VELOCITY DEPENDENCE OF THE IONIZATION OF GAS MOLECULES ON IMPACT OF METASTABLE ATOMS

By

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VELOCITY DEPENDENCE OF THE IONIZATION OF GAS MOLECULES
ON IMPACT OF METASTABLE ATOMS

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Measurements of the velocity dependence of the total ionization
cross section of argon, krypton, xenon, nitrogen, and methane on impact
of metastable neon atoms have been made using a velocity-selected beam
of the metastable atoms. A low voltage D.C. discharge is used as the
source of excited atoms, the velocity selection is accomplished by means
of a rotating slotted-disk selector of standard design, and the particle
density of the target gas is measured using an RCA 1946 thermocouple
gauge which had been calibrated against a McLeod gauge modified so as to
eliminate the mercury pumping effect error. The ionization measurements
were of sufficient precision to allow simultaneous determination of both
the cross section and the secondary electron ejection efficiency. The
secondary electron ejection efficiency from an argon covered gold sur-
face on impact of metastable neon atoms was found to be 0.27 ± 0.14.
In the relative velocity range investigated (v=320-1,700 meters/sec) the cross section, $\sigma_t$, was found to vary as $v^{-s}$ below $v=650$ meters/sec and to deviate positively from the linear $\log \sigma_t - \log v$ relationship at higher relative velocities. The value of $s$ obtained is 0.622 for Ne$^*$-Ar, 0.728 for Ne$^*$-Kr, 0.874 for Ne$^*$-Xe, 0.739 for Ne$^*$-$N_2$ and 0.928 for Ne$^*$-$CH_4$. The velocity distribution of the metastable atoms in the source was verified to be a normal Maxwell-Boltzmann distribution.

The compositions of metastable neon, argon and helium beams obtained from the discharge source have been measured using an inhomogeneous-field deflecting magnet, a low-impedance electromagnet with pole tips of the traditional "two-wire" form. It was found that the composition ($^{3P_2}/^{3P_0}$) of the metastable neon and argon beams is fairly constant over a large range of discharge conditions. This ratio is about 4.8 and 7.2 for the metastable neon and argon atomic beams, respectively, assuming that the electron ejection efficiencies are the same for the two metastable states. For the metastable helium beam, the ratio $\gamma_3^{3S}/\gamma_1^{1S}$ (including the secondary electron emission coefficients, $\gamma_3$ and $\gamma_1$) varies from 0.95 to 2.0 as the discharge current is increased from 0.12 to 0.30 amp.

A simple semi-classical model is formulated in which the transition probability at the turning point is evaluated from perturbation theory. The model predicts both Penning and associative ionization cross sections as well as their dependence on relative velocity. The calculated results based on a step function with two adjustable parameters for the coupling potential fit the experimental results in the linear part of the $\log \sigma_t - \log v$ plot ($v < 650$ meters/sec).
PART I

EXPERIMENTAL
CHAPTER I
INTRODUCTION

Electronically excited atoms or molecules play an important role in many phenomena. Among these, for example, are electrical discharges, flames, shocks, photolysis, etc. These phenomena have been studied extensively and some progress in understanding the behavior of the excited species has been made. However, the achievements by these studies are limited by the nature of the bulk system which in most cases involves more than one excited species. Molecular-beam techniques have been developed to a high degree in recent years and have been used extensively with considerable success to study elastic and inelastic collisions of ground state atoms and molecules. Metastable electronically excited species can be studied by the molecular-beam technique since the free-space lifetime of the excited particles is sufficiently long (of the order of a microsecond or greater). Nonmetastable excited species, which rapidly lose their energy by allowed radiative transitions, have lifetimes too short to be studied by this method.

Two important inelastic collision processes between an electronically excited atom or molecule \( A^* \) and another ground state particle \( B \) are:

\[
\begin{align*}
A^* + B \rightarrow & A + B^+ + e \quad (1) \\
A^* + B \rightarrow & AB^+ + e \quad (2)
\end{align*}
\]

The first process is generally known as Penning ionization and the
second as associative ionization. Both processes have so far been investigated for collisions of rare gas excited atoms in a Maxwellian molecular beam only with the simplest hydrocarbon molecules, several diatomic molecules, and the rare gas atoms themselves.

It is the purpose of this work to investigate the velocity dependence of the total (Penning and associative) ionization of gases on impact of the metastable neon atoms using a velocity-selected beam of metastable neon atoms.
CHAPTER II

THEORETICAL FOUNDATIONS OF THE EXPERIMENTS

A. Metastable Atoms and Their Detection

The strength of a transition in emission is measured by the probability that one excited atom or molecule will emit a photon in unit time. Einstein showed that for an electric dipole transition the transition probability for spontaneous emission, $A$, is related to the transition moment $\hat{\mu}_{mn}$, which is the appropriate matrix element of the dipole moment operator:

$$A_{mn} = \frac{64\pi^3\nu^3}{3\hbar} |\hat{\mu}_{mn}|^2 \nu_{mn} \text{ in cm}^{-1},$$ \hspace{1cm} (2)

where

$$\hat{\mu}_{mn} = \int \psi^*_m \left( \sum_i \vec{r}_i \right) \psi_n \, dr,$$ \hspace{1cm} (4)

$\hat{\mu}_{mn}$ may be interpreted physically as the oscillating dipole moment in the system during the transition from the state $m$ to the state $n$. The mean lifetime of the state $m$ is given by

$$\tau = \frac{1}{\sum_n A_{mn}}.$$ \hspace{1cm} (5)

If ordinary electric dipole radiation is allowed, $\tau$ is about of the order of $10^{-9}$ second. Excited atoms or molecules with lifetimes greater than a microsecond are generally described as metastable, the transition to the ground state being forbidden by the selection rules governing electric dipole radiation. Assuming Russell-Saunders coupling holds for an atom, the electric dipole selection rules are:
If one of electrons in the 2p shell of the ground state
\((1s^22s^22p^6)\) of neon is excited to the 3s state according to the Russell–Saunders coupling, four states are possible for the \(1s^22s^22p^53s\)
configuration, namely, \(3P_2\), \(3P_1\), \(3P_0\), and \(1P_1\).

The \(3P_2\) and \(3P_0\) states of neon are metastable since their electric
dipole radiation to the ground state \(1S_0\) is forbidden by the selection
rules (a) and (b). However, the \(3P_1\) state of neon can radiate to the
ground state due to lack of pure Russell-Saunders coupling, and the \(1P_1\)
state is not metastable because its electric dipole transition to the
ground state is allowed.

Similarly, the \(3P_2\) and \(3P_0\) states of argon, and the \(2^3S_1\) and \(2^1S_0\)
states of helium are metastable states.

Although the electric dipole transition is forbidden, the metastable
atoms can decay to the ground state by double photon emission and magnetic dipole radiation. However, these are at least \(10^5\) times weaker
than an allowed electric dipole transition and thus metastable states will
have lifetimes longer than a microsecond.

Electron ejection from metal surfaces by the incident metastable
atoms has been used to detect them.\(^9\) Auger de-excitation is the main
process of the de-excitation and has been studied in detail by Hagstrum.\(^10\)
The ejection efficiency for the secondary electrons has been measured in
only a few cases. For example, MacLennan\textsuperscript{11} reported the absolute electron yield of helium and neon metastable atoms incident on an atomically clean polycrystalline tungsten surface. The value given for helium is 0.306 ± 0.025 for both the 2\textsuperscript{1}S\textsubscript{0} and 2\textsuperscript{3}S\textsubscript{1} states and the neon value is 0.215 ± 0.020 for the mixed 3\textsuperscript{p}\textsubscript{0} and 3\textsuperscript{p}\textsubscript{2} states.

B. Velocity Distributions of Metastable Atomic Beams

The intensity of metastable atoms with velocity in the range \( v \) to \( v + dv \) remaining in the beam at a distance \( x \) from the point of excitation is\textsuperscript{1,12}

\[
I_x(v)dv = I_0(v)dv\exp(-x/\tau v),
\]

(6)

where \( \tau \) is the mean lifetime which is proportional to the half-life:

\[
\tau_v = \tau \ln 2,
\]

and \( I_0(v)dv \) is the corresponding intensity at the point of excitation. Since the metastable atoms used in these experiments (He\textsuperscript{*}, Ne\textsuperscript{*}, and Ar\textsuperscript{*}) have long lifetimes compared to the times-of-flight from the source to the detector, the factor \( \exp(-x/\tau v) \) in Eq. (6) may be set equal to unity. Eq. (6) is thus reduced to the form

\[
I(v)dv = I_0(v)dv,
\]

(7)

with the subscript \( x \) dropped off. The quantity \( I_0(v)dv \) depends on the excitation method used to produce the metastable atoms.

If an electron impact method is used to produce the metastable atoms, the velocity dependence in the beam intensity before excitation is that of the usual Maxwell-Boltzmann flux distribution. The probability that an atom will be excited by the electron impact is proportional \( v^{-1} \), thus the resultant velocity dependence of the intensity (flux) of the metastable atomic beam is given by
\[ I(v)dv = 4I_0 \frac{1}{\sqrt{\pi}} \frac{1}{\alpha^3} v^2 \exp\left(-\frac{v^2}{\alpha^2}\right)dv, \quad (8) \]

where \( I_0 \) is the total beam intensity, \( \alpha = \sqrt{2kT/m} \), and \( m \) is the mass of the atom.

If a low voltage D.C. discharge method is used to produce the metastable atoms and the discharge source pressure is about 0.1 torr, the mean free path for atoms is very short and the metastable atoms will collide with each other many times before they effuse through the first slit. Therefore, the metastable atoms in the source will probably have the usual Maxwell-Boltzmann velocity distribution, and, consequently, the velocity dependence of the intensity (flux) of the metastable beam is given by

\[ I(v)dv = \frac{2I_0}{\alpha^3} v^3 \exp\left(-\frac{v^2}{\alpha^2}\right)dv. \quad (9) \]

This velocity dependence will be verified experimentally in Chapter IV.

If a beam with velocity dependence of the beam intensity \( I(v)dv \) passes through a velocity selector at a nominal velocity \( v_0 \), the transmission of the rotor is given by

\[ T(v_0) = \int_{v_{\text{min}}}^{v_{\text{max}}} I(v)B(v,v_0)dv, \quad (10) \]

where \( v_{\text{min}} \) and \( v_{\text{max}} \) are the limiting velocities which the velocity selector can transmit at the nominal transmission velocity \( v_0 \), and \( B(v,v_0) \) is the effective slit width (admittance) for different velocities which drops from a maximum at \( v_0 \) to zero at \( v_{\text{min}} \) or \( v_{\text{max}} \) in an approximately linear fashion for a high resolution velocity selector. If the variation of \( I(v) \) over the transmitted band is neglected, the total transmission is given by
\[ T(v_0) = G v_0 I(v_0), \]  

where \[ G = \bar{n} \frac{\gamma}{1 - \gamma^2} \]  
is a geometrical factor, \cite{14}

\[ \gamma = \Delta \phi / \phi, \]  

\( \bar{n} \) is the average fractional open area of the velocity selector, \( \Delta \phi \) the angular width of the slot, and \( \phi \) the total angular shift between the first and the last disks.

C. Metastable Beam Composition Measurements

An atom of mass \( M \) and of total angular momentum quantum number \( J \) moving with velocity \( v \) in an inhomogeneous field will be accelerated transversely with an acceleration \( a \) which is given by \cite{15}

\[ a = \frac{F_z}{M} = \frac{\mu_z}{M} \frac{\partial H}{\partial z}, \]  

where the \( z \)-axis is taken in the direction of the gradient of \( H \),

\[ \mu_z = - \mu_B m_J g, \]  

\( \mu_B \) = the Bohr magneton,

\( m_J \) = the magnetic quantum number = \( -J, -J+1, \ldots, +J \),

and

\[ g = \text{Landé's } g \text{ factor} = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \] (assuming Russell-Saunders coupling)

The magnitude of the deflection in the magnetic field is given by

\[ \Delta z = \frac{1}{2} \frac{\mu_z}{M} \frac{\partial H}{\partial z} t^2 = \frac{\mu_z}{2Mv^2} \frac{\partial H}{\partial z} d_1^2 \]  
or, if the detector is placed at a distance \( d_2 \) behind the far edge of the field region,
\[ \Delta z' = \frac{\mu_z}{2Mv^2} \frac{\partial H}{\partial z} (d_1^2 + 2d_1d_2). \]  

Here, \( t = d_1/v \) is the transit time of the particles through the inhomogeneous field of length \( d_1 \).

An atomic beam which has a uniform distribution of angular momentum directions splits into \((2J+1)\) polarized component beams of equal intensity after passing through the inhomogeneous magnetic field. The magnitude of the deflection will be non-zero for each polarized component except the one with \( m_J = 0 \), and will be proportional to the value of \( m_J \) according to Eqs. (15) and (16). If \( \Delta z' \) for the component \( m_J = \pm 1 \) is larger than the beam width or the slit width for the detector, whichever is larger, then only atoms with \( m_J = 0 \) will be detected. This undeflected fraction has an intensity of \( 1/(2J+1) \) of the total beam intensity, which is measured when the magnetic field is off.

This property of deflection can be used to determine the beam composition if there are two detectable components in the atomic beam with different total angular momentum quantum numbers \( J_1 \) and \( J_2 \). Assume the total measured quantity with the field off is \( S_0 \), and total measured quantity with the field on is \( \delta S_0 \) (assuming the field is strong enough to deflect all components with \( m_J \neq 0 \) from the detector). The following relations hold:

\[ \gamma_1 I_1 + \gamma_2 I_2 = S_0 \]  

and

\[ \frac{\gamma_1 I_1}{(2J_1+1)} + \frac{\gamma_2 I_2}{(2J_2+1)} = \delta S_0 \]  

where \( \gamma_1 \) and \( \gamma_2 \) are detection efficiencies for the components with \( J_1 \) and \( J_2 \), respectively, and \( I_1 \) and \( I_2 \) are their individual intensities.
From Eqs. (17) and (18), we obtain

$$\frac{\gamma_2 I_2}{\gamma_1 I_1} = \frac{(2J_2+1)(2J_1+1)}{(2J_1+1)(1-(2J_2+1)\delta)}.$$  (19)

If \(\gamma_2/\gamma_1\) is known, the ratio \(I_2/I_1\) can be evaluated from Eq. (19).

For example, the metastable neon and argon beams consist of \(^3P_2\) and \(^3P_0\) states with a small energy difference. The \(J\) value is 2 for \(^3P_2\) and 0 for \(^3P_0\) state. Assuming both states have the same detection efficiencies, Eq. (19) is reduced to

$$I(^3P_2)/I(^3P_0) = 5(1-\delta)/(5\delta-1).$$  (20)

D. Total Ionization Cross Section and Electron Ejection Efficiencies for Metastable Atoms

In the reactive scattering of a metastable beam (\(A^*\)) from a target gases (B) in a static gas chamber, the total (Penning and associative) ionization cross section \(\sigma_t\) for the two processes as described in Chapter I,

\[
A^* + B \longrightarrow A + B^+ + e, \quad (1)
\]

and

\[
A^* + B \longrightarrow AB^+ + e, \quad (2)
\]

can be evaluated from some measured quantities. Assume \(I_o\) is the total metastable beam intensity (which is not directly measurable) entering the collision region; \(I_+\) is the intensity of ions produced by the ionization, and \(I_-\) the intensity of electrons. \(I_-\) consists of the sum of the electrons produced by the ionization (equal to \(I_+\)) and those ejected from the metal surface by the impact of the unreacted metastable atoms. If the electron ejection efficiency from the metal surface by a metastable atom is denoted by \(\gamma\), then the intensity of the unreacted metastable atoms is \((I_- - I_+)/\gamma\). Therefore, the total beam intensity \(I_o\) can be expressed as
\[ I_0 = I_+ + \frac{(I_- - I_+) \gamma}{\gamma} \]  

or \[ I_0 = (1 - \frac{1}{\gamma}) I_+ + \frac{1}{\gamma} I_- \]  

If the target particle density \( n \) is sufficiently low so that very few beam particles undergo multiple collisions, the total (Penning and associative) ionization cross section, \( \sigma_t \), may be found from the relation:

\[ I_+ = I_0 [1 - \exp(-\sigma_t n \ell)] \]  

where \( n = Np \) is the number density of target atoms, \( \ell \) is the length of the collision region; \( N \) is the number of atoms or molecules per cm\(^3\) at 300°K and 1 torr pressure = 3.2193 \( \times \) \( 10^{16} \)/cm\(^3\); and \( p \) is the pressure in torr corrected to 300°K. Here, it is assumed that the beam has one component only; \( \sigma_t \) would be the average ionization cross section if the beam has more than one component (assuming \( \sigma_t n \ell \ll 1 \)).

Substituting Eq. (22) in Eq. (23), one obtains

\[ I_+ = [(1 - \frac{1}{\gamma}) I_+ + \frac{1}{\gamma} I_-][1 - \exp(-\sigma_t N \ell p)] \]  

or

\[ \frac{I_-}{I_+} = (1 - \gamma) + \frac{\gamma}{1 - \exp(-\sigma_t N \ell p)} \]  

Using the approximation,

\[ \frac{1}{1 - e^{-x}} = \frac{1}{x} - \frac{x^2}{2!} + \frac{x^3}{3!} - \frac{x^4}{4!} + \frac{x^5}{5!} \]

\[ = \frac{1}{x} + \frac{1}{2} \frac{x}{12} - \frac{x^3}{720} \]

\[ \approx \frac{1}{x} + \frac{1}{2} \quad \text{if} \ x \ll 1. \]

Eq. (24) can be approximated as

\[ \frac{I_-}{I_+} = (1 - \gamma) + \left( \frac{1}{\sigma_t N \ell p} + \frac{1}{2} \gamma \right) \]
The value $I_-/I_+$ as a function of target gas pressure may be studied. A plot of $I_-/I_+$ versus $1/p$ will then yield a straight line with

\[
\text{slope} = \gamma / (\sigma_t N_e^2) \quad (26A)
\]

and

\[
\text{intercept} = 1 - \gamma / 2, \quad (26B)
\]

and, consequently, the total ionization cross section $\sigma_t$ and electron ejection efficiency $\gamma$ can be evaluated.
CHAPTER III
DESCRIPTION OF APPARATUS

A. General Description

The molecular beam apparatus used to make the measurements of total ionization cross sections and metastable beam compositions is shown in Figure 1. It consists of four chambers: the beam source, the fore chamber, the post chamber, and the collision chamber.

The beam gas is introduced through an automatic pressure controller into the beam source where the metastable atoms are produced in a low voltage D.C. discharge. In addition to the metastable atoms, the ions and atoms in various electronic states and photons are produced. This mixture effuses through a narrow slit S₁ into the fore chamber, in which the pressure is about $1.6 \times 10^{-5}$ torr during the experiment. The effusing atoms are collimated by the second slit, S₂, to form an atomic beam in the post chamber. Since S₂ is the only opening between the fore and the post chambers, they can be pumped differentially. The pressure in the post chamber is about $1 \times 10^{-6}$ torr during the experiment, so that collisions between beam atoms and background gas can be neglected.

A potential applied across the plates D deflects from the beam any charged particles that are produced in the source. The highly electronically excited atoms will decay either to the metastable states or to the ground state before traveling any significant distance due to their short radiative lifetimes. Photons will be stopped by the velocity selector.
Figure 1. Cross Section of the Apparatus
in the beam path. Thus, the atomic beam in the post chamber is composed of metastable atoms and ground state atoms only. Since the ground state atoms in the beam will not be detected nor will they affect the detection for the metastable atoms, the beam is effectively a pure metastable atomic beam.

A magnetically operated shutter, BS, is placed directly behind the plates, so that the beam of metastable atoms can be interrupted to obtain a zero intensity reading. $S_3$, $S_4$, and $S_5$ are slits to collimate the atomic beam. Dimensions of the slits are listed in Table 1. The atomic beam of metastable atoms passing through the slotted mechanical velocity selector contains only a narrow band of velocities. This velocity-selected atomic beam is used for the studies of beam composition and ionization cross section. An inhomogeneous deflecting magnet is placed behind the velocity selector for the beam composition study and is removed from the beam path while making the total ionization cross section measurements. The atomic beam finally enters the collision chamber through slit $S_5$ and the target gas is introduced into the collision chamber through small copper tubing mounted on the back side of the scattering chamber. An RCA 1946 thermocouple gauge is used to measure the pressure in the collision chamber. The major parts of the apparatus will be discussed in more detail in the following sections.
Table 1

Dimensions of Slits

<table>
<thead>
<tr>
<th>Slit</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$S_5$</th>
<th>$E_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width (mm)</td>
<td>0.64</td>
<td>0.84</td>
<td>0.64</td>
<td>0.64</td>
<td>0.48</td>
<td>1.56</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>6.35</td>
<td>6.35</td>
<td>5.49</td>
<td>5.49</td>
<td>3.00</td>
<td>6.39</td>
</tr>
</tbody>
</table>
B. Vacuum System

Post Chamber

The post chamber is rectangular in shape with a removable lid, and is made from heavy aluminum alloy of \( \frac{1}{4''} \) thickness, using welded construction throughout. The inside dimensions are \( 10\frac{3}{8''} \times 12\frac{3}{8''} \times 25 \frac{3}{4''} \). Two 5 3/4"-diameter holes covered with lucite flanges, one on the top lid and one on the side wall, act as view ports. The chamber is pumped by a nominal 6" fractionating oil diffusion pump using Convoil-20 pump fluid, with a pumping speed of about 1,000 liters/sec at 1 \times 10^{-6} \) torr. A refrigerated baffle is used to minimize backstreaming of pump fluid. The refrigeration system, which uses Freon-12 as coolant, is operated with a low pressure (about 20-22" Hg of vacuum) in the suction line and cools the baffle to about -40°C. The diffusion pump is backed by a 6 liters/sec mechanical fore pump.

