The velocity dependence
of the absolute total ionization cross section
for collisions of argon atoms with singlet and triplet
metastable helium atoms

By

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Abstract of Dissertation Presented to the
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THE VELOCITY DEPENDENCE
OF THE ABSOLUTE TOTAL IONIZATION CROSS SECTION
FOR COLLISIONS OF ARGON ATOMS WITH SINGLET AND TRIPLET
METASTABLE HELIUM ATOMS

By
Michael Read Woodard

June 1977

Chairman: E. E. Muschliitz, Jr.
Major Department: Chemistry

Measurements of the velocity dependence of the absolute
total ionization cross section of argon atoms upon impact
with selected metastable states of helium atoms are reported.
A low voltage D. C. discharge was used as the source of the
excited atoms, and a rotating slotted disk selector was used
for velocity selection of the excited atoms. Selection of the
electronic spin state of the excited atoms was accomplished
by irradiation of the excited atoms with radiation from a
helium discharge lamp.

Ionization of the argon target atoms by metastable helium
atoms was studied by the gas cell technique in which all ion-
ization products were collected. The ionization measurements
were of sufficient precision to allow simultaneous determina-
tion of the cross section and the secondary electron ejection
efficiency for each metastable state of helium. The secondary
electron ejection efficiency of triplet metastable helium atoms on an electroplated gold surface was determined to be 0.440 ± 0.018 in the presence of argon gas. The secondary electron ejection efficiency of singlet metastable atoms was determined to be 0.582 ± 0.024 under similar conditions.

The total ionization cross section for the He(2^3S)-Ar system was found to increase almost linearly from 8.8 Å^2 to 21.95 Å^2 with an increase of relative velocity from 1162 m/sec to 2787 m/sec. After an initial increase of the cross section from 9.8 Å^2 to 26.2 Å^2 with an increase in relative velocity from 989 m/sec to 2058 m/sec, the velocity dependence of the cross section of the He(2^1S)-Ar system entered a saturation region in which the cross section changed very little with relative velocity. The collision energy dependence of the He(2^3S)-Ar system was also used to determine the values of adjustable parameters present in a current theory based on the potential curve model for Penning and associative Penning ionization.
CHAPTER I
INTRODUCTION

A. Criteria for Chemiionization

Collisions between metastable atoms and target atoms can result in the deexcitation of the electronically excited metastable atom and the formation of an ionic species. These processes are generally referred to as chemiionization if collisions between these neutral reactants result in the formation of one or more charged products.¹

This ionization process is understood to be the collisional autoionization of a two-particle system A* + B, in which the energy of activation \( E(A^*) \) stored in the metastable atom A* exceeds the ionization potential \( IP(B) \) of the target atom B. The two exit channels open to the reaction, in the case where \( E(A^*) - IP(B) > 0 \) are as follows:

\[
A^* + B \rightarrow A + B^+ + e^- \quad (1)
\]

and

\[
A^* + B \rightarrow AB^+ + e^- \quad (2)
\]

where exit channel (1) is commonly called Penning ionization and exit channel (2) is called either associative Penning ionization or simply associative ionization. For collisions occurring at some thermal energy \( E_k(\infty) \), associative ionization will predominate if

\[
E_{el} > E(A^*) - IP(B) + E_k(\infty)
\]
where \( E_{el} \) is the kinetic energy of the electron released by the ionization process. In this case, the electron carries away excess energy since the bound state \( AB^+ \) has a negative energy. Penning ionization occurs in the alternate case where

\[
E_{el} < E(A^*) - IP(B) + E_k(\omega)
\]

and \( A \) and \( B^+ \) are also available to carry off reaction energy.

B. Ionization Models

Hotop and Niehaus have proposed two possible mechanisms which are as follows:2,3

\[
A^*(1) + B(2) \rightarrow A(1) + B^+ + e^-(2)
\]

(a)

and

\[
A^*(1) + B(2) \rightarrow A(2) + B^+ + e^-(1)
\]

(b)

The numbers in parenthesis signify electrons. The direct model (a) is considered to be unlikely since such a process is forbidden by spin selection rules.

The second model (b) shown pictorially in Figure 1, follows the Hagstrum model for Auger deexcitation of metastables at metal surfaces.4 In this model, an electron from target \( B \) tunnels through a barrier of effective width \( d \) into the vacant inner orbital of the metastable \( A^* \) with the subsequent ejection of the high energy metastable electron. The approximate thermal energy of the ejected electron is about \( E(A^*) - IP(B) \). As shown in the figure, \( IP(B) \) is the ionization potential of the tunneling electron, \( IP(A) \) is the ionization potential energy level of the vacant orbital, and \( R_0 \) is the internuclear separation.
Figure 1. Electron Exchange Model for Penning Ionization
The ionization cross section $\sigma$ is computed by the impact parameter method by
\[ \sigma = 2\pi \int_0^\infty P(b,v)b \text{d}b \] (3)
and the ionization probability is written as
\[ P(b,v) = 1 - \exp[-2\int_{R_{c1}}\left(W(R)/v(R)\right) \text{d}R] \] (4)
and $b$ is the impact parameter, $R_{c1}$ the classical turning point, $W(R)$ the transition frequency, and $v(R)$ the radial velocity.

The transition frequency is then calculated from the probability of tunneling through the potential barrier proposed by the model. This method of calculation is complicated by a steric factor introduced by the nonuniformity of the potential barrier surrounding the target and by difficulties in determining the effective width of the potential barrier.\(^5\)

A potential curve model for Penning and associative ionization has been proposed by Herman and Cermak, Niehaus, and quantitatively developed by Miller.\(^6-8\) The ionization process is thought to proceed through the autoionization of a reaction intermediate $[A^* + B]$ into the continuum of $A + B^+ + e^-$. The process is represented in Figure 2. The collision partners $A^*$ and $B$ approach each other along the potential curve $V^*(R)$ with relative kinetic energy $E_k(\omega)$. The curve $V^*(R)$ is embedded in a continuum of potential curves $V^+(R) + E_{e1}$ of the exit channels for the reaction. $V^+(R)$ is taken to represent the lowest available state of the continuum of states $V^+(R) + E_{e1}$.

Transition occurs at some internuclear distance $R_L$ by a
Figure 2. Two State Potential Curve Model for Penning and Associative Ionization
Franck-Condon transition. In the Born-Oppenheimer approximation, the vertical transition electronic energy and the kinetic energy of heavy particle motion are separately conserved. Thus, the initial transition kinetic energy $E_k(R_t)$ of the collision partners is equal to the kinetic energy $E'_k(R_t)$ following the transition and is written as

$$E_k(R_t) = E'_k(R_t)$$

and the total energy of the entrance channel related to the transition kinetic energy $E_k(R_t)$ by

$$E_k(R_t) = E_k^{\infty} + V^*(\infty) - V^*(R_t)$$

The energy of the exit channel is similarly related to the transition kinetic energy by

$$E'_k(R_t) = E_k^{\infty} + V^+(\infty) - V^+(R_t).$$

The conservation of total energy during the Franck-Condon transition is written as

$$E_k(R_t) + V^*(R_t) = E'_k(R_t) + V^+(R_t) + E_{el}(R_t)$$

where $E_{el}(R_t)$ is the energy of the ejected electron. At infinite separation, the kinetic energy of the ionization products, $E'_k(\infty, R_t)$ is given by

$$E'_k(\infty, R_t) = E_k^{\infty} + E_o - E_{el}(R_t)$$

where

$$E_o = V^*(\infty) - V^+(\infty)$$

and

$$E_{el}(R_t) = V^*(R_t) - V^+(R_t).$$

The vertical transition $V^*$ to $V^+$ is similar to the autoionization of a molecule except for the fact that the upper state is continuous with respect to nuclear motion.
Therefore, transitions can occur at all separations $R$. The transition frequency $W(R)$ is connected to the width $\Gamma(R)$ of the potential curve $V^*(R)$ by the expression

$$W(R) = \frac{\Gamma(R)}{\hbar}. \quad (12)$$

The width $\Gamma(R)$ is shown in Figure 2 as an envelope of values for the curve $V^*(R)$ at small nuclear separations. The transition frequency has a particular value for each separation value and does not depend upon the state of particle motion. Furthermore, if the electron exchange mechanism is correct, dipole selection rules are not valid for the population of the different ion electronic states and $\Gamma(R)$ should decrease exponentially with $R$ at large $R$. This conjecture has been well established by numerical calculations.

The importance of expression (9) may now be seen when aided by reference to Figure 2. The relative energy of the reaction products is shown by $E_k'(\infty, R_t)$ plotted as a function of $R$. The ejected electron energy distribution is shown as a projection on an energy scale at the left hand side of the figure. The length of the arrows drawn from energy level $E_k(\infty) + E_o$ to $E_k'(\infty, R_t)$ represent possible energies of the ejected electron. Associative ionization and therefore bound states are possible only when $E_k'(\infty, R_t) < 0$ and $R_t < R_o$. Penning ionization is the only result for transitions occurring at distances $R_t > R_o$ since $E_k'(\infty, R_t) > 0$. As the relative kinetic energy $E_k(\infty)$ increases, the range $R_t < R_o$ and $E_k'(\infty, R_t) < 0$ will decrease and associative ionization will diminish.
Such behavior has been observed for several systems. The fraction of associative ionization was found by Hotop to decrease as a function of relative collision energy (20meV to 300meV) in the systems He(2^1S,2^3S)-Ar and Ne(^3P_0,2)-Kr. This was determined by energy analysis of the Penning ionization electron (PIES) and mass spectrometer ion analysis. A similar trend has been reported for the systems Ne*-Ar, Kr, and Xe in which the ratio of associative to total ionization cross sections decreased from about 0.6 to 0.0 over the relative collision energy range 20 to 350meV.

Pesnelle, et al. have recently reported the velocity dependence of the branching ratio for He(2^1S,2^3S)-Ar using a crossed beam technique. Their determination of the velocity dependence of the ratio of associative to total ionization cross section of the He(2^1S)-Ar system is shown in Figure 3. The individual velocity dependences of the associative and Penning ionization of He(2^3S)-Ar are displayed separately on Figure 4. A fit to the data by the authors, using a theory developed by Nakamura, is also displayed.

C. Quantitative Theory Based on the Potential Curve Model

Miller has developed a classical theory based on the potential curve model discussed previously. The velocity dependence of the total ionization cross can be computed from this theory when information on the potential curve V*(R) and the transition frequency W(R) are available. The theory is classical in its development since the ionization
Figure 3. Dependence of Branching Ratio of Associative to Total Ionization on Relative Velocity for the System He(23S)-Ar (After Ref. 12)
Figure 4. Dependence of the Associative and Penning Ionization Cross Section on Relative Velocity for the System He(2S)-Ar (After Ref. 12)

- - - - - Calculated Values
- I- I- Experimental Values
process is described in probabilities rather than probability amplitudes.

The transition is again viewed as an autoionization process since, for each internuclear distance $R$, the discrete electronic state $V^*(R)$ has an associated width $\Gamma(R)$, in energy units, for decay into its degenerate continuum electronic state $V^+(R) + E_{\text{cl}}$. Thus, the ionization process is a leakage of the discrete state into the continuum state degenerate with it. Each value of angular momentum or partial wave $\ell$ may be treated separately since the potentials are spherically symmetric. The probability density $P_\ell^*(R)$ is defined such that $P_\ell^*(R)dR$ is the probability of leakage into the continuum for an internuclear distance between $R$ and $R + dR$.

