Charge-transfer cross section measurements using laser ablation ion source and reflection time-of-flight mass spectrometer

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CHARGE-TRANSFER CROSS SECTION MEASUREMENTS USING
LASER ABLATION ION SOURCE AND REFLECTION
TIME-OF-FLIGHT MASS SPECTROMETER

Jiebing Wang

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

in

Physics

Department of Physics
University of Nevada, Las Vegas
August 1997
To my parents, and my wife
The dissertation of Jiebing Wang for the degree of Doctor of Philosophy in Physics is approved.

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ABSTRACT

A new method is developed that combines the production of ions by laser ablation with a reflection time-of-flight mass spectrometer (RTOFMS) for charge-transfer cross section measurements. This method allows a specific charge-transfer channel of an ion-neutral pair to be measured at energies of about 0.1 KeV/amu. The charge-transfer cross section is determined by measuring the intensity ratio of the product ions to the parent ions after the charge-transfer reactions occur in the reflection drift tube of the RTOFMS. First, a calibration measurement of C$^{2+}$ with H$_2$ is carried out and the result agrees with previous measurements by other research groups. Then, a first-time measurement of Si$^{3+}$ with He at silicon ion energy of 0.16 KeV/amu is carried out. The single electron charge-transfer cross section of this reaction is $1.27(\pm 0.19) \times 10^{-15}$ cm$^2$. 

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ABSTRACT</strong></td>
<td>iv</td>
</tr>
<tr>
<td><strong>LIST OF TABLES</strong></td>
<td>vi</td>
</tr>
<tr>
<td><strong>LIST OF FIGURES</strong></td>
<td>vii</td>
</tr>
<tr>
<td><strong>ACKNOWLEDGEMENTS</strong></td>
<td>x</td>
</tr>
<tr>
<td><strong>CHAPTER 1  INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Significance of charge-transfer reactions</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Scope of the dissertation</td>
<td>5</td>
</tr>
<tr>
<td><strong>CHAPTER 2  PHYSICS OF CHARGE-TRANSFER REACTIONS</strong></td>
<td>7</td>
</tr>
<tr>
<td>2.1 The classical approach</td>
<td>9</td>
</tr>
<tr>
<td>2.2 The quantum approach</td>
<td>11</td>
</tr>
<tr>
<td>2.2.1 The PSS expansion</td>
<td>12</td>
</tr>
<tr>
<td>2.2.2 Adiabatic representation</td>
<td>14</td>
</tr>
<tr>
<td>2.2.3 Diabatic representation</td>
<td>16</td>
</tr>
<tr>
<td>2.2.4 Landau-Zener model</td>
<td>17</td>
</tr>
<tr>
<td>2.3 Conclusions</td>
<td>18</td>
</tr>
<tr>
<td><strong>CHAPTER 3  LASER-INDUCED PLASMA</strong></td>
<td>20</td>
</tr>
<tr>
<td>3.1 Overview</td>
<td>20</td>
</tr>
<tr>
<td>3.2 Time-of-flight measurements of the laser-induced plasma</td>
<td>21</td>
</tr>
<tr>
<td>3.2.1 Experimental setup</td>
<td>21</td>
</tr>
<tr>
<td>3.2.2 Experimental methods</td>
<td>22</td>
</tr>
<tr>
<td>3.3 Experimental results</td>
<td>24</td>
</tr>
<tr>
<td>3.3.1 Temperature and expansion velocity of the plasma</td>
<td>25</td>
</tr>
<tr>
<td>3.3.2 Total number of ions produced by laser ablation</td>
<td>27</td>
</tr>
<tr>
<td>3.3.3 Ion species and their power dependency</td>
<td>28</td>
</tr>
<tr>
<td>3.3.4 Derived plasma characteristics</td>
<td>28</td>
</tr>
<tr>
<td>3.4 Kinetics of laser-induced plasma</td>
<td>32</td>
</tr>
<tr>
<td>3.4.1 Absorption of the laser light and vaporization of the target material</td>
<td>33</td>
</tr>
<tr>
<td>3.4.2 Plasma formation and heating</td>
<td>34</td>
</tr>
<tr>
<td>3.4.3 Plasma expansion velocity</td>
<td>37</td>
</tr>
<tr>
<td>3.5 Ionization structure in laser-induced plasma</td>
<td>38</td>
</tr>
<tr>
<td>3.5.1 The ionization plasma model</td>
<td>38</td>
</tr>
<tr>
<td>3.5.2 Corona limit</td>
<td>40</td>
</tr>
</tbody>
</table>

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3.5.3 Saha limit .......................................................... 41
3.5.4 Results and discussions .................................. 42
3.6 Conclusions .......................................................... 47

CHAPTER 4 DESIGN AND CONSTRUCTION OF REFLECTION TIME-
OF-FLIGHT MASS SPECTROMETER 48
4.1 Introduction .......................................................... 48
4.2 Optimum parameters for second-order focusing . .... 49
   4.2.1 Grounding of the drift tubes ......................... 49
   4.2.2 Floating of the drift tubes ............................ 53
4.3 Design parameters of the RTOFMS ......................... 55
4.4 Resolution analysis ................................................. 56
   4.4.1 Resolution limited by initial energy spread ...... 56
   4.4.2 Resolution limited by construction factors ...... 57
   4.4.3 Resolution limited by ion detectors ............. 58
4.5 Construction of the RTOFMS .................................. 58
   4.5.1 Incidence drift tube assembly ....................... 58
   4.5.2 Reflectron assembly ................................. 59
   4.5.3 Reflection drift tube assembly ....................... 61
   4.5.4 Ion detector assembly .............................. 61
4.6 Established system ............................................... 63
   4.6.1 Vacuum and electrical system ....................... 63
   4.6.2 Mass spectrum obtained using the RTOFMS system .. 66

CHAPTER 5 CHARGE-TRANSFER CROSS SECTION MEASUREMENT 71
5.1 Experimental setup ................................................. 71
   5.1.1 Ion detector ............................................. 71
   5.1.2 Data acquisition system .......................... 72
   5.1.3 Gas handling system ............................... 73
5.2 Charge-transfer measurement of C^{2+} with H_2 ........ 74
   5.2.1 Experimental method and procedure .............. 74
   5.2.2 Channel electron multiplier gain efficiency calibration .... 78
   5.2.3 Determination of the ion energy and cross section .... 80
   5.2.4 Discussion on the result ............................ 82
5.3 Charge-transfer measurement of Si^{3+} with He .......... 84
   5.3.1 Experiments ............................................. 86
   5.3.2 Determination of the ion energy and cross section .... 90
   5.3.3 Discussion on the result ............................ 91
5.4 Conclusions .......................................................... 93

REFERENCES 96
LIST OF TABLES

3.1 Atomic parameters of molybdenum ions ....................................... 41
4.1 Design parameters of the RTOFMS............................................................. 56
5.1 The potential settings of the RTOFMS in Si^{3+} + He measurements . 87
5.2 Ions received by the CEM in Si^{3+} + He measurements ................. 88
LIST OF FIGURES

2.1 Classical potential curve crossing representing a charge-transfer process between a multiply charged ion and a neutral atom. .......................... 8
2.2 Classical orbiting model of a charge-transfer process. ....................... 10
2.3 Charge-transfer transition in the adiabatic quantum representation. .... 15
3.1 Ion detection by CEM and curve fitting by the translational Maxwellian distribution. ................................................................. 26
3.2 Averaged laser ablation RTOF mass spectrum with the molybdenenum target. ........................................................................... 29
3.3 Power dependency of the ion species of the laser induced plasma ....... 30
3.4 Ionization structure obtained under corona limit. ............................... 43
3.5 Ionization structure obtained under Saha limit. .................................. 44
3.6 Ionization structure in a non-LTE case. ................................................. 46
4.1 Sketch of the RTOFMS configuration. ................................................. 50
4.2 Schematics of the laser ablation ion source and the RTOFMS. .......... 64
4.3 Schematics of the vacuum system associated with the laser ablation ion source and the RTOFMS. ....................................................... 65
4.4 General electrical connections for the RTOFMS. ................................. 67
4.5 A typical RTOF mass spectrum generated by a single laser shot on a pure carbon target. ............................................................. 68
4.6 A typical RTOF mass spectrum generated by a single laser shot on a tungsten disicilide target. ........................................................... 70
5.1 Schematics the ion detector and data acquisition system. ...................... 72
5.2 Two RTOF mass spectra are presented in the diagram. The dotted line is the average RTOF mass spectrum of the parent C^{2+} ions. The solid line is the RTOF mass spectrum of the product C^{+} ions. The overshoot is caused by the preamplifier. ........................................ 79
5.3 A 50 laser-shots averaged time-of-flight spectrum collected by the non-biased extraction plate that serves as a Faraday cup. ......... 81
5.4 Single electron charge-transfer cross sections for C^{2+} + H_{2} at low energies reported by several research groups. ...................... 85
5.5 Two RTOF mass spectra are presented in the diagram. The dotted line is the average RTOF mass spectrum of the parent Si$^{3+}$ ions. The solid line is the RTOF mass spectrum of the product Si$^{2+}$ ions. The overshoot is caused by the preamplifier. 

5.6 Comparison of our measured charge-transfer cross section of Si$^{3+}$ + He with the theoretical calculation by Gargaud and McCarroll.

5.7 Comparison of charge-transfer rate measurements and calculations toward the reaction of Si$^{3+}$ with He.
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CHAPTER 1

INTRODUCTION

1.1 Significance of charge-transfer reactions

A charge-transfer reaction in an atomic or molecular system is one in which an electron, or several electrons, are transferred from one atomic or molecular system to another. The charge transfer process is an important atomic and molecular process in any plasma environment. Specifically, we will focus on the significance of charge-transfer reactions at low collision energies. By low collision energy we mean that the relative nuclear speed is much less than a typical electron speed. A typical electron speed can be estimated from classical dynamics:

\[ \frac{m_e v^2}{r} = \frac{1}{4\pi e} \frac{Ze^2}{r^2}. \]  

(1.1)

If \( Z = 1 \) and \( r = 10^{-10} \) m, then \( v = 1.5 \times 10^6 \) m/s, which corresponds to electron kinetic energy of 6.4 eV. So if a nucleus has the same speed as an electron, its kinetic energy is on the order of 12 KeV/amu. This is much higher than the energy we work with.

We first summarize the significance of measuring the charge-transfer cross sec-
tions at low energies.

1. It serves as a testing ground for theory.

The quantal calculation of charge transfer, especially at low energies, is still far from perfect. Although the theory has improved its accuracy in recent years, many discrepancies exist between the experimentally measured values and the calculated ones. For instance, the charge-transfer cross section of O\(^{2+}\) with He \([1]\) measured in the ion trap disagrees with the recent quantal calculation \([2]\) by as much as three orders of magnitude.

2. It is important to the understanding of the interactions among impurity ions and neutrals at the edges of tokamak fusion plasmas.

A large part of the impurity ions are sputter-generated by the strike of diffused hot plasma ions and neutrals on the vacuum vessel wall, limiter and divertors. As a consequence, the edge plasma has the highest impurity concentration. Although the absolute concentration of impurity ions may be small (less than a few percent in total), charge transfer between those ions and neutrals may be rapid. The captured electrons may initially stay at specific excited levels of the ions and return to the ground state by radiation. This radiation, combining with radiation from other atomic processes, keeps the edge plasma temperature low (100 — 500 eV). Although no clear and self-consistent picture of the coupling of atomic processes and the collective plasma phenomena in the plasma edge
region has emerged so far, there is an overwhelming evidence of its existence, as well as of the fact that the properties and dynamics of the edge plasma have a decisive influence on the overall plasma energy confinement [3]. This is not only because the edge plasma defines the boundary conditions for the whole, but also because the impurities in the edge may migrate into the center plasma and radiate energy through recombination processes. While the radiation from the impurities is detrimental to the energy confinement in the center plasma, it plays a beneficial role at the divertor by helping to damper the thermal energy and cool down the plasma [4, 5].

The charge-transfer reaction can also be used in diagnosis of the concentration of impurity ions in the tokamak plasma. A fast hydrogen atom beam has been used for the diagnosis of fully ionized plasma species such as He$^{2+}$, C$^{6+}$ and O$^{8+}$ [6]. These are highly state-selective electron capture processes:

$$H(1s) + X^{z+} \rightarrow H^+ + X^{(z-1)+}(nlm)$$  \hspace{1cm} (1.2)

In collisions of C$^{6+}$ and O$^{8+}$ with H atoms, the products C$^{5+}$ and O$^{7+}$ are found to be formed selectively in the levels with $n = 4$ and $n = 5$, respectively [7]. The subsequent radiation can be identified, and the impurity density profile can be obtained from a knowledge of the corresponding charge-transfer cross sections. Diagnostics of this type can also be carried out using fast He and Li beams, and applied to other impurity ions.
3. It plays a significant role in the astrophysical plasma.

Ion-atom charge exchange reactions contribute significantly to the ionization balance of complex ions in astrophysical photoionized plasmas such as emission nebulae, planetary nebulae, nova shells, starburst galaxies and probably active galactic nuclei [8, 9, 10]. The ionization structure in a photoionized plasma is balanced by photoionization, radiative, dielectronic, and charge-transfer recombination. For electron temperatures lower than $10^6$ K, the abundance of neutral atomic H or He can be sufficient for the charge exchange rate to exceed the radiative (direct or dielectronic) recombination rate for ions with charge $q \geq 2$.

[11]

4. It is beneficial to the many research areas.

The charge-transfer of ion-atom and ion-molecule is beneficial to widely diverse areas such as aeronomy [12], electrical discharges in semiconductor processing [13], flames and combustion systems [14], design and operation of multi-charged ion sources [15], etc. It also has impact on studies relating to the generation of X-ray or vacuum ultraviolet laser light. The state selective nature of charge transfer may provide a possible pumping mechanism for an X-ray laser [16, 17]. Finally, heavy element charge-transfer processes may provide useful information to the nuclear synthesis in interstellar medium. Heavy elements refer to those whose atomic numbers are greater than 30 (Zn). They have different nucleosynthetic origins from those of the lighter elements ($Z < 30$). Lighter elements are
formed by oxygen and silicon burning, while heavy elements are formed by a
diverse mixture of slow and rapid neutron capture (s- and r-process). Compar­
ison of measured abundances of these heavy elements for different sight lines
provide a unique probe of stellar evolution, nucleosynthetic enrichment, and the
efficiency with which this material is mixed in the interstellar medium. Up to
date, six heavy elements (GaII, GeII, KrI, Sn II [18], As II and Se II) [19] have
been observed in the interstellar medium.