Fore Chamber

The fore chamber is made from a 304 Stainless steel tee 6" in length with 0.109" wall thickness. All components for the source are supported from the lid on top. Two 1/4" holes penetrating both the lid and top flange of the tee are used for reproducible alignment so that the top lid can be removed and replaced without resetting the slit alignment. The fore chamber is pumped by a nominal 4" fractionating oil diffusion pump which uses Convalex-10 pump fluid and is backed by a 1.5 liters/sec mechanical fore pump. A chevron baffle was used to minimize backstreaming. The baffle was cooled only by conduction from the aluminum ring which in turn is cooled by the atmosphere. Special cooling was not necessary, since Convalex-10 pump fluid has a very low
vapor pressure at room temperature. An Ultek fore line trap using molecular sieve material to adsorb oil is used between the mechanical pump and the oil diffusion pump to prevent contamination of the diffusion pump oil by the mechanical pump oil vapor.

**Pressure Measurement**

Ionization gauges are installed in each of the fore and post chambers to monitor the pressures. The pressure is $1 \times 10^{-6}$ torr in both chambers when no gas is entering the source. During the experiment, the pressures are $1.6 \times 10^{-5}$ torr in the fore chamber and $1 \times 10^{-6}$ torr in the post chamber. However, after long periods of operation of the velocity selector, high temperatures in the motor bearings will cause a slight increase in the post chamber pressure.

A sensing tube for the thermocouple pressure gauge is installed at each roughing line between the mechanical pump and the diffusion pump to monitor the roughing line pressures.

**Safety Interlocks**

The diffusion pumps are each controlled by a safety interlock system. If the pressure in the roughing line of the post chamber is higher than 0.1 torr, power to the both diffusion pumps will be automatically turned off. One "Flow-trol" is installed in each water line to the diffusion pumps to monitor the water flow rate. If the flow rate falls below 1/3 gallon per minute, the power to that diffusion pump will be automatically turned off.
C. Auxiliary Vacuum System, Gas Sampling, and Gas Delivery

Auxiliary Vacuum System and Gas Sampling.

An auxiliary vacuum system which contains several 12-liter glass bulbs for gas storage was used for gas manipulation and purification. The system is pumped by a mercury diffusion pump backed by a mechanical pump.

The helium (from Airco\textsuperscript{22}) is introduced into the storage bulb through an absorption trap containing degassed activated charcoal at liquid nitrogen temperature. The impurity in this helium is estimated to be less than one part in \(10^3\) as indicated by mass analysis.\textsuperscript{23} The neon and krypton are taken from cylinders of research grade gases supplied by Matheson Company\textsuperscript{24} without further purification. The reported impurity is 10 ppm for the Neon and less than 67 ppm for the krypton. The xenon and nitrogen are taken from flasks of reagent-grade gases from Airco. The methane used is Phillips\textsuperscript{25} research grade with impurity of 0.37 mole per cent, the most probable impurities being nitrogen, carbon dioxide and ethane.

Beam Gas Delivery

The beam gas is introduced into the source through an automatic pressure controller unit since it is necessary to keep the beam source pressure very constant to obtain a stable beam intensity. This unit consists of a Granville-Phillips\textsuperscript{26} Automatic Pressure Controller( APC) and a high pressure ion gauge, Westinghouse Type WL-7676. A picoammeter\textsuperscript{27} is used to measure the ion current from the ion gauge and supplies an output to the APC, thus serving as a pressure transducer. A 500ml.
flask is also placed downstream of the APC to buffer short term pressure fluctuations. The whole unit is shown in Figure 2.

The WL-7676 ion gauge is designed to measure gas pressures in the range of $1 \times 10^{-5}$ to $5 \times 10^{-1}$ torr, and the APC will automatically regulate the gas pressure in a system from one atmosphere to less than $1 \times 10^{-11}$ torr. The pressure in the source (ranging from 0.08 torr to 0.6 torr) is regulated by this system to better than ± 0.005 torr.

Target Gas Delivery

The target gas is introduced into the collision chamber through a manually controlled variable leak valve. The pressure in the collision chamber was found to be quite constant since the consumption in this case is negligible compared to the amount contained in the supply flask.

D. Beam Source

Configuration

The beam source uses a low voltage D.C. discharge to produce the metastable atoms and is similar to that of Rothe et al. As shown in Figure 1, it consists of a Pyrex tube C, two water-cooled copper end plates A and B, and a filament F and its supporting rods R. The Pyrex tube (5.1cm OD and 6.5cm long) serves both as an envelope for the discharge source and electrical insulation between plates A and B. In addition, the transparent Pyrex tube provides a direct view of the discharge condition. Plate A serves as the anode and supports the source slit $S_1$. Plate B contains electrical feed-throughs R for the filament F and the source gas inlet. Since the discharge produces a
Figure 2. Automatic Pressure Controller Unit
large amount of heat, cooling is provided by water flowing through a ring of copper tubing of 3/16" O.D. silver-soldered onto the outside faces of both plates close to the circumferences.

Filament

A ribbon-type filament is used. The ends are spot-welded to pieces of nickel sheet which are subsequently spot-welded to the flat ends of supporting rods R (inconel rod of 3/16" diameter). It was found that thoriated tungsten cataphoretically coated with thoria is the best material for the filament. The cataphoretic coating procedure has been described by Muschlitz and Randolph et al. The filament dimensions are 0.0254 mm thick, 1.91 to 2.54 mm wide, and 3 cm long. The distance between filament and anode is 2.1 cm.

Power

The filament is powered by a Lambda regulated power supply, the bias potential which is applied on the negative end of the filament F with respect to the end plate B (ground) provided by a Heathkit power supply, and the anode voltage by a Hewlett Packard power supply, operated in the constant current mode.

E. Velocity Selector

Construction

The slotted disk velocity selectros (SDVS) used are patterned after Kinsey's design. This design has the advantage that the velocity selector can be operated with different resolution and transmission
properties without introducing any side bands. Alcoa 2024-T3, an aluminum alloy with a very high tensile strength, was used for the material for the disks, and the saw used for cutting aluminum was 2" diameter, 0.022" thick with 20 teeth, and made of solid tungsten carbide. Each velocity selector consists of five thin disks (0.03125") and one thick disk (0.125"). The disks are clamped together between heavy end pieces for cutting. Two 1/8" diameter aligning holes 180 degrees apart are drilled through each disk separately after cutting at such position that a given particle will pass through slots that were milled by the same cut. Thus, small deviations or inaccuracies in the milling do not impair the performance of the selector. The characteristics of the two sets of the velocity selector disks built are listed in Table 2. A photograph of the velocity selector is shown in Figure 3. Rotor assembly is shown in Figure 4.

Bearing and its Mounting

We initially used Barden bearings of Type SR6K3 for the rotor coated with a special lubricant from Ball Brothers. Both the bearings and lubricant are satisfactory at 25,000 RPM for two to three hours continuous use. The bearings have to be relubricated after a total running time of fifteen hours. The maximum speed of the rotor is 40,000 RPM for a short time (perhaps 15 minutes) without overheating the bearings and the mounting spring. Lately, the SR6K3 type bearings were replaced with Barden Bartemp bearings SR6STB5-DB2 which had been dry-coated by Ball Brothers and did not need to be relubricated. The new bearings work satisfactorily at 25,000 RPM.

Each bearing was mounted inside tight-fitting brass ring of 0.2"
Table 2

Characteristics of the Slotted Disk Velocity Selectors

<table>
<thead>
<tr>
<th></th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of disks</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Diameter of disks</td>
<td>5.652&quot;</td>
<td>5.652&quot;</td>
</tr>
<tr>
<td>Number of slits per disk</td>
<td>360</td>
<td>360</td>
</tr>
<tr>
<td>Length of rotor, L+d</td>
<td>2.031&quot;</td>
<td>2.031&quot;</td>
</tr>
<tr>
<td>L</td>
<td>2.000&quot;</td>
<td>2.000&quot;</td>
</tr>
<tr>
<td>Total angular shift φ</td>
<td>24°</td>
<td>8°</td>
</tr>
<tr>
<td>( \kappa = \frac{dz}{d\phi} = \frac{L}{\phi} = \frac{v}{\omega} )</td>
<td>9.5493&quot;/rad</td>
<td>14.3239&quot;/rad</td>
</tr>
<tr>
<td>(helical path or conversion factor from angular velocity ( \omega ) to transmitted velocity ( v_o ))</td>
<td>(- 2.54\omega (\text{RPM}))</td>
<td>(- 7.62\omega (\text{RPM}))</td>
</tr>
<tr>
<td>Length of slit (in radial direction)</td>
<td>0.312&quot;</td>
<td>0.312&quot;</td>
</tr>
<tr>
<td>Slit width, ( \ell_1 )</td>
<td>0.022&quot;</td>
<td>0.022&quot;</td>
</tr>
<tr>
<td>Angular width at base, ( \Delta \phi )</td>
<td>0.5°</td>
<td>0.5°</td>
</tr>
<tr>
<td>Tooth thickness between slits</td>
<td></td>
<td></td>
</tr>
<tr>
<td>At base of slits</td>
<td>0.022&quot;</td>
<td>0.022&quot;</td>
</tr>
<tr>
<td>At top of slits</td>
<td>0.027&quot;</td>
<td>0.027&quot;</td>
</tr>
<tr>
<td>Average value, ( \ell_2 )</td>
<td>0.0245&quot;</td>
<td>0.0245&quot;</td>
</tr>
<tr>
<td>Average opening fraction, ( \frac{\ell_1}{\ell_1 + \ell_2} )</td>
<td>0.473</td>
<td>0.473</td>
</tr>
<tr>
<td>Thickness of disks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd disk</td>
<td>0.125&quot;</td>
<td>0.125&quot;</td>
</tr>
<tr>
<td>Others</td>
<td>0.03125&quot;</td>
<td>0.03125&quot;</td>
</tr>
</tbody>
</table>
Table 2. Continued

<table>
<thead>
<tr>
<th></th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average radius, $r$</td>
<td>2.670&quot;</td>
<td>2.670&quot;</td>
</tr>
<tr>
<td>Cutting angle for slits, $X = \tan^{-1}\left(\frac{\Sigma}{K}\right)$</td>
<td>15°37'</td>
<td>5°19'</td>
</tr>
<tr>
<td>Position for aligning holes (clockwise with respect to the same cut)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st disk</td>
<td>0°</td>
<td>0°</td>
</tr>
<tr>
<td>2nd disk</td>
<td>1.5°</td>
<td>0.5°</td>
</tr>
<tr>
<td>3rd disk</td>
<td>3°</td>
<td>1°</td>
</tr>
<tr>
<td>4th disk</td>
<td>6°</td>
<td>2°</td>
</tr>
<tr>
<td>5th disk</td>
<td>12°</td>
<td>4°</td>
</tr>
<tr>
<td>6th disk</td>
<td>24°</td>
<td>8°</td>
</tr>
<tr>
<td>$\gamma = \frac{\Delta \phi}{\phi}$</td>
<td>0.0208</td>
<td>0.0625</td>
</tr>
<tr>
<td>Velocity spread</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[R = \frac{\Delta v}{2v_o} = \frac{v_{\text{max}} - v_{\text{min}}}{2v_o}]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>complete set (with six disks)</td>
<td>0.0208</td>
<td>0.0627</td>
</tr>
<tr>
<td>$[R \approx \frac{\gamma}{1-\gamma^2}]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>partial set with last $n$ disks removed, $R_n$</td>
<td>$R_n \approx 2^n R_o$</td>
<td>$R_n \approx 2^n R_o$</td>
</tr>
<tr>
<td>$v_{\text{min}}/v_o = 1/(1+\gamma)$</td>
<td>0.980</td>
<td>0.941</td>
</tr>
</tbody>
</table>
Table 2. Continued

<table>
<thead>
<tr>
<th></th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_{\text{max}}/v_o = 1/(1-\gamma)$</td>
<td>1.021</td>
<td>1.067</td>
</tr>
<tr>
<td>Geometrical Factor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G = \bar{n} \gamma/(1-\gamma^2)$</td>
<td>0.0098</td>
<td>0.0297</td>
</tr>
<tr>
<td>$[T(v_o)=Gv_oI(v_o)]$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. Velocity Selector
Figure 4. Velocity Selector Rotor Assembly (After Ref. 34)

1, 2, 4 - 6 . 1/32" thickness disks
3 . 1/8" thickness disk
7 - 12 . spacers
13 . bearings
14, 16 . collars
15 . 1/4-28 N.F. Allen screw
17 . 3/8-24 N.F. nut
18 . 3/8" rotor shaft
thickness which in turn was supported by four tension springs. The mounting is shown in Figure 5. Each end of each spring is threaded a few times around a screw about the same size as spring and secured by a brass sleeve and set screw. The screw on one end is then screwed into the tapped hole on the mounting ring, and the other end connected to a supporting block. A piece of rubber tubing is fitted closely over each spring before the ends are fastened on the screws to act as a damper. The rotor can be balanced by adjusting the spring tensions. The housing blocks can be moved up and down by means of a geared shaft which passes through an O-ring seal in the wall of the vacuum system so that the whole rotor assembly can be lowered out of the beam path if necessary.

Motor and its Controller

The rotor is driven by a Syntorque two-pole, two-phase hysteresis synchronous motor, which is mounted on four posts extending from the rotor assembly housing blocks so that the motor and the rotor assembly can be moved as a unit. The motor is connected to the velocity selector rotor by 1.48-inch length of No. 13 piano wire (0.031" diameter) using suitable couplings.

Two CML variable frequency (50-1,800 Herz) power supplies furnish the power to the motor. The input to the motor is controlled by ganged variacs as shown in Figure 6.

Rotor Frequency Measurement

The rotor frequency is measured by an optical method. A high-output lens-end miniature lamp is placed in one of the housing blocks at the same height as the aligning holes of the rotor so that light can
Figure 5. Velocity Selector Bearing Mounting
(A). General View (shown with one spring only)
(B). Details about spring connection
CML Two Phase Power Supplies

120 V A.C.

Frequency control knob

Master

Slave

Output Voltages from power supplies

Ganged Variables

Output currents

Red

Green

Yellow

Blue

Motor Controller

Hysteresis Motor

EF17H71

Syntorque

Corp.

Figure 6. Velocity Selector Motor and Controller
pass through the aligning holes as they pass the lamp. A photo-diode placed in the other housing block at the same position as the lamp is conductive when it is exposed to light and thus produces a pulse in the circuit. This pulse is sent to a Baird-Atomic scaler for counting, thus, giving a direct measurement of the rotor frequency. The circuit is shown in Figure 7. A General Radio Strobotac is also used to observe the rotor as a frequency check.

F. Inhomogeneous Deflecting Magnet

The inhomogeneous deflecting magnet, which is "Model B" with a modified length of 4-9/16" as described by Herm and Herschbach, is a low-impedence electromagnet with pole tips of the traditional "two-wire" form. The schematic drawing and the relative location of the pole tips are shown in Figure 8. The pole tips (parts A and G) are made from Vanadium Permendur, the yoke parts (parts B, C, D, E, and F) from Armco magnetic ingot iron, and the clamps from stainless steel. All the iron parts (A to G) were nickel plated to prevent corrosion.

The energizing current and cooling water is carried by forty-two turns of 3/16" O.D. copper tubing wound about the yoke, twenty-one turns about each of the sides (parts C and E). Woven fiber glass tape is wound about the yoke to prevent chafing, and the copper tubing is insulated with woven fiber glass tubing. The energizing current is furnished by a Sorensen D.C. power supply, which has been modified with a Variac input so the output can be varied from 0 - 100 amps at 0 - 10 volts. The reported magnetic induction in the air gap is about 12kG at an energizing current of about 100 amps, and the nominal gradient-to-field ratio, \( (1/\mu)(\partial H/\partial Z) \), of the magnet is about 3cm\(^{-1}\).
Figure 7. Rotor Frequency Measurement
Figure 8. Inhomogeneous Deflecting Magnet (After Ref. 45)
(A). Schematic Drawing
(B). Relative Location of the Pole Tips
(Number in inches)
C. Collision Chamber and Detecting System

The collision chamber is a modified version of that used by Smith and Muschlitz.\textsuperscript{51} As shown in Figure 1, a brass can $G$ with only one opening $S_5$ (across which a differential pressure can be maintained) envelops the whole collision chamber. Inside can $G$, there are scattering elements, a thermocouple gauge for measuring the target gas pressure, and an inlet for the target gas.

The scattering elements consist of the scattering cylinder lid $E_1$, the scattering cylinder $E_2$, and the scattering cylinder bottom $E_3$. $E_1$ contains a slit which is large enough to pass the beam without interference. $E_1$ is connected to a current measuring device and $E_3$ to the draw out potential supply. $E_2$ can be electrically connected to either $E_1$ or $E_3$. The dimensions of the scattering elements are given in Table 3. The scattering elements have been heavily gold-plated to obtain surfaces with equal electron-ejection efficiency and to minimize contact potential differences.

In the measurements for the total ionization cross section, $E_2$ is connected to $E_3$. The metastable atoms entering through slit $S_5$ in can $G$ pass through the slit opening in $E_1$ into the scattering region. The atom may undergo an elastic or inelastic collision with the target particle. Penning and associative ionization are the main inelastic processes producing ions and electrons. Elastically scattered and unscattered metastable atoms will hit either $E_2$ or $E_3$. If $E_2$ and $E_3$ are positive with respect to $E_1$, all positively charged particles will be collected on $E_1$ and be measured as $I_+$. Electrons will be collected on $E_2$ or $E_3$ with no effect on $I_+$. If a negative potential is applied
Table 3

Dimensions of Scattering Elements

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of scattering region</td>
<td>2.15 cm</td>
</tr>
<tr>
<td>Diameter of scattering cylinder (E_2)</td>
<td>1.91 cm</td>
</tr>
<tr>
<td>Slit opening on E_1</td>
<td>1.56 mm x 6.39 mm</td>
</tr>
</tbody>
</table>
on $E_2$ and $E_3$, both electrons produced by inelastic collision and secondary electrons ejected from $E_3$ or $E_2$ by the unreacted metastable atoms will be collected on $E_1$ and be measured as $I$. The detecting system is shown in Figure 9. The draw out potential applied on $E_3$ is furnished by a battery whose voltage is divided by a Helipot precision potentiometer. Current measurements on $E_1$ are made by means of a Cary Instruments vibrating-reed electrometer. The maximum sensitivity is $1 \times 10^{-14}$ ampere for full scale deflection of the output meter using an input resistance of $10^{11}$ ohms. Shielding of the leads for both $E_1$ and $E_3$ are necessary to reduce the noise level.

The measuring device for the beam composition studies is the same as for the cross section measurement except $E_2$ is connected to $E_1$ to increase the collection efficiency for the electrons ejected from $E_3$. The can $G$ is completely shielded from the fringing magnetic field of the deflecting magnet by means of Conetic foil.

The output from the Cary electrometer is fed into a chart recorder for continuous monitoring of current measurement and into an integrator to sum the signal for a certain period of time to average out noise. The main component of the integrator is an operational amplifier. A logic control circuit controls the integration time which may be 1, 10, 100, or 200 sec. The result of the integration is displayed by a digital voltmeter and permanently recorded by a printer.

The pressure inside the scattering chamber is controlled by a leak valve and measured by an RCA 1946 thermocouple gauge. The gauge has four leads, two for the heater connected to a DC power supply through a rheostat, and two for the EMF measurement. The measurements of EMF
Figure 9. Detecting System
are made by means of a Leeds and Northrup universal potentiometer\textsuperscript{59a} and galvanometer\textsuperscript{59b} utilizing a standard cell.\textsuperscript{60} The potentiometer is powered by a high capacity, long life Willard battery.\textsuperscript{61}
Chapter IV
EXPERIMENTAL PROCEDURE AND DATA TREATMENT

A. Calibration of RCA 1946 Thermocouple Pressure Gauge against McLeod Gauge

A simple device consisting of a magnetic ball valve and condenser as described by Colgate and Genre 62 has been added to a previously calibrated McLeod gauge manometer. Using appropriate coolant this modified McLeod gauge can eliminate almost completely the observed mercury pumping error. The procedure is described in Ref. 62 in detail. When a coolant at -10°C is passed through the condenser before the mercury is raised to the measuring flask, the mercury pumping error effect is made negligible. The RCA 1946 thermocouple pressure gauge, which was installed inside the collision chamber, was calibrated against the modified McLeod gauge with the whole collision chamber inside the bell jar to which the modified McLeod gauge was attached. The calibration procedure is as follows. A current of 70mA was supplied to the heater leads of the RCA 1946 gauge, the EMF was measured as $E_o$ at vacuum, then a small amount of gas was introduced into the bell jar (with bottom gate to pump closed). The EMF was again measured as $E$, meanwhile, the gas pressure was measured using the McLeod gauge as $p$. The value of $(E_o - E)/E_o = \Delta E/E_o$ is very constant and is a function of the gas pressure $p$ only. Since the absolute values of $E_o$ and $E$ vary with the ambient temperature, the time between measurements for $E_o$ and $E$
cannot be too long. About 10 to 15 points were recorded between 0.1 and 10 mtorr pressure for each gas. With the help of the WL-7676 high pressure ion gauge, it was not difficult to introduce the right amount of gas to the vacuum to obtain the required pressure. A plot of $p$ versus $\Delta E/E_0$ yields a straight line. The calibration curves are shown in Figures 10 and 11, and the results are given in Table 4.

B. **Slit Alignment**

Slit alignment was checked optically. An intense small commercial light bulb was placed at the position of the filament inside the source. All slits were adjusted to such a position that the center of the beam coincided with the slit centers.

