Chapter 5

Inner- and outer-shell electron dynamics in H$^+$+Na(3s) collisions

5.1 Introduction

Collisions between protons and alkali atoms have been studied extensively in the past. In 1964 Donnally et al. [178] reported first measurements on cross sections for the production of metastable H(2s) in H$^+$+Cs collisions. The study of this charge exchange reaction was motivated by the development of spin polarized ion sources. The choice for an alkali target over the earlier proposed molecular hydrogen target as donor to feed the H(2s) channel [179] was taken because for alkalis the ionization energies are lower and the energy defects with the H(2s) state smaller. This leads to larger cross sections which maximize at lower impact energies. The latter facilitates the separation of the metastable hydrogen atoms from the beam of protons by electric or magnetic fields. Soon after, charge exchange on alkalis was proposed to be the first step in the production of polarized negative hydrogen ions [180]. From the 1970’s on the motivation to study collisions between protons and alkali atoms shifted towards fusion research (see e.g. [181,182]).

From a theoretical perspective, an appealing feature of ion–alkali-atom collision systems is the shell structure of the alkalis, i.e., a single valence electron outside closed inner shells. It suggests the applicability of quasi-one-electron models in which the dynamics of the loosely bound outermost electron is governed by the joint Coulomb potential of projectile and target nuclei and an effective potential due to “frozen” inner-shell electrons. Ion–alkali-atom collisions have been valuable test beds for advancing methods to solve the one-electron time-dependent Schrödinger equation because true one-electron systems, i.e., collisions of bare ions on atomic hydrogen, are difficult to handle and control experimentally. Almost all reported quantum mechanical and classical calculations concerning alkali-atom targets rely on the one-electron approximation.

For the H$^+$+Na(3s) collision system, measurements of total cross sections for one-electron capture in the low keV/amu impact energy range are manifold [183–185]. At higher impact energies, also cross sections for two-electron removal were obtained [13,186]. These studies
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Figure 5.1: Q-value spectrum of Na\(^+\) recoil ions after p-Na collisions at 14 keV/amu. Main contributions come from outer-shell capture (OSC), of which capture into H(1s) and H\((n = 2)\) are indicated. Outer-shell ionization starts beyond \( Q = 5.14 \text{ eV} \). On top of the ionization tail the inner-shell capture (ISC) contributions appear. Clearly visible are the two contributions from ISC into H(1s) in combination with Na\(^+\)(2\(p^5\)3s) and Na\(^+\)(2\(p^5\)3p) as final state. The line through the data is drawn to guide the eye.

showed that the cross sections for single electron capture are around \( 1 \times 10^{-14} \text{ cm}^2 \) below 5 keV/amu, after which they decrease to about \( 3 \times 10^{-17} \text{ cm}^2 \) at 100 keV/amu. From impact energies of 20 keV/amu on ionization dominates the production of Na\(^+\) ions. Besides total one-electron cross sections, experimental work has been done on measuring the Lyman-\( \alpha \) emission, i.e. H(2\(p \rightarrow 1s\)) decay [187–189]. The resulting line-emission cross sections represent the partial cross sections for capture into the 2\(p\) subshell, which is the main channel for one-electron capture. In a similar way, using quenching methods, cross sections for capture into the metastable 2\(s\) subshell were obtained [190, 191].

These experimental studies were followed and inspired by theoretical progress in coupled channel calculations, using molecular [192–194] or two-center atomic basis set expansions [195–197]. Most recent theoretical work on charge transfer in keV \( \text{H}^+ + \text{Na}(3s) \) collisions is based on two-center 36 atomic orbital expansion (TCAO36) [198], two-center 70-state Sturmian-pseudostate expansion (TCSAO70) [199] and classical trajectory Monte Carlo (CTMC) calculations [90].

These one-electron models have been employed with some success. However, the theoretical calculations typically showed a much steeper decrease of the cross section towards higher impact energies than experimentally observed. The cross sections even seem to flatten out. The necessity to improve the models became apparent already some twenty years ago, when measurements of multiple-electron removal from lithium and sodium atoms by proton
or helium-ion impact were reported [13].

