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SINGLE AND MULTIPLE IONIZATION OF SULFUR ATOMS BY
ELECTRON IMPACT

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SINGLE AND MULTIPLE IONIZATION OF SULFUR

ATOMS BY ELECTRON IMPACT

by

Daniel L. Ziegler

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IN PARTIAL FULFILLMENT OF THE
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DOCTOR OF PHILOSOPHY

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MARCH 1982

ABSTRACT

SINGLE AND MULTIPLE IONIZATION OF SULFUR ATOMS BY ELECTRON IMPACT

by

Daniel L. Ziegler

Laboratory measurements of the cross sections for single, double, triple, and quadruple ionization of sulfur atoms by electron impact are presented for collision energies from threshold to 500 eV. The cross sections for single ionization of sulfur are measured relative to those of several elements whose absolute cross sections for single ionization are known. Cross sections for each multiple ionization process are then measured relative to those for single ionization. The configuration and operation of the apparatus for these measurements are described. The possible effects of excited sulfur reactants are examined, and the reported cross sections are felt to be characteristic of ground state sulfur atoms.

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF FIGURES	vii
1. INTRODUCTION	1
2. APPARATUS	6
2.1 Neutral Beam Production	6
2.2 Signal Production and Detection	8
2.3 The Electron Gun	10
2.4 Beam Purity Tests	15
3. SINGLE IONIZATION MEASUREMENTS	21
3.1 Definition of Cross Sections for Single Ionization	21
3.2 Measurement of Parameters	22
3.2.1 Measurement of the Signal Count Rate	23
3.2.2 Measurement of the Detection Efficiency	29
3.2.3 Electron Beam Current Measurement	30
3.2.4 Neutral Beam Flux Measurement	30
3.2.5 Determination of the Geometric Overlap	33
3.3 Electron Energy	38
4. MULTIPLE IONIZATION MEASUREMENTS	43
4.1 Derivation of Cross Section Ratios	43
4.2 Measurement of Parameters for Double Ionization	44
4.2.1 Measurement of the Count Rates	44
4.2.2 Measurement of the Detection Efficiency	47
4.3 Measurement of Parameters for Triple and Quadruple Ionization	51
5. NEUTRAL BEAM STATE ANALYSIS	52
5.1 Effect of Excited Atoms on Single Ionization Measurements	54
5.2 Effect of Excited Atoms on Multiple Ionization Measurements	55
6. THEORY	57
6.1 Quantum Calculations for Single Ionization	57

	v
6.1.1 The Born Calculation	57
6.1.2 The Bethe Approximation	62
6.2 Empirical Theories for Single Ionization	63
6.3 Classical Theories for Ionization	64
7. RESULTS AND DISCUSSION	68
REFERENCES	80

LIST OF TABLES

Table	Page
1-1 Sulfur ion concentrations in the Io torus as determined from Voyager EUV spectrometer observations.....	4
1-2 Sulfur ion concentrations in the Io torus as determined from Voyager Plasma Science observations.....	4
3-1 Electron beam energy correction.....	42
7-1 Cross sections for single ionization of sulfur atoms by electrons.....	70
7-2 Cross sections for double ionization of sulfur atoms by electrons.....	73
7-3 Cross sections for triple ionization of sulfur atoms by electrons.....	78
7-4 Cross sections for quadruple ionization of sulfur atoms by electrons.....	79

LIST OF FIGURES

Figure	Page
2-1 Schematic diagram of apparatus.....	7
2-2 Fast beam energy analyses.....	11
2-3 Schematic diagram of electron gun.....	12
2-4 Energy analysis of oxygen dissociation products.....	18
3-1 Beam modulation scheme.....	24
3-2 Cross section for single ionization versus electron current.....	28
3-3 Geometric overlap versus electron energy.....	36
3-4 Cross sections for single ionization of helium near threshold.....	39
4-1 Ratio of double and single ionization count rates versus electron current.....	46
4-2 Detection efficiency for S^{++} versus Kr pressure.....	50
5-1 Low lying states of S^0 and S^+	53
7-1 Cross sections for single ionization of sulfur atoms by electrons.....	69
7-2 Ratio of the cross sections for double and single ionization of sulfur atoms by electrons.....	71
7-3 Cross sections for double ionization of sulfur atoms by electrons.....	72
7-4 Ratios of the cross sections for multiple and single ionization of sulfur atoms by electrons.....	76
7-5 Cross sections for multiple ionization of sulfur atoms by electrons.....	77

