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Osama Abu-Haija
Western Michigan University

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SINGLE-ELECTRON CAPTURE PROCESSES IN SLOW COLLISIONS OF He^2+ IONS WITH MOLECULAR TARGETS

by

Osama Abu-Haija

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Physics

Western Michigan University
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This dissertation is dedicated to my parents, Abdulla and Najah.

Osama Abu-Haija
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CHAPTER I

INTRODUCTION

Amongst the fundamental topics for research in atomic physics is the study of collisions of particles, and especially collisions of projectile ions with neutral atoms or molecules. There are three major categories of events that may occur in an ion-atom/molecule collision: ionization, excitation, and charge transfer or electron capture. These processes can occur in either collision partner or in both, and it is important to note that combinations of these processes can occur as well. Each process takes place due to the interaction between the nucleus of one colliding partner and the electrons of the other, or between the electrons of the projectile ion and the electrons of the target. Of primary interest is the single-electron capture, by which an electron from the neutral target is captured by the projectile ion, since frequently this is one of the dominant processes in low-energy collisions.

The process of charge transfer can be described by the following reaction (Kamber and Cocke, 1991)

\[ A^{q+} (n_0, l_0, m_0) + B \rightarrow A^{(q-1)+} (n, l, m) + B^+ + \Delta E. \]  

(1.1)

where A is the projectile ion with initial charge q and B is the neutral target atom or molecule, \( \Delta E \) is the energy defect of the reaction channel involved (see Chapter II), and \((n_0, l_0, m_0)\) and \((n, l, m)\) are the quantum numbers of initial and final states, respectively, of the projectile ion.
The interaction of atomic ions with molecules leads to a variety of processes which are important from the viewpoint of gaining a better, more quantitative insight into the structure of the molecular targets and molecular product ions themselves, and the mechanisms and dynamics involved in their ionization and dissociation.

The need to understand ion-atom/molecule collision processes is important in a number of applications such as material science and plasma science, where low temperature plasmas play a key role in determining characteristics of target materials and of plasma behavior (Pequignot, 1980). These processes not only strongly influence the charge state balance but also give rise to light emission, which arises from electron capture into excited states. Another important application is toward the studies of astrophysics, comets, the aurora and corona discharges (Merrill et al., 1987). Also atmospheric molecular ions (O$_2^+$, N$_2^+$, CO$^+$, and CO$_2^+$) are important constituents of the earth’s upper atmosphere. Information on mechanisms responsible for their excitation is crucial to a complete understanding of auroral and other atmospheric phenomena (Bulter et al., 1980). In addition, single-electron capture processes in collisions of He$^{2+}$ ions (solar wind ions) with cometary gases H$_2$O and CO$_2$ have been observed by Giatto Spacecraft using the Ion Mass Spectrometer/High Energy Range Spectrometer (IMS/HERS) during a close encounter with Comet Halley in 1986 (Greenwood et al., 2000). Therefore, state selected studies of the electron capture processes can contribute significantly to a better understanding of the observed spectra of the atmospheric molecular ions.

When doubly charged helium ions collide with molecules, a variety of reaction channels are possible through which electron capture may take place. These processes, which are energetically possible, are described below:

Non-dissociative single-electron capture (pure single-electron capture (SEC)):
He$^{2+}$ + AB $\rightarrow$ He$^+$ (n = 1 or 2) + AB$^+$ + $\Delta$E.

(1.2)

Single-electron capture accompanied by molecular target-ion excitation (transfer excitation (TE)):

He$^{2+}$ + AB $\rightarrow$ He$^+$ (n = 1 or 2) + AB$^+$ + $\Delta$E.

(1.3)

Single-electron capture accompanied by dissociative molecular target-ion (dissociative transfer excitation (DTE)):

He$^{2+}$ + AB $\rightarrow$ He$^+$ (n = 1 or 2) + AB$^{++} \rightarrow$ He$^+$ + A$^+$ + B + $\Delta$E.

(1.4)

Single-electron capture accompanied by ionization of molecular target-ion (dissociative transfer ionization (DTI)):

He$^{2+}$ + AB $\rightarrow$ He$^+$ (n = 1) + AB$^{++} + e \rightarrow$ He$^+$ + A$^+$ + B$^+$ + e + $\Delta$E.

(1.5)

In recent years, the study of single-electron capture processes in collisions of low-energy doubly charged ions with molecular targets has attracted theoretical and experimental attention (Fukuroda et al., 1989, Rohmund et al., 1995, Kearns et al., 2001). However, only few measurements of state-selective single-electron capture by doubly charged ions from molecular targets have been made using translational energy-gain spectroscopy techniques (Fárník et al., 1993, Hodgkinson et al., 1995, Burns et al., 1997, Albu et al., 2004). Much of the early work has concentrated on measurements of total cross sections for single-electron capture by doubly charged...

Previous measurements of state-selective single-electron capture by low-energy doubly-charged helium ions from O$_2$, H$_2$O, CO$_2$, N$_2$, and NH$_3$ molecular targets have been studied by a number of investigators. Among them Rogers et al. (1978) have investigated inelastic and charge transfer scattering in collisions between He$^{2+}$ ions and molecular nitrogen. Hanaki et al. (1982) have bombarded N$_2$ with He$^{2+}$ ions in the energy range from 0.7 - 4.5 keV and obtained single and double electron capture cross sections. Furthermore, Kobayashi et al. (1984) have employed the translational energy-gain spectroscopy technique to measure the energy gain spectra of 0.8 keV He$^{2+}$ ions with N$_2$. Rudd et al. (1985) have measured the cross sections for single and double electron capture by 5$-$150 keV/amu He$^{2+}$ ions from a variety of different atomic and molecular targets using a transverse-field technique. Single-electron capture and direct scattering have been studied in collisions of He$^{2+}$ with N$_2$ and O$_2$ at an impact energy of 4 keV (Martin et al., 1991). McCullough et al. (1992) have obtained the energy-gain spectrum of He$^+$ ions produced by 8 keV He$^{2+}$ ions in collision with O$_2$. Fárník et al. (1995) have observed the vibrational state populations of NH$_3^+$ formed in single-electron capture processes in collisions of 70 eV He$^{2+}$ ions with NH$_3$ at three laboratory scattering angles. Recently, Albu et al. (2004) have used translational energy-gain spectroscopy to study state-selective single-electron capture for impact of slow He$^{2+}$ ions on H$_2$, O$_2$, and CO at impact energies $\leq$ 1 keV. In their work, a comparative study for these three collision systems has been made on the relative importance of pure single-electron capture versus single-electron capture accompanied by target excitation. Very recently, Seredyuk et al. (2005) have carried out experimental and theoretical studies of charge transfer in collisions of He$^{2+}$ ions.
with H$_2$O molecules at an energy range from 0.025 - 12 keV/amu by means of translational energy spectroscopy, photon emission spectroscopy, and fragment ion spectroscopy.

In this thesis, we carry out doubly differential cross section measurements, in energy and angle, for state-selective dissociative and non-dissociative single-electron capture processes in collisions of low-energy He$^{2+}$ ions with O$_2$, H$_2$O, CO$_2$, N$_2$, and NH$_3$ molecular targets by means of a translational energy-gain spectroscopy technique. The method of translational energy spectroscopy allows the identification of the initial as well as the final states of the colliding particles by measuring the total change in internal energy of the colliding system during the collision.

The scope of this dissertation is to present experimental work that measured the translational energy-gain spectra, the differential cross sections, and the absolute total cross sections for single-electron capture in collisions of He$^{2+}$ ions with O$_2$, H$_2$O, CO$_2$, N$_2$, and NH$_3$ at impact energies between 100 eV and 1600 eV and scattering angles between 0° and 8°. A differential energy gain spectrometer, capable of simultaneously measuring the scattering angle and energy spectrum of the capturing projectile, will be used to obtain measurements on state-selective dissociative and non-dissociative single-electron capture of low-energy doubly-charged helium ions in collisions with molecular targets. The measurements of the energy gain spectra are discussed by comparing them with different theoretical models which have been used for a qualitative explanation of the main features of the state-selective single-electron capture processes by low-energy multiply and doubly charged ions. The Landau-Zener model (Landau, 1932, Zener, 1932) and the Extended Classical-Over-Barrier model (Niehaus, 1986) have been used to calculate the location of the “reaction window” (see the section on Reaction Window in Chapter II). Differential cross
section values are also compared with a multi-state collision model (Andersson et al., 1987) based on classical trajectories for nuclear motion and multi-channel Landau-Zener transition probabilities. Experimental values of total cross sections are compared with the predictions of multi-channel Landau-Zener model calculations and with the results from the Demkov model (Demkov, 1963).

In the next chapter, the theoretical background is given. The experimental procedure is discussed in detail in Chapter III, and the data analysis techniques are presented in Chapter IV. In Chapter V, the experimental results, discussion of the results and comparisons of the present results with previous studies and theoretical models are made. Finally, conclusions are given in Chapter VI.
CHAPTER II

THEORETICAL BACKGROUND

In this chapter we will describe the mechanisms which govern low energy ion-atom/molecule collisions. In addition, we review the major theoretical models used in describing single-electron capture by projectile ions from neutral targets—either atoms or molecules—at low collision energies. Throughout this chapter atomic units are used except where otherwise stated.

Kinematics

A general schematic description of an inelastic collision process involving single-electron capture in the laboratory frame is shown in Fig. 1. Here a projectile ion A with charge $q$ strikes a target B, which is normally neutral and considered to be stationary. As a result of their mutual interaction, the projectile ion is scattered through the angle $\theta$ away from the direction of beam incidence while the target leaves the collision region at the angle $\varphi$. The distance $b$ is the impact parameter of the collision. The energy gained by the projectile ion during a collision can be expressed using classical two-body dynamics as a difference between the final kinetic energy $E_f$ of the scattered projectile ion and the initial kinetic energy $E_0$ of the incident projectile ion, that is

$$Q = E_f - E_0.$$  \hspace{1cm} (2.1)
Figure 1. Typical electron capture reaction in the laboratory frame. The scattering angles $\theta$ and $\varphi$, and the impact parameter $b$ are indicated (Cooks, 1978).

From two-body kinematics, the relationship of the energy gain $Q$ to the energy defect $\Delta E$, which is defined as a difference in the binding energies of the collision products, is found to be (Kamber and Cocke, 1991)

$$ Q = \Delta E - \Delta K. $$

where $\Delta K$, defined below, is the translational energy given to the target, and $\Delta E$ is calculated from spectroscopic data according to the following formula

$$ \Delta E = I_p(A^{(q-1)^+}) - I_p(B) - E_x, $$

(2.3)
where \( I_p(A^{(n-1)+}) \) and \( I_p(B) \) are, respectively, the ionization potentials of the projectile product ion \( A^{(n-1)+} \) and the target molecule \( B \), and \( E_x \) is the excitation energy of the \( x \)th level of the projectile product ion \( A^{(n-1)+} \) or the target product ion \( B^+ \). However, \( \Delta E \) can either be positive (a decrease in the internal energy with corresponding increases in kinetic energy) or negative. The former is called an exothermic reaction and the latter an endothermic one.

The general expression of the translational energy \( \Delta K \) given to the target is given by (Cooks, 1978)

\[
\Delta K = \frac{M}{M + m} \left(1 - \cos \theta \right) \left[ \frac{2mE_0}{M + m} - \Delta E \right] + \frac{M(\Delta E)^2}{4mE_0} \cos \theta, \tag{2.4}
\]

where \( M \) and \( m \) are, respectively, the projectile and target masses, \( E_0 \) is the laboratory translational energy of the projectile, and \( \theta \) is the laboratory scattering angle of the projectile. In the forward scattering angle, Eq. (2.4) reduces to

\[
\Delta K = \frac{M(\Delta E)^2}{4mE_0}, \tag{2.5}
\]

If the mass of the low-energy projectile ion is much lighter than that of the target then the translational energy given to the target, calculated on the basis of zero and nonzero scattering angles, is negligibly small. Then the energy gain \( Q \) can be written as

\[
Q = \Delta E. \tag{2.6}
\]
Landau-Zener Model

In an ion-atom collision the electrons to be captured are not free but bound to the target nucleus, and therefore have a momentum distribution. If the relative velocity of the colliding particles is considerably of the same order of magnitude or smaller than the orbital velocity of the target electron to be captured, then an electron capture reaction can be best viewed as transitions between a set of quasi-molecular electronic states formed by the collision partners. Associated with each state is an interaction potential which depends on the internuclear separation $R$, and which is represented as a potential curve that is a sum of the repulsive energy of the two nuclei and the electronic binding energy. Electron capture is considered to take place over a localized region of internuclear distance, where the potential energy curves dominated by the Coulomb repulsion between the two ions in the outgoing channel and nearly constant (small polarization attraction) potential curves characterizing the ion-neutral interaction in the incoming channel become strongly coupled.

A schematic diagram of two distinct representations of the potential energy curves describing the behavior of the ion-atom system during the collision is shown in Fig. 2. The adiabatic representation (solid lines) may be determined by solving the Schrodinger equation for the molecular electronic states. Furthermore, the adiabatic curves obey the Neuman-Winger non-crossing rule (Cooks, 1978) which forbids molecular energy stats of the same symmetry from crossing each other. However, the diabatic representation (dashed lines) associated with the states of the same symmetry may cross (i.e., become degenerate at finite value of the internuclear distance) and violate the non-crossing rule because they are not exact solutions to the Schrodinger equation. Nevertheless, such diabatic curves are most useful when discussing charge
transfer reactions. The basic idea of the Landau-Zener (LZ) model (Landau, 1932, Zener, 1932) is formed by finding a solution for the transition probability $P_{i\rightarrow f}(b)$ to transfer an electron from initial state $i$ to the final state $f$. According to this model, the transition is assumed to occur at an avoided crossing with efficient coupling between a pair of diabatic potential curves which correspond to incoming $(A^+ + B)$ and outgoing $(A^{(q-1)+} + B^+)$ channels.