Here electron capture and ionization processes in H+ + Na(3s) collisions have been studied in the energy range of 4–25 keV/amu. Cross sections for capture and ionization, as well as state selective and differential cross sections for outer-shell capture (OSC) into the n = 1, n = 2, and n ≥ 3 shells of hydrogen have been obtained. Besides charge transfer processes involving the outer-shell electron of Na, also inner-shell capture (ISC) processes have been observed. Note that while OSC in this collision system has been studied extensively, direct identification of pure ISC has not been reported so far.

To introduce this collision system a Q-value spectrum of Na+ recoils is shown in figure 5.1. Several processes can be recognized in this spectrum. In the OSC part of the spectrum (Q < I, where I = 5.14 eV is the ionization potential of Na) one can distinguish the contributions of OSC into H(1s) (Q = −8.46 eV) and H(n = 2) (Q = +1.74 eV) which is the main capture channel. Capture into higher n states cannot be resolved. Ionization of the outer-shell electron leads to Q > I. On top of the ionization tail the ISC contribution from the 2p shell is found. Although ionization and ISC can have the same Q-value, the latter can be recognized because it gives rise to capture peaks on top of the continuous ionization spectrum. The two main peaks in this part of the Q-value spectrum arise when an inner-shell 2p electron is captured into H(1s) and the target is left in either an excited Na+(2p53s) or Na+(2p53p) state. The smaller peaks are not identified unambiguously, but are related to more highly excited Na+ states or ISC into excited hydrogen, H(n ≥ 2). The Q-values of the relevant OSC and ISC channels are given in table 5.1. The maximum Q-value for ISC is Q = 52.3 eV and occurs when the outer-electron is just excited to the continuum of the target and the inner-shell electron is captured into the continuum of the projectile.

To summarize the processes under investigation, we distinguish between processes in

<table>
<thead>
<tr>
<th>final states</th>
<th>Q-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(n = 1) + Na+(2p6)</td>
<td>-8.46</td>
</tr>
<tr>
<td>H(n = 2) + Na+(2p6)</td>
<td>1.74</td>
</tr>
<tr>
<td>H(n = 3) + Na+(2p6)</td>
<td>3.63</td>
</tr>
<tr>
<td>H+ + Na+(2p6) + e−</td>
<td>≥5.14</td>
</tr>
<tr>
<td>H(n = 1) + Na+(2p53s)</td>
<td>24.5</td>
</tr>
<tr>
<td>H(n = 1) + Na+(2p53p)</td>
<td>28.7</td>
</tr>
<tr>
<td>H(n = 1) + Na+(2p53d)</td>
<td>32.5</td>
</tr>
<tr>
<td>H(n = 1) + Na+(2p54s)</td>
<td>32.7</td>
</tr>
<tr>
<td>H(n = 1) + Na+(2p5)+ e−</td>
<td>≥38</td>
</tr>
<tr>
<td>H(n = 2) + Na+(2p53s)</td>
<td>34.7</td>
</tr>
<tr>
<td>H(n = 2) + Na+(2p53p)</td>
<td>38.9</td>
</tr>
<tr>
<td>H(n = 2) + Na+(2p53d)</td>
<td>42.7</td>
</tr>
<tr>
<td>H(n = 2) + Na+(2p54s)</td>
<td>42.9</td>
</tr>
<tr>
<td>H+ + Na2+(2p5)+ 2e−</td>
<td>≥52.3</td>
</tr>
</tbody>
</table>

Table 5.1: Q-values of relevant final states after one-electron capture processes in H+ + Na(3s) collisions, grouped in either OSC or ISC. Also the Q-values related with the onset of single ionization, transfer ionization and double ionization are given.
Inner- and outer-shell electron dynamics in H$^+$+Na(3s) collisions

Figure 5.2: Total one-electron capture cross sections for H$^+$+Na(3s) collisions as function of impact energy. Experiment: Ebel and Salzborn [184] (□); Aumayr et al [185] (■); DuBois [13] (○). Theory: TC-BGM results for total capture (—), and for OSC capture (– –); TCSAO70 [199] (···).