The probability of leakage, while particles approach each other, is denoted as $P_\ell^{\text{in}}(R)$, and the probability of leakage occurring while the particles separate is denoted by $P_\ell^{\text{out}}(R)$. For the case of approaching particles, the probability for leakage at a distance between $R$ and $R + dR$ is written as

$$P_\ell^{\text{in}}(R)dR = [1 - \int_R^\infty P_\ell^{\text{in}}(R')dR']\left[\frac{\Gamma(R)}{\hbar v_\ell(R)}\right]dR.$$  \hspace{1cm} (13)

The first quantity in brackets, the survival factor, is the probability that leakage has not occurred in the interval $\omega \rightarrow R$. The survival probability is multiplied by the rate of leakage [$\Gamma(R)/\hbar$] and by the time [$dR/v_\ell(R)$] spent in the interval [$R, R + dR$]. The term $v_\ell(R)$ is the radial velocity at $R$. 

The author solves Equation (13) by converting it into a differential equation to obtain

\[ P_{\text{in}}^\infty (R) = \frac{\Gamma (R)}{\hbar \nu_\alpha (R)} \exp \left[ - \int \frac{\Gamma (R')}{R \hbar \nu_\alpha (R')} \, dR' \right] \]  

(14)

where the exponential expresses the survival factor. The probability of leakage into a continuum state at any point on the inward trajectory \( R_{\text{cl}} < R \leq \infty \) is written as

\[ \int_{R_{\text{cl}}}^\infty P_{\text{in}}^\infty (R) \, dR = 1 - \exp \left[ - \frac{\int R_{\text{cl}} \Gamma (R) \, dR}{\hbar \nu_\alpha (R)} \right] \]  

(15)

where \( R_{\text{cl}} \) is the classical turning point or the largest value of \( R \) for which the radial velocity is zero.

The outward trajectory is treated similarly where the probability of leakage occurring over \( [R, R + dR] \) is written as

\[ P_{\text{out}}^\infty (R) \, dR = \left[ 1 - \int_{R_{\text{cl}}}^R P_{\text{in}}^\infty (R') \, dR' \right] \int_{R_{\text{cl}}}^R P_{\text{out}}^\infty (R') \, dR' \]

\[ \times \left( \frac{\Gamma (R) \, dR}{\hbar \nu_\alpha (R)} \right) \]  

(16)

The quantity enclosed in brackets is the probability of survival over the entire approach trajectory and the part of the separation trajectory \( R_{\text{cl}} \) to \( R \). Solution of this equation gives

\[ P_{\text{out}}^\infty (R) = \frac{\Gamma (R)}{\hbar \nu_\alpha (R)} \exp \left[ - \int_{R_{\text{cl}}}^{R_{\text{cl}}} \frac{\Gamma (R')}{\hbar \nu_\alpha (R')} \, dR' - \int_{R_{\text{cl}}}^R \frac{\Gamma (R') \, dR'}{\hbar \nu_\alpha (R')} \right] \]  

(17)
and the probability of leakage at any point on the outward part of the trajectory is written as

\[ P^\text{out}_l(R) = \exp \left[ - \int_{R_{cl}}^{\infty} \frac{\Gamma(R)}{\nu_\lambda(R)} dR \right] \times \left[ 1 - \exp \left[ - \int_{R_{cl}}^{\infty} \frac{\Gamma(R)}{h\nu_\lambda(R)} dR \right] \right]. \]  

The probability density that a transition occurs at a particular \( R \) is given by

\[ P^\text{in}_l(R) = P^\text{out}_l(R). \]  

The probability of a transition during the entire collision is given by

\[ P^\text{in}_l = \int_{R_{cl}}^{\infty} P^\text{in}_l(R) dR \]

or

\[ P^\text{in}_l = \int_{R_{cl}}^{\infty} P^\text{in}_l(R) dR + \int_{R_{cl}}^{\infty} P^\text{out}_l(R) dR. \]  

Upon substitution of Equation (15) and Equation (18), the probability of ionization for partial wave \( l \) is written as

\[ P^\text{in}_l = 1 - \exp \left[ -2 \int_{R_{cl}}^{\infty} \frac{\Gamma(R)}{h\nu_\lambda(R)} dR \right] \]

where the radial velocity is given by

\[ \nu_\lambda(R) = \nu_0 \left[ 1 - \frac{\nu^*(R)}{E_k(\infty)} - \frac{\lambda(\lambda+1)/2}{2\mu R^2 E_k(\infty)} \right]^{1/2} \]  

and \( \mu \) is the reduced mass for the \( \Lambda^* \)-B system.

The total cross section for these inelastic transitions is written by the partial wave method by
\[ \sigma(v_o) = \frac{\pi}{k_o^2} \sum (2l + 1) P_l(v_o) \]  

(23)

where

\[ k_o = \left[ \frac{2\mu}{\hbar^2} \left[ E_k(\infty) - V^*(\infty) \right]/\hbar^2 \right]^{1/2}. \]  

(24)

The full quantum mechanism development gives the expected result of eliminating the singularity in the argument \( \Gamma(R) \) at the classical turning point. The quantity is still peaked near the classical turning point but is not infinite. The most probable internuclear distance for ionization transitions is still near the classical turning point.

D. Verification of the Classical Theory

Olson used the classical formulas developed by Miller to fit the velocity dependence of the total ionization cross sections for the system \( \text{Ne}^*(3P_{0,2})-\text{Ar} \) measured by Tang, Marcus, and Muschlitz.\(^8,15,16\) The author used a potential curve of the Lennard-Jones form and an exponential form of the coupling width given by

\[ \Gamma(R) = \exp \left[ -1.53 R \right]. \]  

\(^6,12\)

A very good fit to the experimental data was obtained. The theory successfully predicted the unexpected minimum found in the velocity dependence of the cross section; whereas, the theoretical development advanced by Micha, Tang, and Muschlitz predicted a monotonic decrease of the cross section with increasing relative velocity.\(^17\) This increase in the ionization cross section for thermal energies above
50 meV was attributed to the exponentially increasing nature of the coupling width as the distance of closest approach decreased with increasing energy. The calculations predicted that the cross section would rise to a maximum around 10 eV and then decrease slowly with energy. Figure 5 shows the fit obtained by Olson to the low thermal data of Tang et al. and the high collision energy of Moseley et al.\textsuperscript{16,18}

Olson also used the potential curve classical theory as a basis for calculation of the velocity dependence of the total ionization cross section for the system He(2\textsuperscript{1}S,2\textsuperscript{3}S)-Ar.\textsuperscript{19} The long range van der Waal interaction potentials were obtained from the work of Bell, Dalgarno, and Kingston.\textsuperscript{20} The repulsive interaction potentials were drawn from the results of differential scattering work done by Smith et al. in which screening constants were incorporated to account for pronounced shell structure effects.\textsuperscript{21} The potential was written in the form

\[
V(R) = \frac{2}{R} \left[ C_T \exp \left(-\frac{R}{C_T}\right) + \frac{2}{R} C_L \exp \left(-\frac{R}{C_L}\right) + 2 \exp \left(-\frac{R}{C_K}\right) \right] - \left( \frac{C_{ab}}{R^6} \right) \left[ 1 - \exp \left(-x\right) \right] \\
\left( 1 + x + 1/2x^2 + 1/6x^3 + 1/24x^4 + 1/120x^5 \right) \] (25)
\]

where \( C_K, C_L, \) and \( C_M \) are the screening lengths of the K, L, M shells respectively, \( C_{ab} \) is the long-range coefficient, and \( x = R/C_M. \) The coupling frequency was written as

\[
W(R) = \exp \left[ -\frac{R}{B} \right]
\]

where the adjustable parameter for He(2\textsuperscript{3}S)-Ar was \( B = 0.667 \ a_o \) and for He(2\textsuperscript{1}S)-Ar was \( B = 0.629 a_o. \)

The potential submitted by Olson has been used successfully
Figure 5. Dependence of Total Ionization Cross Section on Relative Velocity for the System Ne$^{2P_0,2}$-Ar (After Ref. 15)

- - - Calculated Values of Ref. 15

o o o Experimental Results of Ref. 16

Δ Δ Δ Experimental Results of Ref. 18
by several groups attempting to obtain theoretical fits to their experimental results on the He(2\(^3\)S)-Ar system.\(^{19}\) Niehaus and Illenberger have recently measured the velocity dependence of the total ionization cross section for the systems He(2\(^1\)S,2\(^3\)S)-Ar, Kr, Xe, N\(_2\), and Hg.\(^{22}\) Using the same \(V^*(R)\) and the values \(B = 0.357a_0\) and \(A = 7400\text{au}\) for the adjustable parameters in the transition frequency for the He(2\(^3\)S)-Ar system, Illenberger and Niehaus obtained good agreement between their experimental results and theory. The experimental results cannot be regarded as absolute cross sections. The absolute values were determined by normalization of their relative cross sections values to absolute destruction rate constants obtained from the flowing after-glow results of Schmeltekopf and Fehsenfeld.\(^{23}\)

Pesnelle, Watel, and Manus have also obtained data on the relative velocity dependences of the total ionization cross section of the systems He(2\(^1\)S,2\(^3\)S)-Ar using a crossed-beam apparatus.\(^{12}\) The results were reported as absolute cross sections obtained by normalizing the relative cross sections to the results of calculations again based on Olson's potential curve and Miller's classical theory. The values \(A = 4000\text{au}\) and \(B = 0.360a_0\) were used for the adjustable parameters in the transition frequency for the He(2\(^3\)S)-Ar system with good results. Pesnelle, et al. also found good relative agreement between their measurements and the absolute destruction rate constants of Lindinger, Schmeltekopf and Fehsenfeld using the approximate expression
2.2 \frac{SKT}{T}^{1/2}

where the value 2.2 is an arbitrary normalization factor.\textsuperscript{12,24}

Velocity-averaged absolute total ionization cross sections of the systems He*\((2^1S, 2^3S)\)-Ar have been obtained by Riola et al. and Rundel et al.; however, comparison with their results is difficult since the velocity distribution of their metastable beam is not known precisely.\textsuperscript{25,26} Assuming a distribution of the type \(v^4 \exp(-v^2/a^2)\) and a beam temperature \(T = 300^\circ\text{K}\) for the velocity averaged absolute cross sections, Illenberger and Niehaus normalized their data to the velocity-averaged absolute cross sections.\textsuperscript{22} If the measured cross sections were so normalized, they estimate that their reported cross sections would be increased by a factor of 2 for the He\((2^3S)\)-Ar case and would be increased by a factor of 1.5 for the He\((2^1S)\)-Ar case.

The strong increase of the total ionization cross section with relative energy predicted by Miller's theory and Olson's potential for the systems He\((2^1S, 2^3S)\)-Ar has been demonstrated very well for He\((2^3S)\)-Ar, but the He\((2^1S)\)-Ar results are conflicting. The Niehaus and Illenberger results for He\((2^1S)\)-Ar show very little relative velocity dependence; whereas, the results of Pesnelle et al. have a much stronger energy dependence.