CHAPTER 1

INTRODUCTION

In 1979 large concentrations of singly and multiply ionized sulfur atoms were detected by the Voyager I spacecraft, in the Io torus around Jupiter. The source of the material in the torus is believed to be the satellite Io. Although the mechanisms are not completely understood at this time, it is likely that atoms and molecules are sputtered from the surface or atmosphere by the impact of energetic ions (Hill et al. 1982; Cloutier et al. 1978), or possibly ejected into space by the volcanoes on Io (Cheng 1980). These particles are then ionized, and captured by Jupiter's magnetic field such that they rotate about the field lines, which corotate with Jupiter (Goertz 1980). The ions, thus accelerated, form a plasma torus which surrounds the orbit of Io.

The Io torus is located at approximately $6 R_J$ (from the center of Jupiter) and has a minor diameter of about $2 R_J$. A sharp temperature gradient at $5.7 R_J$ divides the torus into two distinct parts, a cool inner region in which single ions predominate, and a warm outer region in which multiple ion concentrations can be equal to or greater than single ion concentrations. Sulfur and oxygen ions, which are observed in roughly equal amounts in

in the torus, are the predominant ionic species. Only relatively small amounts of other ionic species, including Na^+ , SO^+ , and SO_2^+ , were reported.

Two instruments aboard Voyager independently measured ionic concentrations in the Io torus. One of these, the Extreme Ultraviolet (EUV) Spectrometer recorded the spectrum of light emitted with wavelengths between 500 and 1700Å. The observed spectral lines and their intensities were used to identify the presence, and concentrations of the various ions. The sulfur ion concentrations derived from these data are shown in Table 1-1 (Shemansky and Smith 1982). These are average concentrations over the field of view of the EUV Spectrometer, which is the torus $\frac{1}{2}$ width.

A second device, the Voyager Plasma Science Instrument (Bridge et al. 1977), consisted of a set of Faraday cups, each with a retarding grid energy/charge/mass separator, operated so as to collect and analyze ions, as it passed through the torus. The analysis of the spectra, thus obtained, was simplified in that all ions corotate with the magnetic field lines, and thus all had the same velocity relative to the collectors. Therefore the energy dependence could be eliminated and each peak could be assigned a unique charge to mass value. A difficulty arose, however, in that the peaks in most spectra were quite broad due to the thermal motion of the ions, and it was therefore necessary to assume a kinetic

model for the ions to resolve the peaks in the spectrum. Unfortunately, as yet there is no information to indicate which kinetic model is the proper one to use, so the concentrations derived from these data are not unique at this time. The concentrations shown in Table 1-2, were derived from these data, first assuming the ions have a common temperature, and then assuming the ions have a common thermal speed (Bagenal and Sullivan 1981). As one can see only the concentrations of minor ions, such as S^{3+} , are greatly affected by the particular choice of kinetic model. If one averages these concentrations over the torus $\frac{1}{2}$ width, they agree with the concentrations derived from the EUV data to within about a factor of 3. This agreement is considered to be good given the uncertainties in each technique (Shemansky and Smith 1981).

Since the basic structure of the torus is now understood, aeronomers are turning their attention to tasks such as identifying the nature of the ionic sources, for which electron impact ionization cross sections will be necessary. Until now no experimental determination of the cross sections for single or multiple ionization of sulfur atoms by electrons have been made. Further, theoretical studies for single ionization of sulfur by electron impact yield results which differ with each other by as much as a factor of two, and there are no reliable estimates at all for the multiple ionization processes. Therefore, an immediate need exists for some

Table 1-1. Average sulfur ion concentrations in the Io torus as derived from the EUV spectrometer observations.