which only the outer-shell is active, i.e.,

\[
\begin{align*}
\text{H}^+ + \text{Na}(2p^63s) & \rightarrow \text{H}(n) + \text{Na}^+(2p^6), & \text{outer-shell capture}, \\
\text{H}^+ + \text{Na}(2p^63s) & \rightarrow \text{H}^+ + \text{Na}^+(2p^6) + e^-, & \text{outer-shell ionization},
\end{align*}
\]

(5.1)

(5.2)

and processes in which also the 2p-shell contributes,

\[
\begin{align*}
\text{H}^+ + \text{Na}(2p^63s) & \rightarrow \text{H}(n) + \text{Na}^+(2p^5n'l'), & \text{n'} \geq 3, \text{ inner-shell capture}, \\
\text{H}^+ + \text{Na}(2p^63s) & \rightarrow \text{H}(n) + \text{Na}^{2+}(2p^5) + e^-, & \text{transfer ionization}.
\end{align*}
\]

(5.3)

(5.4)

The experimental results are presented in conjunction with recent TC-BGM calculations. The general features of this close coupling scheme are discussed in section 2.5.1. For the H$^+$+Na(3s) collision system the basis included the undisturbed states \(\psi^0_v(r)\) of the Na target \((n = 2 - 4\) shells, 19 states) and of the projectile \((n = 1 - 5\) shells, 35 states), as well as 49 pseudostates from the set \(\{\chi^\mu_v(r,t), \mu \geq 1, v \leq V_t\}\) up to order \(\mu = 6\), in which \(V_t\) is the finite set of target states. A set of 26 impact parameters in the range \(0.22 \text{ a.u.} \leq b \leq 30 \text{ a.u.}\) was used, while the integrations have been restricted to impact parameters \(b \leq 5 \text{ a.u.}\) for the inner electrons. Physically this restriction is fully justified, since the inner-shell electrons are tightly bound.

Figure 5.2 summarizes the total cross sections for one-electron capture. Previous experiments [183–185] and theoretical calculations [197, 199] are in very good agreement for low energy, but above 40 keV/amu discrepancies are found. Compared with the measurements of DuBois [13] theory underestimates one-electron capture by up to an order of magnitude. The TC-BGM calculations for total capture, including also the 2s- and 2p-shell, follow the
5.2 Outer-shell processes

First the pure outer-shell processes, i.e. single outer-shell capture or ionization will be considered. In the Q-value spectra these processes appear at $Q < 24.5$ eV. A typical Q-value spectrum of Na$^+$ recoils resulting from 8 keV/amu H$^+$+Na(3s) collisions is shown in figure 5.3. The energy dependence of pure outer-shell processes is illustrated in figure 5.4. Two effects can be seen directly. First of all the state selectivity is lost with increasing collision energy. At 4 keV/amu 85% of the intensity is due to capture into the H($n = 2$) shell, while at 10 keV/amu ionization is equally strong as this channel. Above 16 keV/amu capture into higher shells is equally probable as capture into $n = 2$. Secondly, the ionization distribution is shifted towards higher Q-values. One can show that the Q-values of ionization processes are directly connected to the energy of the emitted electrons in the projectile frame (see appendix C). At low projectile energy most of the emitted electrons are projectile centered (electron capture into the continuum), thus having very low energy in the projectile frame. But with increasing projectile velocity, ionized electrons strand in between the target and the projectile. At $E = 25$ keV/amu target centered electrons would correspond to an energy of 13.6 eV in the projectile frame, appearing at $Q = 18.7$ eV (see chapter 10 for a general discussion on single...
ionization).

The relative contributions of capture into the $n = 1$ and $n = 2$ shells are obtained by fitting the spectra, assuming Gaussian peak shapes. The amount of ionization is determined as described in section 4.3.6. Subtracting these contributions from the spectrum one obtains the partial cross section for capture into $n \geq 3$. Absolute calibration is obtained by normalizing the total one-electron capture contribution to the earlier mentioned absolute cross sections [13,183–185], shown in figure 5.5.