Finding a solution for the transition probability can be achieved by solving the time-dependent Schrödinger equation

$$\left( H - i \frac{\partial}{\partial t} \right) \Psi = 0 \quad (2.7)$$

Figure 2. A schematic diagram of the potential energy curves for the incoming and outgoing channels near a curve crossing versus internuclear distance $R$. The solid lines are adiabatic representation, dashed lines are diabatic representation, and the coupling matrix element $H_{12}$ is one-half the adiabatic splitting at $R_x$. 

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where $H$ is the electronic Hamiltonian and $\Psi$ is the electronic wave function during the collision. The electronic wave function in the coupling region can be written as

$$\Psi = \chi_1 C_1(t) \exp(-i \int_{t}^{t} \omega_1 dt) + \chi_2 C_2(t) \exp(-i \int_{t}^{t} \omega_2 dt).$$

(2.8)

where $C_i (i=1, 2)$ is the probability amplitude of being in the diabatic state $\chi_i$, which corresponds to the diabatic potential curve $U_i$. Solving the time-dependent Schrödinger equation results in two ordinary differential equations:

$$i \frac{\partial C_1}{\partial t} = H_{12} C_2 e^{-i \int (U_2 - U_1) dt},$$

(2.9)

$$i \frac{\partial C_2}{\partial t} = H_{12} C_1 e^{-i \int (U_1 - U_2) dt}.$$

(2.10)

where $H_{12}$ is the coupling matrix and is assumed to be constant at the crossing point $R_x$. The boundary conditions under which Eqs. (2.9) and (2.10) are solved are imposed by knowledge that initially the system is in the diabatic state $\chi_1$ at $t = -\infty$, i.e.

$$|C_1(-\infty)| = 1, \quad |C_2(-\infty)| = 0.$$  

(2.11)

The probability that the system makes an a diabatic transition, remaining in $\chi_1$ after traversing the crossing at $R_x$, is given by

$$p = |C_1(\infty)|^2.$$  

(2.12)

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Applying conservation of probability, the transition probability for an electron to be transferred from initial state $\chi_1$ to the final state $\chi_2$ is given

$$1 - p = |C_2(\infty)|^2.$$  \hspace{1cm} (2.13)

The solutions for Eqs. (2.9) and (2.10) satisfying the initial boundary conditions Eq. (2.11) were shown by Landau and Zener to be given by

$$p = |C_1(\infty)|^2 = e^{-2\pi \gamma},$$  \hspace{1cm} (2.14)

$$1 - p = |C_2(\infty)|^2 = 1 - e^{-2\pi \gamma},$$  \hspace{1cm} (2.15)

where,

$$\gamma = \frac{H^2_{12}}{\frac{d}{dt} (U_1 - U_2)\bigg|_{t=0}} = \frac{H^2_{12}}{V_r \frac{d}{dR} (U_1 - U_2)\bigg|_{R=R_s}},$$  \hspace{1cm} (2.16)

where $V_r$ is the radial velocity. Assuming a classical straight-line trajectory, then the radial velocity is given by (Cooks, 1978)

$$V_r = V_o \left[1 - (b/R_s)^2\right]^{1/2}.$$  \hspace{1cm} (2.17)

where, $b$ is the impact parameter, and $V_o$ is the initial collision velocity.
Therefore, the Landau and Zener probability for a diabatic transition as a function of the impact parameter is written as

$$p = \exp \left( -\frac{2\pi \frac{H^2}{V}}{V \Delta F} \right)$$  \hspace{1cm} (2.18)

where $\Delta F$ is difference in slopes of the corresponding diabatic potential curves at the curving crossing and is given by

$$\Delta F = \frac{d}{dR} (U_1 - U_2) \bigg|_{R=R_x}$$  \hspace{1cm} (2.19)

If we furthermore assume a repulsive Coulomb interaction for exit channel $U_2$ (neglecting the small polarization contribution) and zero interaction for entrance channel $U_1$, then Eq. (2.19) becomes

$$\Delta F = \frac{(q - 1)}{R_x^2}$$  \hspace{1cm} (2.20)

The coupling matrix $H_{12}$ in Eq. (2.18) is assumed to be equal to one-half the adiabatic splitting at the avoided curve crossing $R_x$, as shown in Fig. 2 (Bransden and Joachain, 1983). Olson et al. (1971) proposed an analytical formula of the coupling matrix $H_{12}$, which is based on empirical fits to exact calculations of adiabatic potential curves, and is given by

$$H_{12} = 9.13 q^{-1/2} \exp[-1.324 aR_x q^{-1/2}]$$  \hspace{1cm} (2.21)
where $\alpha$ is a parameter introduced to allow for target atoms other than atomic hydrogen and is given by

$$\alpha = (2I_t)^{1/2},$$  \hspace{1cm} (2.22)

where $I_t$ represents the ionization potential of the target atom. Kimura et al. (1984) have reduced the coefficient of this coupling matrix by 40%, i.e., to 5.48, in order to give a better agreement with their measurements.

For the collision systems involving partially-stripped projectile ions, Taulbjerg (1986) derived a generalized expression for the coupling matrix of the form

$$H_{12} = 9.13 f_{nl} q^{-1/2} \exp[-1.324 \alpha R_x q^{-1/2}],$$  \hspace{1cm} (2.23)

with

$$f_{nl} = (-1)^n + 1 - \frac{\sqrt{2l+1} \Gamma(n)}{\sqrt{\Gamma(n+1+1)\Gamma(n-1)}},$$  \hspace{1cm} (2.24)

where $f_{nl}$ represents a factor to describe capture into the non-degenerate $l$-states of partially-stripped ions. For molecular targets, excitation of vibrational and rotational states of the molecular product must be taken into consideration. Magee (1952) modified $H_{12}$ by including the square root of the Frank-Condon factor $f$ for the specific transition between vibrational levels in Eq. (2.23). Thus, the modified coupling matrix element can be written as
\[ H_{12} = 9.13 \sqrt{f_{nl}} q^{-1/2} \exp[-1.324 \alpha R x q^{-1/2}] . \] 

(2.25)

Figure 3. Two-state picture of trajectories for capture on the way in (above) and capture on the way out (below).

In the Landau-Zener model approach, two possible paths of traversing the potentials when making the transition are considered as shown in Fig. 3. Each path
has a probability $P = p(1-p)$ of being traversed, where $(1-p)$ is the transition probability to transfer an electron from one curve to the other curve during a single pass of the crossing and $p$ is the probability of the diabatic transition at a single potential crossing. Thus, the total probability for making the transition when the crossing is traversed twice (on the way in or on the way out) is given by

$$P = 2p(1-p).$$  \hspace{1cm} (2.26)

**The Multi-Channel Landau-Zener Model**

The Landau-Zener model was originally used to describe charge transfer in a two-state system, but later extended to describe multi-channel states as shown in Fig. 4.

![Figure 4. A plot of potential energy curves versus $R$ for multi-channel states.](image-url)
The extension of the Landau-Zener model to a multi-channel system has been done by Olson and Salop (1976). The general expression of the probability $P_n$ for capture into the $n^{th}$ final state through a system with $N$ crossings, assuming that there is no interference between adjacent exit channels, is given by

$$P_n = p_1 p_2 \ldots p_n (1 - p_n) [1 + (p_{n+1} p_n + 2 \ldots p_N)^2 + (p_{n+1} + 1 - p_n)^2\ldots + (1 - p_{n+2})^2 + (1 - p_{n+1})^2]$$

(2.27)

where single channel probability $p_n$ can be calculated from Eq. (2.18). The cross section for capture into a particular state $n$ is then

$$\sigma_n = 2\pi \int_0^{\infty} p_n b db,$$

(2.28)

and the total cross section is given by

$$\sigma = \sum_n \sigma_n.$$  

(2.29)

It should be noted that the validity of the multi-channel Landau-Zener model is restricted to the adiabatic energy region. Furthermore, the multi-channel Landau-Zener model presented here completely neglects the electron transition caused by the rotation of the internuclear axis.
The classical over barrier (COB) model, which was originally introduced by Bohr et al. (1954), is one of the simpler models used to describe ion-atom collisions. It is widely used because it accurately describes the main features of the single-electron transfer process (Ryufuku et al., 1980). According to this model, as the projectile ion $A^{q+}$ approaches a neutral target atom $B$, the potential energy barrier between the collision partners will be lowered with decreasing internuclear distance $R$, as shown in Fig. 5. As a result, an electron may be transferred from $B$ to $A^{q+}$ at a critical distance $R_c$, where the height of the potential barrier separating the Coulomb potential wells, generated by the ionic charges of the target nucleus and the projectile, is below the binding energy of the electron.

![Diagram](https://example.com/diagram.png)

Figure 5. Schematic diagram illustrating the basic capture process mechanism as described by the classical-over-barrier model.
The potential barrier $V(x)$ seen by the electron is the sum of Coulomb potentials for the projectile ion and the target ion. Along the internuclear axis, this potential is given by

$$V(x) = -\frac{q}{x} - \frac{1}{R-x}.$$  \hspace{1cm} (2.30)

for $0 < x < R$, where $q$ is the charge of the incoming ion, and $x$ is the distance from the projectile measured along the internuclear axis between the target and the projectile. The barrier maximum can be calculated by setting the derivative of Eq. (2.30) to zero. Therefore, the barrier maximum is given by

$$V_{\text{max}} = -\left(\frac{\sqrt{q}+1}{R}\right)^2.$$  \hspace{1cm} (2.31)

The binding energy $I_t$ of the target electron at the internuclear distance $R$ is increased due to the Coulomb field of the approaching ion. Thus, the actual binding energy of the target electron is given by

$$I_t^* = I_t - \frac{q}{R}.$$  \hspace{1cm} (2.32)

The critical internuclear distance $R_c$ at which the electron can transfer from the target to the projectile ion is found by equating Eq. (2.31) to the actual binding energy (2.32), namely

$$R_c = \frac{1+2\sqrt{q}}{I_t},$$  \hspace{1cm} (2.33)
At infinite internuclear distance the binding energy $I_A$ of the captured electron equals the actual binding energy, Eq. (2.32), minus the attractive Coulomb potential induced by the target charge and is given by

$$I_A = I_t(R_c) + \frac{1}{R_c} = -I_t - \frac{q-1}{R_c}. \quad (2.34)$$

Then, combining Eqs. (2.33) and (2.34) yields the following equation for $I_A$:

$$I_A = -I_t \left( 1 + \frac{q-1}{1 + 2\sqrt{q}} \right). \quad (2.35)$$

Within the framework of the hydrogen-like approximation, we can express the binding energy in terms of the principle quantum number $n_c$ as follows:

$$n_c = \frac{q}{\sqrt{2I_A}}, \quad (2.36)$$

One can calculate the effective principle capture quantum number, which is treated as a continuous number, of the projectile having a diabatic crossing near $R_c$ and is written as

$$n_c = \left( \frac{q^2 (1 + 2\sqrt{q})}{2I_t (q + 2\sqrt{q})} \right)^{1/2}. \quad (2.37)$$

Eq. (2.37) will not, in general, yield an integer value for $n_c$. Therefore, the dominant principle quantum number is assumed to be the one most closest to $n_c$. 

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The COB model predicts that the exit channel with largest possible quantum number $n$ satisfying the condition $n \leq n_c$ will be predominantly populated. This is equivalent to taking the exit channel with the largest possible crossing radius $R_x$ satisfying $R_x \leq R_c$, where $R_x = (q-1)27.2/\Delta E(\text{eV})$, neglecting polarization. Moreover, the cross section for the electron capture is simply taken as

$$\sigma_c = A \pi R_c^2. \quad (2.38)$$

where $A$ denotes the capture probability and usually has a value of about 0.5, corresponding to the maximum possible capture probability for a two-state system (neglecting interference effects).

The Extended Classical-Over-Barrier Model

The COB model handles, in principle, only the case of a single-electron capture process in low-energy ion-atom collisions and does not include the collision velocity as a parameter in the calculation. Bárány et al. (1985) extended this model to include multiple electron transfer processes, considered as a sequence of single-electron transfers. However, this modified model only emphasizes the incoming part of the trajectory ("way-in"). The improvements by Niehaus (1986) to include more electron capture processes and some velocity dependence, is referred to as the extended classical over barrier (ECOB) model. In the ECOB model two parts of the collision trajectory are distinguished: the way-in (ion approaching target) and the way-out (ion receding). Moreover, the model allows one to calculate analytically the energy gain ($Q$) distribution of a collision. In what follows, we assume for the
collisions a straight-line trajectories approximation, with turning points $R_t$ equal to the impact parameters of the considered collision.