The strong energy dependence of the total ionization cross section is also demonstrated by results obtained from flowing-afterglow measurements of Lindinger, Schmeltekopf, and Fehsenfeld.\textsuperscript{24} The temperature dependence of the total
destruction rate constants of He($^2S$) by Ar and other gases increased strongly over the thermal energy range 300°K to 800°K.

The approach of the flowing afterglow technique differs from the molecular beam method in that the rate of metastable destruction is measured rather than the appearance of reaction products. The afterglow from a discharge source is allowed to flow down a tube at a velocity of about $10^4$ cm/sec at a pressure of about 1 torr. The afterglow, which persists for about $1 \times 10^{-2}$ sec, will extend down the tube for about 1 meter. The reactant is added downstream from the discharge source, and the destruction of metastable atoms by the reactant gas is determined at various distances along the flow path by selective absorption of radiation at 3889 Å ($^2S$ to $^3P$ optical transition in helium) and 5016 Å ($^1S$ to $^1P$ optical transition in helium) by the helium metastable triplet and singlet states respectively. Flowing afterglow results for He($^1S$) are generally not as reliable as He($^3S$) results since collisions of the type

$$\text{He}(^1S) + e^- \rightarrow \text{He}(^3S) + e^- + 0.79 \text{ eV}$$

provide an additional channel for He($^1S$) metastable destruction.$^{27}$

The relative total ionization cross sections obtained by beam experiments can be related to the destruction rate constants to obtain absolute cross sections. Illenberger and Niehaus normalized their relative cross sections to the destruction rate constant at the known temperature of 300°K.$^{22}$
The proportionality factor $K$ correcting $\sigma_{\text{Rel}}(v)$ to absolute cross sections $\sigma_{\text{Abs}}(v)$ was determined from the expression

$$\int K \cdot \sigma_{\text{Rel}}(v) \cdot f(v) \cdot v dv = \text{Rate Constant (300°K)} \quad (27)$$

where

$$\sigma_{\text{Abs}}(v) = K\sigma_{\text{Rel}}(v)$$

and $f(v)$ is the normalized Maxwellian relative velocity distribution at 300°K.

Relative cross sections may also be normalized to the absolute velocity-averaged total ionization cross sections $\overline{\sigma}_{\text{Abs}}$ obtained by beam techniques by the expression

$$\int K \cdot \sigma_{\text{Rel}}(v) \cdot f'(v)dv = \overline{\sigma}_{\text{Abs}} \quad (28)$$

where $f'(v)$ is the velocity distribution of the metastable beam.

E. Object

The object of the present work is to report the velocity dependence of the absolute total ionization cross section for the systems $\text{He}(2^1S, 2^3S)$-$\text{Ar}$. These results differ from those previously discussed in that the cross sections reported are absolute rather than normalized values. A gas cell technique, in which the metastable beam is allowed to enter a chamber of static target gas, has been used rather than a crossed-beam technique. The gas cell technique is somewhat limited since ionization product branching ratios cannot be determined; however, the method should give reliable absolute cross sections at accurately known beam velocities. The
experimental procedure is basically similar to that of Tang, although the arrangements for signal collection and the data analysis technique have been changed. 28
A. Metastable States

Low voltage discharge sources produce many electronically excited states by collision of ground state atoms with electrons. While a large number of different excited states are possible, the lifetime of most states is very short where electric dipole radiation is allowed. Excited states, however, exist for which the electric dipole matrix transition element for transition to the ground state is zero. These stable excited states, with lifetimes greater than a microsecond, are referred to as metastable excited states.

The selection rules governing electric dipole radiation, where Russell-Saunders coupling is assumed, are as follows:

(a) \( \Delta S = 0 \),
(b) \( \Delta L = 0, \pm 1 \),
and (c) \( \Delta J = 0, \pm 1 \) excepting \( J = 0 \neq J = 0 \),

where \( S \) = total spin angular momentum,
\( L \) = total orbital angular momentum,
and \( J \) = total angular momentum.

Considering the case of helium in particular, two metastable states exist. The \( 1s \ 2s \ (2^3S) \) level in helium is the lowest possible triplet level since the only lower level is the singlet \( 1s^2 \) ground state. Selection rule (a) forbids triplet
to singlet transitions and the resultant lifetime of the state is about $6 \times 10^5$ seconds.\(^{30}\)

The second helium metastable state is the singlet state denoted by $1s^22s^1(2^1S)$ in which the transition to the singlet ground state is forbidden by selection rule (c). The lifetime of the singlet state is of the order $2 \times 10^{-2}$ seconds.\(^{30}\)

B. Spin Selection of $^1S$ or $^3S$ Helium Metastable Atoms from a Mixed Beam

A beam of triplet helium metastable atoms can be obtained from a mixed beam of singlet and triplet helium metastable atoms by irradiation of the mixed beam with radiation from a helium discharge lamp. The $^1S$ to $^1P$, 206 µ radiation emitted by the helium discharge promotes the $^1S$ metastable atom to the $^1P$ state. The $^1P$ state atoms then decay preferentially to the ground state, and the singlet state is said to be "quenched." The triplet $^3S$ state atoms also absorb radiation from the helium discharge lamp; however, the triplet can only radiate back to the $^3S$ spin state since no lower level exists for the triplet system.

C. Detection of Metastable Atoms

Metastable atoms can be detected indirectly by counting the electrons ejected from metal surfaces by incident metastable atoms. This process of deexcitation is thought to occur by Auger deexcitation of the metastable atom in which the metastable atom is ionized by the tunneling of its excited electron into a vacant energy level in the metal. The
resultant ion is then neutralized upon impact with the metal surface and a free electron subsequently ejected. The ratio of free electrons ejected from the metal surface for each incident metastable atom is called the secondary electron coefficient and is usually denoted by the symbol $\gamma$. Dunning and others have measured this ratio for several different metal surfaces and have studied the effect on the ejection coefficient by surface contamination and by the angle of incidence of the metastable with the target surface. The authors conclude that the secondary electron ejection coefficient varies with the condition of the metal surface and that the coefficient is only reliable when determined from surfaces under actual experimental conditions. Using a gas cell technique, the authors measured the value of the secondary electron ejection coefficient for singlet and triplet helium metastables to be 0.46 and 0.63, respectively. The metal surface was gold plated and the target gas was argon.

The values for the secondary electron ejection coefficients for singlet and triplet helium metastables in this work were determined from the same experimental data used to determine the ionization cross section. The expressions used in this analysis are given in the following section on total ionization cross section.

D. Velocity Distribution of a Maxwell-Boltzmann Source Gas

The metastable states of helium are produced by a low
voltage DC discharge with source gas pressures of about 0.1 torr. A Maxwell-Boltzmann velocity distribution may be expected at these gas pressures since the very short mean free path of the atoms leads to thermal equilibrium. The resultant velocity dependence of the intensity (particle flux) of the metastable atomic beam is given by

\[ I(v)dv = 4 \frac{I_0}{\sqrt{\pi}} \frac{1}{\alpha^3} v^2 \exp \left( \frac{-v^2}{\alpha^2} \right) dv \]  

(29)

where \( I_0 \) is the total beam intensity, \( \alpha^2 = \left( \frac{2kT}{m} \right) \), and \( m \) is the mass of the atom. The velocity distribution, however, is altered by the chamber exit slit width which is much smaller than the mean free path of the discharge gas. The gas will escape the chamber by effusive flow with the escape of higher velocity atoms being favored.36, 37 The velocity dependence of the modified Maxwell-Boltzmann gas is given by

\[ I(v)dv = \frac{2I_0}{\alpha^4} v^3 \exp \left( \frac{-v^2}{\alpha^2} \right) dv. \]  

(30)

The velocity selector further alters the velocity distribution of the transmitted beam. In cases (such as the present one) in which the selector transmission band is narrow in comparison to the width of the function \( I(v) \), the distribution function of the transmitted beam intensity becomes38

\[ T(v) = vI(v) \]  

(31)

and the velocity distribution detected at the collision chamber is given by
Experimental verification of this velocity dependence is given in Chapter IV.

**E. Total Ionization Cross Section and Secondary Electron Ejection Coefficients for Metastable Atoms**

The total ionization cross section and the secondary electron ejection coefficient can be evaluated from quantities measured by experiment. The ion and electron current, resulting from the reactive collision between the metastable beam and the static target gas, are measured separately and supply the basic data needed to determine the ionization cross section. The reaction path length is the distance from the entrance slit of the gas cell to the rear wall of the collision cell. The length, \( \ell \), of the reaction path is 2.25 cm. The number density, \( n \), of the target gas is assumed uniform throughout the entire collision chamber. The temperature of the target gas was assumed to be 24°C - the ambient temperature of the apparatus.

The loss, due to chemiionization, of metastable beam intensity, \( dI \), along a small interval, \( dx \), of the reaction path is written as

\[
\frac{dI}{I} = -\sigma_t n dx.
\]

Upon integration over the total reaction path, the intensity, \( I_\ell \), of the remaining metastable atoms including those elastically scattered is given by

\[
I_\ell = I_0 e^{-\sigma_t \ell}
\]
where $\sigma_t$ is the total ionization cross section, $n$ is the target gas number density, $I_o$ is the intensity of metastable atoms entering the collision cell, and $l$ is the total reaction path length. The ion current, $i_+$, collected from this process is obtained from the difference between the metastable beam intensity entering the collision chamber and the intensity at distance $l$ or

$$i_+ = I_o - I_k = I_o (1 - e^{-\sigma_t n l}).$$

(35)

Electrons come from two sources. Ionization will contribute an electron current equal to $i_+$. Electrons are also generated by unreacted metastables striking the rear of the collision cell. The fraction of metastables detected by Auger deexcitation is given by the secondary electron ejection coefficient, $\gamma$, and the electron current generated from the deexcitation process is $\gamma(I_o - i_+)$. The combined electron current, $i_-$, is therefore given by

$$i_- = i_+ + \gamma(I_o - i_+).$$

(36)

The target gas number density is corrected to the density at 300°K and is related to pressure in mtorr units by

$$n = \left(3.2193 \times 10^{13} \text{#/cm}^3\right) \left(\frac{300^{\circ}K}{297^{\circ}K}\right) \left(\frac{P(\text{mtorr})}{1 \text{mtorr}}\right)$$

(37)

where $3.2193 \times 10^{13} \text{#/cm}^3$ is the number density at 300°K and 1 mtorr pressure. For convenience, the argument of the exponential term in expression (35) is consolidated and re-written as

$$i_+ = I_o \left[1 - \exp \left(-\sigma_t n l\right)\right]$$

(38)

where
and the pressure variable is in mtorr units.

