An Experimental Study of Ionising Collisions
Between Metastable Helium and Various
Atoms and Molecules

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Abstract

This thesis presents a study of chemi-ionisation reactions involving the two metastable states of helium He(2^3S) and He(2^1S) with Ar, CO\textsubscript{2}, N\textsubscript{2}O, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and NH\textsubscript{3}, also of He(2^3S) with SF\textsubscript{6}. The experimental techniques developed to measure both the relative total ionisation cross sections and the branching ratios for the different reactions is described, and a theoretical analysis is carried out in the case of collisions between helium atoms in both metastable states and argon.

The relative variation of total ionisation cross section with velocity is carried out using the time-of-flight technique in a computer controlled experiment. The metastable atom source produces a wide velocity distribution (1 - 20 kms\textsuperscript{-1} or 0.02 - 8 eV). A newly-designed quench lamp enables the removal of fast He(2^1S) metastable atoms from the beam. In every case except that of Ar + He(2^1S) in the range 1 - 5 kms\textsuperscript{-1} measurements with helium atoms in the He(2^1S) state are the first to be made. The measurements made for He(2^3S) with N\textsubscript{2}O and SF\textsubscript{6} are also completely new. To make measurements using He(2^1S) the quench lamp is pulsed giving time-of-flight distributions with and without He(2^1S) information. Measurements with only the He(2^3S) state are subtracted from measurements with both states in order to determine the contribution from the He(2^1S) state. The computer control is essential to store this information simultaneously, but the process is by necessity slow and involves an appreciable amount of time in which data is not being recorded.

To measure branching ratios for the different chemi-ionisation reactions as a function of collision velocity, a time-of-flight mass spectrometer is used to separate the different product ions. The pulsed quench lamp is used again in conjunction with computer control to record metastable atom time-of-flight distributions and ionisation time-of-flight spectra so that the variation of the ion branches with velocity can be seen. As with the relative ionisation cross sections, the He(2^1S) data is new except in the case of argon. The He(2^3S) data is also new in the case of N\textsubscript{2}O and SF\textsubscript{6}.

Various interaction potentials for Ar+He(2^3S) and Ar+He(2^1S) have been used to calculate theoretical ionisation cross sections for comparison with the present experimental data. The potentials have been modified to find the best fit to the present experimental data, and the general applicability of the new potentials has been assessed.
For my loving and supportive parents
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Chapter 1
Introduction

1.1 Background to the present research

Ionisation by metastable helium atoms is an important process both in natural and man-made plasmas. Helium is a major constituent of many planetary and stellar atmospheres and is present in the interstellar medium (Rees et al. 1968). The metastable levels present in helium are important in the production of a population inversion in some lasers, for example He-Ne and He-Cd (Webb 1976). Also metastable atoms give rise to energy loss in experimental fusion reactors because they cannot be contained by magnetic fields.

The interaction of metastable helium with many gases has been studied experimentally for many years (chapter 2) and the theoretical approach has been developed to apply to the case of argon (chapters 3 and 6).

The two electrons of helium combine according to the LS-coupling rule and so the 1s2s lowest excited state gives rise to 2^1S and a 2^3S atomic states. These singlet and triplet states are both metastable; the transition to the 1^1S ground state is optically forbidden by the parity change rule and the ΔL=±1 selection rule. In addition to this the 2^3S state is also forbidden to decay by the ΔS=0 rule. The lifetimes of the 2^3S and 2^1S states are $9 \times 10^3$ and $2 \times 10^2$ s respectively as measured by Woodsworth and Moos (1975).

Because of the large excitation energies of the two metastable states, 19.8 eV for He(2^3S) and 20.6 eV for He(2^1S), collisions with atoms and molecules may lead to ionisation of the target at any collision velocity. In most cases more than one ionisation process is possible:

\[
\begin{align*}
\text{He}^* + AB &\rightarrow \text{He} + AB^+ + e^- & \text{Penning ionisation} \\
\text{He}^* + AB &\rightarrow \text{HeAB}^+ + e^- & \text{Associative ionisation} \\
\text{He}^* + AB &\rightarrow \text{He} + A^+ + B + e^- & \text{Dissociative ionisation} \\
\text{or} &\rightarrow \text{He} + B^+ + A + e^- \\
\text{He}^* + AB &\rightarrow \text{HeA}^+ + B + e^- & \text{Associative-dissociative ionisation} \\
\text{or} &\rightarrow \text{HeB}^+ + A + e^- \\
\end{align*}
\]

where A and B are fragments of a molecule and may be atoms, or molecules in their own
right. Any combination of these processes may be available for a given target; collectively
the processes are known as chemi-ionisation.

Penning (1927) observed the reaction (Equation 1.1) in his studies of the effects of small
amounts of impurities in rare gas discharges and in 1934 he published the first indirect cross
section measurement. However it was not until 1966 that the study of chemi-ionisation
became precise and widespread, with the first experimental measurements of ejected
electron energy distributions by Čermáč. The theory of chemi-ionisation was developed by
Nakamura (1969) and Miller (1970), (chapter 2) and a large number of absolute ionisation
cross sections were measured by Schmeltekopf and Fehsenfeld (1970) using the flowing
afterglow technique (chapter 3). This prompted the development of a wide range of beam
techniques in the following years to measure absolute and relative total ionisation cross
sections and differential elastic cross sections. The techniques of West et al (1975),
Pesnelle et al (1975), Brutschy and Haberland (1977) and Jerram (1985) are described in
chapter 2. The results of these experiments show that total ionisation cross sections can be
strongly dependent on collision velocity, and some large differences may occur in the triplet
and singlet cross sections. Far more work has been carried out with the triplet than with
the singlet metastable atoms.

1.2 Present aims and thesis content

A detailed description of theoretical and experimental advances in the field of chemi-
ionisation is given in chapters 2 and 3 respectively. The present work described in chapter
4 is intended to follow on directly from that described above, particularly that of Jerram
(1985), and to extend it by making relative total ionisation cross section measurements over
a wide velocity range (1 - 20 km s\(^{-1}\)) for both singlet and triplet metastable atoms.

Both He(2^1S) and He(2^3S) are used as the reagent in collision with various atoms and
molecules (Ar, CO\(_2\), N\(_2\)O, CH\(_4\), C\(_2\)H\(_2\), and NH\(_3\)). In the case of SF\(_6\) only enough data could
be accumulated for He(2^3S) data to be recorded.

These targets have been chosen for a number of reasons: Ar because it has been extensively
studied theoretically and will therefore allow measured ionisation cross sections to be
compared to those calculated theoretically; carbon dioxide (CO\(_2\)), nitrous oxide (N\(_2\)O),
methane (CH\(_4\)) and ammonia (NH\(_3\)) are all present in the atmosphere of the earth and other
planets; sulphur hexaphluoride (SF₆) is much used in the electrical industry; and acetylene (C₂H₂) is a combustible fuel. They are expected to interact with helium in a number of ways. CO₂, N₂O and C₂H₂ are expected to show a weak interaction, because of their intermediate polarisability. CH₄ and SF₆ are symmetrical molecules and should show argon-like repulsive interactions. Ammonia is very reactive and should show a much stronger interaction than any of the other molecules.

With the singlet state, except for the case of argon, no previous relative measurements have been made. In the triplet case previous measurements have been made (except in the cases of N₂O and SF₆), but the collision velocity range has been extended in the present experiment.

In addition to the total ionisation cross sections measured, the branching ratios for the reactions shown in Equation 1.1-1.4 are measured over a wide velocity range (1-14kms⁻¹), again using both singlet and triplet metastable species.

In chapter 5 the results are tabulated and presented graphically with relative total ionisation cross sections normalised to absolute measurements. Comparisons with other experimental work are made where possible, and conclusions about the interaction potential characteristics for each target species are made.

In chapter 6 the classical approach described in chapter 2 is used with theoretical interaction potentials derived by several authors to calculate total ionisation cross sections for Ar + He(2¹S) and Ar + He(2³S). These cross sections are compared with the present measured ionisation cross sections and the interaction potentials adjusted to give the best fit. The interaction potentials are examined to find which best represents the present experimental results. The extent to which changes to the potentials has reduced their relevance to differential data, for which they were originally constructed, is also assessed. The approximate cross section technique of Illenberger and Niehaus (1975) is also used to examine all measured ionisation cross sections at intermediate collision velocities.

In chapter 7 the results are summarised, conclusions are drawn from the present work, and ideas are put forward for improvements to the present experiment and future research.
Chapter 2
Theoretical approach to Penning ionisation

2.1 Introduction

A metastable rare gas atom has a more open electronic structure than a ground state atom and therefore its electron orbitals can overlap and interact with those of a target particle, causing ionisation. The ionisation cross section for a target particle with a metastable atom is affected by their separations and the time taken in the collision. Both of these factors are determined by the potential experienced by the particles as they approach and as they move apart. To calculate a theoretical Penning ionisation cross section, therefore, it is necessary to have a knowledge of these potentials.

2.2 The two potential model

The two potential curve model developed by Herman and Čermák (1966) is the basis of all subsequent theoretical treatments such as Katsuura (1965), Mori (1966 and 1969), Nakamura (1969, 71, 75 and 76), Hickman et al. (1977a and b), and most importantly Miller (1970, 72 and 77) whose approach is closely followed later in the chapter.

Figure 2.1 shows schematically the two potential curve model for ionisation. Before ionisation the reactant particles X* and AB form an excited quasi-molecule XAB* and after form an ionised quasi-molecule XAB+. Penning ionisation is caused by an autoionising transition between two adiabatic potential curves V*(R) and V+(R), shown in the following reaction

\[
X^* + AB \rightarrow [X^*AB] \rightarrow [XAB^+e^-] \rightarrow X+AB^+ + e^- \\
V^*(R) \rightarrow V^+(R)
\]  

(2.1)

The probability of ionisation per unit time \(P(R)\) is related to the 'energy width' \(\Gamma(R)\) of \(V^*(R)\) by

\[
P(R) = \frac{\Gamma(R)}{\hbar}
\]

(2.2)

\(\Gamma(R)\) and \(V^*(R)\) combine to form an initial state complex or optical potential \(W^*(R)\)

16
Energy (arb units)

\[ V^*(R) - V^+(R) = \varepsilon \]

Figure 2.1 Two potential model of chemi-ionisation
given by

$$W^*(R) = V^*(R) - \frac{1}{2} \Gamma(R)$$  (2.3)

The energy of the particles before collision is given in Figure 2.1 by the upper horizontal line giving a relative kinetic energy of $E_0$. The energy after collision is given by the lower horizontal line with a relative kinetic energy of $E_0'$. Ionisation takes place by a vertical transition obeying the Born-Oppenheimer approximation, which is to say that the transition is instant with internuclear separation and kinetic energy equal immediately before and after ionisation. The values of $E_0$ and $E_0'$ may be different because of the possibility of conversion of internal energy to translational energy. The total energy $E$ is conserved giving the relation

$$E = V^*(R) + E_0 = V^*(R) + E_0' + \epsilon$$  (2.4)

where $\epsilon$, the electron energy, is the difference between the energy of the initial and final quasi-molecular states at a fixed internuclear distance (the Frank-Condon principle). The final energy of the collision particles can be derived from this expression to give

$$E_0' = E_0 + [V^*(\infty) - V^+(\infty)] - \epsilon$$  (2.5)

From this relation it can be seen that if the difference in the asymptotic potentials plus the initial energy is less than the electron energy $\epsilon$, then the final energy $E_0'$ is negative and a bound state is formed. This is known as associative ionisation. If $E_0'$ is greater than zero then the particles are not bound together and Penning ionisation occurs. Associative ionisation can only occur if the potential $V^+(R)$ contains a well deep enough to support a bound state, for example in the case of the interaction of argon with metastable helium where both species of ion are formed. The branching ratio has been measured in this work and also by Jerram (1985) and Pesnelle et al (1975). Because the electron energy is fixed as a consequence of the Frank-Condon principle and the asymptotic potentials are also fixed, it can be seen from Equation 2.5 that the amount of associative ionisation must decrease with increasing initial energy $E_0$. Above a certain energy, associative ionisation does not occur. This pattern is observed in the experiments carried out in this work. In
the case of He(2^3S) + Ar no associative ionisation is observed above a kinetic energy of 0.7eV and in the case of He(2^1S) + Ar none is observed above 0.2 eV, in good agreement with the experiment of Pesnelle et al (1975).

The Frank-Condon principle is represented clearly by

\[ e = V^*(R_i) - V^*(R_i) \]  

(2.6)

where \( R_i \) is the internuclear separation at ionisation. The important consequence of this is that the energy of an ejected electron gives useful information about the two quasi-molecular potentials. The study of the ejected electron was originated by Čermák (1966 a,b and c). Subsequent Penning ionisation electron spectroscopy or PIES has been carried out by many experimenters notably by Niehaus and his collaborators (Fuchs and Niehaus (1968), Hotop and Niehaus (1969a,b) Hotop et al (1969), Niehaus (1973). Figure 2.1 shows graphically, from a plot of electron energy versus internuclear separation, and an electron energy distribution curve of the type derived by the technique of PIES, the relative proportion of Penning ionisation to associative ionisation (shaded region) for the system. Also shown is \( e_0 \) the energy of an electron ejected at large separation (effectively no collision takes place and \( E_0 = E_0' \)). This value is equal to the energy of an electron ejected due to photoionisation by a photon of energy equal to the metastable excitation energy of the projectile particle.

In the two potential model for Penning ionisation the origin of the ejected electron is not significant. The electron may come from a direct process where the target electron is ejected, or indirectly in which it is ejected from the projectile. If He(2^1S) is the projectile both methods of ionisation are possible from the Wigner spin conservation rule, but if He(2^3S) is the projectile then only the indirect method is allowed. Hotop and Niehaus (1969) first suggested that the ejected electron originates from the projectile even if the direct method is allowed, a proposal which is widely accepted now. Equation 2.7 shows the indirect process which involves electron exchange.

\[ \text{He}^*(2^3S) [\text{11}] + \text{AB}[\text{11}] \rightarrow \text{He}(2^1S) [\text{11}] + \text{AB}^*[\text{1}] + e^-[\text{1}] \]  

(2.7)

An electron from the outer shell of the target atom AB is exchanged into the incomplete
Is shell of the helium atom filling the shell so that the electron in the 2s shell is ejected. The process leaves the helium atom in the ground state and the target molecule ionised. Experiments with spin polarised He(2\textsuperscript{3}S) (such as done by Keliher et al (1975a and b) and Hodge et al (1979)) have confirmed this process.

2.3 Limitations of the two potential model

The two potential model is too simplistic for describing anything but the most simple cases, such as collisions between metastable helium and atoms such as argon and simple molecules. The theory can only describe collisions between metastable atoms and ground state atoms. It is also essential that the metastable energy of the projectile is greater than the ionisation potential of the target. This is the case for most atoms and molecules interacting with metastable helium, which has a large metastable energy (19.8 eV for He(2\textsuperscript{3}S) and 20.6 eV for He(2\textsuperscript{1}S)). Neon has an ionisation energy (21.6 eV) above the metastable energy of both helium species and is thus not ionised by thermal energy helium metastable atoms.

In order for the Born-Oppenheimer approximation to be applicable, the collision energy must be small. This allows two adiabatic potential energy curves to describe the two states in the system. The two curves must be isolated allowing no transitions to other adiabatic potentials. This is a big difficulty in the case of molecular targets for which there will in fact be many adiabatic curves such as those which describe the formation of ground state helium and excited state target species (AB\textsuperscript{+}). In the case of molecular targets there is also the possibility of vibrational, rotational and chemical reactions such as dissociative ionisation and associative-dissociative ionisation taking place. In addition the non-spherical shapes of most molecules means that the potential experienced by the projectile particle is dependent on the orientation of the target molecule. The complex interaction potential must therefore be replaced by a potential surface. The hydrogen molecule has been considered by several theoreticians, notably Cohen and Lane (1976) who have produced a theoretical potential surface, but their calculated total ionisation cross section is in poor agreement with the experimental work of Jerram and Smith (1985).

2.4 Calculation of classical cross sections

In order to calculate the total ionisation cross section as a function of collision energy it is first necessary to devise a theoretical interaction potential. As has been stated above, this
is a particularly difficult process for a molecular target, but can be achieved considerably more easily for a simple target such as argon because the potential is spherically symmetrical. Chapter 6, in which some theoretical cross sections are calculated for the He* + Ar system, describes in detail the construction of such spherically symmetric potentials from the experimental study of differential scattering of helium from argon. However, it is not necessary to have constructed an interaction potential in order to derive an expression for the total ionisation cross section in terms of the interaction energy and a hypothetical potential. The technique used by Miller (1970) is described below.

Miller (1970) has derived expressions for the total ionisation cross sections using classical, semiclassical and quantum mechanical treatments. His classical treatment starts from the assumption of a spherically symmetrical interaction potential, the radial motion can be treated separately at each value of angular momentum \( \ell \hbar \). It is necessary to find an expression for \( P_\ell(R) \) in terms of \( V^*(R) \) and \( \Gamma(R) \), where \( P_\ell(R)dR \) is the probability density function of leakage to the continuum occurring in the region of internuclear separation between \( R \) and \( R + dR \). The value of the function \( P_\ell(R) \) at \( R \) is different for the particles moving together and moving apart. \( P_\ell(R) \) is therefore defined as either \( P_\ell^{\text{in}} \) or \( P_\ell^{\text{out}} \). The expression derived by Miller (1970) is

\[
P_\ell^{\text{in}}(R) \ dR = \left[ 1 - \frac{\int R \Gamma(R) \ dR}{\hbar V_\ell(R)} \right] \frac{\Gamma(R)}{\hbar V_\ell(R)} \ dR \tag{2.8}
\]

The expression in brackets represents the probability that ionisation has not taken place in the region between \( R \) and infinity. The remainder of the equation is simply Equation 2.2, the probability of ionisation at \( R \), multiplied by the time spent in the interval \( R \) to \( R + dR \) given by \( dR/V_\ell(R) \). The radial velocity \( V_\ell(R) \) is given by

\[
V_\ell(R) = V_0 \left[ 1 - \frac{V^*(R)}{E_0} - \frac{1}{2\mu E_0 R^2} \right]^{\frac{1}{2}} \tag{2.9}
\]

where \( V_0 \) is the collision velocity, \( E_0 \) is the asymptotic collision energy and \( \mu \) is the reduced mass of the system. In order to solve Equation 2.8 it must first be turned into a differential equation

\[
P_\ell^{\text{in}}(R) = \frac{\Gamma(R)}{\hbar V_\ell(R)} \exp\left[ -\int_R^{\infty} \frac{\Gamma(R')}{\hbar V_\ell(R')} \ dR' \right] \tag{2.10}
\]
Using the same principle an expression for \( P_1^{\text{out}} \) is derived

\[
P_1^{\text{out}}(R) \, dR = \left[ 1 - \int_{R_0}^{\infty} P_1^{\text{in}}(R') \, dR' - \int_{R_0}^{R} P_1^{\text{out}}(R') \, dR' \right] \frac{\Gamma(R)}{\hbar v_1(R)} \, dR \quad (2.11)
\]

where \( R_0 \) is the classical turning point, the largest value of \( R \) for which \( v_1(R) = 0 \). The brackets now contain the probability that ionisation has not taken place on the inward path from infinity to \( R_0 \) or on the outward path from \( R_0 \) to \( R \). Equation 2.11 is solved to give

\[
P_1^{\text{out}}(R) = \frac{\Gamma(R)}{\hbar v_1(R)} \exp \left[ -\int_{R_0}^{R} \frac{\Gamma(R')}{\hbar v_1(R')} \, dR' - \int_{R_0}^{R} \frac{\Gamma(R')}{\hbar v_1(R')} \, dR' \right] \quad (2.12)
\]

The total probability of ionisation occurring on the inward and outward paths is given by the following expressions

\[
\int_{R_0}^{\infty} P_1^{\text{in}}(R) \, dR = 1 - \exp \left[ -\int_{R_0}^{\infty} \frac{\Gamma(R)}{\hbar v_1(R)} \, dR \right] \quad (2.13)
\]

\[
\int_{R_0}^{\infty} P_1^{\text{out}}(R) \, dR = \exp \left[ -\int_{R_0}^{\infty} \frac{\Gamma(R)}{\hbar v_1(R)} \, dR \right] \left[ 1 - \exp \left( \int_{R_0}^{R} \frac{\Gamma(R)}{\hbar v_1(R)} \, dR \right) \right] \quad (2.14)
\]

The total probability of ionisation occurring at separation \( R \) is

\[
P_1 = P_1^{\text{in}}(R) + P_1^{\text{out}}(R) \quad (2.15)
\]

which is the sum of the probabilities of ionisation at \( R \) on the inward and outward paths, and the total probability of ionisation during the collision \( P_1 \) is

\[
P_1 = \int_{R_0}^{\infty} P_1(R) \, dR \quad (2.16)
\]
The final result then is
\[
P_1 = 1 - \exp \left[ -2 \int_{k_0}^{\infty} \frac{\Gamma(R)}{\hbar V_1(R)} dR \right] \tag{2.17}
\]
which is the sum of 2.13 and 2.14. To determine the total cross section at velocity \( v_0 \) the probability of ionisation must be summed over all \( l \) to give
\[
\sigma_0^{\text{tot}} = \left( \frac{\pi}{k_0^2} \right) \sum_l (2l+1) P_1 \tag{2.18}
\]
where \( k_0 \) is given by
\[
k_0 = \left[ \frac{2\mu [E_0 - v_0(\infty)]}{\hbar^2} \right]^{\frac{1}{2}} \tag{2.19}
\]
The dependence of \( k_0 \) on \( E_0 \) is very important because in the low energy region it causes the cross section to decrease rapidly with increasing energy (Burdensky et al 1981). The cross section begins to increase again above 20 meV because collisions penetrate to lower internuclear separation. Thus \( R_0 \) decreases and so the probability of ionisation increases. The probability of ionisation saturates eventually and the cross section begins to decline again. This behaviour is observed experimentally for many systems (chapter 5).

2.5 Refinements to classical theory

Miller (1970) has derived a semi-classical expression for the total ionisation cross section. The major difference between the classical and semi-classical approaches is the replacement of probabilities with probability amplitudes, that is to say the magnitude of the probability squared. The total ionisation cross section in terms of the S matrix, which possesses a phase as well as a probability, is
\[
\sigma_0^{\text{tot}} = \left( \frac{\pi}{k_0^2} \right) \sum_l (2l+1) |S_l|^2 \tag{2.20}
\]
In this semi-classical case interference terms are present in the summation. These have very little effect on the total ionisation cross section at the collision energies in the present experiment. Because of its relative simplicity the classical approach is used in chapter 6 to calculate the total ionisation cross sections for argon with both metastable species of
helium. Burdensky et al (1981) have made measurements below 1 meV, a region in which resonances are predicted by the semi-classical calculations of Brutschy et al (1976). The semi-classical approach is very useful in calculating the differential cross sections, either for elastic or inelastic scattering. The differential cross section is calculated from the modulus squared of the scattering amplitude given by

\[ \sigma(\theta) = |f(\theta)|^2; \quad f(\theta) = (2ik)^{-1} \sum_j (2l+1) S_1 P_1(\cos\theta) \]  

The quantum mechanical approach is unnecessary in the present experiment for the same reason as the semi-classical approach, but is useful (as is the semi-classical approach) for the calculation of differential cross sections and to compare with the classical calculations of low energy total ionisation cross sections.

2.6 The simplified analytical theory

Illenberger and Niehaus (1974) have identified an energy region in the ionisation cross section in which certain approximations may be made to Equation 2.17. There are two conditions for the applicability of these approximations. Firstly the collision energy \( E_0 > \Delta^* \) where \( \Delta^* \) is the well depth of \( V^* \), the real part of the potential curve. Secondly \( P_I < < 1 \) where \( P_I \) is the ionisation efficiency per collision. The first condition implies that only collisions which penetrate to the repulsive region of the interaction need be considered. The second condition ensures that collisions in the region where \( P_I \) and the total ionisation cross section saturates are not included. The energy range implied by these conditions is between 20 meV and 100 meV.

The major simplification made is the replacement of the angular momentum \( l \) by a continuous function including the impact parameter \( b \) and \( k_0 \) previously defined in Equation 2.19

\[ bk_0 = l + \frac{1}{2} \]  

(2.22)
With \( P(b) \) small, Equation 2.17 can be expanded to give

\[
P(b) = 2 \int_{k_0}^\infty \frac{\Gamma(R)}{\hbar \nu(D, R)} \, dR \tag{2.23}
\]

Now the total ionisation cross section defined in Equation 2.18 can also be turned into an integral:

\[
\sigma(E) = 2\pi \int_0^\infty P(b) b \, db \tag{2.24}
\]

Substituting \( P(b) \) into Equation 2.24 and integrating over \( b \) leaves an integral over \( R \) only:

\[
\sigma(E) = \int_{k_0}^\infty \frac{4\pi \nu^2 \Gamma(R)}{\sqrt{2 \mu (E_0 - V^*(R))}} \, dR \tag{2.25}
\]

\( V^* \) is simplified to the same functional form as \( \Gamma \) (Equation 2.26) because only the repulsive region is used in this analysis.

\[
V^*(R) = C \exp\left(-\frac{R}{D}\right) \quad \Gamma(R) = A \exp\left(-\frac{R}{B}\right) \tag{2.26}
\]

The integration can now be performed to give

\[
\sigma(E_0) = 2A \left( \frac{\mu}{2B} \right)^{1/2} (BD\pi)^{3/2} \left( \ln \frac{E_0}{C} \right)^2 \left( \frac{E_0}{C} \right)^{D/2 - 1/2} \tag{2.27}
\]

It is now possible for a log-log plot of cross section against energy to yield a gradient value approximately equal to \( D/B-1/2 \). The aim of this treatment is simply to gain information about the shape of the coupling width \( \Gamma \) from the already deduced shape of the real part of the interaction potential. In chapter 6 this simple theory will be tested using the present experimental data.
Chapter 3
Experiments with metastable helium

3.1 Introduction

In this section a brief review of the more important and relevant experiments performed up to the present is given. The merits of the various methods are compared, as are their problems.

3.2 Stationary afterglow experiments

The use of gaseous discharges is the oldest method of gaining information about the ionisation by metastable atoms. Observations have usually been made of the afterglow of the discharge. The experiments are of two main types, stationary and flowing afterglow studies.

The stationary afterglow method is simple in principle. A discharge is struck momentarily in a mixture of a rare gas and a reagent gas, and the concentrations of excited atoms in the rare gas is monitored as they decay. By a detailed analysis of the continuity equation which describes this decay, the rate constant $k$ for different reactions can be determined. The cross section $\sigma$ is related to $k$ by the following relation

$$ k = \int_0^\infty \nu \sigma (\nu) f(\nu) \, d\nu \quad (3.1) $$

where $\nu$ is the relative velocity, and $f(\nu)$ is the velocity distribution function at $\nu$.

The concentration of metastables is generally measured by illuminating the gas with a resonance lamp and observing the absorption of line radiation by transitions of known oscillator strength. For example Benton et al (1962) observed the concentration of He$(2^3S)$ and He$(2^1S)$ by monitoring the $3^3P-2^3S$ (388nm) and the $3^1P-2^1S$ (501.6nm) lines respectively.
The major problems with these experiments are in determining absolutely the quantity of reagent gas present in the plasma, the quantity is usually small and measurement is further complicated by the presence of impurities, which outgas from the walls of the container. The importance of this second factor is dependent on the pressure at which the experiments are performed. Pulsed electrolysis experiments, for example, in which the plasma is produced by electron bombardment, are performed at atmospheric pressure. In these experiments the problems are reduced by the high pressure but errors may occur because second and third order reactions may become important.

3.3 Flowing afterglow experiments

Developed by Ferguson, Schmeltekopf and Fehsenfeld (1969) primarily for atmospheric ion-molecule reaction studies and widely applied by Schmeltekopf and Fehsenfeld (1970) the flowing afterglow method is a development which has allowed the total quenching constants for metastable helium by many reagent gases to be measured. Some of the inherent problems with the stationary afterglow system are solved by striking the discharge in a fast-moving gas.

![Flowing afterglow apparatus of Schmeltekopf and Fehsenfeld (1970)](image)

Figure 3.1 Flowing afterglow apparatus of Schmeltekopf and Fehsenfeld (1970)

Figure 3.1 shows the system described by Schmeltekopf and Fehsenfeld (1970). The discharge is struck in a gas at 0.4 torr and with a velocity of $8 \times 10^3$ cm s$^{-1}$. The flow rate is much greater than the rate of outgassing and so there is no problem associated with contamination of the buffer gas, as in the stationary afterglow method. An electron gun
is used to produce a discharge, to produce the triplet state an acceleration of 100eV at 2mA
is used. This produces strong ionisation and results in the conversion of He($2^1S$) to He($2^3S$)
by superelastic collisions with free electrons. In order to produce singlet metastables the
electron gun is operated at an acceleration lower than the ionisation potential of helium, so
that excess free electrons are not present. Metastables are produced in the discharge
region and are transported along the tube. The reagent is added further along the tube, and
because of this separation from the discharge, the reagent is in the ground state.

Further along the tube the concentrations of metastables can be measured by a variety of
methods. In the experiment shown neon is added to the gas flow. The neon is immediately
excited into different radiating states. Depending on which metastable does the exciting
either 568.98 nm (from Ne+He($2^1S$)), or 703.24nm, (from Ne+He($2^3S$)) radiation is
emitted. The absolute determination of the intensity of these lines allows the concentration
of both metastable species to be measured.

The quenching constant $k$ can be determined from the following relation.

$$\ln(X^*) = \ln(X^*_0) - D \cdot \frac{Bk I}{V} Y$$ (3.2)

in this $X^*$ is the concentration of metastables at the point of detection, $X^*_0$ is the initial
concentration, $D$ is the coefficient of diffusion for metastables to the tube walls, $l$ is the
distance between the point at which the reagent is added and the detection region, $Y$ is the
reagent concentration, and $V$ is the mean buffer gas velocity. The constant $B$ is pressure
dependant and corrects for the variation of buffer gas velocity across the tube diameter.
By varying $Y$ a plot of $\ln(X^*)$ against $Y$ will be a straight line with a gradient equal to
$BkI/V$.

The problems with this method are firstly the difficulty in determining the parameters $D$,
$B$ and the effective length $l$. $B$ and $l$ are dependent on the individual flow characteristics
of each apparatus. The other disadvantages of the flowing afterglow method are that large
amounts of expensive gas are used and that secondary reactions may distort the results.
Nevertheless most of these difficulties can be largely overcome and much useful data has
been obtained.
3.4 Beam experiments

The major advantage of beam experiments over the flowing afterglow studies is the ability to study reactions individually and in more detail. It is possible to measure the ionisation cross section $\sigma$ in Equation 3.1 at a single velocity, rather than the quenching rate constant $k$ which is integrated over all velocities. Both the ejected electrons and the positive ions are available for study. It is therefore possible to measure the ionisation cross sections for associative and dissociative reactions as well as examining the Penning ionisation electron spectrum. In addition, it is possible to measure the angular distribution of scattered metastable atoms and product ions.

Beam experiments are of two types, gas cell and crossed beam arrangements. Gas cell experiments are most useful for making absolute measurements of ionisation cross sections. Crossed beam apparatuses are more flexible but are less capable of making absolute measurements.

3.4.1 Gas cell experiments

The gas cell technique was developed by Sholette and Muschlitz (1962) and was the first technique developed to measure the absolute total ionisation cross section of rare gases by metastable helium. The technique has been further developed by many experimenters including several in the present author’s laboratory such as Dunning and Smith (1971) and Jerram and Smith (1985), whose experimental set-up is shown in Figure 3.2.

Jerram and Smith’s apparatus is as follows. The metastable beam source is a constricted-arc hot-cathode type designed by Trujillo (1975) with a wide velocity output (a more detailed analysis of the variety of sources used by experimenters is presented in chapter 4). The velocity selector designed by Trujillo (1975) is used to produce a metastable atom beam of variable velocity. A helical quench lamp of the Hotop et al (1969) type is used to remove singlet metastables from the beam (see chapter 4.3).

The gas cell, shown in some detail in Figure 3.2, is a sophisticated detector consisting of an outer earthed box and an inner box which can be biased positively or negatively and connected to either the slats or grid. Gas is admitted to the cell and the pressure carefully monitored by a calibrated Pirani gauge. Currents due to the metastable flux $J$ are measured.
at the monitor grid and currents due to positive ions $I_g$ are measured at the fine grid. The electron current $I_s$, due to ionisation of the reagent gas and the emission of secondary electrons from the back face of the gas cell is measured at the slats. A computer is used to record and average the outputs from two electrodes connected to the monitor grid and slats.

