Molecular dissociation induced by electron transfer to multicharged ions

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Chapter 1

General introduction
1.1 Introduction

Charge transfer between atoms, molecules and their ions plays an important role in the formation and destruction of molecular species in hot astrophysical plasmas, cold interstellar clouds and atmospheric regions. On earth, these processes occur in laboratory plasmas ranging from plasmas in etching machines and ion sources to fusion reactors. In plasma physics as well as in astrophysics information about complex sets of processes is obtained by the observation of particles and photons emitted from the different objects. To determine the influence and importance of the various contributing processes from this kind of information it is necessary to have accurate knowledge about the most important collision systems.

H, He, C and O are the most abundant elements in the cosmos. In dense interstellar clouds, due to the high density and optical thickness, most of the carbon exist in carbon monoxide and almost all the hydrogen is in its molecular form, while helium is the most found atomic species [1]. But also in diffuse clouds H₂ and CO are the most abundant molecules [2].

Atomic and molecular species can be ionised by interaction with ultraviolet photons, X-rays, cosmic rays and by energetic shock heated particles. Due to Auger processes multicharged ions can be formed up to triply charged and even higher [3–5]. Once ionised, dissociation and charge transfer processes can induce new reactions resulting in the formation of various molecules. For example, ionisation of He by cosmic rays can be followed by dissociative charge transfer with CO leading to the production of C⁺. In collisions of C⁺ with molecular hydrogen hydrocarbon molecules can be formed [6].

The densities of the various interstellar species are determined from the observation of electromagnetic radiation. This radiation results from the decay of excited atoms and molecules. Every decay process is characterised by a specific spectral line. It may be clear that due to the many reactions involving all possible cosmic species the study and interpretation of the observed spectra is very complex. To unravel the observed spectra and to understand the physical and chemical processes involved, atomic and molecular data for a wide variety of collision processes are essential. [7]

About fifty years ago fusion plasma research was started with the goal to achieve controlled thermonuclear fusion as new energy source. The ‘easiest’ fusion process is the reaction of a deuterium and a tritium nucleus. When these two nuclei fuse an alpha particle and a fast neutron are produced. The total energy gain is 17.6 MeV which is released in the form of kinetic energy of the reaction products. To achieve the fusion of light particles, they need to collide with very high velocities to overcome their mutual Coulomb repulsion. Therefore the gaseous particles in a fusion reactor have to be heated to extremely high temperatures, about 100 million °C. At such temperatures all particles are fully ionised and form a hot plasma. Since there are no materials which can stand these high temperatures a fusion plasma is confined by magnetic fields.

The Joint European Torus (JET) in Culham (U.K.) is the largest fusion reactor in the world. It is basically a large doughnut shaped vacuum
vessel which is surrounded by magnetic coils. To obtain the required temperature various heating techniques are used. One of them is heating by neutral beam injection whereby a beam of energetic (\(\sim 40 \text{ keV/amu}\)) neutral particles is injected into the core of the plasma. With the injection of neutral particles, bound electrons are brought into the plasma leading to various excitation and ionisation processes. With the decay of excited atoms and ions in the plasma, photons can be emitted which can leave the plasma. This is a disadvantage because every photon carries away a certain amount of energy at the expense of the heating. However, from the detection of the emitted photons information can be obtained about the processes in the plasma. Therefore charge exchange spectroscopy has developed to an important diagnostic tool.

For example at JET, neutral He-beams are used for plasma heating. This implies that charge exchange involving helium atoms is an important class of processes which takes place in the plasma. Electron capture from neutral He by He\(^{2+}\) ions (one of the major plasma impurities) can lead to excited He\(^+\) ions which decay by photon emission. From the observed emission spectrum, information is obtained about local plasma parameters. To illustrate, the intensity of the emitted light is a measure of the He\(^{2+}\) density, and the broadening of the spectral line is related to the temperature of the plasma [8,9]. Crucial for a reliable determination of these plasma parameters is an accurate knowledge of the underlying cross sections.

From the foregoing part it may be clear that atomic and molecular collision data are essential to the understanding of physical and chemical processes in interstellar clouds and astrophysical and thermonuclear fusion plasmas. A valuable contribution to the cross section database is made by crossed beam experiments. We have used this technique to study various collision systems. In this thesis collisions of He\(^{2+}\) on He, H\(_2\) and CO and collisions of O\(^{7+}\) on CO will be discussed.