C. **Optimum Discharge Condition to Produce Metastable Atoms**

For each metastable atom studied (He*, Ne*, and Ar*), the filament bias was +50 volts with respect to ground and the filament current was 8 to 15 amperes. A 450 volt potential difference across the deflecting plates $D$ was used to deflect any charged particles present in the beam. The beam intensity increases with the discharge current; however, the discharge current was set at 200mA in most cases to lengthen the filament lifetime. The same is true for the anode voltage: a higher anode voltage is required to initiate discharge, but, once started, the anode voltage was set as low as possible. The source pressure was varied until the strongest beam intensity was obtained. The optimum discharge conditions are given in Table 5.
Figure 10. Calibration Curves for RCA 1946 Thermocouple Gauge for Ar, Kr, Xe, O₂, NO, HD, CO₂, and CD₄.
Figure 11. Calibration Curves for RCA 1946 Thermocouple Gauge for $H_2$, $D_2$, $N_2$, $N_2O$, $CH_4$, $C_2H_4$, and $C_2H_6$
Table 4
Calibration for RCA 1946 Vacuum Gauge
in the Range 0.1 to 10 Microns\textsuperscript{a}

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure (Microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>( p = 156.45 \times \frac{\Delta E}{E_0} - 0.01010 )</td>
</tr>
<tr>
<td>Kr</td>
<td>( p = 224.28 \times \frac{\Delta E}{E_0} - 0.01772 )</td>
</tr>
<tr>
<td>Xe</td>
<td>( p = 268.99 \times \frac{\Delta E}{E_0} - 0.03754 )</td>
</tr>
<tr>
<td>H(_2)</td>
<td>( p = 70.060 \times \frac{\Delta E}{E_0} - 0.01034 )</td>
</tr>
<tr>
<td>D(_2)</td>
<td>( p = 78.595 \times \frac{\Delta E}{E_0} + 0.00377 )</td>
</tr>
<tr>
<td>HD</td>
<td>( p = 67.955 \times \frac{\Delta E}{E_0} + 0.00125 )</td>
</tr>
<tr>
<td>O(_2)</td>
<td>( p = 102.76 \times \frac{\Delta E}{E_0} - 0.03748 )</td>
</tr>
<tr>
<td>N(_2)</td>
<td>( p = 98.256 \times \frac{\Delta E}{E_0} - 0.00966 )</td>
</tr>
<tr>
<td>NO</td>
<td>( p = 92.165 \times \frac{\Delta E}{E_0} - 0.01507 )</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>( p = 85.016 \times \frac{\Delta E}{E_0} + 0.00689 )</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>( p = 78.404 \times \frac{\Delta E}{E_0} - 0.01093 )</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>( p = 62.227 \times \frac{\Delta E}{E_0} - 0.01669 )</td>
</tr>
<tr>
<td>CD(_4)</td>
<td>( p = 63.467 \times \frac{\Delta E}{E_0} + 0.00055 )</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>( p = 54.772 \times \frac{\Delta E}{E_0} + 0.00475 )</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>( p = 45.560 \times \frac{\Delta E}{E_0} - 0.00288 )</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Note: Heater current = 70mA
Table 5
Optimum Discharge Conditions to Produce Metastable Atoms

<table>
<thead>
<tr>
<th>Condition</th>
<th>He*</th>
<th>Ne*</th>
<th>Ar*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source Pressure (Torr)</td>
<td>0.08 - 0.12(^a)</td>
<td>0.08 - 0.12(^b)</td>
<td>0.08 - 0.12(^c)</td>
</tr>
<tr>
<td>Anode Voltage (Volts)</td>
<td>65</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>Discharge Current (Ampere)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Filament Bias (Volts)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Typical Beam Intensity</td>
<td>24(^d)</td>
<td>30(^e)</td>
<td>21(^f)</td>
</tr>
</tbody>
</table>

(10\(^{-14}\) Ampere)

\(^a\) APC reference set at 400, WL-7676 read \(\frac{I^+}{I^-} = 0.045\)

\(^b\) APC reference set at 650, WL-7676 read \(\frac{I^+}{I^-} = 0.073\)

\(^c\) APC reference set at 800, WL-7676 read \(\frac{I^+}{I^-} = 0.27\)

\(^d\) At nominal velocity 1,450m/sec using velocity selector Set II.

\(^e\) At nominal velocity 900m/sec using velocity selector Set II.

\(^f\) At nominal velocity 712m/sec using velocity selector Set II.
D. Drawout Potentials

In order to determine the proper potentials to be applied on E3 for the current measurements in the collision chamber, the current intensity was measured as a function of the voltage applied to E3 at some arbitrary nominal velocity of the beam. Measurements were made with and without the target gas inside the collision chamber. Figure 12 shows the plots of current intensities against the drawout potentials. Each curve levels off below -60 volts and above +6 volts. Different velocities of metastable atoms and different scattering gases gave the same dependence, and all subsequent measurements were made at a -65 volt drawout potential for I_- measurement and at a +6.5 volt drawout potential for I_+ measurements.

E. Velocity Distribution of the Metastable Neon Atomic Beam

In order to check the operation of the velocity selectors, the intensity of the metastable neon atomic beam was measured as a function of the rotor frequency, which is proportional to the nominal transmitted velocity, for each set of velocity selectors used. To increase the transmission, only the first four disks were used for Set I with the resultant velocity spread \( R = \Delta v/2v_0 = 0.084 \) (with \( v_{\text{min}} = 0.923v_0 \) and \( v_{\text{max}} = 1.091v_0 \)), and the first five disks were used for Set II with the resultant velocity spread \( R = \Delta v/2v_0 = 0.127 \) (with \( v_{\text{min}} = 0.889v_0 \) and \( v_{\text{max}} = 1.143v_0 \)). Figure 13 shows the plots of measured values and calculated values of the relative beam intensity at different nominal velocities. The dotted line shows the calculated velocity dependence of the intensity (flux) of the metastable neon atomic beam,
Figure 12. Current Intensity Versus Drawout Potential

--- without target gas

---●--- with argon as target gas
Velocity Distribution of the Metastable Neon Atomic Beam

a). Velocity dependence of the intensity (flux) of the metastable neon atomic beam.

\[ I(v) \sim v^3 \exp(-v^2/\alpha^2) \]

\[ \alpha = \sqrt{2kT/m} \]

b). Velocity dependence allowing for transmission of the velocity selector

\[ T(v_0) \sim \int_{v_{\text{min}}}^{v_{\text{max}}} I(v) 3(v, v_0) dv \]

c). Measured beam intensity with velocity selector Set I (using four disks) assuming \( \alpha = 71 \text{ m/sec} \) (\( T = 612^\circ \text{K} \))

d). Measured beam intensity with velocity selector Set II (using five disks) assuming \( \alpha = 70 \text{ m/sec} \) (\( T = 595^\circ \text{K} \))
\[ I(v) = v^2 \exp(-v^2/\alpha^2), \]
where \( \alpha = \sqrt{2kT/m} \) assuming the metastable atoms in the discharge source have a Maxwell-Boltzmann velocity distribution as discussed in Chapter II. The solid line shows the calculated transmitted quantities at different nominal velocities for the velocity selector Set I and Set II,

\[ T(v_o) = \int_{v_{\text{min}}}^{v_{\text{max}}} I(v) B(v,v_o) \, dv, \]
as discussed in Chapter II. Since \( I(v) \) over the transmitted band varies very much at the two ends of the velocity distribution curve, the actual value of \( I(v) \) was used in the numerical integration for \( T(v_o) \).

\( B(v,v_o) \) was approximated by a function that is triangular as a function of \( v \). The absolute values of \( T(v_o) \) are different for Set I and Set II. However, their relative values with respect to the maximum value (about at \( \alpha = 1 \)) are very close for the two sets at the same nominal velocity. Thus, \( T(v_o) \)'s for Set I and Set II can be shown on the same curve using the relative value. The solid circles show the relative measured beam intensity with velocity selector Set I assuming \( \alpha = 710\text{m/sec} \) (\( T = 612^\circ\text{K} \)) for the best fit with the calculated curve, and the open circles show the relative measured beam intensity with velocity selector Set II assuming \( \alpha = 700\text{m/sec} \) (\( T = 595^\circ\text{K} \)). As shown in the plot, the measured values fit the calculated curve in a large range of velocity so well that the assumption that the metastable atoms in the discharge source have a Maxwell-Boltzmann distribution must be valid. Also, these measurements have shown that the temperature in the source is reproducible for the same discharge condition, since these measurements for Set I and Set II were taken at times separated by a few months.
F. Metastable Atomic Beam Composition Measurements

In order to determine the proper currents to be applied to the energizing coils of the inhomogeneous deflecting magnet to deflect all components with \( m_J \neq 0 \) from the detector, the beam intensity of the metastable neon was measured as a function of the current applied to the energizing coils at some arbitrary nominal velocity of the neon beam. Figure 14 shows a plot of the relative undeflected beam intensity of the metastable neon versus the energizing current. The beam intensity dropped quite rapidly at low energizing current and saturated at about 30 amps. Different beam velocities and different beam gases showed a similar dependence, each with the onset saturation occurring at a magnet current lower than 45 amps. All subsequent beam composition measurements were made at 40 amps of energizing current when the deflecting field was required. The total beam intensity was measured when the deflecting field was off.

G. Electron Ejection Efficiency from a Cold Surface on Impact of Metastable Neon Atoms

As discussed in Chapter II, the electron ejection efficiency \( \gamma \) from a metal surface can be evaluated from the intercept of the plot of \( I_-/I_+ \) versus \( 1/p \). However, the probable error of this intercept would be large even with relatively accurate data since a long extrapolation is required. To maximize the accuracy of the \( \gamma \) value obtained, a beam of very high intensity is used. An unselected beam could not be used, since photons would interfere. The thick disk (0.125") of velocity selector Set I is opaque to photons but still has a high transmission for a broad band of velocities. The \( \text{Ne}^+ \) beam obtained in this way with
Figure 14. Deflection of Metastable Neon Atomic Beam in an Inhomogeneous Magnetic Field (Ne* at 875 m/sec)
a nominal velocity of 570 m/sec was used to study the electron ejection efficiency. Both $I_-$ and $I_+$ were measured at different target gas (argon) pressures. Figure 15 shows a plot $I_-/I_+$ versus $1/p$ for these measurements. The least-squares method gives:

$$\text{Intercept} = 1 - \frac{\gamma}{2} = 0.864 \pm 0.070$$

$$\gamma = 0.27 \pm 0.14.$$ 

This $\gamma$ is the electron ejection efficiency from an argon covered gold surface on impact of metastable neon atoms. Since the target gases probably do not effect the $\gamma$ value appreciably, this value was used for all target gases in the collision study with Ne*. No attempt to measure the $\gamma$ values for other metastable atoms was made.

**H. Total (Penning and Associative) Ionization Cross Section Measurement**

The inhomogeneous deflecting magnet was removed from the post chamber when making the total ionization cross section measurements. The systems studied were metastable neon atoms with Ar, Kr, Xe, N$_2$, or CH$_4$ as the target gas. Before making any measurement, the alignment is checked by measuring the current at electrode $E_1$ with no target gas present. If positive current is detected, this implies that metastable atoms are hitting electrode $E_1$ due to the poor alignment.

During the experiment $I_+$ and $I_-$ are measured at a constant nominal beam velocity as a function of the target pressure. Velocity selector Set I has been used for the measurements with the nominal beam velocity lower than 635 m/sec ($\approx$ 25,000 RPM), and the Set II for the remaining measurements. However, velocity selector Set II was also used for some of the measurements with nominal beam velocity lower than 635 m/sec as a
Figure 15. Secondary Electron Ejection Efficiency Measurement
\[ \frac{I_-}{I_+} = 0.27 \pm 0.14 \]
The difference in the measured cross section values due to the different resolutions of the velocity selectors at the same nominal beam velocity is within experimental error.

The pressures are measured as follows. The EMF of the RCA 1946 thermocouple pressure gauge is measured before admitting the target gas and denoted as $E_0$, and is measured again after admitting the target gas and denoted as $E_1$. The pressure can be determined from the value of $\Delta E_1/E_0$ with $\Delta E_1 = E_0 - E_1$ as described in the section A this chapter. The proper way to measure the second pressure is to follow the above procedure, i.e., to evacuate the collision chamber and then repeat measuring $E_0$ and $E_1$, but it will take quite a long time to get reasonable vacuum in the collision chamber due to the small opening of the collision chamber. Also the bearings may become too hot during this delay. Instead, the EMF at the first pressure is measured again and denoted as $E_1'$ ($E_1'$ may be different from $E_1$ due to a change in ambient temperature) after $I_+$ and $I_-$ measurements, then the flow rate of the target gas to the collision chamber is varied and the EMF is measured and denoted as $E_2$. Let $\Delta E_2 = E_1' - E_2$, then the total change in EMF is $\Delta E_1 + \Delta E_2$, and the pressure can be evaluated from the value $\Delta E/E_0$ with $\Delta E = \Delta E_1 + \Delta E_2$.

The variation of $E_0$ is small (for example, from 14.3100 mV to 14.3000 mV in a typical run) and the error in these measurements should be negligible. After two or three of these accumulation measurements, the collision chamber is evacuated to obtain a new value for $E_0$. The target gas pressure in the collision chamber was in the range of 0.5 to 1.5 microns (all pressures were corrected to 300°K). $I_-$ was in the range of $(1 - 30) \times 10^{-14}$ amp and $I_+$ $(0.2 - 4.0) \times 10^{-14}$ amp.
In some cases, $I_+$ and $I_-$ were measured as a function of the nominal beam velocity at a constant target pressure. The results show no difference from that obtained from currents measured as a function of the target pressure at a constant nominal beam velocity. The system Ne$^+$ - Xe was studied by this method.

I. Data Treatment

The total ionization cross section $\sigma_t$ was evaluated from the least-squares slope of a plot of $I_-/I_+$ versus $1/p$:

$$\frac{I_-}{I_+} = (1 - \frac{\gamma}{2}) + \frac{\gamma}{\sigma_t N \ell} \frac{1}{p^q}.$$

Figure 16 shows some of the plots of $I_-/I_+$ versus $1/p$ for Ne$^+$ - Ar system at different beam velocities.

Finally, the total ionization cross sections were corrected according to the method described by Berkling et al. The correction function used was $F_0\sigma(s,x)$ where $x$ is the ratio of the velocity of the atomic beam to the most probable velocity of the scattering particles, and $q$ a parameter expressing the velocity dependence given by

$$\sigma_t(v) = v - \frac{2}{q-1}$$

where $v$ is the relative velocity. The correction was made as follows: an initial value of $q$ was assumed, a correction calculated, and then $q$ was recalculated. This was iterated until $q$ did not change by more than 0.2%.
Figure 16. $\frac{I_\text{--}}{I_\text{+}}$ Versus $1/p$ for the Ne$^*$-Ar System at Different Beam Velocities
Chapter V. EXPERIMENTAL RESULTS AND DISCUSSION

A. Metastable Beam Composition from the Discharge Source

The beam compositions under different discharge conditions have been measured for metastable helium, neon and argon beams. As shown in Table 6, the beam compositions for metastable neon and argon are fairly constant over a large range of source pressures, discharge currents, and anode voltages. However, for metastable helium, the $\gamma I$ ratio (Eq.19) of the $^3S$ state to the $^1S$ state apparently increases as discharge current increases. This may be due to the conversion of atoms in the $^1S$ state to the $^3S$ state by superelastic collisions with electrons. At high discharge currents more electrons are present, so more atoms in the $^1S$ state are converted into the $^3S$ state. The ratio of the atoms in the $^1S$ state to those in the $^3S$ state of metastable helium by electron-impact excitation has been measured as a function of electron excitation energy by Dugan et al. Their results are consistent with this study if one assumes that the helium atoms in the discharge undergo collisions with electrons of energy between 30 and 40 electron volts. This seems a reasonable assumption for an anode potential of 65-volts. The relative abundance of the $^3S$ and $^1S$ states of the metastable helium atoms from a low voltage discharge has been reported by Rothe et al. They concluded that the detected particles were largely in the $^3S$ state, a quite different result from the value obtained in this experiment. The discrepancy may be due to
Table 6

Metastable Beam Compositions From Discharge Sources

(A). Metastable Helium Beam

<table>
<thead>
<tr>
<th>Nominal Beam Velocity (m/sec)</th>
<th>Anode Voltage (Volts)</th>
<th>Discharge Current (Amp)</th>
<th>$\gamma I$ Ratio $^{3S/1S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,448</td>
<td>65</td>
<td>0.12</td>
<td>0.95</td>
</tr>
<tr>
<td>1,448</td>
<td>65</td>
<td>0.20</td>
<td>1.70</td>
</tr>
<tr>
<td>1,219</td>
<td>65</td>
<td>0.30</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Note:  
1) Set II velocity selector was used for the velocity selection  
2) Source pressure = 0.1 torr  
3) Filament bias potential = 50 volts

(B). Metastable Neon Beam

<table>
<thead>
<tr>
<th>Nominal Beam Velocity (m/sec)</th>
<th>Source Pressure (Torr)</th>
<th>Discharge Current (Amp)</th>
<th>$\gamma I$ Ratio $^{3P_2/3P_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>999</td>
<td>0.08</td>
<td>0.19</td>
<td>4.88</td>
</tr>
<tr>
<td>712</td>
<td>0.08</td>
<td>0.19</td>
<td>5.01</td>
</tr>
<tr>
<td>712</td>
<td>0.05</td>
<td>0.19</td>
<td>5.33</td>
</tr>
<tr>
<td>712</td>
<td>0.11</td>
<td>0.19</td>
<td>5.23</td>
</tr>
<tr>
<td>712</td>
<td>0.08</td>
<td>0.10</td>
<td>3.99</td>
</tr>
<tr>
<td>712</td>
<td>0.08</td>
<td>0.20</td>
<td>4.78</td>
</tr>
<tr>
<td>712</td>
<td>0.08</td>
<td>0.30</td>
<td>4.22</td>
</tr>
<tr>
<td>712</td>
<td>0.08</td>
<td>0.40</td>
<td>4.60</td>
</tr>
<tr>
<td>712</td>
<td>0.08</td>
<td>0.50</td>
<td>4.78</td>
</tr>
</tbody>
</table>

Note:  
1) Set II velocity selector was used for the velocity selection  
2) Anode voltage = 45 volts  
3) Filament bias potential = 50 volts
Table 6. Continued

(C). Metastable Argon Beam<sup>c</sup>

<table>
<thead>
<tr>
<th>Anode Voltage (Volts)</th>
<th>( \gamma I ) Ratio ( ^{3P_2}/^{3P_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>6.54</td>
</tr>
<tr>
<td>35</td>
<td>6.92</td>
</tr>
<tr>
<td>45</td>
<td>8.24</td>
</tr>
</tbody>
</table>

<sup>c</sup> Note:  
1). Nominal beam velocity = 712 m/sec using the Set II velocity selector  
2). Source pressure = 0.1 torr  
3). Discharge current = 0.2 Amp.  
4). Filament bias potential = 50 volts
the higher discharge current (250-700mA) and longer discharge tube (10cm) used by these authors. No data is available for comparison with the results for the metastable neon or argon atomic beam composition.

B. Velocity Dependence of the Total Ionization Cross Section of Argon, Krypton, Xenon, Nitrogen, and Methane on Impact of Metastable Neon Atoms

The total ionization cross section (σ_t) as a function of the relative initial velocities (v) are shown in Figures 17 through 20 for the systems Ne* - Ar, Ne* - Kr, Ne* - Xe, and Ne* - N_2 and Ne* - CH_4, respectively. The log σ_t - log v plot is linear in the relative initial velocity range of 320 to 650m/sec. The slopes for the log σ_t - log v plots for these systems in this region are summarized in Table 7.

Since the probable error in the value of γ is ± 50% as shown in Chapter IV, and the probable errors in the values of slope and the scattering path length are relatively small, the probable error in the value of the absolute cross section would be about ± 50%. However, the error in γ will not cause any effect on the velocity dependence calculation. The probable error in the relative cross section (excluding the error in γ) was estimated to be ± 5%. The possible error caused by the recoiling Ne* atoms which hit the collecting plate E_1 has been estimated to be less than 1.4% for all systems studied (See Appendix I for the details of this calculation).

Recently, a simple model has been proposed to explain Penning ionization. In this model the Penning ionization cross section σ_{PI} is expressed as

\[ \sigma_{PI} = P_{c} Q_{c} \]
Figure 17. Velocity Dependence of the Total Cross Section for Ionization of Argon on Impact of Metastable Neon Atoms

--- Calculated Values

---○--- Experimental Values
Figure 18. Velocity Dependence of the Total Cross Section for Ionization of Krypton on Impact of Metastable Neon Atoms

--- Calculated Values

---O----- Experimental Values
Figure 19. Velocity Dependence of the Total Cross Section for Ionization of Xenon on Impact of Metastable Neon Atoms

--- Calculated Values

--- Experimental Values
Figure 20. Velocity Dependence of the Total Cross Section for Ionization of Methane and Nitrogen on Impact of Metastable Neon Atoms

---○----- Ne* → CH₄

---○----- Ne* → N₂
Table 7

Velocity Dependence of the Total Ionization of Gas Molecules on Impact of Metastable Neon Atoms

<table>
<thead>
<tr>
<th>System</th>
<th>Velocity Dependence Parameter, s ((\sigma_t \sim v^{-s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne(^*) - Ar</td>
<td>0.622 ± 0.014</td>
</tr>
<tr>
<td>Ne(^*) - Kr</td>
<td>0.728 ± 0.014</td>
</tr>
<tr>
<td>Ne(^*) - Xe</td>
<td>0.874 ± 0.016</td>
</tr>
<tr>
<td>Ne(^*) - N(_2)</td>
<td>0.739 ± 0.023</td>
</tr>
<tr>
<td>Ne(^*) - C(_2)(_2)</td>
<td>0.928 ± 0.018</td>
</tr>
</tbody>
</table>

\(^a\) Note: Between \(v = 320\) and \(v = 650\) m/sec only.
where $Q_c$ is a "close" or "gas-kinetic" collision cross section calculable from intermolecular potentials, and $P_c$ is the ionization probability per collision. If it is assumed that the van der Waals forces alone determine $Q_c$, $Q_c$ then varies with the relative initial velocity approximately as $v^{-2/3}$. Bates et al., formulates the probability of reaction per collision as $P_c = 1 - \exp(-w)$ with $w \approx v^{-1}$ as a crude approximation. With $w$ small for Penning ionization considered here, $P_c \approx \alpha v^{-1}$, the resultant $\sigma_{PI}$ would vary with the relative initial velocity approximately as $v^{-5/3}$. This velocity dependence is quite different from the experimental value which is between $v^{-0.62}$ and $v^{-0.93}$ in this study. The experimental values are for the total ionization cross section; however, associative ionization is only a small portion of the total. Therefore, this model cannot explain the experimentally observed velocity dependence. Even if $P_c$ is insensitive to the collision energy as assumed by Jones and Robertson, the slow variance of $Q_c$ from system to system still cannot explain the quite different results for the different systems. Jones and Robertson have calculated the collision cross section for diffusion using the Lennard-Jones (6-12) potential to compare with the experimental Penning ionization results and it appears that the velocity dependence of the calculated cross section is too strong in the low velocity range.