In this model, the binding energies of the $r$th electron, in the case of $r$ capture by the projectile of charge $q$ or the target, are given by

$$E_{P,t} = I_t + \frac{q}{R_{t,\text{in}}} \cdot \frac{t + r}{R_{t,\text{out}}}$$

and

$$E_{T,t} = I_t + \frac{q}{R_{t,\text{in}}} \cdot \frac{q - r}{R_{t,\text{out}}}$$

respectively, where $I_t$ is the ionization potential of the $r$th electron, and $R_{t,\text{in}}$ and $R_{t,\text{out}}$ are the critical internuclear distances of the $r$th electron on the way in and on the way out, respectively. These critical internuclear distances are given by

$$R_{t,\text{in}} = \frac{t + 2\sqrt{qt}}{I_t}$$

and

$$R_{t,\text{out}} = R_{t,\text{in}} \left(\frac{\sqrt{q - r + \sqrt{t + r}}}{\sqrt{q + \sqrt{t}}}\right)^2.$$
The energy gain $Q$ is defined as

$$Q = \sum_{t} \left( E_{p/T,t} - I_{t} \right).$$  \hfill (2.43)

The distribution of the binding energies (reaction window) around the most probable value is assumed to be Gaussian shaped and is given by (Niehaus, 1986)

$$W(E) = \left( \Delta E \pi^{1/2} \right)^{-1} \exp \left[ - \left( \frac{E - E_{p/T,t}}{\Delta E} \right)^2 \right],$$  \hfill (2.44)

where $\Delta E$ is the width and is given by

$$\Delta E = \sqrt{\left( \Delta V_{m,in}^2 + \Delta V_{m,out}^2 \right)},$$  \hfill (2.45)

with $\Delta V_{m,in}$ and $\Delta V_{m,out}$ equal to

$$\Delta V_{m,in/out} = \left| \frac{dV_{m,in/out}}{dR} \right|^{1/2},$$  \hfill (2.46)

where $dV_{m}/dR$ is the change of the barrier height with internuclear distance, and $V_{r}$ can be obtained from Eq. (2.17).
In discussing charge transfer mechanisms for collision systems, two different types of mechanisms must be considered. In the first type, electron capture occurs at the avoided crossings of potential energy curves, where in most cases the energy separation between the reactants and the products at infinite internuclear separation is large. This case was treated by the LZ model, as discussed earlier in this chapter. The second type of mechanism applies to systems in which several potential energy curves lie very close together asymptotically. Here, electron capture doesn’t occur because of a localized curve crossing, but rather because the coupling between the states is comparable in magnitude to the potential energy separation. A theoretical framework for this type of mechanism was introduced by Demkov (1964).

According to the Demkov model, electron transfer occurs at the internuclear distance $R_c$ where the coupling matrix element equals one half of the energy difference $\Delta E(R) = E_f - E_i$ between the initial and the final potential curves. The coupling matrix element at the internuclear distance $R_c$ may be approximated by

$$H_{12} = \exp(-\lambda R).$$

(2.47)

with $\lambda$ adjustable. In this model, the transition probability from the initial state to the final state at impact parameter $b$ is given by

$$P(b) = \text{sech}^2\left(\frac{\pi \Delta E}{2\hbar \lambda V_r}\right) \sin^2\left(\frac{1}{\hbar} \int_{-\infty}^{\infty} H_{12}(t) \, dt\right).$$

(2.48)

where $V_r$ is the radial velocity of the projectile at a specific impact parameter.
Seredyuk et al. (2005) have carried out the calculations of the cross sections for charge transfer in collisions of He\(^{2+}\) ions with H\(_2\)O using the Demkov model for transitions between quasi-parallel potential curves and the Landau-Zener model for transitions at curve crossings (see below).

For the Demkov model, the coupling matrix element is given by (Seredyuk et al., 2005)

\[ V_{ij} = 3.6\alpha^2 \exp(-0.86\alpha R), \quad (2.49) \]

where the velocity parameter \( \alpha = (\sqrt{2I_i} + \sqrt{2I_f}) / 2 \) is obtained from the ionization energies \( I_i \) and \( I_f \) of the electron in the initial and final levels, respectively. Also, the energy difference is given by (Seredyuk et al., 2005)

\[ \Delta E(R) = \Delta E_\infty + 1/R, \quad (2.50) \]

where \( \Delta E_\infty \) is the asymptotic energy difference for \( R \to \infty \). Thus, the internuclear distance \( R_c \) is obtained by solving the equation \( \Delta E(R_c) = 2 H_{12} \). The expression used for the cross section at an internuclear distance \( R_c \) is given by (Seredyuk et al., 2005)

\[ \sigma_{if} = P_{if}(R_c) \pi R_c^2, \quad (2.51) \]

where \( P_{if} \) is the total transition probability since the system makes two passages through the transition region, first on the way in and again on the way out. Therefore,
\[ P_{\gamma} = 2p(1-p), \quad (2.52) \]

with \( p \) defined as

\[ p = \exp \left( -\frac{\Delta E(R_c)}{\alpha V_r} \right), \quad (2.53) \]

and \( V_r \) is the radial velocity of the projectile taken to be the collision speed, and \( \Delta E(R_c) \) is obtained from Eq. (2.50). It is important to note that Eq. (2.51) implies that \( P_{\gamma}(R) = P_{\gamma}(R_c) = \text{constant for } R < R_c \) and \( P_{\gamma}(R) = 0 \) elsewhere.

For the Landau-Zener model, the probability \( P_{\text{LZ}} \) for the transition to remain in the initial diabatic state in a single crossing is given by (Seredyuk et al., 2005)

\[ P_{\text{LZ}} = \exp \left( \frac{-2\pi H_c^2}{F_c V_p} \right), \quad (2.54) \]

where the "force" \( F_c \) is obtained as the derivative of the energy difference Eq. (2.50) at \( R_c \), and \( H_c \) is matrix element evaluated at \( R_c \) and may be approximated by (Seredyuk et al., 2005)

\[ H_c = 0.15a^2\exp(-0.86aR), \quad (2.55) \]

where \( a \) is the velocity parameter already given in conjunction with the Demkov theory. For \( P_{\text{LZ}} \ll 1 \), the probability for populating the number \( v \) of final states is obtained as (Seredyuk et al., 2005)
The unknown number of final states was set to \( v = 20 \). For such a large number, the results do not change significantly with increasing \( v \). Therefore, the choice of \( v \) is uncritical for the transition probability. After the transition probability is evaluated, the corresponding cross section is again obtained using Eq. (2.51).

**Semi-Classical Curve-Crossing Model**

For slow collisions, where the velocities of the projectiles are much lower than those of the captured electrons, one can treat the motion of the electrons and that of the nuclei separately. In this regime, the so-called semi-classical model may be used, whereby the nuclear motion is described classically while the electron motion is described quantum mechanically. Therefore, the deflection functions and differential cross sections are determined classically, while the electronic probabilities are determined using the Landau-Zener formula.

**Classical Differential Cross Section**

The classical differential cross section \( d\sigma/d\Omega \), differential with respect to the solid angle \( \Omega \), relates the incoming intensity of the particles to the number of particles scattered into an element of solid angle, \( d\Omega \), in the direction specified by the scattering angle \( \theta \). The relationship between the impact parameter \( b \) and the deflection angle \( \theta(b) \) of the projectile ion in the center-of-mass coordinate is given by (Goldstein, 1980)
\[
\theta = \pi - \frac{b|dr|}{r^2 \sqrt{1 - (V(r)/E_{cm}) - (b/r)^2}}.
\] (2.57)

where \(E_{cm}\) is the projectile center of mass initial kinetic energy, \(V(r)\) is the scattering potential, and \(r\) is the internuclear separation. Integrating Eq. (2.57) for any impact parameter \(b\) yields the classical deflection angle \(\theta(b)\) as a function of \(b\), which can be transformed to a laboratory scattering angle for comparison with experimental results. Therefore, the differential cross section for scattering into the solid angle \(d\Omega\) is obtained from \(\theta(b)\) and given by (Goldstein, 1980)

\[
\frac{d\sigma}{d\Omega} = \frac{b}{\sin \theta} \left| \frac{db}{d\theta} \right|.
\] (2.58)

It should be noted that in general the integral in Eq. (2.57), however, is not analytic for most potentials and thus evaluation of \(\theta(b)\) requires numerical calculation. Moreover, it is difficult to obtain calculated potentials accurate over the localized curve crossing region. Therefore using diabatic Coulomb potential curves will simplify the problem. Such curves yield an analytical expression for the deflection function, which is differentiable. \(d\sigma/d\Omega\) may therefore be calculated using Eq. (2.58). In order to perform the calculation, several assumptions have to be considered: (1) the colliding partners do not interact until they reach the crossing point \(R_x\); (2) after reaching \(R_x\), the reaction along diabatic curves corresponds to capture on the way in or capture on the way out; (3) the diabatic potential curves used in Eq. (2.58), assuming zero interaction in the initial channel, are obtained from
\[ V(r) = \frac{(q-1)}{r} - Q. \]  

For simplicity, let us consider the two-state interaction in which two different trajectories are possible (way in and way out, see Fig. 3). By using the Landau-Zener transition probability for each trajectory, \( p_1 \) and \( p_2 \), the total differential cross section can be written as (Andersson et al., 1987)

\[ \frac{d\sigma}{d\Omega} = p_1 \left( \frac{d\sigma}{d\Omega} \right)_1 + p_2 \left( \frac{d\sigma}{d\Omega} \right)_2, \]  

where the indices 1 and 2 refer to the two trajectories. This idea can be extended to include multi-channel systems with more than one outgoing channel (see Fig. 4). Therefore, the total semi-classical differential cross section for single-electron capture into a particular final state of the projectile product is given by

\[ \frac{d\sigma}{d\Omega} = \sum_i p_i \left( \frac{d\sigma}{d\Omega} \right)_i. \]  

**Critical and Rainbow Angles**

As discussed early, for a two state-system (see Fig. 3), there are two possible paths that the system can follow for electron capture, resulting in a double-branched angle deflection \( \theta(b) \), as shown in Fig. 6. The upper branch of the deflection function corresponds to the projectile trajectory followed by capture on the way in, while the lower branch pertains to the trajectory followed by capture on the way out. The two
branches meet at a critical angle $\theta_c$, which corresponds to capture at an impact parameter equal to the crossing radius $R_x$. On the basis of the semi-classical two-state scattering model, the critical angle $\theta_c$ has been estimated by assuming that capture occurs at a localized curve crossing between the potential energy curves for the entrance and exit channels.

Figure 6. Typical deflection function for a two-state collision process.

For small laboratory scattering angles, $\theta_c$ is given by (Cocke et al., 1987)

$$\theta_c = \frac{Q}{2E_o}, \quad (2.62)$$
where $Q$ is the energy gain of the reaction channel and $E_0$ is the initial kinetic energy of the projectile. This angle separates the events scattered at smaller angles due to capture on the way out and events scattered at larger angles due to capture on the way in.

At smaller internuclear distances, inside the crossing radius, there are usually exit reaction channels with a higher $Q$-value than the dominant exit channel which behave adiabatically at the crossing with the entrance channel. Therefore, the entrance channel is not flat but promoted to a repulsive potential energy curve inside the active crossing. This promotion causes the lower branch of the deflection function to rise at small angles, producing a maximum in the differential cross section (i.e., $d\sigma/d\theta \to \infty$) at a scattering angle $\theta_r$ as shown in Fig. 6. This rainbow angle $\theta_r$ which corresponds to the smallest angle for which two impact parameters result in the same scattering angle.

**Reaction Window**

The important curve crossing between the diabatic potential energy curves associated with the entrance channel and the various exit channels are those which occur at moderate internuclear separations, where the probability for single-electron capture is large. This range of intermediate radii (3-10 a.u) is the so-called “reaction window” for the electron capture process. Taulbjerg (1986) has found that the position of the reaction window for any collision system depends mainly on the collision energy of the projectile. When the collision energy is reduced, the adiabaticity at the inner crossing becomes increasingly pronounced, while the transition probability at a distant crossing becomes larger. Therefore, the reaction
window shifts toward larger internuclear separations if the collision energy is reduced and vice versa.

In most cases, the location of the reaction window is calculated as a function of the internuclear separation. This location is then compared to the crossing radii of specific final states. Those crossing radii falling within the reaction window are expected to have the largest cross section. It is also possible to find the location of the reaction window in terms of the Q-values of the final states which will give a qualitative interpretation of the relative importance of each final state.
CHAPTER III

EXPERIMENTAL PROCEDURE

In atomic collisions many processes leave the neutral target atom/molecule positively charged as it loses to the projectile or to the continuum one or more of its electrons. This new ion is called a recoil ion. In this work the recoil ions were produced in a recoil-ion source after a fluorine ion beam from the Western Michigan University tandem Van de Graaff accelerator bombarded helium target gas. The recoil ions were used as slow projectile ions in low energy ion-molecule studies.

In this chapter we describe the production of the fluorine ion beam from the tandem accelerator, the differential energy–gain spectrometer, and our data acquisition procedure.

Production of the Fluorine Beam

A general schematic of the Western Michigan University tandem Van de Graaff accelerator is shown in Fig. 7. This accelerator facility has two negative ion sources: a source of negative ions by cesium sputtering (SNICS) and a direct extraction negative ion exchange source. The SNICS ion source, which makes negative ions from solids, was used to produce a fluorine ion beam for the work described here. Inside the SNICS, the cesium boiler and the cesium valve are heated so that the cesium vapor flows into the ion source. After cesium atoms are ionized by contact with the hot tungsten coil, they are attracted to the sputter cathode which is
packed with CaF₂ and held at 6 kV negative with respect to the ionizer. The energetic cesium ions sputter atoms from the surface of the cathode.