![Diagram of Gas Cell Apparatus](image)

Figure 3.2 Gas cell apparatus of Jerram and Smith (1985)

To determine the absolute ionisation cross section the following relation is used

$$\ln \left( \frac{I_s^- + I_s^+ - 2I_g^+}{I_s^+} \right) = -n\sigma J + \ln (\gamma K)$$

(3.3)

where $I_s^-$ and $I_s^+$ are measured with the box and grid negative or positive respectively.
relative to the slats. With the box and slats positive relative to the grid $I_{g}^{+}$ is measured. The secondary emission coefficient for metastable helium atoms on gold (all surfaces are coated with gold) is $\gamma$. The length of the gas cell is $l$, the number density of reagent gas atoms in the gas cell is $n$ and $K$ is a constant.

The derivation of Equation 3.3, is given by Jerram and Smith (1985) and will not be repeated here. It is clear that a plot of $\ln((I_s^-+I_s^+\cdot2I_g^+)/J)$ against $n$ will be a straight line with gradient $-\sigma l$, so that $\sigma$ can be determined if currents and $n$ and $l$ are known. The number density $n$ is deduced from an absolute measurement of the pressure of the gas in the cell.

The advantage of this method over other gas cell experiments such as Woodard et al (1978) is that it is not necessary to determine $\gamma$. Also the use of slats in place of the grid wires used by Dunning and Smith (1971) eliminates a problem identified by Jerram (1985) of extra ionisation caused by electrons orbiting the grid wires. The biggest problem with the experiment are the small current magnitudes and the necessity to determine the absolute number density of the reagent gas. Also the path length $l$ may be larger than assumed due to elastic scattering, but this effect is likely to be small. Despite the difficulties of the measurements, fewer assumptions and uncertain calculations are necessary than in the afterglow experiments. Nevertheless the earlier flowing afterglow results are generally consistent with the results of Jerram and Smith (1985).

3.4.2 Simple crossed beam experiments

The most adaptable experimental arrangement is one in which the reagent gas is introduced to the metastable beam not in a cell but in the form of a beam. However the results are usually not absolute and have to be normalised, for example to the flowing afterglow rate constants or absolute cross sections as measured by Jerram and Smith (1985). The crossed beam technique was used for the work described in this thesis. The two beams cross at right angles and the ionisation products are separated in a mass spectrometer or detected in total. The remaining metastables may be detected as may those which have been elastically scattered. The electrons produced are also available for study.

The simplest system is that used by West et al (1975) (Figure 3.3) to measure the branching ratios of Penning and dissociative ionisation. No velocity selector is used and so
measurements can only be made over a distribution of collision velocity. This means that

![Diagram of crossed beam apparatus]

Figure 3.3 Crossed beam apparatus of West et al (1975)

the variation of cross section with velocity is not directly measurable. To make absolute measurements is complicated however by the need to know the absolute densities of both the metastable and reagent species in the interaction region. West et al used an ingenious method devised by Dunning, Smith and Stebbings (1971) by which the target beam is chopped, and the difference in the ejected electrons measured by the metastable detector is compared with the change in total ion count rate. From this can be deduced the secondary ejection efficiency $\gamma$ of the metastable detector and thus the density of metastables. The density of reagent gas is found by replacing the metastable beam by an electron beam and measuring the current of ions produced at a collision energy $1 \text{ keV}$ for which the ionisation cross section is well known. This method although original, is quite crude compared to the gas cell method, because it is dependent on small signal changes for the value of $\gamma$ and an assumption of the overlap of the target and electron beams.

3.4.3 Crossed beam experiments incorporating time-of-flight

A much more sophisticated (but not absolute) time-of-flight technique has been developed
by experimenters such as Pesnelle et al (1975), Illenberger and Niehaus (1975), Parr et al (1980), Jerram (1985), and Kroon (1985). These experiments although not absolute can measure the velocity dependence of Penning ionisation cross sections. Figure 3.4 shows the apparatus of Pesnelle et al, in which the metastable beam is chopped by a slotted wheel and pulses of metastable atoms result. Because the beam produces a range of velocities (section 4.5.1), the pulse of metastables spreads out in the drift region and the atoms arrive at the detector at different times. At the moment a pulse of metastables is produced, a start pulse from the photo-diode is fed into a multi-channel analyser, which then begins to record either the detection of metastables or ions in the interaction region. The TOF distributions of ions and metastables are built up over many revolutions of the chopper wheel taking a number of hours. A relative ionisation cross section as a function of velocity is eventually calculated by converting the TOF spectra into velocity spectra and dividing the ion distribution by the metastable distribution. In order to make measurements with the singlet state, TOF spectra are recorded with the quench lamp on and off and a subtraction is made of the triplet distribution from the triplet plus singlet distribution. Thus four distributions must be recorded, each at a different time, in the Pesnelle et al experiment. Similarly if the partial cross sections of individual ion species are to be measured, the mass spectrometer must be used to build up a TOF distribution for each ion species individually.

Figure 3.4 Crossed beam apparatus of Pesnelle et al (1975) incorporating the time-of-flight technique

The disadvantage of this is clearly that any change in the conditions of the experiment between the recording of distributions will result in a systematic error occurring in the results. For example this could be due to the gradual rise in background gas pressure with
time, quite common in crossed beam experiments, or due to gas freezing on a liquid nitrogen trap. This effect would be made worse in the Pesnelle et al experiment because there is no way of determining the origin of an ion detected by the total ion detector.

This latter problem has been overcome by Jerram (1985) by the substitution of the total ion detector by a TOF mass spectrometer. Now it is necessary for a coincidence to occur between the detection of a positive ion and an electron before a count is made, thereby ensuring that only ions produced in the interaction region are recorded (chapter 4.5.3).

Another improvement in the experimental set-up of Jerram is the replacement of the multi-channel analyser by a CAMAC interface unit and an LSI-11 microcomputer. This allows ten ion mass spectra to be recorded simultaneously, each at a different velocity. Similarly, for total cross sections, both the ion and metastable TOF distributions are recorded simultaneously. Because the computer is much slower at recording information than the multi-channel analyser, it is only possible to record one metastable and one ion in each chopper wheel cycle, making the acquisition of data rather slow in this experiment. No experiments were performed by Jerram using the singlet state but a development of his apparatus is used to do so in the work described in chapters 4 and 5 of this thesis.

3.4.4 Crossed beam differential scattering experiments

The apparatus for measuring differential elastic cross sections by Brutschy et al (1976) is shown in Figure 3.5. To provide a velocity-selected beam a supersonic nozzle source is used, as is generally the case in differential experiments. The supersonic nozzle source provides a narrow velocity range which can be varied over a small range by changing the helium gas temperature. The metastable states are induced after the nozzle by an axial electron beam. A fixed detector (not shown) is used with the TOF technique to determine the velocity distribution from the source. As usual a quench lamp is used to remove singlets when necessary, a second lamp has been added to provide adequate quenching at high velocity.

The target beam source is also of the supersonic nozzle type. Two more detectors which are not shown are used one out of the plane of Figure 3.5 at a fixed position to monitor changes in the experimental conditions with time, and the other, which can be moved, to measure the intensity of scattered metastable atoms as a function of angle. A stepping
Figure 3.5 Crossed beam apparatus of Brutschy et al (1976) for measuring elastic scattering cross sections

Figure 3.6 Differential elastic scattering cross sections for Ar + He(2^3S) at several energies
motor and a system of counters is used to record the elastic differential cross section. Figure 3.6 shows the results of a typical experiment using triplet helium and argon, the full curves are calculated from a proposed optical potential developed by the Freiburg group.

3.4.5 Crossed beam Penning-ionisation-electron-spectroscopy experiments

A typical apparatus for observing Penning ionisation electron spectra (PIES) is shown in Figure 3.7 taken from Yencha's review article (1984). The presence of the velocity selector means it is possible to observe the ejected electron energy distribution (EEED) from Penning ionisation as a function of metastable atom velocity. As usual, state selection is performed by a helical quench lamp and Rydberg atoms are removed by the electric field plates. A photon source can be substituted for the metastable beam in order to observe photoelectron peaks. Ejected electrons can pass from the ionisation chamber through a small aperture into an electrostatic energy analyser. Apparatuses of this type have been used successfully by Čermák (1966a,b,c), Hotop et al (1979) and Ohno et al (1983) among others.

![Figure 3.7 Apparatus for performing Penning ionisation electron spectroscopy](image)
Figure 3.8 (Čermák 1976) shows a typical EEED curve for the $^2P_{3/2}$ and $^2P_{1/2}$ ionic fine structure states of argon by the two species of metastable helium and the resonance photons also produced by the source. The positions shown by arrows are those of the energy difference between the metastable energy and the ionisation potential of argon $E_0$. The peaks are displaced by $\Delta E$ the energy shift given by

$$E_e = E_0 + \Delta E$$

where $E_e$ is the ejected electron energy and $E_0$ is the difference in the ionisation potential of the reagent gas and the metastable energy. Important information can be obtained simply from the width of the Penning ion peaks and the magnitude and direction of their shift. In the case of argon the peaks are narrow and slightly positively shifted. The implications of this is that the incoming potential curve $V^*$ is largely repulsive with a well depth much less than the relative kinetic energy of the particles $E_k$. Figure 3.9 (Yencha 1984) shows how ionisation takes place largely at the repulsive wall, a region in which $E_e$ varies only slowly with internuclear separation, and gives rise to narrow Penning peaks. The electron energy is positively shifted because, $E_e$ is greater than $E_0$ at the repulsive wall.

As described in chapter 2, associative ionisation is predicted by the possibility of $E_e$ being greater than the sum $E_0 + E_k$. With $E_0$ and $E_k$ both known, the amount of associative ionisation can be deduced from the relative area under the EEED curve at energy greater than $E_0 + E_k$. This implies that the outgoing potential $V^+$ is not completely repulsive but has a small attractive well.

Other interaction potential systems can also be deduced from their EEED, for instance a strongly attractive incoming potential for which the well depth is much greater than the relative collision energy shown in figure 3.10 (Yencha (1984)). This situation applies in the case of water shown in Figure 3.11, (Čermák and Yencha (1976)) and is signified by a broad energy distribution, a consequence of the wide range of internuclear separations at which ionisation can occur. The peak will be negatively shifted as a result of the well depth.

Many rare gases have been studied in this way. The information gained about the interaction potentials can be compared with the information derived from total ionisation and differential cross section measurements. The advantage of PIES over other techniques is that the properties of the interaction potentials are more readily derived from the experimental results. However, it is also possible to obtain detailed information from the
Figure 3.8 Ejected electron energy distribution for Ar + He$^*$
Čermáck (1976)

Figure 3.9 Potential model for Ar + He$^*$ showing a repulsive wall in the incoming potential and a well depth $E_{W0}$ much smaller than the relative kinetic energy $E_{k}(\alpha)$ of the colliding particles (Yencha 1984)
Figure 3.10 Potential model for $\text{H}_2\text{O} + \text{He}$ showing an attractive potential with $E_{\text{WD}}$ much greater than the relative kinetic energy $E_k(\infty)$ of the colliding particles (Yencha 1984).

Figure 3.11 Ejected electron energy distribution for $\text{H}_2\text{O} + \text{He}$ Čermák and Yencha (1977)
variation of differential and total ionisation cross sections with collision velocity by the construction of theoretical interaction potentials.

This PIES technique continues to be used by workers such as Hotop et al (1979), Munakata et al (1979), and Ohno et al (1983), giving extensive information about the final vibrational and electronic states of the molecular ions formed. Also the technique of Penning ionisation electron-ion coincidence spectroscopy, (PIECOS) has been developed by Münzer (1978) from photo-ionisation work by Brehm and Von Puttkamer (1967) and has allowed the EEDC corresponding to individual dissociative branches to be studied. The technique, which is described in detail by Elland (1979), involves observing a coincidence between a specific positive ion (using a TOF mass spectrometer) and the ejected electron.
Chapter 4
Experimental Method and Apparatus

4.1 Introduction and general experimental arrangement

Figure 4.1 shows schematically the experimental arrangement used to measure both total ionisation cross sections and branching ratios. The basic crossed beam apparatus has been modified by several experimenters over a period of twenty five years.

The experimental setup is housed in four tanks, but only tanks T1, T2, T3 are shown because T4, which contains the target beam source, is located behind the experimental tank. Tank T1 has a hot cathode effusive gas source attached to one end and inside is a chopper wheel which pulses the metastable atom beam. A slotted switch situated below the chopper wheel provides start pulses for the time-of-flight system. In tanks T1, T2, T3 differential pumping is provided and the beam is collimated by the intervening apertures. Tank T2 houses the helical quench lamp used to eliminate He(2$^1S$) metastable atoms. The electrostatic pusher plates in tank T3 remove highly excited states from the beam. The metastable beam and target beam, which is perpendicular to the plane of Figure 4.1, cross in the interaction region. The positive ions and electrons produced are drawn out by an electric field and are detected by the electron and ion detectors situated below and above the interaction region respectively, and providing the start and stop pulses for a time-of-flight (TOF) mass spectrometer. The channel electron multiplier is used to detect the metastable atoms that pass through the target beam. The metastable atom velocity and identification of ion products are obtained by time-of-flight techniques.

Two separate experiments are performed with the apparatus described above. To determine the relative variation of ionisation cross section with velocity two sets of TOF distributions are recorded, one generated by stop pulses from the channeltron, produced by unscattered helium metastable atoms, and one generated by stop pulses from the interaction region, the result of ionising collisions with particles in the target beam. The two TOF distributions are converted into velocity distributions and a division of the latter by the former gives the relative variation of cross section as a function of collision velocity.

In the second experiment the information from the channeltron is discarded. Again a TOF distribution is recorded from stop pulses produced at the interaction region but this time the
Figure 4.1 Schematic diagram of the apparatus
distribution is divided into ten time bins each representing ionisation occurring at a different collision velocity. The TOF mass spectrometer is used to record ten ion mass spectra, one for each time bin. In this way the variation of branching ratio for one or more product ions can be observed as a function of collision velocity.

For both experiments the quench lamp is rapidly turned on and off by the computer. This pulsing of the quench lamp is necessary to provide two sets of data simultaneously, one using only the He(2^3S) content of the beam and one using both He(2^3S) and He(2^1S) metastables. By subtracting the former from the latter, data for collisions involving atoms in the He(2^1S) state are obtained. This means that when measuring branching ratios not ten but twenty ion mass spectra must be recorded.

It is necessary to perform the two experiments separately because of the limited memory space and speed of the computer, which in the first experiment records four TOF distributions and in the second records one TOF distribution and twenty mass spectra. It also turns the quench lamp on and off and monitors its performance. A detailed account of the computer control system and individual pieces of apparatus is given in the rest of this chapter along with descriptions of the techniques used to analyse the data.

4.1.1 The vacuum system

The four vacuum tanks T1, T2, T3, and T4 are each pumped by an oil diffusion pump stack (Edwards type EO6, EO4 EO6 and EO4 respectively), those attached to tanks T1, T2, and T4 containing Apiezon C oil. Convalex 10 oil, because of its lower vapour pressure and back-streaming rate, is used in the pump on the experiment tank T3. To back the diffusion pumps a larger backing pump (Edwards ED660) has been installed, with a pumping speed (660 l/minute) double that used in previous experiments. This allows a greater amount of helium to be passed through the system than was previously possible.

4.2 The metastable atom beam and target beam

4.2.1 Construction of metastable atom beam source

The constricted arc hot cathode source was designed by Trujillo and is described in detail in his thesis. Figure 4.2a shows the source in cross section. It consists of a glass tube
36mm inside diameter and 40mm long held between copper front and back plates. The cathode filament, fixed to the back plate by two terminals, (one is insulated from the back plate, the other is in electrical contact with it) is made of folded nickel gauze with an overall area of 24 cm², and is coated with electron emissive material (see section 4.2.2). The disc-shaped filament shield, which is made of stainless steel, is also fixed to the back plate. The shield protects the cathode by masking it from the anode. Without it the cathode coating would quickly be lost due to localised discharges on the cathode surface. The cathode lifetime is 20 - 30 hours, after which the emissivity of the coating is reduced to such an extent that it is no longer possible to strike a discharge.

The anode and the intermediate electrode are parts of the front plate, as shown in Figure 4.2a. The rectangular aperture in the intermediate electrode is 0.5mm wide by 3mm long. The electrode is made from magnesium, which has a low sputtering yield, and it is insulated from the anode by a mica annulus. The anode, which is copper, contains the aperture through which the beam emerges. This is 3mm high and between 0.02mm and 0.08mm wide, (see section 4.2.5) depending on the required source output. The desired aperture width is achieved by separating two copper knife edges with strips of aluminium foil, above and below the desired aperture position. The intermediate electrode and the anode are separated by 0.25mm. The dimensions are designed to ensure a high current density in the region between these electrodes, giving rise to the characteristically wide metastable velocity distribution and high flux.

The current regulated supply was designed by and is described in detail by Trujillo (1975). It is capable of supplying 5 A with a voltage up to 90 V. The intermediate electrode is always at earth potential, and the cathode and anode are allowed to float during operation. However, a switch is provided to connect the intermediate electrode and anode when striking a discharge. A separate AC cathode heater supply allows up to 45 A to be passed through the cathode filament at 3.5 V. A glass U-tube manometer (see Figure 4.2b) containing diffusion pump oil is connected between the source and the adjoining vacuum tank to measure the source gas pressure, which during operation is between 0.5 and 1 torr. The manometer can be bypassed to pump the source directly through the vacuum tank, providing greater pumping speed during cathode outgassing.
Figure 4.2a Cross section through the metastable atom source designed and built by Trujillo (1975)
Figure 4.2b Photograph of the metastable atom source
4.2.2 Cathode preparation

The cathode filament is made from a strip of nickel gauze 80mm long and 30mm wide, folded three times to make it 10mm wide and then spot-welded along the open edge. The strip is wound around a jig to give it a zig-zag shape and the ends are each spot welded to a stainless steel support. The cathode filament is cleaned ultrasonically in pure acetone, dried with a hot air gun and coated with a highly electron-emissive triple-carbonate mixture of barium, strontium and calcium, (Derby Luminescents, type EEM/36A). The cathode filament is heated to approximately 100° C to evaporate the butyl acetate solvent, and four more coats are carried out in a similar way until the gauze is completely filled and evenly covered. The cathode filament is once more thoroughly heated to remove as much solvent as possible and is then carefully fixed by its supports to the source back plate. The back plate is fitted to the glass tube and the assembly is secured in position on four studs protruding from the front plate (Figure 4.2b).

The source is pumped down by a backing pump to 10⁻³ torr and then through the source tank, via the manometer bypass, until the pressure stabilises below 10⁻⁶ torr. A small current is then passed through the cathode (1-5 A) and is gradually increased to 20 A at a rate which ensures that the tank pressure does not exceed 2×10⁻⁵ torr. A higher pressure (5-10×10⁻⁵ torr) indicates that the cathode coating is being shed and that the lifetime of the cathode filament will be significantly reduced. At 20 A the carbonates in the coating begin to dissociate to form oxides and a large amount of CO₂ is given off. The current is slowly increased to 30 A where it is maintained until the reaction is complete and the source tank pressure is below 10⁻⁶ torr.

4.2.3 Operation and characteristics of the source

With a cathode filament current of 30 A and the pressure in the vacuum tank less than 10⁻⁶ torr the source can be operated. The manometer bypass valve is then closed, and helium is slowly leaked into the source. When the pressure reaches 1.3 torr, (the manometer reads 20 mm of oil) a discharge may be struck. To strike the discharge, the anode and intermediate electrode are connected together and 100 V is applied between cathode and anode. When the discharge is bright and covering the intermediate electrode, the anode is disconnected from the intermediate electrode and the discharge strikes through the slit in the intermediate electrode and onto the anode. If the anode does not strike, the cathode
filament current is increased and the above procedure repeated until a discharge is achieved. The discharge current quickly increases from 0.2 to 0.5 A, along with an increase in discharge brightness and beam intensity. Initially the discharge colour is light blue, indicating the presence of impurities from the cathode filament, but over several hours the colour changes to a light pink. The change of colour is accompanied by a change in the velocity distribution of the metastable beam. Figure 4.3 shows two TOF distributions, 4.3a is produced by a new cathode and 4.3b by a cathode several hours old. Initially the presence of impurities in the source prevents the appearance of the characteristic high velocity peak visible in figure 4.3b. The high velocity peak which is present until near the end of the cathode life, has been explained by Trujillo (1975) as due to a region of high temperature (greater than $10^4$K), which is not in thermal equilibrium. Such a high temperature does not seem feasible and a more likely source of the high velocity peak is the dissociative recombination of He$_2^+$. The low velocity or thermal distribution is however characteristic of a temperature in the source of 540K.

As the filament ages the coating is depleted due to sputtering. To strike a discharge, the cathode current must then be increased sometimes up to 40 A. However, eventually it is no longer possible to strike the discharge and the filament must be replaced.

4.2.4 Production of metastable He(2$^1$S)

The present source has been used in the work of Jerram (1985), Harper (1977) and Trujillo (1975), which were all concerned almost entirely with the He(2$^3$S) metastable state. Only Harper and Davies (1980) made preliminary measurements with He(2$^1$S) metastable atoms using a velocity selector. Trujillo found the percentage of He(2$^1$S) metastables in the beam to be $12 \pm 1\%$ at $1.59 \times 10^3$ ms$^{-1}$ and $8 \pm 4\%$ at $1.12 \times 10^4$ ms$^{-1}$, and these figures were considered by Harper (1977) and Jerram (1985) to be low enough to rule out experiments using He(2$^1$S). Present measurements of beam composition agree quite well with those of Trujillo (1975), indicating that He(2$^1$S) metastables make up no more than 15% of the beam content at any velocity.

A high total flux of metastable atoms is vital to the speed of data collection and reliability of an experiment using the He(2$^1$S) state. Table 4.1 shows a comparison between the Trujillo source and several others used in different beam experiments. An alternative design would have been considered if it could have given a good velocity range with an improved
Figure 4.3a Metastable TOF distribution from source with new cathode

Figure 4.3b Metastable atom TOF distribution after several hours use
singlet flux. The velocity range produced by the Trujillo source (1-30 kms$^{-1}$) is superior to the other designs, although the Kroon (1985) source is quite good at 7-17kms$^{-1}$. However the percentage of He(2$^1$S) from the Kroon source is low at 5%, although the beam intensity is high. A big disadvantage of this source is that it uses a 1000 W power supply (Theuws et al 1982). The Fahey et al (1980) cold-cathode-arc supersonic-nozzle source produces a large He(2$^1$S) flux but with only a narrow velocity range of 1.3-2.3kms$^{-1}$. Brutschy et al (1976) give a figure of 85% for the He(2$^1$S) content of their beam with a good beam intensity, but again the velocity range is far too limited at 0.8-3 km$^{-1}$. Parr et al (1981), Illenberger and Niehaus (1975) and Pesnelle et al (1975) have used sources with moderately good velocity ranges (1-5kms$^{-1}$), but the percentages of He(2$^1$S) are small, and their beam intensities, although not reported, are probably similar to the Trujillo source as they are also hot cathode designs. The Trujillo source offers the best combination of velocity range and He(2$^1$S) flux required for the present purposes, provided it is operated near its maximum output, and has therefore been used throughout the experiments described in this thesis. The mode of operation has been thoroughly investigated to ensure that a good beam intensity is always achieved.

4.2.5 Maximising the metastable atom beam intensity

In his thesis Jerram (1985) indicates that the beam intensity obtained in his experiments was approximately $10^{12}$ s$^{-1}$sr$^{-1}$. An initial goal in the present work was to improve this figure to $10^{13}$ s$^{-1}$sr$^{-1}$. This would then allow experiments to be performed in a relatively shorter time and make He(2$^1$S) experiments feasible. The limited flux of He(2$^1$S) metastables in the beam as operated by Jerram implies that an experimental duration of up to 300 hours would be necessary to record a complete data set. This would be reduced to 30 hours if a factor of ten increase in beam intensity could be achieved. Maintaining such an increased output is initially dependent upon finding the optimum operating conditions. All of the design parameters which influence the beam intensity have been identified and where possible steps have been taken to improve the design and thus the source performance. Each of the parameters and the improvements made is described below.

a) Filament heater current: this has an effect on the density of free electrons in the plasma. It is set to the minimum level necessary to maintain a steady discharge and prolong the lifetime of the cathode. Increasing the current is found not to give a better metastable intensity, but does increase the photon flux.
Table 4.1
Comparison of metastable helium sources

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type of source</th>
<th>Intensity (sr(^{-1})s(^{-1}))</th>
<th>Percentage He((^2^S))</th>
<th>Velocity range kms(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trujillo (Present) (1975)</td>
<td>Constricted arc</td>
<td>(10^{12})</td>
<td>12</td>
<td>1-20</td>
</tr>
<tr>
<td>Fahey et al (1980)</td>
<td>Supersonic nozzle</td>
<td>(3 \times 10^{12})</td>
<td>5</td>
<td>1.3-2.3</td>
</tr>
<tr>
<td>Pesnelle et al (1975)</td>
<td>Hot cathode</td>
<td>-----</td>
<td>33</td>
<td>1.2-4.5</td>
</tr>
<tr>
<td>Illenberger and Niehaus (1975)</td>
<td>Hot cathode</td>
<td>-----</td>
<td>&lt; 50</td>
<td>1-5</td>
</tr>
<tr>
<td>Kroon (1985)</td>
<td>Cold cathode</td>
<td>(1-2 \times 10^{14}) *</td>
<td>5</td>
<td>7-17</td>
</tr>
<tr>
<td>Brutschy et al (1976)</td>
<td>Supersonic nozzle</td>
<td>(3 \times 10^{14})</td>
<td>85</td>
<td>0.8-3</td>
</tr>
</tbody>
</table>

* Units of sr\(^{-1}\)s\(^{-1}\)mm\(^{-2}\)
b) Discharge current and voltage: these control the electron density and energy in the anode aperture region and therefore the amount of excitation and ionisation taking place. The constant current supply is normally set to 0.5 A and the voltage varies from 70-90 V. Higher current gives a minor improvement in the metastable intensity, but a much greater photon flux.

c) Pressure in the source and adjoining vacuum tank: elastic scattering of metastable atoms in the vacuum tank is a major limiting factor on the intensity of the metastable beam. Collisions which excite helium into its metastable states are thought to occur in the constricted arc region of the source, where the electron density and temperature are highest. Collisions between metastables in the beam and background helium which occurs in tank T1 just outside the exit aperture remove atoms from the beam by scattering. Figure 4.4a and 4.4b show the relationship between source and tank pressure and beam intensity. Increasing the source pressure leads to a corresponding increase in the tank pressure and a drop in the metastable atom signal. The source pressure is set at 0.5-1.3 torr for the best performance. Although the optimum pressure varies for each cathode, it has been found that the beam intensity is higher towards the lower end of the pressure range. Typically Jerram (1985) operated the source at pressures of over 1 torr resulting in a poor beam intensity. The vacuum tank pressure does not rise above $3 \times 10^{-6}$ torr when the source is in use.

d) Anode slit width: This is the primary controlling factor for the beam intensity by setting the rate of effusion of helium into the vacuum tank. The width has been increased from 0.02 mm to 0.08 mm without causing the rapid increase in the vacuum tank pressure and a marked loss of beam signal as experienced by Trujillo (1975), probably because he did not compensate by lowering the source pressure. With the present combination of slit width and source pressure, beam intensities have been recorded of up to thirty times the level reported by Trujillo (1975) and Jerram (1985) and typically a factor of 10 is achieved.

e) Intermediate electrode slit width: This has some control on the electron density in the region of the anode slit. No adjustment to this width has been made; it remains 0.5 mm.

f) Impurities: these cause collisional quenching of metastables within the source. The cathode coating is an important source of impurities, mainly CO$_2$, which continues to be produced by the cathode for some hours after a discharge has been struck. A black substance builds up on all of the surfaces inside the source, over the lifetime of each cathode, particularly on the intermediate electrode and filament shield. If this build up is not removed before a new cathode filament is fitted, the beam intensity is reduced drastically.
Figure 4.4a Metastable atom intensity verses source pressure

Figure 4.4b Pressure in source verses pressure in tank T1
g) Cathode coating thickness: this affects the electron density in the source and also the amount of impurity in the discharge. The quantity of coating used is such as to maximise the lifetime of the cathode and the discharge current for a given heater current and to minimise impurities given off by the coating. The coating procedure described in section 4.2.2 was arrived at by trial and error and normally four to five coats are applied.

Figure 4.5 shows a plot of the intensity against beam velocity distribution before and after the changes were implemented. A very similar velocity distribution is apparent in the graphs, but with an increased intensity in the latter case. The improvements in the metastable beam intensity have also given rise to an increased photon flux. This is not a problem because the photon peak in the TOF spectrum arrives as a prompt pulse and is easily distinguished from the slower metastable flux.

No factor has been discovered which controls the ratio of the number of metastables in the high velocity distribution to the number in the thermal distribution and normally the peak of the high velocity part of the distribution is only about half that of the thermal part, although sometimes the two peaks are about equal. The amount of coating on the cathode may affect this ratio because each cathode appears to have a characteristic ratio associated with it.

4.2.6 The target beam

The target beam is formed in a tank adjacent to the experimental chamber. Gas is admitted through a needle valve and passes along a tube cooled by a cold trap before emerging through a multi-channel aperture array. The beam enters the interaction region through a small aperture placed 10mm from the multi-channel array, to provide collimation.

Cooling the gas reduces the thermal velocity of the cross beam. For gas in the form of a beam, the mean velocity is proportional to the square root of the gas temperature. Consequently when liquid nitrogen at 80K is used in the cold trap the gas temperature is reduced by a factor of approximately four and the mean velocity is approximately halved. Section 5.2 describes the corrections made to cross section measurements to compensate for the target beam velocity. Not all target gases can be cooled to such a low temperature because they condense in the multi-channel array. Only Ar and CH\textsubscript{4} can be cooled to liquid nitrogen temperature. N\textsubscript{2}O is cooled to the freezing point of carbon dioxide (194K)
Figure 4.5  Comparison of new and old metastable atom intensity

Intensity (arb units)

Typical new beam intensity

Typical old beam intensity

velocity km/s
but the other target gases could only be used at room temperature.

The gas pressure is measured in the experimental tank T3 using an ionisation gauge. When a stable pressure of $1.2 \times 10^{-6}$ torr is reached, then data acquisition may begin. The ionisation gauge produces a background of ions so is switched off during data acquisition.

It is necessary to monitor the pressure in tank T3 between data runs because most of the gases freeze on the liquid nitrogen trap and then slowly evaporate as the liquid coolant level decreases. This is particularly true of $N_2O$, $SF_6$ and $NH_3$. In addition to this problem, $NH_3$ also tends to condense in the needle valve due to adiabatic expansion. The target beam intensity then decreases continuously and the needle valve must be frequently adjusted.

Gases used in the target beam were always of at least 99% purity and were supplied in lecture bottles (Cambrian Gases or Argo International). The purities are, Ar 99.995%; $CH_4$ 99.995%; $NH_3$ 99.96%; $CO_2$ 99.99%; $N_2O$ 99.5%; $C_2H_2$ 99.5%; $SF_6$ 99.9%.

4.3 The quench lamp

4.3.1 Introduction

To perform experiments using $He(2^3S)$ or $He(2^1S)$ it is necessary to separate atoms in the two states. A beam of nearly pure $He(2^2S)$ can be achieved by passing the beam through a region illuminated with radiation from a helium-filled discharge lamp. For earlier experiments using this apparatus a helical lamp of the type described by Hotop et al (1969) was developed by Allison (1978) and Harper (1977) in which the beam passes along the axis of the helix. In the previous experiments it was only necessary to remove most of the singlet metastable population, but in the present work where the difference in signal between the quench lamp on and off states is measured, it has been necessary to consider carefully how the quench lamp performance could be improved. The Harper lamp was used initially but a new lamp has also been built which is of superior performance.

4.3.2 The quenching process

Figure 4.6 shows the energy levels of helium and the transitions excited by the quenching radiation. 2058nm and other singlet radiation excites the $He(2^1S)$ metastable to the $2^1P$ or
Figure 4.6 The energy levels of helium
higher $^1P$ states. These preferentially decay to the $^1S$ ground state with 98% probability. Ground state atoms cannot be excited to the He($^21S$) state by the 58.4 nm line because UV radiation of this wavelength does not pass through the glass quench lamp tube. He($^23S$) metastables are predominantly excited to the $^3P$ state by the 1083 nm radiation, and other triplet radiation may excite higher $^3P$ states. These can only decay to the $^2S$ state, leaving the He($^23S$) beam content intact.

4.3.3 Lamp performance

The performance of a quench lamp can be quantified in terms of the quenching efficiency, a measurement of the fraction of metastable atoms in the $^1S$ state which is quenched by the lamp. It is desirable to have a quenching efficiency approaching 100% for metastables of all velocities, allowing the full He($^21S$) signal to be observed as the difference between signals with the lamp on and off.

The quench lamps used by Allison, Harper and Jerram were developed from the design described by Hotop in 1969. The lamps consist of six turns of a 6mm diameter Pyrex glass tube containing helium at a pressure of approximately 3 torr. Figure 4.7 shows the lamp built by Harper (1977) and used by Jerram (1985), and inherited by the present author. The performance of this lamp is estimated using three different expressions to calculate the quenching efficiency as a function of velocity. The first expression was devised by Parr et al in 1982 and recognises that the probability of a metastable absorbing a photon of quenching radiation is proportional to the amount of time spent in passing through the lamp.