Miller and Schaefer have recently presented "Theoretical Treatment of Penning Ionization -- He(ls2s 1S, 3S) + H(ls 2S)." They present a simplified model for Penning ionization: "auto-ionization (PI or AI) occurs if, and only if, the collision energy and orbital angular momentum are such that the relative motion of $A^*$ and
B surmounts the maximum of the effective radial potential (the actual \( A^* - B \) potential plus the centrifugal potential); moreover, auto-ionization takes place only at the classical turning point in the effective radial potential." "The resulting expression for the total ionization cross section is

\[
\sigma_{\text{tot}}(E) = \pi R^2 \left[ 1 - V_e(R)/E \right], \tag{27A}
\]

where \( R = R(E) \) is the larger root of the equation

\[
E = V_e(R) + \frac{1}{2} R V_o'(R); \tag{27B}
\]

\( V_o(R) \) is the \( A^* - B \) potential (with the asymptotic limit subtracted out, so that \( V_o(\infty) = 0 \)), and \( E \) is the collision energy.

Their expression can be derived alternately as follows. Assume there is a relative maximum in the effective potential. The criterion for the system to pass over this maximum is that the impact parameter be less than some critical impact parameter \( b_c \), which is evaluated by letting the relative initial energy \( E \) equal to the effective potential at the relative maximum \( R_m \), i.e.,

\[
E = V_o(R_m) + \frac{E_b}{R_m^2}, \tag{27C}
\]

or

\[
b_c = R_m^2 \left[ 1 - \frac{V_o(R_m)}{E} \right]. \tag{27D}
\]

Since at \( R = R_m \), the effective potential has a zero slope,

\[
\left. \frac{d}{dr} \left[ V_o(R) + \frac{Eb_c^2}{R^2} \right] \right|_{R=R_m} = 0,
\]

or

\[
Eb_c^2/R_m^2 = \frac{1}{2} R_m V_o'(R_m). \tag{27E}
\]

Substituting Eq. (27E) into Eq. (27C), we obtain

\[
E = V_o(R_m) + \frac{1}{2} R_m V_o'(R_m). \tag{27F}
\]
The total ionization cross section is

\[ \sigma_{tot}(E) = \frac{\pi b^2}{c} = \pi R^2_m(1 - \frac{V_0(R_m)}{E}). \]  

(Eqs. (27G) and (27F) are identical to Eqs. (27A) and (27B), respectively.

Since this simplified model implies the existence of a relative in the effective potential, it is good for collisions with very small total angular momentum only. At higher energies this model breaks down as either no relative maximum in the effective potential or no real root for \( R \) in Eqs. (27B) or (27F) exists. For instance, if the reduced relative initial kinetic energy, \( E/\epsilon \) (\( E \) is the relative initial kinetic energy, and \( \epsilon \) is the well depth of the Lennard-Jones potential), is larger than 0.8 for a system with a Lennard-Jones potential, there is no real root for \( R \) in Eq. (27B). This would mean that the transition is classically impossible if \( E/\epsilon \) is larger than 0.8. Therefore, a new model will be presented in the following chapter to calculate the velocity dependence of the total ionization cross section.

The experimental results show that the total ionization cross section starts to level off or to increase slightly at the relative initial velocity 700 m/sec for each system. The corresponding reduced relative initial kinetic energy, \( (E/\epsilon) \), is 7.09 for \( \text{Ne}^* - \text{Ar} \), 6.99 for \( \text{Ne}^* - \text{Kr} \), and 5.99 for \( \text{Ne}^* - \text{Xe} \). It may be possible that a new channel of reaction opens at about these energies and predominates thereafter. The ions produced are assumed to be in their ground states. The energy difference between the first excited state \( (2P_{3/2}) \) and the ground state \( (2P_{1/2}) \) of the ions increases in the order \( \text{Ar}^+ < \text{Kr}^+ < \text{Xe}^+ \), while the amount of deviation from the linear \( \log \sigma_t - \log v \) plot at high collision energy has a reverse order (i.e., \( \text{Ne}^* - \text{Xe} < \text{Ne}^* - \text{Kr} < \text{Ne}^* - \text{Ar} \)) which seems reasonable if one assumes that the \( 2P_{3/2} \) state of the ion is the
second channel product. This would be true for the systems of Ne\(^*\) \(-\) N\(_2\) and Ne\(^*\) \(-\) CH\(_4\) too since N\(_2^+\) and CH\(_4^+\) have a number of low energy excited states. Another possibility causing the increase of ionization cross section at high velocity may be that the \(^3\)P\(_0\) atoms are de-excited to the \(^3\)P\(_1\) state by collision with the target gas molecules at high velocities and subsequently radiate to the ground state. Thus the measured total beam intensity would be decreased and the measured ionization cross section would be larger than it should be. Phelps\(^{73}\) has reported that at 300°K the average cross section for collisional de-excitation of the \(^3\)P\(_0\) neon atoms to the \(^3\)P\(_1\) state is about 6 \times 10^{-20} \text{cm}^2, which is too small to explain the present data. This explanation must still be considered, however, since the cross section for collisional de-excitation of the \(^3\)P\(_0\) neon atoms to the \(^3\)P\(_1\) state may be much larger at higher temperatures.
PART II

THEORETICAL
CHAPTER VI
A SIMPLE MODEL FOR PENNING AND ASSOCIATIVE IONIZATION

Two important inelastic collision processes between a metastable excited atom or molecule (A*) and another ground state particle (B), as described in Chapter I, are:

\[ A^* + B \rightarrow A + B^+ + e, \]  

(1)

and

\[ A^* + B \rightarrow AB^+ + e. \]  

(2)

Reaction (1) is called Penning ionization (PI) and reaction (2), associative ionization (AI). The PI/AI cross sections may be evaluated from a simple model:

i). Transition (PI or AI) occurs if and only if the collision energy and orbital angular momentum are such that the distance between A* and B becomes smaller than the range of the coupling potential responsible for the transition.

ii). The relative motion is semi-classical and the transition takes place only at the classical turning point.\(^{74}\)

iii). The transition probability at the turning point can be evaluated by perturbation theory.

iv). The transition may lead to either PI or AI depending on the relative kinetic energy and the relative minimum of the effective radial potential for the final state (A + B\(^+\)). If no relative minimum exists in the effective radial potential for the final state, the transition leads to PI only.
Figure 2.1 shows the schematic representation of the transition and the coupling potential. The subscripts 1 and 2 denote the initial state (the upper state, $A^* - B$) and the final state (the lower state, $A - B^+$), respectively. The effective radial potentials with zeroes at $R \to \infty$ are denoted by $V_{01}$ and $V_{02}$, the asymptotic relative kinetic energies by $E_1$ and $E_2$, the difference between the excitation energy of the metastable atom and the ionization potential of its collision partner by $\Delta E$, the classical turning point by $R_{cl}$, the energy of the electron ejected in the ionization by $e$ with a maximum value $e_m$, and the relative maximum value of $V_{02}$ at $R = R_{m2}$ by $M_2$. Some other notations and relations are listed in the following.

\begin{align*}
  e^* &= E_1 + \Delta E - M_2 \\
  e_m &= V_{01}(R_{cl}) + \Delta E - V_{02}(R_{cl}) = E_1 + \Delta E - V_{02}(R_{cl}) \\
  E_2 &= E_1 + \Delta E - c \\
  E_2 - V_{02}(R_{cl}) &= e_m - e
\end{align*}

The coupling potential $U$ is shown at the bottom of Figure 2.1. It is assumed that $U$ is a non-zero number if $R$ is equal to or smaller than $R_c$, and is zero if $R$ is larger than $R_c$.

According to the proposed model, the system in the initial state $(A^* - B)$ will come to the classical turning point $R_{cl}$. If $R_{cl}$ is larger than $R_c$, no transition is possible. On the contrary, if $R_{cl}$ is equal to or smaller than $R_c$, the system may transit from the initial state $(A^* - B)$ to the final state $(A - B^+)$. It is assumed that the transition probability can be evaluated by perturbation theory. The magnitude of the relative final kinetic energy $E_2$ depends on how much energy is carried away by the ejected electron as described by Eq. (3). If $E_2$ is smaller than $M_2$,
Figure 21. A Schematic Representation of Penning and Associative Ionization
the system cannot pass over the rotational barrier and associative
ionization results. otherwise Penning ionization occurs. The quantity
$\varepsilon^*$ is the critical value of the electron energy, $\varepsilon$, which determines
which process occurs.
CHAPTER VII

EVALUATION OF THE TRANSITION PROBABILITY
AND THE TOTAL IONIZATION CROSS SECTION

The general wave function normalized by the delta function of energy in the \( p \) (momentum) representation for a particle in a homogeneous external field is of the form

\[
a_{\theta}(p) = \frac{1}{\sqrt{(2\pi\hbar F)}} \exp\left[ \frac{i}{\hbar F} (E \cdot p - \frac{p^3}{6m}) \right], \quad (32)
\]

where \( F \) is the force acting on the particle due to this field, \( m \) is the mass of the particle, and \( E \), the kinetic energy, is the eigenvalue of the Hamiltonian operator

\[
H = \frac{p^2}{2m} - \hbar F \frac{\partial}{\partial p}. \quad (33)
\]

In the case of \( A^* - B \), near the transition point, \( R_\star \), the curves \( V_{\theta 1}(R) \) and \( V_{\theta 2}(R) \) are approximated by the straight lines,

\[
V_{\theta 1}(R) = V_{\theta 1}(R_\star) - F_1 \xi, \quad (34A)
\]

and

\[
V_{\theta 2}(R) = V_{\theta 2}(R_\star) - F_2 \xi, \quad (34B)
\]

where

\[
F = -(\frac{2V}{3R})_{R=R_\star} \quad (35)
\]

and

\[
\xi = R - R_\star.
\]

These represent one-dimensional motion in a homogeneous field, and thus Eq. (32) can be applied here. Therefore, the wave function for the initial state \( (A^* - B) \) can be expressed as
where $a_1$ has been normalized to unit current density and $\mu$ is the reduced mass of the system. Since $E_1 = V_{G}$ at the transition point (assumed to be the classical turning point), Eq. (36) is reduced to the form

$$a_1 = \frac{1}{\sqrt{|F_1|}} \exp\left\{ \frac{i}{\hbar F_1} \left[ (E_1 - V_{G}) p - \frac{p^3}{\hbar \mu} \right] \right\}. \tag{37}$$

The reflected waves or the waves for the final state (A-B$^+$) have the same form as Eq. (36) except for a factor of $\sqrt{2\hbar n}$,

$$a_2 = \frac{1}{\sqrt{2\hbar n |F_2|}} \exp\left\{ \frac{i}{\hbar F_2} \left[ (E_2 - V_{G}) p - \frac{p^3}{\hbar \mu} \right] \right\}, \tag{38}$$

or

$$a_2 = \frac{1}{\sqrt{2\hbar n |F_2|}} \exp\left\{ \frac{i}{\hbar F_2} \left[ (E_m - e) p - \frac{p^3}{\hbar \mu} \right] \right\}, \tag{39}$$

where $a_2$ is normalized by the delta function of energy.

The required transition probability is given by the expression

$$w = \frac{2\pi \hbar}{\hbar n} \left| \int a_1^* \cdot U \cdot a_2 dp \right|^2, \tag{40}$$

where $w$ is the transition probability, and $U$ is the perturbation energy or the coupling potential. Since the term $(a_1^* \cdot a_2)$ varies more rapidly than $U$, $U$ may be taken outside the integral and replaced by its value at the point of transition, giving

$$w = \frac{2\pi \hbar}{\hbar n} \left| U(R_d) \int_{-\infty}^{\infty} a_1^* \cdot a_2 dp \right|^2. \tag{41}$$

Substituting Eqs. (37) and (39) to Eq. (41), one has

$$w = \frac{U^2}{\hbar^2 |F_1 F_2|} \tau^2, \tag{42}$$
where \( I = \int_{-\infty}^{\infty} \exp\{ i \left[ \frac{(e_m - e)}{\eta F_2} p + \frac{1}{6\iota \eta} \left( \frac{1}{F_1} - \frac{1}{F_2} \right) p^3 \right] \} dp. \)

Let \( \delta(p) = \frac{e_m - e}{\eta F_2} p + \frac{1}{6\iota \eta} \left( \frac{1}{F_1} - \frac{1}{F_2} \right) p^3. \)

Since \( \delta(-p) = -\delta(p), \)
\[
\sin[\delta(-p)] = -\sin[\delta(p)],
\]
and \( \cos[\delta(-p)] = \cos[\delta(p)], \)
then
\[
I = \int_{-\infty}^{\infty} \exp\{ i \delta(p) \} dp = \int_{-\infty}^{\infty} \{ \cos[\delta(p)] + i \sin[\delta(p)] \} dp
\]
\[
= 2 \int_{0}^{\infty} \cos[\delta(p)] dp,
\]
or
\[
I = 2 \int_{0}^{\infty} \cos\left( \frac{e_m - e}{\eta F_2} p + \frac{1}{6\iota \eta} \left( \frac{1}{F_1} - \frac{1}{F_2} \right) p^3 \right) dp.
\]

Since \( \int_{0}^{\infty} \cos(at^3 \pm ct) dt = (\frac{1}{3}) \pi Ai[(\pm a)\frac{1}{3} c], \)
where \( Ai \) is Airy function, it follows that
\[
I = 2\pi \left( \frac{1}{6\iota \eta} \right)^{\frac{1}{3}} \left( \frac{1}{F_1} - \frac{1}{F_2} \right)^{\frac{1}{3}} Ai(-x),
\]
where \( x = (e_m - e) \left( \frac{2\iota}{\eta^2} \right)^{\frac{1}{3}} \left( \frac{1}{F_2} - \frac{1}{F_1} \right)^{\frac{1}{3}} \frac{1}{F_2}. \)

The value of \( x \) is a non-negative number in the region of interest.

Finally, \( w = \frac{U^2}{\eta^2 |F_1 F_2|} T^2 = \frac{4 \pi^2 U^2}{|F_1 F_2|^3 |F_1 - F_2|^2} \left( \frac{2\iota}{\eta^2} \right)^{\frac{2}{3}} Ai^2(-x), \)
\[
\text{All values in Eq.}(45) \text{ are the values at the transition point.}
\]
The variable $F_1$ in Eqs. (44) and (45) can be calculated for each energy and impact parameter if the potential functions for the both states are known, but, $U$, $V_{02}$, and $F_2$ remain unknown. In order to calculate $V_{02}$ and $F_2$, we have to know the orbital angular momentum for the final state. Fortunately, we can assume that the orbital angular momentum is almost conserved even when the electron carries away part of it by the following arguments. Let $L_e$ and $L_2$ be the orbital angular momentum for the ejected electron and the final state, respectively. Velocity, impact parameter, and energy are denoted by $v$, $b$, and $E$, respectively. Since

$$\frac{L_e}{L_2} = \frac{m_e v e^e}{\mu_2 v_2 b_2} = \left( \frac{m_e E_e}{\mu_2 E_2} \right)^{\frac{1}{2}} \frac{b_e}{b_2} \approx (\frac{m_e}{\mu_2})^{\frac{1}{2}} \ll 1,$$

(46)

where we have assumed that $E_e = E_2$ and $b_e = b_2$.

Thus, $L_2 = L_1$,

$$E_2 \left( \frac{b_2}{R} \right)^2 = E_1 \left( \frac{b_1}{R} \right)^2,$$

(47)

and

$$V_{02} = V_2 + \frac{E_2}{2} \left( \frac{b_2}{R} \right)^2 = V_2 + \frac{E_1}{2} \left( \frac{b_1}{R} \right)^2.$$

Dropping off the subscript for the impact parameter, one obtains

$$V_{02} = V_2 + \frac{E_1}{2} \left( \frac{b}{R} \right)^2.$$

(48)

Once $L_2$ is calculated, $F_2$ can be evaluated also.

Finally, we have to assume some functional form for the coupling potential, $U(R)$. We have chosen a step function,

$$U(R) = 0 \quad \text{for} \quad R > R_c,$$

(49A)

and

$$U(R) = U_0 \quad \text{for} \quad R \leq R_c,$$

(49B)
where $R_c$ is the cut-off point for the coupling and $U_0$ is a constant.

Now we are ready to evaluate the transition probability. Eq. (45) may be rewritten in a simple form

$$w(E_1, b, e) = 6_1(E_1, b) A e^2 [-I_m - e] 6_2(E_1, b),$$

where

$$6_1(E_1, b) = \frac{4 \pi^2 U^2}{|F_1 F_2|^{\frac{2}{3}} |F_1 - F_2|^{\frac{2}{3}}} \left( \frac{2 \mu}{\hbar^2} \right)^{\frac{2}{3}},$$

and

$$6_2(E_1, b) = \left( \frac{2 \mu}{\hbar^2} \right)^{\frac{1}{3}} \left( \frac{1}{F_2} - \frac{1}{F_1} \right)^{\frac{1}{3}} \frac{1}{F_2}.\quad (52)$$

The functions $6_1(E_1, b)$ and $6_2(E_1, b)$ are functions of the initial relative energy and impact parameter.

Eq. (50) gives the transition probability at some fixed energy for the ejected electron. In order to evaluate the total transition probability at each impact parameter and each initial relative energy, Eq. (50) has to be multiplied by the density of states of the electron and integrated over the range of the electron energies, i.e.,

$$w(E_1, b) = \int_0^{e_m} w(E_1, b, e) \rho(e) de,$$

where $\rho(e)$ is the density of states of the electron per unit energy.

Since the energy carried away by the ejected electron is about the same as the difference in the excitation energy of the metastable atom and the ionization energy of the ground state colliding partner and is smaller than the ionization energy of the ground particle, the ejected electron will feel a quite strong coulomb field. Thus, we will use the density of states of an electron in a coulomb field for $\rho(e)$, which is inversely proportional to the square root of the electron energy.
Eq. (53) becomes

\[ \omega(E_1, b) = k \int_0^{e_m} \omega(E_1, b, e) \frac{1}{\sqrt{e}} \, de, \]  

(54)

where \( k \) is a proportionality constant. We will leave \( k \) in Eq. (54) and \( u_0 \) in Eq. (49) undetermined, and use their product, \( k u_0 \), as an adjustable parameter.