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Figure 7. Schematic drawing of the Western Michigan University tandem Van de Graaff accelerator and associated beam lines (S. M. Ferguson 2005).
A number of these sputtered fluorine atoms collide with cesium atoms near the cathode, capture an electron and become negative ions. These ions are repelled by the cathode and accelerated towards an extraction electrode with an acceleration voltage of -27 kV and subsequently towards a final focus electrode, which is held at ten kV. Negative Fluorine ions (q = -1) are analyzed by a 20° inflection magnet and focused by an einzel lens into the low energy end of the accelerator tube. Since this accelerator is a tandem, the negative ions are accelerated towards the positive terminal voltage, set at approximately 5 MV in this instance, where electrons are stripped off by a low density oxygen gas and the ions become positively charged ions. The ions are then repelled by the positive terminal voltage and accelerated a second time thereby gaining a total kinetic energy \((Q + 1)V\), where \(V\) is the positive voltage on the terminal and \(Q\) \((Q = 1, 2, \ldots)\) is the charge state of the positive ions emerging from the striper gas. After the beam leaves the high-energy end of the accelerator, it is focused on a set of defining slits to form an object for the analyzing magnet. The analyzing magnet bends the beam through a 90° angle and forms an image at the second set of slits. The strength of the field in the analyzing magnet is set to select the energy and the charge state of the ions, which reach the target. The currents produced by the portion of the beam striking the image slits is converted into a signal which can also be fed back to the corona system to stabilize the terminal voltage. Finally, the ion beam is directed into the target room through the selected atomic physics beam line using a switching magnet. The selected beam is collimated by a set of four-jaw slits and guided to the recoil ion source, where doubly charged helium ions are produced. For convenient ion current tuning, a small Faraday cup located behind the recoil ion source was used (see Fig. 8). Typical beam currents collected by the Faraday cup were between 0.5 and 1 µA.
Differential Energy-Gain Spectrometer

The differential energy–gain spectrometer described here was used to study low energy electron capture processes. A schematic illustration of the experimental apparatus is shown in Fig. 8. It consists of a recoil ion-source, analyzing magnet, deflecting plates, a target collision cell, electrostatic analyzer, and a detector.

Figure 8. Schematic illustration of the experimental apparatus. Recoil ion source, double focusing magnet, target cell, electrostatic energy analyzers, channeltrons, and position sensitive channel plate detector.
Recoil-Ion Source

The recoil-ion source is made up of a collision chamber, a pusher, a gas nozzle, and two lenses (L₁ and L₂). The helium gas atoms flowed into the source through a 3 cm long copper nozzle with an inside diameter of 120 microns, which was placed at the center between the pusher and L₁. The gas pressure in the recoil ion source was adjusted until the pressure of the main chamber was raised to ~ 4.5×10⁻⁶ Torr from the background pressure of ~ 3.5×10⁻⁶ Torr.

A well-collimated beam of 25-MeV F⁺ (in this case) was collected by a Faraday cup after it passed through the collision chamber which has entrance and exit apertures of 2.5 mm and 3 mm in diameter, respectively. Slow recoil ions of He⁺ and He²⁺ formed in the ion source were extracted perpendicular to the pump beam with an acceleration voltage \( V_{\text{acc}} \), which is equal to the voltage applied on the pusher, through a 2.5 mm diameter aperture in L₁ and 4 mm in L₂, under the influence of a potential field set up by positive voltages imposed to the pusher and lenses L₁ and L₂. The recoil ion beam extracted from the recoil source was focused by an einzel lens into the entrance aperture of an 180° double-focusing analyzing magnet, of radius 11.5 cm, where mass-to-charge selection of the ions was accomplished. Following momentum analysis, the ion beam was guided with the aid of horizontal and vertical parallel deflection plates into the entrance of 5.56 mm-long collision cell which has entrance and exit apertures of 1 mm and 2 mm in diameter, respectively. The collision cell pressure was monitored by noting an increase in the background pressure, when no target gas was admitted, in the main chamber from ~ 4.5×10⁻⁶ Torr to ~ 5.5×10⁻⁶ Torr. As the beam passes through the gas cell, a fraction of the incident particles undergo charge exchange with the target gas.
**Electrostatic Analyzer**

The scattered ions composed of He$^+$ and He$^{2+}$ were electrostatically energy analyzed and detected by a particle detector. Two types of the electrostatic analyzer, namely, a 90° double-focusing analyzer equipped with a one-dimensional position sensitive channel-plate detector (DFA, right insert in Fig. 8) and a 45° parallel-plate analyzer equipped with two channeltrons (PPA, left insert in Fig. 8), were used separately to perform the measurements of the translational energy-gain spectra for single-electron capture by He$^{2+}$ ions from O$_2$, H$_2$O, CO$_2$, N$_2$, and NH$_3$.

**90° Double-Focusing Analyzer (DFA)**

A 90° double-focusing electrostatic analyzer was used to analyze the energy of the projectile ions that had undergone capture. These ions were scattered through a nominal angle $\theta$ into a solid angle of about $3 \times 10^{-3}$ sr. The scattering angle $\theta$ is selected by means of aperture A1 (1mm Diameter) located in front of the DFA.

The voltage applied across the plates of the DFA is related to the energy of the transmitted projectile ions by

$$E = q V_{\text{acc}} = q k V$$  \hspace{1cm} (3.1)$$

where $q$ is the atomic charge of the projectile ion and $k$ is the DFA constant and is given by (Pool et al., 1972/73)

$$k = \frac{2R_i R_o}{R_o^2 - R_i^2}$$  \hspace{1cm} (3.2)$$

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with $R_i$ and $R_o$ are the radii of the inner and outer electrodes of the DFA, respectively.

For the present DFA, the measured values of the inner and outer radii are 27.6 and 42.4 mm, respectively. Thus the calculated value of $k$ is 2.3, while the measured value was determined from the slope of a curve of the $V_{acc}$ plotted as a function of DFA Voltage (see Fig. 9) and found to be 2.6.

![Graph showing linear relationship between acceleration voltage $V_{acc}$ and DFA voltage (V). The slope is equal to the analyzer constant $k$.](image)

Figure 9. Schematic diagram representing the linear relationship between acceleration voltage $V_{acc}$ and DFA voltage (V). The slope is equal to the analyzer constant $k$.

The measured energy resolution ($\Delta E$) of DFA for a 100 eV He$^{2+}$ projectile beam (direct beam) was found to be 0.98 eV as determined from the full width at half maximum (FWHM) of the energy distribution of the direct beam as shown in Fig. 10.
Figure 10. Energy resolution of the DFA. The full width at half maximum (FWHM) for the 100 eV He$^{2+}$ projectile beam is 0.98 eV.

The analyzed ions were then detected by a one-dimensional position sensitive channel-plate detector located at the focal plane of the DFA. The detector assembly was composed of two 3.25 cm diameter microchannel plates (MCPs) preceded a position-sensitive anode (PSA). The voltage across the front MCP was about -1800 V, while the rear MCP was grounded. The detector operates in the following manner. When an ion strikes the front channel plate the resulting electron cascade from the MCPs was accelerated towards and collected by the anode. The charge gathered by the PSA was used to determine the position of events along a single dimension. Electrodes on either side of the resistive anode collect fractions of total charge deposited. The larger the fraction of the charge collected at an electrode, the closer
the event location was to that electrode. The relative position of an event is then
determined by the ratio between the resulting voltage pulse at one electrode and the
sum of the voltage pulses at both electrodes, that is (Kamber and Cocke, 1991)

\[ X = \frac{V_U}{V_U + V_L} \]  

where \( X \) is the relative position along the PSA axis, and \( V_U \) and \( V_L \) are the voltage
pulse heights at the upper and lower electrodes, respectively (see Fig. 14).

**45° Parallel-Plate Electrostatic Analyzer (PPA)**

A 45° parallel-plate analyzer was mounted after the collision cell instead of
DFA to analyze the energy, ranged from 100 eV to 1600 eV, of the scattered ions that
had undergone capture at forward scattering angle. When the voltage across the
analyzer set to zero, the scattered ions were made to pass through the analyzer and
detected by channeltron 1 (see Fig. 11). For energy analysis, the scattered ions were
detected by a channeltron 2 with the correct voltage across the analyzer (see below).
A uniform electric field is applied between the two parallel plates, where the upper
plate was kept at positive potential, while the lower plate was grounded. Positive ions
entered the field at 45° through the first slit, traveling in parabolic paths, were
refocused upon the exit slit, and then detected by channeltron 2.

The resolution of the PPA depends on the widths of the entrance and exit slits
and the separation distance between the slits. An approximate theoretical resolution
given by Harrower (1955) was used to estimate the energy resolution of our analyzer
for the case of equal entrance and exit slits, that is
where $\Delta E$ is the range of energy, which ions at an average energy $E$ may posses and still pass through the two slits of the analyzer with a given value of a deflecting voltage $V_d$, $X_0$ is the separation between slits, and $\Delta S$ is the slit width.

\[
\frac{\Delta E}{E} = \frac{2\Delta S}{X_0}
\] (3.4)

Figure 11. Diagram of the parallel-plate electrostatic analyzer (PPA).

For the present analyzer, we used $X_0 = 106$ mm and $\Delta S = 0.5$ mm, then

\[
\frac{\Delta E}{E} = 0.94\% 
\] (3.5)
The energy resolution of PPA was measured by changing the applied voltage on the upper plate and measuring the corresponding counts for a fixed time at channeltron 2. A typical energy resolution spectrum is shown in Fig. 12.

Figure 12. Energy resolution of the PPA. The full width at half maximum (FWHM) for the 201 eV He\textsuperscript{2+} projectile beam is 1.9 eV.

The deflecting voltage to be used between the parallel plates to deflect a beam of energy $E = q V_{\text{acc}}$ entering the entrance slit at an angle of $\theta = 45^\circ$ is given by (Harrower, 1955)

$$V_D = 2\frac{d}{X_o} V_{\text{acc}}$$

(3.6)
where d is the separation between the plates (d = 34.14 mm, in our case). Thus, Eq. (3.6) reduces to

\[ V_D = 0.64 V_{\text{acc}} \] (3.7)

Figure 13 shows that the relation between the acceleration voltage and the deflecting voltage is linear. The slope of this curve is equal to the parallel-plate analyzer constant (in this case k = 0.62). The discrepancy between the theoretical and the measured values for the analyzer constant could be due to the inaccuracies in the measurement of the distances, acceleration voltage, and deflecting voltage.
Data Acquisition

An electronic block diagram for data acquisition is shown in Figure 14. The output signals from each electrode of the position sensitive anode (PSA) were first amplified by using pre-amplifiers (Ortec model 109A), amplified by using amplifiers (Ortec model 451), and then summed using a dual sum/invert amplifier (DSI, Tennelec model TC253). The signal, along with the signal pulse from the lower electrode, were then fed to the energy and position inputs of the position sensitive detector analyzer (PSD Analyzer, Ortec model 466), respectively.

The voltage signals were divided within the PSD, producing a voltage signal whose height was proportional to the location of the incident ion's position on the PSA. These analog signals of the position output were directed into an analog-to-digital converter (ADC), which was gated by the counter timer, preset for some maximum number of counts of integrated fast beam current accumulated by the Faraday cup. The pulse rate of the output signal (energy output of the PSD) was measured using a ratemeter (RM, Ortec model 744). Digital position signals from the ADC go to the input module of the CAMAC crate. A STARBUST interface module was used to transfer data to a MicroVAX computer system enabling conversion from position distribution to energy distribution information.

The detector was periodically calibrated by positioning the direct beam at different locations by varying the applied voltage across the DFA. Spectra were gathered at each voltage in order to obtain a calibration curve (see Fig. 15). However, we minimize the distortion due to small changes in linearity near the edges of the PSA by using only the central portion of the PSA.
Figure 14. Electronic block diagram for angular distribution measurements.
Figure 15. Position of the projectile peaks as a function of the DFA voltages.

A separate electronic configuration was used for scanning the voltage across the parallel-plate analyzer and the current of the 180° double-focusing magnet. This electronic block diagram is illustrated in Fig. 16. KSCAN, a program written in FORTRAN for the VAX WORKSTATION, controls the magnetic current and the voltage applied to the parallel-plate analyzer. Commands and data are transferred between the VAX workstation and crate controller over a serial interface. The crate controller is a PDP 11/83 microprocessor based STARBUST unit (Creative Electronic Systems S.A.). It has been programmed to accept and execute the standard set of CAMAC commands. The magnetic current and parallel-plate voltage ($V_D$) are set by commands to a DAC (digital-to-analog converter). The DACs have 12 bits, so
their resolution is 0.02%. The digitized integrated beam current and channeltron counts are read from the scalars. Using KSCAN the operator can choose to scan stepwise either the magnet or the parallel-plate analyzer. Energy-gain spectra were recorded by scanning the deflecting voltage $V_D$ applied to the parallel-plate analyzer controlled by one of the DACs. The integrated main beam current from the Faraday cup was used to normalize each scan step.

Figure 16. Electronic block diagram for recoil ion charge state analysis and parallel plate voltage scans of reaction products.
CHAPTER IV

DATA ANALYSIS

In this chapter, we describe the procedure used to obtain charge state spectrum for the recoil ions produced in the recoil ion source and the translational energy-gain spectra for single electron capture by He\(^{2+}\) ions from O\(_2\), H\(_2\)O, CO\(_2\), N\(_2\), and NH\(_3\) measured at selected projectile scattering angles and different impact energies. In addition, we discuss the determinations of the differential and absolute total cross section.

Charge-State Spectroscopy

In order to analyze the ion beam produced in the ion source, it is necessary to separate out the components of different charges and to focus each of these discrete beams so that their intensities can be measured. This is usually accomplished by the use of magnetic field in a direction perpendicular to the direction of ion motion. Figure 17 shows a charge-state spectrum obtained by varying the magnet current of the 180°-double focusing magnet. He\(^{q+}\) ions (where \(q = 1\) and 2) are obtained with intensities sufficient for energy-gain studies. The main peaks correspond to \(^4\)He\(^{q+}\), whereas the small peak corresponds to H\(^+\). However, the identification of the charge state of each peak was achieved by plotting the square root of the mass to charge ratio versus the magnet current for each peak (see Fig. 18). The linearity of this plot was used to verify the correct identification of each charge state.
Figure 17. He\textsuperscript{+} recoil ion charge state spectrum for 25 MeV F\textsuperscript{+} beam incidents on helium gas.

