in the ring. Therefore, the product fragments from DR events essentially have the same velocity and the detector can be regarded as mass sensitive.

![Figure 3.3](Photo by Mathias Hamberg)
The signals from the detector are monitored either by an MCS or a multi-channel analyzer (MCA) depending on whether the cross section or branching fractions are being investigated. For cross section measurements the output pulse is transferred via a discriminator to the MCS and the number of DR events versus time is recorded. For branching fraction measurements the output pulse goes directly to an MCA which monitors the number of events versus the pulse height i.e. the kinetic energy (or mass) of the incoming fragments.

The integration time of the detector-electronics is \( \sim \mu s \), which is much longer than the differences in the time-of-flight for fragments from a single DR event (\( \sim \text{ns} \)). This means that fragments from a particular DR reaction are recorded simultaneously and that the output pulse corresponds to their total kinetic energy. By inserting a grid (see section 3.1.5) in front of the detector the pulse height spectrum splits up into a series of peaks, their relative intensities being dependent on the branching ratios and the transmission of the grid. The resolution of the detector is determined mostly by the leakage current of the detector, which gives rise to electrical noise. This means that fragments with low kinetic energy or which differ little in kinetic energy cannot be resolved individually. Two IISDs, with the same working principles but differing in size, were used for the DR experiments. The active areas of the detectors are \( \sim 900 \, \text{mm}^2 \) and \( \sim 3000 \, \text{mm}^2 \), respectively. While the former has better resolution, the latter is in some cases more appropriate for fragment detection. Light product fragments may receive high enough transversal velocity in the DR reactions so that they can miss the active area of the detector. The risk for this to occur is reduced with an increased detector size.

It should be noted that the recorded signals, both for cross section and branching fraction measurements, are contaminated by signals arising from reactions between ions and residual gas molecules. These signals can be corrected for as will be explained in the next chapter on data analysis.

### 3.1.5 Grid technique

As mentioned, fragments from a single recombination event hit the IISD within such a short time interval that only their total kinetic energy is recorded by the MCA-card. To enable the extraction of branching fractions a moveable stainless steel grid (50 \( \mu \text{m} \) thick) with holes having diameters of \( \sim 80 \, \mu \text{m} \) is inserted in front of the detector. This grid has a transmission probability of \( P = 0.297 \pm 0.015 \) [24] for each product fragment.

If a DR event results in two fragments with kinetic energies \( E_1 \) and \( E_2 \) it can be detected either at the energy \( E_1 \), \( E_2 \) or \( E_1 + E_2 \), with probabilities of \( P(1-P) \), \( P(1-P) \) and \( P^2 \), respectively, depending on which fragments pass the grid.

### 3.2 Other techniques used for DR investigations

Storage rings were first used in the field of DR in the early 1990s following a proposal by Datz and Larsson published in 1992 [74]. Apart from CRYRING other magnetic storage rings where DR has been studied are ASTRID (Denmark), Test Storage Ring (Germany) and TARN II (Japan) [2]. The main benefits of using storage rings for DR studies is the possibility
to determine the absolute cross section at different collision energies and to extract detailed information about the products for many systems. DR can also be studied by other methods than by the use of ion storage rings equipped with electron coolers. In this subsection a few basic principles are presented for some of these other methods.

### 3.2.1 Stationary and flowing afterglow technique

The stationary afterglow technique was the first method used in the experimental study of DR and, as mentioned in the introduction, it was through this technique that it was realized that DR indeed is an efficient reaction. The main steps in the determination of a DR rate coefficient are introduction of a precursor gas into a cavity, formation of ions and free electrons, switch-off of the plasma inducing device, and finally measurement of the decay in electron density through time (for example by the use of a Langmuir probe) [75]. Drawbacks of the stationary afterglow technique are the limited number of molecular ions that can be studied and the fact that the DR reaction is studied in the same region as where the ions are produced.

A development of this technique was the Flowing Afterglow Langmuir Probe (FALP) method (see e.g. [76]). In a FALP study aimed to determine the rate coefficient for the DR of a molecular ion \( \text{M}^+ \), a carrier gas, usually helium, is partly ionized and flows with known velocity, \( v_p \), through a tube. Different gases are injected downstream through inlets in the tube with the aim of converting the \( \text{He}^+ \) plasma to one totally dominated by \( \text{M}^+ \). A moveable Langmuir probe is used to measure the electron density, \( n_e \), at different positions, \( z \), downstream of the injection inlets, with a particular value of \( z \) corresponding to a particular time \( t \) through \( t = (z_1 - z_0)/v_p \). The DR rate coefficient, \( k(T) \), of \( \text{M}^+ \) can be found by the assumption that \( n_e \) is similar to the concentration of \( \text{M}^+ \) and that DR is the only removal mechanism of the electrons. In such a situation it can be derived that

\[
\frac{1}{n_e(z_1)} - \frac{1}{n_e(z_0)} = k(T) \left( \frac{z_1 - z_0}{v_p} \right)
\]

where \( n_e(z_0) \) and \( n_e(z_1) \) are measured electron concentrations at positions \( z_0 \) and \( z_1 \), respectively, and \( v_p \) is the plasma velocity.

To determine the thermal rate coefficient at a particular temperature \( T \) it is required that the entire flow tube (or cavity in the case of stationary afterglow experiments) is set to that temperature. Many afterglow experiments have therefore only been conducted at \( \sim 300 \) K. One benefit for the determination of the thermal rate coefficient is that the internal temperature of the ions matches the kinetic temperature due to efficient relaxation through collisions with the carrier gas. A drawback is the lack of mass selection which could cause undesired by-products of the ion formation. To overcome this problem stationary or moveable mass spectrometers have been used in order to characterize the ion population.

To extract information on branching fractions different techniques have been applied including e.g. VUV-absorption and laser induced fluorescence [77]. These techniques generally do not allow for a detailed insight into the branching ratios but can be used e.g. to investigate specific product fragments.
3.2.2 Single pass merged beams experiments

Similar to the storage ring technique, in the Merged Electron-Ion Beam Experiment (MEIBE) apparatus DR is studied by the merging of a mass-selected ion beam with an electron beam [78, 79]. Neutral products are separated from charged particles and detected with an energy sensitive detector. The electron and ion currents are measured by Faraday cups. The maximum kinetic energy of ions in MEIBE is significantly lower than in storage rings, and the upper mass limit of singly charged molecular ions that can be studied is at present 32 amu [2]. Branching fractions can be investigated by applying a similar grid technique as done in the experiments at CRYRING [80]. Such measurements are however challenging due to limited resolution of the detector and the long time needed to acquire reasonable statistics since each produced ion travels through the interaction region only once. Another drawback is that the ions react with the electrons almost immediately after production, which implies that the ions could be in highly excited states.
Chapter 4

Data evaluation

In this chapter the data analysis procedures used to extract absolute cross sections, thermal rate coefficients and branching fractions from the DR reaction measurements are presented.

4.1 Cross sections and thermal rate coefficients

The DR cross section depends on the relative velocity, $v_{rel}$, between the reactants and tends to increase as $v_{rel}$ decreases due to Coulombic attraction. In natural environments where electron velocities are expected to follow Maxwellian distributions the thermal rate coefficients of the DR reaction, $k_{DR}$, is defined by $k_{DR}(T_e) = \langle \sigma_{DR} v_{rel} \rangle$, where $T_e$ is the electron temperature.

The extraction of absolute DR cross sections from the CRYRING experiments are based on count rates measured at different relative velocities of the reactants. For the extraction to be possible, different experimental parameters and corrections need to be taken into account. The thermal rate coefficient as a function of $T_e$ is then determined from the retrieved cross section data.

4.1.1 Relative kinetic energy and detuning energy

The relative kinetic energy, $E_{rel}$, for ion – electron collisions is given by

$$E_{rel} = \frac{\mu v_{rel}^2}{2},$$

(4.1)

where $\mu$ is the reduced mass

$$\mu = \frac{m_e m_{ion}}{m_e + m_{ion}},$$

(4.2)

Since $m_{ion} >> m_e$ it follows that $\mu$ is very well approximated by $m_e$. The magnitude of the relative velocity for electrons crossing an ion beam at angle $\theta$ is according to the cosine law given by

$$v_{rel} = \sqrt{v_e^2 + v_i^2 - 2v_e v_i \cos \theta},$$

(4.3)
The relative kinetic energy is thus equal to

\[ E_{rel} = \frac{m_e (v_e^2 + v_i^2 - 2v_e v_i \cos \theta)}{2} \]  

(4.4)

In the case of parallel beams, \( \theta = 0 \) and equation (4.4) simplifies to

\[ E_{rel} = \frac{m_e (v_e - v_i)^2}{2} \equiv E_d \]

(4.5)

The relative kinetic energy as given by (4.5) is defined as the detuning energy and expressed as \( E_d \). This is the relative kinetic energy when the two beams are parallel and when transversal velocity spreads of the particles are ignored. Similarly we define the detuning velocity \( v_d \) as the relative velocity when the velocity vectors are parallel and thus, \( v_d = |v_e - v_i| \).

4.1.2 Determining rate coefficient versus detuning energy

During cross section measurements the cathode voltage of the electron cooler is linearly decreased from a value corresponding to a detuning energy between the electrons and the ions of 1 eV with \( v_e > v_{ion} \) to a value which again corresponds to a detuning energy of 1 eV but now with \( v_e < v_{ion} \). Simultaneously, counts versus time are recorded by means of having the IISD connected to an MCS card. As an example, the cathode voltage ramp and the recorded MCS spectrum for the DR of CD\(_3\)CND\(^+\) are shown in Figure 4.1.

![Figure 4.1](image)

**Figure 4.1** The cathode voltage of the electron cooler (a) and the recorded signal of neutral fragments (b) versus storage time. At cooling energy, where the electrons and the ions have the same average velocity, the DR is most efficient (from the DR experiment on CD\(_3\)CND\(^+\)).
The measured counts do not only originate from DR reactions but also from reactions between the ions and the residual gas present in the ring. To subtract these background-related signals, and enable the extraction of a pure DR count rate, the assumption is made that at ~1 eV relative kinetic energy essentially all counts are due to non-DR processes, since the DR cross section normally is very low at such collision energies, see e.g. [81]. Data points in the regions with collision energies close to 1 eV are fitted to an exponential decay with a decay constant being similar to that of the signals detected by the MCP from collisions between ions and the residual gas. This curve is then subtracted from the MCS spectrum. To extract counts per time from the background subtracted MCS spectrum each data point in the spectrum is divided by the number of experimental cycles (typically ~1000) and the dwell time of the MCS card (usually 2 ms).

The number of DR reactions occurring per second in a volume \( V \) is proportional to the concentrations of the reactants.

\[
\frac{1}{V} \frac{dN_{\text{DR}}}{dt} = R n_{\text{ion}} n_e
\]  

(4.6)

The proportionality constant, \( R \), is the DR rate coefficient with the unit of cm\(^3\)s\(^{-1}\).