Once the transition probability is evaluated, the total ionization cross section may be obtained from

\[ \sigma_t = 2\pi \int_0^{b_m} \omega(E_1, b) b \, db, \]  

(55)

where \( b_m \) is the impact parameter for which the turning point has a value equal to \( R_c \). It can be evaluated from the following equation.

\[ E_1 - V_1(R_c) - E_1 \left( \frac{b_m}{R_c} \right)^2 = 0 \]

or

\[ b_m = R_c \left( 1 - \frac{V_1(R_c)}{E_1} \right)^{1/2}. \]  

(56)
CHAPTER VIII
EVALUATIONS OF PENNING AND ASSOCIATIVE IONIZATION CROSS SECTIONS

As it is easily seen in Figure 21, if most of the excess energy is carried away by the electron, the final state does not have enough kinetic energy to pass over the rotational barrier and the atoms remain in the potential well. Such a collision will lead to associative ionization. Otherwise, Penning ionization will occur. Thus, Eq.(54) can be divided into two parts, one part giving the transition probability \( w_{PI}(E_1, b) \) for Penning ionization, the other giving \( w_{AI}(E_1, b) \) that for associative ionization. At some fixed initial relative energy \( E_1 \) and impact parameter \( b \) in the collision, \( w_{PI}(E_1, b) \) and \( w_{AI}(E_1, b) \) can be evaluated as follows:

1). If no relative minimum exists in \( V_{\delta^2} \) as in the case of very large orbital angular momentum (See Appendix II for calculating the critical value for the existence of the relative minimum), only Penning ionization is possible.

\[
\begin{align*}
    w_{PI}(E_1, b) &= \int_0^e \frac{w(E_1, b, e)}{\sqrt{e}} \, de \\
    w_{AI}(E_1, b) &= 0
\end{align*}
\]  \hspace{1cm} (57)

2). If there is a relative minimum if \( V_{\delta^2} \), this collision may lead to either Penning or associative ionization depending on the location of the relative maximum \( R_{m2} \) and on how much energy
is carried away by the ejected electron.

a). If $R_t > R_m$, only Penning ionization is possible.

$$w_{PI}(E_1,b) = k \int_{0}^{e_m} \omega(E_1,b,e) \frac{1}{\sqrt{e}} \, de$$

$$w_{AI}(E_1,b) = 0$$

b). If $R_t < R_m$, both ionization processes are possible:

i). $E_2 > M_2$ or $e < e^*$ leads to Penning ionization.

ii). $E_2 < M_2$ or $e > e^*$ leads to associative ionization.

$$w_{PI}(E_1,b) = k \int_{e}^{e^*} \omega(E_1,b,e) \frac{1}{\sqrt{e}} \, de$$

$$w_{AI}(E_1,b) = k \int_{e^*}^{e_m} \omega(E_1,b,e) \frac{1}{\sqrt{e}} \, de$$

Finally, Penning and associative ionization cross sections are evaluated from their corresponding transition probabilities and given by:

$$\sigma_{PI}(E_1) = 2\pi \int_{0}^{b} \omega_{PI}(E_1,b) b \, db,$$

and

$$\sigma_{AI}(E_1) = 2\pi \int_{0}^{b} \omega_{AI}(E_1,b) b \, db.$$
In the calculations, we have changed the variables to

\[ x = (e_m - e) \delta_2(E_1, b), \]  

\[ dx = - \delta_2(E_1, b) \, de. \]  

For \( e = 0 \), \[ x = e_m \delta_2(E_1, b) = \alpha. \]  

For \( e = e^* \), \[ x = (e_m - e^*) \delta_2(E_1, b) = \alpha \left( 1 - \frac{e^*}{e_m} \right) = \beta. \]  

For \( e = e_m^* \), \[ x = 0. \]  

Then \[ e = e_m - \frac{x}{\delta_2(E_1, b)} = \frac{1}{\delta_2(E_1, b)} [x - x]. \]  

Utilizing above equations and Eq. (50), Eqs. (57) and (58) may be rewritten as

\[ w_{\text{pl}}(E_1, b) = k \int_{0}^{\alpha} A^2(-x) \frac{1}{\sqrt{\alpha - x}} \, dx, \]  

and Eqs. (59) and (60) as

\[ w_{\text{pl}}(E_1, b) = k \int_{\beta}^{\alpha} A^2(-x) \frac{1}{\sqrt{\alpha - x}} \, dx, \]  

and

\[ w_{\text{al}}(E_1, b) = k \int_{0}^{\beta} A^2(-x) \frac{1}{\sqrt{\alpha - x}} \, dx. \]  

Since \( A^2(-x) \) has to be evaluated very often for very large negative arguments, the square of the Airy function has been approximately expressed as
\[ \text{Ai}^2(-x) = x^{-\frac{3}{2}} \{ 0.159155 \left[ 1 - \exp(-2.7170x^{0.26625}) + 0.159155 \left] - \exp(-2.7170x^{0.26625}) + 0.159155 \right\} + 0.0442 \left[ 1 - \exp(-2.7170x^{0.26625}) + 0.159155 \right]\} \]

\[ \text{Ai}^2(-x) \text{ for } x \geq 10, \quad (72) \]

where \( \zeta = \frac{2}{3} x^\frac{3}{2} \). The absolute error given by this approximate expression is less than 8.0x10^{-6}. Unless it happens that \( \text{Ai}(-x) = 0 \), the relative error is very small in general (See Appendix III for more detail). The integration involving the square of the Airy function can be divided into two parts,

\[ \int_a^b \text{Ai}^2(-x) \delta(x) \, dx = I_1 + I_2, \]

where \( \delta(x) = \frac{1}{\sqrt{|x-x'|}} \),

\[ I_1 = \int_a^1 \text{Ai}^2(-x) \delta(x) \, dx \text{ using the accurate values of } \text{Ai}^2(-x), \]

and \( I_2 = \int_1^b \text{Ai}^2(-x) \delta(x) \, dx \text{ using the approximated values of } \text{Ai}^2(-x). \)

The Lennard-Jones (6-12) potentials are used for the initial states,

i.e., \[ V_1(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right], \]

and the final states are assumed to have potentials of the form,

\[ V_2(R) = \frac{C(12)}{R^{12}} - \frac{C(6)}{R^6} + \frac{C(4)}{R^4}. \]

The potential parameters used in the calculations are listed in Tables 8 and 9. Due to lack of precise information, these values are only approximate. Values of ionization potentials and excitation energies of interest are summarized in Table 10.
Table 8

Lennard-Jones (6-12) Potential Parameters for Some Systems Involving Metastable Neon

\[ V(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right] \]

<table>
<thead>
<tr>
<th>System</th>
<th>( \varepsilon ) (10^{-15}\text{erg})</th>
<th>( \sigma ) (Å)</th>
<th>( C(6) ) (10^{-99} \text{erg-cm}^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne* - Ar</td>
<td>7.69</td>
<td>4.32</td>
<td>2.00</td>
</tr>
<tr>
<td>Ne* - Kr</td>
<td>9.47</td>
<td>4.46</td>
<td>2.98</td>
</tr>
<tr>
<td>Ne* - Xe</td>
<td>11.88</td>
<td>4.63</td>
<td>4.68</td>
</tr>
</tbody>
</table>

\(^a\) See Appendix IVA for the method of estimation.

Table 9

Potential Parameters for Some Ion-molecule Systems Involving Neon

\[ V(r) = \frac{C(12)}{R^{12}} - \frac{C(6)}{R^{6}} - \frac{C(4)}{R^{4}} \]

<table>
<thead>
<tr>
<th>System</th>
<th>( C(12) ) (10^{-6}\text{erg-Å}^{12})</th>
<th>( C(6) ) (10^{-9}\text{erg-Å}^6)</th>
<th>( C(4) ) (10^{-12}\text{erg-Å}^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne - Ar(^+)</td>
<td>0.72503</td>
<td>1.9618</td>
<td>4.553</td>
</tr>
<tr>
<td>Ne - Kr(^+)</td>
<td>1.0353</td>
<td>2.3038</td>
<td>4.553</td>
</tr>
<tr>
<td>Ne - Xe(^+)</td>
<td>1.5597</td>
<td>2.7671</td>
<td>4.553</td>
</tr>
</tbody>
</table>

\(^b\) See Appendix IVB for method of estimation.
Table 10

Energy Levels Used in the Calculation\(^c\)

<table>
<thead>
<tr>
<th>Atom or Ion</th>
<th>Designation</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>(^3)P(_2)</td>
<td>16.619</td>
</tr>
<tr>
<td>Ne</td>
<td>(^3)P(_0)</td>
<td>16.715</td>
</tr>
<tr>
<td>Ar(^+)</td>
<td>(^2)P(_{3/2})</td>
<td>15.759</td>
</tr>
<tr>
<td>Kr(^+)</td>
<td>(^2)P(_{3/2})</td>
<td>13.999</td>
</tr>
<tr>
<td>Xe(^+)</td>
<td>(^2)P(_{3/2})</td>
<td>12.130</td>
</tr>
</tbody>
</table>

Since it is very difficult to estimate the parameters for the potential functions necessary for the calculation for the systems Ne* - CH₄ and Ne* - N₂ no attempt to calculate cross sections for these systems was made. Calculation has been made for three systems, Ne* - Ar, Ne* - Kr, and Ne* - Xe. In the calculation, the energy of the \( ^3P_2 \) state is used for Ne*, and that of the \( ^2P_{3/2} \) state for Ar⁺, Kr⁺, and Xe⁺ unless otherwise specified. In each calculation, a value of \( R_C \) is assumed and if the result gives the right velocity dependence, \( kl^2 \), which has no effect on the velocity dependence, is adjusted until the calculated results fit the experimental results in the low velocity region.

The flow chart and the computer program for cross section calculations are given in Appendix V. It takes about 0.1 minute of computer time to evaluate cross sections at one energy for the Ne* - Ar system, and slightly more for the Ne* - Kr and Ne* - Xe systems.
CHAPTER X

THEORETICAL RESULTS AND DISCUSSION

The calculated results which agree best with the experimental values for the velocity dependence are shown in Tables 11, 12, and 13 for the systems Ne\(^+\) - Ar, Ne\(^+\) - Kr, and Ne\(^+\) - Xe, respectively. These calculated values are shown together with the experimental results in Figures 17, 18, and 19. The parameters used for the coupling potential along with the velocity dependence and percentages for Penning and associative ionization at 500 m/sec relative velocity are summarized in Table 14. Since the results calculated with these parameters and the potential parameters in Tables 8 and 9 fit the experimental results, we will consider these as standard values and then investigate the effect of a variation in some of these parameters.

A. Comparison Between Experimental Results and Calculated Results

As far as the velocity dependences are concerned, calculated results fit very well with the experimental results in the linear portion in the \(\log \sigma - \log v\) plot as shown in Figures 17, 18, and 19. No meaningful correlation has been found for the values of the constant \(kU_0^2\) for the three systems, Ne\(^+\) - Ar, Ne\(^+\) - Kr, and Ne\(^+\) - Xe.

The calculated results do not fit the experimental results in the high velocity region. There may be some factors which could cause the experimental result to deviate from a linear \(\log \sigma - \log v\) relation at
Table 11

Calculated Ionization Cross Section of Argon on Impact of Metastable Neon Atoms

<table>
<thead>
<tr>
<th>Relative Initial Velocity, $v$, m/sec</th>
<th>Total Ionization Cross Section, $\sigma_t$, Å²</th>
<th>Penning Ionization, $\sigma_{PI}$, %</th>
<th>Associative Ionization, $\sigma_{AI}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>6.7093</td>
<td>73.59</td>
<td>26.41</td>
</tr>
<tr>
<td>400</td>
<td>5.9885</td>
<td>73.06</td>
<td>26.94</td>
</tr>
<tr>
<td>500</td>
<td>5.1972</td>
<td>72.68</td>
<td>27.32</td>
</tr>
<tr>
<td>600</td>
<td>4.5281</td>
<td>72.21</td>
<td>27.79</td>
</tr>
<tr>
<td>700</td>
<td>3.9867</td>
<td>71.81</td>
<td>28.19</td>
</tr>
<tr>
<td>800</td>
<td>3.6199</td>
<td>72.24</td>
<td>27.76</td>
</tr>
<tr>
<td>900</td>
<td>3.2253</td>
<td>71.95</td>
<td>28.05</td>
</tr>
<tr>
<td>1,100</td>
<td>2.6713</td>
<td>72.24</td>
<td>27.76</td>
</tr>
<tr>
<td>1,300</td>
<td>2.2544</td>
<td>72.73</td>
<td>27.27</td>
</tr>
<tr>
<td>1,500</td>
<td>1.9514</td>
<td>73.81</td>
<td>26.19</td>
</tr>
<tr>
<td>2,000</td>
<td>1.4556</td>
<td>77.12</td>
<td>22.88</td>
</tr>
</tbody>
</table>

Slope = -0.625 in the $\log \sigma_t - \log v$ plot between $v=320$ and $v=600$ m/sec

---

Table 12

Calculated Ionization Cross Section of Krypton on Impact of Metastable Neon Atoms

<table>
<thead>
<tr>
<th>Relative Initial Velocity, $v$, m/sec</th>
<th>Total Ionization Cross Section, $\sigma_t$, Å²</th>
<th>Penning Ionization, $\sigma_{PI}$, %</th>
<th>Associative Ionization, $\sigma_{AI}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>7.2844</td>
<td>84.33</td>
<td>15.67</td>
</tr>
<tr>
<td>400</td>
<td>6.2608</td>
<td>84.16</td>
<td>15.84</td>
</tr>
<tr>
<td>500</td>
<td>5.3084</td>
<td>83.89</td>
<td>16.11</td>
</tr>
<tr>
<td>600</td>
<td>4.5937</td>
<td>83.77</td>
<td>16.23</td>
</tr>
<tr>
<td>700</td>
<td>4.0371</td>
<td>83.70</td>
<td>16.30</td>
</tr>
<tr>
<td>800</td>
<td>3.5858</td>
<td>83.69</td>
<td>16.31</td>
</tr>
<tr>
<td>900</td>
<td>3.2160</td>
<td>83.74</td>
<td>16.26</td>
</tr>
<tr>
<td>1,100</td>
<td>2.6254</td>
<td>83.88</td>
<td>16.12</td>
</tr>
<tr>
<td>1,300</td>
<td>2.2277</td>
<td>84.45</td>
<td>15.55</td>
</tr>
<tr>
<td>1,500</td>
<td>1.9219</td>
<td>85.33</td>
<td>14.67</td>
</tr>
<tr>
<td>2,000</td>
<td>1.4207</td>
<td>87.71</td>
<td>12.29</td>
</tr>
</tbody>
</table>

Slope = -0.734 in the $\log \sigma_t - \log v$ plot between $v=320$ and $v=600$ m/sec
Table 13
Calculated Ionization Cross Section of Xenon
on Impact of Metastable Neon Atoms

<table>
<thead>
<tr>
<th>Relative Initial Velocity, ( v ), m/sec</th>
<th>Total Ionization Cross Section, ( \sigma_t ), ( \text{A}^2 )</th>
<th>Penning Ionization, ( \sigma_{PI} ), %</th>
<th>Associative Ionization, ( \sigma_{AI} ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>9.7670</td>
<td>88.54</td>
<td>11.46</td>
</tr>
<tr>
<td>400</td>
<td>8.0278</td>
<td>88.38</td>
<td>11.62</td>
</tr>
<tr>
<td>500</td>
<td>6.6060</td>
<td>88.26</td>
<td>11.74</td>
</tr>
<tr>
<td>600</td>
<td>5.6121</td>
<td>88.16</td>
<td>11.84</td>
</tr>
<tr>
<td>700</td>
<td>4.8664</td>
<td>88.13</td>
<td>11.87</td>
</tr>
<tr>
<td>800</td>
<td>4.2864</td>
<td>88.16</td>
<td>11.84</td>
</tr>
<tr>
<td>900</td>
<td>3.8212</td>
<td>88.23</td>
<td>11.73</td>
</tr>
<tr>
<td>1,100</td>
<td>3.1236</td>
<td>88.49</td>
<td>11.51</td>
</tr>
<tr>
<td>1,300</td>
<td>2.6283</td>
<td>88.99</td>
<td>11.01</td>
</tr>
<tr>
<td>1,500</td>
<td>2.2607</td>
<td>88.78</td>
<td>10.22</td>
</tr>
<tr>
<td>2,000</td>
<td>1.6613</td>
<td>92.11</td>
<td>7.89</td>
</tr>
</tbody>
</table>

Slope = -0.881 in the log \( \sigma_t \) - log \( v \) plot between \( v=320 \) and \( v=600 \) m/sec.

Table 14
Summary for the Coupling Potentials and Velocity Dependence of the Ionization Cross Section

<table>
<thead>
<tr>
<th>System</th>
<th>( R_c )</th>
<th>( kU_c^2 )</th>
<th>( s )</th>
<th>Per Cent Abundance at ( v = 500 \text{m/sec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ne}^* - \text{Ar} )</td>
<td>1.0005</td>
<td>5.3412</td>
<td>0.625</td>
<td>0.622, 72.68, 27.32</td>
</tr>
<tr>
<td>( \text{Ne}^* - \text{Kr} )</td>
<td>1.0075</td>
<td>4.5404</td>
<td>0.734</td>
<td>0.729, 83.89, 16.11</td>
</tr>
<tr>
<td>( \text{Ne}^* - \text{Xe} )</td>
<td>1.018</td>
<td>4.5034</td>
<td>0.881</td>
<td>0.874, 82.86, 11.74</td>
</tr>
</tbody>
</table>

Note: 
\( \text{Ne}^* \) is assumed to be at the state \( ^3P_2 \) and \( \text{Ar}^+, \text{Kr}^+, \text{Xe}^+ \) at \( ^2P_3/2 \)

\( R_c \) is in units of \( \sigma \), one of the potential parameters for the Lennard-Jones (6-12) potential for the initial state

\( \sigma \sim v^{-s} \) between \( v=320 \) and \( v=600 \text{m/sec} \)
high velocities as discussed in Part I of this dissertation. However, if a suitable coupling potential function which increases as $R$ decreases is used for the calculation, a calculated result which fits the experimental result for the whole range of velocity studied can be obtained. Therefore, an investigation of other forms for the coupling potential function should prove fruitful.

The per cent abundances for Penning and associative ionization have been measured by Herce\(^{23}\) for the Ne\(^*\) - Ar and Ne\(^*\) - Kr system using an electron impact source for metastable neon atoms at different electron energies. His results are shown in Appendix VI for comparison. Although the experimental results cannot be compared directly with the calculated results since Herce's Ne\(^*\) beam was not velocity-selected, a qualitative comparison may be made. For the system Ne\(^*\) - Ar associative ionization is about 25 per cent of the total ionization in the low relative initial velocity part for the calculated results, and it is about 20 per cent for the experimental results. For the system Ne\(^*\) - Kr, associative ionization is about 16 per cent for the calculated results, and about 20 per cent for the experimental results. Considering that the parameters for the potential functions used for the calculation are very rough, the comparison between the calculated results and the experimental results is quite good.

B. Effect of the Coupling Potential on the Ionization Cross Section

In order to compare the effects of changes in the coupling potential on the ionization cross section, a series of values of $R_c$'s have been used for the calculation in each system. The results are summarized in
Table 15. As easily seen in Table 15, the velocity dependence parameter $s (\sigma_v - v^2)$ is very sensitive to a change in the value of $R_C$. There is about 30 per cent increase in $s$ at $R_C = 1.00$, and about 10 per cent at $R_C = 1.03$ for a one per cent increase in the value of $R_C$. The total ionization cross section, which increases as $R_C$ increases, is relatively insensitive to $R_C$. The ratio of Penning ionization to associative ionization is almost constant at each case. It is not too difficult to see the logic of these effects. Since we are using a step function for the coupling potential, any increase in the value of $R_C$ will result in a larger range of impact parameters for which the value of the turning point is less than or equal to $R_C$ and consequently the total ionization cross section increases. However, the increase in the maximum impact parameter due to the increase in $R_C$ may have two opposite effects on the relative abundance of Penning and associative ionization. If the original value of $R_C$ is already relatively large, as in the cases of Ne* – Kr and Ne* – Xe, the increase of the maximum impact parameter will bring about more collisions which have higher total angular momentum. The relative maximum in the effective potential for the lower state may disappear if the system has a too high a total angular momentum, and consequently the increase in the ionization cross section will predominately be in the form of Penning ionization rather than associative ionization. Therefore, the percent of Penning ionization will increase slightly, and that of associative ionization decrease slightly if the original value of $R_C$ is relatively large. On the contrary, if the original value of $R_C$ is relatively small, as in the case of Ne* – Ar, again the increase of the maximum impact parameter will bring about more collisions with high total angular momentum, but this total angular
Table 15

Effect of the Coupling Potential

<table>
<thead>
<tr>
<th>System</th>
<th>$R_c^a$</th>
<th>$\sigma_t$ at $v = 500\text{m/sec}$</th>
<th>Per Cent Abundance at $v = 500\text{m/sec}$</th>
<th>Calculated $s^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne - Ar</td>
<td>1.00</td>
<td>5.1686</td>
<td>72.69</td>
<td>27.31</td>
</tr>
<tr>
<td>Ne - Ar</td>
<td>1.0005</td>
<td>5.1972</td>
<td>72.68</td>
<td>27.32</td>
</tr>
<tr>
<td>Ne - Ar</td>
<td>1.001</td>
<td>5.2256</td>
<td>72.67</td>
<td>27.33</td>
</tr>
<tr>
<td>Ne - Ar</td>
<td>1.0020</td>
<td>5.2825</td>
<td>72.66</td>
<td>27.34</td>
</tr>
<tr>
<td>Ne - Ar</td>
<td>1.0065</td>
<td>5.5190</td>
<td>72.51</td>
<td>27.49</td>
</tr>
<tr>
<td>Ne - Ar</td>
<td>1.03</td>
<td>7.1642</td>
<td>73.66</td>
<td>26.34</td>
</tr>
<tr>
<td>Ne - Kr</td>
<td>1.007</td>
<td>5.2579</td>
<td>83.82</td>
<td>16.19</td>
</tr>
<tr>
<td>Ne - Kr</td>
<td>1.0075</td>
<td>5.3084</td>
<td>83.89</td>
<td>16.11</td>
</tr>
<tr>
<td>Ne - Kr</td>
<td>1.008</td>
<td>5.3718</td>
<td>84.00</td>
<td>16.00</td>
</tr>
<tr>
<td>Ne - Kr</td>
<td>1.02</td>
<td>6.1424</td>
<td>84.35</td>
<td>15.65</td>
</tr>
<tr>
<td>Ne - Kr</td>
<td>1.03</td>
<td>6.7340</td>
<td>84.54</td>
<td>15.46</td>
</tr>
<tr>
<td>Ne - Xe</td>
<td>1.008</td>
<td>5.8424</td>
<td>88.08</td>
<td>11.92</td>
</tr>
<tr>
<td>Ne - Xe</td>
<td>1.018</td>
<td>6.6060</td>
<td>88.26</td>
<td>11.74</td>
</tr>
<tr>
<td>Ne - Xe</td>
<td>1.0185</td>
<td>6.6448</td>
<td>88.27</td>
<td>11.73</td>
</tr>
<tr>
<td>Ne - Xe</td>
<td>1.019</td>
<td>6.6831</td>
<td>88.28</td>
<td>11.72</td>
</tr>
<tr>
<td>Ne - Xe</td>
<td>1.020</td>
<td>6.7583</td>
<td>88.30</td>
<td>11.70</td>
</tr>
<tr>
<td>Ne - Xe</td>
<td>1.030</td>
<td>7.5166</td>
<td>88.51</td>
<td>11.49</td>
</tr>
</tbody>
</table>

Note: 

- $R_c$ is in units of $\sigma$, one of the potential parameters used in the Lennard-Jones potential for the initial state.
- $\sigma_t \sim v^{-s}$ between $v=320$ and $v=600\text{m/sec}$.
- Standard parameters for Ne - Ar, results are listed in Table 11.
- Standard parameters for Ne - Kr, results are listed in Table 12.
- Standard parameters for Ne - Xe, results are listed in Table 13.
momentum is far below the critical angular momentum above which no relative maximum exists. Therefore, the effect on the percentages of associative ionization and Penning ionization is negligible.

Finally, the increase of the maximum impact parameter due to an increase in the value of $R_c$ will have more effect on a collision with low relative initial velocity than on one with high relative initial velocity, and it will therefore determine the velocity dependence of the total ionization cross section.