1.2 Scope of the dissertation

A new method is developed in this dissertation to measure the charge-transfer cross
sections at low energies. This method combines a laser ablation ion source and a
reflection time-of-flight mass spectrometer (RTOFMS). It allows a specific charge-
transfer channel of an ion-neutral pair to be measured.

In chapter 2, the theory of charge-transfer reactions will be introduced. A clas­
ical approach and a simplified quantum approach (Landau-Zener model) will be
discussed to explore the physics behind such reactions.

In chapter 3, the laser-induced plasma will be diagnosed by using the time-of-
flight mass spectrometric method. The measured plasma temperature is compared
with a theory provided by Puell [20, 21]. An ionization model is built to explain the
ionization structures in the laser-induced plasma. All these will help to understand
the process of using laser-induced plasma as an ion source.
RTOFMS is introduced in chapter 4. It is designed and built at UNLV. The
discussions on its resolution and construction are given in full detail.

In chapter 5, we use the laser ablation ion source and RTOFMS to conduct the
charge-transfer cross section measurements. First, a calibration measurement between
C$^{2+}$ and H$_2$ is carried out with the incident energy of C$^{2+}$ at 3045.6(σ = 12.4) eV and
H$_2$ at room temperature. We show that the metastable state ion fraction in the laser
ablation beam is negligible. And our measured cross section of 6.90(±0.78) × 10$^{-16}$
cm$^2$ is consistent with the ground state measurement reported previously. Next,
for the first time, we measured the the single electron charge-transfer cross section
between Si$^{3+}$ and He with incidence of Si$^{3+}$ at 4524(±7.2) eV or 0.16 KeV/amu and
He at room temperature. The measured cross section is 1.27(±0.19) × 10$^{-15}$ cm$^2$. 

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CHAPTER 2

PHYSICS OF CHARGE-TRANSFER REACTIONS

The charge-transfer reaction was first discovered by Henderson [22] during his experiments in which \( \alpha \)-particles were passed through absorbing screen of mica. Thomas [23] came up with the first theoretical model to explain such reactions, based on classical mechanics. The first applications of quantum mechanics to charge transfer were perturbation treatments by Oppenheimer [24] and by Brinkman and Kramers [25]. At low energies, the charge exchange cross section is usually large and the perturbation treatment is not adequate. Note that at low energies, the characteristic times of the electrons in the bound state orbits are much longer than the interaction time between the two approaching nuclei or molecular cores so that a quasi-molecule may be assumed. During the quasi-molecular state, the electron to be captured is shared between the two nuclei, which distinguish this theory from the direct perturbation theory. Massey and Smith [26] first described such a mechanism. The modern form of the charge-transfer theory presented by Bates and McCarroll [27] corrected some serious difficulties with the previous models.

We will first discuss the quasi-molecular model. A classical potential energy
Figure 2.1: Classical potential curve crossing representing a charge-transfer process between a multiply charged ion and a neutral atom.

A diagram of a charge-transfer process involving multiply charged ions is shown in Fig. 2.1. A quasi-molecule formed when \( A^{q+} \) and \( B \) approach each other is represented by an attractive potential curve for the electron. As the two nuclei separate, there is a probability that the electron will slip into the \( A^{(q-1)+} \) and \( B^+ \) channel, represented by a repulsive Coulomb potential. If we view the system as an ion and a neutral all the time, then the interaction between the two when they are far apart is mainly the ion-induced dipole attractive interaction. The dipole interaction is proportional to \( \mathbf{p} \cdot \mathbf{E} \), where \( \mathbf{p} \) is the dipole moment and \( \mathbf{E} \) is the Coulomb field strength. Since \( \mathbf{p} \propto \mathbf{E} \) and the magnitude of \( \mathbf{E} \) is inversely proportional to \( R^2 \) with \( R \) being the internuclear distance, the interaction potential has an inverse \( R^4 \) relationship. The potential will quickly decrease to zero as the two particles separate. When the two particles are close enough that the electron is shared by the two nuclei, the interaction is dominated by the Coulomb repulsion between the two nuclei and the interaction potential has an
inverse $R$ relationship. If we view the system as two ions all the time, the interaction potential is inversely proportional to $R$ at all ranges. If the charge-transfer process is exothermic, the two curves will definitely cross. The charge-transfer occurs at about the "cross" region, as can be explained from Massey adiabatic criterion which says that transitions are improbable unless $\frac{\Delta E}{\hbar \nu} \ll 1$, where $\Delta E$ is the energy separation, $d$ is the range of interaction, $\hbar$ is the Planck constant and $\nu$ is the relative speed of the colliding atoms. This is, in fact, a statement of the Heisenberg uncertainty principle. In slow collisions, $\nu$ is small, and $\Delta E$ has to be small to make a probable transition. It is easy to see the other hand, when $\nu$ is large the transitions can occur to a broad spectrum of final states, no crossing is required, and many channels become strongly coupled. The processes that are not mediated by an energy degeneracy are called "direct impact processes".

2.1 The classical approach

The induced dipole interaction between an atom B and an ion $A^{q+}$ is inversely proportional to $R^4$. In cgs units, the interaction can be written as:

$$V_p = -\frac{\alpha q^2}{2R^4},$$

(2.1)

where $\alpha$ is the polarizability of the neutral. The total macroscopic energy $E_0$ of the ion-neutral pair is:

$$E_0 = T(R) + V_p(R) = T(R) - \frac{\alpha q^2}{2R^4},$$

(2.2)
where $T(R)$ is the kinetic energy at the internuclear separation of $R$. At the point of the closest approach, $R = R_0$, the radial velocity of the ion along the internuclear distance becomes zero. Orbiting of one nucleus around another could occur if the radial acceleration is neglected and the attractive dipole force balances the centrifugal force at $R_0$. Then the target and projectile would remain in close proximity with each other for a long period of time, and it is expected they would have the most opportunity to exchange an electron.

\[
\frac{2\alpha q^2}{R^5} = \frac{2T(R_0)}{R_0}.
\]  

Solving Eq.(2.3), and inserting the result into Eq.(2.2), we have:

\[
T(R_0) = \frac{\alpha q^2}{R_0^5} = 2E_0,
\]  

\[
R_0 = \left(\frac{\alpha q^2}{2E_0}\right)^{1/4}.
\]

Using the angular momentum conservation $T(R_0)R_0^2 = E_0b^2$, where $b$ is the impact parameter (see Fig.2.2), we get:

\[
b = \left(\frac{2\alpha q^2}{E_0}\right)^{1/4}.
\]
The charge transfer can be estimated to be:

\[ \sigma \approx \pi b^2 \approx \pi \left( \frac{2\alpha q^2}{E_0} \right)^{1/2}. \]  

(2.7)

Based on classical kinetic theory, Eq.(2.7) indicates that the charge-transfer cross section is proportional to the ionization state of the ion and to the square root of the polarizability of the neutral, and inversely proportional to their relative velocity. Although this model is crude, it can provide a first estimate for the more complex theoretical modeling.

2.2 The quantum approach

The simplest charge-transfer model consists of an electron and two nuclei, a quantum mechanical three-body system which is not solvable analytically. For the most accurate model, the calculation can become a horrendous task, even with a powerful computer. Here we will only discuss simplified quantum approaches. More extended treatment of charge-transfer process can be found in [28]. The quantum approaches can be divided into two major categories. They are the perturbative methods and the close-coupling methods. The former is adequate to treat collisions at high energies due to a relatively small charge-transfer cross section, while the latter is able to treat collisions at low and intermediate energies. We will focus on the close-coupling methods. The close-coupling methods are based on an expansion of the total wave function into a complete set of basis functions. Schrodinger equation is then transformed into an infinite system of coupled first-order differential equations for the expansion.
2.2.1 The PSS expansion

For charge transfer between two atomic particles (a system of two nuclei and $N$ electrons), if we assume the nuclei and electrons to be point masses and neglect spin-orbit and other relativistic interactions, the total Hamiltonian is:

$$H = -\frac{1}{2M} \nabla_{R_1}^2 - \frac{1}{2M} \nabla_{R_2}^2 - \frac{1}{2m} \sum_{i=1}^{N} \nabla_{r_i}^2 + \frac{Z_1 Z_2 e^2}{|R_1 - R_2|}$$

$$- \sum_{i=1}^{N} \frac{Z_1 e^2}{|R_1 - r_i|} - \sum_{i=1}^{N} \frac{Z_2 e^2}{|R_2 - r_i|} + \sum_{i \neq j}^{N} \frac{e^2}{|r_i - r_j|}$$

$$= -\frac{1}{2M} \nabla_{R_1}^2 - \frac{1}{2M} \nabla_{R_2}^2 + \frac{Z_1 Z_2 e^2}{|R_1 - R_2|} + H_{el},$$

(2.8)

where $H_{el}$ is the Hamiltonian related to the electrons, $R_1$ and $R_2$ are the vectors specifying the coordinates of the two nuclei respectively, and $r_i$ is the vector representing the coordinates of the $i$th electron.

Further assume that: (1) one atom can be viewed as standing still, while the other ion is approaching; (2) the atom can be viewed as a neutral core by the approaching ion nucleus, but not the electron in the ion, while the ion can be viewed as a neutral core with an electron to the neutral atom. The total Hamiltonian is simplified to be:

$$H = -\frac{1}{2M} \nabla_R^2 + H_{el} = T_R + H_{el},$$

(2.9)

where $R$ specifies the internuclear distance.

Because the nuclear motion is much slower than the electronic motion at low...
energy collisions, we can separate the nuclear motion from the electronic motion according to Born and Oppenheimer. Therefore, a simplified quantum mechanical charge-transfer model is to solve the following time-dependent Schrödinger equation of the electrons:

\[ H_d \Psi(R, r, t) = i \frac{d}{dt} \Psi(R, r, t). \]  \hspace{1cm} (2.10)

In the closing coupling method, the PSS (perturbation stationary state) expansion is usually used to expand the total wavefunction into a MO (molecular orbital) basis set \( \{|\chi_i(R, r)\rangle = |i\rangle\} \):

\[ \Psi(R, r, t) = \sum_i a_i(t)\chi_i(R, r)e^{-i \int U_i(R)dt'} \text{,} \]  \hspace{1cm} (2.11)

where \( |a_i(t)|^2 \) represents the probability that the colliding system be in the state \( |i\rangle \) at time \( t \), \( U_i(R) \) can be viewed as the potential energy corresponding to state \( |i\rangle \). The PSS approximation is known for years to have problems that the expansion does not satisfy the asymptotic boundary condition correctly because it completely neglects the momentum possessed by the electrons as they travel with the nucleus to which they belong. Bates and McCarroll [27] amended this deficiency by replacing each static MO basis with a traveling one. A detailed discussion of this problem is out of the scope of this dissertation. We will continue by still using the static MO basis. Inserting Eq.(2.11) into Eq.(2.10), multiplying at left by \( \langle j | \) and integrating over the electronic coordinates, one gets:

\[ i \frac{da_j}{dt} = -U_j a_j + \sum_i \left( \langle j | H_{el} | i \rangle - i \langle j | \frac{d}{dt} | i \rangle \right) a_i e^{-i \int (U_i - U_j)dt'} \text{.} \]  \hspace{1cm} (2.12)
In the following sections, we will introduce two representations that are commonly used to solve Eq.(2.12).

2.2.2 Adiabatic representation

In this representation, the MO basis set \{\{|i\}\} is chosen to be the eigenfunctions of \(H_{el}\):

\[
\langle j | H_{el} | i \rangle = U_j \delta_{ij},
\]

so that Eq.(2.12) becomes:

\[
i \frac{d a_j}{dt} = -\left( \sum_i i \langle j | \frac{d}{dt} | i \rangle \right) a_i e^{-i \int (U_i - U_j) dt}.
\]

The reason behind such representation is that electron velocity is much larger than the collision velocity so that the electron motion adapts itself adiabatically to the nuclear motion as in a molecule. In other words, the electron has sufficient time to experience molecular states at every nuclear separation. Since \(\frac{d}{dt}\) is an energy term that can be split into the radial energy with movement along the internuclear axis and the rotational energy with movement perpendicular to the internuclear axis, the coupling term \(\langle j | \frac{d}{dt} | i \rangle\) can be written as:

\[
\langle j | \frac{d}{dt} | i \rangle = v_R \langle j | \frac{\partial}{\partial R} | i \rangle + \frac{v_0 b}{R^2} \langle j | \hat{L}_y | i \rangle,
\]

where \(v_0\) is the incident collision velocity, \(v_R\) is the radial velocity and \(b\) is the impact parameter. The first term, called the radial coupling, couples molecular states having the same symmetry. The same symmetry refers to the same spin, same spin projection.
and angular momentum projection on the internuclear axis. The second term, called rotational coupling, couples molecular states obeying the selection rule $\Delta L = \pm 1$ with $L$ being the projection of the angular momentum along the internuclear axis. In many cases, at low energies the rotational coupling is much smaller than the radial coupling at the crossing point and is often ignored [28], which means that the charge-transfer transitions is driven by the radial coupling. As a consequence, charge-transfer transition becomes most probable for adiabtic states of the same symmetry.

The Wigner-Von Neuman non-crossing rule based on quantum mechanical principles states that for a many-electron diatomic system the potential curves of the same symmetry do not cross. The proof is a bit subtle [29] and will not be covered here. Fig.2.3 shows the charge-transfer transition in the adiabatic representation.

The adiabatic states and potentials are obtained as numeric solutions of the time-independent Schrödinger equation: $H_d \chi_i(R, r) = U_i(R) \chi_i(R, r)$. The techniques include molecular orbital technique, valence bond technique and etc [30].

Figure 2.3: Charge-transfer transition in the adiabatic quantum representation.
2.2.3 Diabatic representation

The diabatic states are approximate eigenfunctions of the electronic Hamiltonian $H_{el}$ such that, on the one hand, they account for the electronic interatomic interaction to a considerable extent but, on the other hand, the radial nonadiabatic coupling $\langle j | \frac{d}{dt} | i \rangle$ is minimized and may be ignored [31]. In this representation, suppose:

$$\langle j | H_{el} | i \rangle = U_j \delta_{ji} + U_{ji} .$$  \hspace{1cm} (2.16)

Then Eq.(2.12) becomes:

$$i \frac{d a_j}{dt} = - \sum_{i \neq j} U_{ji} a_i e^{-i \int (U_i - U_j) dt} .$$  \hspace{1cm} (2.17)

In the asymptotic region, i.e., at large $R$, the adiabatic and diabatic potential curves are identical. In the molecular region the diabatic and adiabatic curves differ significantly. The avoided crossings in the adiabatic picture are real crossings in the diabatic picture. In the diabatic representation, the charge-transfer transition is driven by the off-diagonal elements of the diabatic potential matrix.