The total ionization cross section could, in principle, be determined from expression (38) if the pressure dependence of \( I_0 \) were known. It is more expedient, however, to develop expressions in which \( I_0 \) is eliminated and involve only the experimentally measured values of \( i_+ \) and \( i_- \) at known target gas pressures. This is accomplished upon division of (36) by (38) with the result

\[
\frac{i_-}{i_+} = 1 + \gamma \left[ \frac{\exp(-cp)}{1 - \exp(-cp)} \right]
\]

simplifying to

\[
\frac{i_-}{i_+} = 1 + \gamma \left[ \frac{1}{\exp(cp) - 1} \right]
\]

Following Tang, the expansion

\[
\frac{1}{\exp(x) - 1} = \frac{1}{x} - \frac{1}{2} + \frac{x}{12} - \frac{x^3}{720} + \frac{x^4}{720} \ldots
\]

can be used to obtain

\[
\frac{i_-}{i_+} = (1 - \frac{\gamma}{2}) + \frac{\gamma}{c} \frac{1}{p} + \frac{\gamma c}{12} p - \frac{\gamma c^3}{720} p^3 - \frac{\gamma c^4}{720} p^4 \ldots
\]

and the linear approximation

\[
\frac{i_-}{i_+} \approx (1 - \frac{\gamma}{2}) + \frac{\gamma}{c} \frac{1}{p}
\]

where \( cp \ll 1 \). An alternative analytical expression is developed by multiplication of (40a) by pressure and is written as
\[
\frac{i}{i_+} P = P + \gamma \left( \frac{P}{\exp(cp) - 1} \right) \quad (41a)
\]

where the same expansion gives

\[
P \left( \frac{i}{i_+} \right) = \frac{\gamma}{c} + (1 - \frac{\gamma}{2})P + \frac{\gamma c p^2}{12} - \frac{\gamma c^3 p^4}{720} \ldots \quad (41b)
\]

and finally the linear approximation

\[
P \left( \frac{i}{i_+} \right) = \frac{\gamma}{c} + (1 - \frac{\gamma}{2})P. \quad (41c)
\]

The linear approximation (41c) gives very little error for target pressures up to 5.0 mtorr. This was determined by comparison of calculations using (41a) and (41c) and appropriate values for \(\sigma\) and \(\gamma\). Both (40c) and (41c) appear to be suitable for data analysis, but (41c) should give a more reliable intercept. It may be shown that

\[
\lim_{P \to 0} P \left( \frac{i}{i_+} \right) = \frac{\gamma}{c}
\]

for both (41a), using L'Hospital's rule, and (41c), whereas for (40a)

\[
\lim_{P \to \infty} P \left( \frac{i}{i_+} \right) = 1.
\]

Thus, if Equation (40c) is to remain reliable, care must be exercised to insure that the condition \(cp \ll 1\) is met. Expression (41c) was therefore used to determine both \(\gamma\) and \(\sigma\) from experimental measurements of \(i_+\) and \(i_-\) for a series of common target gas pressures.
Other expressions can be used with varying success to evaluate $\sigma$ and $\gamma$. Using (36) and (38), the expression

$$\frac{i_+}{i_- - i_+} = \frac{1}{\gamma} \left| \exp(cp) - 1 \right|$$

(42a)

can be written, which upon expansion of the exponential term gives

$$\frac{i_+}{i_- - i_+} = \frac{c}{\gamma} p + \frac{c^2}{2\gamma} p^2 + \frac{c^3}{6\gamma} p^3 \ldots$$

(42b)

The values of $\sigma$ and $\gamma$ can be determined as adjustable parameters from a least squares fit of experimental data to the form of expression (42a). Relative cross section can be determined from the linear (first approximation) part of expression (42b). This final procedure is reliable only for data taken at very small target gas pressures.
CHAPTER III
DESCRIPTION OF APPARATUS

A. General Description

The molecular beam apparatus shown in Figure 6 is a modification of the apparatus previously described by Tang.\textsuperscript{28} The apparatus has four separate chambers: the discharge chamber, the fore chamber, the post chamber, and the collision chamber.

Admission of the beam gas into the discharge chamber is controlled by an automatic pressure controller. Production of metastable atoms in the discharge chamber is achieved using a low-voltage DC discharge. The gas exits the discharge chamber through slit S-1 and enters the fore chamber. The beam gas then passes through a second slit, S-2, into the post chamber.

Charged particles formed in the discharge are removed from the beam when it passes between two parallel deflection plates. A 450 VDC potential is applied across the plates. A solenoid driven beam stop, BS, is located directly behind the deflection plates so that background readings may also be taken during the experiment.

The beam is further collimated by slits S-3 and S-4 which are positioned at the ends of the velocity selector. In addition to mechanically selecting the velocity range to be studied, the selector prevents any photons generated in the discharge from reaching the collision chamber. Some
Figure 6. Cross Section of Apparatus
states with high electronic excitation energy are also produced by the discharge; however, their radiative lifetimes are short compared to the time required to traverse the distance to the collision chamber. Their fast decay leaves only metastable and ground state atoms in the beam. Since the detector system in this apparatus is insensitive to ground state helium atoms, the beam may be considered a pure metastable beam.

The quench lamp, located between the final two disks of the velocity selector, is coiled around the beam path to obtain maximum photon flux across the beam path. Helium $^1S^1$ metastable atoms are removed from the beam during the operation of the lamp in a process where the $2s$ electron of the $^2S^1$ state is promoted to a $2p$ state by 2.06 μ photons from the lamp. Transition from this state to ground is heavily favored and the $^1S^1$ state is subsequently quenched. Thus, measurements are performed on a beam of mixed metastable atoms or on a pure beam of triplet metastable atoms. Information on singlet state metastable atoms is obtained from the difference of the two experimental measurements.

The beam is collimated a final time by slit S-5 in the collision chamber superstructure and then enters the collision chamber. The target gas is admitted into the collision chamber by a feed-through in the rear of the collision chamber. Also located in the rear of the collision chamber are the heater and thermocouple from an RCA 1946 thermocouple gauge which are used to measure the target gas
pressure. A more detailed description of the experimental apparatus is given in the following sections.

B. Vacuum System

Fore Chamber

The fore chamber was constructed from a 304 stainless steel tee 6" in length with a 0.109" wall thickness. The vacuum equipment was a nominal 4" fractionating oil diffusion pump, containing Convalex-10 pump fluid, backed by a 1.5 liters/sec mechanical fore pump. An air-cooled chevron baffle was inserted between the chamber and diffusion pump. A chilled baffle was unnecessary since the pump fluid has a very low vapor pressure at room temperature. Contamination of the diffusion pump fluid by mechanical pump oil vapor was prevented by an Ultek fore line trap installed between the two pumps.

Post Chamber

The post chamber was constructed from heavy aluminum alloy of 1.25" thickness. The chamber walls were welded together. The top and bottom of the chamber, made from the same metal stock, were secured to the sides by a number of bolts. Arrangements for o-rings in the lid and bottom insured a vacuum-tight seal. The chambers inner dimensions were 10 1/2" x 12 1/2" x 25 3/4". A 5 3/4"-diameter hole, covered with a lucite flange, provided a viewport through one side wall. Two vacuum-tight feed-throughs for the gas input and output tubes of the quench lamp were located in the window of a similar viewport in the lid.
A nominal 6" fractionating oil diffusion pump, using Convoil-20 pump fluid, backed by a 6 liters/sec mechanical fore pump comprised the vacuum system of the post chamber. The diffusion pump had a pumping speed of about 1,000 liters/sec at 1 x 10^{-6} torr. Pump fluid backstreaming was minimized by a refrigerated baffle. The refrigeration system cooled the baffle to about -40°C using Freon-12 as the coolant.

Pressure Measurement

Pressures in the fore and post chambers were measured by vacuum ionization gauges. With no gas entering the two chambers, the fore chamber pressure was 2 x 10^{-7} torr and the post chamber was 6 x 10^{-7} torr. The fore chamber maintained a pressure of 2 x 10^{-5} torr when beam gas was admitted into the discharge chamber. The pressure in the post chamber fluctuated slightly with the pressure of the target gas in the collision cell. The post chamber maintained a 3 x 10^{-6} torr pressure when the target gas pressure was 4 mtorr.

Safety Provisions

Several methods were used to protect the diffusion pumps during operation. Sensing tubes for a thermocouple pressure gauge controller were installed between the backing pump and diffusion pump of each chamber. If the backing pressure of the post chamber exceeded 50 mtorr, the controller automatically shut off the power to both diffusion pumps. The system was also protected from any malfunction of the servo-mechanism controlling the gas pressures in the discharge chamber. A full-scale reading of 10 x 10^{-5} torr on the
ionization gauge controller monitoring the fore chamber terminated a switched output to the Automatic Pressure Controller.\textsuperscript{43,44} The controller automatically closed its leak valve servomechanism.

The pressure in the water lines to the two diffusion pumps was monitored by "Flowtrol" units.\textsuperscript{45} These devices automatically terminated power to the diffusion pumps if the water line pressure dropped below a critical level. These units have some shortcomings in their ability to protect the diffusion pumps. The units measure the water pressure drop across a narrow orifice which also restricts the flow rate of the water. The flow of water is stopped completely if the orifice becomes obstructed by debris or mineral deposits. Unfortunately, however, the unit will continue to sense a safe pressure drop across the orifice and fail to shut down the diffusion pump.

C. Gas Source

Auxiliary Vacuum System and Gas Storage

A glass vacuum system with 10 glass 12-liter storage bulbs was used for gas manipulation and purification. The system was pumped by a mercury diffusion pump backed by a mechanical pump. The gas was admitted into the storage bulbs after purification by either a degassed, activated charcoal absorption trap at liquid nitrogen temperature in the case of helium or a degassed wool trap at acetone-dry ice bath temperature in the case of argon.
Target Gas Delivery

The target gas, argon, was admitted into the collision chamber from its storage bulbs through a manually controlled Vactronic leak valve.\textsuperscript{46,47} Two or more argon storage bulbs were used simultaneously to enlarge the volume of gas backing the leak valve. In spite of this precaution, the target gas pressure still decreased slowly with time. This difficulty was circumvented by making pressure readings as quickly as possible before or after pressure related measurements.

Beam Gas Delivery

The flow rate of the helium beam gas from the storage bulbs to the discharge chamber was controlled by the servomechanism of a Granville-Phillips Automatic Pressure Controller (APC).\textsuperscript{44} The Automatic Pressure Controller and related equipment are shown in Figure 7. The servomechanism consists of a motor-driven leak valve. A high pressure WL-7676 ion gauge, placed between the leak valve and discharge chamber, measured the line pressure and the gauge's ion current served as an input signal to a picoammeter.\textsuperscript{48,49} The picoammeter then supplied the APC with a signal proportional to the line pressure. Supplied with this signal, the automatic controller functioned as a proportional controller, adjusting the leak rate by driving its servomechanism. A 500 ml bulb buffered short-term pressure fluctuations in the line following the leak valve.
Figure 7. Beam Gas Delivery System
D. Discharge Chamber

Construction

The discharge chamber was patterned after a low voltage DC discharge source designed by Rothe et al. Basic details of the discharge chamber may be seen in Figure 6. The chamber was mounted to the removable lid of the fore chamber. The chamber consisted of a Pyrex tube C, water-cooled copper end plates A and B, and a filament F, supported by Inconel rods R. The ends of the Pyrex tube (5.1 cm OD and 6.5 cm long) were sealed by plates A and B. The source slit, S, was located on the anode plate A. Plate B contained the source gas inlet and the electrical feed-throughs for the Inconel rods supporting the filament.

Filament

The ends of the tungsten ribbon filament were spot welded to nickel tabs which were in turn spot welded onto the flattened ends of the support rods. The filament was then cataphoretically coated with thoria following the procedure described by Muschlitz et al. The dimensions of the filament were 0.0254 mm thick, 2.5 mm wide, and 3.8 cm long. The distance between the filament and anode was 2.0 cm.