In the experiments at CRYRING the DR reactions occur predominantly in the part of the electron cooler region where the ion beam and the electron beam are parallel. The length of this region is \( l = 85 \) cm. The radius of the electron beam is \( r_e = 2 \) cm and it completely envelops the ion beam. Hence the volume of the interaction region is given by

\[
V = \pi r_{\text{ion}}^2 l
\]  

(4.7)

where \( r_{\text{ion}} \) is the radius of the ion beam. The concentration of the electrons and ions are given by

\[
n_e = \frac{I_e}{q v_e r_e^2}
\]  

(4.8)

and

\[
n_{\text{ion}} = \frac{I_{\text{ion}}}{q v_{\text{ion}} r_{\text{ion}}^2}
\]  

(4.9)

where \( I \) denotes current, \( v \) velocity, and \( q \) is the elementary charge. By combining the equations (4.6)-(4.9) it is found that

\[
R = \frac{dN_{\text{DR}}}{dt} \frac{q^2 v_e v_{\text{ion}} r_e^2 \pi}{l e I_{\text{ion}} l}.
\]  

(4.10)
The electron and ion currents are measured during the experiments. The ion velocity is known and the electron velocity can be determined from the cathode voltage, $U_{\text{cath}}$, of the electron cooler via

$$qU_{\text{cath}} = \frac{m_e v_e^2}{2}.$$  \hspace{1cm} (4.11)

However, the electron velocity as determined by (4.11) will be overestimated due to the space charge effect, which is explained in the upcoming section.

**4.1.3 Space charge correction**

In the DR experiment of CD$_3$CND$^+$ the ions circulated with a velocity of $\sim 2.96 \cdot 10^6$ ms$^{-1}$. For the electron beam to match that velocity it would according to (4.11) require a cathode voltage of $\sim 25$ V. A glance at Figure 4.1 shows that the cathode voltage during cooling was $\sim 27.5$ V. Hence, the effective potential-difference experienced by the electrons was reduced by about 2.5 V at cooling condition. This effect is due to electron-electron repulsion which gives rise to a space charge potential, $U_{sp}$. The effective voltage is then given by

$$U_{\text{eff}} = U_{\text{cath}} - U_{sp}$$  \hspace{1cm} (4.12)

From Gauss’s law [82] it can be derived that the space charge potential

$$U_{sp} = \frac{I_e}{2\varepsilon_0 v_e \pi} \left( \frac{1}{2} + \ln \left( \frac{r_t}{r_e} \right) \right)$$  \hspace{1cm} (4.13)

with $\varepsilon_0 = 8.854 \cdot 10^{-12}$ C$^2$N$^{-1}$m$^{-2}$ being the permittivity constant and with $r_t$ being the radius of the grounded vacuum tube (=5 cm). Typically the electrons have velocities above the ionization threshold of H$_2$, which is the most abundant rest gas molecule in the ring. Ions generated by collisions of H$_2$ with electrons can then be trapped in the beam and act to reduce the space charge potential. In our analysis we assume that this effect is proportional to the ionization cross section, $\sigma_i$, of H$_2$. The effective potential, which governs the true electron velocity, is then given by

$$U_{\text{eff}} = U_{\text{cath}} - (1 - C \sigma_i(v_e)) \frac{I_e}{2\varepsilon_0 v_e \pi} \left( \frac{1}{2} + \ln \left( \frac{r_t}{r_e} \right) \right)$$  \hspace{1cm} (4.14)

A fit of the electron-impact ionization cross section of H$_2$ [83] is used in the correction. The value of the constant $C$ is determined at cooling conditions, when all other values of (4.14) are known.
Due to the fact that

$$U_{\text{eff}} = \frac{m_e v_e^2}{2q}$$  \hspace{1cm} (4.15)

equation (4.14) can be rewritten as

$$U_{\text{cath}} = \frac{m_e v_e^2}{2q} + (1 - C\sigma_i(v_e)) \frac{I_e}{2e_0v_e\pi} \left( \frac{1}{2} + \ln\left(\frac{r_i}{r_e}\right) \right)$$  \hspace{1cm} (4.16)

By using (4.16) $U_{\text{cath}}$ can be plotted versus $v_e$. It is typically a steadily increasing function meaning that for each value of $U_{\text{cath}}$ there is a single corresponding value of $v_e$. This means that for a given value of $U_{\text{cath}}$ the true electron velocity can be extracted.

Now all parameters of the right hand side of (4.10) are known and the DR rate coefficient versus detuning energy can be found. However, the obtained rate coefficient will be overestimated. Not all recorded counts emerge from the 85 cm long region where the two beams are parallel. Signals also originate from the regions where the electrons are bent into and out of the ion beam by the toroidal magnets. In these regions the interaction energy between the electrons and ions is higher than in the merged zone, see for example eq. (4.4). To correct for these counts an iterative procedure [84] is utilized described in the next section.

### 4.1.4 Correcting for reactions in toroidal regions

Let $R(E)$ be the energy dependent DR rate coefficient. From equation (4.6) we then have

$$\frac{dN_{\text{DR}}}{dt} = R(E)Vn_{\text{ion}}n_e$$  \hspace{1cm} (4.17)

In the toroidal regions the electron beam is bent into and out of the ion beam. Each toroidal region is 25.5 cm long. For an electron in any of the two toroidal regions we denote the distance to the merged region as $x$. It has been shown that the angle $\theta$, between the ion beam and the electron beam, varies with $x$ as

$$\theta(x) [\text{rad}] = 0.76 \left( 1 - \frac{1}{1 + (x/31.38)^{2.35}} \right)$$  \hspace{1cm} (4.18)

For $x=0$, $\theta = 0$ radians and for $x=25.5$ cm, $\theta = 0.29$ radians. Equation (4.18) is a fit based on magnetic field measurements. It follows from equation (4.4) and (4.5) that the relative kinetic energy between the electrons and the ions can be expressed as

$$E_{\text{rel}} = E_d + m_e v_1 v_e (1 - \cos \theta)$$  \hspace{1cm} (4.19)
Note that the ion velocity is fixed during experiments and for a certain value of \( E_d \), \( v_e \) is restricted to follow (4.5). Hence in (4.19) there are only two variables; \( E_d \) (or \( v_e \)) and \( \theta \). Since \( \theta \) in turn is a function of \( x \) it is possible to compute \( E_{rel} \) as a function of \( E_d \) and \( x \),

\[
E_{rel}(E_d, x) = E_d + m_e \left( v_i \pm \sqrt{2E_d/m_e} \right) v_i (1 - \cos \theta(x))
\] (4.20)

The “± sign” is replaced by “+” for \( v_e > v_i \) and by “−” for \( v_e < v_i \). The toroidal correction described below can be done separately for \( v_e > v_i \) and for \( v_e < v_i \).

Let \( S \) be the overlapping area between the ion beam and the electron beam. The number of DR events recorded per second will according to (4.17) be

\[
\frac{dN_{DR}}{dt} = Sn_{ion} n_e \left( 2 \int_0^{5.5} R(E_{rel}(E_d, x))dx + lR(E_d) \right)
\] (4.21)

The factor 2 appears since there are two toroidal regions. Note that \( l \) is the length of the region in which the two beams travel parallel. Dividing both sides of (4.21) by \( lSn_{ion}n_e \) gives

\[
\frac{dN_{DR}}{dt} = \frac{1}{lSn_{ion}n_e} \left( 2 \int_0^{5.5} R(E_{rel}(E_d, x))dx + R(E_d) \right)
\] (4.22)

The left hand side of (4.22) is the rate coefficient as determined before the toroidal correction, i.e. by equation (4.10) with space charge corrected \( v_e \). We call this rate coefficient \( R_0(E_d) \). The second term on the right hand side of (4.22) is the rate coefficient which we wish to find. To do this we use an iterative procedure and rewrite (4.22) into

\[
R_n(E_d) = R_0(E_d) - \frac{2}{l} \int_0^{5.5} R_{n-1}(E_{rel}(E_d, x))dx
\] (4.23)

In the first step the integral is solved by using rate coefficients according to \( R_0(E_d) \). Figure 4.2 shows \( R \) versus \( E_d \) from the investigation on \( \text{CH}_3\text{CH}_2\text{CNH}^+ \) before and after the correction.

![Figure 4.2](image.png) Rate coefficient versus detuning energy from the DR investigation of \( \text{CH}_3\text{CH}_2\text{CNH}^+ \) before (black squares) and after (red line) the toroidal correction.
4.1.5 Extracting absolute cross sections

We now know the DR rate coefficient as a function of the detuning energy (or the detuning velocity). For high detuning energies the cross section versus relative kinetic energy is well approximated by $R_{\text{meas}}(v_d)/v_d$. However for lower detuning energies the velocity spreads of the reactants need to be taken into account. The obtained DR rate coefficient, $R_{\text{meas}}$, as a function of the detuning velocity should equal

$$R_{\text{meas}}(v_d) = <v_{\text{rel}}\sigma(v_{\text{rel}})> = \int_{0}^{\infty} v_{\text{rel}}\sigma(v_{\text{rel}}) f(v_{\text{rel}}) dv_{\text{rel}} \quad (4.24)$$

where $f(v_{\text{rel}})$ is the relative velocity distribution. As discussed in chapter 3 the transverse temperature of the electrons is estimated to be $k_B T_{\perp} \approx 2 \text{ meV}$. The longitudinal temperature of the electrons is much lower and is neglected in the analysis. Both transversal and longitudinal ion velocity spreads are neglected as well due to the high mass of the ions. Let $v_{\perp}$ be the transversal velocity of the electrons. The relative velocity between the ions and the electrons is then

$$v_{\text{rel}} = \sqrt{v_d^2 + v_{\perp}^2} \quad (4.25)$$

The transversal velocity distribution of the electrons has a plane Maxwellian distribution

$$f(v_{\perp}) = A(T_{\perp}) v_{\perp} e^{-m_{e} v_{\perp}^2 / 2 k_B T_{\perp}} \quad (4.26)$$

with $A(T_{\perp}) = \frac{m_e}{k_B T_{\perp}}$. Equation (4.24) can now be expressed as

$$R_{\text{meas}}(v_d) = <v_{\text{rel}}\sigma(v_{\text{rel}})> = \int_{0}^{\infty} \sqrt{v_d^2 + v_{\perp}^2} \sigma(\sqrt{v_d^2 + v_{\perp}^2}) v_{\perp} e^{-m_{e} v_{\perp}^2 / 2 k_B T_{\perp}} dv_{\perp} \quad (4.27)$$

It follows from (4.26) and (4.27) that

$$R_{\text{meas}}(v_d) = A(T_{\perp}) \int_{0}^{\infty} \sqrt{v_d^2 + v_{\perp}^2} \sigma(\sqrt{v_d^2 + v_{\perp}^2}) v_{\perp} e^{-m_{e} v_{\perp}^2 / 2 k_B T_{\perp}} dv_{\perp} \quad (4.28)$$

For a given $v_d$ (if corresponding to an $E_d$ in the investigated energy range) the left hand side of (4.28) is known. The cross section can be extracted either numerically by using Fourier transform techniques as outlined in [85] or by using an iterative method in which one uses the fact that the transversal velocity spread is negligible at high $E_{\text{rel}}$ and calculate the cross section at $v_d(j) \leq v_{\text{rel}} < v_d(j+1)$ for smaller and smaller $j$-values, which represents the detuning velocities for which $R_{\text{meas}}(v_d)$ exists.
For all ions studied in this thesis it was observed that the cross section below interaction energies of 0.1 eV were well described by expressions on the form

\[
\sigma(E_{rel}) = A \cdot E_{rel}^{-B}
\]  

(4.29)

This cross section behaviour has also been observed for the majority of ions studied at CRYRING. One can therefore in principle, as a strategy to extract cross sections, perform trial-and-error calculations and fold equation (4.28) with cross section relations on the form \( A \cdot E_{rel}^{-B} \) until the best match to the measured rate coefficients is found. Figure 4.3 shows the retrieved DR cross section for \( \text{CH}_3\text{CH}_2\text{CNH}^+ \) versus relative kinetic energy for the cases when excluding and including the transversal velocity spread of the electrons.