### 5.2.1 One-electron capture

In this section results on one-electron capture from the outer-shell will be discussed. Our partial cross sections together with the TC-BGM results for capture into $n = 1$, $n = 2$ and $n \geq 3$ are shown in figure 5.6. Capture into the hydrogen ground state, H($n = 1$), shows
5.2 Outer-shell processes

Figure 5.5: Experimental total one-electron capture cross sections for $H^+ + Na(3s)$ collisions: Ebel and Salzborn [184] (□); Aumayr et al [185] (■); DuBois and Toburen [183] (△); DuBois [13] (○). The solid curve indicates the cross sections used to put our data on an absolute scale.

only a weak dependence on the projectile energy. Good agreement is found between the experimental results and the TC-BGM calculations.

Figure 5.7 shows the partial cross sections in comparison with previous theoretical work employing close-coupling [197–199] and CTMC [90] methods. The TC-BGM results for capture into $n = 1–4$ are generally in good agreement with previous calculations. Nevertheless, some remarks can be made. The high energy behavior of the $n = 1$ capture channel coincides with TCAO36 [198], but deviates from TCSAO70 [199], which predicts a steeper decrease of the cross section. Cross sections for capture into $n = 5$ have not been considered earlier. The TC-BGM calculations for this channel show a shape similar to H($n = 4$), but are smaller by a factor of 2. The good agreement between experimental results and TC-BGM for H($n ≥ 3$) suggests that the inclusion of projectile states up to the $n = 5$-shell is sufficient to model electron capture at energies <50 keV/amu. Here also the sum cross sections of capture into $n = 3$ and $n = 4$ for TCAO36 and CTMC are included.

Despite many experimental investigations, systematic studies of the $n$-shell selective cross sections are rather scarce. Besides the already mentioned cross sections for capture into H($2s$) and H($2p$), relative cross sections in the energy range of 0.3–3 keV/amu for capture into H($n = 2$) and H($n ≥ 3$) have been obtained by Royer et al by means of time-of-flight energy loss measurements [200]. By normalizing their H($n = 2$) results on theoretical calculations of Allan et al [193], absolute cross sections for capture into H($n ≥ 3$) were obtained, which are also shown in figure 5.7.
5.2.2 Single ionization

Figure 5.8 shows the cross sections for single outer-shell ionization. Our experimental results and TC-BGM calculations are compared with TCSAO70 [199], CTMC [90] and previous experiments [13,186]. From the TC-BGM calculations the total single ionization cross sections and the contribution of outer-shell ionization are shown. Obviously – and in contrast to the capture case – contributions from inner shells are unimportant over the whole range of impact energies (2 – 100 keV/amu). This is of course no surprise, since ionization yields are mainly determined by the binding energies of the electrons in the initial state.

The present experimental data show the strong increase of the ionization cross section up to 20 keV/amu. There is reasonable agreement with TC-BGM up to $E = 20$ keV/amu. At higher energies TC-BGM underestimates experimental data, although the difference decreases towards the highest energies. A possible reason for this discrepancy could be contributions from autoionizing doubly-excited Na states, which are ignored in the TC-BGM calculation. However, an estimation using a multinomial evaluation of multiple excitation yielded contributions two orders of magnitude smaller than the total single ionization cross section [72]. The contributions are that small because of the high binding energy of the $2p$-shell electrons. Therefore, the discrepancies above $E = 20$ keV/amu remain unexplained at present. At low energy the CTMC calculations show a similar energy dependence as obtained by TC-BGM but yield somewhat lower values.
Figure 5.7: Similar as figure 5.6, including previous theoretical work and partial cross sections for capture into $H(n = 3)$, $H(n = 4)$ and $H(n = 5)$. Present experimental data (■), Royer et al [200] (□); theory: TC-BGM (—), TCAO36 [198] (—), TCSAO70 [199] (···), CTMC [90] (---). Note that the panels have different scales.
5.2.3 Transverse momentum distributions