Figure 18. Mass to charge ratio of helium recoil ions plotted as a function of the magnet current.
Energy Analysis

The expression, given below, for calculating the energy gain $Q$ of the projectile following single electron capture in terms of the acceleration voltage and the voltage applied across the electrostatic analyzer was used for both electrostatic analyzers (DFA and PPA).

The energy gain $Q$ is given by (Kamber et al., 1987)

$$Q = \left[ \frac{qV}{qV_o} - 1 \right] qV_{\text{acc}}$$

(4.1)

where $V_o$ and $V$ are the applied voltage to the analyzer, either DFA or PPA, for which the primary beam and ions undergone capture are passed, respectively, and $q$ and $q'$ are the atomic charges of the projectile before and after the collision, respectively. However, for DFA the energy gain $Q$ can be expressed in terms of the position of projectile peak as follows (Kamber et al., 1987)

$$Q(x) = \left[ \frac{(S(0) - S(x))}{(FV_o - S(0) + S(x))} \right] qV_{\text{acc}}$$

(4.2)

where $S(0)$ and $S(x)$ are the positions of the main peak of the uncharged exchanged projectile and product ions respectively, and $F$ is the slope of a curve of the position of the projectile peak plotted as a function of DFA voltage (see Fig. 19).

For convenience of analysis and discussion, ionic energy levels and associated energy defect ($\Delta E$) values for single-electron capture reaction channels of the collision systems studied in this thesis, are listed in tables 1 through 5. The projectile
outgoing reaction channels observed in the collision process were identified by comparing the measured energy gain $Q$ from the translational energy-gain spectra with the calculated $Q$-values from Eqs. (2.2) to (2.4).

Figure 19. A typical calibration showing channel number versus DFA voltage.

The $Q$-value corresponding to each of the observed states is represented by a vertical line in the energy-gain spectrum. The energy levels used in calculating the energy defect were taken from published tables. The energies ($\Delta E$) were calculated assuming that the molecular targets and their product ions were at the lowest vibrational levels ($\nu = 0$) and for some cases at different vibrational levels (see table 6).

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Table 1

Single-electron capture reaction channels for collisions of He\(^{2+}\) ions with O\(_2\).

<table>
<thead>
<tr>
<th>Reactant and Initial State</th>
<th>Products and Final States</th>
<th>(\Delta E) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(^{2+}) + O(_2) ((X^3\Sigma_g^-))</td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^+) ((X^2\Pi_g))</td>
<td>42.33</td>
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<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=2)) + O(_2^+) ((X^2\Pi_g))</td>
<td>1.53</td>
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<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((X^1\Sigma_g)) + e</td>
<td>18.9</td>
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<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Sigma_u)) + e</td>
<td>16.34</td>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((A^3\Sigma_u)) + e</td>
<td>14.8</td>
</tr>
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<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Delta_u)) + e</td>
<td>13.83</td>
</tr>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Pi_u)) + e</td>
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</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Sigma_u)) + e</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((B^3\Pi_u)) + e</td>
<td>12.3</td>
</tr>
<tr>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((B^3\Sigma_u)) + e</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^1\Sigma_u)) + e</td>
<td>11.64</td>
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<tr>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^1\Pi_u)) + e</td>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^1\Delta_u)) + e</td>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((W^1\Delta_u)) + e</td>
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</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Delta_g)) + e</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Pi_u)) + e</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Pi_u)) + e</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^1\Sigma_u)) + e</td>
<td>6.9</td>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^1\Delta_g)) + e</td>
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<td>(\rightarrow) He(^+) ((n=1)) + O(_2^{++}) ((^3\Sigma_g)) + e</td>
<td>4.45</td>
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</tbody>
</table>

Source: (1) WWW homepage of the NIST Atomic Spectra Database

(http://physics.nist.gov/).

(2) Leputsch et al., (1997).


(4) Beebe et al., (1976).
Table 2

Single-electron capture reaction channels for collisions of He$^{2+}$ ions with CO$_2$.

<table>
<thead>
<tr>
<th>Reactant and Initial State</th>
<th>Products and Final States</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^{2+}$ + CO$_2$ ($^1\Sigma_g$)</td>
<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($X^2\Pi_g$)</td>
<td>40.6</td>
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<td>$\rightarrow$ He$^+$ (n=2) + CO$_2$ $^+$ ($X^2\Pi_g$)</td>
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<td>$\rightarrow$ He$^+$ (n=2) + CO$_2$ $^+$ ($A^2\Pi_u$)</td>
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<td>$\rightarrow$ He$^+$ (n=2) + CO$_2$ $^+$ ($B^2\Sigma_u$)</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($X^3\Sigma_g$) + e</td>
<td>16.7</td>
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<tr>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($A^1\Delta_g$) + e</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($B^1\Sigma_u$) + e</td>
<td>14.9</td>
</tr>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($C^1\Sigma_u$) + e</td>
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<td></td>
<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Pi_u$) + e</td>
<td>13.5</td>
</tr>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Pi_u$) + e</td>
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</tr>
<tr>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Sigma_u$) + e</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Pi_u$) + e</td>
<td>11.9</td>
</tr>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Pi_u$) + e</td>
<td>11.6</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Delta_u$) + e</td>
<td>11.4</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Pi_u$) + e</td>
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<td>8.82</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Sigma_u$) + e</td>
<td>8.76</td>
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<td>8.71</td>
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<td>7.38</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Delta_u$) + e</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Sigma_u$) + e</td>
<td>5.09</td>
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<td>$\rightarrow$ He$^+$ (n=1) + CO$_2$ $^+$ ($\Sigma_u$) + e</td>
<td>4.67</td>
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</tbody>
</table>

Source: (1) WWW homepage of the NIST Atomic Spectra Database
(http://physics.nist.gov/).

(2) Millie et al., (1986).

Table 3

Single-electron capture reaction channels for collisions of He\(^{2+}\) ions with N\(_2\).

<table>
<thead>
<tr>
<th>Reactant and Initial State</th>
<th>Products and Final States</th>
<th>(\Delta E) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(^{2+}) + N(_2) ((X^1\Sigma_g^-))</td>
<td>(\Rightarrow) He(^+) (n=1) + N(_2^+) ((X^2\Sigma_g^+))</td>
<td>38.82</td>
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<td></td>
<td>(\Rightarrow) He(^+) (n=2) + N(_2^+) ((X^2\Sigma_g^+))</td>
<td>-1.98</td>
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<td>(\Rightarrow) He(^+) (n=1) + N(_2^+) ((A^2\Pi_u))</td>
<td>37.68</td>
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<td>(\Rightarrow) He(^+) (n=2) + N(_2^+) ((A^2\Pi_u))</td>
<td>-3.12</td>
</tr>
<tr>
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<td>(\Rightarrow) He(^+) (n=1) + N(_2^+) ((B^2\Sigma_u^+))</td>
<td>35.64</td>
</tr>
<tr>
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<td>(\Rightarrow) He(^+) (n=2) + N(_2^+) ((B^2\Sigma_u^+))</td>
<td>-5.16</td>
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<tr>
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<td>(\Rightarrow) He(^+) (n=1) + N(_2^{++}) ((X^1\Sigma_g^-)) + e</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>(\Rightarrow) He(^+) (n=1) + N(_2^{++}) ((a^3\Pi_u)) + e</td>
<td>10.5</td>
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<td></td>
<td>(\Rightarrow) He(^+) (n=1) + N(_2^{++}) ((b^1\Pi_u)) + e</td>
<td>10.4</td>
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<tr>
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<td>(\Rightarrow) He(^+) (n=1) + N(_2^{++}) ((c^1\Delta_u)) + e</td>
<td>10.2</td>
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<tr>
<td></td>
<td>(\Rightarrow) He(^+) (n=1) + N(_2^{++}) ((c^1\Sigma_u^-)) + e</td>
<td>8.9</td>
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<tr>
<td></td>
<td>(\Rightarrow) He(^+) (n=1) + N(_2^{++}) ((A^3\Pi_u)) + e</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Source: (1) WWW homepage of the NIST Atomic Spectra Database
(http://physics.nist.gov/).
(2) Leutsch et al., (1997).
Table 4

Single-electron capture reaction channels for collisions of He\(^{2+}\) ions with H\(_2\)O.

<table>
<thead>
<tr>
<th>Reactant and Initial State</th>
<th>Products and Final States</th>
<th>(\Delta E) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(^{2+}) + H(_2)O ((^1)A(_1))</td>
<td>He(^+) (n=1) + H(_2)O(^+) ((^2)B(_1))</td>
<td>41.8</td>
</tr>
<tr>
<td></td>
<td>He(^+) (n=2) + H(_2)O(^+) ((^2)B(_1))</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>He(^+) (n=1) + H(_2)O(^+) ((^2)B(_1)) + e</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>He(^+) (n=1) + H(_2)O(^+) ((^1)A(_1), (^2)B(_1)) + e</td>
<td>12.4-13.7</td>
</tr>
<tr>
<td></td>
<td>He(^+) (n=1) + H(_2)O(^+) ((^2)A(_1)) + e</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Source: (1) WWW homepage of the NIST Atomic Spectra Database (http://physics.nist.gov/).

(2) Reutt et al., (1986).

(3) Richardson et al., (1986).
Table 5

Single-electron capture reaction channels for collisions of He^{2+} ions with NH_3.

<table>
<thead>
<tr>
<th>Reactant and Initial State</th>
<th>Products and Final States</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He^{2+} + NH_3 (X^1A_1)</td>
<td>→ He^+ (n=1) + NH_3^+ (X^2A_1)</td>
<td>44.22</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=2) + NH_3^+ (X^2A_1)</td>
<td>3.417</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=2) + NH_3^+ (^2E)</td>
<td>-2.2</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=1) + NH_3^{2+} (X^1A_2) + e</td>
<td>20.72</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=1) + NH_3^{2+} (^1E)   + e</td>
<td>17.36</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=1) + NH_3^{2+} (^3A_2) + e</td>
<td>12.84</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=1) + NH_3^{2+} (^1A_1) + e</td>
<td>10.41</td>
</tr>
<tr>
<td></td>
<td>→ He^+ (n=1) + NH_3^{2+} (^1A_1) + e</td>
<td>7.85</td>
</tr>
</tbody>
</table>


Table 6

The calculated energies $\Delta E$ for the $\text{NH}_3(X^1A_1, 0) \rightarrow \text{NH}_3^+(X^2A_1, v)$ transitions and the calculated populations of vibrational states of $\text{NH}_3^+$. 

<table>
<thead>
<tr>
<th>Final State</th>
<th>Vibrational Level ($v$)</th>
<th>$\Delta E$ (eV)</th>
<th>Calculated Populations of Vibrational States of $\text{NH}_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rightarrow \text{He}^+ (n=2) + \text{NH}_3^+ (X^2A_1, v)$</td>
<td>0</td>
<td>3.417</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.306</td>
<td>0.127</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.188</td>
<td>0.293</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.067</td>
<td>0.507</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.941</td>
<td>0.725</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.811</td>
<td>0.897</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.679</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.544</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.406</td>
<td>0.931</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.266</td>
<td>0.813</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.123</td>
<td>0.668</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1.979</td>
<td>0.522</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.833</td>
<td>0.389</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.686</td>
<td>0.276</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>1.537</td>
<td>0.189</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.387</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>1.235</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>1.082</td>
<td></td>
</tr>
</tbody>
</table>

Source: (1) Ågren et al., (1982).
The errors in the measured Q-value are mainly caused by the least-square fit to the calibration curve, the channel number versus the applied voltage across the analyzer in the case of DFA, and the stability of the voltage applied across the analyzer. In this respect, errors in the energy gain scale were always less than ±1 eV.

**Differential Cross Sections**

The differential cross sections \( \frac{d\sigma}{d\Omega} \) were determined using the translational energy gain technique, by finding the areas under the peaks (total intensity) in the energy gain spectrum obtained at different projectile laboratory scattering angles. The areas were calculated using Gaussian fitting of fixed positions and widths to the observed spectra after normalizing each spectrum to the total amount of the pump beam charge collected at the Faraday cup.

**Total Cross Sections**

In order to measure the absolute total cross sections for single-electron capture by doubly charged helium ions from \( \text{O}_2, \text{H}_2\text{O}, \text{CO}_2, \text{N}_2, \) and \( \text{NH}_3 \) molecules, the aperture A1 located in front of the DFA (see Fig. 8 in Chapter III) was removed. This provides an angular acceptance of almost ±10°.

Measurements of the absolute total cross sections were carried out with projectile energies ranged from 100 to 1600 eV for \( \text{He}^{2+} \) on \( \text{O}_2, \text{H}_2\text{O}, \text{CO}_2, \text{N}_2, \) and \( \text{NH}_3 \). For each particular projectile energy, measurements were taken at least for three different gas pressures. The molecular target pressure was sufficiently low to ensure that single-collision conditions satisfied in the interaction region. Maintaining a
constant pressure within the gas cell was accomplished by means of an automatic valve controller. The pressure was monitored by an MKS Baratron type 690A capacitance manometer which sent a signal to the valve controller (to open or to close a valve to the gas cell) whenever the pressure deviated from the desired set point value. In addition, the target pressure used in all measurements was \( \leq 3 \) mTorr.

