Chapter 10

Single ionization

10.1 Introduction

Single ionization is the most basic ionization process. By impact of the projectile one target electron is emitted into the continuum. For a projectile of charge $q$ and velocity $v_p$ pure single ionization is rather well understood for small values of the Sommerfeld parameter $q/v_p$ [264]. The process can be treated perturbatively and the continuum electron spectrum is dominated by low-energy electrons centered around the target (so-called ‘soft-electrons’). Also two other classes of electrons can be identified, namely ‘binary encounter electrons’ resulting from hard projectile-electron collisions and ‘cusp electrons’ from electron capture into the continuum.

Single ionization represents a basic three-body problem in which the projectile - electron, projectile - target nucleus and target nucleus - electron interactions can all play a role. Measuring the fully differential cross sections provides a stringent test to theory and reveals the few-body dynamics (see e.g. [265] and reference herein). Such studies are usually performed in the high energy region (> 0.1 MeV/amu).

In slow ion-atom collisions, where the projectile velocity is lower than the classical Bohr velocity of the target electron, the probability of ionization is very small compared to that of capture. Mechanisms which promote the electrons into the continuum and the associated electron-momentum distributions have been heavily discussed. Especially the role of the saddle point electrons, introduced by Olson [266] and observed experimentally by e.g. Pieksma et al [267], has stimulated many experimental and theoretical studies (for a review, see e.g. [268]). In the classical saddle point mechanism the electrons, stranded at the equiforce or saddle point between the projectile and residual target ion, will follow this point as the projectile and target separate.

The ejected electron momenta have been measured in COLTRIMS experiments (see e.g. [123–126,269]) revealing that the electrons stay at the target with low kinetic energy (electron excitation into the continuum, EEC), travel along with the projectile (electron capture into the continuum, ECC) or are found in between the target and projectile (including the saddle point electrons). The relative importance of each of them depends on projectile charge state, velocity and target structure. Note that by far most experiments are done on He and Ne.
Theoretically single ionization in slow ion-atom collisions has been addressed by various methods including CTMC [266, 270, 271] and (triple-center) close-coupling calculations [272, 273]. Especially the theory of hidden crossings has been successfully applied [274–276]. In this theoretical framework electronic transitions are associated with the branching points of the adiabatical potential energy surfaces which are analytically continued in the complex plane. Ionization at low velocities is explained as a multistep promotion process in the quasi-molecule formed during the collision. Emphasis is put on two distinct mechanisms which are called S and T superpromotion. The S mechanism is related to unstable trajectories of the electrons located on the top of the centrifugal barrier on the incoming stage of the collision while the T promotion is related to the saddle point mechanism on the receding part of the collision. The hidden crossing calculations have been limited to H as target (see e.g. [19]). Experimental evidence of the molecular orbital promotion mechanism has been found for non-H targets [123, 269, 277, 278].

Total cross section measurements in the threshold region below the ionization maximum are scarce. Wu et al reported single ionization cross sections for collisions between highly charged ions (q=6–30) and He at energies down to 1 keV/amu [279], while Shah et al studied the H$^+$+H system down to 1.25 keV/amu [280]. For alkali targets such cross sections are basically lacking. In this chapter we have compiled our ionization data on Na(3s) and Na$^\ast$(3p) targets. Scaling properties of the ionization cross sections will be investigated and compared to scaling laws deduced from ionization of H and He targets. The measured Q-value spectra contain some information on the momentum distributions of the emitted electrons and on basis of these spectra the importance of EEC and ECC as well as their dependencies on the collision parameters will be discussed.

### 10.2 Total cross sections

The amount of single ionization compared to one-electron capture can be directly extracted from the Q-value spectra. The ionization potential serves as a strict boundary between the two processes (see appendix C). In figure 10.1 we show the compilation of the ratios of cross sections for single ionization and one-electron capture for the collision systems investigated here. For all systems the ratios are characterized by a steep increase with collision energy, but their exact values depend on the projectile and target initial states. For each initial target state one sees that for increasing projectile charge the probability of ionization, with respect to capture, decreases. The role of the initial binding energy can be investigated by comparing data for Na(3s) and Na$^\ast$(3p). Here one observes that ionization increases with decreasing binding energy.