The expression given is

\[ q(v) = 1 - e^{-c/v} \] (4.1)

where $q$ is the quenching probability, $c$ is a constant characteristic of the quench lamp, and $v$ is the metastable velocity. Clearly a fast metastable is less likely to be quenched than a slow metastable because it spends less time passing through the lamp coils. Kroon (1985) has derived a more realistic expression as follows

\[ q(v) = 1 - e^{-n_1/v_3} \] (4.2)
Figure 4.7 The quench lamp used by Harper (1977)
where $B$ is a constant characteristic of the lamp and $l$ is the length of the path followed by the beam through the lamp. The dependence on the square of velocity comes from consideration of the Doppler effect. A metastable atom passing through the lamp sees a shift in the frequency of the quenching radiation, due to its velocity component in the direction of the incident radiation. If the shift is greater than the width of the resonance line, the metastable atom does not absorb the radiation and quenching does not take place. The Doppler effect becomes significant above 10 kms$^{-1}$ reducing the quenching efficiency of the lamp. Jerram (1985) has derived a rigorous form of the quenching efficiency as a function of velocity

$$q(v) = 1 - \exp\left\{\left(\frac{D}{v}\right)^\frac{n}{2} \int_0^\infty e^{-\left(\frac{M}{kT}\right) v^2 \sin^2 \theta} d\theta\right\}$$

(4.3)

where $D$ is a constant characteristic of the quench lamp, $m$ is the mass of the helium atom and $k$ the Boltzmann constant. Jerram has shown that the Kroon expression is a good approximation to the rigorous formula. The three constants $C, B, D$ from Equations 4.1, 4.2, and 4.3 are calculated by examining the variation of beam intensity, at a given velocity, as a function of quench lamp current. This can best be done by using a velocity selector to produce a beam of small velocity width. The flux from the lamp is assumed to be proportional to the discharge current.

Data recorded by Harper (1977) using a velocity selector is reanalysed in Appendix (1) using a more rigorous technique than used by either Harper or Jerram. Figure 4.8 shows a plot of quenching efficiency as a function of velocity for the Harper (1977) lamp with the efficiency calculated using expressions 4.1 and 4.2. It is clear that the Parr expression is inadequate at high velocities, because it does not consider the Doppler effect, and therefore greatly overestimates the quenching efficiency. The newly calculated figure of 47% quenching efficiency at 18 kms$^{-1}$ using both the Kroon and Jerram expressions is lower than the figure of 55 % calculated by Jerram using the same formulae.

The quenching efficiency of the lamp (47%) was considered inadequate for a singlet experiment to be performed with good resolution at high velocity, because more than half of the He(2$^1$S) signal would be lost.
Figure 4.8 Variation of quenching efficiency with velocity

Figure 4.9 Variation of q(v) with quench lamp length
4.3.4 The new quench lamp

Figure 4.9 shows the theoretical quenching efficiency of a Hotop-type lamp but with eighteen turns compared to the six turns of the Harper (1977) lamp. This would give the lamp an emitting length superior by a factor of three. Such a lamp would have a quenching efficiency, calculated using expression 4.2, of 85% at 18 kms$^{-1}$ compared to 47% calculated for the Harper (1977) lamp. This would give an improvement in the singlet metastable signal by a factor of nearly two.

A quench lamp with eighteen turns of Pyrex glass tube was constructed at UCL. Unfortunately, a discharge could not be struck with the supply which is available at UCL (5kV), unless the gas pressure in the lamp is less than 1 torr. This is comparable to the lamp used by Kroon (1985) which has ten turns of glass tube, with inner diameter 3mm. This lamp also operates at a pressure of 1 torr and has a performance similar to the Harper (1977) lamp. Taking this into account it is unlikely that the new lamp could supply a quenching power even double that of the Harper lamp and certainly not the desired factor of three improvement.

The requirement of a lower operating pressure can be overcome by increasing the tube diameter. Thus another lamp has been constructed using tubes of internal diameter 12mm, and 12 turns, shown in Figure 4.10 compared to the lamp used by Allison (1978).

The new lamp has an emitting length of 144mm (12mm × 12 turns) compared to 24mm (4mm × 6 turns) in the Allison and Harper lamps. A discharge can be struck at 5 kV and operated with a current of 56mA, double the current used by Jerram, in order to minimise the effect of the lower current density. This lamp has been used in the collection of all the data presented in this thesis, except for the total and partial cross sections of N$_2$O which were measured using the old lamp.

The lamp is enclosed in an air jacket for cooling, air circulation is provided by a diaphragm pump (Compton type D/1351VM). Circulating air is cooled by passing it through a cold trap containing solid CO$_2$ and solvent at -70°C. A trap containing activated alumina is included in the air circuit to remove water vapour. The large size of the lamp causes it to be prone to overheating; however the operation of the lamp in an "on/off" manner helps to prevent this.
Figure 4.10 The new lamp shown next to an old lamp for scale
4.3.5 Comparison of new and old lamps

An assessment of the performance of the new lamp has been made by comparing the observed singlet to triplet intensity ratio with that for the old lamp. Figure 4.11a shows the singlet to triplet ratio measured using the old lamp during the recording of N$_2$O data. This is compared to the ratio using the new lamp measured during the recording of argon data. The percentage is always higher for the new than it is for the old lamp, but the ratio of the efficiencies of new to the old increases with velocity, as clearly shown in Figure 4.11b. The new lamp has a greater quenching efficiency than the old lamp at high velocity as desired, and is twice as efficient at 19 km/s. The improvement is better than would be expected for a lamp three times the length of the old lamp shown by the solid line in Figure 4.11b.

The fact that the new lamp has a greater efficiency at low velocity (approximately a factor of 1.25), suggests that the old lamp is not as good as previously thought. However, it is possible that the metastable beam source now produces a larger fraction of singlet metastable atoms since the overall performance has been optimised.

The singlet to triplet ratio is not a smooth function of beam velocity, indicating that the velocity distribution of the singlet population is not the same as the triplet population. This is not surprising in the superthermal region where the metastable atoms are probably produced from the dissociative-recombination of He$_2^+$ (section 4.2.3). The different velocity distributions are the result of the dissociation of different ionic states of He$_2^+$. In the thermal velocity range it is likely to be due to regions of different temperature near the source aperture.

4.4 Utilising He($^2\text{S}$) and He($^3\text{S}$)

To measure the total and partial ionisation cross sections for metastable He($^2\text{S}$) with a reagent gas it is necessary to record TOF distributions with the quench lamp on (He($^3\text{S}$) metastable atoms only) then with the lamp off (He($^3\text{S}$) and He($^2\text{S}$) metastable atoms). The singlet distributions are then derived from a subtraction of the first set from the second, as described by

\[ f_{i,m}(v)[\text{singlet}] = f_{i,m}(v)[\text{quench off}] - f_{i,m}(v)[\text{quench on}] \]  

(4.4)
Figure 4.11a Singlet to triplet ratio for new and old lamp

Figure 4.11b Improvement in quenching efficiency (q)

q(new lamp)/q(old lamp)

Ratio of quenching efficiencies for a lamp three times the length of the old lamp
q(3L)/q(old lamp)
where \( f_{i,m}(v) \) is an ion (i) or metastable (m) distribution as a function of velocity.

For this procedure to give a true singlet distribution it is essential that the experimental conditions do not change between the recording of the two distributions. The conditions which must remain constant between quench on and quench off distributions are the target beam intensity, the metastable beam intensity, the background pressure in the experimental tank and the detection efficiencies of metastable atom and ion detectors. All of these conditions change, but slowly over several hours and in the case of detection efficiency over several days. Only the metastable atom beam intensity varies at all significantly over a time scale of minutes, and, as described in section 4.2.3, the high velocity part of the beam output varies from zero to maximum intensity over a period of hours. The presence of an automatic pressure control such as used by Pesnelle et al (1975), would have helped to reduce this, but the short life of the cathodes used and the resulting drift in source output, would not be affected. With only a small fraction of singlets present in the beam (10-15%) it is very important that the signal is not swamped by small drifts in beam intensity between on and off periods. If the variation of beam intensity takes the form of brief fluctuations about a constant level, then it is possible to accumulate each distribution over a long period of time, in order to average these variations out. Pesnelle et al (1975) have used this technique, taking one hour to record each distribution and recording four distributions in turn. This technique would be useless in the present experiment, because of the drifting metastable atom intensity. Consequently a switching technique has been devised to record all distributions in rapid sequence. In the case of a total cross section experiment four distributions are recorded (ion and metastable distributions with lamp on and off), but for branching ratios twenty mass spectra must be obtained (10 mass spectra with the lamp on and off).

Figure 4.12 shows the data recording cycle in the form of a flow chart. The short data recording times ensure that no appreciable change in conditions takes place between the recording of quench on and off distributions. To test the effectiveness of this procedure the data recording cycle has been performed without operating the quench lamp so that the singlet distributions for metastables and ions should be empty. In fact the number of counts in the singlet distributions was less than 0.1 \% of the number of counts in each parent distribution. With the singlet flux expected to be over 10\% of the beam intensity this means that the singlet distribution would contain a background of less than 1\%. This was judged to be very satisfactory.
In the data recording cycle 77% of experimental time is spent recording data. A short time has to be allowed for the quench lamp to achieve equilibrium, either on or off. To ensure that the lamp strikes, an oscillating high voltage from a Tesla coil is applied to the foil wrapping of the quench lamp (Figure 4.10), for 0.2 seconds at the moment the lamp is switched on. Without such an impulse the lamp may fail to strike. The lamp and tesla coil are controlled by the computer through a CAMAC interface and a dual digital-to-analogue converter (DAC Hytec 620). This drives two relays; the first switches the Tesla coil and the second, through an intermediate logic circuit, the lamp supply. This intermediate step is necessary because the CAMAC crate is initialised immediately before data is collected and after the quench lamp is turned on or off, which means that all of the units interfaced with the CAMAC crate are reset. The constant quench lamp supply must be supplied by a unit which is not reset but which can be turned on or off by a signal from the DAC. This is achieved by a simple monostable circuit shown in Appendix 2. It is necessary to initialise the CAMAC crate before data is recorded because otherwise there is a tendency for spurious counts to be recorded in the TOF distributions, which can seriously distort the singlet distributions. The origin of these counts seems to be in the counting registers which
are affected by the Tesla coil. An optically activated switch (RS 305-434) is used to look at the lamp, communicating with the computer via an amplifier circuit (Appendix 3) connected to an input/output unit (Nuclear Enterprises type 9017), again interfaced through the Camac crate. If the lamp has not successfully been turned on or off a message appears on the monitor screen and the switching procedure is repeated.

4.5 Total ionisation cross section measurement

4.5.1 The TOF system and metastable atom detection

The chopper wheel, which has only one slit 5mm wide and 53mm from the centre of the shaft, rotates once every 4.5ms (222Hz) releasing a pulse of metastables and photons 6.5μs long. Figure 4.13 shows the photon peak profile, recorded over several hours, with its characteristic peak shape, a consequence of high count rate (section 4.5.5). The width is approximately 6.5μs indicating a stable chopper wheel speed. The chopper slit passes through a slotted switch (Schmidt type SW 304-560) 10° in angle before passing in front of the source aperture. The pulse from the switch is electronically delayed to compensate for the angular displacement and is applied as the start pulse for the timing system. Metastable flight times vary from 45μs to 1500μs giving a variation in resolution from 14% to 0.4%.

Metastables are detected with a channel electron multiplier (Mullard type B410 AL) which is separated from the chopper wheel by a TOF (time-of-flight) region of 1090mm. The channeltron is also sensitive to the $^1S - ^1P$ (584nm) radiation emitted by the source and so photons are recorded. The pulses are amplified by a fast preamplifier and then fed into a timing filter amplifier (Ortec 454). Background noise is eliminated by an integral discriminator (Nuclear Enterprises 4623). These pulses are used to provide stop signals for the counting system.

4.5.2 The photon masking circuit

A single shot time-of-flight system is used in both experiments, this means that for each start pulse only the first stop pulse contributes to a TOF distribution. As a consequence of the single-shot TOF system, metastables which arrive at the channeltron later than a photon (but in the same cycle) do not contribute to the metastable TOF distribution. As a
Figure 4.13 Start pulse

Intensity (arb units)

Time (micro seconds)
result of increasing the metastable count rate from 0.01 to 0.1 - 0.3 counts per cycle (section 4.2.5), the flux of photons has increased from 0.1 to 0.6 counts per cycle. The effect of this is thus that only 40% of the metastables which reach the detector contribute to the metastable TOF distribution. No distortion of the distribution results from this effect, but the statistical accuracy is reduced.

The high count rate experiment being performed makes it desirable to eliminate the recording of photons from the data collection process. This has been done by modifying the TOF logic circuit for the single-shot TOF system designed by Allison (1978) by adding a photon masking circuit (Appendix 4). This ensures that signals from the channeltron do not become stop pulses unless they occur more than 50μs after the delayed start pulse. The photon peak occurs approximately 36μs after the delayed start and the fastest metastables are detected a further 45μs later.

The photon masking circuitry is switched off to allow the photon peak to be observed, which is needed for determining the zero offset of the TOF distribution. The photons are usually recorded at the beginning and end of a data run in case there is any drift in the zero. The high flux of photons means that the peak channel can be determined accurately in a short time.

A photon masking circuit is not needed in the ion part of the TOF circuit because the photoionisation peak is not of sufficient magnitude to reduce the recorded ion signal. The photo-ionisation count rate is approximately 0.01 per cycle and so only one percent of the ions detected do not contribute to the ionisation TOF distribution.

4.5.3 The TOF mass spectrometer

Figure 4.14 shows a cross section through the interaction region and the ion drift tube, which constitute the TOF mass spectrometer. Allison (1978) designed the spectrometer and has described it in detail along with calculations of the resolution and the correct extraction voltages. Subsequent modifications were made by Harper (1977) who introduced grids of higher transparency. For the present work the only additional modification was that a multi-channel plate detector was substituted for one of the venetian blind electron multipliers previously used. The electrons from ionising collisions in the interaction region are accelerated through 600V by the electron extraction electrode C and are detected by a pair of multichannel plates (Mullard G25-20 ×50). The mounting shown in Figures 4.15a and
Figure 4.14 Cross section through the interaction region

[Diagram of a cross-section showing components labeled as ION DETECTOR and ELECTRON DETECTOR]
Figure 4.15a Cross section through the multi-channel plate mounting

- PHOSPHOR BRONZE SPRING AND SHIM
- GOLD WIRE
- CLAMP
- MULTI-CHANNEL PLATES
- P.T.F.E MOUNT
- SIGNAL AND POTENTIAL SUPPLY TO BACK OF PLATES
- POTENTIAL TO TOP OF PLATES SUPPLIED THROUGH CLAMP AND SPRING
- POTENTIAL BETWEEN PLATES SUPPLIED BY GOLD WIRE
Figure 4.15b Photograph of the multi-channel plate mounting, also showing guard
4.15b was designed to hold one of two old and damaged multi-channel plates, donated by the Mullard Space Science Laboratory of the author's department. The plate was cut in half and the two halves used as a sandwich, to give a detecting area 20×25mm. The mounting is designed to expose the maximum amount of channel plate area to incident electrons (greater than 90%). Good electrical contact is provided on the top face by means of two phosphor bronze springs (0.1mm thick) which run along the edge of the top plate. The springs press down on phosphor bronze shims (0.9mm wide) to increase the electrical contact with the top plate. The shims prevent the springs from damaging the channel plates by distributing the pressure from the springs evenly. Channel plates are very brittle; a figure of 1 g/mm² is quoted as the maximum pressure which should be applied to the surface. Gold wires (0.15mm diameter) are used to provide a potential to the middle of the sandwich, because of their high conductivity and small diameter. A stainless steel collector maintains the bottom of the back plate at ground potential and feeds pulses to a preamplifier. Each plate has a published gain of 10³ at 1kV. The pair configuration is used with 1.5 kV across each plate (see Appendix 5a for circuit) and a gain of approximately 10⁷ was achieved. No appreciable increase in electronic noise was observed after the installation of the channel plate detectors, indicating that the mounting design is satisfactory.

Positive ions from ionising collisions in the interaction region are extracted by the grid B in Figure 4.14 and are accelerated through grid A to 3000 eV. They then cross a 361mm drift region and are detected by an eighteen-stage venetian-blind electron multiplier (EMI 9642/2A), with copper-beryllium dynodes (see Appendix 5b for circuit). At manufacture the multiplier had a gain of 5×10⁷ at the operating potential of 3kV.

The charge pulses from the electron and ion detectors are amplified by fast preamplifiers and then fed into amplifiers (Ortec type 454). Noise is eliminated by two constant fraction discriminators (Ortec type 463). The electron and ion signals are used to give start and stop pulses respectively for a time-to-amplitude converter (TAC) (Ortec 467), as shown in Figure 4.1. Mass information is derived from the amplitudes of the TAC pulses. Ions from background gas can in most cases be filtered out by passing the signal through a single-channel analyzer window (Ortec 406A), which allows pulses only of the desired height to pass through. This procedure is valid provided the background ions have a different mass to the target ions. Usually only one window is used to cover all the ionisation products because the gases used are of high purity and the residual background gas pressure of 2×10⁻⁸
torr is less than 1% of the experimental running pressure of $2 \times 10^{-6}$ torr. Finally the pulses from the TAC (irrespective of their amplitude) are used to provide stop signals for the flight of the metastables.

4.5.4 Data recording for total ionisation cross sections and high count rate corrections

A Quad Preset Counting Register (Hytec 351A), is used to measure the flight times of metastables. Counters 2 and 3 are used to count pulses from a clock pulse generator (Hytec type 95) set to 1 pulse per microsecond. The counters are interfaced via a CAMAC crate to an LSI-11/23 mini computer (DEC). A pulse from the metastable detector is used to stop counter 3. A pulse from the ion detector stops counter 2.

When determining total ionisation cross sections, information concerning the exact mass of individual ions is discarded. This is unfortunate but is necessary because the computer used to record the data is not able to do so quickly enough. Only 3ms is available to the computer to read information from the units in the Camac crate, and this is only sufficient to read two data registers.

If no metastable or ion is detected, counters 2 and 3 are stopped by an electronically generated end pulse which is automatically sent to the counters after 1600μs. The end pulse is also sent to counter 1 which acts as a flag to instruct the computer to record the contents of registers 2 and 3, irrespective of whether or not stop pulses have been received from the metastable or ion detectors.

Total cross section data is recorded by running a program called TOF3 (see Appendix 6). As described in section 4.4, four distributions are recorded simultaneously so that both singlet and triplet information is available. The data recording cycle is described below and is performed in an identical fashion for triplet and singlet distributions.

The computer reads the register of counter 1, if this is 0 then the register is read again. When the register reads 1, indicating the end of a cycle the computer reads the contents of registers 2 and 3. If a register contains a number greater than 1536 then the data is discarded, since 1536 μs is the flight time of the slowest metastable. Otherwise the data
is stored, and a new cycle begins.

The computer completes 1000 cycles and then sorts the data into 512 channels each of 3μs to make one TOF distribution. The data from the counting registers is divided by 3 to convert from microseconds to TOF distribution channel number. When the distribution has acquired data from $10^4$ cycles it is plotted on the VDU (along with three other similarly recorded TOF distributions). After sixty to one hundred sets of $10^4$ cycles the distributions are transferred to floppy disk.

Before data analysis is carried out, the TOF distributions are corrected for the effects of the high count rate. This is a consequence of the single-shot TOF system, which assumes that in every cycle not more than one metastable will reach the channeltron, and no more than one ionisation event will take place. If this condition is broken then the TOF distributions are distorted. This can be seen graphically in Figure 4.16, by a comparison of photon peak shapes observed, in high and low count rate experiments. The width of the peaks is a consequence of the time which the chopper slit takes to pass in front of the source slit. Photons arrive at the channeltron instantaneously. Figure 4.16a shows the flat trapezium shaped photon peak obtained from a weak source. In this experiment the chance of more than one photon being detected during the 6.5μs pulse width is very small because on average only one photon is detected for every ten chopper wheel cycles. By contrast the photon peak observed with the present high output source shown in Figure 4.16b is dominated by a sharp rise in counts and a more gradual fall. Several photons may be detected by the channeltron in the 6.5μs interval, but only the first to be detected can contribute to the TOF distribution. The photon peak shows this bias towards the photons detected first. The average number of photons detected per cycle is 0.5 in Figure 4.16b.

The chance of more than one event occurring is determined by the Poisson distribution

$$P(r) = \frac{m^r e^{-m}}{r!}$$  \hspace{1cm} (4.5)

where $r$ is the number of events in a cycle, $P(r)$ is the probability of $r$ events occurring in one cycle and $m$ is the mean number of events per cycle. Table 4.2 shows the variation of $P(r)$ with $r$, for various values of $m$ and the last column shows the probability that more than one event occurs in a cycle and thus the fraction of events that will be missed by the counting system.

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Table 4.2
Probability $P(r)$ calculated using the Poisson distribution

<table>
<thead>
<tr>
<th>m</th>
<th>$P(r)$</th>
<th>$r=0$</th>
<th>$r=1$</th>
<th>$r=2$</th>
<th>$r=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.990</td>
<td>0.009</td>
<td>0.00005</td>
<td>0.00005</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.9048</td>
<td>0.09</td>
<td>0.0045</td>
<td>0.0015</td>
<td>0.0047</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8187</td>
<td>0.164</td>
<td>0.0164</td>
<td>0.0011</td>
<td>0.0176</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6703</td>
<td>0.268</td>
<td>0.053</td>
<td>0.0071</td>
<td>0.0616</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6065</td>
<td>0.3033</td>
<td>0.0758</td>
<td>0.0126</td>
<td>0.0902</td>
</tr>
</tbody>
</table>

The probability of more than one event occurring per cycle becomes significant when the mean number of events per cycle exceeds 0.2. This represents the upper limit of the count rate for both metastables and ions that could be expected in the current experiment. Clearly there will be some distortion of the kind shown on the photon peak for any distribution recorded from a high count rate. A cross section measurement, which is derived from the division of an ion distribution by a metastable distribution, will be affected if the two distributions are not identical (in which case they would be equally distorted). The cross section will be deformed at low velocity (high TOF times) where the counts per channel is more drastically reduced (see Figure 4.16). Some reduction of the deformation of the cross section can be achieved by making the ion and metastable atom count rates approximately equal. To compensate more fully for the effect of high count rate the data can be corrected retrospectively by using a program called HIGHCOUNT (Appendix 7). The number of cycles in which the data was recorded and the photon peak channel number are fed into the computer. The program then scans through the channels of a given TOF distribution from 1 to 512 and makes a running total of counts. Each count in channels 1 to i-1 represents a cycle in which channel i cannot record an event. The number of counts in channel i is corrected as follows
\[ C_i' = \frac{C_i T}{\sum_{j=1}^{i-1} C_j} \] (4.6)

\( C_i' \) the new total in a channel \( i \)
\( C_i \) = the original total in channel \( i \)
\( T \) = the number of cycles over which the data was recorded
\( \sum_{j=1}^{i-1} C_j = \) the running total of counts in channels 1 to \( i-1 \)

The validity of this procedure can be shown by applying it to the sloping photon peak shown in Figure 4.16b. The saw tooth shape of Figure 4.16b is transformed to become the flat topped trapezium shaped peak of figure 4.16c. In Figure 4.17 a cross section in which the ion and metastable TOF distributions have both been corrected for a high count rate is shown, and compared with the uncorrected cross section. The difference is small, but not insignificant. In this case the count rates were both approximately 0.2 counts per cycle.

4.5.5 Data analysis

Data analysis is carried out using a computer program CROSCAL (Appendix 8). Firstly the four original TOF distributions are read into the computer and converted into velocity distributions. This is simply done by dividing the distance between the chopper wheel and metastable detector, or interaction region in the case of ionisation distributions, (1030mm and 860mm ± 0.1 % respectively) by the flight times. The photon peak channel number is subtracted from the TOF channel number and the result multiplied by three to give the time of flight in microseconds. The TOF distributions start a short time before the actual zero, which is given by the channel which contains the photon peak or the photo-ionisation peak. A zero offset occurs because of electronic delay and because the start pulse does not exactly coincide with the release of a pulse of metastables atoms from the source and chopper wheel. The ion distributions have a larger offset because of a delay caused by the ion flight time in the TOF mass spectrometer.

First the triplet cross section is determined. The metastable atom and ion velocity distributions are divided into 30 velocity bins and the weighted mean velocity of each bin is calculated. The bins are chosen to maximise velocity resolution while making sure that each bin contains enough information to ensure that the data is statistically meaningful. Some of the bins overlap in order to make the variation of cross section with velocity as continuous as possible.
Figure 4.16 Comparison of photon peak shapes

Intensity (arb units)

A Low count rate

B Uncorrected

C Corrected

High count rate

Time
The effective cross section $\sigma_{\text{eff}}(v)$ can be calculated as follows:

$$\sigma_{\text{eff}}(v) = \frac{i+di}{\sum_i n(i) - di} \frac{b_n}{\sum_j m(j) - dj} c_m$$

(4.7a)

where $v$ is the average of the weighted mean velocities calculated for the ion and metastable atom velocity bins, $n(i)$ and $m(j)$ are the number of counts in channels $i$ and $j$ respectively, $b_n$ and $c_m$ are the mean number of the background counts in each channel, and $i$ and $di$ are related to $j$ and $dj$ by $j = i \times l_m/l_n$ and $dj = di \times l_m/l_n$ in which $l_n$ and $l_m$ are the distances from the chopper wheel to the interaction region and the channeltron respectively.

The error on each sum is given by the square root of the sum and the fractional error on the effective cross section is given by summing in quadrature the fractional errors on the two sums. To calculate the singlet cross section a subtraction procedure is used as follows.
where \( k(i) \) and \( l(j) \) are the number of counts in channels \( i \) and \( j \) respectively and \( q(\text{off}) \) and \( q(\text{on}) \) signify the state of the quench lamp. CROSCAL calculates the error on the numerator and denominator of Equation 4.7b from the addition in quadrature of the errors on the sums. The fractional error on the effective cross section is calculated by adding together in quadrature the fractional errors on the numerator and denominator. This means that the errors on singlet cross sections are much larger than they are on the triplet cross sections.

The velocity calculated by CROSCAL in this case is simply the average of the four weighted mean velocities, and is not sufficiently precise. In order to calculate the precise velocity a simple program which subtracts the distributions recorded with the quench lamp on from those recorded with the quench lamp off is used. The resulting singlet distributions are used to determine accurately the velocity dependence of the singlet ionisation cross section. This is done using CROSCAL but reading the two singlet distributions into the computer in the position that is normally occupied by the triplet distributions. Thus Equation 4.7a is used to calculate the singlet total ionisation cross section; the errors calculated are incorrect and are discarded, but the velocity calculated is more precise because the weighted mean velocity is calculated after the subtraction procedure has been carried out.

The resulting effective total ionisation cross sections as a function of collision velocity are in some cases rather incomplete, with information lacking particularly at low velocity. To give a more continuous picture of the velocity dependence of the ionisation cross section a second analysis computer program CROSS2 (Appendix 9) is used. This program is similar to CROSCAL except that the ionisation cross section is calculated at a velocity decided by the program user, with the velocity bin size and position entered by hand. In this way the total ionisation cross section can be calculated at velocities between those determined using CROSCAL. CROSS2 is also used to extend the velocity range of the experiment in cases where sufficient raw information exists at very low or very high velocity.

Both the effective cross section and beam velocity calculated above must be corrected for
the relative velocity of the target beam to obtain a true cross section at the collision velocity. The technique used to perform these corrections is described later in section 4.7.

4.6 Branching ratios

4.6.1 Data collection and analysis

With the present apparatus the variation of the branching ratio with velocity can be measured for each ion product of chemi-ionisation. The TOF mass spectrometer shown in Figure 4.11 is used to distinguish between ion products of different mass in the way described in section 4.5.3. In this experiment no channeltron pulses are recorded and so no information is available about the metastable beam intensity distribution and thus the cross section cannot be determined. Only the relative production of the various ion products at the same collision velocity is revealed. However when this information is coupled with the previously measured total cross sections, the partial cross sections can be obtained. As with the total cross section experiments, the TAC output is used to provide a stop pulse to the timing system, but now the TAC pulses are also fed into a fast analogue-to-digital converter (Nuclear Enterprises NE 9060) which is interfaced to the LSI-11 minicomputer via the CAMAC crate.

To produce an ion mass spectrum as a function of collision velocity, the metastable TOF distribution determined from the ion production in the interaction (ie the 'ion TOF distribution' region is split up into ten time bins. To do this it is important to know the zero offset of the distribution before the experiment begins, simply done by recording the TOF distribution of ionisation. The photo-ionisation peak is observed and incorporated in the branching ratio program TOF1M (Appendix 10). TOF1M records the mass spectra due to ionisation occurring with the quench lamp on and off, in the same way that TOF3 records total cross section data, by using the data recording cycle described in section 4.4 and shown in Figure 4.12. The computer reads the contents of counting register 1; if this is 0 then the register is read again. When the register contains a 1 the computer reads the contents of counting register 2 (ionisation time) and the ADC register (mass information). Data is rejected if it does not fall within the correct range of the ADC register (1-512). TOF1M builds up a two-dimensional array in which the channel number is determined by the ion mass and the bin number is determined by the time of ionisation. The result is a set of ten mass spectra, each recorded at a different velocity. Periodically an overall mass
spectrum is displayed on the VDU.

Before the singlet data can be examined a simple program is used to subtract the ten mass spectra recorded with the quench lamp on from the ten spectra recorded with the quench lamp off. This gives ten ion mass spectra due to ionisation by singlet metastable atoms.

Analysis of a set of ten mass spectra is carried out using the programs BRCAL (Appendix 11). Firstly a simple plotting program is used to look at the mass spectra and determine the range of channels occupied by each mass peak. The mass spectrometer is calibrated before the experiment by examining the mass peaks produced by background gases in the tank and observing their channel numbers. Then ANYJS is used to examine each mass spectrum in turn, adding up the number of events in each mass range and the total number of counts in the spectrum. The fraction of an ion product is then found by dividing the number of counts in the mass range which it occupies by the total number of counts in the mass spectrum. The beam velocity which corresponds to each spectrum is determined as follows. An ion TOF distribution is recorded before and after the data run, so as to average any fluctuation in the source. These are added together and a modified form of CROSCAL is then used to divide the distribution up into ten TOF bins corresponding to those used by TOF1M. The weighted mean velocity of each bin is then determined. The percentage of each ion species is thus calculated, as a function of beam velocity. To convert from beam velocity to collision velocity the procedure described later in section 4.7 is used.

The accuracy of branching ratios decreases with velocity, especially if the fraction of a particular ion is low. Therefore measurements of branching ratios are made for velocities only as high as 14 kms$^{-1}$, considerably lower than for total cross sections measurements.

To convert branching ratios into partial cross sections they are simply multiplied by the total ionisation cross sections, calculated by the method described in section 4.5.4. This is done after the velocity corrections have been carried out. As with branching ratios the partial cross sections cover a much more limited velocity range than the total cross sections.

Each mass spectrum is 256 channels long and the channel number of a given ion product is roughly proportional to the square root of its mass (the precise relationship is given by Allison 1978). A variable mass range is achieved in cases where the ion mass produces a channel number between 256 and 512. A channel offset is read into the computer at the
beginning of a TOF1M run and the offset is subtracted from the ion channel number, in order to fit the ion peak into the mass spectrum. Thus the mass resolution of a 512 channel spectrum is achieved and the limited capacity of the computer memory is not exceeded.

The ion peak width is approximately four channels at half maximum and the resolution of light ions is good, for example ten channels separate the peaks of NH$_3^+$ and NH$_2^+$ (masses 17 and 16). The mass resolution declines with increasing mass, but no heavy rare gases have been used so the problem of separating close mass peaks has not arisen. SF$_6$ (mass 146), which is heavier even than xenon, has been examined, but it produces ion fragments which differ by nineteen mass units (SF$_5^+$ 127 and SF$_4^+$ 108) and so are easily separated.

In the case of argon, the tail of the Ar$^+$ peak overlaps the much smaller ArHe$^+$ peak and thus the latter is significantly increased by the additional counts. To correct this, the lower-mass tail of the Ar$^+$ peak is measured and assuming the peak is symmetrical, the contribution to the ArHe$^+$ channels due to the higher-mass tail is subtracted.

Since the background mass spectrum is very small (section 4.2.6), no background subtractions have been necessary. The amount of background is easily monitored by observing the size of the H$_2$O$^+$ mass peak, which is always visible, because its position is different from any of the peaks produced in the experiment.

4.6.2 Detection efficiencies

The detection efficiencies of both the electron and ion detectors have been determined as a function of target atom mass. In order to make corrections to the branching ratio measurements such corrections are necessary if detection efficiencies vary significantly with target mass. The same procedure as was used by both Allison (1978) and Jerram (1985) has been applied.