Power

A Lambda regulated power supply, operated in the current regulated mode, supplied current to the filament. To reduce backspattering, the filament was floated 50 volts above ground by a Heathkit power supply. The anode voltage was
supplied by a Hewlett Packard power supply operating in the constant current mode. 54

E. Velocity Selector

Construction

The velocity selector was patterned after a slotted-disk design of Kinsey, in which the helical slot path is approximated by machining slots tangential to the desired helical path. 55 This procedure offers several advantages over other slotted-disk designs. The advantages are as follows: 1) simplification of machining procedures; 2) accommodation of higher helical angles without serious loss of transmitted intensity; and 3) incorporation of one disk of greater thickness than the remaining disks reduces the total number of disks.

The disks were made from sheets of very high tensile strength aluminum alloy, Alcoa 2024-T3. A tungsten carbide saw, 0.022" thick with 20 teeth, was used to cut the slots. 56 The disks were stacked in the appropriate order and clamped between thick end pieces. Thus, the respective slots in each disk were cut simultaneously. Two 1/8" diameter holes were then drilled through each separate disk 180° apart to serve as alignment aids during the assembly of the velocity selector.

Table 1 contains information pertinent to the physical configuration and operating parameters of the velocity selector. The rotor assembly is shown in Figure 8.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Set V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of disks</td>
<td>6</td>
</tr>
<tr>
<td>Diameter of disks</td>
<td>5.652&quot;</td>
</tr>
<tr>
<td>Number of slots per disk</td>
<td>360</td>
</tr>
<tr>
<td>Length of rotor, L+d</td>
<td>4.031&quot;</td>
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<tr>
<td>L</td>
<td>4.000&quot;</td>
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<tr>
<td>Total angular shift $\phi$</td>
<td>5°</td>
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<td>Helical pitch $\frac{dz}{d\phi} = \frac{L+d}{\phi} = \frac{v}{\omega}$</td>
<td>46.1919&quot;/rad</td>
</tr>
<tr>
<td>Conversion factor for angular velocity $v$ to transmitted velocity $v_0$</td>
<td>$v_0 (\text{cm/sec}) = 737.2v(l/l_z)$</td>
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<tr>
<td>Length of slot (in radial direction)</td>
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<td>Slot width, $l_1$</td>
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<tr>
<td>Angular width at base, $\Delta \phi$</td>
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<tr>
<td>Tooth thickness between slots</td>
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<tr>
<td>At base of slots</td>
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</tr>
<tr>
<td>At top of slots</td>
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</tr>
<tr>
<td>Average value, $l_2$</td>
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<td>Thickness of disks</td>
<td></td>
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<tr>
<td>3rd disk</td>
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<tr>
<td>Others</td>
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<tr>
<td>Average radius, $r$</td>
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<tr>
<td>Cutting angle for slots, $\chi = \tan^{-1}(\frac{l_1}{A})$</td>
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Table 1 - continued

<table>
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<th>Parameters</th>
<th>Set V</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Position of aligning holes (clockwise with respect to the same cut)</th>
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</thead>
<tbody>
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<td>1st disk</td>
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<td>2nd disk</td>
<td>5/16°</td>
</tr>
<tr>
<td>3rd disk</td>
<td>5/8°</td>
</tr>
<tr>
<td>4th disk</td>
<td>1 1/4°</td>
</tr>
<tr>
<td>5th disk</td>
<td>2 1/2°</td>
</tr>
<tr>
<td>6th disk</td>
<td>5°</td>
</tr>
</tbody>
</table>

\[ \gamma = \frac{\Delta \phi}{\phi} \]

<table>
<thead>
<tr>
<th>Velocity spread</th>
<th></th>
</tr>
</thead>
</table>

\[ R^{-1} = \frac{\Delta v}{2v_o} = \frac{v_{\text{max}} - v_{\text{min}}}{2v_o} = \frac{\gamma}{1 - \gamma^2} \]

\[ v_{\text{min}}/v_o = 1/(1 + \gamma) \]

\[ v_{\text{max}}/v_o = 1/(1 - \gamma) \]

Geometric factor

\[ G = \frac{\gamma}{1 - \gamma^2} \]

\[ T(v_o) \approx G v_o I(v_o) \]
Figure 8. Velocity Selector Rotor Assembly (After Ref. 28)
1, 2, 4, 5, 6 .... 1/32" thickness disks
3. .......... 1/8" thickness disk
7 - 12. .... spacers
13. .......... bearings
14, 16. ...... collars
15. .......... 3/28 N. F. Allen screw
17. .......... 3/8-24 N. F. nut
18. .......... 3/8" rotor shaft
Rotor Mounting and Bearings

Barden Bartemp bearings SR6SSTB-DB2, lubricated by Ball Brother's vacuum coating process, were press fitted onto the rotor shaft. Each bearing was then mounted inside a brass ring enclosure. Each end of the rotor assembly was supported by 4 tension springs attached to a vertically movable block and to the brass enclosure. Rubber tubing was placed around each spring to dampen mechanical vibrations associated with the spring suspension system. This flexible support system allowed the rotor to spin about its own axis of rotation; eliminating the necessity of balancing the rotor to a very high degree of accuracy. The rotor assembly could be lowered out of the beam path by a gear shaft passing through an o-ring seal in the vacuum chamber wall.

Motor and Power Supply

A Globe two-phase, two-pole, hysteresis synchronous motor was used to drive the rotor. The motor was secured within an aluminum housing for shielding purposes and the motor housing mounted on four posts extending from the rotor assembly housing blocks. Thus, the motor and rotor could be moved as a unit. Piano wire (No. 13, 0.031" diameter) was used to couple the shafts of the motor and rotor assembly. Barden Bartemp SR4SSTB5 bearings with Ball Brother's dry vacuum coating were used in the motor to insure long operating lifetimes.

The power to the motor was supplied by two CML variable frequency (50 - 1800 Hz) power amplifiers. The input signal to the motor was controlled by ganged variacs as seen in Figure 9.
Figure 9. Power Supply for Velocity Selector Motor
Rotor Frequency Measurement

The rotor frequency was measured by taking advantage of the optically clear path through the alignment holes of the rotor disks. A high-output lens-end miniature lamp was inserted into one of the housing blocks and a photodiode inserted into the opposite housing block. The lamp and diode were positioned in the housing blocks at the same height as the alignment holes. Thus, the photodiode sensed chopped light pulses which were proportional to the operating frequency of the rotor. The diode became conductive when exposed to the light pulses and produced a pulse in the current which is shown in Figure 10. These pulses were counted and displayed by a Transistor Specialties, Incorporated counter.

F. Quench Lamp

Construction

The design of the quench lamp was somewhat restricted since the quench coils were placed between the last two disks of the velocity selector. This placement was chosen to limit the beam path, thus avoiding loss of beam intensity. The glass coil part of the lamp assembly was constructed from 5/16" OD Pyrex glass tubing of standard wall thickness. The coil consisted of 4 1/2 loops, its length 1 1/2", and inner diameter 3/4". The glass envelope for the electrodes was formed from 7/8" glass to metal Kovar seals. The aluminum electrodes were 1 1/4" in length and 1/2" in width.
The ends of the electrodes were threaded into brass plugs as may be seen in Figure 11. The brass plugs and the electrode metal envelopes were soldered together to insure a vacuum-tight seal and maximum ohmic contact. Small 1/8" holes, drilled through each of the brass plugs and the threaded ends of the electrodes, allowed a steady gas flow through the electrode-coil assembly. Hard drawn copper tubes, 1/4" OD, were soldered onto the brass plugs and passed through vacuum-tight fittings in the main vacuum chamber wall.

The ground electrode of the lamp was clamped directly to an aluminum plate support to insure a good electrical ground and to provide a good heat sink. The floating electrode was clamped to the plate with insulating plexiglass spacers.

**Lamp Vacuum Line**

Vacuum rubber hose was used throughout the quench lamp's vacuum manifold. The entire manifold could be pumped down to 0.2 torr when no gas was admitted into the manifold. A constant flow of gas was admitted to the manifold from a tank of commercial grade helium. The gas was then purified by a liquid N₂ trap. The lamp operating pressure was regulated by a Vactronic leak valve placed between the trap and the high voltage electrode of the lamp. Pressure measurements were taken with a Hastings Vacuum Gauge placed between the ground electrode and the mechanical pump.

The lamp operated with a constant flow of helium gas to
Figure 11. Helium Quench Lamp
remove impurities resulting from the elevated temperature of the lamp during operation. The discharge gas flowed from the positive, high voltage electrode toward the ground electrode. The reasons for this arrangement were as follows: a) most of the energy produced from the discharge was carried by positive ions to the ground electrode which had an excellent heat sink; b) aluminum sputtered from the ground electrode by positive ions was carried downstream, away from the coil by the helium carrier gas; and c) electrons, which carried much less thermal energy, went to the positive electrode which had little heat sinking capabilities.

The voltage to start and maintain discharge was supplied by a Hewlett-Packard DC power supply. A high-power, 10K ohm, 500 watt resistor was placed in series with the lamp on the high voltage line to maintain a base resistance during the initiation of the discharge. This was necessary to circumvent the instrument's current limiting protective circuitry which would have been activated by the apparent short applied across its output terminals.

G. Collision Chamber and Detecting Systems

Construction

The collision chamber was a modified version of chambers used by Smith and Muschlitz and later by Tang. The basic details of the collision chamber are shown in Figure 12. The chamber consisted of 4 parts which were as follows: a) gas cell, b) collision cell, c) superstructure, and d) pressure-sensitive thermocouple.
Figure 12. Collision Chamber and Detecting System
The gas cell, GC, was a brass cylinder with a single slit opening, S-5, through which the metastable beam entered. Table 2 is a listing of the dimensions of slits used to define the beam. The gas cell slit was much smaller than the expected mean free path of any atomic gas contained within the gas cell. Thus, the gas would exit the cell by Knudsen flow and a high pressure differential between the gas cell and the main vacuum chamber be maintained. 68

Target gas was introduced into the cell by a feed-through in the rear of the collision cell from the glass bulbs of purified gases. The target gas pressure was controlled by a Vactronic leak valve placed between the gas cell and the glass bulbs. The gas cell was electrically insulated from all other parts of the collision chamber and could be electrically biased with respect to ground.

The collision cell (CC), mounted inside the gas cell, was a three-part assembly. The cylindrical side (CC2) and the cylinder bottom (CC3) were electrically common and could also be biased with respect to ground. The beam gas was admitted into the collision chamber through a slit, S-6, in the cylinder top (CC3). This slit was slightly larger than the gas cell slit to avoid obstruction of the metastable beam path.

Signal Detection

All electrical charges resulting from collisions of metastables with target atoms or with the rear collision cell wall were collected at the collision cell lid (CCl) when
Table 2. 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>$S_6$</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>
appropriate repulsive potentials were used on all other surfaces. These charges were then measured by a Cary Vibrating Reed Electrometer using an input resistor of $10^{11}$ ohms. Positive ions resulting from ionizing collisions were collected on CC1 by applying equal, repulsive, positive potentials on GC, CC2, and CC3. The potential applied to the gas cell prevented ions focused by the cylindrically-symmetric field from exiting the collision chamber. Conversely, all electrons were collected at surfaces having a positive potential.