One reason behind the diabatic representation is that adiabatic one does not represent the correct correlation behavior in the molecular region, where the strong electrostatic Coulomb interaction and the spin-orbit coupling will substantially decrease the state symmetry. A state becomes a mixture of states with different symmetries so that the non-crossing rule does not hold.

Although any collision can be described in either adiabatic or diabatic basis set, normally it is more convenient to use the diabatic one in which radial couplings are
small [32, 31]. Refer to [32, 31] for how to obtain the diabatic states and potential curves.

2.2.4 Landau-Zener model

In many cases of practical interest, the coupling between many states can be seen as a successive set of coupling between two states. Concerning only two states, and using the diabatic representation, we have,

\[
\begin{align*}
\frac{d a_1}{dt} &= U_{12}(R)a_2 e^{-i \int \Delta U dt}, \\
\frac{d a_2}{dt} &= U_{12}(R)a_1 e^{-i \int \Delta U dt},
\end{align*}
\]

where \( \Delta U = U_2 - U_1 \). The two-state coupled equations are analytically solved by Landau and Zener [33, 34] under the approximations that the interaction is mainly confined in a small region of crossing, and thus

\[
\Delta U = -\alpha(R - R_c) = -\alpha v_{R_c} t,
\]

where \( v_{R_c} \) is the radial velocity at the crossing point and \( \alpha \) is a constant, representing the slope difference of the two potential curves at the crossing point:

\[
\alpha = \left| \frac{dU_1}{dR} - \frac{dU_2}{dR} \right|_{R=R_c},
\]

The transition probability for charge-transfer between two coupling states is given as

\[
P_{12} = |a_2(\infty)|^2 = 1 - e^{-\eta},
\]
where

\[ \eta = \frac{\pi^2}{4\hbar v_{Rc}} \frac{U_{12}^2(R_c)}{\alpha} . \]  

(2.23)

With the transition probability the Landau-Zener charge-transfer cross section can then be readily derived at the relative energy of \( E \) [35, 36]:

\[ \sigma(E) = 4\pi R_c^2 p(1 + \lambda) \int_1^{\infty} e^{-\eta x} (1 - e^{-\eta x}) x^{-3} dx , \]  

(2.24)

where \( \lambda = [U_{11}(\infty) - U_{11}(R_c)]/E \), \( p \) is a probability, equal to the fraction of the initial state that is also the final state.

2.3 Conclusions

While the classical model indicates the charge-transfer cross section is proportional to the ionization degree of the ion, the square root of the polarizability of the neutral and inversely proportional to their relative velocity, the Landau-Zener model based mostly on quantum mechanics indicates:

1. The crossing distance \( R_c \) is crucial to the calculation of charge transfer probability. \( R_c \) is in the range of 7\( a_0 \) to 13\( a_0 \) (\( a_0 \) is the Bohr radius) for most charge-transfer reactions. The Landau-Zener model suggests that the reaction is improbable if \( R_c \) is either small or large but may proceed rapidly if \( R_c \) lies at some intermediate value [37].

2. The transition probability of charge-transfer is favorable toward low radial velocity passing the crossing point. This is meaningful in that if the two particle
have a longer time to interact in the crossing region a charge-transfer transition is more likely to happen.

3. The transition probability of a charge-transfer is inversely proportional to $\alpha$ which represents the abruptness in the crossing region.

Landau-Zener model has provided a useful guide to the identification of those reactions that are rapid at low energies [8]. But serious defects in this model have also been found [38, 39].

In summary, the theoretical treatment of a charge-transfer reaction is a very complicated process. Many details, such as the accuracy in calculation of the potential curves, location of the crossing radii, treatment of the core electrons and inclusion of the translation factors in the basis sets, etc., are all factors that may affect the outcome.
CHAPTER 3

LASER-INDUCED PLASMA

3.1 Overview

The interaction of light with materials depends on the power density of the light and the duration of irradiation. With the current laser technology, power density of the laser beam can be as high as $10^{18}$ W/cm$^2$ and the irradiation time can be as short as femtoseconds. We can compare it with the power density that sun light irradiates on the earth’s surface on a summer day, which is about 0.14 W/cm$^2$. For densities below $10^8$ W/cm$^2$, ordinary heating, melting and some evaporation describe most of the effects. The generation of plasma from the laser-target interaction occurs at laser power density of about $10^8$ W/cm$^2$.

Laser ablation usually refers to power densities above $10^8$ W/cm$^2$. The first laser ablation experiment was done by Breech and Cross in 1962 [40], only several years after the invention of the optical laser. They used a ruby laser to vaporize a solid for the purpose of elemental analysis. Since then, a considerable amount of research, both theoretical and experimental, has been devoted to the subject of laser
interaction with solids. Applications include laser propulsion from laser sustained plasma generated by a continuous high power laser, production of high-particle flux atomic and molecular beams, spectrochemical analysis, chemical synthesis, materials processing, and pulsed laser deposition to prepare high temperature superconductive thin films [41]. Here, we are primarily interested in using the laser-induced plasma as an ion source. The laser power adopted for the current studies ranges from $10^8$ to $10^9$ W/cm$^2$.

To better characterize the laser-induced plasma as an ion source, we need to understand some of the physical processes involved. In the following sections, we will show the time-of-flight results that reveal some of the characteristics of the laser-induced plasma. Then, we will describe a physical picture of laser-solid interaction, introduce Puell's model [20, 21] and compare the model with our experimental results. Next, a simplified ionization model is established to explore the ionization structure in the laser-induced plasma.

3.2 Time-of-flight measurements of the laser-induced plasma

3.2.1 Experimental setup

The experimental setup includes a laser ablation ion source and two mass spectrometers, a linear one (LTOFMS) and a reflection one (RTOFMS). The RTOFMS and its associated vacuum and electrical system will be described exclusively in chapter 4.
1. Laser ablation ion source.

The laser is Nd:YAG Q-switched laser from Quanta-Ray. We use the fundamental frequency output at 1.06 μm. The pulse width is ~ 50 ns. A planar molybdenum target with purity of 99.95% is installed in a vacuum chamber. The laser beam incident on the target with a 45° angle. The motivation to use the molybdenum target is because we have some ablation research on the same target using an ion trap.

2. The LTOFMS.

The LTOFMS was designed and built by Dr. Kwong and later modified by the author. It consists of an extraction plate, a 1.0 m long drift tube and a slightly off-centered channel electron multiplier (CEM) detector. The off-center position of the CEM will help to shield it from the UV blast generated by the laser-induced plasma. The CEM is floated and can be biased so that either ions or electrons can be detected. The extraction plate is a circular plate of 5.3 cm in diameter with a center aperture of 0.06 cm in diameter. The surface of the extraction plate is perpendicular to the axial direction of the drift tube, and is parallel to the surface of the target with a separating distance of 6.7 cm.

3.2.2 Experimental methods

The LTOFMS is used to measure the ion and electron temperature and the expansion velocities of the laser-induced plasma. The extraction plate of the LTOFMS is used
to measure the total number of ions produced by the laser ablation. The RTOFMS is used to identify the ion species in the laser-induced plasma. Here we will derive a formula for the temperature and expansion velocity measurement by the LTOFMS. By directly grounding the LTOFMS drift tube, the time-of-flight profile will directly relate to the initial velocity distribution of the ions.

We will assume the following physical picture. The deposited laser energy vaporizes and ionizes $N_0$ particles. A plasma bubble is formed and heated to a certain temperature. It begins to expand against the substrate and gains recoil momentum. This momentum will give the plasma bubble a center-of-mass velocity $v_{\text{cm}}$ in the laboratory frame. As the plasma bubble expands in size and moves away from the surface, the number density of the particles decreases. At some time, $t$, after the laser ablation, the velocity distribution of the particles is frozen. Accordingly, the velocity distribution of the charged particles is Maxwellian with a translational component:

$$f(v_x, v_y, v_z) = 4\pi N_0 \left( \frac{m}{2kT} \right)^{3/2} \exp \left\{ -\frac{m}{2kT} \left[ (v_x - v_{\text{cm}})^2 + v_y^2 + v_z^2 \right] \right\} , \quad (3.1)$$

where $v_{\text{cm}}$ is the expansion velocity and $x$ is the expansion direction of the plasma. Since the drift tube is aligned with the expansion direction, the number of charged particles that arrive at the CEM during the time interval $t$ to $t + \Delta t$ is

$$N(t)\Delta t = \int_{-D/2t}^{D/2t} dv_y \int_{-D/2t}^{D/2t} dv_z \int_{t/\Delta t}^{t/t} dv_x f(v_x, v_y, v_z) , \quad (3.2)$$

where $l$ is the length of the flight path and $D$ is the diameter of the CEM detector.
Using \( \frac{1}{t + \Delta t} \approx \frac{1}{t} - \frac{\Delta t}{t^2} \), we have

\[
\int_{l/(t+\Delta t)}^{l/t} dv_x f(v_x, v_y, v_z) \approx f\left(\frac{l}{t}, v_y, v_z\right) \frac{\Delta t}{t^2}.
\] (3.3)

And because

\[
\int_{-D/2t}^{D/2t} dv_y \int_{-D/2t}^{D/2t} dv_z e^{-v_{z,0}^2/(2kT)} = \frac{2\pi kT}{m} \left(1 - e^{-\frac{mD^2}{8kTt^2}}\right);
\] (3.4)

We finally have:

\[
N(t) = \frac{4\pi^2 N_0 t}{t^2} \left(\frac{m}{2kT}\right)^{1/2} (1 - e^{-\frac{mD^2}{8kTt^2}}) e^{-\frac{m}{2kT} \left(\frac{l}{v_m}\right)^2}.
\] (3.5)

If the CEM works in the linear range, then the output current \( I(t) \) from the CEM will be proportional to \( N(t) \). For the ions, it can be shown that:

\[
\frac{mD^2}{8kTt^2} \ll 1,
\] (3.6)

Therefore, for ions:

\[
I(t) \propto \frac{N_0 l D^2}{t} \left(\frac{m}{2kT}\right)^{3/2} e^{-\frac{m}{2kT} \left(\frac{l}{v_m}\right)^2}.
\] (3.7)

### 3.3 Experimental results

The experiments are carried out in an ultrahigh vacuum of \( 2 \times 10^{-9} \) Torr. The results shown in section 3.3.1 and 3.3.2 are carried out with laser pulse energy \( \sim 20 \) mJ depositing on the target surface. The power density is estimated to be \( \sim 10^9 \) W/cm\(^2\).
3.3.1 Temperature and expansion velocity of the plasma

These characteristics are measured by using the LTOFMS with the CEM as the charged particle detector. The drift tube is grounded. The entrance of the CEM is floated to $-1020$ volts to collect the ions, and is floated to $+1020$ volts to collect the electrons. The CEM DC-bias voltage is set to be $+1000$ volts to accelerate the secondary electrons for multiplication. Laser shots were fired alternately with the CEM entrance floated to $-1020$ volts and $+1020$ volts. The averaged ion signal and the fitting result according to Eq. (3.7) are presented in Fig. 3.1. The initial dip in the ion signal is caused by the UV emission generated by the laser-induced plasma. The fitting shows good agreement with the raw data and thus indicates the laser induced plasma is indeed close to a thermal equilibrium state. The fitting gives:

1. Ion temperature: $2.9 \times 10^5$ K, corresponds to mean thermal energy of $\frac{3}{2}kT = 38$ eV, and mean thermal velocity of $\left(\frac{8kT}{\pi m}\right)^{1/2} = 8.0 \times 10^3$ m/s.

2. Ion expansion energy: $1.5 \times 10^2$ eV, corresponds to an expansion velocity of $1.7 \times 10^4$ m/s.

The averaged electron signal obtained by floating the CEM entrance to $+1020$ volts is surprisingly similar (in both the peak arriving time and the signal width) to the ion signal shown in Fig. 3.1. However, these electrons may be secondary electrons generated from the bombardment of the ions with the metallic surfaces near the CEM, we have inconclusive results on whether these electrons are directly from laser-induced
Figure 3.1: Ion detection by CEM and curve fitting by the translational Maxwellian distribution.
plasma.

If some of the electrons are directly from the laser-induced plasma, possibly trapped in the Coulomb potential well of the ions, they cannot account for the heating of the plasma because their temperature is rather low (\(\sim 1.5\) K). The electrons that heat up the ions will have a temperature above \(2.9 \times 10^5\) K, corresponding to a mean electron thermal energy of \(\frac{3}{2}kT = 38\) eV, and mean thermal velocity of \((\frac{8kT}{m})^{1/2} = 3.3 \times 10^6\) m/s. So these electrons will reach the CEM within \(1\mu s\). Since the thermal velocity of the these heating electrons is much larger than the ion expansion velocity, they will fly apart uniformly in \(4\pi\) solid angle. The fraction of electrons that reach the CEM is limited by the solid angle of the detector, and only \(10^{-4}\%\) of the total amount of electrons could be collected. Because of this and the intense UV emission from the plasma, we have not been successful in identifying the presense of the fast heating electrons.

3.3.2 Total number of ions produced by laser ablation

The total number of ions produced by the laser ablation can be obtained by using the extraction plate of the LTOFMS as the charge collector. Also this detection method can be used to determine the kinetic energy of the ions with moderate accuracy. The extraction plate (5.3 cm in diameter) will collect almost all of the ions because its size is larger than that of the ion sphere, which expands to about 3.6 cm in diameter (the thermal expansion velocity perpendicular to the expansion direction of the ions is \(\sim\)
4.6 × 10³ m/s from the thermal energy measured by the CEM). A small negative DC voltage (−2 volt) is applied to the extraction plate which is capacitively coupled to the oscilloscope. The DC-bias prevents the changing of the plate potential from the deposition of ions, and also repels the electrons that may travel with the ions. A clean ion signal is thus obtained. The total number of ions is calculated by integrating the ion signal over time. It is on the order of 10¹¹ at this laser power.

3.3.3 Ion species and their power dependency

RTOFMS is used to identify the ion species due to its high resolution power. Ions of differently charged states have been identified with the RTOFMS by comparing the measured time-of-flight with the calculated one. Fig.3.2 shows a RTOF mass spectrum averaged over 500 laser shots with laser pulse energy of 20 mJ deliver to the molybdenum target. Fig.3.3 shows the molybdenum ions production with higher laser powers. We have observed Mo⁸⁺ when the laser power reaches 80 mJ.