Ion	Concentration (particles/cc)
S^+	44
S^{++}	160
S^{3+}	216
S^{4+}	<11

Table 1-2. Sulfur ion concentrations derived from the Voyager Plasma Science observations, as a function of radial distance from Jupiter, L , on a path passing within $\frac{1}{2} R_J$ of the central axis of the torus. The reported values are computed using an isothermal model, except for those in square brackets, which are computed using a common thermal speed model.

Ion	Concentration (particles/cc)			
	$L = 4.96 R_J$	$5.3 R_J$	$6.0 R_J$	$8.6 R_J$
S^+	91	1100	430 [470]	18 [17]
S^{++}	14	39	430 [560]	19 [14]
S^{3+}	5.6	3.5	27 [170]	0.5 [11]
S^{4+}	----	----	----	----

determination of the values of the cross sections for ionization of sulfur atoms by electron impact, particularly for the multiple ionization processes. The data presented in this thesis provide a determination of these cross sections which is adequate to satisfy the needs of the space scientists who model the Io torus.

CHAPTER 2

APPARATUS

The apparatus for this experiment is shown in Figure 2-1. It has been described by Rundel et al. (1979) and Ziegler et al. (1982), therefore only a brief outline is given here.

2.1 Neutral Beam Production

An ion beam is extracted from a magnetically confined electron arc ion source containing CS_2 . Typically the gas pressure in the source is maintained at about 120 mTorr, and the electron arc voltage is 8 volts. The ions formed in the source are accelerated to 1500 eV and then focused by an electrostatic einzel lens. After collimation the ion beam is magnetically momentum analyzed to produce a pure S^+ beam.

The S^+ beam is partially neutralized by charge transfer with O_2 or NO in the Charge Transfer Cell (CTC). A 10 KV/cm field between two plates following the CTC ionizes the highly excited sulfur atoms with $n \geq 19$ (cf. Bamberg and Kolosov 1979), and deflects the resulting ions out of the beam, along with the ions that were not neutralized in the CTC. Procedures to assess the effects of long lived excited atoms in the neutral beam with $n < 19$ are described later in this thesis.

After neutralization the beam is collimated by two 5 mm diameter circular apertures separated by 60 cm. Just

Figure 2-1. Schematic diagram of apparatus.

after entry into the interaction chamber the beam passes through a 140 V/cm field between two small plates, which sweeps out ions formed from the neutral beam by collisions with the background gas. Typical neutral beam fluxes in the interaction chamber are on the order 10^{10} atoms per second.

2.2 Signal Production and Detection

The electron beam crosses the neutral beam in a field free interaction region. Product ions are formed by means of the reactions

Since the momentum of the sulfur atoms is large relative to that of the electrons, the product ions are not appreciably scattered off axis.

Immediately following entry into the detection region sulfur ions of each charge state can be directed individually into a five grid retarding potential energy analyzer by means of an electrostatic deflection system. After passage through the energy analyzer the ions are deflected upward, by a pair of cylindrical electrostatic deflection plates, into a Johnston Laboratories MM1 electron multiplier (see enlargement in Figure 2-1).

The primary purpose of the retarding potential energy analyzer is to reject ions formed in stripping collisions of S with the background gas,

Even though the background gas pressure in the interaction and detection chambers is about 3×10^{-9} Torr, reaction (2-5) produces typically about ten times as much S^+ as the electron impact reaction. It is important to observe, however, that due to the kinematics of reaction (2-5) a sulfur atom will lose at least 10.4 eV of kinetic energy in the stripping process. Therefore the S^+ ions formed in stripping reactions will have at least 10.4 eV less energy than the S^+ produced by electron impact. Since the retarding potential energy analyzer has about 0.3% resolution (4.5 eV for a 1500 eV beam, see Figure 2-2 and Cogan 1978), and the energy spread in the product beam is about 5 eV, the energy analyzer can be set to accept the signal while rejecting the ions formed by stripping reactions.