The electron signal was collected at CC1 after application of negative voltages on GC, CC2, and CC3. The voltage on GC was again primarily designed to insure total charge collection by preventing any focused beam of electrons from exiting the collision chamber through slits S-5 and S-6. The voltage on GC was larger than CC2 and CC3 to prevent the creation of additional secondary electrons through collisions of highly energetic electrons with the surface of the gas cell near slit S-5.

The superstructure, mounted on the exterior front of the gas cell, was a precaution against inadvertent collection of electrons formed by metastable collisions with the edges of the gas cell entrance slit. This structure was insulated from the gas cell and biased positive 90 V with respect to ground.

The output from the electrometer was monitored by a chart recorder and integrated over a period of time to average out noise. An operational amplifier was the main
component of the integrator and a logic control circuit controlled the integration time.\textsuperscript{71} The integrated signal was displayed by a Newport digital voltmeter and recorded on a Digitec printer.\textsuperscript{72,73}

**Pressure Measurement**

The pressure of the target gas inside the collision chamber was controlled by a Vactronic high vacuum leak valve. The heater and thermocouple elements of an RCA 1946 thermocouple gauge, located in the rear of the gas cell, measured the target gas pressure. The two heater leads were connected across a DC constant current supply.\textsuperscript{74} The DC current level was determined by measuring the potential drop across a precision 2 ohm resistor located in series with the thermocouple gauge.

The EMF measurement was taken across a second pair of thermocouple leads. This measurement was made by a Leeds and Northrup universal potentiometer and galvanometer with an Eppley Laboratory standard cell.\textsuperscript{75,76} The working voltage source powering the potentiometer was obtained from Leeds and Northrup.\textsuperscript{75}
A. Calibration of Target Gas Pressure Gauge

The RCA 1946 thermocouple, mounted within the collision chamber, was used to measure the target gas pressure. The collision chamber and thermocouple pressure gauge assembly was placed inside a vacuum bell jar and the thermocouple calibrated at known argon pressures with a MKS Baratron.77

The calibration procedure was as follows. A current of 70 mA was supplied to the heater leads of the RCA 1946 gauge, and the EMF \( (E_0) \) was measured at a high vacuum of \( 1 \times 10^{-7} \) torr. The bell jar was then isolated from its diffusion pump by a butterfly valve, and a small amount of argon introduced into the bell jar. Following equilibration of the argon, the EMF \( (E) \) of the gauge and the Baratron pressure reading \( P \) (mtorr) were taken simultaneously. The bell jar and its contents were evacuated after each pressure reading to minimize contamination by atmospheric gases. Contamination by atmospheric gases, however, was not a serious problem since the leak rate of the system was about \( 2.2 \times 10^{-3} \) mtorr/min with the butterfly valve closed. Since the absolute values of \( E_0 \) and \( E \) vary with ambient temperature, the pressure dependence of the RCA gauge was determined as a function of \( (E_0 - E)/E_0 = \Delta E/E_0 \) which depends on gas
pressure only. Several pressure readings were taken between 0.2 mtorr and 8.0 mtorr.

The linear relationship between the quantities $\Delta E/E_o$ and $P$ (mtorr) is demonstrated by Figure 13. The parameters $m$ and $b$ of the relationship $P$ (mtorr) = $m (\Delta E/E_o)$ - $b$ were determined by a linear least squares fit to the data with the results being

$$P \text{ (mtorr)} = 148.502 (\Delta E/E_o) - 0.2096$$

with a correlation coefficient of 0.9999.

B. Conditions for Metastable Production

The filament was operated +50 volts with respect to ground at a current between 12.0 and 14.5 A. The helium discharge gas pressure was maintained at 0.09 torr as determined by the WL - 7676 high-pressure gauge. The corresponding reference setting on the automatic pressure controller was 880.

The anode current was set at 400 mA to obtain the optimum metastable intensity. The anode voltage varied between 60 and 65 volts depending on the condition of the filament. Any charged particles produced by the low-voltage discharge were deflected from the beam by a 450 volt potential across the deflection plates (D).

C. Distribution of Metastable Velocities

The height of the $5^\circ$, 6-disk velocity selector was adjusted with respect to the beam path to insure optimum
Figure 13. Calibration Curve for RCA 1946 Thermocouple Gauge for Argon
beam transmission. No signal was detected in the collision chamber when the rotor was not turning; therefore, no optically clear path to the collision chamber was open to photons or metastable atoms produced by the discharge. The velocity spread transmitted by the selector was calculated to be

\[ R = \frac{V_{\text{max}} - V_{\text{min}}}{V_0} = 0.101 \]

where \( V_{\text{max}} = 1.111 V_0 \) and \( V_{\text{min}} = 0.909 V_0 \).

Figure 14 shows a plot of measured and calculated values of the relative beam intensity for the helium metastable atoms at various nominal velocities. The points represent the experimentally measured transmitted beam intensity adjusted to unity at maximum intensity and the solid line is the corresponding theoretical velocity distribution of the intensity predicted by

\[ T(v) = v^4 \exp \left( -\frac{v^2}{a^2} \right) \]

where \( a^2 = 2kT/m \), \( k = 1.38 \times 10^{-16} \text{ erg}/^\circ\text{K} \), and \( m = 6.6488 \times 10^{-24} \text{ g/atom} \) for helium. The characteristic beam temperature was calculated to be \( T = 463^\circ\text{K} \) where \( a^2 = 1.92235 \times 10^{10} \text{ cm}^2/\text{sec}^2 \).

The good theoretical fit strongly supports the assumption of a Maxwell-Boltzmann velocity distribution inside the discharge source. The disagreement between the theoretical and experimental intensity at the lowest beam velocities is due to a cloud-like formation of helium atoms outside the exit slit of the source. This accumulation of gas will selectively scatter the low velocity beam atoms.
Figure 14. Velocity Distribution of Detected Metastable Beam Intensity

---

Calculated Values

O O Experimental Values
D. Charge Collection Potentials

To insure complete collection of the ionization products, the current collected on CCl was studied for several biasing arrangements on CC2, CC3, and GC. From these series of intensity saturation studies, it was found necessary to keep \( V_{GC} \) at a voltage equal to or greater than the voltages \( V_{GC2} \) and \( V_{CC3} \). The collection plate CCl was essentially situated in a potential well by this arrangement. Furthermore, any charged particles focused by the cylindrical field inside the collision cell were prevented from exiting the collision chamber by the repulsive potential at the front of the gas cell.

The saturation curves shown in Figure 15 indicated that virtually all the desired reaction products were collected with the voltage arrangements given in Table 3.

The beam velocity during this study was 1290 m/sec. The saturation characteristics were studied with 3 mtorr argon target gas pressure and also with no target gas. Depending on which charged species was to be collected, the voltage on GC was maintained at the voltage given in Table 3 and the voltages on CC2 and CC3 were varied from +120 V for positive ion collection to -120 V for negative charge collection. Changing the voltage on the superstructure had no noticeable effect since its function was essentially duplicated by the potential \( V_{GC} \).

E. Operation of Quench Lamp

The quench lamp was placed between selector disks 5 and
Figure 15. Charge Collection Versus Drawout Potential

--- Signal intensity without target gas
- - o - - Signal intensity with argon target gas
Table 3. Current Collection Potentials

<table>
<thead>
<tr>
<th>Charge Collected</th>
<th>Repulsive Potentials with Respect to Ground</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{GC}$</td>
</tr>
<tr>
<td>Positive Ions</td>
<td>+45 V</td>
</tr>
<tr>
<td>Electrons</td>
<td>-135 V</td>
</tr>
</tbody>
</table>
6 and carefully aligned along the beam axis to avoid obstruction of the metastable beam. The quenching efficiency of the lamp was studied by the saturation technique. Thus, the ratio of the quenched to unquenched metastable beam intensity was measured at different discharge currents. This procedure was repeated for a series of discharge gas pressures and discharge gas flow rates.

Although the flow rates were not measured, the effect on the quenching efficiency by flow rate could be observed by partially closing a vacuum shut-off valve between the lamp and the mechanical vacuum pump. A constant discharge gas pressure was maintained in the lamp during this series of studies. The quenching efficiency improved noticeably with increases in the discharge gas flow; therefore, a maximum pumping rate was maintained throughout the remaining studies. Efficient removal of degassed impurities in the lamp, cooler operating temperatures of the lamp, and transport of sputtered Al away from the lamp coils were other benefits of fast flow rates.

The effect of quench gas pressure on the quenching efficiency of the lamp was then determined at different discharge currents. The quenching efficiency was studied over a pressure range of 0.5 torr to 7.0 torr. The optimum gas pressure fell between 1.5 and 4.0 torr, since the onset of quench saturation occurred at lower discharge currents as the pressure was increased. The maximum range of discharge currents over which saturation occurred was realized at 3.0 torr discharge gas pressure.
Figure 16 shows the ratio of quenched to unquenched beam intensity at various discharge currents and a discharge gas pressure of 3.0 torr. Quenching saturation is seen to extend from 30 mA to 50 mA. The beam velocity was 1327 m/sec and the maximum beam current was approximately $10^{-12}$ A. From these studies, the optimum operating conditions of the lamp were as follows: 3.0 torr discharge gas pressure, 40 mA lamp discharge current, and maximum flow rate of quench gas. Also, the lamp's efficiency was severely affected by impurities in the discharge gas supply; therefore, the helium was purified by passage through a liquid $N_2$ trap before entering the lamp.

F. Procedure of Experiment

The charge drawout voltages were first set for the collection of electrons ($V_{GC} = -135$ V, $V_{CC2} = V_{CC3} = -95$ V). Using the quench lamp, signals proportional to the unquenched (singlet + triplet) and quenched (triplet) metastable beam intensity were measured without target gas. The difference in these two measurements gave the signal proportional to the singlet metastable beam intensity. The relationship between the beam intensity ($I_o$) and the measured signal ($i_o$) is given by $i_o = \gamma I_o$. A background thermocouple EMF reading ($E_o$) was also taken in the absence of the target gas.

Target gas was then introduced into the target chamber and allowed to equilibrate and a second thermocouple EMF ($E_1$) taken. The unquenched and quenched electron signals were measured and the singlet electron signal obtained from the difference of the two experimentally measured signals.
Figure 16. Saturation of Quench Lamp Efficiency
The charge drawout potentials were then changed to the appropriate arrangement for collection of positive charges \((V_{CC} = V_{CC2} = V_{CC3} = 445 \text{ V})\). The ion current resulting from the unquenched and quenched metastable beam were again measured and an additional thermocouple EMF reading was taken. The target gas flow to the collision chamber was interrupted and a background EMF measurement taken.

The second pair of EMF thermocouple measurements was taken to obtain the target pressure during the collection of positive charges. Although the setting on the leak valve regulating gas flow into the chamber was not altered, the final target gas pressure was invariably lower than the initial target gas pressure by approximately 0.2 mtorr. This was not unexpected in view of the long period of time between the two pairs of thermocouple readings.