![Graph showing relative intensities versus gas cell pressure for 200 eV He\(^{2+}\) on O\(_2\).](image)

**Figure 20.** Plot of relative intensities versus the gas cell pressure for 200 eV He\(^{2+}\) on O\(_2\).

The measured spectra were analyzed by integrating the number of counts in each peak and the relative intensities, \( I/I_0 \), where \( I_0 \) is the number of the incoming He\(^q^+\) ions in an unit of time and \( I \) is the number of He\(^{(q-1)^+}\) ions produced in the same time interval, were measured as a function of the collision gas pressure after normalizing to the total pump amount beam charge collected at the Faraday cup. By
plotting relative intensities versus the gas cell pressure, one can verify the linear dependence of the measured relative intensities with respect to the gas cell pressure (see Fig. 20). A linear least-squares fit to the plotted data was used to obtain the slope \((I/I_0)/P\) from which the cross sections were determined.

To obtain the absolute cross section values, the data were analyzed as described immediately below. The number of the detected particles following passage through the target region is given by

\[
I = I_0 \sigma T
\]  

(4.3)

where \(I_0\) is the number of incident particles in atoms, \(\sigma\) is the cross section in \(\text{cm}^2\), and \(T\) is the target thickness in atoms/cm\(^2\) which can be expressed as

\[
T = C_0 P L
\]  

(4.4)

where \(C_0 = 3.3 \times 10^{13}\) atoms/mTorr cm\(^3\), \(P\) is the gas pressure in mTorr, and \(L\) is the length of the gas cell (5.65 mm). Combining Eqs. (4.3) and (4.4) gives

\[
\sigma = 5.41 \times 10^{-14} \frac{I/I_0}{P}
\]  

(4.5)

where \((I/I_0)/P\) represents the slope of the relative intensities versus pressure plot (Fig. 20) which can be obtained directly from the linear least-squares fit. The experimental uncertainties for the absolute values of the total cross sections were obtained by the quadratic sum of the statistical deviations, determination of target thickness, and counting efficiency and were less than 12 %.
CHAPTER V

RESULTS AND DISCUSSION

In this chapter, measurements for single-electron capture processes in collisions of He\(^{2+}\) projectile ions with O\(_2\), H\(_2\)O, CO\(_2\), N\(_2\) and NH\(_3\) molecular targets are presented and discussed. The measurements are classified according to translational energy-gain spectra, differential cross sections, and energy dependence total cross sections.

**Translational Energy-Gain Spectra**

**He\(^{2+}\) + O\(_2\) Collisions**

Figure 21 shows the translational energy-gain spectra for the formation of He\(^+\) ions from the reaction of 100 eV He\(^{2+}\) ions with O\(_2\) at different projectile laboratory scattering angles. At 0° scattering angle, two peaks are clearly resolved. The dominant peak is due to dissociative single-electron capture by the projectile He\(^{2+}\) ions into the n=1 state of the He\(^+\) product ions with simultaneous ionization of the target product (i.e., DTI) via the reaction channel

\[
\text{He}^{2+} + \text{O}_2 (X^3\Sigma_g^-) \rightarrow \text{He}^+ (n=1) + \text{O}_2^{2+} + e. \quad (5.1)
\]

Energetically, O\(_2^{2+}\) is identifiable with the production in the excited state \(^1\Pi_u\), which
lies about 10-11 eV above the ground state \( \left( X \ \Sigma_g^+ \right) \), which dissociates into the ground state ionic pair \( O^+ (4S) + O^+ (4S) \).

Figure 21. Translational energy-gain spectra for single-electron capture by 100 eV \( \text{He}^{2+} \) ions from \( \text{O}_2 \) at different projectile laboratory scattering angles.
The small peak centered around $Q = 1.5$ eV is due to non-dissociative single-electron capture (SEC) into the $n=2$ states of $\text{He}^+$ with production of $O_2^+$ in the ground state $(X^2\Pi_g)$. As the scattering angle is increased, the DTI process remains dominant, but the relative importance of the SEC process strongly decreases. This indicates that the angular distribution for the SEC process is more strongly peaked in the forward direction than for a process associated with dissociative electron capture in the $\text{He}^{2+}$ - $O_2$ collisions. In dissociative transfer ionization processes, on the other hand, projectile ions are scattered into larger angles compared with pure single-electron capture because of a strong Coulomb repulsion between collision products after the collision. Furthermore, as the scattering angle is increased, a relative shift of about 1 - 2 eV in the energy gain of the DTI channel is observed going from a scattering angle of $0^\circ$ to $6^\circ$. This is attributed to the contributions from avoided crossings at smaller internuclear separations (larger Q values), which gradually become more important at large scattering angles. In general, at forward scattering angle, the large impact parameter collisions play an important role in the electron capture process since the avoided crossings at small internuclear separation cannot be reached and make small contribution. As the angle is increased, contributions from successively smaller internuclear separation regions make their appearance.

The electron capture probabilities (i.e., relative values only) for the reaction channels corresponding to DTI and SEC processes produced in $\text{He}^{2+}$ - $O_2$ collisions are displayed in Fig. 22. The electron capture probability is determined from the ratio of the area under each reaction channel to the total area of the spectrum. The areas under the DTI and SEC reaction channels were determined by fitting Gaussian peak shapes of fixed positions and widths to the measured spectra presented. Referring to Fig. 22, we see that the DTI reaction channel is a dominant process over the angular
range $0^\circ \leq \theta \leq 7.4^\circ$, and the probability for capture into this channel increases with increasing scattering angle. The figure also indicates that the $n=2$ states of He$^+$ produced in the SEC process are strongly forward scattered.

![Graph](image)

Figure 22. Probability of single-electron capture by 100 eV He$^{2+}$ ions from O$_2$ at different projectile laboratory scattering angles. ■, DTI; ●, SEC. Smooth lines are drawn to guide the eye.

The variation of the translational energy-gain spectra for single-electron capture processes as a function of collision energy for the He$^{2+}$ - O$_2$ collision system is illustrated in Fig. 23. For these measurements, we used a 45° parallel plate analyzer with an angular acceptance of about $\pm 8^\circ$. As can be seen, the relative importance of the SEC channel with respect to the DTI channel increases with increasing collision energy.
Figure 23. Translational energy-gain spectra for single-electron capture by He\(^{2+}\) ions from O\(_2\) at different collision energies.

In greater detail, the dependence of the cross section ratio \(\sigma(\text{DTI})/\sigma(\text{SEC})\) on the collision energy \((E_{\text{lab}})\), which is determined from the areas under the dissociative and non-dissociative reaction channels by fitting Gaussian peak shapes of fixed positions and widths to the measured spectra presented in Fig. 23, is displayed in Fig. 67.

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24 along with the recent measurements by Albu et al. (2004). While they both show the same monotonic decrease with energy, the present experimental results tend to be larger than those of Albu et al. (2004). This is because they performed their measurements using a hemispherical energy analyzer with an angular acceptance of about ± 0.5°.

Similar observations have been seen in single-electron capture by 2 - 8 keV He\(^{2+}\) ions from D\(_2\) (Martin et al., 1991) and H\(_2\) (Hodgkinson et al., 1995), and more recently by Kearns et al. (2001) in collisions of 0.8 - 4 keV He\(^{2+}\) ions with CO, in which the relative importance of the non-dissociative electron capture with respect to the dissociative electron capture increases with increasing collision energy.

![Graph](image)

Figure 24. The ratio \(\sigma(\text{DTI})/\sigma(\text{SEC})\) for single-electron capture by He\(^{2+}\) ions from O\(_2\) plotted versus collision energy E. ●, present work; ○, Albu et al. (2004).
To understand the SEC and DTI processes, we used the correlation diagrams of molecular orbitals (MO) and the corresponding potential curves to visualize the different capture mechanisms and to show the transition energies involved for the collision systems studied here. Figures 25 (a) and (b) show the molecular diagram and the corresponding potential curves, respectively, for the He\(^{2+}\) - O\(_2\) collision system.

![Correlation diagrams and potential curves](image)

**Figure 25.** (a) Correlation diagrams of molecular orbitals and (b) Corresponding potential curves for the He\(^{2+}\) - O\(_2\) system. Single-electron transitions populating the n = 1, 2, and 3 states of He\(^+\) ions are denoted by 1, 2, and 3, respectively. Dielectronic transitions populating the n = 1 state and the continuum state \(\varepsilon\) are denoted as (1,\(\varepsilon\)).

As seen in Fig. 25 (b), transitions into n = 2 occur at distances near 4.4 a.u. (see the arrow labeled 2) initiated by mechanisms treated by the Demkov model.

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Similarly, transitions into the \( n = 3 \) level of \( \text{He}^+ \) occur at about 3 a.u. (arrow labeled 3). It should be emphasized that Demkov-type transitions occur at locations where the potential energy difference is equal to twice the interaction matrix element \( V_{ij} \). This indicates that the \( \text{He}^+(n=2) \) formation proceeds via a single-electron process governed by the nucleus-electron interaction.

The population of the \( n = 1 \) state of \( \text{He}^+ \) occurs near \( R=2.5 \) a.u. as a result of a two-electron (dielectronic) process, where one electron is transferred into the MO correlated with the \( n = 1 \) level and another electron is ionized. This transfer ionization (TI) process is produced by the electron-electron interaction, where the potential energy, liberated by the transition into the deeply lying \( n = 1 \) orbital, is used to ionize another electron (the sum of potential energy changes is equal to zero) thereby, resulting in fragmentation of the \( \text{O}_2 \) molecule. In Fig. 25 (b), the dielectronic transitions, denoted as \( (1, \varepsilon) \), occur at the locations where the incident channel \( \text{He}^{2+} + \text{O}_2 \) crosses a series of potential curves \( \text{He}^+ + \text{O}_2^{2+}(\varepsilon) \). This results in the transfer of one electron of \( \text{O}_2 \) to the \( \text{He}^{2+} \) ion while a second electron is transferred into the continuum of \( \text{O}_2 \) with an energy \( \varepsilon \).

**He\(^{2+}\) + \text{H}_2\text{O} Collisions**

Figure 26 shows the translational energy-gain spectra obtained for single-electron capture by 100 eV \( \text{He}^{2+} \) ions from \( \text{H}_2\text{O} \) at different scattering angles. At 0° scattering angle, two peaks are clearly seen. The strongest peak at about 10 eV can be correlated with dissociative transfer ionization, i.e., single-electron capture into the \( n=1 \) state of the \( \text{He}^+ \) product ions with production of \( \text{H}_2\text{O}^{2+} \) into \( ^1\text{A}_1, ^1\text{B}_1 \) and \( 2^1\text{A}_1 \) states of \( \text{H}_2\text{O}^{2+} \) to produce \( \text{OH}^+ + \text{H}^+ \) (Richardson et al., 1986). The weaker peak at 1

70
eV corresponds to non-dissociative single-electron capture into He$^+$ (n=2) with production of H$_2$O$^+$ in the ground state (X $^2$B$_1$).

Figure 26. Translational energy-gain spectra for single-electron capture by 100 eV He$^{2+}$ ions from H$_2$O at different projectile laboratory scattering angles.

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As the scattering angle is increased, the dissociative transfer ionization channel remains dominant but the relative importance of non-dissociative single-electron capture into the n=2 states is strongly decreased. This indicates that the angular distribution for the SEC process is strongly peaked in the forward direction. In addition, another particularly interesting feature of the scattering angle dependence of single electron capture spectra is that, with increasing scattering angle, contributions from avoided crossings at smaller internuclear separations (larger Q values) become gradually more important, as one would expect.

Figure 27. Probability of single-electron capture by 100 eV He\textsuperscript{2+} ions from H\textsubscript{2}O at different projectile laboratory scattering angles. ■, DTI; ○, SEC. Smooth lines are drawn to guide the eye.
The electron capture probabilities for DTI and SEC processes produced in He$^{2+}$ - H$_2$O collisions are displayed in Fig. 27, where it is again demonstrated that the dissociative reaction channel is dominant over the angular range $0^\circ \leq \theta \leq 6^\circ$.

![Figure 27. Electron capture probabilities for DTI and SEC processes.](image)

Figure 27. Electron capture probabilities for DTI and SEC processes produced in He$^{2+}$ - H$_2$O collisions.

Figure 28. Translational energy-gain spectra for single-electron capture by He$^{2+}$ ions from H$_2$O at different collision energies.

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The observed translational energy-gain spectra for single-electron capture by He\(^{2+}\) ions from H\(_2\)O at 0° scattering angle and different collision energies are shown in Fig. 28. As the collision energy is increased, the contributions from the SEC process increase and become the dominant process at collision energies \(E \geq 800\) eV in agreement with the recent measurements of Seredyuk et al. (2005). Figure 29 displays the dependence of the cross section ratio \(\sigma(\text{DTI})/\sigma(\text{SEC})\) on the collision energy. It can be seen that the ratio decreases with increasing collision energy indicating that the SEC process becomes gradually more important than the DTI process.

![Graph showing the ratio of cross sections for DTI and SEC versus collision energy](image)

Figure 29. The ratio \(\sigma(\text{DTI})/\sigma(\text{SEC})\) for single-electron capture by He\(^{2+}\) ions from H\(_2\)O plotted versus collision energy \(E\).

The correlation diagrams of molecular orbitals (MO) and the corresponding potential curves for the single-electron capture in He\(^{2+}\) - H\(_2\)O collision are shown in

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Fig. 30. Again transitions into He\(^+\) (n=2) states occur at an internuclear distance of about 4 a.u. and are due to nucleus-electron interaction while, transitions into He\(^+\) (n=1) state occur at about 2 a.u. as a result of dielectronic process. Transitions can be explained using the Demkov and the Landau-Zener models as was done for O\(_2\) target.

![Diagram](image)

Figure 30. (a) Correlation diagrams of molecular orbitals and (b) Corresponding potential curves for the He\(^{2+}\)-H\(_2\)O System. Notations are the same as in Fig. 25.