From the experimental data transverse momentum distributions or differential cross sections (DCS) for capture into the $n = 1$, $n = 2$, $n \geq 3$ and ionization have been extracted. Due to low statistics DCS for $n = 1$ could only be obtained for $E \geq 7$ keV/amu. DCS for $n \geq 3$ are only presented for $E \leq 14$ keV/amu because at higher energies separation from $n = 2$ and ionization becomes difficult. The experimental transverse momentum distributions for several impact energies are shown in figure 5.9. All data are normalized to their peak maximum to facilitate the comparison between the different channels. All channels show narrow distributions in which the peak positions never even exceed 0.3 a.u.. Further inspection shows that the differences between the $n = 2$, $n \geq 3$ and ionization channels are within the resolution (0.1 a.u.), except for the lowest energies at which ionization extends to somewhat higher momenta. At all energies the $n = 1$ distribution is broader than that of the other channels. Relative differential cross sections as a function of scattering angle are shown in figure 5.10 for 4 and 25 keV/amu. While the transverse momentum distributions broaden with increasing impact energy, a slight narrowing is observed in figure 5.10. This is due to the velocity dependence of the transformation from transverse momenta to scattering angles (see equation 4.10).

Previous experimental studies on DCS are mainly limited to lower energies. Note that usually the so called ‘reduced DCS’, defined as $\sigma(\theta) \sin(\theta)$, is plotted to enhance the large angle scattering part of the cross section. At 1–5 keV/amu DCS for capture into H(2p) were determined by measuring the Lyman-\(\alpha\) photons in coincidence with the scattered H
Figure 5.9: Experimental transverse momentum distributions at several impact energies for capture into $n = 1$ (---), $n = 2$ (—), $n \geq 3$ (– –), and ionization (· · ·). All distributions are normalized to their peak values.
projectile [201]. The data did not cover the peak region of the DCS because the smallest scattering angle measured was 0.9 mrad. However the supporting calculations, folded with the experimental resolution of about 0.2 mrad, showed a reduced DCS peak around 0.4 mrad at 3.5 keV/amu and 0.3 mrad at 5 keV/amu. Our MOTRIMS data show a peak position of 0.15 mrad in the DCS at 4 keV/amu. In the reduced DCS this leads to a peak position at 0.23 mrad. Finally, time-of-flight energy loss measurements at 2 keV/amu found equal DCS distributions for capture into \( n = 2 \) and \( n = 3 \) [202]. At higher energy we also observe that capture into \( n = 2 \), \( n \geq 3 \) and ionization have more or less similar DCS. This implies that these channels are populated in the same impact parameter range. Only capture into the endothermic channel, \( n = 1 \), shows larger transverse momenta, implying smaller impact parameters than for the other channels.

### 5.3 Inner-shell processes

A first indication of the participation of inner-shell electrons in ion-atom collisions was found in the high-energy behavior of the total capture cross section (see e.g. [203] and references therein). The flattening out of the total cross section instead of a rapid decrease was explained by an increased participation of core electrons. At higher energies the incident ion’s velocity approaches that of the core electrons. In general, the capture cross section is expected to maximize if there is “velocity matching” between the target electron and the projectile. Total one-electron capture cross sections for the \( \text{H}^+ + \text{Na}(3s) \) collisions also exhibit this trend (see figure 5.2).

A RIMS technique enables the direct observation of (sub-) shell-specific processes, as the Q-value of a specific reaction can be determined. Previously, this level of detail was accessible only indirectly via spectroscopy of Auger electrons or photons, which are charac-
5.3 Inner-shell processes

5.3.1 Inner-shell one-electron capture

From the assignment of the ISC part of the Na$^+$ recoil spectrum (see figure 5.1) it is clear that most of its contribution is related to capture into the hydrogen ground state. Therefore in the following inner-shell capture is specified for the processes

$$\text{H}^+ + \text{Na}(2p^6 3s) \rightarrow \text{H}(1s) + \text{Na}^+(2p^5 nl), \quad n \geq 3.$$  \hfill (5.5)

One of the 2$p$ inner-shell electrons is captured into the hydrogen ground state while the outer-shell 3$s$ electron remains bound to the target. In the rest of the discussion the term ISC is used for processes given by equation 5.5.
Figure 5.12: MOTRIMS and TC-BGM results for the different contributions to ISC into H(n = 1): Na\(^+\)\((2p^53s)\) (■, ‒ ‒ ) and Na\(^+\)\((2p^53p)\) (□, ‒ ‒ ).