Apart from the applied physics interest there is a considerable fundamental interest in these collision systems as a test for various theoretical models. One-electron capture processes in (quasi-) one-electron atomic collision systems can be described appropriately by close-coupling methods [10,11]. It is only very recent that these models are applied to one-electron capture from two-electron targets like He and H\(_2\). The symmetric He\(^{2+}\) + He collision system, discussed in chapter 2, may be regarded as the simplest two electron system. However, the symmetry between projectile and target states together with the large exo- or endothermicity of the various one-electron transfer channels makes a theoretical description rather complicated.

Compared to He, capture from H\(_2\) presents an extra challenge since the molecular nature of H\(_2\) has to be taken into account, for example the orientation of its molecular axis with respect to the velocity of the projectile. Furthermore, compared to ion-atom collisions, collisions with molecules are more complicated due to the possible dissociation of the molecular ions produced by charge transfer. In chapter 3 dissociative and non-dissociative one-electron capture in He\(^{2+}\) on H\(_2\) collisions will be discussed. In this chapter it
will be shown that in spite of the molecular nature of \( \text{H}_2 \) the overbarrier model (next section) which is proposed for ion-atom collisions can be used for a qualitative explanation of an important feature.

The validity of this classical model for the description of charge transfer in ion-molecule collisions is very valuable, especially for a better understanding of charge transfer processes in collision with multi-electron targets. Up till now collision systems like \( \text{He}^{2+} \) and \( \text{O}^{7+} \) on \( \text{CO} \), as presented in this thesis, are too complicated for a full theoretical description. But information on the stability of multicharged molecules and the energetics involved in their dissociation is important for testing of computing methods for molecular potential curves [12]. Also for experimentalists ion-molecule collisions are rather complicated due to the various charge transfer channels together with the many excited states with various possibilities for dissociation. In the experiments described in chapter 5 we focus on the determination of the various dissociation channels, while in chapter 6 the charge exchange processes will be stressed. To explain the experimental results we have used potential energy curves of several electronic states of \( \text{CO}^{q+} \), with \( q \leq 3 \), which have been determined by various groups using \textit{ab initio} molecular orbital calculations.

### 1.2 The overbarrier model

Charge exchange processes in keV ion-atom collisions can be described with the overbarrier model as proposed by Niehaus (1986) [13]. This model considers the binding energies of the electrons in the joint Coulomb field of the colliding particles. If a highly charged ion approaches a neutral target the potential barrier between the target and the projectile will decrease. If the barrier is below the ionisation energy of a particular target electron, this electron can cross the barrier and move in the compound potential well of target and ion. On the way out, when the collision partners separate, electrons can be captured by the projectile or recaptured by the target. So the maximum number of captured electrons depends on the closest internuclear distance reached in the collisions. With the overbarrier model we can calculate the internuclear distance at which capture takes place and the binding energy of an electron after capture. Figure 1.1 shows the situation for \( \text{O}^{7+} \) colliding on \( \text{Ar} \) at an internuclear distance of 0.43 nm. The third electron can just cross the barrier. The energy levels of the electrons are the successive ionisation potentials of the argon electrons which are shifted due to the electric field of the projectile ion.

We can also apply the overbarrier model to ion-molecule collisions if the molecular structure does not influence the collision too much. This is the case if (i) the collision time is short compared to the vibration time of the nuclei in the molecule and (ii) the electron capture takes place at internuclear distances which are large compared to the size of the molecule. The first assumption holds for collisions at keV energies as will be discussed in the next section. The second assumption will be discussed now.

Consider a \( \text{CO} \) molecule. This has almost the same ionisation energies for the outer elec-
Electrons as argon. Therefore capture distances in collisions with O$^+$ are comparable to the O$^+$ + Ar system displayed in figure 1.1. So up to three electrons can be captured at a rather large impact parameter of around 0.4 nm, while the equilibrium internuclear distance of the CO ground state is 0.11 nm. Therefore, at least for the capture of outer electrons also the second assumption holds which means that the overbarrier model is applicable for ion-molecule collisions considered here.

1.3 Ion–molecule collisions

Ionisation and dissociation of molecules in ion-molecule collisions is assumed to proceed in a two step process [14]. This is shown in figure 1.2 together with the time scales of the relevant processes. The first step is the direct interaction between the projectile and the electrons of the molecule leading to ionisation, excitation and electron capture by the projectile:

$$A^q^+ + BC \rightarrow A^{(q-r+s)^+} + BC^{r+s} + te^- \quad (1.1)$$

During the collision a quasi-molecular ion (ABC)$^q^+$ is formed by the projectile and the molecular target. This complex exists for $10^{-16}$ to $10^{-15}$ s, dependent on the collision energy. In this time the charge exchange processes take place. The collision time is much shorter than the molecular dissociation time which is larger or equal to the vibration time which is typically around $10^{-14}$ s. So during the charge exchange process we can assume the internuclear distance of the molecule to be fixed.