**Figure 4.3** The black squares represent the DR cross section for \( \text{CH}_3\text{CH}_2\text{CNH}^+ \) obtained ignoring the transversal energy spread of the electrons (it is given by \( R_{\text{meas}} (v_d/v_d) \)). The red triangles represent the cross section when the transversal velocity spread of the electrons has been taken into account and the solid black line is the best fit of these data points, with \( \sigma(E_{rel}) = 1.1 \cdot 10^{-15} \cdot E_{rel}^{-1.26} \) cm\(^2\).

### 4.1.6 Determining the thermal rate coefficient

The thermal rate coefficient is an important parameter for modelling the chemical evolution of environments such as molecular clouds and planetary ionospheres. It is the temperature dependent proportionality constant \( k(T) \) in the expression

\[
\frac{dn_{\text{ion}}}{dt} = -k(T) \cdot n_{\text{ion}} \cdot n_e
\]

(4.30)

To determine the thermal rate coefficient it is assumed that the electrons in the medium have an isotropic Maxwellian speed distribution.
\[ f(v) = A(T) v^2 e^{-\frac{m_e v^2}{2k_B T}} \tag{4.31} \]

where \( A(T) = 4\pi \left( \frac{m_e}{2\pi k_B T} \right)^{3/2} \).

Since electrons (due to their lower mass) move much faster than molecular ions in e.g. molecular clouds the relative velocity for collisions is well approximated by the electron velocity. The thermal rate coefficient \( k(T) \) is the expectation value of \( v\sigma \) at temperature \( T \), and as such

\[ k(T) = \langle v\sigma \rangle = \int_{0}^{\infty} v\sigma f(v) \, dv = A(T) \int_{0}^{\infty} v\sigma v^2 e^{-\frac{m_e v^2}{2k_B T}} \, dv \tag{4.32} \]

This approach of finding \( k(T) \) is repeated for temperatures ranging from ~10 to 1000 K. Note that the variable substitution \( mv^2 / 2 = E \) makes it possible to express the thermal rate coefficient as

\[ k(T) = \frac{8\pi m_e}{(2\pi m_e k_B T)^{3/2}} \int_{0}^{\infty} E\sigma e^{-E/2k_B T} \, dE \tag{4.33} \]

For electron temperatures below 1000 K, \( k(T) \) is typically well fitted by expressions of the form \( \alpha \cdot (T/300)^\beta \, \text{cm}^3 \, \text{s}^{-1} \) with \( \alpha \) and \( \beta \) usually having values between \( 10^{-7} \) and \( 2 \cdot 10^{-6} \, \text{cm}^3 \, \text{s}^{-1} \) and -0.5 and -1, respectively.

### 4.1.7 Estimating uncertainties

Statistical errors arise from the counting of DR reactions and reactions between the ions and the residual gas. Systematic uncertainties are mainly due to uncertainties in current measurements, the length of the interaction region and the radius of the electron beam. The total uncertainty is estimated by taking the quadratic sum of the individual errors. Below \( E_{\text{rel}} \sim 0.1 \, \text{eV} \) the statistics are in general good and overall uncertainties are typically less than 20%. At higher relative kinetic energies the statistics are poorer and uncertainties become more pronounced. The uncertainty in the thermal rate coefficient follows from the uncertainty in the DR cross section. The high uncertainty in the DR cross section for higher energy ranges (above 0.1 eV) has no major impact on the uncertainty of the thermal rate coefficient for temperatures below 1000 K.
4.2 Branching fractions

When a reaction between two species is incorporated in a model that is aimed to predict the chemical evolution of an environment not only the thermal rate coefficient is important. It is also vital to know the products of the reaction. Typically there are several product channels in a DR reaction. The branching fractions give the probability of the different channels.

4.2.1 Available product channels

If not considering internal excitation one can imagine four ways in which a DR reaction of a molecular ion $\text{ABC}^+$ can occur

$$\text{ABC}^+ + e^- \rightarrow \begin{cases} \text{AB} + \text{C} \\ \text{AC} + \text{B} \\ \text{BC} + \text{A} \\ \text{A} + \text{B} + \text{C} \end{cases}$$ \tag{4.34}

At low relative kinetic energies it is not certain that all of these channels are energetically accessible. If all reaction energy is transformed into kinetic energy of the products the kinetic energy released ($\text{KER}$) can be calculated if the heats of formation, $\Delta H$, for the ion and all products in the reaction are known. As such the $\text{KER}$ of the reaction $\text{ABC}^+ + e^- \rightarrow \text{AB} + \text{C}$ is

$$\text{KER} = \Delta H(\text{ABC}^+) - \Delta H(\text{AB}) - \Delta H(\text{C})$$ \tag{4.35}

The heat of formation (which in principle relates to binding energies) for relevant species, have been compiled from the literature, in particular through reference series such as [86, 87].

4.2.2 Extraction of branching fractions

The branching fractions of the DR reactions were investigated at relative kinetic energies of ~0 eV. It should be remembered that the IISD/MCA recorded the total kinetic energy of impinging product fragments from single DR events. Count rates were typically below a few kHz, which resulted in a very small probability that products from two DR events were recorded simultaneously. Subtraction of signals emerging from reactions between the ions and the residual gas was done by recording spectra at $E_{\text{rel}} \sim 1$ eV where the DR contribution to the signal is negligible [81]. For the background subtraction the MCA spectra were normalized according to the intensity of the ion beam measured by the MCP during each run.

Measurements were first performed without the grid (see section 3.1.5) in front of the detector in order to ensure that losses of product fragments did not present a problem. These losses arise when a product fragment in a DR reaction has enough transversal velocity that it misses the active area of the detector. Those product fragments that do hit the detector from such events give rise to signals at lower energies than the events in which all product
fragments are detected. Figure 4.4 shows the recorded MCA spectra from the investigation of CH$_3$CH$_2$CNH$^+$ at (a) $E_{\text{rel}} \sim 0$ eV and (b) $E_{\text{rel}} \sim 1$ eV when the grid was not inserted in front of the IISD. In panel (c) of the same figure the background subtracted spectrum is displayed showing a single peak, which ensured that losses of fragments carrying heavy atoms did not occur during the recording of the data. If losses had been observed it would have had to be accounted for in the determination of branching fractions (see e.g. [88]).

![Figure 4.4](image_url)

**Figure 4.4** Fragment energy spectra of the DR of CH$_3$CH$_2$CNH$^+$ without the grid inserted at (a) $E_{\text{rel}} \sim 0$ eV and (b) $E_{\text{rel}} \sim 1$ eV. At $E_{\text{rel}} \sim 0$ eV both DR and background (BG) reactions are recorded while at $E_{\text{rel}} \sim 1$ eV it is expected that only BG reactions are recorded. Panel (c) shows the background subtracted energy spectrum, which indicated that no losses of product fragments carrying heavy atoms occurred during the measurement.

Figure 4.5 displays the MCA spectra recorded in the study of CH$_3$CH$_2$CNH$^+$ with the grid in front of the detector at (a) $E_{\text{rel}} \sim 0$ eV and (b) $E_{\text{rel}} \sim 1$ eV. The pure DR spectrum resulting from background subtraction is shown in panel (c) of the same figure.
Figure 4.5 Fragment energy spectra of the DR of CH$_3$CH$_2$CNH$^+$ with the grid inserted at (a) $E_{\text{rel}} \sim 0$ eV and (b) $E_{\text{rel}} \sim 1$ eV. At $E_{\text{rel}} \sim 0$ eV both DR and background (BG) reactions are recorded while at $E_{\text{rel}} \sim 1$ eV it is expected that only BG reactions are recorded. Panel (c) shows the background subtracted energy spectrum, which was used to determine the branching ratios of the available product channels.

For CH$_3$CH$_2$CNH$^+$ (to give an example), the peak areas of Figure 4.5 (c) were used in the extraction of the DR branching fractions of the available channels by considering the probability for a given reaction channel to contribute to a given peak taking into account that the grid, with transmission probability $P \sim 0.297$ for each product fragment, was inserted in front of the detector. Due to limitations in the detector resolution (see the labeling of the peaks in Figure 4.5 (c)) it was not possible to study the branching fractions in detail and therefore the analysis focused on determining to what extent ruptures of different bonds between heavy atoms occurred. If we by $X_n$ denote a fragment carrying $n$ heavy atoms (C or N atoms) and $\{H\}$ denote an unknown number of hydrogen atoms (or H$_2$ molecules) the DR of CH$_3$CH$_2$CNH$^+$ can occur through the following types of channels at $E_{\text{rel}} = 0$ eV

$\alpha$) $X_4 + \{H\}$ e.g. CH$_3$CH$_2$CN + H + 5.2 eV

$\beta$) $X_3 + X + \{H\}$ e.g. CH$_2$CN + CH$_3$ + H + 1.7 eV

$\gamma$) $X_2 + X_2 + \{H\}$ e.g. C$_2$H$_5$ + HNC + 4.7 eV

$\delta$) $X_2 + X + X + \{H\}$ e.g. HNC + CH$_3$ + CH$_2$ + 0.4 eV
The peaks in Figure 4.5 (c) are labeled 1-4 indicating the number of heavy atoms carried by the product fragments that hit the detector. A DR reaction in which all heavy fragments pass the grid contributes to the peak labeled with 4. Consider channel $\beta$ producing two heavy fragments, one carrying three heavy atoms and one carrying one heavy atom. Such an event contributes to peak 1 with a probability of $P(1-P)$ since it requires that the $X$ fragment passes the grid (probability $P$) whereas the $X_3$ fragment is stopped (probability $1-P$). In analogy with these examples, a linear equation system is set up

$$
\begin{bmatrix}
I(1) \\
I(2) \\
I(3) \\
I(4)
\end{bmatrix}
= 
\begin{bmatrix}
0 & P(1-P) & 0 & 2P(1-P)^2 \\
0 & 0 & 2P(1-P) & P(1-P) \\
0 & P(1-P) & 0 & 2P^2(1-P) \\
P & P^2 & P^2 & P^3
\end{bmatrix}
\times
\begin{bmatrix}
N_{\alpha} \\
N_{\beta} \\
N_{\gamma} \\
N_{\delta}
\end{bmatrix}
$$

(4.36)

In the equation system $I(1)$-$I(4)$ denote the intensities of the four peaks in Figure 4.5 (c) and $N_{\alpha,\beta,\gamma,\delta}$ denote the unknown number of DR reactions of the types $\alpha$, $\beta$, $\gamma$ and $\delta$ that occurred during the measurement. Solving (4.36) by Gaussian elimination gives $N_{\alpha,\beta,\gamma,\delta}$ and the branching fractions are determined by normalization of the obtained result.