The detection efficiencies are determined by recording the ion counts $N_1$, the electron counts $N_2$ and the number of coincidences $N_3$ in a given time. The counts are related to the ion detection efficiency ($A_1$), and the electron detection efficiency ($A_2$) as follows

$$N_1 = A_1 N$$

$$N_2 = A_2 N$$

$$N_3 = A_1 A_2 N$$

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where \( N \) is the total number of ionisation events occurring. The detection efficiencies are thus

\[
A_1 = \frac{N_3}{N_2} \quad (4.11)
\]
\[
A_2 = \frac{N_3}{N_1} \quad (4.12)
\]

The values of \( A_1 \) and \( A_2 \) determined in this way are shown in table 4.3 and plotted in Figure 4.18a and their product plotted in Figure 4.18b giving the combined detection efficiency of the two detectors.

**Table 4.3**

Detection efficiencies for positive ions and electrons

<table>
<thead>
<tr>
<th>Ion species</th>
<th>Mass</th>
<th>Electron (%)</th>
<th>Ion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>16</td>
<td>49.9 ± 0.4</td>
<td>12.26 ±0.17</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>17</td>
<td>52.17 ± 0.66</td>
<td>11.43 ± 0.32</td>
</tr>
<tr>
<td>N(_2)</td>
<td>28</td>
<td>50.17 ± 0.42</td>
<td>11.14 ± 0.09</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>46.4 ± 0.66</td>
<td>11.7 ± 0.25</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>44</td>
<td>49.39 ± 0.44</td>
<td>11.43 ± 0.51</td>
</tr>
<tr>
<td>Kr</td>
<td>83.8</td>
<td>49.9 ± 1</td>
<td>7 ± 0.3</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>146</td>
<td>50 ± 0.6</td>
<td>7.98 ± 0.14</td>
</tr>
</tbody>
</table>

The detection efficiencies are determined by the area of the detectors, the secondary emission coefficients, the transparency of the extraction grids, and the sensitivity of the electronic counting system.

As would be expected the electron detection efficiency does not vary with mass. The ion
Figure 4.18a Detection efficiency for positive and negative ions and electrons

![Figure 4.18a Detection efficiency for positive and negative ions and electrons](image1)

Figure 4.18b Combined detection efficiency of ion and electron detectors ($A_1 \times A_2$)

![Figure 4.18b Combined detection efficiency of ion and electron detectors ($A_1 \times A_2$)](image2)

Present results
Jerram (1985)
detection efficiency is also virtually constant in the range 16 - 44 mass units, in agreement with the results of Allison (1978). No corrections are therefore made to the branching ratios of CO₂ or N₂O which produce ion fragments spanning this range. In most hydrocarbon cases the masses of ion fragments lie in a small range, for example, CH₄⁺ and CH₃⁺, and so these are left uncorrected. Above 44 mass units there is a clear decline in the ion detector efficiency with increasing mass. This is seen more clearly in a plot of combined detection efficiency A₁ × A₂ in Figure 4.18b. The present results are shown compared to those measured by Jerram (normalised to the present efficiency for mass 44). Thus there may be significant differences in detection fragments of the branches of SF₆, because of the large differences in their masses, and their large mass numbers (108-146).

The variation in detection efficiency for these target masses could not be measured and so no corrections can be made to their branching ratios.

4.7 Correction for the thermal motion of target atoms

The effective cross sections described in section 4.5.6 must be corrected to take into account motion of the target particle. Because of this the relative collision velocity of a target atom and metastable helium atom is greater than the calculated metastable beam velocity.

The most probable velocity in the target beam is given by

$$\alpha = \sqrt{\frac{3kT}{m}}$$

(4.13)

where k is the Boltzmann constant, T is the gas temperature in the source and m is the mass of a target gas atom.

A slow metastable atom has a greater probability of undergoing a collision with a target atom than a fast metastable atom, because it spends a longer time in the beam. This effect is dependent on the ratio of the metastable atom velocity to the most probable atom velocity in the target beam. The desired final result is a true cross section σ(g) at a mean relative velocity g between the target atom and a metastable helium atom.

The corrections for a beam and for a gas cell target have been calculated by several authors notably Pauli (1960), Berkling et al (1962) and Lang et al (1971). The Berkling et al
corrections give a cross section $\sigma_{\text{ion}}(v_i)$,

$$\sigma_{\text{ion}}(v_i) = \sigma_{\text{eff}}(V) \frac{1}{\mathcal{F}_b(s,x)}$$  \hspace{1cm} (4.14)

where $v_i$ is the beam velocity and $\sigma_{\text{eff}}(v_i)$ is the effective cross section measured in section 4.5.5, $\mathcal{F}_b(s,x)$ is a correction tabulated by Berkling et al, and defined in Massey and Burhop (1971) as follows

$$\mathcal{F}_b(s,x) = 4\pi \frac{1}{2} x^{-2} \beta \int (x^2 + z^2)^{\beta} z^2 e^{-z^2} \, dz$$ \hspace{1cm} (4.15)

$$\beta = \frac{(s-3)}{2(s-1)}$$ \hspace{1cm} (4.16)

where $s$ derives from the form of interaction potential chosen

$$V \propto x^{-a}$$ \hspace{1cm} (4.17)

$x$ is the ratio of the metastable atom beam velocity $v_i$ to the target beam velocity $\alpha$

$$x = \frac{v_i}{\alpha}$$ \hspace{1cm} (4.18)

A similar function $\mathcal{F}_{a0}(s,x)$ for a gas cell is also tabulated. The advantage of this method is that only the cross section must be adjusted, the collision velocity becomes the beam velocity. The disadvantage is that the cross section corrections can be large, and they depend strongly on the assumed form of the interaction potential, which may introduce large errors.

The correcting method described by Lang et al (1971) also depend on the same assumed interaction potentials, but the cross section $\sigma_{\text{ion}}(g)$ is given at the mean collision velocity of the two beams $g$, not the beam velocity $v_i$. The corrected cross section $\sigma_{\text{ion}}(g)$ is given by:

$$\sigma_{\text{ion}}(g) = \frac{\sigma_{\text{eff}}(v_i)}{\mathcal{F}(s,x) \, w(x)}$$ \hspace{1cm} (4.19)

$$w(x) = \frac{g}{v_i}$$ \hspace{1cm} (4.20)

$w(x)$ is equivalent to $\mathcal{F}_{b0}(\infty,x)$ the Berkling et al correction for a hard sphere interaction.
potential. The function \( f(s,x) \) is not tabulated by Lang et al but a conversion from the function \( F_{b_0}(s,x) \) of Berkling et al (1962) is given by

\[
f(s, x) = F_{b_0}(s, x) \left[ F_{b_0}(\infty, x) \right]^{\frac{(3-s)}{(s-1)}}
\]

(4.21)

In the case where \( s = \infty \), the function \( f(\infty, x) = 1 \); in the case where \( s = 6 \), over the range of the present experiments, \( f(6, x) = 1 \) to within 1%.

The cross section corrections of Lang et al (1971) are more reliable than those of Berkling et al because they are much less dependent on \( s \). Also a more physical solution is achieved, because the cross sections are determined at the relative collision velocity and so the true energy range of the experiment is apparent. Thus the correction procedure of Lang et al has been chosen to calculate the values of \( \sigma_{\text{ion}}(v_i) \) in chapter 5. It has been assumed that \( f(s, x) \) is always 1. The corrections are most necessary for light targets and are greatest at low collision velocity. For collisions at \( 1 \text{km/s} \), \( w \) varies from 1.2 for collisions with ammonia to 1.03 for collisions with sulphur hexafluoride.
Chapter 5
Results and discussion

5.1 Introduction

In this chapter the ionisation cross sections and branching ratios of Ar, CO₂, N₂O, CH₄, C₂H₂, NH₃ and SF₆ are presented. The data, which has been corrected as described in chapter 4 for the effects of relative collision velocity and high count rate, is tabulated in Tables 5.2 to 5.14 and is presented graphically in Figures 5.2 to 5.33.

The relative data has in every case been normalised to absolute measurements. Table 5.1 indicates to which absolute data the present results have been normalised together with the normalisation error and a key to Figures 5.2 to 5.33.

The triplet data for Ar, CH₄ NH₃ are normalised to the gas cell measurements of Jerram (1985) carried out on the present apparatus and measured as a function of collision energy. This is important because it makes the normalisation procedure simple.

Other cross sections are normalised to the flowing afterglow results of Schmeltekopf and Fehsenfeld (1970) for SF₆, N₂O, CO₂ or the pulsed radiolysis results of Ueno et al (1980) in the case of C₂H₂. These results are presented as an absolute rate constant k at a particular temperature. To derive the normalisation factor a rate constant is calculated from the relative cross section measurements using the following relationship:

\[ k' = \int_{0}^{\infty} f(v)\sigma'(v)v \, dv \]  \hspace{1cm} (5.1)

where \( \sigma' \) and \( k' \) are the measured cross section and calculated rate constant respectively and \( f(v) \) is the Maxwellian velocity distribution function. The normalisation constant is simply given by \( k = Nk' \), where \( N \) is the normalisation constant and \( k \) is the reported rate constant. The normalised cross section can now be found from \( \sigma(v) = N\sigma'(v) \).

The absolute afterglow cross sections shown in Figures 5.2 to 5.32 have been calculated by the authors of the papers from their absolute rate constant \( k \) by assuming that the cross
section $\sigma$ is independent of velocity. $k$ is measured at a given temperature which is converted to a mean collision energy. To do this the average collision velocity is first calculated using Equation 5.2, where $m$ is the mass of the target particle, $k_B$ is the Boltzmann constant and $T$ is the given temperature:

$$
\bar{v} = \left(\frac{8 k_B T}{\pi m}\right)^{1/2}
$$

(5.2)

In the present work the singlet cross sections are normalised using the same factor as for the corresponding triplet cross sections. The assumption implicit in this is that the detection efficiency of the channeltron is equal for the two metastable species. Evidence for the validity of this assumption is given in section 5.2.

The total ionisation cross sections are shown in figures 5.2 to 5.32 as discrete points, along with partial cross sections shown as smooth curves drawn through the data points. In the case of argon the partial cross sections have not been shown because of the large amount of information given on these graphs. Error bars are shown on the total cross sections and the branching ratios. Error bars are shown at three points only on the partial cross sections. These are calculated by adding the errors from the branching ratio and total cross section in quadrature.

No error bars are shown on the triplet cross sections because the errors are so small. The errors for the singlet cross sections are larger and in general the amount of data taken is enough to ensure that the error bars are less than ten percent in the mid energy range (0.04 eV - 0.3 eV) where the population of He($2^1S$) is at its highest. This criterion means that data acquisition can be completed for one target species in roughly one week, though more in the case of argon. At high energy, where the singlet fraction is low, the error bars are much larger because of the subtraction procedure described in section 4.5.5. It would be necessary to record ten times as much data, to reduce the errors in these regions to one third of their present level which was impractical.

For the same reasons the error bars shown on the singlet branching ratios are very large at high and low energy. However, again the errors on the triplet data are very small and no error bars are shown.
The total ionisation cross sections for argon with both metastable species are compared with the plentiful relative measurements of other experimenters. The variation of branching ratios for argon have been compared with the data of Jerram (1985) and Pesnelle (1975) in the triplet case; in the singlet case only the data of Pesnelle (1975) is available for comparison.

The triplet ionisation cross sections and branching ratios of CO$_2$, CH$_4$, C$_2$H$_2$, and NH$_3$ are compared with the only relative data available, that of Jerram (1985). No relative data is available to compare with the present singlet cross sections and branching ratios of these molecules, nor with the singlet and triplet data of N$_2$O and SF$_6$.

Figure 5.1 Energy resolution of experiment

![Energy resolution of experiment](image)

The energy resolution as a function of energy is shown graphically in Figure 5.1, calculated for the molecules at two extremes of mass, methane and sulphur hexafluoride. The major energy broadening is due to the width of the TOF bins. The resolution is poorer for branching ratio results than for total ionisation cross section results because the TOF bins used are wider for these measurements. The effects of the finite width of the start pulse
and the spread in thermal motion of the target beam are also important. An expression for
the latter is given by Chantry (1971) as follows

\[ W_{1/2} = (11.1 y k_B T E_0)^{1/2}, \quad y = \frac{m}{(m+M)} \]  

(5.3)

where \( W_{1/2} \) is the width at half maximum, \( k_B \) is the Boltzmann constant, \( T \) is the
temperature of the beam and \( E_0 \) is the mean beam energy. \( M \) and \( m \) are the masses of the
projectile and target particles respectively. The total energy resolution is the quadrature
sum of these three factors.

5.2 Ar + He(\( ^2S \))

In Figure 5.2 the present data is compared with the relative data of Kroon (1985), Jerram
identical to the data of Illenberger and Niehaus (1975) which is not shown. The data of
Parr et al (1982) is shown only where it diverges from the data of Jerram (1985) to which
it is also identical below 0.2 eV.

Figure 5.2 shows a good agreement with the magnitude and variation of the relative data
of Jerram (1985). Below 0.04 eV the present measurement is higher than the data of
Jerram. This effect could be due to differential scattering of metastable atoms in the
experimental chamber by a high background gas pressure, but this is not thought to be the
case. The low energy data agrees well with the absolute measurement of Schmeltekopf
and Fehsenfeld (1970), better than does the relative data of Jerram. The cross section rises
smoothly from 0.04 eV to a maximum at 0.5 eV, and agrees well with Jerram (1985) and
Parr et al (1982). However, agreement is poor with the data of Woodard et al (1978). This
has been accounted for by Jerram (1985) as a result of the design of their gas cell.

The small dip at 0.7 eV shown in the present data is better defined than in the relative data
of Jerram (1985). Above 2 eV there is possibly some oscillatory structure, superimposed on
to a slowly declining cross section.

Associative ionisation is at its maximum of 20\% at the lowest collision energy of 0.02 eV
and decreases rapidly to below 0.2\% at 1 eV. This is in good agreement with the
measurements of Jerram (1985) and Pesnelle et al (1975), although, as figure 5.3 shows,
the present measurements show slightly more associative ionisation. This is most likely to be due to the overlap of the two mass peaks. The single energy measurements (Table 5.15) of Herce et al, (1968a) Hotop et al (1969) and West et al (1975) show considerably less associative ionisation than the present results, whereas the data of Allison (1978) using the present mass spectrometer is in good agreement. The most likely explanation is that the collision energies reported in the other work are lower than the actual values, because as Figure 5.3 shows, the fraction of ArHe$^+$ decreases rapidly with energy. The single-energy experiments do not employ the TOF technique and so the reported energies are less reliable than the energy dependent measurements.

5.3 Ar + He(2$^1$S)

The relative total ionisation cross section for argon with He(2$^1$S) has been normalised using the same factor as for the triplet data, assuming that the detection efficiency of the channeltron used is equal for the two metastable species. This assumption is supported by the agreement between the present data and the relative data of Burdenski et al (1981), Sidiqui et al (1984) and Parr et al (1982). Good agreement is also found with the absolute measurements of Schmeltekopf and Fehsenfeld (1970) and Riola et al (1974).

A much steeper rise in cross section is apparent in Figure 5.4 at lower energy than in the triplet case, following the data of Parr et al closely at the lowest energy and showing no signs of a minimum in the cross section (Burdenski et al 1981). The small magnitude of the cross section at low energy eliminates the possibility of differential scattering in the experimental tank, which would have boosted the observed cross section. The cross section reaches a maximum between 0.1 and 0.2 eV where it lies between the diverging data of Parr et al and Burdenski et al. The data of Kroon shows a similar shape to the present data but with much lower magnitude. Kroon (1985) has made the same assumption as has been made in the present work, that the detection efficiency of his metastable detector is equal for both metastable species. Kroon's triplet data, normalised to the theoretical cross section of Siska (1979), is in good agreement with the present results. Kroon has multiplied the singlet cross section by the same normalisation factor as for the triplet cross section.

The implication, therefore, from the discrepancy between the cross section measured by Kroon and the cross section measured by the other experimenters including the present author, is that the detection efficiency of his metastable detector is in fact higher for
He(2^3S) than it is for He(2^1S). This could be due to the indirect method of detection used involving an electron multiplier detecting electrons ejected from a stainless steel surface. Dunning and Smith (1971) and Dunning et al (1971) have considered the detection efficiency for metastable helium by several targets. Although the detection efficiency determined is the same for the two metastable species with a target of chemically cleaned stainless steal, the detector used by Kroon is untreated and so it is reasonable that the detection efficiencies be different.

Above 0.3 eV there is no data with which to compare the present results, and between 0.3 and 0.9 eV the statistical accuracy of the results is quite low. Above 0.9 eV the cross section declines slowly in a similar fashion to the triplet cross section and with a similar magnitude to it as Figure 5.6 shows.

The fraction of associative ionisation at low energy is almost double that in the triplet case (43% at 0.031 eV). The fraction decreases more rapidly however, and is in good agreement with the data of Pesnelle et al (1975), though slightly larger (Figure 5.5). The other single energy measurements (Table 5.16) all show much less associative ionisation than either the present data or that of Pesnelle et al, (Figure 5.5) indicating that the collision energies reported in Table 5.16 are lower than the actual values.

### 5.3 CO_2+ He(2^3S)

The cross section for ionisation of carbon dioxide by He(2^3S) shows a continuous decline in magnitude with increasing energy (Figure 5.7), indicating that the interaction potential is weakly attractive. This is in agreement with the PIES results of Hotop et al (1979). The present results show a good agreement with the data of Jerram (1985), continuing the trend of his data into both low and high energy regions (the present results extend the energy range of measurements by a factor of two).

No associative ionisation occurs and Penning ionisation accounts for more than sixty percent of the ionisation products (Figure 5.8), with dissociative ionisation providing the rest. The amounts of each branch detected agree well with the data of Jerram, with better accuracy in the case of the smallest branch, CO^+. The single energy measurements (Table 5.15) are in good agreement with the present results excepting those of Hotop et al (1969) which
gives a low percentage of O$^+$. 

5.4 CO$\text{}_2 + \text{He}(2^1S)$

The total ionisation cross section of carbon dioxide by He(2$^1S$) shows a good agreement with the absolute measurements of Riola et al (1974) and is within the errors of Schmeltekopf and Fehsenfeld (1970). Figure 5.9 shows the cross section declining with energy below 0.2 eV with only small fluctuations. This is expected from the PIES data of Tuffin et al (1981), which indicates the presence of a slightly more attractive potential than in the triplet case. At 0.2 eV the singlet and triplet cross sections are equal, and at higher energy the cross section oscillates about the level of the triplet cross section (Figure 5.11). This may be due to a genuine structure in the cross section, but fluctuations due to the lower statistical accuracy at high energy cannot be ruled out.

The branching ratios of Figure 5.10 show more CO$^+$ Penning ionisation than in the triplet case and less O$^+$. There is a cross over in the magnitude of CO$^+$ and O$^+$ above 0.6 eV. The single energy measurements in Table 5.16 show good agreement with the present results except for the O$^+$ percentages, which are roughly double. Again no associative ionisation occurs.

5.5 N$\text{}_2$O + He(2$^3S$)

The total ionisation cross section of nitrous oxide by He(2$^3S$) shown in Figure 5.12 has the smallest variation with energy of any measured. The cross section rises slightly with energy below 0.05 eV, but the trend over the remaining energy range is downwards, suggesting, as in the case of carbon dioxide, a weak attractive potential in agreement with the PIES results of Hotop et al (1979).

The branching ratios (Figure 5.13) are more interesting than the total ionisation cross section. Penning ionisation accounts for only half of the ionisation products at low energies and is overtaken by the NO$^+$ branch above 0.7 eV, which increases over the energy range as do the other three dissociative branches.

West et al (1975) do not record any N$^+$ or N$^+$ (Table 5.15), as have been detected in
present measurements. This may be due to inadequate resolution of the mass spectrometer used by West et al. The mass peaks of NO+ and N2+ are very close (30 and 28 atomic mass units respectively) and could easily appear as one peak. The percentage of NO+ recorded by West et al is similar to the combined percentage of NO+ and N2+ recorded in the present experiment, which suggests that the explanation is reasonable. In addition the data of Hotop et al (1979) gives a percentage of N2+ and O2+ in agreement with the present data and they also report some N+.

West et al (1975) report detection of HeO+ (1%) but none has been detected in the present experiment or by Hotop et al (1979). This is almost certainly a spurious detection, due to dissociation of N2O molecules in the drift space between the interaction region and the analysing magnet, the possibility of which is admitted in their paper.

5.6 N2O + He(21S)

The total ionisation cross section for nitrous oxide by He(21S) shows a much more pronounced energy dependence than in the triplet case (Figure 5.14) indicating a more attractive interaction potential. There is a smooth fall in cross section up to 0.15 eV where a small hump appears; the decline continues to 0.5 eV where the singlet and triplet cross sections are equal. Above 0.5 eV the cross section oscillates about the level of the triplet cross section (Figure 5.16). As in the case of carbon dioxide this oscillation may be due to statistical fluctuation, but the spiked structure at 0.8 eV is more than twice the length of its error bar from the value of the triplet cross section, and is therefore likely to be real physical structure.

The branching ratios shown in Figure 5.5 show a lower fraction of Penning ionisation than in the triplet case (30% compared with 50%). Once again the data of West et al disagrees with the present results in the case of NO+, N2+ and N+ but the percentages of N2O+ and O+ are in good agreement. Hotop et al (1979) report a much greater fraction of N+; the ratio of N+ to N2O+ agrees with the present results.

5.7 CH4 + He(23S)

The cross section for ionisation of methane by He(23S) increases with energy in a similar fashion to that of argon, indicating that the interaction potential is repulsive in an argon-
like way. The present data shows good agreement with the results of Jerram (1985) up to 0.3 eV, but above this energy there is significant disagreement (Figure 5.17). A dip is observed between 0.3 and 2 eV, where the data of Jerram is at a maximum. This is the only case of such a divergence in the two sets of data. An explanation for this difference may be found in the comparison of triplet and singlet cross sections shown in Figure 5.21. The total ionisation cross section of methane by He(21S) shows a pronounced maximum in the same energy region as the peak detected by Jerram. The quench lamp used by Jerram (Chapter 4.3.4) was not as effective at high energy as the one used in the present experiment, and so the cross section measured by Jerram at high energy may contain a contribution from the singlet cross section.

Figure 5.18 shows that the dissociative channel of ionisation is predominant; Penning ionisation declines over the energy range and is overtaken by the CH3+ dissociative branch above 0.04eV. This is in good agreement with the results of Jerram (1985) and the single energy measurements in Table 5.15. No associative ionisation has been observed.

5.8 CH4 + He(21S)

The total cross section for ionisation of methane by He(21S) shows evidence of an argon-like repulsive interaction potential as for the triplet case. There is evidence of a minimum in the cross section at 0.033eV. As with argon the cross section reaches its maximum at a lower energy than for the triplet case (Figure 5.19) where it is in good agreement with the data of Schmeltekopf and Fehsenfeld (1970) and Lindinger (1974). Unusually a second sharper and higher maximum is visible at 1 eV which may be due to structure in the repulsive wall of the interaction potential such as the small attractive region suggested by Brutschy et al (1982) for the Ar + He(21S) system (Chapter 6.1).

Figure 5.20 shows that the fraction of Penning ionisation is lower for the singlet than for the triplet interaction, as in the cases of nitrous oxide and carbon dioxide. The fraction of CH2+ is higher at low energy than it is for the triplet case, and is in good agreement with the single energy measurements of Table 5.16.

5.9 C2H2 + He(23S)

The total cross section for ionisation of acetylene by He(23S) shows a gradient similar to
that recorded by Jerram (1985) in the mid-energy region, but with a slightly higher gradient at low energy (Figure 5.22). The present cross section is normalised, as is that of Jerram (1985), to the absolute measurement of Ueno et al (1980), which is at low energy. This means that the present cross section is generally lower than that of Jerram. The shape of the cross section indicates a weakly attractive system, in agreement with the PIES data of Ohno et al (1983). Above 4.5eV there is a small rise in the cross section (Figure 5.22) which may be due to a repulsive wall at small interatomic separation.

Penning ionisation is the predominant branch of ionisation (Figure 5.23) but declines with energy and is equalled by the increasing dissociative channel $C_2H^+$ at 4 eV. The measurements of Jerram show a cross over in the branches at 2.5 eV; this is probably due to lower statistical accuracy in his measurements. There is good agreement with the measurements of Hotop et al (1969) shown in Table 5.15. No associative ionisation has been observed.

5.10 $C_2H_2 + He(2^1S)$

The total ionisation cross section of acetylene by He($2^1S$) shows a more rapid decline with increasing energy than the triplet case (Figure 5.24), as for nitrous oxide and carbon dioxide, and again indicates a more attractive potential than in the triplet case. A small hump is apparent at 0.16 eV and a second larger hump at 0.35 eV. Above 0.4eV the cross section is similar to the triplet cross section (Figure 5.26) without any appreciable structure.

Figure 5.25 shows the fraction of Penning ionisation to be lower than in the triplet case as in all other cases. The data of Hotop et al (1969) also shows a lower percentage of Penning ionisation (Table 5.16), but not as pronounced as in the present results. Penning ionisation remains predominant over the entire range of energy, with the dissociative channel highest at mid energies (0.35-1.3 eV) and no associative ionisation observed.

5.11 $NH_3 + He(2^3S)$

The total cross section for ionisation of ammonia by He($2^3S$) shows a rapidly declining cross section with energy (Figure 5.27). The present data is in good agreement with that of Jerram (1985), with the trends shown by Jerram continued at low energy. This rapid decline would be expected from the PIES data of Ohno et al (1983) which shows that the
NH₃ + He(2^3S) system is strongly attractive. At high energy (above 9eV) the cross section is constant, and may have reached a minimum because collisions are penetrating to a repulsive wall in the interaction potential. At higher energies still, the cross section may be expected to increase as the imaginary part of the potential rises.

Penning ionisation provides the major branch in Figure 5.28, but declines with energy and is overtaken by the NH₂⁺ branch above 1 eV, as compared to 2eV in the work of Jerram (1985). The variation of the NH⁺ branch is better defined than by Jerram, because of the superior statistical accuracy of the present data. No associative ionisation has been observed.

5.12 NH₃ + He(2^1S)

The total cross section at 0.03 eV is the largest cross section of any recorded in this work. Figure 5.29 shows good agreement with the absolute measurement of Schmeltekopf and Fehsenfeld (1970). The cross section declines in a similar fashion to the triplet cross section (Figure 5.31), with the exception of a maximum at 0.3 eV. The hump appears in only the Penning ionisation cross section. As would be expected, the singlet interaction potential is even more strongly attractive than is the triplet potential.

Penning ionisation provides the major branch in Figure 5.30, with the predominant dissociative channel NH₂⁺ unusually declining with energy. There is not enough NH⁺ data at high and low energy to make reasonable measurements in these regions. The error bars are very large over most of the energy range, but the measurements vary smoothly.

5.13 SF₆ + He(2^3S)

The total ionisation cross section for sulphur hexafluoride with He(2^3S) shown in Figure 5.32 behaves in a very similar way to that of argon. The cross section rises smoothly with energy, before reaching a maximum at 0.28 eV. This suggests that the interaction potential is repulsive as in the case of argon. A gentle argon-like decline is interrupted by a peak at 0.83eV, suggesting there is some structure, either in the repulsive wall of the interaction potential, or in the imaginary part of the interaction potential. Penning ionisation is the major branch of ionisation as in the case of argon, although no associative ionisation has been detected (Figure 5.33).
Table 5.1
Normalisation errors for total and partial cross sections given in tables 5.2 to 5.14 and key to figures 5.2 to 5.33

<table>
<thead>
<tr>
<th>Target species</th>
<th>Normalised to</th>
<th>Normalisation error (%)</th>
<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>Jerram (1985)</td>
<td>6</td>
<td>■</td>
</tr>
<tr>
<td>CO₂</td>
<td>Schmeltekopf and Fehsenfeld (1970)</td>
<td>30</td>
<td>○</td>
</tr>
<tr>
<td>N₂O</td>
<td>Schmeltekopf and Fehsenfeld (1970)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>Jerram (1985)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>C₂H₂</td>
<td>Ueno et al (1980)</td>
<td>15</td>
<td>□</td>
</tr>
<tr>
<td>NH₃</td>
<td>Jerram (1985)</td>
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</tr>
<tr>
<td>SF₆</td>
<td>Schmeltekopf and Fehsenfeld (1970)</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

**Other absolute measurements**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
</table>
### Table 5.2 Relative cross sections and branching ratios for Ar + He(2^3S)

#### Total cross section

<table>
<thead>
<tr>
<th>g km⁻¹</th>
<th>σ(g) ( \times 10^{-16} \text{cm}^2 )</th>
<th>E meV</th>
<th>g km⁻¹</th>
<th>σ(g) ( \times 10^{-16} \text{cm}^2 )</th>
<th>E meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97</td>
<td>4.27 ± 0.05</td>
<td>0.018</td>
<td>2.88</td>
<td>14.9 ± 0.1</td>
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</tr>
<tr>
<td>1.00</td>
<td>4.32 ± 0.05</td>
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<td>2.89</td>
<td>15.0 ± 0.1</td>
<td>0.159</td>
</tr>
<tr>
<td>1.12</td>
<td>4.48 ± 0.12</td>
<td>0.023</td>
<td>3.03</td>
<td>15.1 ± 0.1</td>
<td>0.174</td>
</tr>
<tr>
<td>1.12</td>
<td>4.47 ± 0.05</td>
<td>0.024</td>
<td>3.21</td>
<td>16.6 ± 0.1</td>
<td>0.196</td>
</tr>
<tr>
<td>1.19</td>
<td>4.59 ± 0.06</td>
<td>0.027</td>
<td>3.25</td>
<td>16.6 ± 0.1</td>
<td>0.200</td>
</tr>
<tr>
<td>1.29</td>
<td>4.75 ± 0.06</td>
<td>0.029</td>
<td>3.69</td>
<td>18.5 ± 0.2</td>
<td>0.259</td>
</tr>
<tr>
<td>1.35</td>
<td>5.25 ± 0.05</td>
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<td>4.33</td>
<td>19.4 ± 0.2</td>
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<tr>
<td>1.42</td>
<td>5.47 ± 0.05</td>
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<td>5.22</td>
<td>19.7 ± 0.3</td>
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<tr>
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<td>19.1 ± 0.4</td>
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<tr>
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<tr>
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<td>7.07</td>
<td>19.3 ± 0.3</td>
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<tr>
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<td>8.00</td>
<td>19.4 ± 0.3</td>
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</tr>
<tr>
<td>1.92</td>
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<td>0.070</td>
<td>9.21</td>
<td>19.6 ± 0.3</td>
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</tr>
<tr>
<td>2.22</td>
<td>10.93 ± 0.09</td>
<td>0.093</td>
<td>10.6</td>
<td>18.0 ± 0.3</td>
<td>2.15</td>
</tr>
<tr>
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<td>18.4 ± 0.2</td>
<td>3.12</td>
</tr>
<tr>
<td>2.62</td>
<td>13.5 ± 0.1</td>
<td>0.130</td>
<td>15.7</td>
<td>15.9 ± 0.2</td>
<td>4.69</td>
</tr>
<tr>
<td>2.63</td>
<td>13.5 ± 0.1</td>
<td>0.132</td>
<td>19.7</td>
<td>16.6 ± 0.1</td>
<td>7.39</td>
</tr>
<tr>
<td>2.73</td>
<td>14.1 ± 0.1</td>
<td>0.142</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Partial cross sections \( (10^{-16} \text{cm}^2) \)

<table>
<thead>
<tr>
<th>g km⁻¹</th>
<th>E meV</th>
<th>Ar⁺ ( \sigma )</th>
<th>ArHe⁺ ( \sigma )</th>
<th>( \sigma ) Ar⁺</th>
<th>( \sigma ) ArHe⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13</td>
<td>0.031</td>
<td>76.2 ± 2.5</td>
<td>23.8 ± 1.5</td>
<td>3.6</td>
<td>1.1</td>
</tr>
<tr>
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<td>0.050</td>
<td>77.6 ± 0.8</td>
<td>22.8 ± 0.4</td>
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<td>1.46</td>
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<tr>
<td>2.11</td>
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<td>81.3 ± 0.5</td>
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<td>1.75</td>
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<tr>
<td>2.5</td>
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<td>1.60</td>
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<tr>
<td>3.0</td>
<td>0.170</td>
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<td>6.6 ± 0.2</td>
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<td>1.01</td>
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<td>3.5</td>
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<td>96.9 ± 0.8</td>
<td>3.1 ± 0.1</td>
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<td>4.6</td>
<td>0.400</td>
<td>99.1 ± 1.4</td>
<td>0.9 ± 0.1</td>
<td>19.3</td>
<td>0.16</td>
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<td>6.0</td>
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<td>99.8 ± 1.7</td>
<td>0.2 ± 0.06</td>
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<td>0.03</td>
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<tr>
<td>8.5</td>
<td>1.37</td>
<td>100 ± 1.6</td>
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<td>19.4</td>
<td></td>
</tr>
</tbody>
</table>