A different leak rate of target gas was admitted into the collision chamber and another series of EMF and ion charge currents measured. After changing the drawout potential, the electron currents and EMF's were again measured. The target gas flow was again interrupted and background EMF's and metastable intensities measured. This procedure was repeated until ion and electron currents were measured for at least 10 different target gas pressures in the range from 0.5 mtorr to 4.5 mtorr of argon. Using this procedure, the target gas pressures and the beam flux were always known accurately both during the collection of ionic charges and during collection of electrons.
G. Reduction of Raw Data

The data were corrected for variations in the metastable beam intensity by division of the pressure dependent signal by the signal obtained with no target gas in the collision chamber. The pressure dependence of the reduced ion current can be written as

\[ \frac{i_d}{i_0} = \frac{E(P)}{\gamma_o} \left[ 1 - \exp(-cp) \right] \]  (43)

and the pressure dependent reduced electron current written as

\[ \frac{i_e}{i_0} = \frac{E(P)}{\gamma_o} \left[ 1 - (\gamma - 1) \exp(-cp) \right] \]  (44)

where \( E(P) \) is the target gas pressure dependence of elastic and inelastic scattering of the metastable beam in the main chamber, \( \gamma_o \) the secondary electron ejection coefficient with no target gas, and \( \gamma \) the secondary electron ejection coefficient with target gas in the collision chamber. Equation 40a is regained upon division of Equation (44) by Equation (43).

The experimental pressures and the reduced ion and electron currents were fit to a 4th degree polynomial in order to obtain data at common pressures. Comparison of the experimental data and data obtained from the polynomial fit showed no discernible bias resulting from the polynomial fit. Although some smoothing occurred, the polynomial was of sufficiently high degree to reproduce any major variations in the slowly varying pressure data. For each beam velocity used, the pressure dependent data were then fit to the
\[ \frac{j}{i_+} P = (1 - \frac{\gamma}{2}) P + \frac{\gamma}{c} \] (41c)

using a linear least squares technique. The secondary electron ejection coefficient \( \gamma \) was obtained from the slope, \( m \), by the expression \( \gamma = 2 - 2m \). The absolute total ionization cross section at each beam velocity was determined from the intercept \( (\gamma/c) \) by the expression

\[ \sigma(A^2) = \left( \frac{c}{\gamma} \right) \frac{\bar{\gamma}}{7.317 \times 10^{-3}} \] (45)

where \( \bar{\gamma} \) is the average of all values of \( \gamma \). Representative samples of the least square fit to the data for several relative beam velocities are shown for the system \( \text{He}(2^3S) - \text{Ar} \) in Figure 17 and for the system \( \text{He}(2^1S) - \text{Ar} \) in Figure 18.
Figure 17. $P \cdot (i_t^2 / i_t^1)$ Versus $P$ for He$(2^3S)$-Ar at Different Relative Velocities
Figure 18. $P \cdot (i_- / i_+)$ Versus $P$ for He(2$^1$S)-Ar at Different Relative Velocities
A. Secondary Electron Ejection Coefficients

The secondary electron ejection coefficients for He \( (2^1S, 2^3S) \) on the electroplated gold surfaces of the collision chamber were determined experimentally as discussed in the previous chapter. The average value of the secondary electron ejection coefficient of \( 2^3S \) He* for all beam velocities was \( \overline{\gamma}_t = 0.582 \pm 0.024 \) where 0.024 was the standard deviation of all values. The average value for \( (2^1S)\)He* was \( \overline{\gamma}_s = 0.440 \pm 0.018 \). The ratio of the two coefficients was \( \overline{\gamma}_s/\overline{\gamma}_t = 0.756 \). The results of other experimental determinations of \( \gamma \) on different surfaces and with different target gases suggest caution when comparing published values.

Dunning, Rundel, and Stebbings report \( \overline{\gamma}_s = 0.53, \overline{\gamma}_t = 0.69 \), and \( \overline{\gamma}_s/\overline{\gamma}_t = 0.768 \) on a stainless steel surface and \( \gamma_s = 0.51, \gamma_t = 0.63 \), and \( \gamma_s/\gamma_t = 0.81 \) on a Cu-Be surface. Dunning and Smith have also published values of the coefficients for an electroplated gold surface where \( \gamma_t = 0.63 \pm 0.07, \gamma_s = 0.46 \pm 0.09 \), and \( \gamma_s/\gamma_t = 0.73 \). These last results agree with the present results within experimental error. This should be expected since a gas cell method with argon as the target gas was similarly employed. The variation of \( \gamma \) with different target gases reported by
Dunning et al. indicated an adsorbed gas surface effect. This is somewhat puzzling since atomic gases such as Ar and Kr apparently do not adsorb appreciably on metal surfaces at room temperature and low pressures. However, further indication of possible adsorbed gas surface effect may be seen in Figure 17, where the experimental data in some cases depart from the linear relationship with pressure at low target gas pressures.

B. Relative Velocity Dependence of the Total Ionization Cross Section

Present Results

The relative velocity dependence of the absolute total ionization cross section for the He* (2^3S)-Ar and He* (2^1S)-Ar systems are given by Figure 19 and Figure 20 respectively. The experimentally determined cross sections are represented by the points joined by the solid line with the vertical bars representing estimates of the experimental error. The error for each relative velocity was determined from the standard deviation of the intercept \( \frac{Y}{c} \) in the linear least squares fit of

\[
P \left( \frac{i^-}{i^+} \right) = (1 - \frac{Y}{c})P + \frac{Y}{c}.
\]

The uncertainty of \( Y \) is not reflected in the error bars. The values \( \overline{Y}_t = 0.582 \) and \( \overline{Y}_s = 0.440 \) were used in the calculation of the absolute total ionization cross sections. The methods for calculation of the relative velocity and of correction for the random motion of the target gas are
Figure 19. Dependence of Absolute Total Ionization Cross Section on Relative Velocity for the System He$^{2+}$-Ar
Figure 20. Dependence of Absolute Total Ionization Cross Section on Relative Velocity for the System He(2S)-Ar
given in the Appendix. The ratio of the triplet to singlet cross sections at various relative velocities are shown in Figure 21.

It should be noted that the uncertainty in the values for the cross sections are large in the low relative velocity range. This is due primarily to the very small metastable beam intensity at low velocities. The He*($2^1S$)-Ar cross sections at low beam velocities are particularly difficult to obtain since the data for this system are determined from the difference in two experimental measurements.

The qualitative behavior of the ionization cross section may be explained in terms of the potential curve and its associated coupling frequency to the continuum. To the lowest order of approximation, the "classical" theory of ionization gives the approximation

$$
\sigma(v) \propto R_{c1}^2 W(R_{c1})v^{-1}.
$$

At very low collision energies ($E_k(\infty) \ll \epsilon$, where $\epsilon$ is the well depth of the potential energy of interaction), the collision is sensitive only to the attractive part of the potential curve. If $W(R) \sim \exp(-R)$, then the coupling between the discrete state $V^*(R)$ and the continuum of states $v^+(R) + E_{c1}$ is very weak and only "close collisions" will result in ionization. Therefore, ionization will be dominated by the $v^{-1}$ factor and the ionization cross section will decrease with increasing relative velocity.

The region ($E_k(\infty) \approx \epsilon$) is viewed as a transition region in which the collision energy is approximately equal to the
Figure 21. Dependence of the Ratio of Absolute Total Ionization Cross Section of Ne(2^1S)-Ar to Ne(2^3S)-Ar on Relative Velocity
well depth of the interaction potential. In this region, the cross section will pass through a minimum value. However, the collision energy at which the cross section is at a minimum does not correspond exactly to the minimum energy of the potential curve. The exact position of the minimum involves the degree of coupling given by $W(R)$ as well as the interaction potential.

As the collision energy is increased beyond the minimum of the potential curve ($E_k(\infty) \ll \epsilon$), the interaction enters the "hard core" region. In this region, the collision energy is sufficiently high to probe the repulsive part of the potential curve. The factor $v^{-1}$ is overcome by the transition coupling factor. The classical turning point decreases with increasing collision energy, and the exponential nature of $W(R)$ will be strongly probed. Thus, the cross section will follow the coupling frequency and increase with collision energy.

At very high collision energies, the repulsive potential becomes very steep. As a result, the classical turning point $R_{cl}$ and therefore $W(R_{cl})$ will remain relatively constant and the $v^{-1}$ factor will again predominate. The ionization cross section will decrease with increasing collision energy.

The present measurements are the only absolute cross section measurements so far reported. The results reported by Pesnell et al. are relative cross sections which have been normalized to theoretical calculations of the cross sections based on Miller's classical development and the potential
curve suggested by Olson for the He(2⁴S)-Ar system. Pesnelle et al. employed a crossed beam technique in which both beams were generated by effusive sources. The results for He-(2⁴S,2¹S)-Ar reported by Illenberger and Niehaus are also relative cross sections which were normalized to the destruction rate constant of He(2⁴S) by argon at 300°K. The technique of crossed beams from effusive sources was also employed by Illenberger and Niehaus.

The cross sections reported by both Pesnelle et al. and Illenberger et al. for the system He(2¹S)-Ar are relative to the normalized cross sections for the He(2⁴S)-Ar system. This procedure may be subject to systematic error in the case of Pesnelle et al., for example, since the authors assume \( \gamma_s/\gamma_t = 1 \) for the first CuBe dynode of their detector. Dunning, Rundel, and Stebbings have found experimentally that \( \gamma_s/\gamma_t = 0.81 \) for metastable helium atoms incident on a CuBe surface. In the present work, the absolute cross sections for both the He(2⁴S)-Ar and He(2¹S)-Ar systems are measured independently.

Riola, Howard, Rundel, and Stebbings have measured the velocity-averaged absolute cross section for the He(2⁴S,2¹S)-Ar system. Since their absolute cross sections are velocity-averaged, direct comparison with their results is difficult. For a mean center-of-mass collision energy of about 60 meV, their velocity-averaged absolute cross section for He(2⁴S)-Ar is \( \bar{\sigma}_t = 16.9 \text{ Å}^2 \) and for He(2¹S)-Ar \( \bar{\sigma}_s = 22.7 \text{ Å}^2 \) and the ratio of the two values is \( \bar{\sigma}_s/\bar{\sigma}_t = 1.34 \).
The velocity dependence of the ionization cross section appears to pass through a minimum $E_{\text{min}}$ at 950 m/sec of 15 meV. The well depth calculated from Olson's potential is approximately 5.4 meV leading to the ratio $\frac{E_{\text{min}}}{E} = 2.78$. As was pointed out previously, the coupling frequency also has a decisive role in determining the exact position of $E_{\text{min}}$. Also, the rather large uncertainty in the experimentally determined cross section at low velocities may cause considerable error in $E_{\text{min}}$. A more precise determination of $E_{\text{min}}$ should be possible with the theoretical fit of the experimental cross sections. Nevertheless, the interaction passes through the transition region somewhere below 20 meV and enters the "hard core" region.

The ionization cross section rises linearly with relative velocity from 1100 m/sec to 2800 m/sec or from collision energies 25 meV to 150 meV. The dependence of the ionization cross section on collision energy is somewhat weaker in the present results than the dependence found by Illenberger and Niehaus and by Pesnelle et al.\textsuperscript{12,22}

The energy dependence of the total ionization cross section does not appear to follow the expected behavior. The collision energy dependence seems to be following a hard core potential before the condition $E_k^{(c)} \gg \epsilon$ is well met. The potential well depth calculated from the potential given by Olson is $\epsilon = 12.26$ meV which corresponds to a relative velocity of 806 m/sec.
In general, the collision energy dependence found by Pesnelle et al. closely resembles the present results. The energy dependence reported by Illenberger and Niehaus deviates from the present results in the low energy region where these authors found a weak energy dependence.