The experimental ISC cross sections obtained are shown in figure 5.11 together with the TC-BGM calculations, in which the total ISC contribution is obtained from the difference between total one-electron capture \((\sigma^0)\) and outer-shell capture \((\sigma^{10}_{ISC})\). Clearly, the dominant contribution to ISC is due to the Na\((2p)\) electrons. The MOTRIMS results agree very well with the calculations. However, this agreement may be somewhat fortuitous, since the calculations are not restricted to the final states probed by the experiments. The experimental ISC excludes the possibility that more than one electron is removed. The Q-value spectra are taken for Na\(^+\) recoil ions and do not include Na\(^2+\) recoils. This situation is not respected by taking the difference of net- and single-electron transfer cross sections, but can be modelled by multinomial statistics [72]. The result of such an analysis is shown figure 5.11. This multinomial ISC is somewhat lower than the difference of net- and single-particle cross sections, which is a direct consequence of the condition that the other electrons – in particular Na\((3s)\) – remain bound to the target.

The two main ISC peaks in the Q-value spectrum (figure 5.1) are due to capture into H\((1s)\) leaving the excited Na\(^+\) recoil in either a \(2p^53s\) or \(2p^53p\) state. Their relative contributions are shown in figure 5.12. These two channels contribute about 75% of the total ISC. The other 25% can be ascribed to the formation of higher \(2p^5nl\) states. The main trends in the MOTRIMS data are supported by the calculations: \(2p^53p\) gives the largest contribution below \(E = 18\) keV, and \(2p^53s\) dominates at higher energies. Below \(E = 6\) keV/amu theory shows again a dominance of \(2p^53s\), which is not supported by the measurements.

To understand a dominance of the \(2p^53p\) final state at low energy the following explanation is proposed. This final state implies that the capture of one inner-shell \(2p\) electron is accompanied by the excitation of the outer-shell \(3s\) electron to the \(3p\) orbit, i.e. an active role of the outer-shell electron. In this process the two active electrons form a system with total
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Figure 5.13: Reduced DCS of OSC into $H(n=2)$ and ISC into $H(1s)$ leading to Na$^+$($2p^53p$) at 14 keV/amu collision energy. In order to compare these processes, in both cases the integral over $\sigma(\theta)$ is normalized. The line is to guide the eye.

The energy dependence of the $2p^53s$ population suggests that with increasing projectile velocity the $3s$ electron does not change its initial orbital and becomes more of a spectator. In fact this is a situation typically assumed in high energy ISC, i.e., charge transfer from different shells can be treated independently (see e.g. [208]). The present data clearly show the transition between ISC with and without outer-shell participation. The transition occurs at about 1.4 $v_{orb}$ of the outer-shell electron, i.e. at much lower velocity than $v_{orb}$ of the $2p$ electron (which corresponds to a collision energy of 90 keV/amu).

Further differences between OSC and ISC are seen in the DCS of both processes. Figure 5.13 compares DCS for outer-shell capture into $H(n=2)$ and ISC into $H(1s)$ leading to Na$^+$($2p^53p$). One should note that in order to extract the DCS of ISC we have to correct for the presence of outer-shell ionization events in the relevant Q-value region. This is done by subtracting the ionization DCS at large Q-values (around Q=20 eV) from the DCS at Q-values at which the ISC processes occur. This procedure introduces some uncertainty because one has to assume that the ionization momentum distribution is constant over a (small) range of Q-values. Measuring the Na$^+$ recoils in coincidence with neutral hydrogen could resolve this
Figure 5.14: Transfer ionization cross section $\sigma_{10}^{2}$ and its components for $H^+ + Na$ collisions as functions of impact energy. Experiment: present data $\sigma_{2}^{10}$ (■); $\sigma_{2}^{10}$ DuBois [13] (○). Theory: TC-BGM results $\sigma_{2}^{10}$ (—), $\sigma_{3s}^{2p\text{cap}} + \sigma_{3s}^{2p\text{ion}}$ (—), and $\sigma_{2p}^{2p\text{cap}}$ (···).

problem. Here the inverse Abel transformation is directly applied to the raw data. For ISC the data was collected in larger bins than for OSC in order to improve the statistics.