3.3.4 Derived plasma characteristics

It is interesting to look at other plasma characteristics based on our experimental measurements. Here, an electron temperature of 38 eV and an averaged electron density of 10¹⁸ cm⁻³ will be adopted. The estimate of the electron temperature is based on our ion temperature measurement, and estimate of the electron density is based on a heating zone volume of ~ 10⁻⁷ cm³ and total electron number of ~ 10¹¹.
Figure 3.2: Averaged laser ablation RTOF mass spectrum with the molybdenum target.

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Figure 3.3: Power dependency of the ion species of the laser induced plasma
from our total ion number measurement.

1. Electron Debye length.

It is a characteristic length beyond which the electrons shield out the electric field of a discrete charge.

\[ \lambda_{De} = \left( \frac{T_e}{4 \pi n_e e^2} \right)^{1/2}. \]  

(3.8)

With \( T_e = 38 \text{ eV} \) and \( n_e = 10^{18} \text{ cm}^{-3} \), \( \lambda_{De} \) is estimated to be \( 6.8 \times 10^{-2} \mu \text{m} \), which is much smaller than the laser wavelength. The number of electrons in the Debye sphere \( N_D \) is calculated to be \( \sim 1000 \), which means that the standard plasma kinetic theory may have a valid place here.

2. Electron-ion collision frequency.

The collision frequency can be estimated from \( f_{ei} \approx n_i \sigma v_e \), where \( n_i \) is the ion density, \( \sigma \) the collisional cross section, and \( v_e \) the electron thermal velocity. \( \sigma \) can be estimated from the elastic cross section: \( \sigma = \pi b^2 \), where \( b \) is the impact parameter and is about \( 10^{-8} \text{ cm} \). \( n_i \sim 10^{18} \text{ cm}^{-3} \). \( f_{ei} \) can therefore be estimated to be \( \sim 10^{11} /\text{s} \). This evidently shows the tendency of temperature equilibrium between the ions and the electrons during the plasma heating because time interval between the electron-ion collisions is much shorter than the laser pulse duration.

3. Electron's coherent motion.
The electron's coherent oscillatory motion in the laser electric field can be expressed as:

\[ v_{\text{coherent}} = \frac{eE_L}{m_e\omega_L}, \tag{3.9} \]

where \( \omega_L \) is the laser light frequency and \( E_L \) is the laser electric field. \( E_L = \frac{\Phi}{\alpha_0} \sim 6 \times 10^5 \) volt/cm, where \( \Phi \) is taken as \( 10^9 \) W/cm\(^2\). \( v_{\text{coherent}} \) is calculated to be \( 4.7 \times 10^3 \) m/s, which is much smaller than the thermal velocity of the electrons. So it is not expected for such coherent motion to modify much either the ion-electron collision frequency or the inverse Bremsstrahlung absorption coefficient [42]. This also diminishes the possibility that the electrons gain energy from the laser faster than their distribution can become Maxwellian [43].

### 3.4 Kinetics of laser-induced plasma

Laser ablation is a very complex phenomenon involving many processes: absorption, electronic excitation, vaporization, rapid heating, plasma generation, expansion, sputtering, and etc. It depends strongly on the power density and irradiation time. Here we will only discuss a simplified theoretical treatment of the laser-induced plasma at the power density of \( 10^8 - 10^{10} \) W/cm\(^2\) and the laser irradiation time on the nanosecond scale. Under these conditions, the laser ablation process can be roughly divided into three stages: (1) absorption of the laser radiation and vaporization of the target material; (2) plasma formation and heating; and (3) plasma expansion. We will discuss each in turn.
3.4.1 Absorption of the laser light and vaporization of the target material

Different laser power densities will have different absorption effects at the opaque surfaces. When the power density is low, heating without phase change occurs. When the power density is increased to a certain regime, laser-induced melting occurs. When the power density is further increased to above $10^8 \text{ W/cm}^2$, laser-induced vaporization becomes the main effect [44]. The minimum flux density for the vaporization process to play the principle role can be estimated from the following model. Suppose a laser pulse with a beam diameter of $r$, duration of $\tau$, and flux density of $\Phi$, we can estimate the depth of the heating layer by using a simplified solution of the time-dependent heat conduction equation:

$$\frac{dT}{dt} = \frac{K}{\rho c} \nabla^2 T,$$

(3.10)

where $T$ is the temperature, $\rho$ the density, $c$ the specific heat and $K$ the thermal conductivity. A simplified solution gives the depth of the heating layer during the laser pulse:

$$d = \frac{\pi}{2} \left( \frac{K \tau}{\rho c} \right)^{1/2},$$

(3.11)

If all the laser light energy is converted into the thermal energy, we can estimate the minimum flux density to vaporize the target by:

$$\Phi \pi \left( \frac{r}{2} \right)^2 \approx d \pi \left( \frac{r}{2} \right)^2 \rho \left( \frac{N_A}{M} \right) B,$$

(3.12)

where $N_A$ is the Avogadro constant, $M$ is the atomic weight of the target element. $B$ is the binding energy of the target atoms, and can be estimated from the vaporization...
temperature: \( B \sim kT_v \). Insert Eq.(3.11) into Eq.(3.12) and replace \( B \) with \( kT_v \), we obtain:

\[
\Phi = \frac{1}{2} \pi \left( \frac{K \rho}{\tau c} \right)^{1/2} \left( \frac{N_A}{M} \right) kT_v.
\]

For molybdenum, \( K = 138 \text{ W/m K, } c = 251 \text{ J/kg K, } T_v = 4639 \text{ K, } \rho = 10.2 \text{ g/cm}^3, \)
\( M = 0.096 \text{ kg. For a pulse of 50 ns, we estimate that the minimum flux density to have the vaporization take place is } \sim 2 \times 10^7 \text{ W/cm}^2. \)

This model suggests that less laser flux density is required to vaporize an element that is heavy, or of small thermal conductivity. Also, a laser pulse with shorter duration offers an advantage of vaporizing the target. The dynamics of the vaporization is certainly of interest [45] but is out of the scope of this dissertation.

### 3.4.2 Plasma formation and heating

At high laser flux densities, the thermal energy of the vaporized material exceeds the ionization energy and some electrons and ions are produced. Some electrons and ions may also come from the multiphoton ionization process. The ionized gas can not be treated as independent groups of electrons and ions. Our experiment indicates that the temperature of the ions during the laser ablation is on the order of \(10^5 \text{ K} \). This temperature is much higher than the phase-change (solid \( \rightarrow \) gas) temperature of the target, which is on the order of \(10^3 \text{ K} \). That means ions continue to gain energy after the ionized gas is formed. The increased energy could not be from the direct interaction between the ions and the laser field because neither the oscillation and
collision of the ions in the intense laser field nor the photon scattering contribute much to the energy gain due to the large mass of an ion. On the other hand, it is easier for an electron to gain energy in the oscillating laser field due to its small mass. Therefore, the energy gain of the ions can only be attributed to the interaction between the ions and electrons. There are three main mechanisms accounting for laser light absorption by the plasma. They are (a) inverse Bremsstrahlung, (b) resonance absorption and (c) absorption due to ion-acoustic turbulence. In the power density regime of \(10^8\) to \(10^{10}\) W/cm\(^2\), inverse Bremsstrahlung is the dominant effect [46].

Inverse Bremsstrahlung is a process in which an electron gets accelerated by absorbing a photon in the intense laser electric field. And then the electrons' gained momentum is transferred to the ions by collisions. In this picture, the electron temperature should be equal to or slightly higher than that of the ions. They tend to be equal if the collision frequency is high enough. This tends to be the case for our laser ablation ion source. A Maxwellian distribution of ions and electrons produces the following inverse Bremsstrahlung absorption coefficient [46]:

\[
K_{ib} = \frac{16\pi (2\pi)^{1/2}}{3} \frac{Z^2 n_e n_{ie} e^6 \ln \Gamma}{c (m_e T_e)^{3/2} \omega_L^2 \left(1 - \frac{n_e}{n_c}\right)^{1/2}},
\]

where \(n_e\), \(T_e\), and \(m_e\) are the density, temperature and the mass of the electrons, \(n_i\) and \(Z\) are the density and charge of the ions. \(n_c\) is the electron critical density at which the corresponding plasma frequency \(\omega_p = (4\pi e^2 n_e/m_e)^{1/2}\) equals the frequency \(\omega_L\) of the incident light. \(\Gamma = \frac{\omega_L}{\omega_p b_{\text{min}}}\), and \(b_{\text{min}} = \max\left(\frac{Ze^2}{T_e}, \frac{h}{(m_e T_e)^{1/2}}\right)\). \(v_{te}\) is the electron thermal velocity. \(\Gamma\) is the ratio of the maximum and the minimum impact
parameters and is estimated to be in the range of 1 to 10. The laser light cannot penetrate densities above \( n_c \). All laser light absorption and reflection processes occur at electron densities \( n_e < n_c \), in the 'underdense plasma'.

The heating of the plasma from the laser light can last for the duration of the laser pulse. The velocity of the ions is on the order of \( 10^4 \) m/s, as we measured from the linear time-of-flight experiment (see section 3.3.1). Thus, during a 50 ns laser pulse an ion electron pair can move as far as \( 5 \times 10^{-4} \) m. This length scale is larger than the radius of the focal spot. This means the plasma will not keep building up the temperature during the whole course of the laser shot because the plasma keeps moving out of the heating zone. A steady state can be assumed when the plasma exhibits a stationary flow, where the laser energy carried into the heating zone is equal to the energy flow carried out by the plasma coming away from the heating zone. Furthermore, this leads to a picture in which the temperature of the plasma will be increased to a certain value during the first few nanoseconds and then, kept constant for the remaining time of the laser pulse.

Puell's model \[20, 21\] of calculating the temperature of the laser-induced plasma assumes stationary flow. Although many other models exist, Puell's model is easy to understand and provides good physical senses. In the following, his theory will be applied toward our experimental situation.

According to Puell, the electron temperature right after a laser pulse is:

\[
kT_e = a^{-\frac{3}{2}} \left( \frac{3MCR}{50} \right)^{\frac{3}{2}} \Phi^{\frac{4}{3}},
\]  

(3.15)
where $a = \frac{Z^{+1}}{Z}$, $M$ is the ion mass, $R$ is the radius of the focal spot, $\Phi$ is the incoming light flux density and $C = 2.5 \times 10^{-55} \left(\frac{\omega_R}{\omega}\right)^2$ (cgs units), $\omega$ is the angular frequency of the employed laser, and $\omega_R$ is the angular frequency of the ruby laser. With laser emission at 1.06 \mu m, power density of $\Phi$ of $10^9$ W/cm$^2$, a focal radius of $5 \times 10^{-3}$ cm and averaged ion charge $Z$ to be 2, the electron temperature of a molybdenum laser-induced plasma is calculated to be 22 eV. This means the ion temperature should also be $\sim 22$ eV. Although it does not match our measurement exactly, it is not far away from the measurement either. We are satisfied because we are using a very crude model.

An interesting point can be drawn from Puell’s equation. The larger the ion mass, the higher the plasma temperature would be. This is understandable because the plasma will move slower with larger ion mass, resulting in more heating time from the laser pulse. Our experimental results on a carbon target support this argument, though do not agree quantitatively. Using comparable laser power density on a pure carbon target, we estimate the ion temperature of carbon to be $\sim 12$ eV (see chapter 5), about three times lower than that of the molybdenum target.

### 3.4.3 Plasma expansion velocity

It is also called plasma blow-off velocity. A simple estimate is that the blow-off velocity is roughly equal to the local sound velocity, for $n_e = n_i$,

$$v = \left(\frac{ZT_e}{m_i}\right)^{1/2},$$  

(3.16)
which is close to $10^6$ cm/s. Several different types of analytic theories [47, 48] indicate that the blow-off velocity should be at least sonic at the critical density surface, and it should then rise to supersonic values for densities $n_e < n_c$. So this is basically in agreement with our experiments.

3.5 Ionization structure in laser-induced plasma

In the following, we will discuss the ionization structure of the laser-induced plasma. This is important since we often want to maximize the production of ions in a specific charge state.

3.5.1 The ionization plasma model

Due to the complexity of the problem, it is very difficult to completely solve the ionization structure in the laser-produced plasma. Here we present a qualitative idea of the concentrations of various ions in the initial plasma stage. The following assumptions are made:

1. The plasma is optically thin and photoionization can be neglected.

2. Each ionization stage has only a ground state.

3. Ionization equilibrium is reached, that is, we have a steady state ionization structure.

The above conditions may not be exactly valid, but can nevertheless serve as a useful first approximation. With these assumptions, the ionization process is controlled
by electron impact (Eq. (3.17) with $\rightarrow$), while recombination may be either by
three-body collisional (Eq. (3.17) with $\leftarrow$) or radiative processes (Eq. (3.18)).

$$e + A^{z+} \leftrightarrow A^{z+1} + e + e,$$
(3.17)

$$e + A^{z+1} \rightarrow A^{z+} + h\nu.$$
(3.18)

The ionization equilibrium equation is established as the balance between the ioniza­
tion and recombination [49]:

$$\frac{c_{z+1}}{c_z} = \frac{S(T_e)}{\alpha(T_e, n_e)},$$
(3.19)

where $c_{z+1}, c_z$ are the concentrations of ions in stages $z+1, z$, respectively, $c_1$ is the
concentration of the neutral atom, $S(T_e)$ is the collisional ionization coefficient, and
$\alpha(T_e, n_e)$ is the recombination coefficient including two parts:

$$\alpha(T_e, n_e) = \alpha_r(T_e) + n_e \beta(T_e),$$
(3.20)

where $\alpha_r(T_e)$ the radiative recombination coefficient and $\beta(T_e)$ the collisional three-
body recombination coefficient. The empirical expressions for these rate coefficients
will be adopted here. They are adjusted to give good fits to reliable data [50].

$$S(T_e, z) = 2.34 \times 10^{-7} \sigma T_e^{\frac{1}{2}} \chi(z)^{-\frac{1}{2}} e^{-\frac{\chi(z)}{k T_e}} \text{cm}^3\text{s}^{-1},$$
(3.21)

$$\alpha_r(T_e, z) = 2.05 \times 10^{-12} \frac{\chi(z)^{\frac{1}{2}}}{T_e} \text{cm}^3\text{s}^{-1},$$
(3.22)

$$\beta(T_e, z) = 4.78 \times 10^{-23} \sigma T_e^{-\frac{3}{2}} \chi(z)^{-\frac{1}{2}} \frac{g_z}{g_{z+1}} \text{cm}^6\text{s}^{-1},$$
(3.23)

where $\sigma$ is the number of outer electrons, $T_e$ is the absolute electron temperature in the
unit of K, $\chi(z)$ is the ionization potential (in eV) of the ion of charge $z$ in its ground
state, and $g$ is the statistical weight of the ground state. Generally, three cases can be distinguished: (1) corona limit, $n_e \beta \ll \alpha_r$. The radiative recombination dominates over the three body recombination and the ionization equilibrium is independent of $n_e$; (2) Saha or LTE limit, $n_e \beta \gg \alpha_r$. The equilibrium is controlled entirely by collisions; (3) non-LTE case, $n_e \beta$ and $\alpha_r$ are comparable. Radiative and three body recombination are both important.