Branching ratios (\%)

#### Partial cross sections \( (10^{-16} \text{cm}^2) \)
Figure 5.2  Ar + He(2^3S)  
Cross section ($10^{-16}$ cm$^2$)

Figure 5.3  
Branching ratio (%)
Table 5.3 Relative cross sections and branching ratios for Ar + He(21S)

**Total cross section**

<table>
<thead>
<tr>
<th>g (kms(^{-1}))</th>
<th>(\sigma(g)) ((10^{-16})cm(^2))</th>
<th>E (meV)</th>
<th>g (kms(^{-1}))</th>
<th>(\sigma(g)) ((10^{-16})cm(^2))</th>
<th>E (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.04</td>
<td>4.1 ± 1.5</td>
<td>0.021</td>
<td>3.20</td>
<td>26.4 ± 1.2</td>
<td>0.173</td>
</tr>
<tr>
<td>1.09</td>
<td>5.8 ± 1.4</td>
<td>0.023</td>
<td>3.16</td>
<td>27.4 ± 1.4</td>
<td>0.196</td>
</tr>
<tr>
<td>1.16</td>
<td>7.4 ± 1.4</td>
<td>0.025</td>
<td>3.22</td>
<td>27.2 ± 1.4</td>
<td>0.199</td>
</tr>
<tr>
<td>1.22</td>
<td>9.8 ± 1.4</td>
<td>0.028</td>
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<td>24.0 ± 1.4</td>
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<td>1.26</td>
<td>11.4 ± 1.3</td>
<td>0.030</td>
<td>3.69</td>
<td>24.2 ± 1.6</td>
<td>0.258</td>
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<tr>
<td>1.31</td>
<td>12.0 ± 1.4</td>
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</tr>
<tr>
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<tr>
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<tr>
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<td>0.600</td>
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<tr>
<td>1.93</td>
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<td>2.62</td>
<td>28.7 ± 1.3</td>
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<td>16.3 ± 5.1</td>
<td>6.70</td>
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</table>

**Branching ratios (%)**

<table>
<thead>
<tr>
<th>g (kms(^{-1}))</th>
<th>E (meV)</th>
<th>Ar+ (%)</th>
<th>ArHe+ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13</td>
<td>0.031</td>
<td>57.4 ± 13</td>
<td>42.6 ± 7.1</td>
</tr>
<tr>
<td>1.62</td>
<td>0.050</td>
<td>71.9 ± 2.7</td>
<td>28.1 ± 1.4</td>
</tr>
<tr>
<td>2.11</td>
<td>0.084</td>
<td>92.7 ± 2.7</td>
<td>7.3 ± 1.0</td>
</tr>
<tr>
<td>2.5</td>
<td>0.118</td>
<td>97.6 ± 2.5</td>
<td>2.4 ± 0.7</td>
</tr>
<tr>
<td>3.0</td>
<td>0.170</td>
<td>98.9 ± 3.0</td>
<td>0.1 ± 0.05</td>
</tr>
<tr>
<td>3.5</td>
<td>0.230</td>
<td>100 ± 1.5</td>
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</table>

**Partial cross sections (\(10^{-16}\)cm\(^2\))**

<table>
<thead>
<tr>
<th>g (kms(^{-1}))</th>
<th>(\sigma(Ar^+)) ((10^{-16})cm(^2))</th>
<th>(\sigma(ArHe^+)) ((10^{-16})cm(^2))</th>
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</thead>
<tbody>
<tr>
<td>1.13</td>
<td>11.8</td>
<td>8.8</td>
</tr>
<tr>
<td>1.62</td>
<td>17.7</td>
<td>6.9</td>
</tr>
<tr>
<td>2.11</td>
<td>28.5</td>
<td>2.2</td>
</tr>
<tr>
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</table>
Figure 5.4 Ar + He(2S)
Cross section ($10^{-16}$ cm$^2$)

- Parr et al (1982)
- Kroon (1985)

Collision energy (eV)

Figure 5.5
Branching ratio (%)

- Ar$^+$
- ArHe$^+$

Collision energy (eV)
Figure 5.6

Cross section (10^{-6} cm^2)

Collision energy (eV)

Ar + He(2S)
Ar + He(2'S)
Table 5.4 Relative cross sections and branching ratios for CO$_2$ + He(2$^3$S)

<table>
<thead>
<tr>
<th>$g$ (kms$^{-1}$)</th>
<th>$\sigma(g)$ ($10^{-16}$cm$^2$)</th>
<th>$E$ (meV)</th>
<th>$g$ (kms$^{-1}$)</th>
<th>$\sigma(g)$ ($10^{-16}$cm$^2$)</th>
<th>$E$ (meV)</th>
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<td>30.1 ± 0.2</td>
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<tr>
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<td>3.21</td>
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<td>1.25</td>
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<td>29.8 ± 0.3</td>
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<td>43.9 ± 0.2</td>
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<td>29.2 ± 0.3</td>
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Branching ratios (%)

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<th>CO$^+$</th>
<th>O$^+$</th>
<th>$\sigma$(CO$_2^+$)</th>
<th>$\sigma$(CO$^+$)</th>
<th>$\sigma$(O$^+$)</th>
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<tr>
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<td>2.0</td>
<td>10.9</td>
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<td>26.0 ± 0.2</td>
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<td>8.6</td>
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<tr>
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Figure 5.7  CO$_2^+$ He($2^3$S)
Cross section (10$^{-16}$ cm$^2$)

Figure 5.8
Branching ratio (%)
Table 5.5 Relative cross sections and branching ratios for carbon CO₂ + He(2¹S)

<table>
<thead>
<tr>
<th>g (kms⁻¹)</th>
<th>σ(g) (10⁻¹⁶cm²)</th>
<th>E (meV)</th>
<th>g (kms⁻¹)</th>
<th>σ(g) (10⁻¹⁶cm²)</th>
<th>E (meV)</th>
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<tr>
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Branching ratios (%)

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<th>CO⁺</th>
<th>O⁺</th>
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<th>σ(CO⁺) (10⁻¹⁶cm²)</th>
<th>σ(O⁺) (10⁻¹⁶cm²)</th>
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<td>21.0</td>
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Figure 5.9 $\text{CO}_2 + \text{He}(2^1\text{S})$
Cross section ($10^{-16}\text{ cm}^2$)

Figure 5.10
Branching ratio (%)
Figure 5.11

Cross section (10^{-16} \text{ cm}^2)

Collision energy (eV)

CO_2 + He(2^3 S)
CO_2 + He(2^1 S)
Table 5.6 Relative cross sections and branching ratios for N$_2$O + He(2$^3$S)

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<th>E (meV)</th>
<th>$g$ (kms$^{-1}$)</th>
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Branching ratios (%)

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<th>N$_2^+$</th>
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Figure 5.12 $\text{N}_2\text{O} + \text{He}(2^3\text{S})$

Cross section ($10^{-16}\text{ cm}^2$).

Figure 5.13

Branching ratio (%)

Collision energy (eV)
Table 5.7 Relative cross sections and branching ratios for N₂O + He(2¹S)

Total cross section

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<th>g (kms⁻¹)</th>
<th>σ(g) (10⁻¹⁶cm²)</th>
<th>E (meV)</th>
<th>g (kms⁻¹)</th>
<th>σ(g) (10⁻¹⁶cm²)</th>
<th>E (meV)</th>
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<tr>
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Branching ratios (%)

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<th>NO⁺</th>
<th>N₂⁺</th>
<th>O⁺</th>
<th>N⁺</th>
<th>σ(N₂O⁺)</th>
<th>σ(NO⁺)</th>
<th>σ(N₂⁺)</th>
<th>σ(O⁺)</th>
<th>σ(N⁺)</th>
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<td>3.1 ± 0.5</td>
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<td>49.9</td>
<td>11.6</td>
<td>3.0</td>
<td>2.9</td>
</tr>
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Figure 5.14  $\text{N}_2\text{O} + \text{He}(2^1\text{S})$

Cross section ($10^{-16} \text{ cm}^2$)

Collision energy (eV)

Figure 5.15

Branching ratio (%)

Collision energy (eV)
Figure 5.16

Cross section ($10^{-16}$ cm$^2$)

- $\Box$ N$_2$O + He($2^3S$)
- $\Diamond$ N$_2$O + He($2^1S$)

Collision energy (eV)
Table 5.8 Relative cross sections and branching ratios for CH₄ + He(2³S)

### Total cross section

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<tr>
<th>g (kms⁻¹)</th>
<th>σ(g) (10⁻¹⁶cm²)</th>
<th>E (meV)</th>
<th>g (kms⁻¹)</th>
<th>σ(g) (10⁻¹⁶cm²)</th>
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### Branching ratios (%)

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<th>E (meV)</th>
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<th>CH₃⁺</th>
<th>CH₂⁺</th>
<th>σ(CH₄⁺)</th>
<th>σ(CH₃⁺)</th>
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### Partial cross sections (10⁻¹⁶cm²)

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Figure 5.17 CH$_4$+ He($2^3S$)
Cross section ($10^{-16}$ cm$^2$)

Collision energy (eV)

Figure 5.18
Branching Ratio (%)

Collision energy (eV)
Table 5.9 Relative cross sections and branching ratios for CH$_4$ + He($2^1S$)

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<th>g (kms$^{-1}$)</th>
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<th>E (meV)</th>
<th>g (kms$^{-1}$)</th>
<th>$\sigma$ (g) $10^{-16}$cm$^2$</th>
<th>E (meV)</th>
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Branching ratios (%)

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<th>CH$_3^+$</th>
<th>CH$_2^+$</th>
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<th>$\sigma$ (CH$_3^+$)</th>
<th>$\sigma$ (CH$_2^+$)</th>
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<td></td>
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<td>8.4 ± 0.3</td>
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<td>11.4</td>
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</table>
Figure 5.19 \( \text{CH}_4 + \text{He}(2^1S) \)
Cross section \( (10^{-16} \text{ cm}^2) \)

Figure 5.20 Branching Ratio (%)
Figure 5.21

Cross section ($10^{-16}$ cm$^2$)

- □ CH$_4$ + He($2^3$S)
- ◇ CH$_4$ + He($2^1$S)

Collision energy (eV)
Table 5.10 Relative cross sections and branching ratios for C$_2$H$_2$ + He(2$^3$S)

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<tr>
<th>$g$ (kms$^{-1}$)</th>
<th>$\sigma(g)$ ($10^{-16}$cm$^2$)</th>
<th>$E$ (meV)</th>
<th>$g$ (kms$^{-1}$)</th>
<th>$\sigma(g)$ ($10^{-16}$cm$^2$)</th>
<th>$E$ (meV)</th>
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Branching ratios (%)

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<th>$E$ (meV)</th>
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<th>C$_2$H$^+$</th>
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<th>$\sigma$(C$_2$H$^+$)</th>
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Figure 5.22 $\text{C}_2\text{H}_2^+ + \text{He}(2^3\text{S})$

Cross section ($10^{-16}\text{ cm}^2$)

Collison energy (eV)

Figure 5.23

Branching ratio (%)

Collison energy (eV)
Table 5.11 Relative cross sections and branching ratios for C$_2$H$_2$ + He(2$^1$S)

<table>
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<th>g (kms$^{-1}$)</th>
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<th>E (meV)</th>
<th>g (kms$^{-1}$)</th>
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<th>E (meV)</th>
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<td>47.2 ± 8.4</td>
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<td>5.75</td>
<td>27.4 ± 9.3</td>
<td>0.565</td>
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<td>2.80</td>
<td>45.1 ± 3.8</td>
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<td>6.38</td>
<td>31.2 ± 12</td>
<td>0.745</td>
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<td>2.95</td>
<td>50.9 ± 4.2</td>
<td>0.159</td>
<td>7.05</td>
<td>41.0 ± 14</td>
<td>0.907</td>
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<td>2.96</td>
<td>51.9 ± 4.2</td>
<td>0.160</td>
<td>8.21</td>
<td>31.0 ± 9.5</td>
<td>1.23</td>
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<td>3.10</td>
<td>47.9 ± 3.8</td>
<td>0.175</td>
<td>9.09</td>
<td>24.2 ± 7.9</td>
<td>1.51</td>
</tr>
<tr>
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<td>10.7</td>
<td>30.6 ± 11</td>
<td>2.07</td>
</tr>
<tr>
<td>3.30</td>
<td>42.1 ± 3.7</td>
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<td>12.5</td>
<td>25.5 ± 10</td>
<td>2.85</td>
</tr>
<tr>
<td>3.43</td>
<td>38.0 ± 3.7</td>
<td>0.215</td>
<td>15.9</td>
<td>22.9 ± 8.7</td>
<td>4.58</td>
</tr>
<tr>
<td>3.48</td>
<td>37.0 ± 3.6</td>
<td>0.221</td>
<td>17.8</td>
<td>21.1 ± 16</td>
<td>5.81</td>
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<tr>
<td>3.75</td>
<td>29.8 ± 3.1</td>
<td>0.256</td>
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</tbody>
</table>

Branching ratios (%)

<table>
<thead>
<tr>
<th>g (kms$^{-1}$)</th>
<th>E (meV)</th>
<th>C$_2$H$_2^+$</th>
<th>C$_2$H$^+$</th>
<th>$\sigma$(C$_2$H$_2^+$) $10^{-16}$cm$^2$</th>
<th>$\sigma$(C$_2$H$^+$) $10^{-16}$cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.27</td>
<td>0.029</td>
<td>59.6 ±13</td>
<td>40.4 ±7.6</td>
<td>50.2</td>
<td>34.1</td>
</tr>
<tr>
<td>1.73</td>
<td>0.054</td>
<td>63.2 ±3.4</td>
<td>36.8 ±2.1</td>
<td>38.5</td>
<td>22.4</td>
</tr>
<tr>
<td>2.20</td>
<td>0.088</td>
<td>67.1 ±2.5</td>
<td>32.9 ±1.6</td>
<td>37.8</td>
<td>18.5</td>
</tr>
<tr>
<td>2.58</td>
<td>0.120</td>
<td>69.4 ±2.8</td>
<td>31.6 ±1.9</td>
<td>32.9</td>
<td>14.9</td>
</tr>
<tr>
<td>3.67</td>
<td>0.170</td>
<td>61.4 ±3.3</td>
<td>38.6 ±2.1</td>
<td>28.1</td>
<td>12.3</td>
</tr>
<tr>
<td>3.72</td>
<td>0.250</td>
<td>66.5 ±3.5</td>
<td>33.6 ±2.8</td>
<td>20.4</td>
<td>10.3</td>
</tr>
<tr>
<td>4.4</td>
<td>0.350</td>
<td>54.5 ±8.5</td>
<td>45.5 ±5.3</td>
<td>41.2</td>
<td>21.5</td>
</tr>
<tr>
<td>6.0</td>
<td>0.625</td>
<td>54.9 ±16</td>
<td>45.1 ±14</td>
<td>15.7</td>
<td>13.1</td>
</tr>
<tr>
<td>8.5</td>
<td>1.31</td>
<td>54.2 ±12</td>
<td>45.8 ±11</td>
<td>11.9</td>
<td>10.0</td>
</tr>
<tr>
<td>14.7</td>
<td>3.92</td>
<td>64.3 ±10</td>
<td>35.7 ±5.9</td>
<td>15.3</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Partial cross sections ($10^{-16}$cm$^2$)
Figure 5.24  \( \text{C}_2\text{H}_2^+ \text{ He}(2^1\text{S}) \)

Cross section \( (10^{-16} \text{ cm}^2) \)

Collision energy (eV)

Figure 5.25

Branching ratio (%)

Collision energy (eV)
Figure 5.26

Cross section ($10^{-16}$ cm$^2$) vs. Collision energy (eV)

- $C_2H_2^+ + He(2^3S)$
- $C_2H_2^+ + He(2^1S)$
Table 5.12 Relative cross sections and branching ratios for NH\textsubscript{3} + He(2\textsuperscript{3}S)

<table>
<thead>
<tr>
<th>Total cross section</th>
<th></th>
<th>Partial cross sections (10\textsuperscript{-16}cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>g (kms\textsuperscript{-1})</td>
<td>E (meV)</td>
<td>NH\textsubscript{3}\textsuperscript{+}</td>
</tr>
<tr>
<td>1.36</td>
<td>0.031</td>
<td>64.6 ± 0.9</td>
</tr>
<tr>
<td>1.79</td>
<td>0.054</td>
<td>64.5 ± 0.4</td>
</tr>
<tr>
<td>2.25</td>
<td>0.085</td>
<td>64.1 ± 0.4</td>
</tr>
<tr>
<td>2.62</td>
<td>0.116</td>
<td>63.2 ± 0.4</td>
</tr>
<tr>
<td>3.11</td>
<td>0.163</td>
<td>62.8 ± 0.5</td>
</tr>
<tr>
<td>3.59</td>
<td>0.218</td>
<td>61.1 ± 0.7</td>
</tr>
<tr>
<td>4.7</td>
<td>0.371</td>
<td>56.5 ± 1.4</td>
</tr>
<tr>
<td>6.0</td>
<td>0.600</td>
<td>55.1 ± 1.7</td>
</tr>
<tr>
<td>8.3</td>
<td>1.16</td>
<td>48.0 ± 1.7</td>
</tr>
<tr>
<td>13.9</td>
<td>3.26</td>
<td>42.7 ± 1.5</td>
</tr>
</tbody>
</table>
Figure 5.27 NH$_3$+ He($2^3$S)

Cross section ($10^{-16}$ cm$^2$)

Jerram (1985)

Collision energy (eV)

Figure 5.28

Branching Ratio (%)

Jerram (1985)

Collision energy (eV)
Table 5.13 Relative cross sections and branching ratios for NH$_3$ + He($2^1S$)

**Total cross section**

<table>
<thead>
<tr>
<th>$g$ (km$^{-1}$)</th>
<th>$\sigma(g)$ ($10^{-16}$cm$^2$)</th>
<th>E (meV)</th>
<th>$g$ (km$^{-1}$)</th>
<th>$\sigma(g)$ ($10^{-16}$cm$^2$)</th>
<th>E (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.34</td>
<td>141 ± 35.0</td>
<td>0.03</td>
<td>3.50</td>
<td>57.8 ± 4.9</td>
<td>0.207</td>
</tr>
<tr>
<td>1.45</td>
<td>117 ± 13.2</td>
<td>0.036</td>
<td>3.77</td>
<td>68.4 ± 7.5</td>
<td>0.240</td>
</tr>
<tr>
<td>1.22</td>
<td>100 ± 8.8</td>
<td>0.042</td>
<td>3.80</td>
<td>66.7 ± 6.7</td>
<td>0.249</td>
</tr>
<tr>
<td>1.75</td>
<td>92 ± 8.8</td>
<td>0.052</td>
<td>3.99</td>
<td>67.0 ± 9.3</td>
<td>0.264</td>
</tr>
<tr>
<td>1.83</td>
<td>89.4 ± 8.8</td>
<td>0.057</td>
<td>4.39</td>
<td>62.4 ± 10</td>
<td>0.362</td>
</tr>
<tr>
<td>1.90</td>
<td>86.3 ± 8.8</td>
<td>0.061</td>
<td>4.73</td>
<td>51.1 ± 9.3</td>
<td>0.381</td>
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<tr>
<td>1.97</td>
<td>91.7 ± 7.0</td>
<td>0.065</td>
<td>4.79</td>
<td>61.6 ± 9.3</td>
<td>0.387</td>
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<tr>
<td>2.28</td>
<td>73.3 ± 5.7</td>
<td>0.088</td>
<td>6.38</td>
<td>45.4 ± 13</td>
<td>0.688</td>
</tr>
<tr>
<td>2.35</td>
<td>79.8 ± 5.3</td>
<td>0.093</td>
<td>7.05</td>
<td>36.4 ± 11</td>
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<tr>
<td>2.55</td>
<td>76.1 ± 4.0</td>
<td>0.110</td>
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<tr>
<td>2.74</td>
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<td>26.9 ± 5.8</td>
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<td>2.76</td>
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<td>2.85</td>
<td>63.5 ± 4.0</td>
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<td>0.151</td>
<td>15.2</td>
<td>29.0 ± 6.6</td>
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<tr>
<td>2.99</td>
<td>64.8 ± 3.6</td>
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<tr>
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<td>27.5 ± 7.9</td>
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<tr>
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<td>0.189</td>
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<td>17.9 ± 8.0</td>
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</table>

**Branching ratios (%)**

<table>
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<tr>
<th>$g$ (km$^{-1}$)</th>
<th>E (meV)</th>
<th>NH$_3^+$</th>
<th>NH$_2^+$</th>
<th>NH$^+$</th>
<th>$\sigma$(N$_3^+$)</th>
<th>$\sigma$(NH$_2^+$)</th>
<th>$\sigma$(NH$^+$)</th>
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</thead>
<tbody>
<tr>
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<td>0.031</td>
<td>74.3 ±13.0</td>
<td>25.7 ±9.4</td>
<td>105</td>
<td>36.2</td>
<td>30.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1.79</td>
<td>0.054</td>
<td>66.2 ±4.4</td>
<td>32.9 ±3.2</td>
<td>0.9 ±0.5</td>
<td>60.5</td>
<td>39.6</td>
<td>28.3</td>
</tr>
<tr>
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<td>0.085</td>
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<td>31.9 ±2.5</td>
<td>0.9 ±0.4</td>
<td>36.0</td>
<td>24.6</td>
<td>19.6</td>
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<tr>
<td>2.62</td>
<td>0.116</td>
<td>62.7 ±3.6</td>
<td>29.6 ±2.6</td>
<td>0.7 ±0.4</td>
<td>34.2</td>
<td>19.5</td>
<td>11.1</td>
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<tr>
<td>3.11</td>
<td>0.163</td>
<td>65.2 ±4.2</td>
<td>34.2 ±3.2</td>
<td>0.6 ±0.4</td>
<td>34.2</td>
<td>24.1</td>
<td>17.9</td>
</tr>
<tr>
<td>3.59</td>
<td>0.218</td>
<td>70.0 ±5.8</td>
<td>29.4 ±6.2</td>
<td>0.6 ±0.6</td>
<td>42.9</td>
<td>18.0</td>
<td>9.1</td>
</tr>
<tr>
<td>4.7</td>
<td>0.371</td>
<td>83.9 ±13</td>
<td>15.9 ±13</td>
<td>0.2 ±1.0</td>
<td>47.8</td>
<td>47.8</td>
<td>9.1</td>
</tr>
<tr>
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<td>0.600</td>
<td>77.5 ±27</td>
<td>22 ±14</td>
<td>0.6 ±3.0</td>
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<td>11.1</td>
<td>0.3</td>
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<td>8.3</td>
<td>1.16</td>
<td>76.5 ±31</td>
<td>24 ±15</td>
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<td>7.9</td>
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</tr>
<tr>
<td>13.9</td>
<td>3.26</td>
<td>88.4 ±24</td>
<td>11.6 ±16</td>
<td>21.5</td>
<td>2.8</td>
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</table>
Figure 5.29 \( \text{NH}_3^+ \text{ He}(2^1 S) \)

Cross section \( (10^{-16} \text{ cm}^2) \)

Figure 5.30

Branching Ratio (%)
Table 5.14 Relative cross sections and branching ratios for SF$_6$ + He(2$^3$S)

Total cross section

<table>
<thead>
<tr>
<th>g (kms$^{-1}$)</th>
<th>E ($10^{-16}$ cm$^2$)</th>
<th>E (meV)</th>
<th>g (kms$^{-1}$)</th>
<th>E ($10^{-16}$ cm$^2$)</th>
<th>E (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.974</td>
<td>14.8 ± 0.6</td>
<td>0.019</td>
<td>2.88</td>
<td>32.0 ± 0.9</td>
<td>0.169</td>
</tr>
<tr>
<td>1.02</td>
<td>15.3 ± 2.0</td>
<td>0.021</td>
<td>2.89</td>
<td>32.8 ± 1.2</td>
<td>0.170</td>
</tr>
<tr>
<td>1.06</td>
<td>16.3 ± 1.5</td>
<td>0.023</td>
<td>3.02</td>
<td>31.2 ± 0.9</td>
<td>0.185</td>
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<td>16.5 ± 1.0</td>
<td>0.025</td>
<td>3.21</td>
<td>31.7 ± 0.9</td>
<td>0.209</td>
</tr>
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<td>1.20</td>
<td>16.7 ± 0.5</td>
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<td>3.24</td>
<td>31.8 ± 1.0</td>
<td>0.214</td>
</tr>
<tr>
<td>1.24</td>
<td>17.5 ± 0.5</td>
<td>0.031</td>
<td>3.68</td>
<td>33.6 ± 1.4</td>
<td>0.276</td>
</tr>
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<td>18.0 ± 0.8</td>
<td>0.034</td>
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<td>32.2 ± 2.4</td>
<td>0.311</td>
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<td>1.37</td>
<td>18.4 ± 0.8</td>
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<td>4.32</td>
<td>33.4 ± 2.1</td>
<td>0.379</td>
</tr>
<tr>
<td>1.42</td>
<td>19.1 ± 0.7</td>
<td>0.041</td>
<td>4.72</td>
<td>33.0 ± 2.0</td>
<td>0.453</td>
</tr>
<tr>
<td>1.51</td>
<td>20.9 ± 0.6</td>
<td>0.046</td>
<td>5.20</td>
<td>32.9 ± 3.2</td>
<td>0.550</td>
</tr>
<tr>
<td>1.59</td>
<td>21.8 ± 0.8</td>
<td>0.052</td>
<td>5.70</td>
<td>33.4 ± 3.3</td>
<td>0.660</td>
</tr>
<tr>
<td>1.67</td>
<td>23.2 ± 0.5</td>
<td>0.057</td>
<td>6.39</td>
<td>38.9 ± 3.4</td>
<td>0.832</td>
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<td>23.7 ± 0.5</td>
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<td>7.11</td>
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</tr>
<tr>
<td>1.84</td>
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<td>0.069</td>
<td>8.07</td>
<td>29.6 ± 2.8</td>
<td>1.32</td>
</tr>
<tr>
<td>1.92</td>
<td>26.0 ± 0.5</td>
<td>0.075</td>
<td>9.25</td>
<td>31.9 ± 2.2</td>
<td>1.74</td>
</tr>
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<td>2.23</td>
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<td>0.101</td>
<td>10.7</td>
<td>27.9 ± 1.8</td>
<td>2.32</td>
</tr>
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<td>2.24</td>
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<td>0.119</td>
<td>12.9</td>
<td>31.3 ± 1.5</td>
<td>3.39</td>
</tr>
<tr>
<td>2.62</td>
<td>29.4 ± 0.8</td>
<td>0.140</td>
<td>15.8</td>
<td>31.1 ± 1.0</td>
<td>5.09</td>
</tr>
<tr>
<td>2.63</td>
<td>30.3 ± 0.8</td>
<td>0.141</td>
<td>19.9</td>
<td>30.9 ± 0.9</td>
<td>8.03</td>
</tr>
<tr>
<td>2.73</td>
<td>30.6 ± 0.8</td>
<td>0.151</td>
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</tr>
</tbody>
</table>

Branching ratios (%)

<table>
<thead>
<tr>
<th>g (kms$^{-1}$)</th>
<th>E (meV)</th>
<th>SF$_6^+$</th>
<th>SF$_5^+$</th>
<th>SF$_4^+$</th>
<th>SF$_6^+$</th>
<th>SF$_5^+$</th>
<th>SF$_4^+$</th>
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</thead>
<tbody>
<tr>
<td>1.1</td>
<td>0.024</td>
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<td>9.4 ± 0.8</td>
<td>4.9 ± 0.6</td>
<td>14.1</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>1.6</td>
<td>0.051</td>
<td>84.4 ± 0.7</td>
<td>9.8 ± 0.2</td>
<td>5.8 ± 0.2</td>
<td>18.4</td>
<td>2.2</td>
<td>1.3</td>
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<tr>
<td>2.1</td>
<td>0.088</td>
<td>83.6 ± 0.5</td>
<td>10.0 ± 0.2</td>
<td>6.4 ± 0.1</td>
<td>22.2</td>
<td>2.6</td>
<td>1.7</td>
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<tr>
<td>2.5</td>
<td>0.125</td>
<td>83.8 ± 0.6</td>
<td>9.9 ± 0.2</td>
<td>6.3 ± 0.2</td>
<td>24.5</td>
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Partial cross sections ($10^{-16}$ cm$^2$)

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<th>SF$_5^+$</th>
<th>SF$_4^+$</th>
<th>SF$_6^+$</th>
<th>SF$_5^+$</th>
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132
Figure 5.32 \( \text{SF}_6 + \text{He}(2^3S) \)
Cross section \( (10^{-16} \text{ cm}^2) \)

![Graph showing cross section data for \( \text{SF}_6 + \text{He}(2^3S) \).](image)

Figure 5.33
Branching ratio (%)

![Graph showing branching ratio data.](image)
Table 5.15
Comparison of present branching ratios with other data

Collisions with He(2^3S)

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Table 5.16
Comparison of present branching ratios with other data

Collisions with He(2^1S)

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Comparison of theoretical and experimental results for collisions of He($2^3$S) and He($2^1$S) with Ar

6.1 Introduction

In this section experimental measurements of the total ionisation cross sections for Ar by He($2^3$S) and He($2^1$S), are compared with theoretical results calculated from model interaction potentials.

The first potential developed to describe the interaction of He$^*$ and Ar was devised by Olsen (1972). It is a simple interaction potential, the real part of which (Figure 6.1) is defined at all separations $R$ by a single expression (Appendix 12), which is a modified form of the Ar + He$^+$ potential of Smith et al (1967). The simple form of the Olsen potential makes it relatively easy to convert into a computer subroutine which is also readily adaptable between the singlet and triplet cases. The Olsen potential has been employed by several experimenters and is used here to make a comparison with the later more sophisticated potentials.

The imaginary part of the potential is given by Olsen as a simple exponential.

$$\Gamma (R) = e^{-BR} \quad (6.1)$$

However, a more adaptable exponential form given by

$$\Gamma (R) = Ae^{-BR} \quad (6.2)$$

has been used by Illenberger and Niehaus (1975), Pesnelle et al (1974), Woodard et al (1978) and Jerram (1985) to fit experimental results more closely. In Equation 6.1 and Equation 6.2 $A$ and $B$ are constants chosen to give the best fit to the experimental results and $\Gamma$ is the imaginary part or coupling width of the optical potential. Olsen's form of coupling width was chosen with the minimum number of parameters which would give a theoretical cross section that fitted the limited experimental results available at the time.
Equation 6.2 has been used in this work.

The Freiburg group (Brutschy et al 1976 (triplets) and Haberland and Schmidt al 1977 (singlets)) have performed high resolution differential cross section experiments on argon with both singlet and triplet helium metastable species (Figures 6.1 and 6.5). They have devised several interaction potentials which deserve analysis. As with Olsen the short range repulsion is represented by a shielded Coulomb potential. However, the potential is not defined by a single expression but by several expressions each in a different region, that is to say it varies in a piece-wise continuous fashion (Appendices 13 and 14). The Coulomb potential is interpolated by means of an exponential spline function to a Morse potential in the case of the triplet interaction (Brutschy et al 1976), and by a double Morse potential in the case of the singlet potential (Haberland and Schmidt 1977). This is in turn interpolated to a Van der Waals potential by a cubic spline function. The potentials are considerably different from the Olsen potential at small separations. Again, Equation 6.2 is used to describe the coupling widths.

The Pittsburg group (Siska 1979 (triplets) and Martin et al 1978 (singlets)) have performed differential cross section measurements on both singlet and triplet metastable states and have devised their own interaction potentials (Appendices 15 and 16). They use a third method to describe the functional form of the interaction potential, which they refer to as Ion-Atom-Morse-Morse-Spline-Van der Waals (IAMMSV). Two piece-wise functions describe the interaction, one at small separations and the other at large separations. The transition between the two functions is provided by a switching function which allows a smooth change to take place. Once again Equation 6.2 is used to represent the coupling width.

The work of the Pittsburg group took place after the work of the Freiburg group. In both singlet and triplet cases a better velocity resolution for their differential cross section measurements is claimed and the work shows smaller experimental errors. There is close agreement between the triplet potentials of Siska (Pittsburg group 1979) and Brutschy et al (Freiburg group 1976) (Figure 6.1), but less good agreement between the singlet potentials (Figure 6.5). Martin et al (1978) have used a local gradient maximum in the real part of their potential (Figure 6.5) in order to produce the so-called rainbow effect in their differential cross sections. Haberland and Schmidt (Freiburg 1977) have introduced a minimum in the real part of their potential in order to produce the same effect (Figure 6.5).
Where possible all three potentials are used to calculate the theoretical cross sections described in section 6.3.