In figure 10.2 the single ionization cross sections are put on an absolute scale by normalization to absolute cross sections for one-electron capture. For H$^+$ and He$^{2+}$ impact on Na(3s) we have used recommended cross sections, as discussed in chapter 5 and 6, respectively. In case of O$^{6+}$ impact on Na(3s) experimental one-electron capture cross sections are not available and therefore the TC-BGM calculations (chapter 7) are used for normalization. The absolute cross sections for single ionization of Na$^\ast$(3p) were obtained using the cross sections for capture from Na(3s) and using the capture cross section ratio between Na(3s)
Figure 10.1: Single ionization and one-electron capture cross section ratios for different projectiles colliding on Na(3s) and Na\(^*\)(3p) (chapter 8). Explicitly,

\[
\sigma_{\text{ion}}(3s) = \left( \frac{\sigma_{\text{rel}}^{\text{ion}}(3s)}{\sigma_{\text{rel}}^{\text{cap}}(3s)} \right) \sigma_{\text{cap}}(3s),
\]

(10.1)

\[
\sigma_{\text{ion}}(3p) = \left( \frac{\sigma_{\text{rel}}^{\text{ion}}(3p)}{\sigma_{\text{rel}}^{\text{cap}}(3p)} \right) \left( \frac{\sigma_{\text{rel}}^{\text{cap}}(3p)}{\sigma_{\text{rel}}^{\text{cap}}(3s)} \right) \sigma_{\text{cap}}(3s),
\]

(10.2)

where the quantities between brackets are ratios obtainable from our experiments and \(\sigma_{\text{cap}}(3s)\) are the one-electron capture cross sections.

Theoretical cross sections were obtained by TC-BGM for H\(^+\)+Na(3s) (chapter 5) and CTMC calculations for He\(^{2+}\)+Na(3s) (chapter 6). Note that single ionization in H\(^+\)+Na(3s) and H\(^+\)+Na\(^*\)(3p) collisions has been investigated by earlier by means of CTMC calculations [90]. The results for the excited state have been included in figure 10.2. The CTMC calculations for H\(^+\)+Na(3s) yielded about 20-25% smaller cross sections than the ones of TC-BGM (see figure 5.8).

For each projectile charge state the ionization cross sections show an enhancement when going from Na(3s) to Na\(^*\)(3p). The energy dependence, i.e. the slope of the curves in figure 10.2, seems not to vary strongly with binding energy, but is different for different projectile charges. At low energies the ionization cross section is larger for a lower charge state.
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Figure 10.2: MOTRIMS and theoretical single ionization cross sections for different projectiles colliding on Na(3s) and Na∗(3p), including TC-BGM calculations for H+ + Na(3s) (—) and CTMC calculations for H+ + Na∗(3p) [90] (— —) and He2+ + Na(3s) (···).

projectile. However, for ions in higher charge states the cross sections increase more rapidly with energy and ultimately exceed the ones for lower charge states. A crossing behavior at intermediate energies is also seen in CTMC calculations on fully stripped ions (q=1–36) colliding on H [79].

In the threshold region below the cross section maximum scaling properties of ionization cross sections for He have been considered by Wu et al [279]. Later a generalized scaling law was obtained by Wu et al [281] by including also experimental and theoretical data on ionization of H by highly charged ions. The scaling involves the reduced cross section \( \tilde{\sigma} = \sigma l^{1.3}/q \) and the reduced energy \( \tilde{E} = E/Iq^{1/2} \). The energy scaling is derived from the Bohr-Lindhard model [35]. However, it is of note that the experimental data for H targets only covered a small part of the threshold region. Therefore the scaling law is mostly determined by single ionization of He. In figure 10.3 the proposed scaling is applied to our data and compared to the He data of Wu et al [279, 281]. Our scaled data show a similar dependence on the scaled energy as the He cross sections, but yield clearly larger values. In order to describe the ionization data from Na(3s), Na∗(3p) and He an alternative scaling law have to be found.

Our findings could be useful to estimate single ionization cross sections for similar collision systems, i.e., ion-atom collisions involving weakly bound electrons, e.g., alkali and metastable atoms. For example, the ionization potential of metastable helium (4.8 eV) lies in between that of Na(3s) and Na∗(3p). The present study can also be regarded as an intermediate step between ionization of atoms in which the electrons are strongly bound, such as in H
and He, and that of Rydberg atoms, in which the ionization potentials are smaller than 1 eV.