### 3.5.2 Corona limit

If we assume a corona plasma model, and consider up to $n$ ionization stages, then we have a set of linear equations:

$$
\frac{c_i}{c_{i+1}} = \frac{\alpha_i(T_e)}{S_i(T_e)},
$$

where $i = 1, 2, ..., n-1$ and $c_1$ is the concentration of the neutral atom, $c_i (i = 2, 3, ..., n)$ is the concentration of $i-1$ charge state ions. Their summation are normalized to unity.

$$
c_1 + c_2 + ... + c_n = 1.
$$

These equations can be used to solve $n$ concentrations that are corresponding to $n$ ionization stages. The answer can be easily seen:

$$
c_1 = \frac{1}{1 + \frac{\alpha_1}{\alpha_1} + \frac{\alpha_1 \alpha_2}{\alpha_1 \alpha_2} + \cdots + \frac{\alpha_1 \alpha_2 \cdots \alpha_{n-1}}{\alpha_1 \alpha_2 \cdots \alpha_{n-1}}},
$$

$$
c_2 = \frac{c_1 \beta_1}{\alpha_1},
$$

$$
c_3 = \frac{c_1 \beta_1 \beta_2}{\alpha_1 \alpha_2},
$$

...
Table 3.1: Atomic parameters of molybdenum ions

<table>
<thead>
<tr>
<th>Atomic term</th>
<th>$\sigma$</th>
<th>$g$</th>
<th>$\chi$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoI $^7S_3$</td>
<td>6</td>
<td>7</td>
<td>7.10</td>
</tr>
<tr>
<td>MoII $^6S_{5/2}$</td>
<td>5</td>
<td>6</td>
<td>16.15</td>
</tr>
<tr>
<td>MoIII $^5D_0$</td>
<td>4</td>
<td>5</td>
<td>27.13</td>
</tr>
<tr>
<td>MoIV $^4F_{3/2}$</td>
<td>3</td>
<td>28</td>
<td>46.4</td>
</tr>
<tr>
<td>MoV $^3F_2$</td>
<td>2</td>
<td>35</td>
<td>61.2</td>
</tr>
<tr>
<td>MoVI $^2D_{3/2}$</td>
<td>1</td>
<td>20</td>
<td>68</td>
</tr>
<tr>
<td>MoVII $^1S_0$</td>
<td>6</td>
<td>1</td>
<td>126</td>
</tr>
<tr>
<td>MoVIII $^2P_{3/2}$</td>
<td>5</td>
<td>12</td>
<td>153</td>
</tr>
<tr>
<td>MoIX $^2D_{5/2}$</td>
<td>4</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

\[ c_i = \ldots, \]
\[ c_n = \frac{c_1s_1s_2\ldots s_{n-1}}{\alpha_1\alpha_2\ldots\alpha_{n-1}}. \]  

(3.29)

This model will be applied to the laser-induced molybdenum plasma at various electron temperatures, and the results will be discussed later. The ionization potential and other atomic parameters of molybdenum ions are listed in table 3.1 [51].

3.5.3 Saha limit

If we assume a Saha limit, where only three-body recombination is considered, then we have a set of nonlinear equations:

\[ \frac{c_i}{c_{i+1}} = \frac{n_e\beta(T_e)}{S_i(T_e)}, \]  

(3.30)

where $i = 1, 2, \ldots, n - 1$, and

\[ n_e = n_i(c_2 + 2c_3 + 3c_4 + \ldots + (n - 1)c_n), \]  

(3.31)
where \( n_i \) is the number density of ions in the plasma. Eq.(3.30) is actually the Saha equation. The system of equations Eq.(3.30), Eq.(3.31), together with Eq.(3.25) can be numerically solved by using the Newton-Raphson method. The results will be discussed next.

### 3.5.4 Results and discussions

Fig.3.4 and Fig.3.5 display the electron temperature dependence of the concentrations of differently charged ions in the corona limit and in the Saha limit, respectively.

First, it is obvious that the concentrations of various ionization stages are strongly dependent on the plasma temperature. At certain temperatures, ions with few ionization stages will dominate the concentration. As the temperature increases, the ions in the lower ionization stage decreases. This is in agreement with the RTOFMS measurement of the ion species. At lower laser pulse energy of less than 5 mJ, the ion peak intensity of Mo\(^+\) dominates over the other Mo\(^q+\) with \( q \leq 2 \), while at laser energy of 20 mJ, the the peak intensity of Mo\(^2+\) and Mo\(^3+\) exceed that of Mo\(^+\) (see Fig.3.2).

Secondly, an obvious difference in Fig.3.4 and Fig.3.5 is the concentration profile of Mo\(^6+\) ions. In the corona limit, this is understandable because Mo\(^6+\) has a very high ionization potential which makes it hard to be ionized and easy for Mo\(^7+\) to recombine radiatively. Meanwhile, Mo\(^5+\) has a relative low ionization potential which makes it easy to be ionized and hard for Mo\(^6+\) to recombine radiatively. In the Saha limit,
Figure 3.4: Ionization structure obtained under corona limit.
Figure 3.5: Ionization structure obtained under Saha limit.
this is also explainable because the three body recombination coefficient is inversely proportional to $\chi^{1.75}$, which means Mo$^{6+}$ has a high collisional recombination rate due to its high ionization potential. The RTOFMS experiments (see Fig.3.3) shows a large amount of Mo$^{5+}$ being produced, while the ion trap experiment shows the relative easiness for trapping Mo$^{6+}$ ions.

Finally, the ionization structure in a non-LTE case is shown in Fig.3.6, in which the concentration profiles of Mo$^{5+}$ and Mo$^{6+}$ become close.

After the heating stage, the plasma begins to expand. Both the density of the electrons and ions will quickly drop, leading to fast decaying ionization rates and recombination rates, and 'ionization frozen' state is said to take place.

The ionization models described above only agree qualitatively with the experimental measurements. Quantitatively, noticeable discrepancies exist between the two. The ionization structure is more broadened in our measurement as compared with Fig.3.6. The model-predicted temperature, at which a similar concentration is produced as that in Fig.3.2, is about five times smaller than the experimental value. And when the laser pulse energy is increased significantly, Mo$^+$, Mo$^{2+}$ ions are expected to disappear according to the model, but the experiments show that a significant number of singly and doubly charged ions are always there. Some of the discrepancies between the theory and the experiment may arise from the laser pulse intensity-vs-time profile and the transverse mode of the laser spot.
Figure 3.6: Ionization structure in a non-LTE case.
3.6 Conclusions

In summary, we have measured some characteristics of the laser-induced plasma through the time-of-flight mass spectrometric method. The simplified kinetic theory and ionization model offers approximate yet not perfect agreement with the experiments. For a thorough understanding of the laser-induced plasma, further experiments using various techniques and more complicated theory are needed.

The present experiment indicates some advantages using the laser-induced plasma as the ion source: (1) it has a copious supply of ions per pulse; (2) it offers flexibility in generating multiply-charged ions of a wide variety of element species; (3) it has the absence of any carrier gas; (4) it is simple in design and construction and (5) it is suitable for time-of-flight measurement because of the short laser pulse.
CHAPTER 4

DESIGN AND CONSTRUCTION OF REFLECTION TIME-OF-FLIGHT MASS SPECTROMETER

4.1 Introduction

The reflection time-of-flight mass spectrometer (RTOFMS) is a type of nonmagnetic time-of-flight mass spectrometer in which ions from a point source with an initial velocity spread are reflected and time focused into a detector. It is designed to improve the mass-to-charge resolution. Here, the design and construction of a RTOFMS was first motivated to probe the laser-induced plasma, and was found later that it could be used to measure the charge-transfer cross sections.

The RTOFMS compensates for the difference in the time-of-flight of the ions of different energies by means of an ion reflector. The ions with greater velocity will spend less time in the field-free drift region, however, they will have to spend more time in the reflection region because ions with greater velocity will penetrate a greater distance into the reflection region than the ions with slower velocity. The RTOFMS is designed so that ions with different initial velocity will arrive at the
detector at almost the same time. The idea of RTOFMS can be traced back to Karataev, et al [52]. Since then RTOFMS has been developed into two forms: linear RTOFMS (ions will be reflected at 180°) and V-shaped RTOFMS (ions will follow a V-shaped trajectory). RTOFMS has found applications in laser photodissociation [53], identification of cluster ions [54], trace detection of organic molecules, etc.

In the following sections, the optimal parameters and resolving power for a V-shaped RTOFMS are examined. Factors that influence the the resolution are also discussed. The design and construction are given in detail, and finally two mass spectra of laser ablated ions from a carbon target and a tungsten disicilide target will be shown.

4.2 Optimum parameters for second-order focusing

4.2.1 Grounding of the drift tubes

The general configuration for a V-shaped RTOFMS with grounded drift tubes is shown in Fig.4.1. The total time-of-flight is,

\[ t = t_L + t_D + t_R, \quad (4.1) \]

where \( t_L \) is the time-of-flight through the field-free region, \( t_D \) is the time-of-flight through the deceleration space, and \( t_R \) is the time-of-flight in the reflecting region.

Suppose the initial velocity of an ion in the expansion direction is \( v \), and the average initial velocity of the ions in the expansion direction is \( v_0 \), and the ion charge
Figure 4.1: Sketch of the RTOFMS configuration.
is $q$. Define:

$$U_0 = \frac{1}{2} \frac{mv_0^2}{q}, \quad (4.2)$$

$$k = \left( \frac{v}{v_0} \right)^2, \quad (4.3)$$

where $U_0$ represents the average equivalent potential applied to the initial-still ions to achieve the same initial kinetic energy, and $k$ represents the initial kinetic energy spread. With these definitions, $t_L, t_D$ and $t_R$ can be derived using Newtonian mechanics:

$$t_L = L \left( \frac{2qU_0}{m} \right)^{\frac{1}{2}} k^{-\frac{1}{2}}, \quad (4.4)$$

$$t_D = 4d_D \left( \frac{U_0}{U_D} \right) \left( \frac{2qU_0}{m} \right)^{-\frac{1}{2}} k^{\frac{1}{2}} - \left( k - \frac{U_D}{U_0} \right)^{\frac{1}{2}}, \quad (4.5)$$

$$t_R = 4d_R \left( \frac{U_0}{U_R} \right) \left( \frac{2qU_0}{m} \right)^{-\frac{1}{2}} \left( k - \frac{U_D}{U_0} \right)^{\frac{1}{2}}, \quad (4.6)$$

where $L$ is the total drift tube length: $L = L_I + L_R$. The total time-of-flight can be written as:

$$t = C F(k), \quad (4.7)$$

where

$$C = 4d_R \left( \frac{U_0}{U_R} \right) \left( \frac{2qU_0}{m} \right)^{-\frac{1}{2}}, \quad (4.8)$$

$$F(k) = Ak^{-\frac{1}{2}} + nA \left( k^{\frac{1}{2}} - (k - p)^{\frac{1}{2}} \right) + (k - p)^{\frac{1}{2}}. \quad (4.9)$$

Here,

$$A = \left( \frac{L}{4d_R} \right) \left( \frac{U_R}{U_0} \right), \quad (4.10)$$
\( n = \left( \frac{i d_D}{L} \right) \left( \frac{U_0}{U_D} \right), \)

\( p = \frac{U_D}{U_0}. \)

\( A, n, p \) and \( C \) are constants that are independent of \( k \). The resolution is defined as

\[ R = \frac{t_0}{2\Delta t} = \frac{t_0}{2(t - t_0)}. \]

From Eq.(4.7), the resolution is only restricted by the initial energy spread of the ions and can be expressed as:

\[ R = \frac{F(1)}{2[F(k) - F(1)]}. \]

In order to have a high resolution time-of-flight mass spectrometer, \( F(k) \) should be very close to \( F(1) \). Making Taylor expansion of \( F(k) \) at \( k = 1 \), we have

\[ F(k) = F(1) + \left( \frac{dF}{dk} \right)_{k=1} (k - 1) + \left( \frac{d^2F}{dk^2} \right)_{k=1} \frac{(k - 1)^2}{2} + \cdots. \]

Assuming that \( n \) is much smaller than 1 (\( n \) will be enforced to be a small value during the later design and construction), we obtain the derivatives of \( F \) versus \( k \) from Eq.(4.9):

\[
\frac{dF}{dk} \approx -\frac{1}{2} Ak^{-\frac{3}{2}} + \frac{1}{2}(k - p)^{-\frac{1}{2}},
\]

\[
\frac{d^2F}{dk^2} \approx \frac{3}{4} Ak^{-\frac{5}{2}} - \frac{1}{4}(k - p)^{-\frac{3}{2}},
\]

\[
\frac{d^3F}{dk^3} \approx -\frac{15}{8} Ak^{-\frac{7}{2}} + \frac{3}{8}(k - p)^{-\frac{5}{2}},
\]

\[
\frac{d^4F}{dk^4} \approx \frac{105}{16} Ak^{-\frac{9}{2}} - \frac{15}{16}(k - p)^{-\frac{7}{2}},
\]
By setting the first- and second-order terms to be zero we will achieve the second-order focusing and high resolving power. The solutions are:

\[ P = \frac{2}{3}, \quad A = 3^{\frac{1}{2}}. \]

\subsection{4.2.2 Floating of the drift tubes}

In order to extract the ions in a more efficient way, floating of the drift tubes is preferred. There are two cases we would like to discuss under the floating category. In both cases, we have taken the acceleration length as part of the drift tube length for convenience. The resulting error here will be insignificant and if it does affect the performance of the RTOFMS, we believe that the second-order focusing can still be achieved by tuning variable parameters, such as the potentials on the deceleration and the reflection plates.

\textbf{case 1.} The reflection and deceleration plates are not floated to the drift tube level.