6.2 Fitting Procedure

Equation 2.17 is used as the basis of the calculations made in this chapter. However, there is a problem in the expression derived by Miller (1970) because the integral is defined as being from \( R_0 \) to infinity. \( R_0 \) is defined as the point at which \( V_0 = 0 \) and therefore the integral is infinite for all \( l \). This gives the meaningless result that all \( P_l = 1 \). In order to resolve this, a substitution is made which makes \( R = R_0 \sec(\theta) \) to give

\[
P_l(R) = P_l(\theta) = 1 - \exp \left[ -2 \int_0^{\frac{\pi}{2}} \frac{\Gamma(\theta)}{hV_2(\theta)} R_0 \sec(\theta) \tan(\theta) \, d\theta \right]
\]

in which as \( R \) tends to \( R_0 \), \( \theta \) tends to 0 and so the tendency of \( v_0 \) to go to 0 is countered by the \( \sec(\theta)\tan(\theta) \) term in the numerator (Equation 6.3), which also tends to zero. As a result the equation no longer tends to infinity and can be used for calculation. The theoretical ionisation cross section has been calculated for nine velocities (from 1 - 20 km/s) and the value of \( \chi^2 \) calculated from

\[
\chi^2 = \frac{1}{N-n} \sum_{i=1}^{N} \left( \frac{\sigma_{\text{calc}} - \sigma_{\text{exp}}}{\Delta \sigma_{\text{exp}}} \right)^2
\]

In the cases where one or more parameters have been varied to find the best fit, i.e. the lowest value of \( \chi^2 \), the method of Marquand (Bevington 1969) has been used. The computer programs used to perform the analysis were written in Fortran 77 and run on a Dell PC AT computer. They are described in Appendices 17 and 18.

6.3 Comparison of theoretical and experimental results for He(2^3S) + Ar

To examine the fit of the Olsen curve to the present data over the whole velocity range it is reasonable to adjust the parameters \( A \) and \( B \) in Equation 6.2, as has been described above. Olsen chose the value of \( B \) (using Equation 6.1) which best fitted his theoretical cross section calculations to the limited total ionisation cross section data which was
Figure 6.1 Interaction potentials for $\text{Ar} + \text{He}(2^3S)$
Figure 6.2 Coupling width $\Gamma$ for Ar + He($^3S$)

- Siska
- Brutschy et al
- Olsen

$\Gamma_{\text{sat}} = 0.136$
$\Gamma_{\text{sat}} = 0.128$
$\Gamma_{\text{sat}} = 0.081$

Internuclear distance $R$ (a.u.)
available at the time; i.e. at low energy to the absolute measurements of Schmeltekopf and Fehsenfeld (1970) at 0.03 eV, and at high energy to the data of Mosely et al (1972) from 100 - 1000 eV. However, the data of Mosely et al is now thought to be outside the range of validity of the theoretical treatment used in the present work. The best values of A and B were calculated using the program CRS (Appendix 17) to fit the data over the whole velocity range using nine data points. However, the fit was very poor with a value of $\chi^2$ over 100. The procedure was repeated but for only the low velocity data below 4Km/s. The best values of A and B were determined and $\Gamma$ is plotted in Figure 6.2. The fit is now good with $\chi^2$ equal to 3.7 over the fitted range. The calculated cross section is plotted in Figure 6.3 over the complete velocity range. Clearly the Olsen potential (the combination of real and imaginary parts) represents the low velocity interactions well. These interactions are at relatively large internuclear separation ($R > 4$ a.u.),

The Siska and Brutschy et al potentials (Figure 6.1 and 6.2) are more closely defined than that of the Olsen potential because they have been designed to fit differential cross section measurements. This does not allow any variation of A and B without causing a distortion of the theoretical differential cross sections to take place. The aim of this analysis has therefore been to calculate the ionisation cross sections from the theoretical potentials of these two groups as given by them in their papers. Unfortunately the value of A given by Brutschy et al does not reproduce the theoretical ionisation cross section shown in their paper. The value of A has therefore been varied to find the best fit to this theoretical cross section. An exact fit has been achieved indicating that the value of A calculated here is in fact the one used by Brutschy and the value quoted in their paper is incorrect.

Figure 6.3 shows the calculated cross sections using both the Brutschy et al and Siska potentials. Clearly both potentials give a better fit to the present experimental results at low velocity than at high velocity, as with the Olsen potential, but the Siska potential gives the better agreement of the two. Once again the cross sections are too large at high velocity, though not to the same extent as the cross section calculated from the Olsen potential. In order to obtain a better fit to the experimental data a modification to $\Gamma$ has been used which was proposed first by Nakamur (1975). The modification consists of a saturation of $\Gamma$ at small separation, given by

$$\Gamma(R) = A \exp(-BR) \quad \text{for } R > R_{sat}$$

$$\Gamma'(R) = A \exp(-BR_{sat}) \quad \text{for } R < R_{sat} \quad (6.5)$$
Figure 6.3 Theoretical cross sections calculated using interaction potentials for the Ar+He(2^3S) system and compared with the present experimental results.

Cross section ($10^{-16}$ cm$^2$)

Collision energy (eV)

Figure 6.4 Theoretical cross sections calculated with a saturating form of \( \Gamma \) the imaginary part of the Ar+He(2^3S) interaction potential.

Cross section ($10^{-16}$ cm$^2$)

Collision energy (eV)
and supported by the calculations of Miller et al (1972) and Bieniek (1978) which show a
maximum in $\Gamma$ at internuclear separation between $R=2$ a.u. and $R=8$ a.u. for the $\text{He}(^2S) + \text{H}$ reaction. This saturation in $\Gamma$ has been used by Kroon (1985) and Jerram (1985) to
explain the high velocity decline in their triplet cross sections. The form of $\Gamma$ suggested
is given in equation 6.3. Kroon (1985) has also introduced a form in which $\Gamma$ decreases for
small $R$, but this has not been used here as it is considered over-elaborate.

The new form of $\Gamma$ has been used to calculate the total ionisation cross section using the
Olsen potential with the values of A and B calculated above. The fitting procedure has been
used to find the best value of $R_{\text{sat}}$ (5.62 a.u.). The resulting cross section is shown in
figure 6.4 along with the cross sections calculated in the same way for the Siska and
Brutschy potentials, using the A and B values given in their work. It is clear from figure
6.4 that a much better fit is now possible for all the potentials. The Brutschy et al potential
gives a cross section in the middle velocities somewhat higher than the other two and the
Olsen potential is high at the lowest velocities. Only the Siska potential is in very close
agreement over the complete velocity range (although even this potential cannot produce
the slight dip in the cross section at 0.8 eV). The value of $R_{\text{sat}}$ determined for the Siska
potential is the lowest for the three potentials $R_{\text{sat}} = 4.9$ a.u. ($T_{\text{sat}} = 1.36 \times 10^{-3}$ a.u.)
compared to $R_{\text{sat}} = 5.06$ a.u. for Brutschy et al ($T_{\text{sat}} = 1.28 \times 10^{-3}$ a.u.) and $R_{\text{sat}} = 5.62$
a.u. for Olsen ($T_{\text{sat}} = 0.87 \times 10^{-3}$ a.u.). This is very important because collisions which
penetrate to small $R$ result in large-angle differential scattering. The high-energy large-angle
differential cross section calculations made using the Siska and Brutschy et al potentials will be distorted if $R_{\text{sat}}$ is too large. Such measurements have been made by
Brutschy et al at energies as high as 0.48 meV and 0.245 meV, for which collisions may
approach $R = 4.5$ a.u. and $R = 4.9$ a.u. respectively, using a classical calculation and the
interaction potential of Brutschy et al. The theoretical differential cross sections calculated
at large angle for these energies are boosted by the reduction in $\Gamma(R)$ to the extent that they
lie above the experimental data and do not fall within the error bars. This means that none
of the potentials can satisfactorily represent both differential and ionisation cross sections
at the higher energies. What may be stated is that the saturation needed to make the Siska
potential fit the experimental results is slightly less distorting to differential cross section
calculations than that for the Brutschy et al potential. The Olsen potential is known to give
a poor fit to differential cross section data even without a saturating $\Gamma$. 

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Figure 6.5 Interaction potentials for Ar + He(2\(^1\)S)

\[ V \text{ (a.u.)} \]

- Martin et al
- Haberland + Schmidt
- Olsen

Internuclear distance \( R \) (a.u.)

V (a.u.)

-0.001
0
0.001
0.002
0.003
0.004

0  2  4  6  8  10  12  14  16

Internuclear distance \( R \) (a.u.)
Figure 6.6 Coupling width $\Gamma$ for Ar + He(2$^1$S)

$\Gamma$ (10$^{-2}$ a.u)

- Martin et al
- Haberland et al

$\Gamma_{sat} = 0.095$

$\Gamma_{sat} = 0.073$

Internuclear distance $R$ (a.u)

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6.4 Comparison of theoretical and experimental results for He\(^{2\text{S}}\) + Ar

An attempt has been made to find the best values of the parameters \(A\) and \(B\) in the imaginary part of the Olsen potential to fit the experimental results at low velocity, as was done successfully with the triplet potential. However in this case it is not possible to get a good fit. The real part of the potential will only allow a gently sloping rise in the ionisation cross section (Figure 6.7) similar to that found in the triplet case. Because of this no theoretical cross sections calculated from the Olsen potential are shown in Figure 6.8.

Figure 6.7 shows the ionisation cross sections calculated using the potentials as given by Martin et al (1978), Olsen (1972) and Haberland and Schmidt (1977). The real and imaginary potentials of Martin et al are used in their given form so that the differential calculations for which they were derived are not altered (Figure 6.5). For the Haberland and Schmidt potential only the real part is used in this work. The imaginary part of the potential \(\Gamma\) has been modified by Haberland and Schmidt, introducing a gradient minimum at \(R=5.75\) a.u. by means of a second exponential term. In a later publication by Brutschy et al (1982) they have used a nearly identical real potential but have reverted to the simple form of \(\Gamma\), as used in the present calculations (Figure 6.6). Because the potentials are so similar, it is reasonable to use the exact form of \(\Gamma\) given by Brutschy et al (1982).

Unfortunately it has not been possible to use this later real potential devised by Brutschy et al (1982) for any calculations because the potential, which includes two switching functions, cannot be constructed correctly from the information given in the Brutschy et al paper. The only difference between the two potentials of the Freiburg group is the depth of the intermediate minimum. In the Brutschy et al (1982) paper the minimum introduced by Haberland and Schmidt (1977) has been reduced in depth by a factor of two for better agreement with differential cross section data.

As in the case of the triplet interaction, the calculated singlet cross section does not decrease at high velocity in the same way that the experimental cross section does. Once again a saturating form of \(\Gamma\) has been used to fit the high end of the velocity range. The saturation gives a good agreement between experiment and theory at high velocity (Figure 6.8) with \(\Gamma\) saturating at \(R_{\text{sat}} = 5.16\) a.u. for the Martin et al potential \(T_{\text{sat}} = 0.95\times10^3\) a.u. and \(R_{\text{sat}} = 5.6\) a.u for the Haberland and Schmidt potential \(T_{\text{sat}} = 0.73\times10^3\) a.u.)
Figure 6.7: Theoretical cross sections calculated using interaction potentials for the Ar+He(2^1S) system and compared with the present experimental results.

Cross section (10^{-16} \text{cm}^2)

Figure 6.8: Theoretical cross sections calculated with a saturating form of \Gamma the imaginary part of the Ar+He(2^1S) interaction potential.

Cross section (10^{-16} \text{cm}^2)
As Figure 6.8 shows, the cross section calculated using the potential of Martin et al fits the experimental data better than the cross section calculated from the work of Haberland and Schmidt, because the latter lies above the experimental measurements at low velocities. Neither cross section shows a maximum at 0.11 eV as does the experiment; the Martin et al potential gives a maximum at 0.2 eV and the Haberland and Schmidt potential shows a better agreement with a maximum at approximately 0.15 eV.

Burdenski et al (1981) have made measurements of the total ionisation cross section for He(2\textsuperscript{1}S) + Ar up to a velocity of 3 km/s and have calculated theoretical cross sections using the potentials of the Freiberg group. By adopting the same saturating form of $\Gamma$ as used here the value of $R_{\text{sat}}$ was found to be 5.93 a.u., which is a higher value than calculated in this work ($R_{\text{sat}} = 5.6$ a.u.). This may be due to the more pronounced decline in their measured cross section over their much shorter velocity range. The value of $R_{\text{sat}}$ determined by Burdenski et al is large enough to affect the differential cross section calculations of the Freiberg group down to 100 meV, boosting the large-angle cross sections to the extent that they fall outside the experimental errors of the work. The value of $R_{\text{sat}}$ determined here for the Martin et al potential, $R_{\text{sat}} = 5.16$ a.u., is in much better agreement with the differential measurements of the Freiburg and Pittsburg groups.

Figure 6.9 Variation of turning point with angular momentum

![Graph showing turning points with angular momentum]

Turning Point (a.u.)
- 0.97 km/s\textsuperscript{-1}
- 1.51 km/s\textsuperscript{-1}
- 3.25 km/s\textsuperscript{-1}
- 9.21 km/s\textsuperscript{-1}
- 19.7 km/s\textsuperscript{-1}

---

Ar+He(2\textsuperscript{3}S)
Ar+He(2\textsuperscript{1}S)
Figure 6.10 Variation of cross section with angular moment

Cross section (arb units)

(a) Ar+He(2\(^3\)S)

1.51 km s\(^{-1}\)

3.25 km s\(^{-1}\)

0.97 km s\(^{-1}\)

9.21 km s\(^{-1}\)

19.7 km s\(^{-1}\)

Angular Momentum (l)

Cross section (arb units)

(b) Ar+He(2\(^1\)S)

1.51 km s\(^{-1}\)

3.25 km s\(^{-1}\)

0.97 km s\(^{-1}\)

9.21 km s\(^{-1}\)

19.7 km s\(^{-1}\)

Angular Momentum (l)

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differential cross sections at 180 meV are affected by the saturation at 5.16 a.u. The classical turning point for 180 meV interactions with low values of angular momentum ($L<40$) can penetrate to $R = 5.03$ a.u., the region in which $\Gamma$ is saturated. Interactions of less than 180 meV cannot penetrate to the saturated region, and so the calculated differential cross sections at these energies remain the same.

Figures 6.9 shows how the turning points at zero angular momentum and collision velocities between 1.15 kms$^{-1}$ and 3.25 kms$^{-1}$ (48 meV - 200 meV) begin to reach the region in which $\Gamma$ is saturating (4.5 a.u. - 5.5 a.u.). Also shown graphically is the fact that colliding particles which have large angular momentum may have lower turning points than particles with low velocity and with low angular momentum. As a consequence of this (Figure 6.10a and b) collisions with large angular momentum remain important at high collision velocity.

In conclusion there is still a discrepancy between the ionisation and differential cross sections, but at higher energy than reported by Burdensky et al. Burdenski et al have suggested that an extra channel for de-excitation of the $2^1S$ state may be important at higher energies, and put forward radiative de-excitation as the most likely explanation for this discrepancy.

### 6.5 Approximate cross sections

The expression for the approximate cross section derived by Illenberger and Niehaus (Equation 2.27) suggests that for a range of energies between 20 meV and 100 meV a log-log plot of cross section versus energy will result in a straight line. The gradient of this line $M$ is approximately given by

$$M = \frac{D}{B} - \frac{1}{2}$$

(6.6)

where $D$ and $B$ are given by equation 2.26. Oddly, the target which fulfils this condition least in Figures 6.11 and 6.12 is argon. The triplet interaction can be represented by a straight line, but clearly not the singlet interaction, where the simplification is valid at a lower range of collision energy (0.02 - 0.06). For the other molecules studied, quite good agreement is obtained, confirming the validity of the simplification adopted by Illenberger and Niehaus.
Figure 6.11 Log-Log plot of cross section against energy for collisions with He(2^3S)

Cross section \(10^{-16} \text{ cm}^2\)

Collision energy (eV)

- $\text{SF}_6$
- Ar
- $\text{C}_2\text{H}_2$
- $\text{CO}_2$
- $\text{CH}_4$
- $\text{N}_2\text{O}$
- $\text{NH}_3$
Figure 6.12 Log-Log plot of cross section against energy for collisions with He(2\textsuperscript{1}S)

Cross section ($10^{-16}$ cm$^2$)

Collision energy (eV)

- $+$ for Ar
- $\times$ for CH$_4$
- $\times$ for C$_2$H$_2$
- $\triangle$ for CO$_2$
- $\square$ for N$_2$O
- $\diamond$ for NH$_3$
Chapter 7
Conclusions and suggestions for further work

7.1 Conclusions

Total and partial cross sections for collisions of Ar, CO₂, N₂O, CH₄, C₂H₂, NH₃ with helium atoms both in the He(2³S) and He(2¹S) metastable states of helium have been made and also for SF₆ with the triplet state only. The total ionisation cross section for He(2¹S)+Ar is in good agreement with other available data at low collision velocity (below 5 km/s⁻¹), and there is no reason to believe that the results at high velocity (5-20 km/s⁻¹) are not equally reliable, although the error bars are larger. In every other case the variation of total ionisation cross section for collisions with He(2¹S) are the first to be measured.

The procedure of normalising the singlet cross section with the same normalisation constant as for the corresponding triplet cross section has been tested in the case of argon and is found to be very satisfactory. This technique has allowed comparisons to be made between absolute measurements of total ionisation cross sections and both present triplet and singlet results, where several absolute measurements exist. The other available absolute results are at single energies, and normally fall within the error bars of the present cross sections.

The triplet measurements agree well with the previous results of Jerram (1985) and in most cases extend his measurements into higher and lower energy regions. The only significant disagreement is in the case of methane, which is likely to be the result of much better performance of the present quench lamp than that used by Jerram.

The branching ratios are the first energy-dependent ratios measured in the case of collisions with the singlet metastable state, as are the cases of N₂O and SF₆ for the triplet metastable state. Where comparisons are possible in the singlet case, agreement with other single energy measurements is within the error bars, which are large at energies above 0.2 eV. For the triplet case, the agreement with the energy-dependent measurements of Jerram is good, and the present results increase the accuracy by an order of magnitude. In most cases the fraction of Penning ionisation decreases with energy and associative ionisation is only apparent for argon.
The present total ionisation cross sections for both metastable species with argon have been compared with theoretically generated cross sections. In the triplet case it is possible to obtain a good agreement between experiment and cross sections calculated using any of the model potentials, provided a saturating form of imaginary potential is used. The potential which gives the best agreement is that of Siska (1979).

In the singlet case, the potential devised by Olsen (1972) is not satisfactory, as it does not reproduce the steeply rising cross section at low energy. The interaction potential derived by the Pittsburg group (Martin et al 1978) is superior to that of the Freiburg group (Haberland and Schmidt 1977), again using the saturating form of imaginary potential.

In both singlet and triplet cases, the necessary saturation in the imaginary part of the interaction potential reduces the ability of these potentials to produce theoretical high energy differential elastic cross sections which fit experimental data. To reproduce the present experimental results, the saturation in the imaginary part of the interaction potential was introduced at lower internuclear separation than in the work of Burdenski et al (1981). The present work allows the theoretical interaction potentials to describe both elastic and inelastic processes satisfactorily to higher interaction energies than any previous experiments.

### 7.2 Possible improvements and suggestions for further work

It is almost certainly possible to improve the detection efficiency of the present ion detector. This would be done by replacing the electron multiplier with the available multi-channel plates of larger detecting area (1000 mm\(^2\) compared with 314 mm\(^2\)). A mounting identical to that described in chapter 4 could be used.

The quench lamp used in the present experiment has proved to be more than three times as effective as the previous lamp introduced by Harper (1977). However it is not ideal, tending to overheat. This leads to unwanted outgassing in the lamp and makes refilling and baking the lamp frequent necessities. This might be overcome if the present air cooling system were replaced by a water cooling system. Alternatively the 2058 nm resonant radiation could be produced by means of a 1064 nm YAG laser pumping a tunable dye laser. This would be expensive but is the most likely way to achieve full quenching at velocities up to and above 20 kms\(^{-1}\).
As stated in chapter 5, in order to reduce by a factor of three the magnitude of the error bars in the present experiment, it would be necessary to increase the amount of data recorded by a factor of ten. This would best be achieved by increasing the count rate of the experiment but to do this it would be necessary to change from a single-shot to a multi-shot TOF system. This would require a change to a faster computer, fast enough to accept counts a few microseconds apart, and to operate in the multi-channel-analyser mode. The TOF mass spectrometer would need to be replaced in favour of a quadropole mass spectrometer because the time delay between the detection of electron and ion in the TOF type would lead to multiple start pulses in a very high count rate experiment.

With a redesigned interaction region it would be possible to observe the ejected electron energy distributions for different molecules. This could be done by using the multi-channel plate detector to its full capacity as a position sensitive device. Electrons would be collimated as in the Hotop et al (1977) system and then spread out according to energy by passing them through an electric field perpendicular to their trajectory. The multi-channel plates could be inclined with respect to this trajectory to increase sensitivity. A one-dimensional position sensitive anode would be used (or a combination of a phosphor strip and charge-coupled device). The present TOF system would be useful for recording ejected electron energy distributions (EEED) as a function of collision energy, which has been rarely done.

By further collimation of the metastable atom beam and the introduction of a second channeltron detector displaced from the present one by several degrees, it would be possible to perform differential elastic scattering experiments, in a similar manner to that of Kroon (1985), with the cross section measured as a function of energy at a fixed angle. This would help, as it already has in the case of argon, in the formulation of theoretical potential surfaces for the interaction of the systems described in this thesis.
Appendix 1
Analysis of efficiency of the quench lamp built by Harper (1977)

The quenching efficiency as a function of current is given by equation A1:

\[ q(I) = 1 - e^{-kI} \quad \text{A1} \]

Where \( K \) is a constant. Figure A1.1 shows the metastable atom count rate as a function of current \( C(I) \), for a velocity of 7.6 \( \text{km/s} \). From this the value of \( q \) can be derived, as a function of current and more importantly velocity. Equation A2 shows how \( q(I) \) is related to the count rate information of Figure A1.1:

\[ q(I) = \frac{C(I) - C_{\text{min}}}{C_{\text{max}} - C_{\text{min}}} \quad \text{A2} \]

where, \( C_{\text{min}} \) is the count rate achieved with 100% quenching, and \( C_{\text{max}} \) is the count rate measured with no quenching (when the lamp is off). Equations A1 and A2 are simply rearranged to give equation A3:

\[ C(I) = C_{\text{min}} + (C_{\text{max}} - C_{\text{min}}) e^{-kI} \quad \text{A3} \]

A least squares fitting program has been used to find the values of \( C_{\text{min}} \), and \( K \). Previously \( C_{\text{min}} \) has only been estimated. The values calculated are given below.

\[ K = 0.1267 \quad C_{\text{min}} = 4192 \quad \chi^2 = 0.47 \]

The new value of \( K \) is replaced in equation A1, to find \( q \), at 7.6 \( \text{km/s} \), and at a quench lamp current of 28 mA (the normal operating current). The value of the quenching efficiency \( q \) is 98.3%.

By substituting the values of \( q \) and \( v \) into equations given in chapter 4.3 (4.1, 4.2, 4.3) the constants \( C \), \( B \) and \( D \) in these equations have been calculated as \( C = 2.7 \times 10^4 \text{ ms}^{-1} \), \( B = 3.49 \times 10^9 \text{ ms}^{-1} \) and \( D = 1.81 \times 10^5 \text{ ms}^{-1} \).
Figure A1.1

Counts (per 20 seconds)

- Computed fit

Quench lamp current mA

Cmax = 4750

Cmin = 4192
Appendix 2 Relay logic circuit

Appendix 3 Optical switch circuit
Appendix 4 TOF logic circuit with photon mask
Appendix 5 Detector supply circuits

Multi-channel plate supply

![Multi-channel plate supply diagram]

Electron multiplier supply

![Electron multiplier supply diagram]
Appendix 6

TOF3 Provides data collection for total cross section experiments

C
C TOF3
C COLLECTS TIME OF FLIGHT DATA, PLOTS AND FILES
C LINKS WITH SUBPROGRAMS CAMCUL FOR INTERFACE WITH THE CAMAC CRATE,
C PLOTS55 TO SHOW TOF SPECTRA ON THE VDU AND
C FILE TO SAVE THE DATA ON DISK
C
COMMON FNAM(3), COM(18), PAR(18), VAL(10), DAT(520), VALON(10)
DIMENSION DATON(520), DATI(520), DATION(520), VALI(10)
DIMENSION IMSTOR(1001), IONSTOR(1001), IONPLT(512), IONPTL(512)
DIMENSION VALION(IO)
DATA Y/'Y'/
NDATST=1
1 FORMAT(10I6)
2 FORMAT(18A4)
3 FORMAT(10F8.1)
C
C THE VAL* ARRAYS RECORD INFORMATION ABOUT THE DATA WHICH IS BEING COLLECTED
C 'I' INDICATES AN ION SPECTRA AND 'ON' INDICATES THE LAMP IS ON
C
VAL(1)=512.0
4 DO 6 I=2,10
VAL(I)=0.0
VALON(I)=0.0
VALI(I)=0.0
VALION(I)=0.0
6 CONTINUE
NREP=0
C
C TOF SPECTRA ARE STORED IN DAT* ARRAYS
C
DO 8 I=1,520
DAT(I)=0.0
DATON(I)=0.0
DATI(I)=0.0
DATION(I)=0.0
8 CONTINUE
C
C ONE 'CYCLE' REPRESENTS $10^4$ START PULSES
C
TYPE 10
10 FORMAT(' NUMBER OF CYCLES? ')$
ACCEPT 1,ICYC
NCY=1
C
C FIRST INITIALIZE CAMAC CRATE
C
ICOUNT=1
C
C WHEN ICOUNT = 1 THE LAMP IS OFF WHEN ICOUNT = 2 THE LAMP IS TURNED ON
C
12 DO 32 N=1,ICYC
DO 860 L=1,20
CALL CAMAC(11,0,0)
CALL CAMAC(8,0,0)
CALL CAMAC(10,0,0)
C
C RECORD DATA WITH LAMP OFF
C
DO 25 I=1,1001
20 CALL CAMAC(0,21,1,2,IL)
IF(IL.EQ.0)GOTO 20
CALL CAMAC(0,21,3,2,IL)
CALL CAMAC(0,21,2,2,IL)
DATA IS TEMPORARILY STORED IN THE IONSTOR (IONS) AND IMSTOR (METASTABLE) ARRAYS

IONSTOR(I)= JL
IMSTOR(I)= IL

THE DATA IS SORTED INTO TOF SPECTRA

THE DATA IS SORTED INTO TOF SPECTRA

IF(ICOUNT.EQ.2)GOTO 700
DO 30 I=2,1001
IF(IMSTOR(I).GE.1536)GOTO 30
J=IFIX(IMSTOR(I)/3 +1)
DAT(J)=DAT(J)+1.0

IF(DAT(J).LE.VAL(2))GOTO 29
VAL(2)= DAT(J)
VAL(5)=J
29 VAL(3)= VAL(3)+1.0
30 CONTINUE

SECONDLY THE IONS

DO 300 I=2,1001
IF(IONSTOR(I).GE.1536)GOTO 300
J=IFIX(IONSTOR(I)/3 +1)
DAT(I)=DAT(I)+1.0

IF(DAT(I).LE.VAL(2))GOTO 290
VAL(2)= DAT(I)
VAL(5)=J
290 VAL(3)= VAL(3)+1.0
300 CONTINUE

VAL(4)= VAL(4)+1.0

TURN THE QUENCH LAMP ON

GO TO 1200
1100 TYPE 1102
1102 FORMAT( ' LAMP HAS FAILED TO STRIKE ' )
CALL CAMAC(0,8,1,16,0,0)
CALL CAMAC(0,4,0,0,0,0)

LAMP RELAY ON

DO 100 K=1,500
100 CONTINUE

TESLA RELAY ON

DO 150 K=1,500
150 CONTINUE

TURN TESLA RELAY OFF

0.0

wait
DO 200 K=1,100
DO 175 I=1,500
175 CONTINUE
200 CONTINUE
CALL CAMAC(0,4,0,10)
CALL CAMAC(0,4,0,26)
C
C LOOK AT LAMP WITH PHOTODIODE
C
CALL CAMAC(0,4,0,8,DL,DH,IQ,)
TYPE 1,IQ
C
C IF THE LAMP HAS NOT STRUCK REPEAT PROCESS AGAIN
C
IF(IQ.EQ.1)GOTO 1100
TYPE 170
170 FORMAT( ' LAMP ON ')
C
C RECORD DATA WITH QUENCH LAMP ON
C
ICOUNT=2
DO 271 I=1,100
DO 281 K=1,500
281 CONTINUE
271 CONTINUE
GOTO 860
700 CONTINUE
C
C SORT METASTABLE ATOM DATA INTO TOF SPECTRA
C
DO 795 I=2,1001
IF(IMSTOR(I).GE.1536)GOTO 795
J=IFIX(IMSTOR(I)/3+1)
DATON(J)=DATON(J)+1.0
IF(DATON(J).LE.VALON(2))GOTO 790
VALON(2)=DATON(J)
VALON(5)=J
790 VALON(3)=VALON(3)+1.0
795 CONTINUE
C
C SORT ION DATA INTO TOF SPECTRA
C
DO 400 I=2,1001
IF(IONSTOR(I).GE.1536)GOTO 400
J=IFIX(IONSTOR(I)/3+1)
DATION(J)=DATION(J)+1.0
IF(DATION(J).LE.VALION(2))GOTO 390
VALION(2)=DATION(J)
VALION(5)=J
390 VALION(3)=VALION(3)+1.0
400 CONTINUE
800 CONTINUE
VALON(4)=VALON(4)+1.0
C
C TURN LAMP OFF
C
GOTO 1400
1300 CALL CAMAC(0,4,0,10,)
TYPE 1302
1302 FORMAT( ' THE LAMP HAS FAILED TO GO OFF ')
CALL CAMAC(0,8,1,16,0,0)
1400 CALL CAMAC(0,8,1,16,10200,0)
DO 850 K=1,100
DO 825 I=1,500
825 CONTINUE
850 CONTINUE
C
C LOOK AT LAMP WITH PHOTODIODE
C
CALL CAMAC(0,4,0,10)
CALL CAMAC(0,4,0,26)
CALL CAMAC(0,4,0,8,DL,DH,IQ,)
TYPE 1,IQ

C
C IF THE LAMP HAS FAILED TO GO OFF THEN REPEAT THE PROCEDURE
C
IF(IQ.EQ.0)GOTO 1300
TYPE 822

822 FORMAT( ' LAMP OFF ' )
DO 857 I=1,100
DO 856 K=1,500
856 CONTINUE
857 CONTINUE

RETURN TO BEGINNING OF CYCLE
C
ICOUNT=1
860 CONTINUE
TYPE 1,NCY
NCY=NCY+1
32 CONTINUE
NREP=NREP-1
IF(NREP.GT.0)GOTO 12

C AT THE END OF A RUN OF CYCLES THE TOF SPECTRA ARE SCROLLED ON THE VDU ALONG WITH THEIR
C VAL ARRAY AND THEN THE C SPECTRA ARE PLOTTED ON THE SCREEN
C
DO 37 I=1,512,10
TYPE 3,(DAT(I),J=I,I+9)
37 CONTINUE

DO 40 I=1,512,10
TYPE 3,(DATON(I),J=I,I+9)
40 CONTINUE
IF(VAL(2).EQ.0)VAL(2)=0.1
SCAL=235.0/(VAL(2)*2)
DO 41 I=1,512
IPLT(I)=IFIX(DAT(I)*SCAL+0.5)
41 CONTINUE

DO 42 I=1,512
IONPLT(I)=IFIX(DATON(I)*SCAL+0.5)
42 CONTINUE
FILPLOT=0.0
GOTO 44

DO 500 I=1,512,10
TYPE 3,(DAT(I),J=I,I+9)
500 CONTINUE
DO 510 I=1,512,10
TYPE 3,(DATON(I),J=I,I+9)
510 CONTINUE
IF(VAlI(2).EQ.0)VALI(2)=0.1
SCAL=235.0/(VALI(2)*2)
DO 520 I=1,512
IPLT(I)=IFIX(DATI(I)*SCAL+0.5)
520 CONTINUE

DO 530 I=1,512
IONPLT(I)=IFIX(DATON(I)*SCAL+0.5)
530 CONTINUE

CALL PLOT55(2,1+2+4+32+512,511)
CALL PLOT55(9)
CALL PLOT55(10)
IF(FILPLOT.NE.1)GOTO 52

CALL PLOT55(3,1+2+4+32+512,511)
CALL PLOT55(9)
CALL PLOT55(10)
CALL PLOT55(7)
GOTO 51

CALL PLOT55(3,1)
CALL PLOT55(4,1)
CALL PLOT55(7)