Another very interesting point in Table 15 is that the three systems (Ne$^*$ - Ar, Ne$^*$ - Kr, and Ne$^*$ - Xe) have about the same value of $s$ for the same value of $R_c$. For instance, at $R_c = 1.03$ reduced units, $s($Ne$^*$ - Ar$) = 0.986$, $s($Ne$^*$ - Kr$) = 0.993$, and $s($Ne$^*$ - Xe$) = 1.003$; at $R_c = 1.02$ reduced units, $s($Ne$^*$ - Kr$) = 0.902$, and $s($Ne$^*$ - Xe$) = 0.904$; at $R_c = 1.008$ reduced units, $s($Ne$^*$ - Kr$) = 0.738$, and $s($Ne$^*$ - Xe$) = 0.738$. The reason for this coincidence is not clear.

C. Effect of the Potential Parameters on the Ionization Cross Section

In order to test the sensitivity of the ionization cross section to changes in the potential parameters used for the calculation, a series of potential parameters have been used. First of all, the energy of the $^3P_0$ state has been used for metastable neon in the calculation summarized in Table 16. Comparing Table 16 with Table 11, in which the energy of $^3P_2$(Ne) state was used, the variation of the cross sections is found to be very small and is less than 1 percent at most energies. The variation of the percentage of Penning ionization is less than 2 percent and the change in the velocity dependence is also very small.
Table 16

Calculated Ionization Cross Section of Argon on Impact of Metastable ($^3$P$_0$) Neon Atoms

<table>
<thead>
<tr>
<th>Relative Initial Velocity, $v$, m/sec</th>
<th>Total Ionization Cross Section $\sigma_t$, $\text{Å}^2$</th>
<th>Penning Ionization $\sigma_{PI}$, %</th>
<th>Associative Ionization $\sigma_{AI}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>6.7041</td>
<td>74.69</td>
<td>25.31</td>
</tr>
<tr>
<td>400</td>
<td>5.9367</td>
<td>73.97</td>
<td>26.03</td>
</tr>
<tr>
<td>500</td>
<td>5.1539</td>
<td>73.60</td>
<td>26.40</td>
</tr>
<tr>
<td>600</td>
<td>4.6140</td>
<td>73.85</td>
<td>26.15</td>
</tr>
<tr>
<td>700</td>
<td>4.0021</td>
<td>73.07</td>
<td>26.93</td>
</tr>
<tr>
<td>800</td>
<td>3.6116</td>
<td>73.30</td>
<td>26.70</td>
</tr>
<tr>
<td>900</td>
<td>3.2398</td>
<td>73.19</td>
<td>26.81</td>
</tr>
<tr>
<td>1,100</td>
<td>2.6977</td>
<td>73.59</td>
<td>26.41</td>
</tr>
<tr>
<td>1,300</td>
<td>2.2669</td>
<td>73.94</td>
<td>26.06</td>
</tr>
<tr>
<td>1,500</td>
<td>1.9632</td>
<td>74.93</td>
<td>25.07</td>
</tr>
<tr>
<td>2,000</td>
<td>1.4570</td>
<td>77.94</td>
<td>22.06</td>
</tr>
</tbody>
</table>

Slope = -0.600 in the log $\sigma_t$ - log$v$ plot between $v=320$ and $v=600$ m/sec.
Therefore, comparison of experiment with calculations using $^{3}P_2$ Ne is sufficient.

An initial state with double the potential well depth, and two final states with different well depths have been used for calculation. The results are shown in Tables 17, 18, and 19, and also shown in Figure 22. The results are summarized in Table 20. As easily seen in Table 20, variation of the potential well depth in the initial state has a larger effect on the velocity dependence of the ionization cross section than similar variations in the final state. However, the change in the ratio $\sigma_{PL}/\sigma_{AI}$ due to a change in the potential well depth of the initial state is small. On the contrary, the potential well depth in the final state has a much larger effect on this ratio and less effect on the velocity dependence.

The effect of a change in $k_{C}$ on the velocity dependence parameter $s$ is large (10-30% for a 1% change in $R_c$ in the region of interest). Changes in the potential parameters of the initial and final states on the velocity dependence parameter $s$ can be neglected, however. The conclusion is that the most important factor determining the velocity dependence is the cut-off point $R_c$ of the coupling potential and that other factors can be neglected.
### Table 17

Calculated Ionization Cross Section of Argon on Impact of Metastable Neon Atoms with Double the Potential Well Depth in the Initial State

<table>
<thead>
<tr>
<th>Relative Initial Velocity, ( v ), m/sec</th>
<th>Total Ionization Cross Section ( \sigma_t ), ( \AA^2 )</th>
<th>Penning Ionization ( \sigma_{PI} ), %</th>
<th>Associative Ionization ( \sigma_{AI} ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>5.1486</td>
<td>73.36</td>
<td>26.64</td>
</tr>
<tr>
<td>400</td>
<td>4.7496</td>
<td>73.51</td>
<td>26.49</td>
</tr>
<tr>
<td>500</td>
<td>4.2735</td>
<td>73.39</td>
<td>26.61</td>
</tr>
<tr>
<td>600</td>
<td>3.8243</td>
<td>73.03</td>
<td>26.97</td>
</tr>
<tr>
<td>700</td>
<td>3.4030</td>
<td>72.59</td>
<td>27.41</td>
</tr>
<tr>
<td>800</td>
<td>3.1412</td>
<td>73.13</td>
<td>26.87</td>
</tr>
<tr>
<td>900</td>
<td>2.8455</td>
<td>73.06</td>
<td>26.94</td>
</tr>
<tr>
<td>1,100</td>
<td>2.3942</td>
<td>73.47</td>
<td>26.53</td>
</tr>
<tr>
<td>1,300</td>
<td>2.0351</td>
<td>73.98</td>
<td>26.02</td>
</tr>
<tr>
<td>1,500</td>
<td>1.7910</td>
<td>75.36</td>
<td>24.64</td>
</tr>
<tr>
<td>2,000</td>
<td>1.3344</td>
<td>78.70</td>
<td>21.30</td>
</tr>
</tbody>
</table>

Slope = -0.471 in the \( \log \sigma_t - \log v \) plot between \( v = 320 \) and \( v = 600 \) m/sec
### Table 18

Calculated Ionization Cross Section of Argon on Impact of Metastable Neon Atoms with One-Half the Potential Well Depth in the Resulting Molecular Ion

<table>
<thead>
<tr>
<th>Relative Initial Velocity, ( v ), m/sec</th>
<th>Total Ionization Cross Section ( \sigma_t, \text{Å}^2 )</th>
<th>Penning Ionization ( \sigma_{PI}, % )</th>
<th>Associative Ionization ( \sigma_{AI}, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>9.0327</td>
<td>81.05</td>
<td>18.95</td>
</tr>
<tr>
<td>400</td>
<td>8.0217</td>
<td>80.74</td>
<td>19.26</td>
</tr>
<tr>
<td>500</td>
<td>6.8626</td>
<td>80.31</td>
<td>19.69</td>
</tr>
<tr>
<td>600</td>
<td>6.0463</td>
<td>80.51</td>
<td>19.49</td>
</tr>
<tr>
<td>700</td>
<td>5.2839</td>
<td>80.40</td>
<td>19.60</td>
</tr>
<tr>
<td>800</td>
<td>4.6852</td>
<td>80.49</td>
<td>19.51</td>
</tr>
<tr>
<td>900</td>
<td>4.2395</td>
<td>80.95</td>
<td>19.05</td>
</tr>
<tr>
<td>1,100</td>
<td>3.4797</td>
<td>81.80</td>
<td>18.20</td>
</tr>
<tr>
<td>1,300</td>
<td>2.9482</td>
<td>83.22</td>
<td>16.78</td>
</tr>
<tr>
<td>1,500</td>
<td>2.5454</td>
<td>85.08</td>
<td>14.92</td>
</tr>
<tr>
<td>2,000</td>
<td>1.8462</td>
<td>90.09</td>
<td>9.91</td>
</tr>
</tbody>
</table>

Slope = -0.644 in the \( \log \sigma_t - \log v \) plot between \( v=320 \) and \( v=600 \) m/sec

**Note:** The potential parameters for NeAr\(^+\) with one-half the potential well depth are:

\[
\begin{align*}
C(12) &= 3.5753 \times 10^{-7} \text{erg.Å}^{12} \\
C(6) &= 9.5357 \times 10^{-10} \text{erg.Å}^6 \\
C(4) &= 4.553 \times 10^{-12} \text{erg.Å}^4
\end{align*}
\]
Table 19

Calculated Ionization Cross Section of Argon on Impact of Metastable Neon Atoms with One and One-Half the Potential Well Depth in the Resulting Molecular Ion

<table>
<thead>
<tr>
<th>Relative Initial Velocity, ( v ), m/sec</th>
<th>Total Ionization Cross Section, ( \sigma_t ), ( \text{Å}^2 )</th>
<th>Penning Ionization, ( \sigma_{PI} ), %</th>
<th>Associative Ionization, ( \sigma_{AI} ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>5.5126</td>
<td>68.54</td>
<td>31.46</td>
</tr>
<tr>
<td>400</td>
<td>4.9749</td>
<td>67.64</td>
<td>32.36</td>
</tr>
<tr>
<td>500</td>
<td>4.3383</td>
<td>67.26</td>
<td>32.75</td>
</tr>
<tr>
<td>600</td>
<td>3.7874</td>
<td>66.51</td>
<td>33.49</td>
</tr>
<tr>
<td>700</td>
<td>3.3335</td>
<td>65.87</td>
<td>34.13</td>
</tr>
<tr>
<td>800</td>
<td>2.9737</td>
<td>65.54</td>
<td>34.46</td>
</tr>
<tr>
<td>900</td>
<td>2.7268</td>
<td>65.90</td>
<td>34.10</td>
</tr>
<tr>
<td>1,100</td>
<td>2.2717</td>
<td>66.01</td>
<td>33.99</td>
</tr>
<tr>
<td>1,300</td>
<td>1.9002</td>
<td>65.90</td>
<td>34.10</td>
</tr>
<tr>
<td>1,500</td>
<td>1.6894</td>
<td>67.42</td>
<td>32.58</td>
</tr>
<tr>
<td>2,000</td>
<td>1.2787</td>
<td>70.31</td>
<td>29.69</td>
</tr>
</tbody>
</table>

Slope = -0.623 in the log \( \sigma_t \) - log \( v \) plot between \( v=320 \) and \( v=600 \) m/sec

Note: The potential parameters for NeAr\(^+\) with one and one-half the potential well depth are:

\[ c^{(2)} = 1.0925 \times 10^{-6} \text{ erg. Å}^{12} \]

\[ c^{(6)} = 2.9700 \times 10^{-9} \text{ erg. Å}^{6} \]

\[ c^{(4)} = 4.553 \times 10^{-12} \text{ erg. Å}^{4} \]
Figure 22. Effects of the Potential Parameters on the Ionization Cross Sections

- Normal Condition
- One-half Potential Well-depth in NeAr^+
- Double Potential Well-depth in Ne^+ - Ar
- One and One-half Potential Well-Depth in NeAr^+
The graph shows the relationship between the relative initial velocity (m/sec) and the total ionization cross section (Å²). The data points are represented by various symbols, with lines connecting them to illustrate the trend. The y-axis represents the total ionization cross section in Å², while the x-axis represents the relative initial velocity in m/sec. The graph includes data points at different velocities, indicating a decreasing trend in cross section as velocity increases.
Table 20

Effect of the Potential Parameters on the Ionization Cross Section for the Ne* - Ar System

<table>
<thead>
<tr>
<th>Variation of Parameter</th>
<th>Total Ionization Cross Section at 500m/sec, $\sigma_t$, Å²</th>
<th>Per Cent Abundance at 500m/sec $\sigma_{PL}$</th>
<th>$\sigma_{AI}$</th>
<th>$s^{a}$ ($\sigma_t - v^{-s}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard $^b$</td>
<td>5.1972</td>
<td>72.68</td>
<td>27.32</td>
<td>0.625</td>
</tr>
<tr>
<td>Double potential well depth for (Ne* - Ar) $^c$</td>
<td>4.2735</td>
<td>73.39</td>
<td>26.61</td>
<td>0.471</td>
</tr>
<tr>
<td>1/2 potential well depth for (Ne - Ar$^+$) $^d$</td>
<td>6.8626</td>
<td>80.31</td>
<td>19.69</td>
<td>0.644</td>
</tr>
<tr>
<td>3/2 potential well depth for (Ne - Ar$^+$) $^e$</td>
<td>4.3383</td>
<td>67.26</td>
<td>32.75</td>
<td>0.623</td>
</tr>
</tbody>
</table>

Note:
- $^a$ Between $v=320$ and $v=600$m/sec
- $^b$ Results shown in Table 11
- $^c$ Results shown in Table 17
- $^d$ Results shown in Table 18
- $^e$ Results shown in Table 19
APPENDICES
APPENDIX I

PARTIAL BACK ELASTIC SCATTERING CROSS SECTION

As shown in the above figure, positive ions in the reactive scattering of a Ne* beam (for example, Ne* + Ar → Ar⁺ + Ne + e) are collected on plate A. One expects that the Ne* atom from large angle elastic scattering can hit the collecting plate A and knock out electrons, and thus can contribute some error when positive ions are being measured. This partial back elastic scattering where the Ne* atom recoils and hits the collecting plate A can be estimated as follows.

At an arbitrary point x along the scattering path $\chi_a$ is the scattering angle for the beam particle in the laboratory coordinates.

If

$$\pi \leq \chi_a \leq \theta_m(x),$$

where

$$\theta_m(x) = \frac{\pi}{2} + \arctan\left(\frac{x}{r}\right),$$

then the beam particle will recoil back and hit plate A. The partial
back elastic scattering cross section, \( q(x) \), can be expressed as

\[
q(x) = 2\pi \int_{\theta_m(x)}^{\pi} \sigma_a(x_a) \sin x_a \, dx_a,
\]

where \( \sigma_a(x_a) \sin x_a \) is the differential cross section in the laboratory coordinates for the elastic scattering. \( \sigma_a(x_a) \sin x_a \) can be evaluated from the center of mass differential cross section, \( \sigma(x) \sin x \), which has been tabulated by Mason\(^{77}\) for systems with an exp-six potential,

\[
V(R) = \frac{\epsilon}{1-6\alpha} \left[ \frac{6}{\alpha} \exp\left[ \alpha (1- \frac{R}{R_m}) \right] - \left( \frac{R_m}{R} \right)^6 \right],
\]

where \( \epsilon \) and \( R_m \) are well depth and its location, respectively, and \( \alpha \) is a constant. The relations required for the transformation are

\[
tan x_a = \frac{m_2 \sin x_a}{m_1 + m_2 \cos x_a},
\]

and

\[
\sigma_a(x_a) \sin x_a = \left( 1 + \frac{m_1}{m_2} \left( \frac{m_1 + m_2 \cos x}{m_2 + m_1 \cos x} \right) \right) \sigma(x) \sin x,
\]

where \( m_1 \) is the mass of the beam particle and \( m_2 \) is the mass of the scattering particle. Therefore, \( q(x) \) can be evaluated by numerical integration provided that the exp-six potential for the system is known. However, as a first approximation, the well depth and its location for a Lennard-Jones (6-12) potential can be used for the exp-six potential, and some value between 12 and 15 can be chosen for \( \alpha \) since \( q(x) \) is relatively insensitive to a change in \( \alpha \) in the range \( 12 < \alpha < 15 \). The beam intensity at point \( x \) is

\[
I(x) = I_0 \exp(-Q \cdot x \cdot n),
\]
where $n$ is the density of the scattering particles, and $Q$ is the total scattering cross section which is taken as approximately equal to the total elastic scattering cross section. $q(x)$ is multiplied by a weighting factor $\exp(-Qx_n)$ to allow for the variation in beam intensity with $x$. The average value of $q(x)$ can be expressed as

$$q(x) = \lim_{N \to \infty} \frac{N \sum_{k=1}^{N} \exp(-Qx_k n) 2\pi \int_{\theta_k}^{\pi} \sigma_a(x_a) \sin x_a dx_a}{\sum_{k=1}^{N} \exp(-Qx_k n)},$$

where

$$\theta_k = \theta_m(x_k),$$

$$x_k = (k - 1) \ell / N,$$

and

$$\ell = \text{the scattering path length}.$$

The value of $Q$ can be expressed as

$$Q = 4.9926 \cdot 10^{11} \left( \frac{C^{(6)}}{v} \right)^{0.4},$$

(All in c.g.s. units),

where $C^{(6)}$ is the van der Waals attraction, and $v$ is the relative initial velocity. Using the values of the Lennard-Jones (6-12) potential listed in Table 8, and using $a = 12$, $q(x)$'s for 1 mtorr pressure inside the scattering chamber are calculated and listed Table 21 together with the experimental values of the total ionization cross section, $\sigma_t$, for the comparison.

As shown in Table 21, values of $\overline{q(x)}/\overline{\sigma_t}$ are very small, less than 1% in most cases with a maximum value of 1.4% in the Ne* - Xe case. Therefore, the error due to partial back elastic scattering can be neglected.
Table 21
Partial Back Elastic Scattering Cross Section

A. Ne - Ar System

<table>
<thead>
<tr>
<th>Reduced Relative Initial Kinetic Energy</th>
<th>Relative Initial Velocity, m/sec</th>
<th>$\overline{q}(x)/\sigma_t A^2$</th>
<th>$\sigma_t A^2$</th>
<th>$\overline{q}(x)/\sigma_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>332.4</td>
<td>0.0361</td>
<td>6.62</td>
<td>0.55</td>
</tr>
<tr>
<td>3.0</td>
<td>455.2</td>
<td>0.0299</td>
<td>5.44</td>
<td>0.55</td>
</tr>
<tr>
<td>5.0</td>
<td>587.6</td>
<td>0.0252</td>
<td>4.64</td>
<td>0.54</td>
</tr>
<tr>
<td>20.0</td>
<td>1,175.3</td>
<td>0.0166</td>
<td>4.32</td>
<td>0.38</td>
</tr>
</tbody>
</table>

B. Ne$^*$ - Kr System

<table>
<thead>
<tr>
<th>Reduced Relative Initial Kinetic Energy</th>
<th>Relative Initial Velocity, m/sec</th>
<th>$\overline{q}(x)/\sigma_t A^2$</th>
<th>$\sigma_t A^2$</th>
<th>$\overline{q}(x)/\sigma_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>334.9</td>
<td>0.0704</td>
<td>7.08</td>
<td>0.99</td>
</tr>
<tr>
<td>3.0</td>
<td>458.7</td>
<td>0.0589</td>
<td>5.63</td>
<td>1.05</td>
</tr>
<tr>
<td>5.0</td>
<td>592.1</td>
<td>0.0499</td>
<td>4.67</td>
<td>1.07</td>
</tr>
<tr>
<td>20.0</td>
<td>1,184.2</td>
<td>0.0333</td>
<td>4.24</td>
<td>0.79</td>
</tr>
</tbody>
</table>
Table 21. Continued

C. Ne* – Xe System

<table>
<thead>
<tr>
<th>Reduced Relative Initial Kinetic Energy</th>
<th>Relative Initial Velocity, m/sec</th>
<th>$\bar{q}(x)$</th>
<th>$\sigma_{t}$</th>
<th>$\bar{q}(x)/\sigma_{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>313.3</td>
<td>0.1390</td>
<td>9.92</td>
<td>1.40</td>
</tr>
<tr>
<td>1.6</td>
<td>361.8</td>
<td>0.0924</td>
<td>8.75</td>
<td>1.06</td>
</tr>
<tr>
<td>3.0</td>
<td>495.4</td>
<td>0.0774</td>
<td>6.65</td>
<td>1.16</td>
</tr>
<tr>
<td>5.0</td>
<td>639.5</td>
<td>0.0658</td>
<td>5.32</td>
<td>1.24</td>
</tr>
<tr>
<td>20.0</td>
<td>1,279.0</td>
<td>0.0442</td>
<td>4.40</td>
<td>1.00</td>
</tr>
</tbody>
</table>

D. Ne* – N₂ System

<table>
<thead>
<tr>
<th>Reduced Relative Initial Kinetic Energy</th>
<th>Relative Initial Velocity, m/sec</th>
<th>$\bar{q}(x)$</th>
<th>$\sigma_{t}$</th>
<th>$\bar{q}(x)/\sigma_{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>329.0</td>
<td>0.0188</td>
<td>5.78</td>
<td>0.33</td>
</tr>
<tr>
<td>3.0</td>
<td>450.5</td>
<td>0.0151</td>
<td>4.59</td>
<td>0.33</td>
</tr>
<tr>
<td>5.0</td>
<td>581.6</td>
<td>0.0127</td>
<td>3.80</td>
<td>0.33</td>
</tr>
<tr>
<td>20.0</td>
<td>1,163.2</td>
<td>0.0085</td>
<td>3.36</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*Note:  
1) $\ell = 2.15$cm and $r = 0.955$cm  
2) Assume pressure inside the scattering chamber is $1 \times 10^{-3}$mmHg  
3) Assume scattering particles are initially at rest  
4) No back elastic scattering for Ne* – CH₄ system
APPENDIX II

EVALUATION OF THE CRITICAL VALUE FOR THE EXISTENCE OF A RELATIVE MINIMUM IN THE EFFECTIVE POTENTIAL

In general, the effective potentials may be expressed as

\[ V_\delta(r) = \frac{C^{(12)}}{r^2} - \frac{C^{(6)}}{r^6} - \frac{C^{(4)}}{r^4} - \frac{C^{(2)}}{r^2}, \]

(1)

where \( C^{(12)} = L^2/(2m) = E_b^2 \) (\( L \) is the orbital angular momentum, \( E \) the collision energy, and \( b \) the impact parameter), and \( C^{(2)}/r^2 \) is the rotational barrier. If there is no relative minimum in the effective potential, the effective potential is monotonically decreasing, and the slope of the curve must be always negative for all values of \( r \), i.e.,

\[ \frac{dV_\delta}{dr} < 0, \]