10.3 Momentum distributions

Not only the amount of ionization can be extracted from the Na⁺ Q-value spectra, but also some aspects of the emitted electron dynamics. One can show that the energy above the ionization potential, \( Q - I \), is equal to the kinetic energy of the emitted electron in the projectile frame \( E_{e,pf} \) (see appendix C). Under the assumption that the electron travels close to the projectile axis distinct features in the spectra can be assigned. The threshold of ionization at \( Q = I \) is connected to ECC in which the free electron travels with the projectile (at rest in the projectile frame), which can be seen as a continuation of capture into high \( n \)-states. On the other hand, emitted electrons which remain near the target, i.e. EEC, have a kinetic energy in the projectile frame of \( \frac{1}{2}v_p^2 \) and can be found at \( Q = I + \frac{1}{2}v_p^2 \). While the ECC boundary is independent of the projectile velocity, the EEC shifts to higher Q-values with increasing impact energy. Saddle point (SP) electrons are characterized by their velocity \( v_s \), given by \( v_s = v_p \left( 1 + q^{1/2} \right)^{-1} \) in the laboratory frame [124] and can be found at \( Q = I + \frac{1}{2}q(1 + \sqrt{q})^{-2}v_p^2 \) in the spectra.

An overview of the Q-values spectra for H⁺+Na(3s) is shown in figure 10.4 in which...
the ECC, EEC and SP positions are indicated. At our lowest collision energies the Q-value spectra decrease smoothly through $Q = I$ and have very low intensity at the EEC boundary. With increasing projectile energy ionization increases and a maximum in the spectrum at $Q > I$ starts to appear for $E > 16$ keV/amu. The maximum gets rather broad when reaching the highest energy of $E = 25$ keV/amu. Due to the finite resolution, also events resulting from one-electron capture into high $n$-states appear around $Q = I$, which excludes a quantitative comparison of the relative importance of ECC and EEC. However, a qualitative analysis seems possible.

In the projectile frame the electron’s kinetic energy can be expressed in terms of the projectile velocity:

$$E_{e,pf} = Q - I = \frac{1}{2} \eta v_p^2,$$

which defines the scaled projectile frame electron energy $\eta$. The advantage of using $\eta$ rather then the $Q$-value itself is that now the positions of SP and EEC are independent of the collision energy. Figure 10.5 shows the $\eta$ dependence of the electron spectra for the highest projectile energies. The distributions are normalized to their maximum value. ECC corresponds to the situation that $\eta = 0$, EEC to $\eta = 1$ and SP corresponds to $\eta = 0.25$. With increasing projectile velocity the electron is found closer to the target ($\eta = 1$), indicating an increasing role of EEC.
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Figure 10.5: Kinetic energy distributions of the emitted electrons in the projectile frame for single ionization in $H^+ + Na(3s)$ collisions in terms of $\eta$ (see equation 10.3).

on the cost of ECC. This feature has also been observed in $H^+ + He$ collisions [124]. At low velocity the emitted electron is able to follow the projectile. At high velocity the projectile is too fast and therefore leaves the electron near to the target nucleus. Note that at the highest energies the maxima do not coincide with the saddle point velocity and most electrons are found between the saddle point and the target, having kinetic energies $\lesssim 5$ eV.

An overview of the Q-value spectra for $He^{2+} + Na(3s)$ collisions is shown in figure 10.6(a). The range of measured collision energies is so low that a maximum for $Q > I$ is not observed. In the Q-value spectra for $He^{2+} + Na(3s)$ one observes less intensity between SP and EEC than between ECC and SP as compared to equal projectile velocity $H^+ + Na(3s)$ collisions. This indicates that for increasing projectile charge state the role of EEC decreases, which is also observed for ionization of He and Ne by bare ions [125]. This can be understood by an argument similar to that used to explain the velocity effect. The attractive force which pulls the electron towards the projectile increases with increasing projectile charge, leaving less electrons near the target nucleus.

Finally, we can compare the ionization patterns in $He^{2+} + Na(3s)$ and $He^{2+} + Na^*(3p)$ collisions (see figure 10.6), to investigate the dependence on the initial binding energy. For equal projectile velocity one observes higher intensities between SP and EEC than between ECC and SP for $Na^*(3p)$ as compared to Na(3s). One has to realize that with decreasing binding energy the projectile velocity relative to the classical orbital velocity of the target electron increases, such that the observed effect might simply be a velocity effect. Taking this into account $13$ keV/amu for Na(3s) corresponds to $\sim 8$ keV/amu for Na*(3p), nevertheless the EEC process still seems somewhat stronger for Na*(3p). Such an effect has not been observed before, because most experiments were done with He and Ne target and their difference in binding energies is relatively small.
To conclude, from a detailed analysis of the ionization part of the Q-value spectrum the influence of the projectile charge state and velocity and of the initial target state on the electron emission patterns could be qualitatively investigated. With increasing projectile velocity or decreasing charge state the electron is found closer to the target in line with experiments on noble gases. For the first time a similar trend is observed for a decreasing binding energy. Measuring the momenta of the emitted electrons in coincidence with the target recoils is needed to study single ionization of Na more precisely and quantitatively. However, the present study shows that the recoil-ion spectrum alone does already provide a wealth of information.