### 4.2.3 Estimating uncertainties

Uncertainties to branching fractions are rather small and are mainly due to the uncertainty in the grid transmission probability and in peak intensities given that peaks in some cases are partly overlapped. Considering the amount of acquired data, statistical uncertainties are very small. Error bars are found by varying the transmission probability and the peak areas within reasonable limits and by then observing the variations in the obtained results for the branching ratios.
Chapter 5

Gas phase model of a dark cloud

Chemical models are used for different astronomical environments including e.g. different types of interstellar clouds, early stages of star formation and cometary comae. The model mostly used in the papers presented in this thesis is a pure gas-phase model of the dark cloud TMC-1, and this model is briefly described here.

5.1 Brief description of the model

The model calculates the abundance of species in a dark cloud with similar physical conditions as TMC-1 as a function of time by numerically solving a system of coupled differential equations which describe the rate of change in abundance of each species. At the time $t = 0$ the elemental abundances listed in Table 5.1 are used as suggested in [89]. At this instant it is assumed that the abundance of free electrons equals the sum of all cation abundances. Physical parameters, also suggested in [89], are kept constant in time and are listed in Table 5.2. The rate coefficients used for individual chemical reactions are taken from the dipole-enhanced version of the latest release of the UMIST Database for Astrochemistry (UDFA), henceforth referred to as Rate06 [89, 90]. Alongside a chemical network provided by the Ohio State University (OSU) [91] UDFA is the most widely used database for interstellar and circumstellar modelling.

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance</th>
<th>Element</th>
<th>Abundance</th>
<th>Element</th>
<th>Abundance</th>
<th>Element</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.14</td>
<td>C$^+$</td>
<td>7.3·10$^{-3}$</td>
<td>N</td>
<td>2.14·10$^{-5}$</td>
<td>O</td>
<td>1.76·10$^{-4}$</td>
</tr>
<tr>
<td>F</td>
<td>2.0·10$^{-8}$</td>
<td>Na$^+$</td>
<td>3.0·10$^{-9}$</td>
<td>Mg$^+$</td>
<td>3.0·10$^{-9}$</td>
<td>Si$^+$</td>
<td>3.0·10$^{-9}$</td>
</tr>
<tr>
<td>P$^+$</td>
<td>3.0·10$^{-9}$</td>
<td>S$^+$</td>
<td>2.0·10$^{-8}$</td>
<td>Cl$^+$</td>
<td>3.0·10$^{-9}$</td>
<td>Fe$^+$</td>
<td>3.0·10$^{-9}$</td>
</tr>
</tbody>
</table>

Table 5.1 Initial elemental abundance relative to total hydrogen nuclei used for gas-phase models of the dark cloud TMC-1. (Data taken from [89])

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>Gas temperature</td>
<td>10 K</td>
</tr>
<tr>
<td>$n$(H$_2$)</td>
<td>H$_2$ concentration</td>
<td>10$^4$ cm$^{-3}$</td>
</tr>
<tr>
<td>$A_v$</td>
<td>Visual extinction</td>
<td>15 mag</td>
</tr>
<tr>
<td>$\zeta_0$</td>
<td>Cosmic-ray ionization rate of H$_2$</td>
<td>1.36·10$^{-17}$ s$^{-1}$</td>
</tr>
</tbody>
</table>
5.1.1 Reactions considered in the model and their rate coefficients

The following types of two-body reactions are considered in the model:

- ion-neutral (e.g. $\text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{H}$)
- dissociative recombination (e.g. $\text{H}_3\text{O}^+ + e^- \rightarrow \text{OH} + \text{H} + \text{H}$)
- charge exchange (e.g. $\text{CH}_3\text{CHO} + \text{C}^+ \rightarrow \text{CH}_3\text{CHO}^+ + \text{C}$)
- neutral-neutral (e.g. $\text{CH} + \text{O} \rightarrow \text{CO} + \text{H}$)
- mutual neutralization (e.g. $\text{H}^+ + \text{H} \rightarrow \text{H} + \text{H}$)
- radiative recombination (e.g. $\text{C}^+ + e^- \rightarrow \text{C} + h\nu$)
- associative electron detachment (e.g. $\text{C} + e^- \rightarrow \text{C}^- + h\nu$)
- radiative association (e.g. $\text{CH}_3^+ + \text{CO} \rightarrow \text{CH}_3\text{CO}^+ + h\nu$)

The rate coefficients for two-body reactions are in the Kooij-Arrhenius form

$$k(T) = \alpha(T/300)^\beta e^{-\gamma/T} \text{ cm}^3\text{s}^{-1}$$

(5.1)

where $T$ is the temperature, $\alpha$ and $\beta$ are constants, and $\gamma$ is the activation energy in K. For many reactions $\alpha$, $\beta$ and $\gamma$ have been determined experimentally or theoretically while for other reactions these values are only estimated. For all included DR reactions $\gamma = 0$.

Rate06 also contain two photo-processes:

- photodissociation (e.g. $\text{CN} + h\nu \rightarrow \text{C} + \text{N}$)
- photoionization (e.g. $\text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H}_2^+ + e^-$)

The rate coefficients for these reactions are of the form

$$k = \alpha e^{-\gamma A_v} \text{ s}^{-1}$$

(5.2)

where $\alpha$ is the rate coefficient in the unshielded interstellar UV radiation field, $A_v$ is the extinction at visible wavelengths by interstellar dust, and $\gamma$ is a parameter taking into account the increased extinction at UV-wavelengths. Due to the high visual extinction in dark clouds these photo-processes are not so important for the chemistry in such regions.

The final two types of reactions included in Rate06 involve cosmic ray particles (CRP). Firstly

- direct cosmic-ray reactions (e.g. $\text{H}_2 + \text{CRP} \rightarrow \text{H}_2^+ + e^-$)

that have rate coefficients of the form

$$k = \alpha \text{ s}^{-1}.$$
Secondly

- cosmic ray induced photo-processes (see [92] for precise definition)

which have rate coefficients of the form

$$k = \alpha \gamma / (1 - \omega) \ s^{-1}$$  \hspace{1cm} (5.4)

where $T$ is temperature, $\alpha$ is the direct cosmic-ray ionization rate, $\gamma$ is a factor related to the probability per cosmic-ray ionization that the desired photo-reaction takes place, and $\omega$ is the dust grain albedo.

The rate of change in the density $n$ of each species $i$ with time is given by the formula

$$\frac{dn_i}{dt} \equiv \sum_{a,b} k_{ab} n_a n_b + \sum_{c} k_{c} n_c - n_i \left[ \sum_{d} k_{i d} n_d + \sum_{e} k_{i e} \right]$$  \hspace{1cm} (5.5)

The first term represents the summation over all two-body reactions that lead to the formation of $i$. The second term is the summation over all photo-processes and/or cosmic-ray processes that produce $i$. The final two terms are the equivalent summations over all processes that lead to the destruction of $i$. Coupled with the initial abundances and physical parameters in Table 5.1 and 5.2, respectively, the density of each species can be numerically calculated versus time.

5.1.2 Processes not accounted for in the model

In the model calculations of TMC-1 we have not included grain surface chemistry and reactions involving molecular anions. Grains have been treated in other models incorporating adsorption and desorption [93, 94] of molecules (and atoms) as well as reactions occurring on the grain surfaces [95]. The grains are in these models not treated as species but only as substrate for gas-phase species to stick to, i.e. there is no differential equation for the abundance of grains. It has been discussed that a deterministic rate coefficient approach could be erroneous to use for chemistry that occurs on grains owing to the fact that the number of reactive species on a grain-surface could be low. To this end, stochastic approaches have also been used when modelling grain surface chemistry [96].

It should also be pointed out that molecular anions of the form $C_{2n}H^-$ recently have been observed in circumstellar and interstellar media, including the dark cloud TMC-1 [97, 98]. These anions are believed to have formed mainly by radiative electron attachment onto neutral molecules

$$C_{2n}H + e^- \rightarrow C_{2n}H^- + hv$$  \hspace{1cm} (5.6)

In fact it was calculated by Herbst in 1981 that the large electron affinity of hydrocarbon radicals would give high rate coefficients for such reactions for species with more than 4-5...
atoms and that it could bring about $C_2nH/C_2nH$ ratios of a few percent in dark clouds [99]. This was confirmed by McCarthy et al. in 2006, whose observations toward TMC-1 indicated a $C_6H/C_6H$ ratio of $\sim 2.5\%$ [97]. Walsh et al. ran models to investigate the effects of molecular anions on the chemistry of dark clouds [100]. In their study they used the pure gas-phase model of TMC-1 described above with and without the addition of chemistry associated with molecular anions (the OSU database was also used in their work). Apart from $C_2nH^-$ ions, with $n = 2, 3, 4, 5$, also $C_{2n}^-$ ions, with $n = 2, 3, 4, 5$ and $C_3N^-$ and $C_5N^-$ were considered. In the model the anions were destroyed by photo-detachment, mutual neutralization and through reactions with atoms. The main finding associated with the inclusion of anion chemistry was an enhanced production efficiency of unsaturated carbon-chain neutral molecules, in particular ones belonging to the $C_nH$, $C_nH_2$ and $HC_nN$ families. The overall effect of the inclusion of anion chemistry was, however, relatively small and the authors argued that this was due to the fact that the abundance ratio between anions and free electrons remained low throughout the model, with a maximum of only a few percent.

5.2 Limitations of chemical modelling

Modelling the chemical evolution of interstellar clouds is difficult and uncertainties to the described type of model are of course pronounced [101]. Uncertainties exist in the rate coefficients, initial elemental abundances and the physical parameters of the system. The supposition of homogeneous number density and temperature may be an oversimplification as it has been found that TMC-1 contains at least six smaller units with distinct chemical properties [102]. Moreover, there are probably many molecules and reactions playing a role for the chemistry that are not yet realized. The model may neglect some species which although minor may play a role in the formation/destruction of more abundant species. Pure gas-phase models suffer from not taking grain processes properly into account while models accounting for such processes are associated with uncertainties regarding surface chemistry, including binding energy of molecules to dust grains [94, 96, 102].

The success of a model can be interpreted as its ability to reproduce observed abundances of as many molecules as possible. However, models should stick to reality; an improved rate file, for example a change of a rate coefficient to an experimentally determined value, does not necessarily mean a more successful model. Given all uncertainties it is interesting to point out that even pure gas-phase models are capable of reproducing the abundances (to within an order of magnitude) for a majority of the molecules observed in TMC-1 [14, 25, 101-103] and such comparisons have lead to estimations on the chemical age of TMC-1 of a few $10^5$ years [25, 101, 103]. The situation is somewhat worse for more complex molecules, the abundances of which are often underestimated [14]. This could be a natural consequence of that these species are the products of long, perhaps various, chains of reactions, with some rate coefficients only estimated and with all formation pathways not yet identified.
Chapter 6

Results and discussion

In this chapter results from the DR experiments on CD$_3$CND$^+$, CH$_3$CHCNH$^+$, CH$_3$CH$_2$CNH$^+$, CD$_3$CDO$^+$, CH$_3$CHO$^+$ and DCOOD$_2$$^+$ are presented and discussed.