(2)

or

\[ C^2 > \frac{2C^{(4)}}{r^2} + \frac{3C^{(6)}}{r^4} - \frac{6C^{(12)}}{r^6} = \delta(r), \text{ for all } r. \]

(3)

Thus, \( C^{(2)} > \max. \delta(r) \), for condition (2) to hold for all \( r \). The maximum value of \( \delta(r) \) can be easily calculated. Letting \( r_m \) be the location of the maximum value of \( \delta(r) \),

\[ \delta'(r) = -\frac{4C^{(4)}}{r^3} - \frac{12C^{(6)}}{r^5} + \frac{60C^{(12)}}{r^7} = 0 \quad |r = r_m, \]

or

\[ C^{(4)} + \frac{3C^{(6)}}{r^2} - \frac{15C^{(12)}}{r^8} = 0 \quad |r = r_m. \]

(4)
Solving Eq. (4) for $r_m$, one can calculate the maximum value of $g(r)$. Let $C^*$ be this maximum value,

$$C^* = \max g(r) = \frac{2C^{10}}{r_m^2} + \frac{3C^{6}}{r_m^4} - \frac{6C^{12}}{r_m^6}.$$ 

If $C^2 > C^*$ for any system, there is no relative minimum or maximum existing in the effective potential. For example, the Lennard-Jones (6-12) potential,

$$V(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right),$$

has

$$C^* = \frac{36}{25} \left( \frac{1}{5^3} \right) \varepsilon \sigma^2 = 2.4624 \varepsilon \sigma^2.$$ 

For values above this critical value the effective potential curves are monotonically decreasing. The $C^*$ values using a 12-6-4 potential for the final states as listed in Table 9 are: 168.58 for Ne-Ar$^+$, 132.02 for Ne-Kr$^+$, and 100.56 for Ne-Xe$^+$, all in units of $\varepsilon \sigma^2$ of their corresponding initial states.
APPENDIX III

APPROXIMATION OF $\text{Ai}^2(-x)$ FOR LARGE $x$

Consider the following table of values\(^a\) where $\zeta = \frac{2}{3} x^{3/2}$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\zeta$</th>
<th>$f_1(\zeta)$</th>
<th>$f_2(\zeta)$</th>
<th>$f_1^2$</th>
<th>$f_1 f_2$</th>
<th>$(f_2^2 - f_1^2)\zeta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.654894</td>
<td>20</td>
<td>0.3975221</td>
<td>0.4002887</td>
<td>0.1580238</td>
<td>0.1591236</td>
<td>0.0441445</td>
</tr>
<tr>
<td>11.203512</td>
<td>25</td>
<td>0.3978114</td>
<td>0.4000258</td>
<td>0.1582539</td>
<td>0.1591348</td>
<td>0.0441683</td>
</tr>
<tr>
<td>13.572088</td>
<td>$\frac{100}{3}$</td>
<td>0.3980983</td>
<td>0.3997597</td>
<td>0.1584823</td>
<td>0.1591437</td>
<td>0.0441854</td>
</tr>
<tr>
<td>17.784467</td>
<td>50</td>
<td>0.3983824</td>
<td>0.3994903</td>
<td>0.1587085</td>
<td>0.1591499</td>
<td>0.0441982</td>
</tr>
<tr>
<td>28.231081</td>
<td>100</td>
<td>0.3986638</td>
<td>0.3992179</td>
<td>0.1589328</td>
<td>0.1591537</td>
<td>0.0442106</td>
</tr>
<tr>
<td>$\infty$</td>
<td>$\infty$</td>
<td>0.3989423</td>
<td>0.3989423</td>
<td>0.1591550</td>
<td>0.1591550</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Note: from p. 477, Ref. 76.

\[ \text{Ai}(-x) = x^{-\frac{1}{3}}[f_1(\zeta) \cos \zeta + f_2(\zeta) \sin \zeta] \]

\[ \text{Ai}^2(-x) = x^{-\frac{1}{3}}[f_1^2(\zeta) + f_1 f_2 \sin 2\zeta + (f_2^2 - f_1^2) \sin^2 \zeta] \]

We can see from this table that $f_1 f_2$ and $(f_2^2 - f_1^2)\zeta$ are quite constant over the large range of arguments. They are approximately expressed as $f_1 f_2 = 0.159155$, and $f_2^2 - f_1^2 = 0.04420/\zeta$.

$f_1^2$, however, is not so stable, but it can be expressed as

\[ f_1^2 = 0.159155[1 - \exp(-2.717 \times 0.26625)]. \]

Therefore, for a large argument, $x \geq 10$, $\text{Ai}^2(-x)$ may be expressed as

\[ \text{Ai}^2(-x) = x^{-\frac{1}{3}}[0.159155[1 - \exp(-2.717 \times 0.26625) + \sin(2\zeta)] + \frac{0.0442}{\zeta} \sin^2 \zeta} \]

(1)
The following table is a comparison of actual values of $A_i^2(-x)$ and its approximated values for a number of arguments.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Approximated Value from Eq. (1)</th>
<th>Actual Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0016176</td>
<td>0.0016209</td>
</tr>
<tr>
<td>15</td>
<td>0.0774036</td>
<td>0.0774068</td>
</tr>
<tr>
<td>30</td>
<td>0.0077311</td>
<td>0.0077288</td>
</tr>
<tr>
<td>35</td>
<td>0.016978</td>
<td>0.016979</td>
</tr>
<tr>
<td>115</td>
<td>0.0007131</td>
<td>0.0007139</td>
</tr>
<tr>
<td>120</td>
<td>0.0102384</td>
<td>0.0102303</td>
</tr>
<tr>
<td>275</td>
<td>0.00003734</td>
<td>0.00003493</td>
</tr>
<tr>
<td>280</td>
<td>0.0190228</td>
<td>0.0190225</td>
</tr>
</tbody>
</table>

The maximum absolute error found is $8.0 \times 10^{-6}$. The relative error should be very small unless it happens that $A_i(-x) = 0$. 
APPENDIX IV

ESTIMATE OF POTENTIAL PARAMETERS FOR SOME SYSTEMS

A. The Initial States

The Lennard-Jones (6-12) potentials,

\[ V(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \]

are used for the initial states of the colliding pairs which are non-polar atoms or molecules. \( V(r) \) has a minimum at \( r = r_m (r_m = 2^{1/6}\sigma) \) with well depth \( \varepsilon \). \( \varepsilon \) and \( \sigma \) are related to the Van der Waals attraction potential by

\[ V_{\text{attraction}} = -\frac{C^{(6)}}{r^6} = -\frac{4\varepsilon \sigma^6}{r^6}, \]

where \( C^{(6)} \) is a constant. \( C^{(6)} \) may be estimated by the Slater-Kirkwood method\(^{79,80} \) which gives

\[ C^{(6)} = \frac{3\alpha \pi \hbar^2}{2(m_e)^{3/2}} \frac{\alpha_{\text{p}}^2}{\left[ \left( \alpha_{1}/N_{1} \right)^{1/2} + \left( \alpha_{2}/N_{2} \right)^{1/2} \right]} \]

where \( \alpha \) and \( N \) refer, respectively, to the polarizability and the number of outer shell electrons of each molecule, \( m_e \) and \( e \) represent the electronic mass and charge, and \( \hbar \) has its usual meaning. \( N \) may be obtained by summing the periodic table group numbers for each constituent atom in the molecule and \( r_m \) may be estimated by using the Rule-of-Thumb of Bernstein and Muckerman,\(^{81} \)

\[ r_m = r_i + r_j + 2.0 \left( \hbar \right), \]

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where \( r_i \) and \( r_j \) are the orbital radii of the atoms \((i,j)\). These have been evaluated for several atoms including Ar, Kr, and Xe. \(^{82}\)

The orbital radius of Ne\(^*\) has been estimated as follows. Rothe et al., \(^{66}\) have measured the elastic scattering of He\(^*\) by Ar and Kr. They have been able to derive the parameters for the Lennard-Jones (6-12) potential for the He\(^*\)-Ar and He\(^*\)-Kr systems. Thus, knowing the orbital radii of Ar and Kr, the orbital of He\(^*\) is estimated to be
\[
r_{\text{He}^*} = 2.32 \text{ Å}.
\]

Compare the orbital radii of He and He\(^*\) with their isoelectronic atoms Li\(^+\) and Li, respectively,
\[
\frac{r_{\text{He}}}{r_{\text{Li}^+}} = 1.54,
\]
and
\[
\frac{r_{\text{He}^*}}{r_{\text{Li}}} = 1.46.
\]

These two ratios should become more nearly equal as the atomic number increases, and it is assumed that two ratios are equal for the Ne case, i.e.,
\[
\frac{r_{\text{Ne}}}{r_{\text{Na}^+}} = \frac{r_{\text{Ne}^*}}{r_{\text{Na}}} = \frac{r_{\text{Ne}}}{r_{\text{Na}^+}} \times \frac{r_{\text{Ne}^*}}{r_{\text{Na}}} = 2.20\text{ Å}.
\]

Finally, \( \sigma \) and \( \epsilon \) may be calculated from \( C(6) \) and the estimated \( \kappa_m \). Values obtained for \( \sigma \) and \( \epsilon \) are listed in Table 8. The polarizability and the orbital radii used are listed in Table 22.

**B. The Final States**

Since the final states (Ne – Ar\(^+\), Ne – Kr\(^+\), Ne – Xe\(^+\), etc.) correspond to an ion and a neutral Ne atom, the potentials are conveniently expressed as
Table 22

The Polarizability and the Orbital Radii of Some Atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\alpha$ (10⁻²⁴ cm³)</th>
<th>Orbital Radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.642⁸³</td>
<td>0.65⁸²</td>
</tr>
<tr>
<td>Kr</td>
<td>2.480⁸³</td>
<td>0.80⁸²</td>
</tr>
<tr>
<td>Xe</td>
<td>4.045⁸³</td>
<td>1.00⁸²</td>
</tr>
<tr>
<td>Ne*</td>
<td>27.6⁸⁴</td>
<td>2.20</td>
</tr>
</tbody>
</table>
\[ V(r) = \frac{C_1}{r^{12}} - \frac{C_2}{r^6} - \frac{C_4}{r^4} \]  

(5)

where

\[ C_4 = \frac{1}{2} \alpha_{\text{Ne}} e^2 = 4.553 \times 10^{-12} \text{erg} \cdot \text{A}^4. \]

Dissociation energies \( D_e \) for \( \text{Ne}_2^+ \), \( \text{Ar}_2^+ \), \( \text{Kr}_2^+ \), and \( \text{Xe}_2^+ \) have been reported by Munson et al.,\(^7\) bond lengths \( r_e = r_m \) for \( \text{Ne}_2^+ \) and \( \text{Ar}_2^+ \) have been reported by Mason and Vanderslice,\(^8\) and Cloney et al.,\(^9\) respectively. For a rough estimation of the dissociation energy and bond length of the heteronuclear diatomic ions, the following averages are used:

\[ D_{eAB} = \sqrt{D_{eA}D_{eB}} \]

and

\[ \sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B). \]

The reported values are:

<table>
<thead>
<tr>
<th>System</th>
<th>( \text{Ne}_2^+ )</th>
<th>( \text{Ar}_2^+ )</th>
<th>( \text{Kr}_2^+ )</th>
<th>( \text{Xe}_2^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation energy (eV)(^7)</td>
<td>0.69</td>
<td>1.08</td>
<td>1.00</td>
<td>0.91</td>
</tr>
<tr>
<td>Bond length</td>
<td>2.1(^8)</td>
<td>3.9(^8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to evaluate the bond length for \((\text{NeKr})^+\) and \((\text{NeXe})^+\), it is assumed that the relative size for \( \text{Ne} - \text{Ar}^+ \), \( \text{Ne} - \text{Kr}^+ \), and \( \text{Ne} - \text{Xe}^+ \) is the same as the relative size for \( \text{Ne}^* - \text{Ar} \), \( \text{Ne}^* - \text{Kr} \), and \( \text{Ne}^* - \text{Xe} \).

The estimated values for dissociation energy and bond length are:

<table>
<thead>
<tr>
<th>System</th>
<th>( \text{Ne} - \text{Ar}^+ )</th>
<th>( \text{Ne} - \text{Kr}^+ )</th>
<th>( \text{Ne} - \text{Xe}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation energy (eV)</td>
<td>0.863</td>
<td>0.830</td>
<td>0.792</td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>3.0</td>
<td>3.10</td>
<td>3.22</td>
</tr>
</tbody>
</table>
Then, finally, Eq. (5) is used to evaluate $C^{(12)}$ and $C^{(6)}$ for each system using the following relations: $V(r)$ is dissociation energy at $r$ = bond length, and $V'(r) = 0$ at $r$ = bond length. Values obtained for $C^{(12)}$, $C^{(6)}$, and $C^{(4)}$ are listed in Table 9.
APPENDIX V
FLOW CHART AND COMPUTER PROGRAM FOR CROSS SECTION CALCULATION

A. Flow Chart

Input: Potential parameters, coupling potential parameters, mass, ΔE, etc., velocities (V_i, l = 1, M)

Evaluate the maximum impact parameter, b_m'
Divide b_m into N parts (b_j, j = 1, N)

Evaluate the turning point, R_t and the effective potential, V_b at R_t for the lower state for particular b_j.

Evaluate the relative maximum (M_2) and its location (R_m2) of the effective potential for the lower state

V_b > M_2
R_t < R_m2
Evaluate ω_PI
ω_AI

V_b = M_2
R_t, R_m2

V_b < M_2
R_t < R_m2
Evaluate σ_AI and σ_PI
(V_i, l = i + 1)

Evaluate w_PI
(0, j; j = j + 1)

Print out σ_AI and σ_PI

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B. Computer Program

C    MU = THE REDUCED MASS OF THE SYSTEM
C    KE = THE REDUCED RELATIVE INITIAL K.E.
C    EP AND SIG ARE PARAMETERS FOR THE LENNARD-JONES(6-12)
C    POTENTIAL FOR THE COLLIDING PAIR
C    C12, C6, AND C4 ARE PARAMETERS FOR THE POTENTIAL OF THE
C    FINAL STATE
C    DISTANCE UNIT IN C12, C6, AND C4 IS ANGSTROM
C    NPARTS = NO. OF PARTS OF IMPACT PARAMETERS TO BE DIVIDED
C    UC = A CONSTANT TERM IN THE COUPLING POTENTIAL ENERGY
C    RMAX = THE CUT-CFF POINT FOR THE COUPLING POTENTIAL ENERGY
C    DELTAE = THE ENERGY DIFFERENCE OF EXCITATION OF NEON AND
C    IGNITION OF ITS COLLIDING PARTNER

C REAL MU, KE, IMPACT(2C)
C COMMON KE, EN, EP, SIG, UC, C12, C6, C4, MU, ALPHA
C COMMON IMPACT, WATT(3C), WPI(30), NPARTS
C DIMENSION VEL(2C)
C REAC(5,1)
1 FORMAT('
WRITE(6,1)
REAC(5,2) EP, SIG, MU, DELTAE, UC, RMAX, RAI
2 FORMAT(7E1C.4)
REAC(5,3) C12, C6, C4
3 FORMAT(3E15.4)
REAC(5,5) EB2MAX, FACTOR, CEXPC
5 FORMAT(3F1C.4)
REAC(5,4) NPARTS, N
4 FORMAT(2I3)
WRITE(6,10) EP, SIG
10 FORMAT('C', T5, 'THE LENNARD-JONES(6-12) POTENTIAL FOR THE',
11X, 'COLLIDING PARTICLES ARE C'/T1G,'EPSILCN = ',1PE11.4,1X, 
2'ERGS'/ T10, 'SIGMA = ',1PE11.4,1X,'CM')
WRITE(6,12) C12, C6, C4
12 FORMAT(T5, 'THE POTENTIAL PARAMETERS FOR THE PRODUCTS 01/
11T10, 'C12 = ',1PE13.6,1X,'ERG-A**12'/T10, 'C6 = ',
21PE13.6,1X,'ERG-A**6'/T10, 'C4 = ',1PE13.6,1X,'ERG-A**4')
WRITE(6,13) EB2MAX, FACTOR, CEXPC
13 FORMAT(T5, 'EB2MAX = ',1PE13.6/T5, 'R2MAX = ', 0PF8.4, 1X,
1'**', 1X, 'EB2**(', CF117.7, ')')
WRITE(6,14) MU, UC, RMAX, DELTAE
14 FORMAT(T5, 'THE REDUCED MASS = ',1PE11.4,1X,'CM'/T5,
1'THE COUPLING = ',1PE11.4,1X,'ERGS'/T5,
2'THE CUT-CFF POINT FOR THE COUPLING POTENTIAL ENERGY = ',
30PF6.4/T5, 'DELTA E = ',1PE11.4'///)
C
C READ NUMBER OF VELOCITIES AT WHICH CROSS SECTION IS TO BE
C CALCULATED
REAC(5,2C) (VEL(I), I=1,N)
20 FORMAT(6E1C.4)
CC 2CCO II=1,N
EN = 0.5C * ML * VEL(II)**2
KE = EN/EP
WRITE(6,3) II, VEL(II), KE
30 FCRMAT('O',T5,'NO.',13/T5,'RELATIVE INITIAL VELOCITY =',
   IPE11.4,1X,'CM/SEC'/T5,'REDUCED RELATIVE INITIAL K.E. =',
   2IPE11.4)

C
C FIND THE LARGEST REDUCED IMPACT PARAMETER BELOW WHICH THE
C ATOMS COLLIDE REACT
C
R6 = (1.0/RMAX)**2
R12 = R6**2
BETMAX = RMAX * SQRT(1.0 - 4.0*(R12-R6)/KE)
WRITE(6,35) BETMAX
35 FCRMAT(T5,'THE LARGEST REDUCED IMPACT PARAMETER FOR',1X,
   1'REACTION = ',F7.4//)
   CE = BETMAX/FLCAT(NPAPRTS)
NP1 = NPAPRTS + 1
WRITE(6,4C)
40 FCRMAT(T5, 'REDUCED IMPACT', T26, 'WPI', T42, 'WAI', T58,
   1'ALPHA', T74, 'BETA', TSC, 'EPSTAR', T106, 'EPMAX'/T8,
   2'PARAMETER'//)
   DO 1CCC I = 1, NP1
   BET = CE * FLCAT(I-1)
   EB2 = KE * BET**2
   IMPACT(I) = BET
   C2 = EB2 * EP *(SIG*1.0E8)**2
   EVALUATE THE TURNING POINT AND MAXIMUM IN THE SECOND
   EFFECTIVE POTENTIAL
   CALL RCCTLJ(KE, BET,RECURT)
   RTMAX = RECURT/RMAX
   RT = RECURT * SIG * 1.0E8
   EVALUATE VEF2RT, F1EB,F2EB
   CALL FCRCE(BET,RECURT,VEF2RT,F1EB,F2EB)
   EPMAX = EN + CELTAE - VEF2RT
   ALPHA = EPMAX*F2EB
   IF (EB2.GE. EB2MAX) GC TC 1C0
   IF(EF2-C.10) 42, 42, 44
42 VEF2MX = C.0E0
   GC TC 46
44 R2MAX = FACTOR * EB2**2*CEXPO
   RP2 = (1.0/R2MAX)**2
   RP4 = RP2**2
   RP6 = RP2*RP4
   RP12 = RP6**2
   VEF2MX = C12*RP12 - C6*RP6 - C4*RP4 + C2*RP2
   IF(RT.GE.R2MAX) GC TC 1C0
   IF(VEF2RT.GE. VEF2MX) GC TO 1C0
46 EPSTAR = EN + CELTAE - VEF2MX
   BETA = ALPHA * (1.0 - EPSTAR/EPMAX)
C
C EVALUATE A.I. PROBABILITY
NAI = INT(BETA*1.5) + 2
CALL INTGRT(1, 0.C, BETA, NAI, C, WAI(I))
WAI(I) = F1EB* WAI(I)