Denote \( U_f \) to be the floating voltage applied to the drift tubes (a negative value for positive ions). The total time-of-flight can still be expressed as:

\[ t = CF(k). \]
However here,

\[ F(k) = A(k - f)^{-\frac{1}{2}} + nA((k - f)^{\frac{1}{2}} - (k - p)^{\frac{1}{2}}) + (k - p)^{\frac{1}{2}}. \]  

(4.25)

where

\[ f = \frac{U_f}{U_0}, \]  

(4.26)

\[ n = \left(\frac{4d_D}{L}\right)\left(\frac{U_0}{U_D - U_f}\right), \]  

(4.27)

and other parameters are of the same definitions as those in the case of grounded drift tubes. As in the treatment of the ground-drift-tube case, by assuming \( n \) to be much smaller than 1, expanding \( F(k) \) into Taylor series, and enforcing the first two terms to be zero to achieve second-order focusing, we will establish two equations. The solutions are:

\[ p = \frac{1}{3}(2 + f), \]  

(4.28)

\[ A = 3^{\frac{1}{2}}(1 - f). \]  

(4.29)

Case 2. The reflection and the deceleration plates are floated to the drift tube level.

With similar treatment, it can be derived that:

\[ F(k) \approx A(k - f)^{-\frac{1}{2}} + (k - f - p)^{\frac{1}{2}}. \]  

(4.30)

By applying the second-order focusing conditions, we have,

\[ p = \frac{2}{3}(1 - f), \]  

(4.31)

\[ A = 3^{\frac{1}{2}}(1 - f). \]  

(4.32)
Comparing the two cases, we prefer the first one, because the $p$ and $A$ values are smaller so that less potentials need to be applied to the deceleration and reflection plates to achieve the second-order focusing.

### 4.3 Design parameters of the RTOFMS

Six parameters need to be determined. They are $L$, $d_D$, $d_R$, $U_D$ and $U_R$ and $U_f$, among which $L$, $d_D$, $d_R$ are the most important because they would be fixed once the construction is completed, while other parameters are adjustable. We start out by summing Eq.(4.28) and Eq.(4.29), where $A$ and $p$ are replaced with their definition in Eq.(4.10) and Eq.(4.12):

$$
\frac{U_R + U_D}{U_0} = \left[ \frac{2}{3} + 3^{1/2} \left( \frac{4d_R}{L} \right) \right] - \left[ 3^{1/2} \left( \frac{4d_R}{L} \right) - \frac{1}{3} \right] f .
$$

(4.33)

We make the following observations:

1. Obviously, $U_R + U_D$ has to be greater than $U_0$, otherwise the ions will not be reflected. Therefore from Eq.(4.33), we have

$$
\frac{d_R}{L} > \frac{3^{1/2}}{36} .
$$

(4.34)

2. We have assumed that

$$
n = \left( \frac{4d_D}{L} \right) \left( \frac{U_0}{U_D - U_f} \right) \ll 1 .
$$

(4.35)

In order to satisfy that, $d_D$ should be as small as possible. It is reasonable to set

$$
\frac{d_D}{L} < 1\% .
$$

(4.36)
Table 4.1: Design parameters of the RTOFMS.

<table>
<thead>
<tr>
<th>$L_i$</th>
<th>$L_r$</th>
<th>$d_D$</th>
<th>$d_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>146.0 cm</td>
<td>42.0 cm</td>
<td>1.7 cm</td>
<td>13.3 cm</td>
</tr>
</tbody>
</table>

3. Although $d_D$ should be as small as possible, it has limits. We have assumed a uniform deceleration field between the float tube termination plate and the deceleration plate. The plates will be in the form of grids to achieve the uniformity. However, if the two grids are mounted too close to each other, the gradient of the electrostatic field near the grid wires will be rather high and the ions will be effectively scattered.

With the above observations, we have decided to use the parameters shown in Table 4.1, where $L_i$ and $L_r$ represent the lengths of the incidence drift tube and the reflection tube, respectively.

4.4 Resolution analysis

4.4.1 Resolution limited by initial energy spread

With the second-order focusing conditions satisfied, it can be shown from Eq.(4.13) – Eq.(4.21, and Eq.(4.25) that:

$$
R \approx \frac{64(1-f)^3}{a(k-1)^3 - b(k-1)^4(1-f)^{-1} + c(k-1)^5(1-f)^{-2} - d(k-1)^6(1-f)^{-3}}
$$

(4.37)
where $a = 24$, $b = 75$, $c = 189$, and $d = \frac{1807}{4}$. In our laser plasma case, $k \sim 1.5$. From Eq.(4.37), a resolution power of more than 1000 is readily achieved. However, many other factors besides the initial velocity spread will degrade the resolution.

4.4.2 Resolution limited by construction factors

Setting $k = 1$, i.e., no initial energy spread, we will look at the resolution limited by the construction factors. An uncertainty analysis on Eq.(4.7) shows that:

$$
\left( \frac{\Delta t}{t} \right)^2 = a_1 \left( \frac{\Delta L}{L} \right)^2 + a_2 \left( \frac{\Delta d_D}{d_D} \right)^2 + a_3 \left( \frac{\Delta d_R}{d_R} \right)^2 + a_4 \left( \frac{\Delta U_D}{U_D} \right)^2 + a_5 \left( \frac{\Delta U_R}{U_R} \right)^2 ,
$$

(4.38)

where $a_1 = 0.53$, $a_2 = 4.7 \times 10^{-4}$, $a_3 = 6.4 \times 10^{-2}$, $a_4 = 7.5 \times 10^{-2}$ and $a_5 = 6.3 \times 10^{-2}$. The values of these coefficients are obtained by inserting the design parameters shown in Table 4.1. One way to have a resolution power of $10^3$ is to require each of the five terms on the right hand side of Eq.(4.38) to be less than $2 \times 10^{-7}$, and then we get:

$$
\left| \frac{\Delta L}{L} \right| \leq 6 \times 10^{-4}, \quad \left| \frac{\Delta d_D}{d_D} \right| \leq 2 \times 10^{-2}, \quad \left| \frac{\Delta d_R}{d_R} \right| \leq 2 \times 10^{-3}, \quad \left| \frac{\Delta U_D}{U_D} \right| \leq 2 \times 10^{-3}, \quad \left| \frac{\Delta U_R}{U_R} \right| \leq 2 \times 10^{-3},
$$

(4.39)

These are very stringent restrictions. However, these are for the ground-drift-tube case. Conditions can be relaxed with floating drift tubes. Efforts have been made to limit the time-of-flight uncertainties caused by these factors. The most degrading factor, we meet during the construction, is the flatness of the mesh plate. It is very difficult to mount the mesh on a plate without distorting the flatness of the mesh.
4.4.3 Resolution limited by ion detectors

The transit time spread for the ion detector is also a limiting factor for the resolution. CEM has a long channel length and a typical transit time spread as long as 20 ns, while MCP (microchannel plate) has a very short channel length and a transit time spread of ~ 2 ns. For a total time-of-flight of 20 μs, the maximum resolution of RTOFMS is limited to $10^3$ for the CEM detector, as compared to $10^4$ for the MCP detector.

4.5 Construction of the RTOFMS

We have adopted a V-shape scheme with a $6^\circ$ reflection angle. The structure of the RTOFMS mainly consists of four parts: the incidence drift tube assembly, the reflectron assembly, the reflection drift tube assembly and the detector assembly. The reflectron is housed in a vacuum chamber that has interfaces with the two drift tubes. The two drift tubes are installed in separate vacuum housing tubes to eliminate stray ions from cross traveling.

4.5.1 Incidence drift tube assembly

The incidence drift tube assembly includes the extraction plate, the insulated drift tube, the extension drift tube to the termination plate, two pairs of deflection plates, and an electrostatic lens.

The extraction plate is used to extract ions into the drift tube. It is a metal
round plate of 3.25" in diameter and a circular aperture of 0.03" in diameter. The insulated drift tube is ~ 2" in diameter and made of 50% steel mesh. It is insulated from the 2.5" vacuum housing tube by 0.25" ceramic standoffs. Two sets of orthogonal positioned steering plates are installed inside the entrance section of the incidence drift tube. Each set consists of two square-shaped parallel plates (1.25" in length) with 1" separation. Close to the far end, a cylindrical metal tube of 1.5" in both diameter and length is installed to serve as an einzel lens or unipotential lens. The lens is coaxial with the drift tube. The focusing ability depends on the potential difference between the lens and the drift tube. At the far end, an extension tube of 1.5" in diameter is used to extend the incidence drift tube to the drift termination plate.

4.5.2 Reflectron assembly

The reflectron assembly includes the drift tube termination plate, the deceleration plate, the supporting rings and the reflection plate. The termination plate is used to ensure the field-free property inside the drift tube. It is a mesh-covered ring structure. The deceleration plate is again a mesh-covered plate to ensure the uniformity of the deceleration field. This is important because we have assumed a uniform electric field in our derivation of the time-of-flight. The mesh we have used to cover the termination and deceleration plates is a photoetched stainless steel 304 mesh produced by Buckbee Mears. It has 50 lines/inch with finished wire size of 0.001". The transmission is about 90%. Although with the same transmission coefficient, the electroformed nickel or
copper mesh will have a higher line density and therefore better uniformity than the etched stainless steel mesh, we did not use them because the etched stainless steel mesh is less likely to warp, especially if heated.

Between the deceleration plate and the reflection plate, we used nine equally-spaced supporting rings, to attain a uniform field. In order to reduce the accumulated attenuation, the supporting rings are not covered with meshes. We have used the Simion program to examine the situation. Simion PC 4.02 is a computer program for designing and analyzing charged particle lenses, ion transport systems, and various types of mass spectrometers. The user specifies the potential on the boundaries, and the program uses finite difference techniques (with self-adjusting over relaxation) to solve the Laplace equation for the potential at nonelectrode points [55]. Equipotential contours inside the reflectron with four supporting rings and nine supporting rings are compared. Nine supporting rings show much better uniformity, and thus are adopted in the final design. The voltages on the supporting rings are from one power supply with vacuum resistors as the voltage dividers. In this way, the feedthrough connections are substantially reduced. The resistance of the resistors should be high enough to prevent them from burning down under high voltages. Notice that the resistors in the vacuum dissipate their heat mainly through the blackbody radiation. Meanwhile, the resistance should not be too high, otherwise charges accumulating on the plates will cause a change in their electrical potentials. After careful considerations, we have chosen to use precision metal oxide high voltage resistors of 1 megohm
resistance. They are from K&M Electronics. Each resistor is rated as having power
dissipation of 1 watt at 70° Celsius, maximum operating voltage of 2500 volt and
maximum surface temperature of 220° Celsius. The resistors are glass coated with
nickel leads.

4.5.3 Reflection drift tube assembly

The reflection drift tube assembly includes an insulated drift tube, an electrostatic
lens, a termination plate on each end, and an extension drift tube. The electrostatic
lens is constructed the same way as the one in the incidence drift tube, and functions
equally. It can be used in the mass spectrometry to increase the sensitivity. However,
as currently we are interested in measuring the charge-transfer cross section in the
reflection drift tube, we have tied its potential with that of the reflection drift tube.
The reflection drift tube is not in touch with the incidence one so that the two drift
tubes can be applied with different voltage potentials. This is a feature that enables
us to measure the charge-transfer cross sections at different energies without losing
much sensitivity.

4.5.4 Ion detector assembly

Two versions of the ion detector have been built. One is CEM-based, the other is
MCP-based. The CEM is a Galileo 4816 high current channel electron multiplier.
Three transparent grids are installed in front of the CEM. The grid immediately
in front of the CEM is held at the same potential as the CEM cathode potential to prevent secondary electrons from being extracted out. The other two grids have nothing to do with the mass spectrometry, but play an essential role in the charge-transfer measurements. They will be fully discussed in chapter 5.

The MCP-based detector assembly is quite similar to the CEM-based one. The MCP is a Galileo Chevron 3025. It is a two-stage microchannel plate detector. Each plate has an active area of 4.9 cm², center-to-center spacing of 12 microns, pore size of 10 microns, minimum OPR (opening-area-ratio) of 55%, the bias angle (the angle of the channel with respect to the surface normal) of 12°, gain of $6.5 \times 10^6$ with maximum voltage of 2000 volts, pulse height distribution of 130% FWHM at 2000 volts and the dark count rate of 4 counts per second per cm². It can be calculated that the total number of channels in each plate is $3.4 \times 10^6$. The detector assembly is put together under class 100 laminar flow clean room conditions. A shielding plate is put in front of the Chevron with $\frac{1}{4}$" distance from the first MCP of the Chevron to prevent the possible backstreaming of the secondary electrons. The anode is connected to an instrumentation feedthrough that is impedance-matched to 50 ohms with 1 Ghz bandwidth (single-ended type N coaxial connector with 500 volts maximum). The connection is made through a 50-ohm vacuum coaxial cable. The other connections are made through spring-connections to feedthrough pins mounted on a tee arm.

The MCP-based detector is motivated by a digital detection scheme designed by the author. This scheme relies on the fact that a MCP offers much higher individual
ion detection resolution than a CEM. However, the MCP has been noisier than the CEM during the charge-transfer measurement.

4.6 Established system

The established RTOFMS with the laser ablation ion source is shown in Fig.4.2

4.6.1 Vacuum and electrical system

The system is designed to work at ultrahigh vacuum. The vacuum system is shown in Fig.4.3. A turbo-molecular pump backed by a fore-vacuum pump is used to pump the entire system including the laser ablation chamber, the reflectron chamber and the drift tubes. The turbo-molecular pump is a Leybold Turbvac 600 with pumping speed of 560 l/s for N₂. The fore-vacuum pump is an Alcatel 2020A oil-sealed mechanical pump with free air displacement of 26.9 m³/h. A molecular sieve trap (MST-200 from Kurt J. Lesker) is installed in the foreline to stop the mechanical pump oil vapors from migrating or backstreaming into the turbo-molecular pump and the RTOFMS system. A safety circuit is built to ensure the protection against electricity, water, temperature and foreline pressure failure. An inline pneumatic value (model BL162 from Kurt J. Lesker) is employed to cut off the connection between the turbo-molecular pump and the fore-vacuum pump during an electricity failure.

The pressure of the vacuum chambers and the drift tubes are monitored by two nude Bayard-Albert ionization gauges with one mounted inside the laser ablation
Figure 4.2: Schematics of the laser ablation ion source and the RTOPMS.
Figure 4.3: Schematics of the vacuum system associated with the laser ablation ion source and the RTOFMS.
chamber and the other inside the reflectron chamber. These two gauges are controlled by a multigauge controller from Varian, and they have been calibrated against the primary standard in our laboratory. The absolute calibration of the primary standard is carried out using a dynamic gauge calibration system [56]. The background pressure in the laser ablation chamber is $2 \times 10^{-9}$ Torr while the background pressure in the reflectron chamber is $2 \times 10^{-8}$ Torr. The background gases are analyzed by a Vacuum General quadruple residual gas analyzer (MassTorr DX-200) and is found to consist mainly of H$_2$, H$_2$O, CO and CO$_2$, which is typical in a stainless steel ultra-high vacuum system.