6.1 The DR of protonated nitriles (Paper I-III)

6.1.1 Motivations for the studies

Nitriles are known to exist in various environments of astrochemical interest. Hydrogen cyanide, HCN, has been detected in diffuse interstellar clouds [104], while dark clouds, such as TMC-1, are known to contain nitriles as complex as HC$_{11}$N [105]. Hot cores contain nitriles in higher relative abundance than dark clouds owing to a more efficient desorption of these compounds from grains in such environments [27]. Absorption features of XCN-molecules (solid phase) have been observed towards a series of obscured young stellar objects [106] and several nitriles, including CH$_3$CN, has been detected in cometary comae [107]. Nitriles are also abundant in the atmosphere of Titan [42, 108].

Nitriles are interesting from an astrobiological viewpoint as they can be involved in the synthesis of simple biomolecules in different ways. Experiments have shown that amino acids can be produced by acid hydrolysis of proton-irradiated CH$_3$CN/H$_2$O ice mixtures [109]. Also, as was mentioned in section 2.3, nitriles are presumably important in the formation of Titan’s aerosols. The hydrolysis of tholins (Titan aerosol analogs) can give rise to amino acids [50, 51] and it has even been shown that adenine, one of the four nucleobases of DNA, can be synthesized from tholins [110, 111].

Motivations for us to study the DR of protonated nitriles were as follows

i) The DR of a protonated nitrile could serve as the final step in the synthesis of the corresponding neutral nitrile. Branching fractions of hydrogen ejection from protonated nitriles upon DR had not been studied for any of the considered species.

ii) Nitriles have high proton affinities and can therefore be lost by the sequence protonation followed by DR in interstellar clouds and Titan’s atmosphere. Studies of the DR branching fractions could provide insight into what extent the neutral nitriles are destroyed or recycled by this sequence.

iii) Models of Titan’s ion-chemistry in combination with ionic measurements (from the INMS on the Cassini spacecraft) can be used to retrieve abundances of neutral molecules in Titan’s...
upper atmosphere [59]. For this purpose it is important to know the thermal rate coefficients for the DR of protonated nitriles at electron temperatures relevant for Titan.

6.1.2 Branching fractions

DR branching fractions, at $E_{rel} \sim 0$ eV, of the three studied protonated nitriles are shown in Table 6.1. The resolution of the detector did not allow for a fully detailed investigation into the branching fractions; fragments differing only by a few amu in mass could not be resolved individually (see sections 3.1.4 and 4.2.2). We therefore had to restrict the study to determine how heavy atoms fragmented from each other, which allowed us to put upper limits on the different possible product channels.

Table 6.1 Branching fractions in the DR of protonated nitriles studied at CRYRING

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products (gross formulas)</th>
<th>Branching fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$CND$^+$ + e$^-$ $\rightarrow$</td>
<td>C$_2$ND$_2$, + aD + bD$_2$</td>
<td>0.65±0.03</td>
</tr>
<tr>
<td></td>
<td>C$_2$D$_2$, + ND$_2$, + aD + bD$_2$, CND$_x$, + CD$_y$, + aD + bD$_2$</td>
<td>0.35±0.03</td>
</tr>
<tr>
<td>CH$_2$CHCNH$^+$ + e$^-$ $\rightarrow$</td>
<td>C$_2$NH$_x$, + aH + bH$_2$</td>
<td>0.50±0.04</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_4$, + NH$_x$, + aH + bH$_2$, C$_2$NH$_x$, + CH$_y$, + aH + bH$_2$</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_4$, + CNH$_x$, + aH + bH$_2$</td>
<td>0.49±0.04</td>
</tr>
<tr>
<td>CH$_2$CH$_2$CNH$^+$ + e$^-$ $\rightarrow$</td>
<td>C$_2$NH$_x$, + aH + bH$_2$</td>
<td>0.43±0.02</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_4$, + NH$_x$, + aH + bH$_2$, C$_2$NH$_x$, + CH$_y$, + aH + bH$_2$</td>
<td>0.43±0.02</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_4$, + CNH$_x$, + aH + bH$_2$</td>
<td>0.14±0.01</td>
</tr>
</tbody>
</table>

We assume that the results for CD$_3$CND$^+$ can be applied to CH$_3$CNH$^+$ considering the similarities in DR branching ratios reported for a series of molecular ions and their fully deuterated isotopologues as discussed further in section 6.2.2.

We believe that the dominant type of channel among those involving a break of a bond between heavy atoms in the DR of CD$_3$CND$^+$ are the ones in which the C-N bond is preserved. The reasons for this are that the C-N bond is much stronger than the C-C bond in CD$_3$CND$^+$ and that CH$_3$ + HNC was observed to be the main dissociation channel apart from the single loss of the imine hydrogen atom in a study by Chen et al. 2004 on collisional neutralization of protonated acetonitrile [112]. In the case of CH$_3$CH$_2$CNH$^+$ we also believe that the C-N bond is preserved in almost all DR events. The reason for this relates to our study of CH$_2$CHCNH$^+$ in which breakage of the C-N bond was observed not to occur. Indeed the terminal C-C bond in CH$_3$CH$_2$CNH$^+$ is substantially weaker than the corresponding C-C bond in CH$_2$CHCNH$^+$, while the strengths of the C-N bonds are nearly the same.

Regarding the branching fractions, the upper limits on the channels involving the sole ejection of the imine hydrogen atom, leading to the unprotonated nitrile are of special astrochemical interest. These upper limits are all relatively high, ranging from 0.43 for CH$_3$CHCNH$^+$ to 0.65 for CD$_3$CND$^+$ suggesting that the DR of protonated nitriles could be an important (final) step in the gas-phase synthesis of aceto-, acrylo- and propionitrile in molecular clouds. These results also show that nitriles that are lost by protonation in Titan’s upper atmosphere, or in molecular clouds, to a large extent may be recycled by DR.
Another conclusion from the branching fraction studies is that the DR reactions of protonated nitriles do not seem to involve ruptures of C-N bonds. Preservation of the C-N bond was also observed for the DR of HCNH\(^+\), DCCCN\(^+\) and DCCCND\(^+\) earlier studied at CRYRING [113, 114]. These findings support a conclusion from a Titan model by Krasnopolsky [54], namely that nitriles are not destroyed to yield N\(_2\) again in Titan’s atmosphere. If breakage of the C-N bond would occur in the DR of a nitrile ion, the product N-atom or NH molecule would have the possibility to react further with NH or N, respectively, to produce N\(_2\) through the reaction NH + N \(\rightarrow\) N\(_2\) + H. Preservation of the C-N bond upon DR was however assumed for all nitrile ions considered in the model and indeed the experimental results favor these assumptions. Given their stability it is instead likely that the fate of nitriles in Titan’s atmosphere is to contribute to the haze formation and eventually precipitate to the surface [54].

### 6.1.3 Cross sections

The best fits of the cross-sections versus \(E_{rel}\) for the DR of the studied protonated nitriles are given in Table 6.2 (for plots of the data, see Paper I-III).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cross section (cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD(_3)CND(^+) + e(^-)</td>
<td>(7.4 \cdot 10^{-16} E_{rel}^{-1.23}) for 1 meV&lt; (E_{rel}) &lt; 0.1 eV (4.1 \cdot 10^{-16} E_{rel}^{-1.46}) for 0.1 eV &lt; (E_{rel}) &lt; 1 eV</td>
</tr>
<tr>
<td>CH(_2)CHCNH(^+) + e(^-)</td>
<td>(1.2 \cdot 10^{-15} E_{rel}^{-1.29}) for 1 meV&lt; (E_{rel}) &lt; 0.1 eV (5.6 \cdot 10^{-16} E_{rel}^{-1.60}) for 0.1 eV &lt; (E_{rel}) &lt; 1 eV</td>
</tr>
<tr>
<td>CH(_3)CH(_2)CNH(^+) + e(^-)</td>
<td>(1.1 \cdot 10^{-15} E_{rel}^{-1.26}) for 1 meV&lt; (E_{rel}) &lt; 1 eV</td>
</tr>
</tbody>
</table>

Below \(E_{rel}=0.1\) eV the estimated overall uncertainty in the cross sections are about 15-20% while for higher \(E_{rel}\) the error bars increase due to poorer statistics. Close to 1 eV the cross sections given in Table 6.2 are not at all reliable since the utilized procedure to subtract signals emerging from reactions between the ions and the residual gas is based on the assumption that the DR cross section close to 1 eV is negligibly small.

It is instructive that the mean collision energies of \(10^{-3},\ 10^{-2},\ 10^{-1}\) and 1 eV roughly correspond to electron temperatures, \(T_e\), of 10, 100, 1000 and 10000 K, respectively. In molecular clouds, where \(T_e\) is expected to range from 10 to a few 100 K, and Titan’s upper atmosphere, where \(T_e\) is below 1000 K [115], insight into DR cross sections at \(E_{rel}>0.1\) eV are typically not required. However, it is interesting to note the change of slopes observed at \(E_{rel}\sim0.1\) eV in the DR cross sections of CD\(_3\)CND\(^+\) and CH\(_2\)CHCNH\(^+\). A potential reason for these slope changes, which also have been observed for other molecular ions, is the opening of autoionization channels into vibrationally excited states of the ions [116, 117]. For CH\(_3\)CH\(_2\)CNH\(^+\) such a slope change was not clear, but by inspection of Figure 1 in Paper III one can notice that the cross section data points at \(E_{rel}>0.1\) eV are rather spread out.
6.1.4 Thermal rate coefficients with Titan implications

The thermal rate coefficients for CD$_3$CND$^+$, CH$_2$CHCNH$^+$ and CH$_3$CH$_2$CNH$^+$, as calculated from the cross section data, are given in Table 6.3.