C

EVALUATE P.I. PROBABILITY
IF(BETA-1C.0) 50,60,C
50 NPI = INT((10.C-BETA)*1.5) + 2
CALL INTGRT(1, BETA, 1C.C, NPI, C, XA)
CALL PIINT(10.C, XB)
WPI(I) = (XA+XB)*F1EB
GO TO 80
60 CALL PIINT(BETA, WPI(I))
WPI(I) = F1EB* WPI(I)
GO TO 80
100 WAI(I) = C.C
CALL INTGRT(1, 0.C, 1C.O, 15, 0, XA)
CALL PIINT(10.C, XB)
WPI(I) = F1EB*(XA+XB)
BETA = 0.C
EPSTAR = C.C
80 CONTINUE
WRITE(6,11C) BET, WPI(I), WAI(I), ALPHA, BETA, EPSTAR, EPMAX
110 FORMAT(T5, 7(1PE13.6, 3X))
1000 CONTINUE
KINT = NPARTS/2
CALL INTGRT(6, 0.C, BETMAX, KINT, 0, XPI)
CALL INTGRT(7, 0.C, BETMAX, KINT, 0, XAI)
CO = 6.283185 * SIG**2
XPI = CC * XPI
XAI = CC * XAI
XTOTAL = XPI + XAI
XAIP = XAI*1.0E2/XTOTAL
XPIP = 1CC.C - XAIP
WRITE(6,15C) XPI, XPIP, XAI, XAIP
150 FORMAT///T10, 'THE PENNING IONIZATION CROSS SECTION = ',
11PE13.6, 1X, 'SQUARE CM', 5X, 'OR', 1X, CPF6.3, 1X, 'PER CENT'/
2/T10, 'THE ASSOCIATIVE IONIZATION CROSS SECTION = ',
31PE13.6, 1X,'SQUARE CM',5X,'OR ',CPF6.3,1X,'PER CENT'/)
WRITE(6,25C) XTOTAL
250 FORMAT(T10, 'THE TOTAL IONIZATION CROSS SECTION = ',
11PE13.6, 1X, 'SQUARE CM')
WRITE(6,15CC)
1500 FORMAT('I')
2000 CONTINUE
STOP
END
SUBROUTINE INTEGRATE(NCFN, LIM1, LIM2, NPART, KPAI, VALUR)
C
C THIS IS A FIVE POINT GAUSS-LEGENDRE INTEGRATION SCHEME
C NCFN = THE STATEMENT NUMBER IN SUBROUTINE FN WHICH
C DEFINES FUNCTIONS FOR THE INTEGRATION
C LIM1 = LOW LIMIT FOR THE INTEGRATION
C LIM2 = HIGH LIMIT FOR THE INTEGRATION
C NPART = THE NUMBER OF PARTS OF ARGUMENTS TO BE DIVIDED
C VALUR = THE INTEGRATION VALUE
REAL INT, LIM1, LIM2
DIMENSION X(5), H(5)
CEL = (LIM2-LIM1)/FLCAT(NPART)
A = LIM1
B = LIM1 + CEL
C1 = C.538469
C2 = C.566180
INT = O.OEC
CC 2 I=1, NPART
C3 = (B-A)/2.0EC
X(3) = (B+A)/2.0EC
X(4) = C3*C1 + X(3)
X(2) = -C3*C1 + X(3)
X(1) = -C3*C2 + X(2)
X(5) = C3*C2 + X(3)
H(1) = C.236977
H(2) = C.473623
H(3) = C.566889
H(4) = H(2)
H(5) = H(1)
SUM = O.OEC
CC 3 J=1, 5
CALL FN(NCFN, X(J), KPAI, FF)
SUM = H(J)*FF + SUM
3 CC CONTINUE
SUM = C3*SUM
INT = SUM + INT
A = B
B = B + CEL
2 CC CONTINUE
VALUR = INT
VALUR = VALUR * (-1.0EC)** KPAI
RETURN
END
SUBROUTINE PI (A, VALUE)
C THIS IS TO EVALUATE THE INTEGRATION FOR PEANING
C IGNITIZATION FOR THE PORTION OF LARGE ARGUMENTS IN AIRY
C FUNCTION
REAL II, I2, I3, I4, MU, KE, IMPACT(30), I41, I42
COMMON KE, EN, EP, SIG, UC, C12, C6, C4, ML, ALPHA
COMMON IMPACT, WAI(30), WPI(30), NPARTS
DIMENSION XX(5), FHSIN(5), FHCSS(5), T(5), YY(5), FSIN(5),
1 SUMSIN(5), SUMCOS(5), X(2), Y(2), FCOS(5)
X(1) = SCRT(A)
X(2) = SCRT(ALPHA)
PAI = 3.141593
CC = ALPFA/A
CK = SCRT(CC-1.0)
I1 = 0.318310C*(1.570796-ARSin(X(1)/X(2)))
CALL INTGRT(2, A, ALPFA, 6, C, VALU2)
I2 = -VALU2*0.155155C
I3 = (3.31E-2)*(CK/X(1)+ALCG(X(2)/X(1)+CK)/X(2))/ALPHA
Y(1) = 1.333333*A**1.5C
ALPAA = ALPHA
IF(ALPAA .GT. 100.0) ALPAA=100.0
Y(2) = 1.333333*ALPAA**1.5C
C4A = Y(1)/PAI
C4ALP = Y(2)/PAI
M4 = INT(C4A)
N4 = INT(C4ALP)
RMP1 = PAI*FLCAT(M4+1)
RN4 = PAI*FLCAT(N4)
CALL INTGRT(3, Y(1), RMP1, 1, 0, I41)
CALL INTGRT(3, RN4, Y(2), 1, 0, I42)
XX(1) = 0.1473721
XX(2) = 0.7248710
XX(3) = 1.570796
XX(4) = 2.416621
XX(5) = 2.994220
FHSIN(1) = 5.464931E-2
FHSIN(2) = 4.585455E-1
FHSIN(3) = 8.936086E-1
FHSIN(4) = FHSIN(2)
FHSIN(5) = FHSIN(1)
FHCSS(1) = 2.681257E-1
FHCSS(2) = 2.627579E-1
FHCSS(3) = 0.030
FHCSS(4) = -FHCSS(2)
FHCSS(5) = -FHCSS(1)
M4P1 = M4 + 1
N4 = N4 - M4P1
TCTSIN = C.CEC
TCTCCS = C.CEC
CC 1CC 1 = 1.5
SUMSIN(I) = 0.CEC
SUBROUTINE INTPLT(A, F, U, V)
C THIS IS A PROGRAM FOR THE SIMPLE SIX-POINT LAGRANGIAN
C INTERPOLATION AT DIFFERENT INTERVALS
C F IS KNOWN FUNCTION VALUE FOR ARGUMENT A
C V IS THE INTERPOLATED VALUE FOR ARGUMENT U
C DOUBLE PRECISION A(6), F(6), H(6,6), C(6), U, V, S
S=1.0
DO 10 K = 1, 6
S=S*(U - A(K))
DO 11 J=2, 6
JM=J-1
H(K,J)=A(K)-A(J)
11 CONTINUE
C(1)=F(1)/(U - A(1))*H(1,2)*H(1,3)*H(1,4)*H(1,5)*H(1,6))
C(2)=F(2)/(A(2) - U )*H(1,2)*H(2,3)*H(2,4)*H(2,6)*H(2,5))
C(3)=F(3)/(U - A(3))*H(1,3)*H(2,3)*H(3,4)*H(3,5)*H(3,6))
C(4)=F(4)/(A(4) - U )*H(1,4)*H(2,4)*H(3,4)*H(4,5)*H(4,6))
C(5)=F(5)/(U - A(5))*H(1,5)*H(2,5)*H(3,5)*H(4,5)*H(5,6))
C(6)=F(6)/(A(6) - U )*H(1,6)*H(2,6)*H(3,6)*H(4,6)*H(5,6))
V =S*(C(1)+C(2)+C(3)+C(4)+C(5)+C(6))
RETURN
END

SUMCOS(I) = 0.0EO
T(I) = XX(I) + PAI*FLOAT(M4P1)
SIGNK = [-1.0]*M4P1
DO 80 K = 1, NMD
YY(I) = (0.75 * T(I))**0.6666666
FSIN(I) = SIGNK/(YY(I) * SQRT(ALPHA-YY(I)))
FCOS(I) = FSIN(I)/T(I)
SUMSIN(I) = SUMSIN(I) + FSIN(I)
SUMCOS(I) = SUMCOS(I) + FCOS(I)
T(I) = T(I) + PAI
SIGNK = -SIGNK
80 CONTINUE
TOTSIN = TOTSIN + SUMSIN(I)*FHSIN(I)
TOTCOS = TOTSIN + SUMCOS(I)*FHCOS(I)
100 CONTINUE
14 = (141+142+0.159155*TOTSIN-(4.42E-2)*TOTCOS)/2.0
VALUE = I1 + I2 + I3 + I4
RETURN
END
SUBROUTINE FN(NCFN, X, KPAI, A)
C THIS IS TO CALCULATE REQUIRED FUNCTION VALUE FOR THE
C NUMERICAL INTEGRATION, X IS ARGUMENT, AND A IS THE
C RETURN FUNCTION VALUE.
REAL MU, KE, IMPACT(3C)
COMMON KE, EN, EP, SIG, LC, C12, C6, C4, MU, ALPHA
COMMON IMPACT, WAI(3C), WPI(3C), NPARTS
PAI = 3.141593
T = X + PAI*FLOAT(KPAI)
GC TC (1,2,3,4,5,6,7), NCFN
1 Y = -X
CALL AIRY(Y,B)
C1 = ALPHA - X
IF(C1 .LE. C) GC TC 12
A = BE**2/SCRT(C1)
RETURN
2 C = 2.717 * X**0.26625
C2 = ALPHA - X
IF(C2 .LE. C) GC TC 12
A = EXP(-C)/SCRT(C2*X)
RETURN
3 Y = (C.75*X)**0.6666666
A = (C.1591590*SIN(X)-(4.42E-2)*CCS(X)/X)/(Y*SCRT(ALPHA-Y))
RETURN
4 C9 = ALPHA - X**2
IF(C9 .LE. C) GC TC 12
A = SCRT(C9)/X**3
RETURN
5 C5 = ALPHA-(C.75*T)**0.6666666
IF(C5 .LE. C) GC TC 12
FT = SCRT(C5)/T**1.666666
A = CCS(X) * FT
RETURN
6 CALL TRANSF(1, X, Y)
A = X * Y
RETURN
7 CALL TRANSF(2, X, Y)
A = X * Y
RETURN
12 A = 0.0EC
RETURN
END
SUBROUTINE TRANSF(NUMBER, X, Y)
CCUBLY PRECISION XE(6), YY(6), XX, YDUB
REAL MU, KE, IMPACT(3C)
COMMON KE, EN, EP, SIG, UC, C12, C6, C4, MU, ALPHA
COMMON IMPACT, WAI(3C), WPI(3C), NPARTS
XX = X
I = 0
2 I = I + 1
IF(IMPACT(I)-X) 2, 4, 16
4 GC TC (11,12), NUMBER
11 Y = WFI(I)
RETURN
12 Y = WAI(I)
RETURN
16 HH = IMPACT(I) - IMPACT(I-1)
SS = X - IMPACT(I-1)
R = SS/HH
IF(R.GT.1.0E-2) GC TC 2C
I = I-1
GC TC 4
20 IF(R.GE.1.0E-9) GO TO 50
GC TC (21,?2). NUMBER
21 CC 3C J =1,6
XB(J) = IMPACT(J)
YY(J) = WPI(J)
30 CONTINUE
GC TC 4CC
32 CC 4C J =1,6
XB(J)=IMPACT(J)
YY(J)=WAI(J)
40 CONTINUE
GC TC 4CC
50 NM1= NPARTS - 1
IF(I.LT.NM1) GC TC 3CC
NM5= NPARTS-5
GC TC (2C1,222), NUMBER
201 CC 220 J=1,6
XB(J)=IMPACT(J+NM5)
YY(J)=WPI(J+NM5)
220 CONTINUE
GC TC 4CC
222 CC 24C J =1,6
XB(J)=IMPACT(J+NM5)
YY(J)=WAI(J+NM5)
240 CONTINUE
GC TC 4CC
300 IMP3=I-3
GC TC (3C1,322), NUMBER
301 CC 32C J =1,6
SUBROUTINE ROOTLJ(KE, BET, RM)

C THIS IS TO CALCULATE THE TURNING POINT FOR THE INITIAL
C STATE WITH LENNARD-JONES (6-12) POTENTIAL
C KE = REDUCED INITIAL KINETIC ENERGY
C BET = REDUCED IMPACT PARAMETER
C RM = REDUCED TURNING POINT

REAL KE
R = 0.75E0
N = 0
5 R6 = (1.0/R)**6
R12 = R6*2
Y = KE*(1.0-(BET/R)**2) - 4.0*(R12-R6)
IF(ABS(Y) .LE. 1.0E-3) GO TO 100
IF(Y-0.0E0) 10, 100, 20
10 RMIN = R
IF(N-1) 11, 12, 12
11 R = R + 0.1
GO TO 5
12 R = (RMAX + RMIN)/2.0
GO TO 5
20 RMAX = R
R = (RMAX + RMIN)/2.0
N = N + 1
GO TO 5
100 RM = R
RETURN
END
SUBRCLTINE FORCE(BET,RM,VEF2RT,F1EB,F2EB)
REAL FL, KE, IMPACT(3C)
COMMON KE,EN,EP,SIG,LC,C12,C6,C4,MU,ALPHA
COMMON IMPACT, WAI(3C), WPI(3C), NPARTS
HBar=1.0545E-27
R=R*M*SIG
RR=R*1.0E0
R3=(1.0/RM)**3
R6=R3**2
R12=R6**2
RP2=RR**2
RP6=RF2*RP4
RP12=RP6**2
V2=EN* (BET/RM)**2
V4=-C4/RP4
V6=-C6/RP6
V12=C12/RP12
VEF2RT=V2+V4+V6+V12
F2=(12.*V12+6.*V6+4.*V4)/R
CC=(2.0*FL/HBAR**2)**(3.0/3.0)
CENFC= 2.0*V2/R
FJ1=24.0*EP*(2.0*R12-R6)/R + CENFC
FJ2=F2+CENFC
C1=ABS(FJ2-FJ1)
C2=ABS(FJ2-FJ1)
C3=1.0/FJ2 - 1.0/FJ1
F2EB=CC*(C2/C1)**(-C.3333333) * SIGN(1.0,C3)/FJ2
F1EB=12.5667*(UC*CC)**2/(C1**0.3333333 * C2**0.6666666)
F1EB = F1EB/F2EB**C.5C
RETURN
END
SUBRCLTNE AIRY(A,D)

THIS IS TO EVALUATE THE AIRY FUNCTION

A = ARGUMENT

B = VALUE OF AIRY FUNCTION

DOUBLE PRECISION CC1, CC2, SLMF, SLMG, RG, RF, FLCATK, BDUB

DOUBLE PRECISION CFLCAT, DBLE

IF (ABS(A) .GT. 5.5) GO TO 200

CC1 = 0.355280538875E2

CC2 = 0.258819403792E1

SLMF = C.CCC

RF = 1.0

K = C

10 K = K + 1

FLCATK = CFLCAT(K)

SUMF = SLMF + RF

RF = RF*A**3/(3.0*FLCATK*(3.0*FLCATK-1.0))

DEL1 = SNGL(RF/SUMF)

DEL1 = AES(DEL1)

IF(DEL1-1.0E-10) 30, 30, 10

30 SUMF = C.CCC

RG = DBLE(A)

K = C

40 K = K + 1

FLCATK = CFLCAT(K)

SUMG = SLMG + RG

RG = RG*A**3/(3.0*FLCATK*(3.0*FLCATK+1.0))

DEL2 = SNGL(RG/SUMG)

DEL2 = AES(DEL2)

IF(DEL2-1.0E-10) 50, 50, 40

50 BDUB = CC1*SUMF - CC2*SUMG

B = SNGL(BDUB)

GO TO 100

200 IF (A.LT.3.0) GO TO 500

C = C.66666666*A**1.5

CK = 1.0

SLM = 1.0E0

RK = C.CEC

K = C

250 K = K + 1

SUM = SUM + RK

FK = FLCAT(K)

CK = CK*(6.0*FK-5.0)*3.0*(6.0*FK-1.0)/(216.0*FK)

RK = CK*C**(-K)

IF(AES(RK/SUM) - 1.0E-5) 300, 300, 250

300 B = C.282548*A**(C-0.25)*EXP(-C)*SUM

GO TO 500

500 C = 0.6666666*ABS(A)**1.5

C2K = 1.0

SUMSIN = 1.0E0

RKSIN = C.CEC

K = C
550 \text{K} = \text{K} + 1 \\
\text{SUM} = \text{SUM} + \text{RKSIN} \\
\text{FK} = \text{FLCAT(K)} \\
F12K = 12.0 \times \text{FK} \\
C2K = -C2K \ast (F12K - 11.0) \ast (F12K - 7.0) \ast (F12K - 5.0) \ast (F12K - 1.0) \\
14.5 / (216.0 \ast (2.0 \times FK - 1.0) \ast FK) \\
RKSIN = C2K \ast C \ast (-2 \ast K) \\
\text{IF(AES(RKSIN/SUM) = 1.0E-5) 6CC, 600, 550} \\
600 \text{C2K1} = 6.944444E-2 \\
\text{SUMCCS} = \text{C2K1/C} \\
\text{RKCSCS} = C \times \text{CEO} \\
\text{K} = 0 \\
650 \text{K} = \text{K} + 1 \\
\text{SUMCCS} = \text{SUMCCS} + \text{RKCSCS} \\
\text{FK} = \text{FLCAT(K)} \\
F12K = 12.0 \times \text{FK} \\
C2K1 = -C2K1 \ast (F12K - 5.0) \ast (F12K - 1.0) \ast (F12K + 1.0) \ast (F12K + 5.0) \\
14.5 / (216.0 \ast (2.0 \times FK + 1.0)) \\
RKCSCS = C2K1 \ast C \ast (-2 \ast K - 1) \\
\text{IF(AES(RKCSCS/SUMCCS) = 1.0E-5) 7CC, 700, 650} \\
700 \text{THETA} = C + 0.7853982 \\
G = \text{ABS(A)} \\
B = 0.5641896 \ast C \ast (-0.25) \ast (\text{SUM} \ast \text{SIN(THETA)} - 1) \ast \text{SUMCCS} \ast \text{COS(THETA + FTA))} \\
1000 \text{RETURN} \\
\text{END}
APPENDIX VI

PER CENT ION ABUNDANCE FOR THE SYSTEMS Ne\(^*\) - Ar AND Ne\(^*\) - Kr\(^a\)

Metastable Neon in Argon

<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Ar(^+)</th>
<th>NeAr(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>80.1</td>
<td>19.9</td>
</tr>
<tr>
<td>40</td>
<td>81.6</td>
<td>18.4</td>
</tr>
<tr>
<td>50</td>
<td>81.3</td>
<td>18.7</td>
</tr>
<tr>
<td>60</td>
<td>82.5</td>
<td>17.5</td>
</tr>
<tr>
<td>80</td>
<td>82.6</td>
<td>17.4</td>
</tr>
</tbody>
</table>

Metastable Neon in Krypton

<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Kr(^+)</th>
<th>NeKr(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>77.4</td>
<td>22.6</td>
</tr>
<tr>
<td>40</td>
<td>77.9</td>
<td>22.1</td>
</tr>
<tr>
<td>50</td>
<td>78.3</td>
<td>21.7</td>
</tr>
<tr>
<td>60</td>
<td>78.9</td>
<td>21.1</td>
</tr>
<tr>
<td>80</td>
<td>79.7</td>
<td>20.3</td>
</tr>
</tbody>
</table>

\(^a\) Note: from Ref. 23

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LIST OF REFERENCES


2. For a general review on the molecular-beam techniques and their applications, see


20. Model 4336-P, W.M. Hicks, Inc., Roslyn, N.Y. This ionization gauge is an exact copy of Veeco ionization gauge, Model RG-75.
21. Edwards High Vacuum (Speedivac), LTD., Manor Royal, Crawley, Sussex.
29. The following materials have been tested for the filament:
   (a). Oxide-coated cathode: RCA 33-C-185A cathode-coating material
       (contains BaCO₃, SrCO₃, and CaCO₃ in ethyl acetate solution)
       coated on a nickel strip.
   (b). Tungsten ribbon (0.001 inch thickness, 0.075 inch width).
   (c). Thoriated tungsten ribbon.
   (d). Iridium ribbon cataphoretically coated with thoria.
   (e). Thoriated tungsten ribbon cataphoretically coated with thoria.


33. Model 6443B, Harrison Division of Hewlett-Packard Company, Berkeley
    Heights, New Jersey.

34. J.L. Kinsey, Drawing No. A-4935-0, Massachusetts Institute of


37. VKX-4-DP-XXG, Ball Brothers Research Corporation, Boulder, Colorado.


39. Type EF17H71, Syntorque Corporation (formerly McLean Syntorque
    Corporation), obtained from Electronic Specialties, Thomaston,
    Connecticut.

40. Model P350-7AM, Communication Measurements Laboratories, Inc.,
    Plainfield, New Jersey.

41. GE 253-X, obtained from Allied Electronics, Chicago, Illinois.

42. TI LS-400 supplied by Allied Electronics, Chicago, Illinois.


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45. R.R. Herm and D.R. Herschbach, UCRL Rept. 10526, University of

46. See, for example, pp. 89-100, 397-402 of Ref. 2a.

48. Armco Steel Corporation, Middletown, Ohio.

49. Size No. 5, Woven Glass Tubing, W.M. Hicks, Inc., West Palm Beach, Florida.

50. Model E-6-100A Nobatron, Sorensen Operation, Raytheon Company, Norwalk, Connecticut.


52. Helipot Division, Beckman Instruments, Inc., Fullerton, California.


54. Servo/riter II from Texas Instruments, Inc., Houston, Texas.

55. Q3-Alp Stabilizer Amplifier, Philbrick Researches, Inc., Dedham, Massachusetts.

56. Darcy Digital Multimeter 440, Darcy Industries, Santa Monica, California.

57. Digitec Printer, United Systems Corporation, Dayton, Ohio.


    (a). 7553-5 Type K-3.
    (b). 2430 Type C.

60. Obtained from The Eppley Laboratory, Inc., Newport, R.I.

61. Type DD-5-1, Electric Storage Battery Co., Racine, Wisconsin.


74. See, for example, E.W. McDaniel, Collisions Phenomena in Ionized Gases (John Wiley & Sons., New York, 1964), pp. 67-75, for related models. The hypothesis has also been made by Ref. 72.


BIографICAL SKETCH

Sheng-Yung Tang was born February 14, 1939, in Taiwan, Republic of China. He received his elementary school, high school and college education in his home country. In June, 1962, he received the degree of Bachelor of Science with a major in Chemistry from the National Taiwan Normal University (formerly the Provincial Taiwan Normal University). In September, 1962, he enrolled in the Institute of Nuclear Science of the National Tsing Hua University in Taiwan, where he received the degree of Master of Science with a major in Nuclear Chemistry in June, 1964. He was stationed in the same institute doing research from 1964 until 1965 while serving in the Army of Republic of China. In 1965 he enrolled in the Graduate School of Yale University, where he received another degree of Master of Science with a major in Chemistry in June, 1967. Since September, 1967, he has been enrolled in the Graduate School of the University of Florida pursuing work toward the degree of Doctor of Philosophy. During that time he held the positions of graduate assistant and Petroleum Research Fellow in the Department of Chemistry.

Sheng-Yung Tang is married to the former Ming-Ju Jan, and is the father of two sons.
This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1970

[Signatures]

Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

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