Doubly ionized sulfur is also produced, in an analogous way, in the reaction

These S^{++} ions will, however, have at least 33 eV less energy than signal S^{++} ions, and therefore, they can also be rejected by the energy analyzer, while the signal S^{++} ions are allowed to pass. Likewise S^{3+} and S^{4+} stripping

ions can be rejected by the energy analyzer since they have, respectively, at least 66 and 113 eV less energy than their corresponding signal ions.

An energy analysis of the S^+ parent ion beam, obtained by recording the current collected at the Faraday cup as a function of retarding voltage, is shown in Figure 2-2a. Along with it are shown an energy analysis of the ions formed, from the neutral beam, by stripping collisions with the background gas, and an energy analysis of the S^+ signal produced by the electron impact process.

An energy analysis of the S^{++} ions produced by electron impact along with the energy analysis of the parent S^+ ion beam is shown in Figure 2-2b. The S^{++} stripping count rate was too small to be observed.

2.3 The Electron Gun

A schematic of the electron gun is shown in Figure 2-3. The source of electrons is an oxide coated cathode taken from a 6L6 electron tube and mounted between a set of beam focusing plates. All the structures shown in Figure 2-3, except the cathode, are made from 302 series stainless steel. During data acquisition all these structures are grounded, except the cathode and beam focusing plates.

An electron beam is produced by biasing the cathode negatively with respect to ground. The beam focusing plates are biased more negatively than the cathode, to

Figure 2-2a. Energy analysis of: S^+ parent ion beam; S^+ ions produced in electron impact reaction (2-1): o; S^+ ions produced by the stripping reaction (2-5): •.

Figure 2-2b. Energy analysis of: S^+ parent ion beam; S^{++} ions produced in electron impact reaction (2-2): o.

Figure 2-3. Schematic diagram of electron gun.

direct the beam through the apertures in the source exit plate and the collector entrance plate and then into the electron collector. Typically 93% of the current leaving the cathode is collected in the electron collector, and to within experimental uncertainty the remaining current goes approximately in equal parts to the source exit plate and collector entrance plate. Typical electron currents range from 0.2 to 1.5 mA.

The electron beam is collected in an electron collector to which a voltage to suppress secondaries can be applied. This collector is surrounded by a housing which shields the interaction region from the potential of the electron collector, and shields the electron collector from stray currents. From the center of the area over which the electron beam strikes the collector the neutral beam only subtends 1% of the total solid angle into which electrons can be scattered. The back wall of the collector makes an angle of 20 degrees to the electron beam which causes the majority of the secondary and reflected electrons to be directed towards the bottom of the collector (Jonker 1951), rather than back through the entrance aperture.

The energy of the colliding particles in the signal production reactions (2-1) through (2-4) is given by

$$E = E_{CM} + E_{COL}$$

where E_{CM} is the energy associated with the baricentric motion and E_{C01} is the relative or collision energy of the two particles. The collision energy can be expressed

$$E_{C01} = (\frac{1}{2})\mu v_{C01}^2 = (\frac{1}{2})\mu (V^2 + v^2 - 2Vv\cos\theta)$$

where: $\mu = (Mm)/(M+m) \sim m$
 M = mass of sulfur
 m = mass of electron
 V = velocity of sulfur
 v = velocity of electron
 θ = angle of collision

In this experiment the beams cross at right angles ($\theta = 90^\circ$) so the collision energy can be expressed,

$$E_{C01} = \frac{1}{2} m (V^2 + v^2)$$

The energy of the sulfur atom beam in these measurements was 1500 eV and the lowest electron beam energy was 5 eV. Therefore

$$V = 9.5 \times 10^6 \text{ cm/sec}$$

$$v = 1.3 \times 10^8 \text{ cm/sec}$$

As one can see the electrons always had velocities at least 10 times greater than those of the sulfur atoms. Therefore

$$v^2 > 100 V^2$$

$$E_{C01} \sim \frac{1}{2} m v^2$$

which is the energy of the electrons. In all measurements reported here the collision energy has been taken to be the electron beam energy.