164
CALL PLOT55(3,-512,IONPLT)
ACCEPT 2,KR
IF(FILPLOT.NE.1)GOTO 53
TYPE 3,VALION
GOTO 54
53 TYPE 3,VALON
54 CONTINUE
CALL PLOT55(1,1,)
CALL PLOT55(3,-512,IONPLT)
ACCEPT 2,KR
CALL PLOT55(2,512,511)
FILPLOT=FILPLOT+1
IF(FILPLOT.EQ.1) GOTO 43
C
C MORE CYCLES MAY BE PERFORMED OR THE DATA STORED ON DISK
C
TYPE 45
45 FORMAT(' MORE DATA(2),FILE(3)? '),$)
ACCEPT 1,IND
IF(IND-2)50,50,60
50 TYPE 55
55 FORMAT(' NUMBER OF REPEATS? '),$
ACCEPT 1,NREP
GOTO 12
C
C TO STORE THE DATA ON DISK THE FILES ARE NAMED IN ORDER
C
60 TYPE 65
65 FORMAT(' IN THE ORDER METS OFF,METS ON,IONS OFF,IONS ON? '),$
63 TYPE 64
64 FORMAT(' FILENAME? ')$
ACCEPT 2,FNAM
TYPE 70
70 FORMAT(' COMMENTS(UP TO 72 LETTERS)? '),$
ACCEPT 2,COM
TYPE 71
71 FORMAT(' FIXED PARAMETERS(UP TO 72 LETTERS)? ')$
ACCEPT 2,PAR
CALL FILE(1,0.0)
IF(NDATST.EQ.4)GOTO 81
IF(NDATST-2)72,75,78
72 DO 73 I=1,512
DAT(I)=DATON(I)
73 CONTINUE
DO 74 1=2,10
VAL(I)=VALON(I)
74 CONTINUE
NDATST=NDATST+1
GOTO 63
75 DO 76 I=1,512
DATG(I)=DATONG(I)
76 CONTINUE
NDATST=NDATST+1
GOTO 63
77 DO 78 I=2,10
VALG(I)=VALONG(I)
78 CONTINUE
NDATST=NDATST+1
GOTO 63
79 DO 80 I=2,10
VALG(I)=VALONG(I)
80 CONTINUE
NDATST=NDATST+1
GOTO 63
81 NDATST=1
TYPE 85
C
C AFTER STORING DATA ON DISK THE PROGRAM MAY BE RUN AGAIN
C
85 FORMAT(' RESTART(Y OR N)? ')
   ACCEPT 2,ANS
   IF(ANS.EQ.Y)GOTO 4
   TYPE 90
   
C IF THE COMPUTER MAKES ANY MISTAKES IN FILLING THEN THE PROCEDURE IS REPEATED
C
90 FORMAT(' REMAKE LAST THREE FILES? ')
   ACCEPT 2,ANS
   IF(ANS.EQ.Y)GOTO 72
   STOP
   END
Appendix 7

HIGHCOUNT Corrects TOF spectra for the effect of the high count rate

C
C HIGHCOUNT
C READS IN DATA FROM DISK USING FILE SUBPROGRAM
C CORRECTS FOR HIGH COUNT RATE
C PLOTS TOF SPECTRA BEFORE AND AFTER CORRECTION USING PLOT55 AND PLOT7 SUBPROGRAMS
C
DATA Y,H/'Y',H/
COMMON FNAM(3),COM(18),PAR(18),VAL(10),DAT(520)
DIMENSION SUM(180),KTF(11),VEL(180),LX(11),DIV(180)
DIMENSION DSUM(180),ADSUM(180),DDIV(180),VELO(180)
3000 CONTINUE
C
C SCROLL AND PLOT ARE BOTH OPTIONAL
C
992 FORMAT( ' IS SCROLL REQUIRED? ' )
ACCEPT 7,SCRO
TYPE 992
991 FORMAT( ' IS A PLOT REQUIRED? ' )
ACCEPT 7,GRPH
13 FORMAT(7F10.4)
8 FORMAT(3I6)
C
C LOAD TOF SPECTRUM FROM DISK
C
1 TYPE 2
2 FORMAT( WHICH MEMORY SET? ')
ACCEPT 7,FNAM
CALL FILE(0,0,0.
C
C TYPE OUT DATA AND PLOT TOF SPECTRUM
C
7 TYPE 7,COM
TYPE 7,PAR
5 TYPE 9,VAL
ACCEPT 7,KR
IF(SCRO.NE.Y)GOTO 88
DO 80,1=1,512,10
80 TYPE 9,(DAT(J),J=I,I+9)
9 FORMAT(10F8.1)
88 IF(GRPH.NE.Y)GOTO 27
83 CONTINUE
CALL PLOT7(DAT,512,AMAX,IEN,IG,)
C
C CORRECT FOR HIGH COUNT RATE
C
1000 FORMAT( ' IS A CORRECTION FOR HIGH COUNT RATE REQUIRED ' )
ACCEPT 7,ATEL
IF(ATEL.NE.Y)GOTO 27
C
167
C TOTS  =  RUNNING TOTAL OF COUNTS
C CYCTO  =  THE NUMBER OF CYCLES IN WHICH THE DATA WAS Recorded (DIVIDED BY 10^4)
C CMIS  =  THE NUMBER OF CYCLES IN WHICH A CHANNEL COULD RECORD DATA

C
1010 FORMAT( ' TYPE IN ZERO OFFSET (INTEGRAL) ' )
   ACCEPT 8,IOF
   TOTS=0.0
   DO 1015 I=1,IOF+10
   TOTS=TOTS+DAT(I)
   1015 CONTINUE

C
1020 FORMAT( ' HOW MANY CYCLES ' )
   ACCEPT 13,CYCTO
   IOF=IOF+10
   CYCTO=CYCTO*10000
   CMIS=0.0
   TNEW=0.0
   DO 1100 I=IOF,512
   TOTS=TOTS+DAT(I)
   CMIS=CYCTO-TOTS
   DAT(I)=DAT(I)*CYCTO/CMIS
   TNEW=TNEW+DAT(I)
   1100 CONTINUE

C THE TOTAL NUMBER OF COUNTS IN THE TOF SPECTRUM BEFORE AND AFTER CORRECTION ARE
C DISPLAYED

1110 FORMAT( ' OLD TOTAL, NEW TOTAL ' )
   TYPE 9, TOTS, TNEW

C THE NEW TOF SPECTRUM IS PLOTTED

GOTO 5

C THE NEW TOF SPECTRUM IS FILED ON DISK

27 TYPE 89
89 FORMAT( ' WHAT IS THE NEW FILE NAME? ' )
   ACCEPT 7,FNAM
   CALL FILE(1,0.0)
   GOTO 3000
STOP
END
Appendix 8

CROSCAL Calculates total ionisation cross section

C
C CROSCAL
C READS IN TOF SPECTRA FROM DISK, USING FILE SUBPROGRAMS
C PLOTS TOF SPECTRA USING PLOT55 AND PLOT7 SUBPROGRAMS
C CORRECTS FOR HIGH COUNT RATE
C AND CALCULATES TRIPLET AND SINGLET CROSS SECTIONS
C
DATA Y,H/'Y'/HV
COMMON FNAM(3),COM(18),PAR(18),VAL(10),DAT(520)
DIMENSION SUM(180),KTF(11),VEL(180),LX(11),DIV(180)
DIMENSION DSUM(180),ADSUM(180),DDIV(180),VELO(180)

3000 CONTINUE
C
C SCROLL AND PLOT ARE BOTH OPTIONAL
C
TYPE 992
992 FORMAT( ' IS SCROLL REQUIRED? ' )
ACCEPT 7,SCRO
TYPE 991
991 FORMAT( ' IS A PLOT REQUIRED? ' )
ACCEPT 7,GRPH
13 FORMAT(7F10.4)
8 FORMAT(3I6)
TYPE 2000
C
C ALL FOUR TOF SPECTRA ARE READ INTO THE COMPUTER. Q REPRESENTS THE QUENCH LAMP.
C
2000 FORMAT( ' INPUT FILES IONS QON, IONS QOFF, 
1 METS QON, METS QOFF ' )
DO 2500 NCYC=0,90,30
1 TYPE 2
2 FORMAT( ' WHICH MEMORY SET? ' )
ACCEPT 7,FNAM
CALL FILE(0,0.0)
C
C COM (COMMENTS), PAR (PARAMETERS) AND VAL ARE ARRAYS WHICH CONTAIN INFORMATION ABOUT 
C THE TOF SPECTRA.
C
7 FORMAT(18A4)
TYPE 9,PAR
5 TYPE 9,VAL
ACCEPT 7,KR
IF(SCRO.NE.Y)GOTO 88
DO 80,I=1,512,10
80 TYPE 9,(DAT(J),J=I,I+9)
88 IF(GRPH.NE.Y)GOTO 27
84 CONTINUE
CALL PLOT7(DAT,512,AMAX,IEN,IG,)
C
C A CORRECTION FOR HIGH COUNT RATE CAN BE MADE.
C
1000 FORMAT( ' IS A CORRECTION FOR HIGH COUNT RATE REQUIRED? ' )

169
ACCEPT 7,ATEL
IF(ATEL.NE.Y)GOTO 27
C
C DAT(I) = THE NUMBER OF COUNTS IN CHANNEL I
C IOF = THE PHOTON PEAK CHANNEL
C TOTS = RUNNING TOTAL OF COUNTS
C CYCTO = THE NUMBER OF CYCLES IN WHICH THE DATA WAS C RECORDED (DIVIDED BY 10^4)
C CMIS = THE NUMBER OF CYCLES IN WHICH A CHANNEL COULD RECORD DATA
C

C TYPE 1010
1010 FORMAT( ' TYPE IN ZERO OFFSET (INTEGRAL) ' )
ACCEPT 8,IOF
TOTS=0.0
DO 1015 I=1,IOF+10
TOTS=TOTS+DAT(I)
1015 CONTINUE
C
C IOF=IOF+10
C CYCTO=CYCTO*10000
C CMIS=0.0
C TNEW=0.0
DO 1100 I=IOF,512
TOTS=TOTS+DAT(I)
CMIS=CYCTO-TOTS
DAT(I)=DAT(I)*CYCTO/CMIS
TNEW=TNEW+DAT(I)
C TYPE 9, TOTS ,TNEW
1100 CONTINUE
C
C THE TOTAL NUMBER OF COUNTS IN THE TOF SPECTRUM BEFORE AND AFTER CORRECTION ARE
C DISPLAYED
C
C TYPE 1110
1110 FORMAT( ' OLD TOTAL, NEW TOTAL ' )
TYPE 9, TOTS, TNEW
GOTO 5
27 TYPE 89
C
C AT THIS POINT THE PROCEDURE MAY BE TERMINATED
C
C 89 FORMAT( ' CONTINUE ? ' )
ACCEPT 7,ADDN
INCI=0
IF(ADDN.NE.Y)GOTO 177
C
C TOF BIN LIMITS KTF(I) ARE READ FROM THE DATSET SUBPROGRAM TWO SETS OF KTF(I) EXIST L (LOW
C VELOCITY) AND H (HIGH VELOCITY). THE KTFE VALUES ARE THEN CORRECTED FOR THE DIFFERENT
C PATH LENGTHS BETWEEN THE CHOPPER WHEEL AND THE METASTABLE ATOM AND ION DETECTORS
C
C TYPE 107
107 FORMAT( ' IS THIS A METASTABLE T.O.F. DISTRIBUTION? ' )
ACCEPT 7,AMET
109 CALL DATSET(L,KTF)
GOTO 102
101 CALL DATSET(H,KTF)
102 DO 103 I=1,11
C
C KTF VALUES ARE CONVERTED FROM MICRO SECONDS TO BIN NUMBER
C
C LX(I)=IFIX(FLOAT(KTF(I))/3.0)
103 CONTINUE
IF(AMET.NE.Y)GOTO 119
DO 108,1=1,11
108  LX(I)=IFIX(FLOAT(LX(I))*101.4/80.0)
119  IF(INCI.LT.20) GOTO 105
104  CONTINUE
105  CONTINUE

C THE TRIPLET VELOCITY SPECTRA ARE FIRST CALCULATED
C THE PHOTON PEAK CHANNEL IS SUBTRACTED TO GIVE THE ZERO OFFSET
C SUM = THE NUMBER OF COUNTS PER CHANNEL IN A GIVEN BIN
C DSUM = THE ERROR ON SUM
C VEL = THE WEIGHTED MEAN VELOCITY FOR A GIVEN BIN
C
DO 110,1=1,11
LX(I)=LX(I)+IOF-1
110 CONTINUE
DO 120,1=1,10
  LX(I)=LX(I)+1
  SUM(I+INCI+NCYC)=0.0
  TOP=0.0
  BOT=0.0
  VEL(I+INCI+NCYC)=0.0
  DO 115,J=LX(I),LX(I+1)
    SUM(I+INCI+NCYC)=SUM(I+INCI+NCYC)+DAT(J)
    TOP=(FLOAT(J-IOF)*DAT(J))+TOP
    BOT=BOT+DAT(J)
 115 CONTINUE
  DSUM(I+INCI+NCYC)-hover(SUM(I+INCI+NCYC))*FLOAT(LX(I+1)-LX(I)+1)
  AVTOF=(3.0*TOP)/BOT
  IF(AMET.NE.Y)VEL(I+INCI+NCYC)=860.0/AVTOF
  IF(AMET.EQ.Y)VEL(I+INCI+NCYC)=1090.0/AVTOF
120 CONTINUE
INCI=INCI+10
IF(INCI.LT.30) GOTO 101

C SUBTRACT ANY BACKGROUND

C
TYPE 121
121 FORMAT( ' IS A BACKGROUND SUBTRACTION REQUIRED? ' )
ACCEPT 7,BGB
IF(BGB.NE.Y)GOTO 129
BGD=0.0
DO 122 I=480,510
  BGD=BGD+DAT(I)
122 TYPE 123
123 ACCEPT13,AFT
C
C THE TRIPLET VELOCITY SPECTRA ARE SHOWN ON THE VDU
C
DO 124 J = 1,30
  SUM(J+NCYC)=SUM(J+NCYC)-(BGD/30.0)
129 TYPE 131
131 FORMAT( ' COUNTS , ERROR , VEL ' )
DO 132,1=1,30
  TYPE 9,SUM(I+NCYC),DSUM(I+NCYC),VEL(I+NCYC)
132 CONTINUE
C
C CALCULATE THE SINGLET VELOCITY SPECTRUM
C
ACCEPT 7,KR
TYPE 2509
2509 FORMAT( ' SINGLET SPECTRA IONS THEN METS ' )
DO 2700 IL=1,2
  ACCEPT 7,KR
  IF(IL.EQ.2)GOTO 2510
  IDIFF=120
  ISTOP=30
2510
ISTART=1
GOTO 2600
2510 ISTOP=90
IDIFF=90
ISTART=61
2600 DO 2650 I=ISTART,ISTOP
   SUM(I+IDIFF)=SUM(I+30)-SUM(I)
   C
   C THE ERROR DSUM IS CALCULATED FROM THE COMBINATION IN QUADRATURE OF THE ERRORS OF C THE
   PARENT TOF SPECTRA
   C
   DSUM(I+IDIFF)=SQRT(DSUM(I+30)**2+DSUM(I)**2)
   C
   C AN APPROXIMATE VELOCITY IS CALCULATED, BUT BECAUSE THE VELOCITY DISTRIBUTION OF
   C SINGLET AND TRIPLET METASTABLE ATOMS IS DIFFERENT THE VELOCITY MUST BE CALCULATED BY
   C PRODUCING ION AND METASTABLE TOF SINGLET SPECTRA USING SUBSING AND RE-ENTERING THEM
   C IN THIS PROGRAM IN THE POSITION OF THE METASTABLE ATOM AND ION TOF SPECTRA WITH QUENCH
   C LAMP ON
   C
   VEL(I+IDIFF)=(VEL(I+30)+VEL(I))/2
2650 CONTINUE
   C
   C THE SINGLET TOF SPECTRA ARE DISPLAYED ON THE VDU
   C
   TYPE 2666
   2666 FORMAT( ' COUNTS , ERROR , VEL ' )
   DO 2675 1=1,30
      TYPE 9,SUM(I+IDIFF),DSUM(I+IDIFF),VEL(I+IDIFF)
   2675 CONTINUE
   C
   C CALCULATE CROSS SECTIONS
   C
   TYPE 140
   140 FORMAT( ' CROSS SECTIONS FIRST THE TRIPLET ' )
   DO 2800 IL=1,2
      ACCEPT 7,KR
      IF(IL.EQ.2)GOTO 2850
      ISTART=1
      ISTOP=30
      IDDIFF=60
      GOTO 2855
   2850 ISTART=121
      ISTOP=150
      IDDIFF=30
   2855 CONTINUE
   C
   C DIV = THE CROSS SECTION
   C ADSUM = THE FRACTIONAL ERROR ON SUM
   C DDIV = THE ERROR ON DIV
   C VELO = THE MEAN VELOCITY
   C
   DO 141,1=ISTART,ISTOP
      DIV(I)=SUM(I)/SUM(I+IDIFF)
      ADSUM(I+IDIFF)=DSUM(I+IDIFF)/SUM(I+IDDIFF)
      ADSUM(I)=DSUM(I)/SUM(I)
      DDIV(I)=SQRT(ADSUM(I)**2+ADSUM(I+IDDIFF)**2)*DIV(I)
      VELO(I)=(VEL(I)+VEL(I+IDDIFF))/2.0
   141 TYPE 13,DIV(I),DDIV(I),VELO(I),VEL(I),VEL(I+IDDIFF)
290 TYPE 300
   C
   C THE RESULTS CAN BE NORMALISED TO ABSOLUTE DATA
   C
   300 FORMAT( ' MULTIPLY UP THESE RESULTS? ' )
   ACCEPT 7,AMUL
   IF(AMUL.NE.Y)GOTO 130
   TYPE 350
350 FORMAT( ' BY WHAT FACTOR? ' )
ACCEPT 13,AMULT
DO 400,1=1ST ART,ISTOP
DIV(I)=DIV(I)*AMULT
DDIV(I)=DDIV(I)*AMULT
400  TYPE 13,DIV(I),DDIV(I),VELO(I)
GOTO 290
130  CONTINUE
    TYPE 159

C
C THE CROSS SECTION DATA CAN BE PRINTED OUT AS A PERMANENT RECORD
C
159  FORMAT( ' IS A PRINT OUT REQUIRED? ' )
    ACCEPT 7,PRI0
    IF(PRI0.NE.Y)GOTO 2800
    TYPE 161
161  FORMAT( ' TYPE IN ANY COMMENTS? ' )
    ACCEPT 77,ACOM
    PRINT 77,ACOM
77  FORMAT(A48)
    ICY=1START
164  PRINT 167
167  FORMAT( ' ' )
    PRINT 162
162  FORMAT( ' SET 1 ERROR VEL SET2 ERROR
           1  SET/SET2 ERROR ' )
    PRINT 167
    DO 163 I=ICY,9+ICY
163  PRINT 13,SUM®,DSUM®,VELO®,SUM(I+IDIFF),
1       DSUM(I+IDIFF),DIV®, DDIV®
    CONTINUE
    ICY=ICY+10
    IF(ICY.LT.ISTOP)GOTO 164
    PRINT 167
2800  CONTINUE
    TYPE 2900
2900  FORMAT( ' BEGIN AGAIN ? ' )
    ACCEPT 7,REA
    IF(REA.EQ.Y)GOTO 3000
C
C CLEAR ALL PLOTS FROM THE VDU
C
177  CALL PLOT55(2,512,511)
STOP
END
Appendix 9

CROSS2 Calculates the total cross section at a velocity read into the computer

C
C CROSS2
C READS IN TWO TOF SPECTRA FROM DISK, PLOTS IT USING PLOT55 AND PLOT7 SUBPROGRAMS
C CROSS SECTIONS ARE CALCULATED FROM TOF BIN RANGES ENTERED BY HAND
C
DATA Y,H/'Y'/HV
COMMON FNAM(3),COM(18),PAR(18),VAL(10),DAT(520)
DIMENSION SUM(2),KTP(2),VEL(2),LX(2,2)
DIMENSION DSUM(2),ADSUM(2)
DIMENSION DATA(2,520),IOF(2)
3000 CONTINUE
C
C SCROLL AND PLOT ARE BOTH OPTIONAL
C
TYPE 992
992 FORMAT( ' IS SCROLL REQUIRED? ' )
ACCEPT 7.SCRO
TYPE 991
991 FORMAT( ' IS A PLOT REQUIRED? ' )
ACCEPT 7.GRPH
13 FORMAT(7F10.4)
8 FORMAT(16)
C
C LOAD TOF SPECTRUM FROM DISK
C
TYPE 2000
2000 FORMAT( ' INPUT FILES IONS THEN METS, ' )
DO 2500 NCE= 1,2
1  TYPE 2
2  FORMAT( ' WHICH MEMORY SET? ' )
ACCEPT 7,FNAM
CALL FILE(0,0,0)
TYPE 7,COM
7  FORMAT(18A4)
TYPE 7,PAR
5  TYPE 9,VAL
ACCEPT 7,VR
IF(SCRO.NE.Y)GOTO 88
C
C TYPE OUT DATA AND PLOT TOF SPECTRUM
C
DO 80,1=1,512,10
80  TYPE 9,(DAT(J),J=1,1+9)
88  IF(GRPH.NE.Y)GOTO 900
83  CONTINUE
CALL PLOT7(DAT,512,AMAX,IEN.IG,)
900  CONTINUE
DO 1100 I=1,512
DATA(NCE,I)= DAT(I)
1100 CONTINUE
2500 CONTINUE
TYPE 106
106  FORMAT( ' TYPE IN THE ZERO OFFSETS (INTEGRAL I,M) ' )
174
ACCEPT 8,1OF(1)  
ACCEPT 8,1OF(2)  
C  
C READ THE RANGE OF HIGH AND LOW RANGE OF THE TOF BIN AND CORRECT TIME BIN FOR THE  
C DIFFERENCE IN PATH LENGTH BETWEEN THE CHOPPER WHEEL AND THE METASTABLE ATOM AND ION  
C DETECTOR  
C  
109 TYPE 107  
107 FORMAT( ' INPUT TOF RANGES, LOW,HIGH ' )  
   ACCEPT 8,KTF(1)  
   ACCEPT 8,KTF(2)  
102 DO 103 I=1,2  
   LX(1,I)=IFIX(FLOAT(KTF(I))/3.0)  
103 CONTINUE  
   DO 108,1=1,2  
108 LX(2,I)=IFIX(FLOAT(LX(1,I))*101.4/80.0)  
   DO 104,J=1,2  
   DO 110,1=1,2  
104 CONTINUE  
   DO 110,1=1,2  
105 LX(J,I)= LX(J,I)+ IOF(J)  
110 CONTINUE  
C  
C SUM = THE NUMBER OF COUNTS PER CHANNEL IN A GIVEN BIN  
C DSUM = THE ERROR ON SUM  
C VEL = THE WEIGHTED MEAN VELOCITY FOR A GIVEN BIN  
C  
DO 120,1=1,2  
   SUM(I)=0.0  
   TOP=0.0  
   BOT=0.0  
   VEL(I)=0.0  
   DO 115,J=LX(I,1),LX(I,2)  
115 SUM(I)= SUM(I)+ DATA(I,J)  
115 TOP=(FLOAT(J-IOF(I))*DATA(I,J))+TOP  
115 BOT=BOT+ DATA(I,J)  
115 CONTINUE  
   SUM(I)=SUM(I)/FLOAT(LX(I,2)-LX(I,1)+1)  
   DSUM(I)= SQRT(SUM(I))  
   DSUM(I)=DSUM(I)/SQRT(FLOAT(LX(I,2)+LX(I,1)))+TOP  
115 CONTINUE  
122 AVTOF=(3.0*TOP)/BOT  
122 IF(I.EQ.1)VEL(I)=860.0/AVTOF  
122 IF(LNE.1)VEL® = 1090.0/AVTOF  
C  
C SUBTRACT ANY BACKGROUND  
C  
TYPE 121  
121 FORMAT( ' IS A BACKGROUND SUBTRACTION REQUIRED? ' )  
   ACCEPT 7,BGB  
   IF(BGB.NE.Y)GOTO 129  
   BGD=0.0  
   DO 122 J=480,510  
122 BGD= BGD+ DATA(I,J)  
122 CONTINUE  
123 FORMAT( ' MULTIPLY THE BACKGROUND BY WHAT FRACTION? ' )  
   ACCEPT13,AFT  
124 SUM(I)=SUM(I)-(BGD/30.0)*AFT  
C  
C THE VELOCITY SPECTRA ARE SHOWN ON THE VDU  
C  
129 TYPE 131  
131 FORMAT( ' COUNTS , ERROR , VEL ' )  
132 TYPE 9,SUM(I),DSUM(I),VEL(I)  
120 CONTINUE  
   ACCEPT 7,KR  
C  
C CALCULATE CROSS SECTION  
C DIV = THE CROSS SECTION  
C ADSUM = THE FRACTIONAL ERROR ON SUM  
C DDIV = THE ERROR ON DIV  

175
C VELO = THE MEAN VELOCITY

C
DIV=SUM(1)/SUM(2)
ADSUM(2)=DSUM(2)/SUM(2)
ADSUM(1)=DSUM(1)/SUM(1)
DDIV=SQRT(ADSUM(1)**2+ADSUM(2)**2)*DIV
VELO=(VEL(2)+VEL(1))/2.0

TYPE 162
162 FORMAT( ' SET 1  ERROR  VEL  SET 2  ERROR ' )
   TYPE 13,SUM(1),DSUM(1),VELO,SUM(2),
   1 DSUM(2),DIV,DDIV
163 CONTINUE

TYPE 2900
2900 FORMAT( ' BEGIN AGAIN ? ' )
   ACCEPT 7,REA
   IF(REA.EQ.Y)GOTO 109

177 CALL PLOT55(2,512,511)
STOP
END
Appendix 10

TOFM1 Collects branching ratio data

C TOFM1
C COLLECTS 20 MASS SPECTRA USING THE CAMCUL SUBPROGRAM AT 10 DIFFERENT VELOCITIES, 10 WITH
C QUENCH LAMP ON AND 10 WITH THE QUENCH LAMP OFF. THE SPECTRA ARE RECORDED
C SYMULTANEOUSLY THE TOTAL MASS SPECTRUM IS PLOTED USING THE PLOT55 AND PLOT7
C SUBPROGRAMS
C THE SPECTRA READ INTO 20 FILES USING THE FILE SUBROGRAM
C
COMMON FNAM(3),COM(18),PAR(18),VAL(10),DAT(256)
DIMENSION IPLT(256)
DIMENSION DATT(20,256),VALT(20,10),SUF(20)
DIMENSION ISTOR(500),JSTOR(500)
DATA Y,SUF/Y,1,’1’,’2’,’3’,’4’,’5’,’6’,’7’,’8’,’9’,’10’,
1 ’11’,’12’,’13’,’14’,’15’,’16’,’17’,’18’,’19’,’20’/
1 FORMAT(10I6)
2 FORMAT(18A4)
3 FORMAT(10F7.1)
4 DO 5 I=2,20
  VAL(I)=0.0
5 CONTINUE
NREP=0
C THE 20 SPECTRA ARE STORED IN A TWO DIMENSIONAL ARRAY DATT(I,J) I IS THE CHANNEL NUMBER
C FROM 1 TO 256 AND J IS THE SPECTRUM NUMBER. THE VALT(I,J) ARRAY CARRIES INFORMATION
C ABOUT THE SPECTRA
C
DO 7 I=1,20
  VALT(I,1)=256.0
DO 6 J=2,10
  VALT(I,J)=0.0
6 CONTINUE
DO 7 J=1,256
  DATT(I,J)=0.0
7 CONTINUE
C THE PHOTOIONISATION PEAK (IN MICRO SECONDS) IS RED INTO THE COMPUTER AS A VELOCITY
C OFFSET AND THE MASS SPECTRUM OOF SET WHICH ALLOWS ALL MASS PEAKS UNDER EXAMINATION
C TO BE RECORDED
C
TYPE 8
FORMAT(‘ VELOCITY OFFSET, MASS OFFSET? ‘)
ACCEPT 1,IOF
ACCEPT 1,JOF
VAL(4)=FLOAT(IOF)
TYPE 10
C
C THE NUMBER OF START PULSES RECORDED PER CYCLE CAN BE VARIED TO ALLOW FREQUENT
C DISPLAY OF THE TOTAL MASS SPECTRA IN CONDITIONS OF LOW COUNT RATE, 1000 IS NORMAL
C
10 FORMAT(‘ NUMBER OF START PULSES? ‘)
ACCEPT 1,NRPT
NEV=0
NRPTS=1
STRT=0.0
C
C THE SUM OF ALL INDIVIDUAL MASS SPECTRA IS RECORDED IN THE DAT ARRAY
C
DO 12 I=1,256
  DAT(I)=0.0
12 CONTINUE
14 TYPE 16
16 FORMAT(‘ NUMBER OF CYCLES? ‘)
ACCEPT 1,NCYC
NCYC=NCYC*2
17 DO 18 I=1,256
 IDAT(I)=0
 JDAT(I)=0
18 CONTINUE
IQUEN=0

C C FIRST RECORD DATA WITH THE QUENCH LAMP OFF
C
19 DO 36 IG = 1,NCYC
24 VAL(9)=VAL(9)+FLOAT(NEV)
 CALL CAMAC(11,0,0)
 CALL CAMAC(8,0,0)
 CALL CAMAC(10,0,0)
 CALL CAMAC(0,20,0,26,)
 CALL CAMAC(0,20,0,17,7,8,)
 NEV=0
 DO 28 I=1,NRTT
25 CALL CAMAC(0,21,2,2,IL)
 IF(IL.EQ.0)GOTO 25
 CALL CAMAC(0,21,3,2,IL1)
 CALL CAMAC(0,20,0,2,IL2)
 IF(IL1.LT.20 OR.IL1.LT.1050.0 OR.IL2.LT.512.0)GOTO 28
 NEV=NEV+1
28 CONTINUE

C C ISTOR = VELOCITY
C JSTOR = MASS
C
C ISTOR(NEV)=IL1
 ISTOR(NEV)=IL2-IOF
28 CONTINUE
C
C VAL5 = THE NUMBER OF START PULSES /100
C
VAL(5)=VAL(5)+FLOAT(NRTT)/100.0
C
C SORT THE DATA INTO ONE OF TEN MASS SPECTRA DEPENDING ON VELOCITY
C
DO 35 I=1,NEV
 K=ISTOR(I)-IOF
 M=1
 IF(K.GE.696)GOTO 30
 M=2
 IF(K.GE.472)GOTO 30
 M=3
 IF(K.GE.372)GOTO 30
 M=4
 IF(K.GE.315)GOTO 30
 M=5
 IF(K.GE.266)GOTO 30
 M=6
 IF(K.GE.216)GOTO 30
 M=7
 IF(K.GE.170)GOTO 30
 M=8
 IF(K.GE.123)GOTO 30
 M=9
 IF(K.GE.84)GOTO 30
 M=10
 IF(K.GE.45)GOTO 30
 GOTO 35
30 N=IFIX(JSTOR(I))
 IF(N.LT.1 OR.N.GT.150)GOTO 35
 IF(IQUEN.EQ.0)GOTO 31
 M=M+10
31 DATT(M,N)=DATT(M,N)+1.0
 IF(DATT(M,N).LE.VAL5(M,2))GOTO 32
178
C VALT(M,2) = THE MAXIMUM NUMBER OF COUNTS IN ONE CHANNEL OF SPECTRUM M
C VAL2 = THE MAXIMUM NUMBER OF COUNTS IN THE COMBINED SPECTRUM
C VALT(M,3) = THE TOTAL NUMBER OF COUNTS
C
VALT(M,2)=DATT(M,N)
IF(DATT(M,N).LE.VAL(2))GOTO 32
VAL(2)=DATT(M,N)
32
VALT(M,3)=VALT(M,3)+1.0
DAT(N)=DAT(N)+1