Table 6.3 Thermal rate coefficients versus electron temperature for the DR of protonated nitriles studied at CRYRING. The rate coefficients are applicable for $10 < T_e < 1000$ K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Thermal rate coefficient (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$CND$^+$ + e$^-$</td>
<td>$8.1 \times 10^{-7} \ (T_e/300)^{-0.69}$</td>
</tr>
<tr>
<td>CH$_2$CHCNH$^+$ + e$^-$</td>
<td>$1.8 \times 10^{-6} \ (T_e/300)^{-0.80}$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CNH$^+$ + e$^-$</td>
<td>$1.5 \times 10^{-6} \ (T_e/300)^{-0.76}$</td>
</tr>
</tbody>
</table>

The thermal rate coefficients for CH$_2$CNH$^+$ and CH$_3$CH$_2$CNH$^+$ have been measured by McLain and Adams using a flowing afterglow Langmuir probe (FALP) apparatus as outlined in section 3.2.1 with the results, $k(T) = 3.4 \times 10^{-7} \ (T/300)^{1.03}$ and $k(T) = 4.6 \times 10^{-7} \ (T/300)^{-0.81}$ cm$^3$ s$^{-1}$, respectively [118]. The results agree with earlier FALP measurements conducted at 300 K by Geoghegan et al. [119], but differ from the rate coefficients obtained in this work. We do not think that the significant difference observed for protonated acetonitrile is due to an isotopic effect, since such effects tend to be in the opposite way, with the fully deuterated molecular ion having the lower rate coefficient (see section 6.2.3). If the disagreements in rate coefficients are related to the fact that the rotational temperature of the ions is the same as the electron temperature in the FALP experiments, whereas not in ours, then we would suppose the results at $T_e = 300$ K to agree better, since the ions have permanent dipole moments and are expected to reach a rotational temperature not very far from 300 K during a few seconds of storage in CRYRING.

One difference between the two approaches, which might play a role, is that mass selection of the ions is performed for DR studies at storage rings but not in the FALP method. For example, the final step in the synthesis of CH$_3$CH$_2$CNH$^+$ in the FALP experiments involved the proton transfer from H$_3^+$ to CH$_3$CH$_2$CN. That reaction was studied in a selected ion flow tube experiment by Geoghegan et al. (as a contributing part to their DR experiment of CH$_3$CH$_2$CNH$^+$) and was shown to lead to dissociation into HCNH$^+$ + C$_2$H$_4$ + H$_2$ with a branching ratio of 0.65 [119]. It was noted that the HCNH$^+$ ions in the DR experiment rapidly transferred protons to CH$_3$CH$_2$CN as only CH$_3$CH$_2$CNH$^+$ and its first cluster ion was observed at the downstream mass spectrometer. On the other hand, since the CH$_3$CH$_2$CN density needed to be kept low in order to avoid cluster formation an uncertainty of 40% was estimated for the rate coefficient for the DR of CH$_3$CH$_2$CNH$^+$ [119]. In the more recent work by McLain and Adams [118] the decay of electron density was studied as a function of the utilized CH$_3$CH$_2$CN concentration. A chemical model was used to determine at what concentrations the plasma was nearly totally dominated by different ions and DR rate coefficients were obtained from the electron decays measured at the corresponding concentrations. In the analysis of CH$_3$CH$_2$CNH$^+$ the proton transfer from H$_3^+$ to CH$_3$CH$_2$CN was treated as being non-dissociative. It would be interesting to see the effects on their analysis of taking into account the dissociative nature of the proton transfer from H$_3^+$ to CH$_3$CH$_2$CN as well as an inclusion of the proton transfer reaction from HCNH$^+$ to...
CH$_3$CH$_2$CN with an appropriate rate coefficient. This could possibly further ensure the absence of HCNH$^+$ ions in the plasma. In this context it should be noted that FALP- and CRYRING results agree on the thermal rate coefficient for the DR of HCNH$^+$, with both methods giving $k(T=300) \sim 3 \cdot 10^{-7}$ cm$^3$s$^{-1}$ [113, 118]. Furthermore, the CRYRING results for the thermal rate coefficients of CD$_3$CND$^+$, CH$_2$CHCNH$^+$ and CH$_3$CH$_2$CHN$^+$ fit well into the trend that larger molecular ions have higher thermal rate coefficients than smaller ones, which will be discussed further in section 6.4.

In section 2.3 it was pointed out that Cui et al. [66] used INMS data collected in the closed source mode (for detection of neutrals) to estimate abundances of neutral molecules in Titan’s upper atmosphere. It was mentioned that their results for the T5 flyby agreed fairly well with results reported by Vuitton et al. [59], who instead used INMS data collected in the open source ion mode and a steady state ion chemistry model to estimate neutral abundances. The results from both works were consistent (within a factor of 4) with the exception of CH$_3$CN, for which Cui et al. and Vuitton et al. estimated mixing ratios of 28±5 ppm and 3 ppm, respectively. The steady state abundance of CH$_3$CN in the work by Vuitton et al. is roughly given by

$$[\text{CH}_3\text{CN}] = \frac{k_{\text{DR}}[\text{e}^-][\text{HCNCH}^+]}{k_1[\text{HCNH}^+] + k_2[\text{C}_2\text{H}_4^+]}$$ (6.1)

with $k_{\text{DR}}$ being the thermal rate coefficient for the DR of CH$_3$CNH$^+$ (at $T_e = 718$ K), and $k_1$, $k_2$ being the rate coefficients for the proton transfer reactions HCNH$^+$ + CH$_3$CN $\rightarrow$ CH$_3$CNH$^+$ + HCN (HNC) and C$_2$H$_5^+$ + CH$_3$CN $\rightarrow$ CH$_3$CNH$^+$ + C$_2$H$_4$, respectively. The value used for $k_{\text{DR}}$ by Vuitton et al. was $1.8 \cdot 10^{-7}$ cm$^3$s$^{-1}$ and derived from the FALP measurement by Geoghegan et al. conducted at 300 K only [119]. The thermal rate coefficient at 718 K for the DR of CD$_3$CND$^+$ obtained from the CRYRING measurement is $4.4 \cdot 10^{-7}$ cm$^3$s$^{-1}$, i.e. a factor of 2.5 higher than the value used for the DR of CH$_3$CNH$^+$ in the model. To a good approximation the predicted mole fraction of CH$_3$CN would, by enhancing the $k_{\text{DR}}$ value in the model by Vuitton et al., increase by a factor of 2.5 reaching ~8 ppm. This would improve the agreement with the result reported by Cui et al.

### 6.1.5 Nitrile chemistry in the dark cloud TMC-1

As a part of Paper II we ran gas-phase models of the dark molecular cloud TMC-1 with a special focus on nitrile molecules. The main purpose of this investigation was to see how well the observed abundances of these nitriles could be reproduced by a chemical model which only included gas-phase reactions. The assumptions regarding temperature, H$_2$ density, visual extinction and initial elemental abundances are given in chapter 5 alongside a description of the numerical approach to simulate the chemical evolution of the cloud through time. The first model we ran utilized the set of reaction rate coefficients given in the dipole enhanced-version of the latest release of the UMIST Database for Astrochemistry [89, 90]; we refer henceforth to this model as the original model. Thereafter we studied the impact of recent experimental findings including ours for the DR of protonated acetonitrile and protonated acrylonitrile on the predicted abundances of nitrile molecules.
For the DR of CH$_3$CNH$^+$ we considered channels leading to CH$_3$CN + H, CH$_2$CN + 2H, CH$_3$ + HNC and CH$_2$ + HCN + H with branching fractions of 0.325, 0.325, 0.175 and 0.175, respectively. Note that the sum of the branching fractions for the two first channels (0.65) and the two latter channels (0.35) agree with the results for CD$_3$CND$^+$ in Table 6.1. For the DR of CH$_3$CHCNH$^+$ we included the channels CH$_2$CHCN + H, C$_2$H$_2$ + HCN + H and C$_2$H$_3$ + HNC (see erratum attached to Paper II). It is noted that if another choice would have been made for the channels on the form C$_2$H$_x$ + CNH$_y$ + aH + bH$_2$ in the DR of CH$_2$CHCNH$^+$, it would not affect the outcome of the model notably. The reason for this is that molecules on the form C$_2$H$_x$ and CNH$_y$ are produced at much higher rates by other reactions than through the DR of CH$_2$CHCNH$^+$. We ran nine models, which differed only in the rate coefficients used for the radiative association reactions CH$_3^+$ + HCN $\rightarrow$ CH$_3$CNH$^+$ + hv and CH$_3^+$ + HNC $\rightarrow$ CH$_3$CNH$^+$ + hv. The rate coefficient for the former reaction has been determined both experimentally and theoretically with results differing by a factor of 45 [120, 121]. The latter reaction is not included in the original model, and was added to the other models since it could be important owing to the relatively high HNC abundance in TMC-1 [122].

For eight out of the ten considered nitriles the predicted abundance at 10$^5$ yr (the estimated chemical age of TMC-1) agreed with the observed value to within an order of magnitude in all models. CH$_2$CN was underpredicted by a factor of 30-270 in the different models, while acrylonitrile was under-predicted by a factor of $\sim$3000 in the original model and by a factor of $\sim$700 in the other models. At a cloud age of 3 · 10$^5$ yr the predicted abundance of acrylonitrile peaked in most models, reaching a density $\sim$100 times lower than the observed value.

The observed abundance of CH$_2$CHCN in TMC-1 is somewhat puzzling. Blake et al. [123] suggested grain surface reactions, such as repeated hydrogenation of HC$_3$N, as an explanation to the absence of acrylo- and propionitrile in the cold ridge of the Orion molecular cloud and the presence of these molecules in the hot core of the same cloud. However, while acrylonitrile has been detected in TMC-1 propionitrile has not [124]. As outlined by Minh & Irvine [124] this points to a gas-phase synthesis of CH$_2$CHCN in TMC-1 because i) grain surface molecules tend to be saturated, meaning that CH$_3$CH$_2$CN is expected to be more abundant than CH$_2$CHCN on grains, ii) the masses of CH$_2$CHCN and CH$_3$CH$_2$CN differ only by 2 amu, implying that the energy required for desorption of these species should not be too different. However, the gas-phase models did, as recently mentioned, under-predict the abundance of CH$_2$CHCN by more than two orders of magnitudes.

To summarize, while it is clear that the gas-phase models are capable of reproducing observed values of many nitriles in TMC-1, they lack some of the most important production routes to acrylonitrile.
6.2 The DR of ionized acetaldehyde (Paper IV and V)

6.2.1 Motivations for the studies

Acetaldehyde, CH₃CHO, is apart from formaldehyde, H₂CO, the most commonly detected aldehyde in extraterrestrial environments. It has been observed in dark clouds, hot cores and in comets [125-127]. It has also been tentatively detected in the solid phase towards the highly obscured young stellar object W33A [128]. Acetaldehyde can be involved in different series of reactions to yield amino acids, including via the Strecker synthesis [129, 130].

Once acetaldehyde molecules are formed or released from grains into the gas phase of interstellar clouds they can be ionized by different means; through charge transfer reactions, by cosmic ray particles, or by UV-photons generated from cosmic ray particles. The acetaldehyde ions can then react with free electrons. Motivations for us to study the DR of CD₃CDO⁺ and CH₃CHO⁺ were as follows:

i) The DR of CH₃CHO⁺ is included in astrochemical models of dark clouds and had not been investigated before. We initially used CD₃CDO⁺ in order to be able to extract detailed branching fraction information.

ii) We later investigated the DR of CH₃CHO⁺ to see whether isotopic effects were present in the branching fractions and/or in the thermal rate coefficients.