2.4 Beam Purity Tests

Since O_2^+ has the same charge to mass ratio as S^+ ($e/m = 32$), it cannot be rejected from the S^+ parent ion beam by mass analysis. It is therefore important to insure that the flux of molecular oxygen in the beam is insignificant. Before every run the stainless steel gas delivery system and the source assembly are thoroughly pumped out, and the CS_2 is admitted from an evacuated lecture bottle, which contains 99% pure CS_2 (Scientific Gas Products, South Plainfield, N.J.). Also, mass analysis scans with He in the source prior to the admission of CS_2 , show no peak at charge to mass ratio 32. These precautions ensure the S^+ parent ion beam, and thus the S neutral beam, is extremely pure.

One test can be performed to show directly that any O_2 flux in the S neutral beam is insignificant. This test essentially consists of comparing the energy analyses of the ionic products in the two reactions:

The energy spectrum of the S^{++} produced in reaction (2-2) will be sharp, as it is in Figure 2-2b. The O^+ produced

in reaction (2-7) will be collected with the S^{++} , however its energy spectrum will be very broad. This broadening arises from the fact that the oxygen molecule will dissociate with a finite energy, $2Q$, in the center of mass frame of reference. Owing to an energy amplification effect, the energy difference between a forward and backscattered ion in the laboratory frame will be many times greater than $2Q$.

To show this quantitatively we first observe that the velocity of the center of mass reference frame relative to the laboratory, is to within 0.05%, equal to the initial velocity of the oxygen molecule. Given that each molecule has an initial kinetic energy, $2T$, the center of mass frame velocity is given by

$$v = \sqrt{\frac{2(2T)}{2M}} = \sqrt{\frac{2T}{M}}$$

where M is the mass of each oxygen atom. In the center of mass frame, prior to collision, the oxygen molecule is at rest. After collision, in the center of mass frame, the dissociation products will move apart, each with velocity

$$v = \sqrt{\frac{2Q}{M}}$$

neglecting the momentum imparted by the impacting electron which will be insignificant in any case. The velocity of an O^+ ion in the laboratory frame that is forward scattered in this reaction will thus be

$$v = \sqrt{\frac{2T}{M}} + \sqrt{\frac{2Q}{M}}$$

and its energy will be

$$E_F = \frac{1}{2} MV^2 = T + Q + 2\sqrt{TQ} \quad (2-8)$$

Similarly a backscattered O^+ ion will have an energy

$$E_B = T + Q - 2\sqrt{TQ} \quad (2-9)$$

In the present case the initial kinetic energy of the oxygen molecule, $2T$, is 1500 eV, and the molecule dissociates with an energy, $2Q$, of up to about 2.5 eV, and so, equations (2-8) and (2-9) give

$$E_F = 812.5 \text{ eV}$$

$$E_B = 690.0 \text{ eV}$$

Thus, the O^+ ions produced in reaction (2-7) will be spread at least 100 eV in energy.

During the course of this experiment a molecular oxygen beam was set up and an energy analysis of the product ions, that would be collected with the S^{++} , obtained. This analysis is shown in Figure 2-4, and as one can see, the O^+ product has kinetic energies ranging from at least 700 to 800 eV. In this energy analysis there is some evidence of O_2^{++} ions produced in the reaction

Figure 2-4. Observed cross section versus retarding voltage for production of O^+ and O_2^{++} ions in reactions (2-7) and (2-10) respectively: ●. Observed cross section versus retarding voltage for production of S^{++} ions in reaction (2-2): ○.

which will have a narrow energy spectrum. These ions probably produce the small sharp step, at 750 eV, in the energy analysis of the oxygen beam. An energy analysis of the S^{++} ions produced in reaction (2-2) is plotted as a function of energy analyzer-retarding voltage so that the energy analyses of each reaction can be compared. The heights of each curve are equal to the signal count rate for each process, divided by their respective electron and neutral beam fluxes. In this way, the observed cross section for the production of S^{++} ions is plotted relative to the observed cross section for production of O^+ (see Chapter 3). Thus, the fact that no signal is observed above 752 V when a sulfur beam is used shows, to within the displayed uncertainty, that the sulfur atom beam contains no molecular oxygen.