35 CONTINUE
C
C WHEN IQUEN = 0 THE LAMP IS OFF WHEN IQUEN = 1 THE LAMP IS TURNED ON
C
IF(IQUEN.EQ.1)GOTO 355
IQUEN=IQUEN+1
GOTO 360
355 IQUEN=0
360 TYPE 1,NRPTS
IF(IQUEN.EQ.0)GOTO 1500
C
C TURN THE QUENCH LAMP ON
C
GOTO 1010
1002 TYPE 1004
1004 FORMAT( ' LAMP HAS FAILED TO STRIKE ' )
CALL CAMAC(0,8,1,16,0,0)
CALL CAMAC(0,4,0,10)
C
C LAMP RELAY ON
C
1010 CALL CAMAC(0,8,1,16,10200,0)
DO 1050 K= 1,500
1050 CONTINUE
C
C TESLA RELAY ON
C
CALL CAMAC(0,9,1,16,20400,0)
DO 1149 K= 1,500
1149 CONTINUE
C
C TURN TESLA RELAY OFF
C
CALL CAMAC(0,9,1,16,0,0)
C
C WAIT
C
DO 1100 K= 1,100
DO 1150 I= 1,1500
1150 CONTINUE
1100 CONTINUE
CALL CAMAC(0,4,0,10)
CALL CAMAC(0,4,0,26)
C
C LOOK AT LAMP WITH PHOTODIODE
C
CALL CAMAC(0,4,0,8,DL,DH,IQ,)
TYPE 1,IQ
C
C IF THE LAMP HAS NOT STRUCK REPEAT PROCESS AGAIN
C
IF(IQ.EQ.1)GOTO 1002
1160 FORMAT( ' LAMP ON ' )
DO 1170 I= 1,100
DO 1165 K= 1,500
1165 CONTINUE
1170 CONTINUE
C
C RECORD DATA WITH QUENCH LAMP ON
C
GOTO 36
1500 CONTINUE
C
C TURN LAMP OFF
C
GOTO 1800
1520 CALL CAMAC(0,4,0,10,)
TYPE 1525
1525 FORMAT( ' LAMP HAS FAILED TO GO OFF ' )
CALL CAMAC(0,8,16,0,0)
1800 CALL CAMAC(0,8,16,10200,0)
DO 1528 I=1,100
DO 1526 K=1,500
1526 CONTINUE
1528 CONTINUE
CALL CAMAC(0,4,0,10,)
CALL CAMAC(0,4,0,26)
C
C LOOK AT LAMP WITH PHOTODIODE
C
CALL CAMAC(0,4,0,8,DL,DH,IQ,)
TYPE 1,IQ
C
C IF THE LAMP HAS FAILED TO GO OFF THEN REPEAT THE PROCEDURE
C
IF(IQ.EQ.0)GOTO 1520
TYPE 1560
1560 FORMAT( ' LAMP OFF ' )
DO 1565 I=1,100
DO 1563 K=1,500
1563 CONTINUE
1565 CONTINUE
36 CONTINUE
NREP=NREP-1
IF(NREP.GT.0)GOTO 19
C
C TYPE AND PLOT DATA ON VDU
C
DO 37 I=1,256,10
TYPE 3,(DAT(J),J=I,I+9)
37 CONTINUE
IF(VAL(2).EQ.0.0)VAL(2)=0.1
SCAL=235.0/VAL(2)
DO 41 I=1,256
IPLT(I)=IFK(DAT(I)*SCAL+0.5)
41 CONTINUE
CALL PLOT55(9,)
CALL PLOT55(10,)
TYPE 3,VAL
CALL PLOT55(1,)
CALL PLOT55(2,553,511)
CALL PLOT55(4,1,)
CALL PLOT55(7,)
CALL PLOT55(3,-256,IPLT)
ACCEPT 2,KR
CALL PLOT55(2,512,511)
50 CONTINUE
54 TYPE 55
55 FORMAT( ' MORE DATA(2),FILE(3)? ' )
ACCEPT 1, IND
IF(IND-2)57,57,60
57 TYPE 58
58 FORMAT( ' NUMBER OF REPEATS ? ' )
ACCEPT 1,NREP
GOTO 19
C
C TO FILE THE DATA A SINGLE NAME IS ENTERED AND THE FILES ARE AUTOMATICALLY NUMBERED

180
C FILE1, FILE2..TO FILE20
C
60   TYPE 65
65   FORMAT( ' FILENAME? ' )
      ACCEPT 2,FNAM
C
C IF THE RETURN KEY OPERATES TWICE AND NO FILE NAME IS ENTERED, THE FILE MAY BE RENAMED
C
   TYPE 69
69   FORMAT( ' CHANGE THE NAME? ' )
      ACCEPT 2,FC
      IF(FC.EQ.Y)GOTO60
   TYPE 70
70   FORMAT( ' COMMENTS(UP TO 72 LETTERS)? ' )
      ACCEPT 2,COM
   TYPE 75
75   FORMAT( ' FIXED PARAMETERS(UP TO 72 LETTERS)? ' )
      ACCEPT 2,PAR
C
C VAL(7) = THE NUMBER OF COUNTS RECORDED WITH THE QUENCH LAMP OFF
C VAL(8) = THE NUMBER OF COUNTS RECORDED WITH THE QUENCH LAMP ON
C
DO 77 I=1,10
   VAL(7)=VAL(7)+VALT(I,3)
77   CONTINUE
DO 79 I=11,20
   VAL(8)=VAL(8)+VALT(I,3)
79   CONTINUE
DO 82 I=1,20
   FNAM(2)=SUF(I)
   TYPE 2,FNAM,FNAM(2)
   DO 80 J=1,256
      DAT(J)=DATT(J,I)
   80   CONTINUE
C
C VAL(2) = THE MAXIMUM NUMBER OF COUNTS IN ANY CHANNEL
C VAL(3) = THE TOTAL NUMBER OF COUNTS IN THE MASS SPECTRUM
C VAL(10) = THE NUMBER OF THE SPECTRUM (1-20)
C
   VAL(2)=VALT(I,2)
   VAL(3)=VALT(I,3)
   VAL(10)=I
   CALL FILE(1,0.0)
82   CONTINUE
   TYPE 85
85   FORMAT( ' RESTART(Y OR N)? ' )
      ACCEPT 2,ANS
      IF(ANS.EQ.Y)GOTO 4
C
C IN CASE THE COMPUTER MAKES A MISTAKE CREATING THE FILES THEY CAN BE REMADE
C
   TYPE 86
86   FORMAT( ' REMAKE FILES ' )
      ACCEPT 2,ANS
      IF(ANS.EQ.Y)GOTO 60
STOP
END
Appendix 11

**BRCALC Calculates the branching ratios**

```fortran
C BRCALC
C READS IN 10 MASS SPECTRA EACH AT DIFFERENT VELOCITY, USING THE FILE SUBPROGRAM
C THE MASS VELOCITY RANGES ARE DEFINED BY THE DATER SUBPROGRAM
C THE SPTL SUBPROGRAM DEFINES THE MASS RANGE FOR THE PARTICLES DESIRED
C THE NUMBER OF EACH PARTICLE PRESENT IN A MASS SPECTRUM IS CALCULATED AS IS THE
C PERCENTAGE OF THE TOTAL NUMBER OF COUNTS WHICH IT REPRESENTS
C
DATA BGND,VELO/'BGND','VELOCITY'/
DATA Y,SUF/Y',1',2',3',4',5',6',7',8',9',10',
1 '11',12',13',14',15',16',17',18',19',20'/
DIMENSION APC(10,8),MAX(8),MIN(8),PTL(8),BGD(10),VEL(10)
DIMENSION AVEL(10),KTF(11)
DIMENSION BDAT(512),ERR(10,8),AX(11),SUF(20),ATOT(10,8),TTOT(10)
COMMON FNAM(3),COM(18),PAR(18),VAL(10),DAT(512)
1 FORMAT (2F6.2)
2 FORMAT(2I6)
C
C DEFINE THE TEN TOF RANGES
C
 TYPE 300
300 FORMAT( ' BRANCHING RACIOS FOR SINGLETS ' )
CALL DATER(HLDAT,KTF)
DO 500, I = 1, 11
      AX(I) = FLOAT(KTF(I))
500 CONTINUE
1 TYPE 4
C
C READ THE SET OF TEN MASS SPECTRA FROM DISK AND THE NUMBER OF PTLS TO BE USED.
C
4 FORMAT ( ' WHICH MEMORY SET? '$)
ACCEPT 7,FNAM(1)
7 FORMAT(18A4)
9 FORMAT(10F8.1)
TYPE 14
DO 111, I = 1, IN
DO 111, J = 1, 8
      ATOT(I,J) = 0.0
111 CONTINUE
C
C A MAXIMUM OF 8 PARTICLES MAY BE USED, AND ARE REPRESENTED BY ABR EVIATIONS SUCH AS AN20,
C ANO ETC
C
14 FORMAT( ' HOW MANY PTLS ARE REQUIRED? ' )
ACCEPT 2,IN
13 TYPE 15
15 FORMAT( ' WHAT PARTICLES ' )
IG = 0
C
C THE SUBROUTINE SPTL IS USED TO GIVE THE PREDETERMINED MASS RANGES OF THE PARTICLES
C FOR EACH PARTICLE THE RANGE IS TYPED IN THE FORM OF THE MAX AND MIN CHANNEL NUMBER
C
DO 17,I = 1, IN
ACCEPT 7,PTL(I)
CALL SPTL(PTL(I),MAX(I),MIN(I))
TYPE 2,MAX(I),MIN(I)
17 CONTINUE
C
DO 61,I = 1, 10
   FNAM(2) = SUF(I)
   CALL FILE(0,0.0)
   PEAK = 0.0
   BGD(I) = 0.0
```

182
DO 68, K=1, IN
ATOT(I,K)=0.0
C
C THE MIN AND MAX VALUES ARE USED TO FIND THE NUMBER OF EACH PARTICLE IN EACH VELOCITY
C RANGE
C
DO 60, J=MIN(K), MAX(K)
ATOT(I,K)=ATOT(I,K)+DAT(J)
60 CONTINUE
TTOT(I)=VAL(3)
IF(IN.EQ.1)GOTO 68
C
C BGD REPRESENTS THE NO. OF BACKGROUND COUNTS PER CHANNEL
C
68 CONTINUE
DO 61, J=160, 240
BGD(I)=BGD(I)+DAT(J)
61 CONTINUE
IF(IN.EQ.1)GOTO 21
C
66 FORMAT( ' IS A BACKGROUND SUBTRACTION REQUIRED? ' )
ACCEPT 7, REA
IF(REA.NE.Y)GOTO 54
DO 71, I=1, 10
DO 71, K=1, IN
ATOT(I,K)=ATOT(I,K)-BGD(I)*FLOAT(MAX(K)-MIN(K))/80.0
71 CONTINUE
54 CONTINUE
C
C TYPE OUT THE NAMES OF EACH PTL AND THE
C NUMBERS OF EACH PTL IN EACH VELOCITY RANGE
C
IF(IN.GT.7) IZ=4
IF(IN.LE.7) IZ=IN
IV=1
107 TYPE 3, (PTL(I), I=IV, IZ), BGD, VELO
3 FORMAT(10A8)
DO 78, I=1, 10
VEL(I)=480.00/((AX(11-I)+AX(12-I))/2.0)
AVEL(I)=ALOG10(VEL(I))
BGD(I)=BGD(I)/80.0
TYPE 9, (ATOT(I,K), K=IV, IZ), BGD(I), VEL(I)
TOT=0.0
DO 84, K=1, IN
TOT=TOT+ATOT(I,K)
84 CONTINUE
DO 85, K=1, IN
APC(I,K)=ATOT(I,K)*100.0/TOT
IF(APC(I,K).EQ.0.0)GOTO 101
ERR(I,K)=APC(I,K)*SQRT(ATOT(I,K))/ATOT(I,K)
GOTO 85
101 ERR(I,K)=0.0
85 CONTINUE
C
IF(IN.EQ.1)GOTO 109
IF(IN.EQ.7)GOTO 109
ACCEPT 7, KR
IV=5
IZ=IN
GOTO 107
109 ACCEPT 7, KR
C
C TYPE OUT THE PERCENTAGE OF THE TOTAL COUNTS
C THAT IS DUE TO EACH PTL.
TYPE 89
FORMAT( ' THE PERCENTAGES OF EACH PTL ARE: ' )
5 FORMAT(6(A8,' ERROR'))
IF(IN.GT.4)KN=4
IF(IN.LE.4)KN=IN
TYPE 5,(PTL(I),I=1,KN)
TYPE 79
DO 83,I=1,10
TYPE 10,((APC(I,K),ERR(I,K)),K=1,KN)
10 FORMAT(10(F6.1,' | '))
83 CONTINUE
IF(IN.LE.4)GOTO 104
ACCEPT 7,KR
TYPE 5,(PTL(I),I=5,IN)
TYPE 79
DO 103,I=1,10
TYPE 10,((APC(I,K),ERR(I,K)),K=5,IN)
103 CONTINUE
104 CONTINUE
GOTO 76
67 CONTINUE
21 TYPE 9,(ATOT(J, 1),J = 1,10)
76 CONTINUE
TYPE 57
57 FORMAT( ' RESTART(Y OR N)? ',A)
ACCEPT 2,ANS
IF(ANS.EQ.Y)GOTO 1
STOP
END

Subprogram OLTP defines the interaction potential according to the theory of Olsen (1972), and can be adapted for use with singlet or triplet cases.

```
C OLTP 5/4/90
C OLSEN POTENTIAL FOR TRIPLET, OR SINGLET
C WHEN COMPILED CALLED FVTOT
C FUNCTION PROGRAM

FUNCTION FVTOT(R)

THE SHIELDING LENGTHS ARE GIVEN AS

CM=0.98
CK=0.057
CL=0.18

CAB =226 FOR TRIPLET
=325 FOR SINGLET

CAB=226.
ECS=R/CM
IF(ECS.GE.88.) THEN
XCS=0.0
ELSE
XCS=EXP(-ECS)
END IF
R1=R/CM
IF(R1.GE.88.) THEN
R1=0.0
ELSE
R1=8*EXP(-R1)
END IF
R2=R/CL
IF(R2.GE.88.) THEN
R2=0.0
ELSE
R2=8*EXP(-R2)
END IF
R3=R/CK
IF(R3.GE.88.) THEN
R3=0.0
ELSE
R3=2*EXP(-R3)
END IF
V1=2/R*(R1+R2+R3)
V2=CAB/R**6
V3=1-XCS*(1+ECS+ECS**2/2+ECS**3/6+ECS**4/24+ECS**5/120)
VTOT=V1-V2*V3
FVTOT=VTOT
RETURN
END
```
Appendix 13

Subprogram BRUTRP defines the interaction potential according to the work of Brutschy et al (1976)

```c

FUNCTION FVTOT(R)
R1=4.6
SM=0.93
SL=0.18
SK=0.057
R2=5.0
A1=-0.499
A2=-2.35
A3=-4.48
A4=-4.08
RMIN=10.7
EPS=0.0037
R4=1.5*RMIN
R3=1.2*RMIN
B1=-2.66E-3
B2=7.17E-4
B3=1.59E-5
B4=-5.84E-5

DETERMINE V(R)

R LT 4.6 IMPLIES V(R)= SHIELDED COULOMB

IF(R.LT.R1)THEN
  IF(R/SM.GE.44.)THEN
    RMK=0.0
  ELSE
    RMK=EXP(-R/SM)
  END IF
IF(R/SL.GE.44.)THEN
  RML=0.0
  ELSE
    RML=EXP(-R/SL)
  END IF
VTOT=2*27.21/R+(8+EXP(-R/SM) + 8*RML+2*RMK)
ELSE

IF R IS LT R2=5 IMPLIES VTOT=EXPONENTIAL SPLINE

IF(R.LE.R2) THEN
  VTOT=EXP(A1 + (R-R1)*(A2+(R-R2)*(A3+(R-R1)*A4)))
ELSE

R LT 12.84=1.2*RMIN IMPLIES VTOT=MORSE

IF(R.LE.R3)THEN
  IF(R.LE.5.37)THEN
    BETA=3.77*(1.86-0.86*EXP(-1.3*(R-5.37)**2))
  ELSE
    BETA=3.77
  END IF
  E=EXP(BETA*(1-R/RMIN))
  VTOT=EPS*E*(E-2.)
ELSE

IF R LT R4=16.05=1.5*RMIN IMPLIES VTOT=SPLINE

IF(R.LE.R4)THEN
  VTOT=B1+(R-R3)*(B2+(R-R4)*(B3+(R-R3)*B4))
ELSE

```
IF R GT R4 THEN VTOT = VAN DER WALL

VTOT = -6173/R**6
END IF
END IF
END IF

CONVERT VTOT FROM EV TO AU

FVTOT = VTOT
RETURN
END
Appendix 14

Subprogram SISK A defines the interaction potential for Ar + He(2^3S) according to the work of Siska (1979)

C SISKA REAL PARTS OF POTENTIALS
C SIMILAR FOR BOTH SINGLET AND TRIPLET
C
C FUNCTION FVTOT(R)
C
C CONSTANTS DEFINED FOR TRIPLET POTENTIAL
C
EPSTR=0.05762
RMSTR=5.811
B1STR=7.108
BSTR2=5.523
C6=3.04 E3
C8=5.34 E4
C10=1.224 E7
R1STR=6.4347
R2STR=9.8787
EPPLS=2.673
RMPLS=2.855
B1PLS=3.942
C4=273
R1PLS=3.2843
R2PLS=5.71
R0=4.728
D=0.7142
B1S=-4.6096008E-2
B2S=1.18563902E-2
B3S=9.8331585E-4
B4S=-9.59378453E-4
B1P=-2.13898993
B2P=0.77593273
B3P=-0.43253151
B4P=7.70151019E-2

C CONVERT R FROM AU TO ANGSTROMS
C
R=R*0.52917706
C
C CALCULATE VTOT AS A FUNCTION OF R
C
IF R LESS THAN R1STR IMPLIES VSTR= A MORSE POTENTIAL
C
IF(R.LE.R1STR) THEN
  IF(R.LE.RMSTR) THEN
    ZSTR=EXP(-B1STR*(R/RMSTR-1.)
  ELSE
    ZSTR=EXP(-B2STR+(R/RMSTR-1.))
  END IF
  VSTR=EPSTR*ZSTR*(ZSTR-2.)
ELSE
  IF R LESS THAN R2STR IMPLIES VSTR= SPLINE INTERPOLATION
  IF(R.LT.R2STR) THEN
    VSTR=B1S+(R-R1STR)*(B2S+(R-R2STR)*(B3S+(R-R1STR)*B4S))
  ELSE
    R GREATER THAN R2STR IMPLIES VSTR= VAN DER WALL
    VSTR=-C6*R**(-6)-C8*R**(-8)-C10*R**(-10)

188
END IF
DTERMINE VPLS
IF R LESS THAN R1PLS IMPLIES VPLS = MORSE POTENTIAL
  IF(R.LE.R1PLS)THEN
    ZPLS=EXP(-B1PLS*(R/RMPLS-1.))
    VPLS=EPPLS*ZPLS*(ZPLS-2.)
  ELSE
    IF R LESS THAN R2PLS IMPLIES VPLS = SPLINE INTERPOLATION
      IF(R.LT.R2PLS)THEN
        VPLS=B1P+(R-R1PLS)*(B2P+(R-R2PLS)*(B3P+(R-R1PLS)*B4P))
      ELSE
        IF R GREATER THAN R2PLS IMPLIES VPLS = VAN DER WALL
          VPLS=-C4*R**(-4)
      END IF
  END IF
END IF
DTERMINE SWITCHING FUNCTION
  FR=(1.+EXP((R0-R)/D))**(-1)
  FVTOT=(1.-FR)*VPLS+FR+VSTR
  FVTOT=FVTOT*1.59477E-3
RETURN R TO AU
  R=R/0.52917706
RETURN
END
Appendix 15

Subprogram HAB77 defines the interaction potential according to the work of Haberland and Schmidt (1977)

C
C HAB77
C CALCULATES V(R) FOR A RANGE OF R
C
C FUNCTION FVTOT(R)
C SHIELDING LENGTHS
FM=0.93
FL=0.18
FK=0.057
C FIRST SPLINE PARAMETERS
A0=-0.654
A1=-2.49
A2=-5.27
A3=5.52
C SECOND SPLINE PARAMETERS
B0=-1.94E-3
B1=4.44E-4
B2=-1.06E-4
B3=8.84E-6
R1 =4.8
R2=5.15
C
R LT 4.8 IMPLIES V(R)= A SHIELDED COULOMB
C
IF (R.LT.4.8) THEN
VA=8*EXP(-1*R/FM)
VB= 8*EXP(-1*R/FL)
VC=2*EXP(-1*R/FK)
VTOT=(VA+VB+VC)*2*27.21/R
ELSE IF(R.LT.5.15) THEN
C
R LT 5.15 IMPLIES V(R)= EXPONENTIAL SPLINE
C
VTOT=EXP(A0+(R-R1)*(A1+(R-R2)*A2-(R-R1)*A3)))
ELSE IF(R.LT.12.84) THEN
C
R LT 12.84 IMPLIES V(R)= DOUBLE MORSE
C
FIRST MORSE
C
IF (R.LT.5.96) THEN
X=R
BETAI=5.44*(0.873+0.127*EXP(-0.4*(R-5.96)**2))
ELSE IF(R.LT.6.7) THEN
X=R
BETAI=5.44
ELSE IF(R.LT.8.7) THEN
X=R-0.43*SIN((R-6.71)/1.27)
BETAI=5.44
ELSE
X=R-0.43*EXP(-0.85*(R-8.7)**2)
BETAI=5.44
END IF
R1 = 10.703
D1=0.00347
El=EXP(BETAI*(1-X/R1))
V1=D1*El*(El-2)
C
C SECOND MORSE
C
190
IF(R.LT.5.63) THEN
  X=R
  BETA2=8.23*(0.668+0.332*EXP(-2*(R-5.63)**2))
ELSE IF(R.LT.6.71) THEN
  X=R
  BETA2=8.23
ELSE IF(R.LT.8.7) THEN
  X=R-0.43*SIN((R-6.71)/1.27)
  BETA2=8.23
ELSE
  X=R-0.43*EXP(-0.85*(R-8.7)**2)
  BETA2=8.23
END IF
R2=5.33
d2=0.549
E2=EXP(BETA2*(1-X/R2))
V2=d2*E2*(E2-2)
VTOT=V1+V2
ELSE IF(R.LT.16.055) THEN
  R LT 1.5*R1 (R1=10.703) IMPLIES V(R)= CUBIC SPLINE
  R1=10.703
  VP=B1+(R-1.5*R1)*(B2+(R-1.2*R1)*B3)
  VTOT=B0+(R-1.2*R1)*VP
ELSE
  VTOT=-8875./(R**6)
END IF
FVTOT=VTOT/27.2
RETURN
END
Subprogram MARTIN defines the interaction potentials for the Ar + He(2^1S) system according to the work of Martin et al (1978)

C MARTIN REAL PARTS OF POTENTIALS
C SIMILAR FOR BOTH SINGLET AND TRIPLET
C
FUNCTION FVTOT(R)
C
CONSTANTS DEFINED FOR SINGLET POTENTIAL
C
EPSTR=0.07709
RMSTR=5.931
B1STR=7.108
BSTR2=5.523
C6=4.45 E3
C8 = 1.039 E5
C10=3.115 E7
R1STR=6.56647
R2STR=10.081
EPPLS=2.673
RMPLS=2.855
B1PLS=3.942
C4=273
R1PLS=3.2843
R2PLS=5.71
R0=4.753
D=0.5513
B1S=-6.16719984E-2
B2S=1.5246608 E-2
B3S=1.81019946 E-3
B4S=-1.251769772 E-3
B1P=-2.13898993
B2P=0.77593273
B3P=-0.43253151
B4P=7.70151019E-2
C
CONVERT R FROM AU TO ANGSTROMS
C
R=R*0.52917706
C
CALCULATE VTOT AS A FUNCTION OF R
C
IF R LESS THAN R1STR IMPLIES VSTR = A MORSE POTENTIAL
C
IF(R.LE.R1STR) THEN
IF(R.LE.RMSTR) THEN
ZSTR=EXP(-B1STR*(R/RMSTR-1.))
ELSE
ZSTR=EXP(-B2STR*(R/RMSTR-1.))
END IF
VSTR=EPSTR*ZSTR*(ZSTR-2.)
ELSE
IF R LESS THAN R2STR IMPLIES VSTR = SPLINE INTERPOLATION
IF(R.LT.R2STR) THEN
VSTR=B1S+(R-R1STR)*(B2S+(R-R2STR)*(B3S+(R-R1STR)*B4S))
ELSE
R GREATER THAN R2STR IMPLIES VSTR = VAN DER WALL
VSTR=-C6*R**(-6)-C8*R**(-8)-C10*R**(-10)
192
DETERMINE VPLS
IF R LESS THAN R1PLS IMPLIES VPLS = MORSE POTENTIAL
IF (R.LE.R1PLS) THEN
ZPLS = EXP(-B1PLS*(R/RMPLS-1.))
VPLS = EPPLS*ZPLS*(ZPLS-2.)
ELSE
IF R LESS THAN R2PLS IMPLIES VPLS = SPLINE INTERPOLATION
IF (R.LT.R2PLS) THEN
VPLS = B1P+(R-R1PLS)*(B2P+(R-R2PLS)*(B3P+(R-R1PLS)*B4P))
ELSE
IF R GREATER THAN R2PLS IMPLIES VPLS = VAN DER WALL
VPLS = -.C4*R**(-4)
END IF
END IF
DETERMINE SWITCHING FUNCTION
FR = (1. + EXP((R0-R)/D))**(-1)
FVTOT = (1.-FR)*VPLS + FR*VSTR
FVTOT = FVTOT*1.59477 E-3
R = R/0.52917706
RETURN
END
Appendix 17

CRS calculates the best constants A and B in Equations 6.2 and 6.5 to fit the experimental data, using a subprogram CURFIT (Bevington 1969) this in turn links with other subprograms (FCHISQ, FDERIV, MATINV, all defined by Bevington and FUNCTN defined in Appendix 18)

```
C CRS2 1/5/90
C CALCULATES THE CROSS SECTION WITH THE
C BEST FIT TO MY DATA, AND FINDS CHI SQUARED
C THE VALUES OF A, AND DA ARE MODIFIED
C LINKS WITH CURFIT, WHICH LINKS WITH FUNCTN, AND
C FCHISQ, FDERIV, MATINV, FUNCTN LINKS WITH FVTOT AND FWTOT
C
DIMENSION X(20),A(10),YFIT(20),Y(20),DELTAA(10),
1 SIGMAA(10),SIGMAY(20)
CK1 =0.
CK2=0.

C FIRST INPUT THE DESIRED VELOCITIES IN KM/S
C THE EXPERIMENTAL Y VALUES AND THEIR ERRORS
C
PRINT*, 'CRS CALCULATES THE THEORETICAL CROSS SECTION'
PRINT*, 'AND THE MINIMUM CHI SQUARED'
PRINT*, 'THREE MODES CAN BE USED TO WEIGHT THE RESULT'
PRINT*,'A MODE= +1 WEIGHT=1/DY**2'
PRINT*,'B MODE=0 WEIGHT=1'
PRINT*,'C MODE=-1 WEIGHT=1/Y'
PRINT*
PRINT*, 'ENTER DESIRED WEIGHTING MODE'
PRINT* READ*,MODE
PRINT*,'MODE= '.MODE
PRINT*
PRINT*,'INPUT THE NUMBER OF DATA POINTS '
PRINT* READ*,NPTS
PRINT*, 'INPUT X(KM/S), Y(CM**2 E-16), DY'
PRINT* DO 10 I=1,NPTS
READ*,X(I),Y(I),SIGMAY(I)
10 CONTINUE
DO 20 I=1,NPTS
WRITE(*,*) I,X(I),Y(I),SIGMAY(I)
20 CONTINUE
C CONVERT Y TO AY BY MULTIPLYING BY 3.57
DO 46 I=1,NPTS
Y(I)=Y(I)*3.57
46 CONTINUE
```

194
INPUT A PARAMETERS AND DA INCREMENTS
PRINT*,'INPUT THE NUMBER OF PARAMETERS'
PRINT*
READ*,NTERMS
DO 47 I=1,NTERMS
SIGMAA(I)=1.
47 CONTINUE
PRINT*,'INPUT PARAMETERS A,DA'
PRINT*
DO 50 I=1,NTERMS
READ*,A(I),DELTAA(I)
50 CONTINUE
DO 60 I=1,NTERMS
WRITE(*,*) I,A(I),DELTAA(I)
60 CONTINUE
PRINT*, 'TO CHANGE A VALUE TYPE ITS LIST NUMBER'
PRINT*,'RETURN THEN THE CORRECTION '
PRINT*,'WHEN FINISHED TYPE 100'
PRINT*
READ*,I
IF(I.EQ.100)GO TO 80
READ*,A(I),DELTAA(I)
GO TO 70
70 READ*,I
IF(I.EQ.100)GO TO 80
READ*,A(I),DELTAA(I)
GO TO 70
80 DO 90 1=1,NTERMS
WRITE(*,*) I,A(I),DELTAA(I)
90 CONTINUE
PRINT*
C USE CURFIT TO MINIMISE CHI SQUARED
C
FLAMDA=0.001
95 CALL CURFIT(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,DELTAA,
1 SIGMAA,FLAMDA,YFIT,CHISQR)
PRINT*, ' I, X, Y, YFIT'
DO 100 I=1,NPTS
WRITE(*,*) I, X(I), Y(I)/3.57, YFIT(I)/3.57
PRINT*
100 CONTINUE
PRINT*, 'I, A, DA, SIGMAA'
DO 105 J=1,NTERMS
WRITE(*,*) J,A(J),DELTAA(J),SIGMAA(J)
PRINT*
105 CONTINUE
PRINT*, 'CHI SQUARED=',CHISQR
PRINT*
C TEST TO SEE IF CHISQR HAS REACHED A MINIMUM
C
CK1=CK2
CK2=CHISQR
DIF=ABS(CK2-CK1)/CK2
IF(DIF.GT.0.001) GO TO 95
PRINT*, 'THE FINAL VALUE OF CHI SQUARED =',CHISQR
STOP
END
subprogram FUNCTN calculates the ionisation cross section at collision velocity defined by CRS and calls the subprograms FVTOT (the real part of the interaction potential given in Appendix 12 - 16) and FWTOT (the imaginary part of the interaction potential)

C
C FUNCTN 4/4/90
C LINKS WITH GRIDLS, FVTOT, FWTOT
C CALCULATES THE CROSS SECTION AT A GIVEN VALUE OF X THE COLLISION VELOCITY
C RTP IS CALCULATED FOR EACH VALUE OF L, THE ANGULAR MOMENTUM, AND USED TO FIND PL THE PROBABILITY OF IONISATION FOR CHANNEL L THE SUM OF PL OVER L IS THE CROSS SECTION QCROS
C
FUNCTION FUNCTN(X,I,A)
DIMENSION X(20), A(10)
C
C R = THE ATOMIC SEPARATION
C IDL = THE INCREMENT OF L
C DRAD = INCREMENT OF R
C RTP = YHE TURNING POINT WHERE VRAD=0
C VRAD = YHE RADIAL VELOCITY FROM SCHRODINGERS EQUATION
C PLA2 = (h/2π)**2 = 1 IN AU
C AMU = THE REDUCED MASS IN AU
C XI = COLLISION VELOCITY IN AU
C E0 = COLLISION ENERGY IN AU
C CKOSQ = K ZERO SQUARED IN AU
C VTOT = REAL POTENTIAL IN AU
C WTOT = IMMAGINARY POTENTIAL IN AU
PI=3.1415926
AL=0.
R= 1.
DL= 1.
QCROS=0.
DRAD=0.2
AMU=3.6364*1836.152
PLA2=1.0
RTP=0.
XI=X(I)*4.5732 E-4
E0=0.5*AMU*XI**2.
C
C FIRST FIND THE TURNING POINTS FOR L
C
CKOSQ=2.*AMU*E0/PLA2
10 CONTINUE
RTP=0.
DRAD=0.2
11 CONTINUE
VTOT=FVTOT(R)
CVRAD=(1.-VTOT/E0-AL*(AL+1.)/(CKOSQ*R**2.))
IF(CVRAD.GT.0.) THEN
IF(DRAD.GT.1E-9) THEN
R=R-DRAD/2.
DRAD= DRAD/2.
ELSE
RTP=R
END IF
ELSE
R=R+DRAD

196
ELSE
R=R+DRAD
END IF
IF(RTP.EQ.0.) GOTO 11

USE RTP TO FIND PL

SUMINT=0.0
THETA=0.001
DTHETA=0.02

INTEGRATE FROM 0 TO PI/2

CONTINUE
R=RTP/COS(THETA)
VTOT=FVTOT(R)
WTOT=FWTOT(R, A)
VRAD=XI*(1.-VTOT/E0-AL*(AL+1.)/(CK0SQ*R**2))**0.5
SINT=WTOT*R*TAN(THETA)*DTHETA/(PLA2*VRAD)
SUMINT=SUMINT+SINT
VUL=SINT/SUMINT
IF(VUL.LT.1.E-10) THEN
THETA=1.57
ELSE
THETA=THETA+DTHETA
END IF
IF(THETA.LE.1.57) GOTO 15
IF(SUMINT.GE.44) THEN
PL=1.
ELSE
PL=1.-EXP(-2*SUMINT)
END IF

ADD PL TOGETHER TO GET THE CROSS SECTION

DCROSS=PI/CK0SQ*(2*AL+1.)*PL*DL
QCROS=QCROS+DCROSS

MOVE ON TO NEXT L, BUT FOR LARGE L

AVERAGE OVER A GROUP OF L BECAUSE OF SLOW VARIATION OF VTOT AT LARGE L

IF(AL.LT.50.) THEN
DL=1.
ELSE IF(AL.LT.100.) THEN
DL=2.
ELSE IF(AL.LT.300.) THEN
DL=5.
ELSE
DL=10.
END IF
AL=AL+DL
R=RTP-1.
FRA=DCROSS/QCROS
IF(FRA.GT.1.E-4) GOTO 10
PRINT*,I,X(I),QCROS/3.57, AL
FINALLY RETURN THE CROSS SECTION TO THE MAIN PROGRAM

FUNCTION= QCROS
RETURN
END
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