Because the scattering angle is related to the impact parameter, the differential cross section reveals the impact parameter range in which a certain process occurs. Because of the small binding energy of the $3s$ electron outer-shell capture is possible at large internuclear distances (10-20 a.u.). This results in scattering over small angles (< 0.5 mrad). In contrast, ISC shows a broad distribution extending to much larger angles. Because ISC processes involve the strongly bound $2p$ electrons, the internuclear distances at which capture can take place are small and consequently larger scattering angles are expected. The strong oscillatory behavior might be due to Fraunhofer-diffraction. The angular spacing between two consecutive maxima is given by $\Delta \theta = \lambda_{dB}/2R$, with $\lambda_{dB} = 240$ fm the de Broglie wavelength for 14 keV/amu protons and $R$ the capture radius. The observed angular spacing of about 1.2 mrad results in $\sim 2$ a.u. for the capture radius. An classical over-barrier estimation gives a maximum distance of 2.8 a.u. at which a $2p$-electron can be transferred.

Fraunhofer-diffraction has been observed experimentally in one-electron capture into Li($2s$) in keV Li$^+$+Na($3s$) collisions by the MOTRIMS experiment of Van der Poel et al [24, 146]. The connection with the well-known Fraunhofer-diffraction in classical optics can be seen from the mathematical similarity between the quantal scattering amplitudes and the angular intensity distribution of a coherent light beam scattered on a circular aperture. One criterion for the appearance of this diffraction phenomenon is that contributions to the probability amplitude stem from only a small range of impact parameters. The observation of an oscillatory structure in the DCS hints towards the presence of a very well defined set of
5.3 Inner-shell processes

Figure 5.15: A simple classical over-barrier model representation, comparing TI and ISC. At closest approach the outer 3s electron and one of the 2p-shell electrons are bound by the quasi-molecular potential formed by projectile and target. In case of ISC the 2p electron is transferred to the projectile, while the outer-shell electron is “recaptured” by the target. For TI the outer-shell electron is emitted into the continuum.

trajectories at which ISC occurs.

5.3.2 Transfer ionization

ISC processes in which the outer-shell electron is excited above the ionization limit, i.e. transfer ionization (TI), lead to Na$^{2+}$ recoil ions and do not show up in the Na$^+$ recoil spectrum. To investigate the importance of TI compared with ISC time-of-flight measurements were performed to obtain the total Na$^{2+}$ production, $\sigma_2$. The resulting cross sections are shown in figure 5.14 and compared with transfer ionization cross sections obtained from TC-BGM and previous experimental data [13], which extends to higher energies.

TI is considered to be the main channel for the Na$^{2+}$ production, because pure double ionization is likely to be weak in this energy range. Also the formation of H$^-$ contributes to the two-electron removal cross section. In fact double capture in collisions between protons and alkali-atoms (Na, K, Rb) has been measured for impact energies $E \leq 5$ keV/amu by Ebel and Salzborn [184], who reported a relatively large cross section of $1 \times 10^{-17}$ cm$^2$ at $E = 5$ keV/amu. Remarkably, this is even larger than our total two electron removal cross section measured at 9 keV/amu. However, very recently new experimental results for double capture in H$^+$+K collisions have been reported [209]. They indicate that the corresponding data of reference [184] are much too high, up to one order of magnitude, due to contributions from successive single-capture processes and non-negligible admixtures of neutral hydrogen atoms in the projectile beam. It is not unlikely that the same problems were present in the case of the H$^+$+Na collision system. In fact, the agreement between the present Na$^{2+}$ and previous TI cross sections [13] suggests that the cross section for both double capture and double ionization are negligible. The TC-BGM calculations for TI are in reasonable agreement with our experimental data for Na$^{2+}$.