The cross section, observed here, for production of O^+ from molecular oxygen in reaction (2-7) is somewhat smaller than that observed previously. This is perhaps due to the fact that the O^+ product is scattered such that only about 37% of it is collected in the present apparatus. This is assuming that the O^+ products are scattered isotropically in 177 eV collisions as they have been observed to be in 50 eV collisions (Stockdale et al. 1973). The cross section, observed here, for 177 eV electrons, is $\sim 0.4 \text{ \AA}^2$. This implies the true cross section has a value $\sim 1.1 \text{ \AA}^2$, at 177 eV, which agrees well with the value $1.0 \text{ \AA}^2$

obtained previously by Rapp et al. (1965a). This measurement serves as a good check on our apparatus.

Since the cross sections for

are comparable (Rapp 1965a,b), any oxygen impurity will clearly contribute negligibly to the single ionization measurement for sulfur.

CHAPTER 3

SINGLE IONIZATION MEASUREMENTS

In this chapter the cross section for single ionization of atomic sulfur by electrons is defined in terms of measurable quantities. Then the actual procedures used to determine these quantities are described.

3.1 Definition of Cross Sections for Single Ionization

The absolute cross section for single ionization of atoms by electron impact, σ_+ , can be written in terms of the parameters:

$$\sigma_+ = \frac{R_+}{D_+} \cdot \frac{e}{J} \cdot \frac{e\gamma}{I} \cdot \frac{vV}{(v^2 + V^2)^{\frac{1}{2}}} \cdot F \quad (3-1)$$

where: R_+ = measured count rate for production of single ions

D_+ = detection efficiency for single ions

e = charge on electron

J = electron beam current

I = current of electrons ejected from neutral beam detector by impact of neutral beam

γ = secondary electron ejection coefficient per incident neutral particle

v = velocity of electron beam

V = velocity of neutral beam

and where F is the geometric overlap of the beams defined by the integration over the vertical dimension z ,

$$F = \frac{\int I(z) dz \int J(z) dz}{\int I(z) J(z) dz} \quad (3-2)$$

The parameter F has dimensions of length, and is approximately equal to the height of the taller beam, which in this case is the neutral beam.

We now observe that because

$$v \gg V$$

$$\frac{vV}{(v^2 + V^2)^{1/2}} = V$$

to within 0.5% for all measurements reported here. Also, we observe:

$$V = \sqrt{\frac{2T}{M}}$$

where T = kinetic energy of atom in neutral beam

M = mass of atom in neutral beam

so equation (3-1) becomes

$$\sigma_+ = \frac{R_+}{D_+} \cdot \frac{e}{J} \cdot \frac{eY}{I} \cdot \sqrt{\frac{2T}{M}} \cdot F \quad (3-3)$$

3.2 Measurement of Parameters

Each of the parameters in equation (3-3) is either known or can be measured. The atomic kinetic energy is easily determined to within 1% from an energy analysis of the parent ion beam. The determination of the other parameters is somewhat more involved.

3.2.1 Measurement of the Signal Count Rate

During a single ionization cross section measurement, about 5% of the observed count rate is due to processes other than electron impact. The majority of this background is caused by secondary particles that are produced when stripping ions strike the energy analyzer. Also some of this background is caused by particles ejected from the neutral beam trap by the impact of the neutral beam. Electron beam background contributes negligibly to the observed count rate.