6.2.2 Branching fractions

The branching fractions obtained for CH₃CHO⁺ and CD₃CDO⁺ are shown in Table 6.4. For none of the species it was possible to extract full information on the branching ratios, only the relative importance of channels leading to conservation or fragmentations of bonds between heavy atoms could be investigated.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products (gross formulas)</th>
<th>Branching fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CHO⁺ + e⁻ →</td>
<td>C₂OHₓ + aH + bH₂</td>
<td>0.28±0.02</td>
</tr>
<tr>
<td></td>
<td>COHₓ + CHₓ + aH + bH₂, C₂Hₓ + OHₓ + aH + bH₂</td>
<td>0.72±0.02</td>
</tr>
<tr>
<td>CD₃CDO⁺ + e⁻ →</td>
<td>C₂ODₓ + aD + bD₂</td>
<td>0.34±0.02</td>
</tr>
<tr>
<td></td>
<td>CODₓ + CDₓ + aD + bD₂, C₂Dₓ + ODₓ + aD + bD₂</td>
<td>0.66±0.02</td>
</tr>
</tbody>
</table>

It is noticeable that fairly similar branching behaviors is observed for the two isotopologues, with roughly ~70% of the DR reactions leading to the break of a bond between heavy atoms, both for CH₃CHO⁺ and CD₃CDO⁺, and with ~30% leading to the conservation of the C-C-O chain. The finding that the two isotopologues have fairly similar branching fractions is in line with other measurements conducted at CRYRING, e.g. CH₃OH⁺/CD₃OD⁺⁺ [11], H₃O⁺/D₃O⁺ [24] and NH₄⁺/ND₄⁺ [131].

For the channels involving a break of a bond between heavy atoms we assume that a break of the C-C bond is more common than a break of the C-O bond due to the weaker bond...
strength. A potential product channel is the one leading to HCO + CH$_3$. We used this channel in a model calculation of TMC-1 further described in 6.2.4, but we note again that the use of another channel on the form COH$_x$ + CH$_y$ + $a$H + $b$H$_2$ would not significantly affect the model calculations since potential products like HCO, CO, CH$_3$ and CH$_2$ surely are produced at much higher rates through other reactions than by the DR of CH$_3$CHO$^+$. In the model calculations we assumed, as in [90], that channels which retain the C-C-O chain leads exclusively to ketene (H$_2$CCO) alongside two hydrogen atoms. At first sight this assumption could appear critical, but as will be addressed later there are also much more efficient production pathways for ketene than through the DR of CH$_3$CHO$^+$.

### 6.2.3 Cross sections and thermal rate coefficients

Table 6.5 summarizes the cross sections and thermal rate coefficients obtained from our studies on the DR of CH$_3$CHO$^+$ and CD$_3$CDO$^+$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cross section (cm$^2$)</th>
<th>Thermal rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CHO$^+ + \text{e}^-$</td>
<td>$1.5 \cdot 10^{-15} E_{rel}^{-1.20}$ for $1 \text{meV} &lt; E_{rel} &lt; 0.2 \text{eV}$</td>
<td>$1.5 \cdot 10^6 \ (T_e/300)^{0.70} \ \text{cm}^3 \text{s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$7.9 \cdot 10^{-16} E_{rel}^{-1.60}$ for $0.2 \text{eV} &lt; E_{rel} &lt; 1 \text{eV}$</td>
<td></td>
</tr>
<tr>
<td>CD$_3$CDO$^+ + \text{e}^-$</td>
<td>$6.8 \cdot 10^{-16} E_{rel}^{-1.28}$ for $1 \text{meV} &lt; E_{rel} &lt; 0.2 \text{eV}$</td>
<td>$9.2 \cdot 10^{-7} \ (T_e/300)^{0.72} \ \text{cm}^3 \text{s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$4.1 \cdot 10^{-16} E_{rel}^{-1.60}$ for $0.2 \text{eV} &lt; E_{rel} &lt; 1 \text{eV}$</td>
<td></td>
</tr>
</tbody>
</table>

The uncertainties in these values are similar to those for the studied nitrile ions (see section 6.1.3). We noticed for both ions a change of energy dependence in the DR cross section at $E_{rel} \sim 0.2$ eV which, as in the case of protonated nitrile ions could relate to opening of autoionization channels into vibrationally excited states of the ions. Again, the data at these high collision energies, which are irrelevant for astrochemical applications, are sparse due to poor statistics.

A significant isotopic effect is observed in the cross sections for the ions, with CH$_3$CHO$^+$, the lighter isotopologue, showing the higher reactivity. Possible reasons for lighter isotopologues to have higher cross sections are discussed in Paper V. One explanation could be that the higher reduced mass of the products results in a slower dissociation along the repulsive surface, which gives more time for autoionization to occur [132]. The effect can also appear due to differences in the Franck-Condon overlaps between the initial bound and dissociate wave functions [133]. The heavier isotopologues have lower zero-point energies, which potentially could reduce some of these overlaps. Higher zero-point energies may also help to overcome energy barriers for tunneling to repulsive potential surfaces that do not cross the ionic state close to its minimum or some of the vibrationally excited intermediates formed Rydberg states in an indirect DR-process. The acetaldehyde ion is among the most complex systems studied at CRYRING for which a pronounced isotopic effect has been observed in the DR cross section. The ions CH$_3$OH$_2^+$ and CD$_3$OD$_2^+$ showed comparable
reactivity, which was also observed to be the case for CH$_2$OH$^+$ versus CD$_2$OD$^+$ [11, 134]. Ions whose isotopologues have been observed to have marked differences in the DR cross sections include H$_3$O$^+/D_3$O$^+$ and NH$_4^+/ND_4^+$ [24, 131].

6.2.4 Implications for dark clouds

The thermal rate coefficients for the DR of CH$_3$CHO$^+$ determined from the CRYRING measurement is at 10 K about 10 times higher than the estimated value used in the latest release of the UMIST Database for Astrochemistry [90]. As for the branching fraction investigation our results also show that the flow into the channel H$_2$CCO + 2H is overestimated in [90].

We have run a chemical model to see the effect of our experimental results for the predicted abundances of acetaldehyde and ketene in TMC-1. It turned out that the new results have no particular effect on these abundances. The abundance of ketene decreased only by a few percent at a cloud age of $3 \cdot 10^5$ yr compared to the density predicted by the original model. The reason for this small decrease was the lowering of the relative importance used for the channel leading to H$_2$CCO + 2H in the DR of CH$_3$CHO$^+$ and the reason why the effect was not more pronounced is that the main route to ketene in the model does not involve the DR of CH$_3$CHO$^+$; instead it is produced mainly through the neutral-neutral reaction O + C$_2$H$_3$ → H$_2$CCO + H. Interstellar ketene is discussed thoroughly by Ruiterkamp et al. [135] in light of observations towards embedded protostars. They address, for example, that the emission lines of ketene indicate it to be primarily present in cold gas and that it can be nearly absent in hot cores.

The formation of CH$_3$CHO in hot cores has been argued to occur mainly on grain surfaces [136], while the formation of the molecule in dark clouds is more uncertain. The pure gas-phase model, employing the latest release of the UMIST database for astrochemistry, is able to reproduce the observed abundance in TMC-1. The leading route to acetaldehyde in that model involves the radiative association H$_3$O$^+$ + C$_2$H$_3$ → CH$_3$CHOH$^+$ + hv followed by the DR of CH$_3$CHOH$^+$ producing CH$_3$CHO + H in 50% of the reactions. It has been shown recently that the channel leading to CH$_3$CHO + H in the DR of CH$_3$CHOH$^+$ in fact has a maximum branching ratio of 0.23 [137]. More significantly the theoretically and experimentally determined rate coefficients of the radiative association reaction leading to CH$_3$CHOH$^+$ yielded values differing nearly by a factor of 100 [138, 139]. The higher theoretical value is used in the model, while if the lower experimental value would have been used, the predicted abundance of acetaldehyde in TMC-1 would go down roughly by two orders of magnitude; no longer reproducing the observed abundance. New experiments on the reaction between C$_2$H$_2$ and H$_3$O$^+$ as well as other reactions involving hydrocarbons/hydrocarbon ions and H$_2$O/H$_3$O$^+$, would be valuable for the understanding of the acetaldehyde chemistry of dark clouds.
6.3 DR of protonated formic acid (Paper VI)

6.3.1 Motivations for the studies

Formic acid (HCOOH) is the simplest organic acid. The molecule has been observed in dark clouds, hot cores and in the coma of comet Hale-Bopp [140-142]. It has been proposed that HCOOH could serve as a potential tracer for glycine (the simplest amino acid), NH$_2$CH$_2$COOH, in hot cores where the reaction NH$_2$CH$_2$OH$_2^+$ + HCOOH $\rightarrow$ NH$_2$CH$_2$COOH$_2^+$ + H$_2$O could find favourable conditions [143]. The DR of protonated formic acid (HCOOH$_2^+$) has been regarded as the final step in the gas-phase synthesis of HCOOH [140, 144] and motivations for us to study the DR of DCOOD$_2^+$ included

i) The DR of protonated formic acid had not been studied before. Knowing the thermal rate coefficient and especially the branching fractions of the reaction would provide clues to the synthesis of formic acid in different interstellar media. We used fully deuterated ions with the hope to be able to extract detailed information on the branching ratios.

ii) The observation of HCOOH in the coma of comet Hale-Bopp [142] was argued, based on chemical modelling, to be indicative of formic acid being present in the cometary nucleus rather than synthesized in the coma from other parent molecules [145]. Investigations into the DR of protonated formic acid could potentially reveal results that would strengthen this hypothesis, as it was assumed in the model that the DR of HCOOH$_2^+$ leads to HCOOH in 100% of the reactions. If this would not be the case it would be even harder to explain the observed HCOOH abundance in the coma as a result of chemical synthesis in the gas-phase.

6.3.2 Branching fractions

We were not able to determine detailed branching ratios from our experiment and could only address the relative importance of channels preserving the heavy atom structure and channels involving ruptures of bonds between heavy atoms. The obtained branching fractions for the DR of DCOOD$_2^+$ are shown in Table 6.6 and we believe that these results can be applied to the DR of HCOOH$_2^+$ as well.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products (gross formulas)</th>
<th>Branching fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCOOD$_2^+$ + e$^-$</td>
<td>CO$_2$D$_x$ + aD + bD$_2$</td>
<td>0.13±0.03</td>
</tr>
<tr>
<td></td>
<td>COD$_x$ + OD$_y$ + aD + bD$_2$. O$_2$D$_x$ + CD$_y$</td>
<td>0.87±0.03</td>
</tr>
</tbody>
</table>

The dominant type of fragmentation behavior involved the break-up of one bond between heavy atoms. We consider reactions leading to products on the form O$_2$D$_x$ + CD$_y$ highly unlikely. Indeed, only two such channels are energetically possible at ~0 eV, CD$_3$ + O$_2$ and CD$_2$ + O$_2$D, both of which require significant rearrangements to occur. The most important finding of the branching fraction studies is the upper limit, of only 13%, for the production of formic acid and the astrochemical implications of this result will be discussed in section 6.3.4.
6.3.3 Cross section and thermal rate coefficient

The best fits of the cross section data and the thermal rate coefficient for the DR of DCOOD$^+$ are presented in Table 6.7. The same uncertainties as given for the nitrile ions (section 6.1.3) are to be considered for the results presented in the table. Possible reasons for the change of slope at $E_{rel} \approx 0.1$ eV are the same as for the ions previously discussed. We note also that the thermal rate coefficient for HCOOH$^+$ may be higher than for DCOOD$^+$ (see section 6.2.3).