One can distinguish two pathways to TI: (i) capture from Na(2p) with simultaneous
ionization of Na(3s) ($\sigma_{3s_{ion}}^{2p_{cap}}$) or ionization of Na(2p) with simultaneous capture of Na(3s) ($\sigma_{3s_{cap}}^{2p_{ion}}$), and (ii) capture and ionization of Na(2p) ($\sigma_{2p_{ion}}^{2p_{cap}}$). Note that the two possible contributions to process (i) are indistinguishable as they lead to the same final states, i.e., the same Q-value. However, because ionization is mainly determined by the initial binding energy, $\sigma_{3s_{ion}}^{2p_{cap}}$ is more likely than $\sigma_{2p_{ion}}^{2p_{cap}}$.

The contributions of these two pathways to transfer ionization are also plotted in figure 5.14. Remarkably, above $E = 50$ keV/amu $\sigma_{3s_{ion}}^{2p_{cap}}$ plays a non-negligible role and is equally strong as $\sigma_{3s_{ion}}^{2p_{cap}} + \sigma_{3s_{cap}}^{2p_{ion}}$ at $E = 100$ keV. In principle, it should be possible to test this prediction by our experimental method, since both processes can be distinguished by their Q-values.

Concluding that the Na$^{2+}$ production can be explained by TI in which a 2p electron is captured and the 3s electron is emitted into the continuum, a comparison can be made with ISC. While for ISC after capture of a 2p electron the outer-shell electron stays at the target, in TI the outer-shell electron is excited to the continuum. A classical over-barrier kind of view is depicted in figure 5.15. Within this classical model the balance between TI and ISC is linked to the “recapture” probability of the outer electron. At small internuclear distances both the 3s and a 2p electron move in the combined target and projectile Coulomb potential. On the way-out the 2p electron is transferred to the projectile, and the 3s is either captured by the projectile or recaptured by the target nucleus. Transfer to the projectile can lead to either H$^-$ production or to electron capture into the continuum [210]. The former process is unlikely as discussed above.

To assess the relative importance of TI and ISC their cross sections are shown in figure 5.16. The cross section for ISC is larger than that of TI by a factor of three, implying

![Figure 5.16: Comparison of TI and ISC transfer cross sections. Present data: TI (■) and ISC (▲). TC-BGM: $\sigma_{cap}^{\text{net}} - \sigma_{Na(3s)}^{\text{cap}}$ (—), $\sigma_{2p_{ion}}^{2p_{cap}}$ (—). Previous experiments: $\sigma_{2p_{ion}}^{10}$ DuBois [13] (○).](image-url)
5.4 Conclusions

In this chapter a detailed study of keV H\(^+\)+Na collisions is presented. The MOTRIMS experiments confirm that capture of the outer-shell 3s electron dominates at low energy. But for higher energies they present the first direct evidence of charge transfer being dominated by capture of a 2p inner-shell electron instead of outer-shell capture. With this observation one-electron capture can be seen as a result of two distinct processes. At low energies, \(E < 10\) keV/amu, it is dominated by outer-shell capture into H\((n = 2)\), while at high energies, \(E > 40\) keV/amu, inner-shell capture from the 2p-shell into H\((n = 1)\) is the main process, i.e. already at energies lower than expected from the “velocity matching” argument (see figure 5.17).

In the Na\(^+\) recoil spectra two inner-shell capture processes could be identified, namely ISC leaving the outer-shell electron in the 3s state or exciting it to 3p. The relative intensities of these processes revealed the prominent role of multi-electron dynamics in low energy inner-shell capture and a transition to ISC without active outer-shell participation occurring at \(\sim 1.4 v_{orb}\) of the outer-shell electron. Inner-shell capture leading to Na\(^+\) recoils has larger cross sections than that of Na\(^{2+}\) production, the latter being dominated by transfer ionization. Good overall agreement between our MOTRIMS data and the TC-BGM calculations has been found.

Figure 5.17: Total one-electron capture \(\sigma_1^{10}\) and its main components: OSC into H\((n = 2)\) and ISC into H\((n = 1)\). Symbols: MOTRIMS; curves: TC-BGM.