The general electrical connections are shown in Fig.4.4. To reduce the employment of too many high voltage power supplies, the deflection plates and the electrostatic lens are floated to the level of the drift tube.

4.6.2 Mass spectrum obtained using the RTOFMS system

The laser ablation ion source is used to provide the charged particles. The ablation target is placed inside the laser ablation chamber on a motion feedthrough (see Fig.4.2). It is positioned 16 cm in front of the extraction plate. In between there is a grid installed that can be used as high-pass energy filter if necessary.

Fig.4.5 shows a RTOF spectrum with laser ablation of a pure carbon target obtained by using the CEM-based ion detector. The mass resolution shown in Fig.4.5 is more than 100.
Figure 4.4: General electrical connections for the RTOFMS.
Figure 4.5: A typical RTOF mass spectrum generated by a single laser shot on a pure carbon target.
Fig. 4.6 shows a RTOF spectrum with laser ablation of a tungsten disilicide (WSi$_2$) target of 99.95% purity obtained by using the CEM-based ion detector. The mass resolution of silicon ions shown in Fig. 4.6 is also more than 100.
Figure 4.6: A typical RTOF mass spectrum generated by a single laser shot on a tungsten disilicide target.
CHAPTER 5

CHARGE-TRANSFER CROSS SECTION MEASUREMENT

5.1 Experimental setup

The laser ablation ion source and the RTOFMS system have been described in the previous chapters. Here we focus on the ion detector arrangement, the data acquisition system and the gas handling system, which are specially designed for the charge-transfer measurements.

5.1.1 Ion detector

The CEM detector is adopted and the schematics of the ion detector assembly and the data acquisition system are shown in Fig.5.1.

Beside the termination grid at the exit of the reflection drift tube, three highly transparent grids are installed between the reflection drift tube and the entrance to the CEM. The grid immediately in front of the CEM is held at the same potential as the CEM cathode potential to eliminate secondary electrons from being extracted by the strong electric field of the retardation grid #2. Retardation grid #1 is maintained at ground potential at all times. The retardation grid #2 is primarily designed to provide
discrimination between the parent and product ions. To ensure a linear response of the CEM, the maximum peak current output of the CEM is kept below 10% of its DC bias current. The linearity of the CEM is further checked experimentally by measuring the pressure dependence of the ion signals for a charge-transfer reaction. Gain calibration for ion energies will be discussed in the C$^{2+}$ with H$_2$ charge-transfer measurement.

5.1.2 Data acquisition system

The data acquisition system consists of a Phillips Scientific low noise preamplifier with a gain of 100. The amplified current signal is digitally recorded by a Tektronix TDS 680B digital oscilloscope. Automated data acquisition control software is used to transfer the digital data to the hard disk of a PC computer for later retrieval and

Figure 5.1: Schematics the ion detector and data acquisition system.
analysis. The scan of the oscilloscope is initiated by an electrical signal from a fast photodiode that samples the laser light.

5.1.3 Gas handling system

During the charge-transfer cross section measurement, the vacuum system will be filled with ultrahigh purity neutral gas from a leak valve. The gas line and the gas reservoir (0.4 liter) are first pumped down to $\sim 10^{-2}$ Torr by a mechanical pump. Ultrahigh purity gas is then released into the reservoir and introduced into the system through the leak valve. The gas pressure in the system is usually set at $8.0 \times 10^{-6}$ Torr, much larger than the background pressure, which is less than $2 \times 10^{-9}$ Torr in the laser ablation chamber and less than $2 \times 10^{-8}$ Torr in the reflectron chamber. At equilibrium, the target gas pressure inside the reflectron chamber and the two drift tubes should have the same value when both the source and the sink of the gas are located at the far end of the ablation chamber. Any difference in the pressure will be equalized by molecular flow inside the drift tubes and the reflectron chamber. This is supported by the same reading of the two ion gauges installed inside the ablation and reflectron chambers.
5.2 Charge-transfer measurement of \( \text{C}^{2+} \) with \( \text{H}_2 \)

5.2.1 Experimental method and procedure

The fundamental 1.06 \( \mu \text{m} \) laser emission of a Q-switched Nd:YAG laser is used to ablate a pyrolytic graphite target (99.999% purity). The beam is incident at 45°, focused by a 33 cm focal length lens placed outside the laser ablation chamber. This configuration allows convenient access to the target by the laser beam as well as extraction of the ions from the target surface. The laser energy used during the first phase of the experiment is about 10 mJ to produce low charge state \( \text{C}^{q+} \) ions with \( q \leq 2 \). \( \text{C}^{3+} \) ions are present in only minute amounts. These ions are extracted from the laser plasma into the RTOFMS by the extraction plate biased at −1500 V. Both the front grid and the target are grounded at 0 V. Both the incidence drift tube and the reflection drift tube are maintained at the same potential as the extraction plate. The potential of the deceleration plate and the reflection plate of the reflectron assembly are set at 0 V and +240 V respectively to limit the energy of the reflected \( \text{C}^{2+} \) ions to less than 480 eV. The present setting of these potentials is primarily dictated by the optimal detection and discrimination of parent and product ions. Mass resolution for the laser ablation ions is only of secondary concern. We find that mass resolution of 15 is adequate to resolve \( \text{C}^{3+} \), \( \text{C}^{2+} \), and \( \text{C}^{+} \) ions.

During the course of the measurement, the vacuum chamber is filled with \( 8.0 \times 10^{-6} \) Torr of ultra-high purity \( \text{H}_2 \) (Linde, 99.999%).

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The RTOFMS serves three basic functions: (a) it focuses ions of the same charge state at the detector so that they can be separated in time. (b) it provides a region where the parent carbon ions can interact with the target H\textsubscript{2} molecules. (c) its reflection plate serves as a low-pass energy filter which is essential to the accuracy of the measurement. Measurements of the charge-transfer cross sections are carried out in the reflection drift tube.

When a pulsed beam of C\textsuperscript{2+} is reflected from the reflectron into the reflection field-free drift tube, charge-transfer between C\textsuperscript{2+} and H\textsubscript{2} takes place with the formation of a product C\textsuperscript{+} in a single electron transfer or a product C\textsuperscript{o} in a double electron transfer. Since energy transfer between C\textsuperscript{2+} and H\textsubscript{2} is negligibly small in the charge-transfer process, both the parent ions and the product ions and atoms will have the same energy. However, when the parent ions exit the drift tube and reach the grounded retardation grid #1, they will lose all the energy they gained from the drift tube potential and return to the initial energy, $E\textsubscript{i}$, they acquired during laser ablation. On the other hand, the product ions, which are singly charged, only lose half of the energy gained from the drift tube. The energy of the product ions is $(1500 + E\textsubscript{i})$ eV. Similarly, the energy for C\textsuperscript{o} is $(3000 + E\textsubscript{i})$ eV. When the retardation grid #2 potential, $V\textsubscript{g2}$, is biased at 0 V, all three groups of ions will pass through and hit the cathode of the CEM. When $V\textsubscript{g2}$ is biased at $+500$ V, the potential barrier is too high for parent C\textsuperscript{2+} to pass through because the maximum kinetic energy of the reflected C\textsuperscript{2+} is 480 V, defined by the potential barrier at the reflection plate in the reflectron.
On the other hand, both the product ions and neutrals have enough energy to pass through the potential barrier at grid #2 and are detected by the CEM. When \( V_{g2} \) is raised to +2000 V, the product \( C^+ \) will be reflected since their kinetic energies are at most, 1980 eV. The neutral product, however, will not be affected by the grid bias at any value and will enter the CEM. We also find that the intensity ratio of \( C^+ \) ions to \( C^0 \) atoms plus background is 3 to 1. This ratio will be used later in the calibration of CEM gain efficiency. By applying a different potential at the retardation grid #2, the parent ions, product ions, and neutral atoms can be separated.

The cathode of CEM is floated to -1600 V. At this potential, the impact energy of the parent \( C^{2+} \) and product \( C^+ \) at the CEM cathode will be almost the same: 3200 eV for \( C^{2+} \) and 3100 eV for \( C^+ \). It would be ideal to keep the impact energy of both the parent and product ions the same. This eliminates the differential gain efficiency on ion energies. However, we find that a significant amount of background noise is generated by secondary electrons created by \( C^{2+} \) when ions impinge on the drift tube and its termination mesh plates. By deliberately floating the CEM to -1600 V instead of -1500 V, we create a 100 V potential barrier at the CEM cathode to reflect all the secondary electrons. Further increase in the potential difference does not reduce the noise. At this bias configuration, we are able to keep the background noise to a minimal level.

A series of measurements are carried out by sequentially switching \( V_{g2} \) to 0 V, +500 V, and +2000 V. The cycle is then repeated. This procedure minimizes
the statistical fluctuations caused by the laser pulse irreproducibility and the target surface conditions. The ion signals are recorded by the Tektronix digital oscilloscope. These ion signals are then binned according to the switching sequence and stored in the hard drive of a PC computer for later analysis. A total of 2500 measurements were made per each \( V_{g2} \) setting. The summed ion spectra are then obtained for data analysis. For single electron capture, the cross section can be derived from the following expression:

\[
\frac{I_p}{I_0} = 1 - e^{-\sigma n L}, \quad (5.1)
\]
\[
\sigma \approx \frac{I_p}{I_0 n L}, \quad (5.2)
\]

where \( I_p \) is the current intensity of the product \( C^+ \) ions, \( I_0 \) is the current intensity of the parent \( C^{2+} \) ions, \( L \) is the length of the reflection drift tube, \( \sigma \) is the single electron charge-transfer cross section and \( n \) is the density of the target \( \text{H}_2 \) gas.

In Eq.(5.2), the approximation is valid because \( I_p/I_0 \ll 1 \) in our measurement, which also ensures the single collision condition. The product ion current intensity \( I_p \) can be determined by subtracting the peak ion current obtained with \( V_{g2} \) at +2000 V from that measured with \( V_{g2} \) at +500 V. \( I_0 \) can be obtained by the peak ion intensity current with the retardation grid #2 biased at 0V. We should also mention that the product ions or atom originating in the incidence drift tube will not be reflected into the reflection drift tube due to their excessive energies. Fig.5.2 shows the TOF mass spectra of the parent ions and the product ions. The above expression can also be used to calculate the cross section of the double electron transfer with the production
of neutral C°. Unfortunately, the presence of the background noise even with the target gas removed from the system created a large uncertainty on the C° signal. However, we place an upper limit on the cross section to be less than 1/10 of the single electron charge-transfer cross section.

5.2.2 Channel electron multiplier gain efficiency calibration

The gain efficiency of the detector is dependent on the charge state of the ion and the incident kinetic energy of the ion [57]. Since we operate the CEM in the analog mode, the gain efficiencies for both C^{2+} and C^+ need to be calibrated. The calibration of the gain efficiency is carried out by measuring the average pulse height distribution of an individual carbon ion of a specific charge state. First, without introducing any target gas into the ultra-high vacuum chamber, we reduce the intensity of the ions by defocusing the ion beam with the electrostatic focusing lens inside the incidence drift tube. The intensity is reduced until individual ions can be detected. The pulse width of an individual ion is about 20 ns. The average pulse height distribution for the parent C^{2+} ion is obtained with \( V_{g2} \) at 0 V. We then fill the chamber with \( 8.0 \times 10^{-6} \) Torr of H\(_2\) and set \( V_{g2} \) to +500 V to screen off all the parent C^{2+}. The pulse height distribution of the product C^+, neutral C as well as other background ions is obtained. Since we are interested in the average pulse height distribution of C^+ ions, pulses contributed by product neutral C and background ions have to be subtracted from this distribution. The pulse height distribution for the background
Figure 5.2: Two RTOF mass spectra are presented in the diagram. The dotted line is the average RTOF mass spectrum of the parent $C^{2+}$ ions. The solid line is the RTOF mass spectrum of the product $C^+$ ions. The overshoot is caused by the preamplifier.
ions and product neutral C is obtained by setting $V_{g2}$ to +2000 V. About 600 ion counts were collected for each distribution. The intensity ratio of product $C^+$ ions and $C^0$ atoms plus background has been measured earlier. The result shows that the gain efficiency for the parent $C^{2+}$ is 3.5% higher than the product $C^+$. This differential gain efficiency has been incorporated into the final cross section calculation.

5.2.3 Determination of the ion energy and cross section

The average initial kinetic energy for the laser ablation ions is determined by measuring the time of flight of the positive ion peak at the extraction plate of the incidence drift tube. During this measurement, the target, the front grid and the extraction plate are grounded. Fig.5.3 shows a 50 laser-shots averaged TOF spectrum collected by the non-biased extraction plate. The average energy of the ions is 45.6 ($\sigma = 12.4$) eV with $\sigma$ being the standard deviation. The standard deviation represents the kinetic energy spread of the laser ablation ions. Thus the total energy of the $C^{2+}$ ion is 3045.6 ($\sigma = 12.4$) eV obtained by summing the energy gained at the drift tube and its average initial kinetic energy. The single electron charge-transfer cross section for $C^{2+}$ ions and $H_2$ is measured to be $6.90(0.78) \times 10^{-16}$ cm$^2$. The major uncertainties come from the absolute ion gauge calibration ($\pm 7.8\%$), the statistical uncertainty of the ion intensities created by the fluctuation of the ablation laser pulses ($\pm 7.5\%$), and the linearity of the channel electron multiplier and the preamplifier ($\pm 3\%$). We estimate that the uncertainty on the measured cross sections introduced by the background
Figure 5.3: A 50 laser-shots averaged time-of-flight spectrum collected by the non-biased extraction plate that serves as a Faraday cup.
gases is less than 1%.

5.2.4 Discussion on the result

Depending on the ion source, one of the major shortcomings of the ion beam technique is its uncertainty on the metastable state ion fraction. Since the potential energy curve for the pseudo-molecule formed during collision is quite different for the ground state parent ion than that for the more energetic metastable ion, the charge-transfer cross section can be quite different. For example, charge-transfer between ground state \( \text{O}^{2+} \) and \( \text{He} \) is about five times larger than that for the metastable \( \text{O}^{2+} \) [58]. In the case of \( \text{C}^{2+} \) and \( \text{H}_2 \), the charge-transfer cross section for the metastable ions is larger than that for the ground state ions by a factor of \( \sim 6 \) [59]. It is of paramount importance that the metastable ion fraction in the ion beam be known. In the second phase of this experiment, we will determine the metastable ion fraction of the laser ablation ion beam by changing the temperature of the laser induced plasma.