Table 6.7 Cross sections versus $E_{rel}$ and thermal rate coefficients versus electron temperature, $10 < T_e < 1000$ K, in the DR of DCOOD$^+$ studied at CRYRING

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cross section (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCOOD$^+$ + e$^-$</td>
<td>$5.8 \cdot 10^{-16} E_{rel}^{-1.28}$ for $1$ meV $&lt; E_{rel} &lt; 0.1$ eV</td>
</tr>
<tr>
<td></td>
<td>$1.5 \cdot 10^{-16} E_{rel}^{-1.88}$ for $0.1$ eV $&lt; E_{rel} &lt; 1$ eV</td>
</tr>
</tbody>
</table>

Thermal rate coefficient: $8.4 \cdot 10^{-7} (T_e/300)^{-0.78}$ cm$^3$ s$^{-1}$

6.3.4 Astrochemical implications

As a part of Paper VI we studied the impact of our experimental results for the predicted abundance of HCOOH in the dark cloud TMC-1. In the rate file used for the original model (see section 6.1.4) of TMC-1 the DR of HCOOH$^+$ is included with the assumption that 100% of the reactions lead to HCOOH + H and that the thermal rate coefficient of the reaction obeys the formula $k(T_e) = 3 \cdot 10^{-7} (T_e/300)^{0.50}$ cm$^3$ s$^{-1}$. The predicted abundance of HCOOH at the estimated chemical age of TMC-1, using the original model, is nearly ten times higher than the observed upper limit inferred from observations [146]. By instead using the thermal rate coefficient presented in Table 6.7 and a branching fraction of 13% for the channel leading to HCOOH + H the agreement with observations improves (see Figure 6.1).

Figure 6.1 Evolution of HCOOH in TMC-1 using the latest release of the UMIST Database for Astrochemistry (solid black curve). The dotted line is the result from the model including the branching fractions and thermal rate coefficient for the DR of protonated formic acid as determined by our experiment. The gray horizontal line represents the upper limit for the abundance of HCOOH in TMC-1 as given in [146]. The bold black part of this line is located roundabout the estimated chemical age of TMC-1 ($\sim 10^5$ yr).
We also ran a model, accounting for cloud contraction and freeze out, of the dark cloud L134N. As was the case for TMC-1 the effect of using our experimental results for the DR of protonated formic acid was a decrease in the predicted abundance of HCOOH. In this model, however, the agreement with observations [140] did not improve; the predicted abundance of HCOOH went from being a factor of ~2 higher than observed to being a factor of ~4 lower.

Concerning the HCOOH observed in the coma of comet Hale-Bopp our results strengthen the hypothesis that formic acid is a parent molecule, directly sublimated from the cometary surface. The reason for this is that in the chemical model used in [145] it was also assumed that HCOOH was produced in 100% of the DR reactions of HCOOH$^+$. If the authors instead would have used a 13% share going into the channel leading to HCOOH it would be even harder to reproduce the observed abundance of HCOOH in the coma of the comet via gas-phase chemistry from other parent molecules.

### 6.4 Size effect in dissociative recombination

The DR of many molecular ions has been investigated at CRYRING. It is interesting to divide these ions into three broad categories relating to their thermal rate coefficients at 300 K, $k(300)$. The ions in the first category have $k(300) < 5 \cdot 10^{-7} \text{ cm}^3\text{s}^{-1}$. The ions in the second category have $k(300)$ between 0.5 and $1 \cdot 10^{-6} \text{ cm}^3\text{s}^{-1}$ while ions in the third category have $k(300) > 1 \cdot 10^{-6} \text{ cm}^3\text{s}^{-1}$. Three of the ions considered in this thesis belong to second category, while the other three belong to the third.

**First category ions:** $\text{H}_2^+$, $\text{D}_2^+$, $\text{HeH}^+$, $\text{HF}^+$, $\text{CF}^+$, $\text{CO}^+$, $\text{O}_2^+$, $\text{N}_2^+$, $\text{CN}^+$, $\text{H}_3^+$, $\text{D}_2\text{H}^+$, $\text{D}_3^+$, $\text{C}_2\text{H}^+$, $\text{HCO}^+$, $\text{BH}_3^+$, $\text{CF}_2^+$, $\text{CO}_2^+$, $\text{N}_2\text{H}^+$, $\text{N}_2\text{O}^+$, $\text{H}_2\text{O}^+$, $\text{SH}_2^+$, $\text{SO}_2^+$, $\text{CF}_3^+$, $\text{D}_3\text{O}^+$, $\text{D}_3\text{S}^+$, $\text{HCNH}^+$, $\text{Na}^+(\text{D}_2\text{O})$, $\text{C}_2\text{D}_5^+$

**Second category ions:** $\text{PD}_2^+$, $\text{CH}_3^+$, $\text{O}_3^+$, $\text{N}_3^+$, $\text{OPCl}^+$, $\text{H}_3\text{O}^+$, $\text{CH}_3^+$, $\text{N}_2\text{OD}^+$, $\text{C}_2\text{H}_3^+$, $\text{CH}_2\text{OH}^+$, $\text{CD}_2\text{OD}^+$, $\text{NH}_4^+$, $\text{ND}_4^+$, $\text{C}_2\text{H}_4^+$, $\text{CD}_3\text{CDO}^+$, $\text{CD}_3\text{CND}^+$, $\text{DCOOOD}^+$, $\text{CH}_3\text{OH}_2^+$, $\text{CD}_3\text{OD}_2^+$, $\text{C}_4\text{D}_9^+$

**Third category ions:** $(\text{NO})_2^+$, $\text{DOCO}^+$, $\text{OPCl}_2^+$, $\text{CCCND}^+$, $\text{CH}_3\text{CHO}^+$, $\text{C}_4\text{D}_2^+$, $\text{CD}_2\text{OD}_2^+$, $\text{DCCCN}^+$, $\text{D}^+(\text{D}_2\text{O})_2$, $\text{CD}_3\text{CDO}^+$, $\text{CD}_3\text{CDO}_2^+$, $\text{CH}_3\text{CHCNH}^+$, $\text{CH}_3\text{CH}_2\text{CNH}^+$, $\text{CH}_3\text{CH}_2\text{OH}_2^+$, $(\text{CD}_3\text{)}_2\text{OD}^+$, $\text{C}_3\text{H}_7^+$, $\text{C}_6\text{D}_6^+$, $\text{C}_6\text{D}_7^+$

Although exceptions exist, the trend is that more complex molecular ions appear to have higher rate coefficients than smaller ones. Indeed all studied diatomic ions belong to the first category and none of the studied tri-atomic ions belong to the third category.

In chemical models of e.g. dark clouds or the atmosphere of Titan there are a number of relevant molecular ions with only estimated values of the DR thermal rate coefficients, since experimental investigations not yet have been conducted. While awaiting new experimental results the reliability of the models would probably benefit by taking into account the presumed size effect of the DR thermal rate coefficient. For example, in the latest release of the UMIST database for astrochemistry [90] the DR of $\text{HC}_3\text{NH}^+$ (a reaction not yet experimentally investigated) is included with a thermal rate coefficient of $3 \cdot 10^{-7} \text{ cm}^3\text{s}^{-1}$ at 300 K, which is very probable too low.
Denna avhandling presenterar experimentella studier beträffande den dissociativa rekombinationen (DR) av de organiska molekylära jonerna CD$_3$CND$^+$, CH$_2$CHCNH$^+$, CH$_3$CH$_2$CNH$^+$, CD$_3$CDO$^+$, CH$_3$CHO$^+$ och DCOOD$_2$$^+$. DR är en reaktion i vilken en positivt enkelladdad molekylär jon fångar in en fri elektron och bildar en högt exciterad, ostabil, neutral molekyl, som snabbt bryts upp i neutrala fragment. Reaktionen spelar viktiga roller i diverse kalla, otäta plasman, likt de som existerar i jonosfärer och i interstella journey. I dessa regioner är DR inte bara den viktigaste mekanismen för neutralisering av plasmat; processen kan också fungera som det sista steget i syntesen av olika molekyler.

Samtliga experiment utfördes vid lagringsringen CRYRING belägen vid Manne Siegbahn Laboratoriet i Stockholm. För var och en av de studerade jonerna har vi från experimentell data kunnat bestämma det absoluta tvärsnittet som funktion av den relativa energin mellan reaktionspartiklarna, termiska reaktionshastigheten som funktion av elektron temperature och även i vilka utsträckningar olika produkter bildas i DR processen. Resultaten har använts, och kommer att användas, som förbättrade parametrar i kemiska modeller av interstella journey och/eller den övre atmosfären av Titan, som är Saturnus största måne.

Observationer har avslöjat att interstella journey innehåller en uppsjö av olika molekyler, inklusive komplexa organiska molekyler, som anses intressanta för den pre-biotiska syntesen av exempelvis aminosyror. Hur dessa organiska molekyler bildas och förstörs i interstella journey är långt ifrån helt klarlagt och för att närmare sig svar på dessa frågor krävs, förutom information som fås från själva observationerna, även detaljerade modellberäkningar, som i sin tur är beroende av studier av kemiska reaktioner, vilka helst ska vara utförda i förhållanden som liknar de i interstella journey.

Titans atmosfär innehåller komplexa kolvätekedjor och nitriler som har bildats genom kemiska reaktioner initierade av jonisation och dissociering av de mest förekommande gaserna, N$_2$ och CH$_4$, orsakad av partikel- och UV-strålning. Vetskap om reaktionshastigheter och produkter av kemiska reaktioner som är relevanta för Titans atmosfärkemi är viktig eftersom det bidrar till förståelsen av den observerade kemin och eftersom kemiska modeller med tillförlitliga reaktionsparametrar också kan användas som en metod att uppskatta i vilka mängder olika molekyler förekommer.

Våra experimentella resultat indikerar exempelvis att nitriler, som går förlorade genom protonering i Titans övre atmosfär eller i interstella journey, till stor utsträckning kan återskapas genom DR. Det framstår också att DR processen för nitriljoner inte involverar brott av kolvätebindingen vilket talar till fördel för hypotesen att nitriler, som bildas i Titans övre atmosfär, inte bryts ned till att så småningom bilda N$_2$ på nytt. Studierna av acetaldehydjonerna CD$_3$CDO$^+$ och CH$_3$CHO$^+$ visar en tydlig isotopisk effekt gällande tvärsnittet för DR, där den lättare isotopen är den mer reaktiva. Ett av resultaten från studien av DCOOD$_2$$^+$ är att andelen reaktioner som leder till produkterna DCOOD + D har en övre gräns på 13%. Under antagandet att inga stora isotopiska effekter förekommer i produktfördelningen får detta resultat stora konsekvenser för den modellberäknade förekomsten av myrsyra i mörka interstella journey eftersom det tidigare antogs att myrsyra bildas i 100% av DR reaktionerna av HCOOH$_2$$^+$. 

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