He\(^{2+}\)+CO\(_2\) Collisions

Figure 31 shows the translational energy-gain spectra for the formation of He\(^+\) ions from the reaction of 100 eV He\(^{2+}\) ions with CO\(_2\) at different projectile scattering angles. The zero-degree spectrum shows only one broad peak centered at about 10
eV; this peak correlates with dissociative transfer ionization, due to single-electron capture into the n=1 state of He$^+$ ions with simultaneous ionization of the target-ion product. With an energy-gain of about 10 eV, the accessible states of CO$_2^{2+}$ may correspond to several singlet and triplet $\Sigma$, $\Pi$, and $\Delta$ states of $4\sigma_g^{-1}1\pi_g^{-1}$, and $1\pi_u^{-2}$ configurations whose calculated energies lie between 42.9 and 44 eV. These states dissociate into O$^+$ + CO$^+$ products (Millie et al., 1986).

Figure 31. Translational energy-gain spectra for single-electron capture by 100 eV He$^{2+}$ ions from CO$_2$ at different projectile laboratory scattering angles.
Figure 32. Translational energy-gain spectra for single-electron capture by He\(^{2+}\) ions from CO\(_2\) at different collision energies.

As the scattering angle is increased, the dissociative transfer ionization channel remains dominant. For a scattering angle of 5.2°, a long tail on the lower energy side of the dominant channel was observed. This is attributed to the formation
of CO$_2^{2+}$ ions into higher excited states with possible dissociation into C$^+$ + O$^+$ + O (Masuoka et al., 1996). These states were also detected at higher collision energies (see Fig. 32). No other experimental data are available for comparison.

Figure 33 shows the molecular diagram and the corresponding potential curves for the He$^{2+}$ - CO$_2$ collision system. It can be seen from the potential curves that the avoided crossings between the incoming molecular state and the outgoing states leading to He$^+$ formation are predicted to occur at an internuclear distance of about 2.3 a.u. Again, the transitions are due to the electron-electron interaction, as illustrated and treated by the Landau-Zener model.

![Figure 33](image)

Figure 33. (a) Correlation diagrams of molecular orbitals and (b) Corresponding potential curves for the He$^{2+}$ - CO$_2$ system. Notations are the same as in Fig. 25.
**He$^{2+}$ + N$_2$ Collisions**

In Fig. 34 are shown the translational energy-gain spectra of the product of He$^+$ ions by 100 eV He$^{2+}$ ions incident on N$_2$ at different projectile scattering angles. The shape and the peak position are almost the same as those for a CO$_2$ target.

Figure 34. Translational energy-gain spectra for single-electron capture by 100 eV He$^{2+}$ ions from N$_2$ at different projectile laboratory scattering angles.
Figure 35. Translational energy-gain spectra for single-electron capture by He$^+$ ions from N$_2$ at different collision energies.

The dominant peak in the zero-degree spectrum is due to the dissociative transfer ionization process. As the scattering angle is increased, the DTI channel remains dominant, but the relative importance of the reaction channels forming N$_2^{2+}$ remains dominant, but the relative importance of the reaction channels forming N$_2^{2+}$.
ions in higher excited states, with possible dissociation into $N^+ (3P) + N^+ (3P)$, increases, which is shown as a long tail at $Q \leq 7$ eV (Rogers et al., 1978). Furthermore, the DTI process is the dominant reaction observed over the entire collision energy region studied (see Fig. 35), in agreement with the measurements of Kobayashi et al. (1984) and Martin et al. (1991).

Figure 36 shows the molecular diagram and the corresponding potential curves for the $He^{2+} - N_2$ collision system. It can be seen from Fig. 36 (b) that the probability for electron capture is greatest where there is a crossing of the potential energy curves for the incoming and the out-going states, which occurs at an internuclear distance of about 2.2 a.u. Again, the transitions are due to the electron-electron interaction, as illustrated and treated by the Landau-Zener model.

Figure 36. (a) Correlation diagrams of molecular orbitals and (b) Corresponding potential curves for the $He^{2+} - N_2$ system. Notations are the same as in Fig. 25.
**He$^{2+}$ + NH$_3$ Collisions**

Figure 37 shows the translational energy-gain spectra obtained for single-electron capture by 100 eV He$^{2+}$ ions from NH$_3$ at different scattering angles. At 0° scattering angle, only one peak is observed which corresponds to SEC into the n=2 states of He$^+$ with production of NH$_3^+$ in the ground state (X $^2$A$_1$, $\nu$), where $\nu$ refers to a vibrational state of the target product. The vertical lines on the upper part of the figure represent the calculated energy gain values for the reaction producing NH$_3^+$ (X $^2$A$_1$, $\nu$) through the process

$$\text{He}^{2+} + \text{NH}_3 (X^1A_1, \nu = 0) \rightarrow \text{He}^+ (n=2) + \text{NH}_3^+ (X^2A_1, \nu).$$  (5.2)

Also shown are the relative populations of each vibrational level of NH$_3^+$ (X $^2$A$_1$, $\nu$). The populations were determined by fitting Gaussian peak shapes with fixed positions and widths equal to the experimental energy resolution to the measured spectra in Fig. 37. The value of the largest population has been normalized to the dominant peak observed in the spectrum. Comparison with the results of Fárník et al. (1995) at 70 eV shows good agreement with the present measurements. However, we were unable to resolve the vibrational states because of the low-energy resolution used in our measurements. It is interesting to note that the position of the peak is centered around $\nu = 7$, in agreement with the calculated populations (see Table 6 in Chapter IV). As the scattering angle is increased, the relative importance of the lower vibrational levels increases and the position of the peak is relatively shifted to $\nu = 4$ at $\theta = 4.1^\circ$. 

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Figure 37. Translational energy-gain spectra for single-electron capture by 100 eV He\textsuperscript{2+} ions from NH\textsubscript{3} at different projectile laboratory scattering angles. The vertical lines represent the relative populations of each vibrational level of NH\textsubscript{3}\textsuperscript{+} (X\textsuperscript{2}A\textsubscript{1}, v) ranging between v = 0 and 17; the vertical line at the highest value of ΔE corresponds to the lowest vibrational level of the NH\textsubscript{3}\textsuperscript{+} product (i.e., v = 0).

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Figure 38. Translational energy-gain spectra for single-electron capture by He$^{2+}$ ions from NH$_3$ at different collision energies. Smooth lines are drawn to guide the eye. Also shown are reaction windows calculated on the basis of a single-crossing LZ model (dashed curve) and the ECOB model (dotted curve).
In Fig. 38 are shown the translational energy-gain spectra obtained for single-electron capture by He$^{2+}$ ions from NH$_3$ at 0° scattering angle and collision energies of 0.1 keV, 0.2 keV, and 0.4 keV. Also shown are our calculated reaction windows, the range of Q values where the probability for SEC is large, using both a single-crossing Landau-Zener model (Landau, 1932, Zener, 1932, Oslo and Salop, 1976) and the extended version of the classical-over-barrier (ECOB) model (Niehaus, 1986). Calculated peak values have been normalized to our observed peak values in the energy spectrum. As the collision energy is increased, contributions from the lower vibrational states increase. This can be qualitatively understood with the LZ model, which predicts that with increasing collision energy, the position of the reaction window shifts towards states with a larger Q value. The reaction windows based on the single-crossing LZ model favor Q values larger than those observed and are positioned near $v \leq 5$. The reaction windows based on the ECOB model, on the other hand, accommodate the observed peaks and provide the best description of the observed spectra.

A study of the potential curves for the He$^{2+}$ - NH$_3$ collision system, shown in Fig. 39, indicates that the non-dissociative single-electron capture process is induced by a Demkov-type transition at an internuclear distance of about 6.3 a.u., which is dominated by the nucleus-electron interaction. However, the formation of $n = 3$ states of He$^+$ occurs at about 3 a.u., which was not observed since it is an endothermic process.
Differential Cross Sections

The measured differential cross sections for non-dissociative single-electron capture process by 100 eV He\textsuperscript{2+} ions from O\textsubscript{2}, H\textsubscript{2}O, and NH\textsubscript{3} are illustrated in Figs. 40 - 42. The differential cross sections were found using a translational energy-gain technique, by calculating the area under the peaks in the energy-gain spectra at different projectile scattering angles. The general features of the measured differential cross sections are qualitatively explained in terms of a multi-state collision-model, which has been described in detail by Andersson et al. (1987), based
on classical trajectories for nuclear motion and multi-channel LZ transition probabilities. The theoretical calculations folded with experimental resolution are also shown in Figs. 40 - 42. The value of the largest calculated cross section has been normalized to the height of the peak observed in the corresponding experimental spectrum.

For He$^{2+}$ - O$_2$ collisions (Fig. 40), the measurements show that the distribution contains a main peak lying just inside the critical angle $\theta_c = 0.44^\circ$ for capture into the He$^+$ (n = 2) states, indicating that the capture took place on the way out of the collision.

![Figure 40](image-url)  
**Figure 40.** Experimental and calculated differential cross sections $d\sigma/d\Omega$ for SEC by 100 eV He$^{2+}$ ions from O$_2$. •, present work; broken curve, theoretical calculation folded with experimental resolution. A spline line is drawn to guide the Eye.
The calculation was carried out assuming that the SEC channel to be the exit channel and $\text{He}^+ (n = 1) + \text{O}_2^{++} (\Sigma_u^+) + \text{e}$ to be the promotion channel. The results appear to be in good qualitative agreement with the experimental data but broader than the experimental distribution.

For $\text{He}^{2+} - \text{H}_2\text{O}$ collisions (Fig. 41), the distribution is peaked in the forward direction close to the critical angle $\theta_c = 0.29^\circ$, which indicates that the capture into the $\text{He}^+ (n=2)$ states took place on the way out of the collision.

![Figure 41](image-url)  

Figure 41. Experimental and calculated differential cross sections $d\sigma/d\Omega$ for SEC by 100 eV $\text{He}^{2+}$ ions from $\text{H}_2\text{O}$. •, present work; broken curve, theoretical calculation folded with experimental resolution. A spline line is drawn to guide the Eye.
The unresolved structure at larger scattering angles > 3° is due to contributions from capture on the way into the collision. The calculation was performed assuming the SEC channel to be the exit channel for the capture, with He⁺ (n = 1) + H₂O⁺⁺ \((2^1A_1) + \text{e}\) channel to be the promotion channel. The calculation reproduces the forward peak, but underestimates the contribution from capture that took place on the way into the collision.

For He²⁺ - NH₃ collisions (Fig. 42), the experimental data show that the distribution is peaked in the forward direction inside the critical angle \(\theta_c = 0.77°\), with unresolved structure at about \(\theta = 2.7°\).

![Figure 42. Experimental and calculated differential cross sections \(d\sigma/d\Omega\) for SEC by 100 eV He²⁺ ions from NH₃. •, present work; broken curve, theoretical calculation folded with experimental resolution. A spline line is drawn to guide the Eye.](image-url)
The forward peak clearly represents contributions from capture on the way out of the collision, while the structure occurring at larger angles is due to contributions from capture on the way into the collision. The calculation was performed assuming that the vibrational states ranging between \( v = 0 \) and 17 contribute to single-electron capture with the vibrational state \( v = 7 \), taken to be the exit channel and the vibrational state \( v = 0 \) taken to be the promoter channel. The theoretical calculation is in good agreement with the measured data, although the calculation underestimates the contribution from capture on the way into the collision.

**Total Cross Sections**

We have measured absolute state-selective and total cross sections for single-electron capture by \( \text{He}^{2+} \) ions from \( \text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{CO}_2 \), \( \text{N}_2 \), and \( \text{NH}_3 \) molecular targets at laboratory energies between 0.1 and 1.6 keV. Experimental data for absolute state-selective and total cross sections, along with the relative uncertainties, are listed in Table 7 and 8. These cross sections, together with other experimental data and theoretical calculations obtained by the models described in Chapter II, are depicted as a function of energy in Figs. 43-47.

For \( \text{He}^{2+} - \text{O}_2 \) collisions (Fig. 43), the measured cross sections for capture into the \( \text{He}^+ (n = 1) \) state increase with increasing energy, peak at a collision energy of \( E = 0.15 \) keV/amu, and show a slightly decreasing trend at larger collision energies. On the other hand, the measured cross sections for capture into the \( \text{He}^+ (n = 2) \) states slowly increase with increasing collision energy and become the dominant process at collision energies of \( E \geq 0.2 \) keV/amu. The increase of the probabilities for single-electron capture into the \( \text{He}^+ (n = 2) \) states with increasing projectile energy as

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Table 7

Cross sections (10^{-16} cm^2) for single-electron capture by He^2+ ions from O_2 and H_2O leading to He^+(n = 1) and He^+(n = 2) formations.