C. Calculation of Relative Velocity Dependence of the Total Ionization Cross Section

The relative velocity, $v_r$, dependence of the total ionization cross section for the system He($2^3S$)-Ar was calculated from Miller's "classical" theory and the potential curve $V'(R)$ given by Olson. The development of the analytical expressions was given in Chapter II. The total cross section for each energy ($E_k(\infty) = 1/2 \mu v_{r0}^2$) is obtained by summing the cross section for each angular momentum or partial wave ($\ell$) and is written in terms of atomic units by

$$
\sigma(v_r) = \frac{\pi}{k_0^2} \sum_{\ell} (2\ell + 1) P_\ell(v_r)
$$

where $k_0 = [2 \mu E_k(\infty)]^{1/2}$,

$$
\mu = 6634 \text{ m}_e,
$$

$$
P_\ell(v_r) = 1 - \exp \left[ - \int_{R_{cl}}^{\infty} \frac{W(R)}{v_{r0}} \, dR \right],
$$

$$
W(R) = A \left( \frac{1}{\epsilon_{a\mu}} \right) \exp \left[ \frac{-R}{B(a_o)} \right],
$$

$R$ = the internuclear separation in terms of Bohr radius ($a_o$),

$$
v_{r0}(R) = v_r \left[ 1 - \frac{W(R)}{E_k(\infty)} = \frac{\ell (\ell + 1)}{2\mu E_k(\infty)R^2} \right]^{1/2},
$$
\[ V^\alpha(R) = \frac{2}{R} \left[ 3 \exp \left( -\frac{R}{C_\infty} \right) + 3 \exp \left( -\frac{R}{C_1} \right) \right. \]
\[ \left. + 2 \exp \left( -\frac{R}{C_k} \right) - \frac{C_{ab}}{R} \left[ 1 - \exp \left( -\frac{R}{C_k} \right) \right] \right] \]
\[ \left( 1 + x + \frac{1}{2} x^2 + \frac{1}{6} x^3 + \frac{1}{24} x^4 + \frac{1}{20} x^5 \right) \]
\[ C_\infty = 0.96 a_o, \quad C_1 = 0.18 a_o, \quad C_k = 0.057 a_o, \quad C_{ab} = 226 (\text{au}) \]

and \( x = (R/0.98) \).

In the atomic units system, \( \hbar, \; \text{au}, \; a_o, \; \text{t}_{\text{au}}, \) and \( m_e \) are set equal to unity.

The lower integration limit \( R_{c1} \) (the classical turning point) was taken to be the largest internuclear separation at which \( \nu_\alpha(R) = 0 \). Since \( \nu_\alpha(R) \) has more than one root, and an irregular shape, a Newton-Raphson technique could not be used safely. Therefore, \( R_{c1} \) was determined by an iteration technique in which decreasing values of \( R \) were substituted into \( \nu_\alpha(R) \) until \( \nu_\alpha(R_{n-1}) > 0 > \nu_\alpha(R_n) \). Using smaller increments of \( R \), the iteration was re instituted at \( R = R_{n-1} \) until \( R_{n-1} - R_{c1} = 1 \times 10^{-6} \).

The integration of the term
\[ \int_{R_{c1}}^{\infty} \frac{A \exp \left( -\frac{R}{B} \right)}{\nu_\alpha(R)} \]
is complicated by the existence of a singularity at \( R = R_{c1} \) since \( \nu_\alpha(R_{c1}) = 0 \). The integrand, however, in these calculations was never truly infinite since \( R_{c1} \) was only determined within \( 1 \times 10^{-6} a_o \). Thus, the calculations gave a lower bound of the theoretical calculations.

Simpson's rule or the trapezoidal rule integration could have been used for these calculations, since the integrand
remained finite at its lower integration limit. However, a 30 point Gaussian Laguerre integration technique was employed for its computational economy. The integration was carried over the range $R_{\text{max}} = 15a_0$ to $R_{\text{cl}}$. The calculation was carried out for each partial wave $\ell$ until $P_{\ell}/P_{\text{max}} = 1 \times 10^{-3}$.

The two adjustable parameters, $A$ and $B$, were varied until the calculated energy dependence of the total ionization cross section agreed with the experimentally determined energy dependence within the energy range 20 meV to 150 meV.

Figure 22 shows the results of the theoretical calculations using the adjustable parameters $A = 3300a_0$ and $B = 0.390a_0$. The line represents the theoretical results and the points are the experimental results. The fit is quite good over the velocity range. From the theoretical calculations, the cross section passes through a minimum at a relative velocity of 710 m/sec. The corresponding collision energy, $E_{\text{min}}'$ is 9.5 meV. The ratio of $E_{\text{min}}$ to the potential well depth is $E_{\text{min}}/\varepsilon = 1.76$.

The calculated total ionization cross sections of the He($2^3S$)-Ar system over an extended collision energy range are shown in Figure 23. The solid line represents the present results using values of the adjustable parameters $A = 3300a_0$ and $B = 0.390a_0$. The broken line represents theoretical calculations using the adjustable parameters $A = 7400a_0$ and $B = 0.357a_0$ found by Illenburger and Michaus. The dot-dash line represents theoretical calculations using the adjustable
Figure 22. Calculated and Experimental Dependence of Total Ionization Cross Section on Relative Velocity for He(2s)-Ar

--- Calculated Values

@ @ Experimental Values
Figure 23. Comparison of Calculated Dependence of Total Ionization Cross Section on Collision Energy for He\(^{(2^3S)}\)-Ar

- Present results
- Calculated results of Illenberger et al. \(^{22}\)
- Calculated results of Pesnelle et al. \(^{12}\)
- Calculated results of Olson \(^{19}\)
- Experimental results of Moselcy et al. \(^{18}\)
parameters $A = 4000\text{au}$ and $B = 0.260 a_0$ determined by Pesnelle et al.\textsuperscript{12} These three sets of calculations display the same general trends. In particular, none give the values of the absolute cross section in the high energy range (100 eV to 500 eV) found experimentally by Moseley et al.\textsuperscript{18}

The dot curve displays the results of theoretical calculations using values for the adjustable parameters $A = 1.0\text{au}$ and $B = 0.667 a_0$ determined by Olson.\textsuperscript{19} Olson adjusted these parameters to fit the energy dependence of the cross sections in the high energy range and a single point in the thermal energy range.\textsuperscript{18,79} As expected, these parameters reproduce the cross sections in the high energy range; but, the results disagree with the collision energy dependence of the ionization cross section in the thermal energy range found by Pesnelle et al., Illenberger et al., and the present work.
APPENDIX
CORRECTIONS FOR THERMAL MOTION OF TARGET GAS

The random motion of the target gas in the collision chamber necessitates correction of both the relative collision velocity and the effective total ionization cross section measured experimentally. The velocity correction for collisions between beam atoms with a well defined velocity and target gases having a Maxwellian distribution of velocities has been treated by Kennard. The average relative velocity, \( \bar{v}_r \), for a beam moving with velocity \( v \) through a homogeneous Maxwellian gas at absolute temperature, \( T \), is given by

\[
\bar{v}_r = \frac{1}{\sqrt{\pi} \beta} \left[ \exp \left( -x^2 \right) + (2x + \frac{1}{x}) \frac{\sqrt{\pi}}{2} \phi(x) \right]
\]

where

\[
\beta = \left( \frac{m}{2kT} \right)^{\frac{1}{2}}, \quad x = v \left( \frac{m}{2kT} \right)^{\frac{1}{2}}, \quad \phi(x) = \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp (-t^2) dt
\]

and \( m \) = mass of a single target atom. Values for the error function \( \phi(x) \) have been tabulated by Abramowitz and Stegun.

The most probable velocity of argon gas atoms at \( T = 297^\circ K \) is \( v_m = (2kT/m)^{\frac{1}{2}} = 35.161 \text{ cm/sec} \) and \( \beta = (m/2kT)^{\frac{1}{2}} = 2.8441 \times 10^{-5} \text{ sec/cm} \). Since the beam velocities used in this experiment are much greater than the velocities of the argon target atoms, the expression for the average relative velocity can be simplified to

\[
102
\]
\[ \bar{v}_r = \frac{1}{\sqrt{\pi} \beta} \left[ \exp \left( -\alpha^2 \right) + \frac{\sqrt{\pi}}{2} \left( 2\alpha + \frac{1}{\alpha} \right) \right] \]

where \( \Phi(x) = 1 \). Very little error results from this simplification for even the lowest metastable helium beam velocity of \( v = 73,720 \text{ cm/sec} \) where \( \alpha = 2.0967 \) and \( \Phi(2.0967) = 0.995 \). The average relative velocity, \( \bar{v}_r \), calculated from the full expression is \( 8.194 \times 10^4 \text{ cm/sec} \) and from the simplified expression is \( 8.235 \times 10^4 \text{ cm/sec} \), and the % error is about 0.5.

The thermal motion of the target gas and the velocity dispersion of the beam also affect the measured cross section. Thus, corrections to the effective total ionization cross section \( Q_{\text{eff}} \) obtained by experiment must be made for averaging over the two velocity distributions. Lang, Lilenfeld, and Kinsey have suggested the following correction procedure. The method deals explicitly with a spherically symmetric interaction potential where the target gas is contained in a collision cell. The correction procedure is based on the product

\[ v Q_{\text{eff}} = \kappa_{\text{eff}} \]

where \( v \) is the beam velocity, \( Q_{\text{eff}} \) is the experimentally measured cross section, and the rate coefficient \( \kappa_{\text{eff}} \) is regarded as determined at the average relative velocity \( \bar{v}_r \).

Correction factors \( f(s,x) \) have been tabulated by Lang et al., which relate \( \kappa_{\text{eff}} \) to the product of the average relative velocity and the true cross section \( \sigma(\bar{v}_r) \) by the expression

\[ \kappa_{\text{eff}} = f(s,x) \bar{v}_r \sigma(\bar{v}_r) \]

The variable \( x \) in \( f(s,x) \) is the ratio of the beam velocity
v to the most probable velocity \( v_m \) of the target gas. The variable \( s \) is determined by the behavior of the interaction potential with internuclear separation as \( V(R) \sim R^{-s} \). The true cross section may be determined from the expression

\[
\sigma(\tilde{v}_r) = \frac{1}{f(s,x)} \frac{v}{\tilde{v}_r} Q_{\text{eff}}
\]

For the present work with \( \text{He}^\ast(2^3S,2^1S)-\text{Ar} \), the range \( 8 < s < 12 \) is probably realistic, and \( x \) changes from 2.097 to 7.863 for beam velocities of 73,720 cm/sec to 276,450 cm/sec. The correction factor \( f(s,x) \) can be regarded as unity since in the worst possible case \( f(8,2.1) \approx 0.992 \). The correction factor is closer to unity for a more realistic choice of variables, for example \( f(12,5.0) \approx 0.9986 \). Thus, the form

\[
\sigma(\tilde{v}_r) = \frac{v}{\tilde{v}_r} Q_{\text{eff}}
\]

is appropriate for correction of the present data. The cross section for the lowest velocity used in this experiment is corrected by the factor \( v/\tilde{v}_r = 0.895 \). The factor becomes progressively smaller with higher beam velocity where for the highest beam velocity used in this experiment \( v/\tilde{v}_r = 0.992 \).
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Chemistry

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