The second step is the decay of the (excited) molecular ions by dissociation into fragments:

$$BC^{r+s} \rightarrow B^{s+s} + C^{(r-s)^+} + U_{KER} \quad (1.2)$$

where $U_{KER}$ is the kinetic energy released in the dissociation and $0 \leq s \leq r$. The dissociation channels depend on the potential energy of the intermediate dissociative state. A certain charge state of the molecular ion can lead to various charge states of the fragments with various

![Figure 1.1: Schematic diagram illustrating the basic charge exchange mechanism as described by the overbarrier model.](chart.png)
amoun ts of kinetic energy. This will be discussed in the next section.

### 1.4 Molecular dissociation

The question whether a molecule or molecular ion is stable or not depends on the shape of its potential energy curve as can be seen in figure 1.3. Consider a molecule BC. At large internuclear distances \( r_{BC} \) the potential energy curve will have a weakly attractive shape due to charge polarisation effects,

![Figure 1.2: Time scales for ionisation and subsequent dissociation in ion-molecule collisions.](image)

\[
V_{B+C} \propto -r_{BC}^{-4}.
\] (1.3)

At short distances where the electron shielding is not effective the nuclei feel a strong Coulomb repulsion,

\[
V_{B+C} \propto r_{BC}^{-1}.
\] (1.4)

By combining these two components there can arise an absolute minimum in the potential energy for a certain internuclear distance \( R_e \) between the two atoms B and C as shown in figure 1.3a. In this case the molecule is stable because energy is needed to increase the internuclear distance from \( R_e \) to infinity. The depth of the minimum depends on the total electron density shared by the two nuclei.

However for a multicharged molecular ion the Coulomb repulsion is dominant at all internuclear distances, e.g. in the case of \( B^+ + C^+ \). Now there is no minimum in the total potential energy of the system and the molecule is unstable (figure 1.3b). The atoms gain energy if the internuclear distance increases.

In figure 1.3c the situation is depicted where the potential energy shows a relative minimum at \( R_e \). The potential energy of the atoms at infinity is lower than at \( R_e \) but due to the barrier a molecule can be trapped in the potential well. Such a molecule is called metastable since it can fragment by tunneling. However, tunneling is not the only possibility for decay. If there exists a coupling between a metastable state and a repulsive (unstable) state the molecule can make a transition between these two states and subsequently dissociate. This process is called predisso-
General Introduction

Potential energy

Internuclear distance

\begin{figure}
\centering
\includegraphics{figure1.png}
\caption{Schematic potential energy curves of a diatomic molecule or molecular ion. a) Stable, b) unstable and c) metastable electronic states are shown. d) A coupling between a metastable molecular state and a repulsive (unstable) state can lead to predissociation. e) A metastable state originated from an avoided crossing of two adiabatic potential energy curves.}
\end{figure}

The lifetime of a metastable state depends on the height and the width of the barrier and on the probability of predissociation. A metastable state can originate from an avoided crossing of two adiabatic potential energy curves as shown in figure 1.3e. Here the energy curves of a hypothetical BC$^{2+}$ are drawn leading to B$^{2+} + C$ and B$^+ + C^+$ dissociation limits.

In a charge exchange process multicharged molecular ions are produced in various repulsive and metastable states. As we assume the internuclear distance of the molecule to be fixed during this processes, the population of the molecular ion states can be described by a vertical transition in the potential energy diagram at the equilibrium internuclear distance of the molecular ground state $R_e$. Dependent on the nature of the populated states the dissociation occurs via various channels. Repulsive states and metastable states can respectively dissociate adiabatically and by tunneling to the associated dissociation limit or by predissociation to the same or other limits. In all cases the total energy gain will be equal to the difference of the potential energy of the populated state at $R_e$ and the potential energy of the dissociation limit. The energy released in the dissociation is distributed over the fragments in accordance with conservation of momentum and is in this thesis referred to as kinetic energy release.
1.5 Experimental methods

In this thesis we have studied processes which are triggered by electron transfer between multi-charged ions and neutral atoms or molecules. We have used two different techniques, photon emission spectroscopy and time-of-flight mass spectrometry, as described in chapter 2. By means of photon emission spectroscopy we have studied capture and excitation processes. The light emitted after the collision can be regarded as a "fingerprint" of the primary electron transfer processes. The subsequent dissociation of molecules is studied by time-of-flight mass spectrometry. To determine the kinetic energy of the fragments, the collision products are extracted from the collision centre by an electric field. Therefore, particles initially ejected towards the detector will have a significant shorter flight time than particles ejected in the opposite direction. From this time-difference we can determine the kinetic energy released in the dissociation.