<table>
<thead>
<tr>
<th>Energy (keV/amu)</th>
<th>O_2</th>
<th>H_2O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He^+(n = 1)</td>
<td>He^+(n = 2)</td>
</tr>
<tr>
<td>0.025</td>
<td>1.51 ± 0.26</td>
<td>0.16 ± 0.06</td>
</tr>
<tr>
<td>0.050</td>
<td>2.46 ± 0.33</td>
<td>0.34 ± 0.12</td>
</tr>
<tr>
<td>0.075</td>
<td>3.07 ± 0.32</td>
<td>0.72 ± 0.17</td>
</tr>
<tr>
<td>0.100</td>
<td>3.50 ± 0.44</td>
<td>1.28 ± 0.19</td>
</tr>
<tr>
<td>0.125</td>
<td>4.05 ± 0.52</td>
<td>1.75 ± 0.26</td>
</tr>
<tr>
<td>0.150</td>
<td>4.15 ± 0.48</td>
<td>2.81 ± 0.38</td>
</tr>
<tr>
<td>0.175</td>
<td>3.93 ± 0.47</td>
<td>3.55 ± 0.42</td>
</tr>
<tr>
<td>0.200</td>
<td>3.65 ± 0.45</td>
<td>4.23 ± 0.51</td>
</tr>
<tr>
<td>0.225</td>
<td>3.46 ± 0.49</td>
<td>4.46 ± 0.61</td>
</tr>
<tr>
<td>0.250</td>
<td>3.43 ± 0.51</td>
<td>4.79 ± 0.57</td>
</tr>
<tr>
<td>0.275</td>
<td>3.38 ± 0.52</td>
<td>5.03 ± 0.72</td>
</tr>
<tr>
<td>0.300</td>
<td>3.37 ± 0.50</td>
<td>5.24 ± 0.64</td>
</tr>
<tr>
<td>0.325</td>
<td>3.37 ± 0.50</td>
<td>5.73 ± 0.69</td>
</tr>
<tr>
<td>0.350</td>
<td>3.27 ± 0.50</td>
<td>5.92 ± 0.71</td>
</tr>
<tr>
<td>0.375</td>
<td>3.12 ± 0.46</td>
<td>5.89 ± 0.78</td>
</tr>
</tbody>
</table>

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Table 8

Absolute total cross sections \((10^{-16} \text{ cm}^2)\) for single-electron capture by \(\text{He}^{2+}\) ions from \(\text{O}_2, \text{H}_2\text{O}, \text{CO}_2, \text{N}_2, \text{and NH}_3\).

<table>
<thead>
<tr>
<th>Energy (keV/amu)</th>
<th>(\text{O}_2)</th>
<th>(\text{H}_2\text{O})</th>
<th>(\text{CO}_2)</th>
<th>(\text{N}_2)</th>
<th>(\text{NH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>1.67 ± 0.28</td>
<td>0.94 ± 0.15</td>
<td>0.48 ± 0.09</td>
<td>1.58 ± 0.17</td>
<td>20.24 ± 0.19</td>
</tr>
<tr>
<td>0.050</td>
<td>2.80 ± 0.37</td>
<td>1.63 ± 0.19</td>
<td>0.84 ± 0.13</td>
<td>2.51 ± 0.27</td>
<td>20.66 ± 0.20</td>
</tr>
<tr>
<td>0.075</td>
<td>3.79 ± 0.38</td>
<td>1.99 ± 0.22</td>
<td>1.42 ± 0.15</td>
<td>2.87 ± 0.30</td>
<td>20.73 ± 0.20</td>
</tr>
<tr>
<td>0.100</td>
<td>4.78 ± 0.47</td>
<td>2.56 ± 0.25</td>
<td>1.76 ± 0.22</td>
<td>3.51 ± 0.35</td>
<td>21.00 ± 0.20</td>
</tr>
<tr>
<td>0.125</td>
<td>5.80 ± 0.56</td>
<td>3.18 ± 0.34</td>
<td>2.02 ± 0.25</td>
<td>3.66 ± 0.37</td>
<td>21.28 ± 0.20</td>
</tr>
<tr>
<td>0.150</td>
<td>6.96 ± 0.68</td>
<td>3.52 ± 0.32</td>
<td>2.47 ± 0.28</td>
<td>3.84 ± 0.42</td>
<td>21.43 ± 0.21</td>
</tr>
<tr>
<td>0.175</td>
<td>7.48 ± 0.76</td>
<td>3.71 ± 0.33</td>
<td>3.23 ± 0.35</td>
<td>3.91 ± 0.44</td>
<td>21.48 ± 0.21</td>
</tr>
<tr>
<td>0.200</td>
<td>7.89 ± 0.78</td>
<td>4.00 ± 0.37</td>
<td>3.51 ± 0.36</td>
<td>3.94 ± 0.42</td>
<td>21.49 ± 0.21</td>
</tr>
<tr>
<td>0.225</td>
<td>7.92 ± 0.20</td>
<td>4.15 ± 0.36</td>
<td>3.70 ± 0.39</td>
<td>3.98 ± 0.44</td>
<td>21.61 ± 0.21</td>
</tr>
<tr>
<td>0.250</td>
<td>8.22 ± 0.80</td>
<td>4.31 ± 0.37</td>
<td>3.83 ± 0.20</td>
<td>4.02 ± 0.45</td>
<td>21.65 ± 0.21</td>
</tr>
<tr>
<td>0.275</td>
<td>8.41 ± 0.82</td>
<td>4.37 ± 0.37</td>
<td>3.85 ± 0.19</td>
<td>4.09 ± 0.47</td>
<td>21.78 ± 0.22</td>
</tr>
<tr>
<td>0.300</td>
<td>8.62 ± 0.83</td>
<td>4.71 ± 0.42</td>
<td>3.93 ± 0.21</td>
<td>4.11 ± 0.48</td>
<td>21.91 ± 0.22</td>
</tr>
<tr>
<td>0.325</td>
<td>9.11 ± 0.88</td>
<td>4.99 ± 0.44</td>
<td>3.99 ± 0.23</td>
<td>4.18 ± 0.48</td>
<td>21.91 ± 0.22</td>
</tr>
<tr>
<td>0.350</td>
<td>9.19 ± 0.89</td>
<td>5.13 ± 0.56</td>
<td>4.07 ± 0.24</td>
<td>4.22 ± 0.49</td>
<td>22.01 ± 0.23</td>
</tr>
<tr>
<td>0.375</td>
<td>5.43 ± 0.58</td>
<td>4.15 ± 0.28</td>
<td>4.27 ± 0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>9.00 ± 0.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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predicted by the Demkov model is due to the fact that the transitions are produced by dynamic coupling effects initiated by the nucleus-electron interaction, which requires kinetic energy from the collision partners. On the contrary, the cross section for dielectronic transitions leading to He$^+$ (n = 1) formation decreases with increasing projectile energy.

Figure 43. Cross sections for single-electron capture by He$^{2+}$ ions from O$_2$. Total cross sections: •, present work; ○, Ishii et al. (1999). Capture into He$^+_2$(n=2) states: ▼, present work. Capture into He$^+_1$(n=1) state: ▲, present work. Theory: solid curve, Demkov model; dot curve, LZ model.

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The dielectronic mechanism resembles the Auger effect caused by the electron-electron interaction and does not require kinetic energy from the collision partners. This becomes less important when the projectile energy increases and the collision time decreases.

The energy dependence of the measured cross sections for capture into the \( \text{He}^+ (n = 1) \) state is fairly well reproduced by the Landau-Zener model at energies above 0.25 keV/amu, while capture into \( \text{He}^+ (n = 2) \) states agrees well with the Demkov results. In addition, the measured total cross section slowly increases with increasing collision energy and is in good agreement with the data obtained by Ishii et al. (1999) in the energy region that overlaps.

For \( \text{He}^{2+} - \text{H}_2\text{O} \) collisions (Fig. 44), the measured cross section for capture into the \( \text{He}^+ (n = 1) \) state increases with increasing energy, passes through a maximum at about \( E = 0.175 \) keV/amu, and then seems to decrease slightly at larger collision energies. On the other hand, the measured cross section for capture into the \( \text{He}^+ (n = 2) \) states slowly increases with increasing collision energy and becomes the dominant process at collision energies \( E \geq 0.25 \) keV/amu. The present measurements show similar energy dependencies as the previous collision system, which can be explained by the nucleus-electron interaction and the electron-electron interaction, as discussed previously. Again, the energy dependence of the measured cross sections for capture into \( n = 1 \) is fairly well reproduced by the Landau-Zener model at energies above 0.25 keV/amu, while capture into \( n = 2 \) is in excellent accord with the Demkov results. In addition, the measured cross sections for capture into the \( \text{He}^+ (n = 1) \) and \( \text{He}^+ (n = 2) \) states are in good agreement with recent results of Seredyuk et al. (2005). It can also be seen that the measured total cross sections are in excellent agreement with the recommended total cross sections of Greenwood et al. (2004) in the energy
region of overlap. However, at energies below 0.1 keV/amu, our results are seen to fall below the recommended values of Greenwood et al. (2004).

Figure 44. Cross sections for single-electron capture by He$_{2}^{2+}$ ions from H$_2$O. Total cross sections: •, present work; ○, Greenwood et al. (2004). Capture into He$_{4}^{+}(n=2)$ states: ▼, present work; V, Seredyuk et al. (2005). Capture into He$_{4}^{+}(n=1)$ state: ▲, present work; Δ, Seredyuk et al. (2005). Theory: solid curve, Demkov model; dot curve, LZ model.

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For He\(^{2+}\) - CO\(_2\) collisions (Fig. 45), we notice that the measured data gradually increase and show very little dependence on collision energy above 0.2 keV/amu. There are no previous data for single-electron capture cross sections for He\(^{2+}\) on CO\(_2\) in this energy range. However, the lower-energy work of Greenwood et al. (2000) appears to extrapolate well to our data. The present results are compared with the Landau-Zener model results. They are in excellent agreement at higher energies, but deviate somewhat at lower impact energies.

![Graph](https://example.com/graph.png)

Figure 45. Total cross sections for single-electron capture by He\(^{2+}\) ions from CO\(_2\). •, present work; ○, Greenwood et al. (2000); dot curve, LZ model.
For He\(^{2+}\) - N\(_2\) collisions (Fig. 46), the measured results behave quite similarly to those of the He\(^{2+}\) - CO\(_2\) collisions. Our present results are somewhat larger than the results from Hanaki et al. (1982) and are seen to be in excellent accord with those obtained by Ishii et al. (1999). As can also be seen, the Landau-Zener results are in good agreement with the experimental data at impact energies above 0.1 keV/amu. The deviation between the results is within one order of magnitude below 0.1 keV/amu.

Figure 46. Total cross sections for single-electron capture by He\(^{2+}\) ions from N\(_2\). •, present work; ○, Hanaki et al. (1982); □, Ishii et al. (1999); dot curve, LZ model.

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It is interesting to note that the energy dependence of the experimental values in the previous two collision systems is reproduced, at least qualitatively, by the Landau-Zener calculations at impact energies $E > 0.1$ keV/amu. In addition, the total cross sections slowly increase with collision energy and can also be understood from the reaction window, which gets broader with increasing energy and therefore capture channel with larger or smaller $Q$ values increases in probability.

Regarding the system of $\text{He}^{2+}$ on $\text{NH}_3$ (see Fig. 47), the measured cross sections are reasonably constant with increasing collision energy, a behavior that is well documented for such collisions at low collision energies. This is probably due to the fact that the dominant reaction channel is situated nearly at the center of the reaction window. The Demkov results lie just below the experimental results and show the same energy dependence. There are no other experimental data available for comparison.
Figure 47. Total cross sections for single-electron capture by He$^{2+}$ ions from NH$_3$. •, present work; solid curve, Demkov model.
CHAPTER VI

CONCLUSIONS

In this dissertation, state-selective differential cross sections for single-electron capture by He\(^{2+}\) projectile ions with O\(_2\), H\(_2\)O, CO\(_2\), N\(_2\) and NH\(_3\) molecular targets have been studied by means of translational energy-gain spectroscopy. Measurements were carried out at laboratory impact energies between 0.1 and 1.6 keV and at laboratory scattering angles between 0° and 8°. As apparent from the state-selective measurements, single-electron capture from O\(_2\) and H\(_2\)O proceeds by both dissociative and non-dissociative channels, whereas for N\(_2\) and CO\(_2\) only DTI has been observed. However, for the NH\(_3\) target, the SEC was found to be predominantly populated. The energy-gain spectra were interpreted qualitatively in terms of the reaction windows, which are calculated using the Landau-Zener model and the extended version of the classical-over-barrier model.

We have also studied differential cross sections for the non-dissociative single-electron capture process for He\(^{2+}\) with O\(_2\), H\(_2\)O, and NH\(_3\) collision systems. The angular distribution spectra contain a main peak lying close to the critical angle \(\theta_c\), corresponding to capture at an impact parameter equal to the crossing radius of the dominant reaction channel. The peaks are qualitatively explained by a multi-channel collision model and are attributed to the capture process on the way out of the collision. The computed results are also shown to be in good agreement with the experimental results. The energy dependence of the absolute state-selective and total...
cross sections for single-electron capture by He$^{2+}$ ions from O$_2$, H$_2$O, CO$_2$, N$_2$, and NH$_3$ of the present work were compared with the available data and the theoretical results based on the Demkov and Landau-Zener models. Our measured state-selective cross sections for O$_2$ and H$_2$O targets have been shown to be in reasonable agreement with the calculated cross sections. The computed results are based on simple MO and potential curves, in which we assumed Coulomb repulsion for the final state and neglected the polarization interaction in the entrance channel. The increase of the probabilities for single-electron capture into the He$^+$ (n = 2) states with increasing projectile energy predicted by the Demkov model is due to the fact that the transitions are produced by dynamic coupling effects initiated by the nucleus-electron interaction. On the other hand, the cross section for dielectronic transitions leading to He$^+$ (n = 1) formation decreases with increasing projectile energy. The dielectronic mechanism resembles the Auger effect caused by the electron-electron interaction. In addition, our present total cross sections for both systems show good agreement with other available data.

For He$^{2+}$ on N$_2$ and CO$_2$ collisions, the energy dependence of the experimental values is reproduced, at least qualitatively, by Landau-Zener calculations and shows good agreement with other available data. For He$^{2+}$ on NH$_3$, the cross sections are almost independent of the collision energies and can be understood from the reaction window.
BIBLIOGRAPHY


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(http://physics.nist.gov/).