The expansion dynamics of the laser induced plasma in a vacuum is quite complex [44]. The properties of the laser induced electrons in carbon plasma have been studied experimentally by Rumsby and Paul [60]. During laser ablation, a high density neutral plasma is formed. This plasma is extremely collisional due to large electron density and as a consequence, local thermodynamic equilibrium can be assumed. The ion density ratio, \( \text{I(C}^3+) / \text{I(C}^2+) \), can be used to estimate the collisional temperature of the ions prior to its free expansion into the vacuum. This density ratio is related
to the temperature by $e^{-E_i/kT}$, where $E_i$ is the ionization potential of the C$^{2+}$ ion. This density ratio can be obtained by measuring the time-of-flight intensity peaks of C$^{3+}$ and C$^{2+}$ ions in the pulsed laser ablation ion beam. During the first phase of the experiment, the ion intensity ratio, $I(C^{3+})/I(C^{2+})$, is about 0.5% at the laser energy of 10 mJ. The corresponding temperature $T$ is estimated to be about 9 eV. In this second phase of the experiment, the energy of the ablation laser is raised to 20 mJ, the ion density ratio increases to 1.9% and the corresponding temperature is estimated to be 12 eV. If we assume that the metastable $2S2P \ ^3P_0^{0,1,2}$ states of C$^{2+}$ ions are in thermal equilibrium with the ground state ions, the population ratio of the metastable states to the ground state will increase by as much as 10%. Using the charge-transfer cross section for the metastable state ($3.9 \times 10^{-15}$ cm$^2$) measured by Unterreiter et al. [59], our measured cross section should have increased by as much as 60% with doubling of the input laser energy. However, our measured cross section remains unchanged within the experimental uncertainty. This suggested that the internal temperature of the laser ablation ions is very cold and the metastable ion fraction in the beam is negligible. One can explain the absence of metastable ions in the laser ablation plasma beam by the presence of low energy electrons in the plasma. During the free expansion phase of the plasma, the electron density decreases as $t^{-1}$ while the electron temperature decreases rapidly as $t^{-3}$ [60]. Since the plasma is still highly collisional, the plasma ions are coupled to the plasma electrons even though the ions themselves exhibit a self similar expansion into the vacuum with a velocity...
distribution corresponding to the freeze-out temperature while the internal energy of the ions will follow the temperature of the rapidly cooling electrons. The population ratio of the metastable state to the ground state of C^{2+} ions drops beyond the observable limit of the current facility. Fig. 5.4 summarizes the measured cross sections at low energies by various researchers in the past [59, 61, 62, 63] as well as our current measurement. It is also of interest to compare our measured result with Langevin cross section. The static average electric dipole polarizability for ground state H_2 is 0.8045 \times 10^{-24} \text{ cm}^3 in cgs units. The Langevin charge-transfer cross section (see Eq. (2.7)) of C^{2+} + H_2 reaction is estimated to be 1.44 \times 10^{-16} \text{ cm}^2 at the C^{2+} ion energy of 0.25 \text{ KeV/amu}, which is five times smaller than our measurement value.

Our measurement is in good agreement with the ground state measurement obtained by Unterreiter et al. [59] and by Nutt et al [61]. We conclude that the laser produced ions are cold and are primarily in their ground state.

5.3 Charge-transfer measurement of Si^{3+} with He

Silicon is commonly found in a variety of astrophysical plasmas. The spectral lines of silicon ions have been observed in interstellar medium [64, 65, 66], circumstellar material [67], quasars, Seyfert galaxies [68], the solar lower transition region [69, 70], and late-type stellar atmospheres [71]. These lines have been widely used as a diagnostic tool for the physical conditions in these low temperature plasma environments. The intensity of these lines can be drastically affected by the ionization equilibrium.
Figure 5.4: Single electron charge-transfer cross sections for $C^2+ + H_2$ at low energies reported by several research groups.
through charge-transfer reactions. Contribution by charge transfer of silicon ions and neutral hydrogen and helium need to be thoroughly investigated for the interpretation of these lines [72]. Besides its importance in the astrophysical plasma, the charge-transfer reactions of silicon with various neutrals are of interest in thermal nuclear fusion plasmas.

Few experimental data are available for the charge-transfer reactions between Si$^{3+}$ and neutrals. A measurement of Si$^{3+}$ with atomic and molecular hydrogen at high silicon ion energies (51—201 KeV/amu) was carried out by Kim et al. [73] using ion beam technique. At first, negative Si ions were extracted from a sputter source and injected into the ORNL tandem accelerator. Then, the energetic negative ions went through a terminal stripper and emerged from the tandem as multiply charged positive ions. Charge-transfer between Si$^{3+}$ and H/H$_2$ was measured by passing the ion beam through the target cell. Another measurement of the charge-transfer rate coefficient between Si$^{3+}$ and He at electron-volt energies was carried out by Fang and Kwong [74] using ion trap technique.

Here we will report a single-electron charge-transfer cross section measurement between Si$^{3+}$ and He at Si ion energy of 0.16 KeV/amu.

5.3.1 Experiments

The experimental setup and method bears much similarity with the C$^{2+}$ + H$_2$ measurement. The fundamental 1.06 μm laser emission of a Q-switched Nd:YAG laser
Table 5.1: The potential settings of the RTOFMS in Si$^{3+}$ + He measurements

<table>
<thead>
<tr>
<th>Potential Setting</th>
<th>Voltage (volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front grid</td>
<td>0</td>
</tr>
<tr>
<td>Extraction plate and both drift tubes</td>
<td>-1500</td>
</tr>
<tr>
<td>Electrostatic lens</td>
<td>-700</td>
</tr>
<tr>
<td>Deceleration plate</td>
<td>0</td>
</tr>
<tr>
<td>Reflection plate</td>
<td>+400</td>
</tr>
<tr>
<td>$V_{g1}$</td>
<td>0</td>
</tr>
<tr>
<td>CEM floating</td>
<td>-1600</td>
</tr>
</tbody>
</table>

is used to ablate a tungsten disicilide (WSi$_2$) target of 99.95% purity at 45° angle. The laser pulse energy used during the experiment is about 15 mJ to produce Si$q^+$ ions with $q \leq 3$. Si$q^+$ ions with $q \geq 4$ ions are present in only minute amounts. The potential settings of the RTOFMS are listed in Table 5.1, where $V_{g1}$ represents the voltage on the retardation grid #1 (see Fig.5.1). At these potential settings, the signal intensity is optimized and Si$^{3+}$ and Si$^{2+}$ are completely separated in their arrival time.

During the course of the measurement, the vacuum chambers are filled with ultrahigh purity He target gas (99.999% from Airco) to $8.0 \times 10^{-6}$ Torr.

The voltage on the retardation grid #2, $V_{g2}$, is again switched among 0, +500 and +2000 volts. Table 5.2 lists the ions that the CEM will receive with different $V_{g2}$ settings, where Si$p^q$ refers to the product ion in charge $q$ stage, $E_{\text{min}}$ and $E_{\text{max}}$ are the minimum and maximum ion kinetic energy right after passing through retardation grid #1, and 'Y' and 'N' represent 'Yes' and 'No', respectively. With the aid of Table
Table 5.2: Ions received by the CEM in Si\textsuperscript{3+} + He measurements

<table>
<thead>
<tr>
<th>$E_{\text{min}} - E_{\text{max}}$ (eV)</th>
<th>$V_{g2} = 0$ V</th>
<th>$V_{g2} = +500$ V</th>
<th>$V_{g2} = +2000$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si\textsuperscript{3+}</td>
<td>$E_i - 1200$</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>Si\textsuperscript{3+}</td>
<td>1500 + $E_i - 2700$</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Si\textsuperscript{2+}</td>
<td>3000 + $E_i - 4200$</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Si\textsuperscript{2+}</td>
<td>4500 + $E_i - 5700$</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

5.2, the product ion current intensity $I(Si^{2+})$ from single-electron charge-transfer process can be determined by subtracting the peak ion current obtained with $V_{g2} = +2000$ V from that measured with $V_{g2} = +500$ V. The parent ion current intensity is obtained from the peak ion current with the retardation grid #2 biased at 0 V. The expression Eq.(5.2) is again used to calculate the cross section.

Due to various reasons, the signal intensity in this experiment is much less than that in the precious $C^{2+} + H_2$ experiment. A total of more than 10000 measurements are made with each $V_{g2}$ setting. Fig.5.5 shows the RTOF mass spectra of the parent and the product ions.

The CEM gain efficiency of $\eta(Si^{3+})$ and $\eta(Si^{2+})$ in this experiment should have the following relationship:

$$\Delta \eta \over \eta = \eta(Si^{2+}) - \eta(Si^{3+}) \over \eta(Si^{2+}) < 3.5\%.$$  

(5.3)

This is based on the calibration in the $C^{2+} + H_2$ experiment. The relative gain efficiency is determined by the relative impact kinetic energy of the ions, when the impact kinetic energy is much larger than the energy released from the recombination of ions and electrons [75]. In this measurement, the parent $Si^{3+}$ ions impact on the
Figure 5.5: Two RTOF mass spectra are presented in the diagram. The dotted line is the average RTOF mass spectrum of the parent $\text{Si}^{3+}$ ions. The solid line is the RTOF mass spectrum of the product $\text{Si}^{2+}$ ions. The overshoot is caused by the preamplifier.
CEM surface with a kinetic energy of $(4800 + E_i)$ eV, and the product Si$^{2+}$ ions with $(4700 + E_i)$ eV, where $E_i$ represents the initial expansion energy of the parent Si$^{3+}$ ions. Therefore, the percentage difference of the kinetic impact energy between the parent Si$^{3+}$ ion and the product Si$^{2+}$ ion is less than 2.1%. This difference is less than that of the C$^{2+}$ + H$_2$ experiment. This indicates the correctness of Eq.(5.3). This uncertainty will be incorporated into the final cross section calculation.

5.3.2 Determination of the ion energy and cross section

The average initial kinetic energy for the laser ablation ions is determined by measuring the time of flight of the positive ion peak at the extraction plate of the incidence drift tube. During this measurement, the target, the front grid and the extraction plate are grounded. The average energy of the ions is $24.0 \ (\pm 2.4) \ eV$. Thus, the total energy of the Si$^{3+}$ ion is $4524 \ (\pm 7.2) \ eV$, obtained by summing the energy gained at the drift tube and its average initial kinetic energy. A 0.15% uncertainty from the extraction voltage is also considered. The single electron charge-transfer cross section for Si$^{3+}$ ions and He is measured to be $1.27(\pm0.19) \times 10^{-15} \ cm^2$. The major uncertainties come from the absolute ion gauge calibration ($\pm9.0\%$), the statistical uncertainty of the ion intensities created by the fluctuation of the ablation laser pulses ($\pm11\%$), the linearity of the channel electron multiplier and the preamplifier ($\pm3.0\%$), and the CEM gain efficiency with respect to the parent and product ions ($3.5\%$). We estimate that the uncertainty on the measured cross sections introduced by the background
gases is less than 1%. Also, it is worth mentioning that the Si\(^{3+}\) ion signal would not be contaminated by the presence of tungsten ions because tungsten is so much heavier that the same time-of-flight position as Si\(^{3+}\) would require a production of W\(^{19+}\). At current laser power, it is impossible to generate as highly charged ions as W\(^{19+}\).

5.3.3 Discussion on the result

Si\(^{3+}\) is hydrogen like and thus, has no metastable states.

A comparison with a theoretical calculation is made in Fig. 5.6. The charge-transfer cross section between Si\(^{3+}\) and He is calculated by Gargaud and McCarroll [76] using an ab-initio configuration-interaction with an effective potential. The interpolated charge-transfer cross section at our current ion energy is \(1.57 \times 10^{-15}\) cm\(^2\), which is 23\% larger than our measured value.

Another comparison of interest is to convert our experimental result into a rate coefficient. The rate coefficient is obtained by integrating \(\sigma v\) over a Maxwellian velocity distribution of the collision particles. Since we only measured the cross section at one kinetic energy point, we are unable to provide the exact rate coefficient. However, the comparison is still meaningful if the cross section does not show drastic change with the ion energy. To start, we first convert Si ion energy of 0.16 KeV/amu into a Si temperature of \(1.7 \times 10^7\) K according to \(\frac{1}{2}mv^2 = \frac{3}{2}kT\), an estimation based on energy conservation. Then, the equivalent temperature for the body of Si and He...
Figure 5.6: Comparison of our measured charge-transfer cross section of Si^{3+} + He with the theoretical calculation by Gargaud and McCarroll.
is estimated to be $2.1 \times 10^6$ based on [77]:

$$\frac{T_{\text{equiv}}}{\mu} = \frac{T_{\text{Si}}}{m_{\text{Si}}} + \frac{T_{\text{He}}}{m_{\text{He}}},$$

(5.4)

where $\mu$ is the reduced mass of Si and He. This temperature is rather high for an astrophysical environment. However, it is still of interest to compare our result with other measurements and calculations to see the relation of the rate coefficient and temperature. The product of the average velocity at the above temperature and our measured cross section results in a rate coefficient of $2.24(\pm 0.34) \times 10^{-8}$ cm$^3$/s$^{-1}$. This result is shown in Fig.5.7 together with a measurement point carried out by Fang and Kwong [74] in an ion trap, Landau-Zener calculation by Butler and Dalgarno [78], and full quantal calculation by Honvault et al [79]. Fang and Kwong’s measured rate coefficient is about 30% larger than that of the Landau-Zener estimation and is a factor of three larger than the full quantal calculation. If a linear extrapolation is made, our measurement result is rather close to both the calculations.

The static average electric dipole polarizability for ground state He is $0.2050 \times 10^{-24}$ cm$^3$ in cgs units. The Langevin charge-transfer cross section (see Eq.(2.7)) of Si$^{3+} +$ He reaction is estimated to be $0.96 \times 10^{-16}$ cm$^2$ at the Si$^{3+}$ ion energy of 0.16 KeV/amu. This is one order of magnitude smaller than our measurement value.

5.4 Conclusions

We have introduced a relatively simple yet highly accurate technique to measure charge-transfer cross sections. It combines a laser ablation ion source and a reflection
Figure 5.7: Comparison of charge-transfer rate measurements and calculations toward the reaction of Si$^{3+}$ with He.
time-of-flight mass spectrometer. We demonstrated this technique by measuring the single electron charge-transfer cross section between ground state C\(^{2+}\) ions and H\(_2\) at the carbon ion energy of 0.25 KeV/amu. We then for the first time measured the charge-transfer cross section between Si\(^{3+}\) and He at the silicon ion energy of 0.16 KeV/amu.

Because of the versatility of the pulsed laser ablation ion source, and the flexibility of the accelerating potential, this facility can also be used to examine the cross sections of a variety of multiple charged ions from refractory to gaseous elements at a wide range of energies.
REFERENCES