In order to separate the signal from these backgrounds a beam modulation scheme similar to the one used by Rundel et al. (1979), is employed. In this scheme both the electron and neutral beams are square wave modulated at 1 KHz, 90 degrees out of phase with each other, as shown in Figure 3-1. Two scalers are gated to count during four separate periods.

<u>PERIOD</u>	<u>MEASURED QUANTITIES</u>
a	electron beam background dark current
b	electron beam background neutral beam background signal dark current
c	neutral beam background dark current
d	dark current

The count rate due to the signal alone, R_+ , can then be determined by subtracting the count rates measured in

Figure 3-1. Beam modulation scheme.

periods a and c from the count rates measured in periods b and d

$$R_+ = (R_b + R_d) - (R_a + R_c) \quad (3-4)$$

The percentage uncertainty in R_+ is given by the square root of the total number of counts recorded in the measurement, divided by the total number of signal counts.

This method for determination of the signal count rate requires that the backgrounds produced when both beams are present are equal to the sum of the backgrounds produced by each beam alone. Clearly, a change in the background of one beam due to the presence of the other would affect the measured signal.

In this experiment such a modulated background could arise if stripping ions, formed in the interaction chamber prior to or during passage through the electron gun, were deflected by the space charge of the electron beam. For example, when the electron beam is present stripping ions could be deflected in such a way that the background they produce is larger than it is when the electron beam is off. In this case the neutral beam background during period b would be larger than the neutral beam background during period c, and thus, this effect would lead to an increase in R_+ .

An effect similar to this can be seen in the energy analysis of the S^+ signal ions, shown in Figure 2-2a. As one can see when the stripping ions are allowed to pass

through the energy analyzer, a spurious contribution to the measured signal is observed. As mentioned earlier, however, the energy analyzer was set high enough to reject all the stripping in the actual data acquisition. In this way only the backgrounds produced by stripping ions can affect the measurements.

Another source of error in signal determination would arise if the signal ions were deflected by the electron beam space charge such that only a fraction of them were collected. It is important to note, however, that the electron space charge potential is at most 4 volts, and thus should deflect the fast ion beams insignificantly. In fact, the scans of the multiplier with a small ion probe beam look essentially the same whether the electron gun is on or off.

It is also important to consider the possibility that the electron beam could sputter ions from surfaces in the collector. Some of these ions could emerge from the collector and undergo charge transfer with the neutral beam, and thus contribute directly to the measured signal. It is important to observe, however, that in general such an ion current is only a very small fraction of the incident electron current. For example, Redhead (1964) measured a maximum of only 10^{-5} ions/electron emitted from a weakly bound layer of oxygen chemisorbed on a substrate of polycrystalline molybdenum, when it was struck with 0-300 eV electrons. Further, such ions are scattered into a range

of angles, with energies of a few eV (Madey and Yates 1977), and so, these "secondary" ions should be collected with a similar efficiency as the secondary electrons, in the present collector.

It is possible that some ions are formed in the electron source chamber by electron impact on the background gas. These ions, however, will have kinetic energies of at most a few eV, and thus would not escape the negative potential of the cathode. Pressures would have to be on the order of 10^{-7} Torr in the inner electron collector in order for enough ions to be formed there to affect the measurements.

During the course of the measurement of the cross sections for double ionization of oxygen atoms by electron impact, recently performed on this apparatus, several tests were done to ensure that spurious contributions to the measured count rate were insignificant. Although these tests, in many instances, also serve for the present measurements, further tests are described here that ensure that several possible sources of error did not significantly affect these measurements.

In order to show the measurements were free from spurious effects that depend on the presence of the electron beam, the cross section for single ionization was measured as a function of electron beam current. The result of this measurement, made at a collision energy of 177 eV, is displayed in Figure 3-2. As one can see, to

Figure 3-2. Observed cross section for the single ionization of sulfur by electrons versus electron current, at an electron energy of 177eV.

within experimental uncertainties, the cross section is constant for electron beam currents from 0.15 to 1.5 mA. This shows the measurements are free from spurious effects such as space charge modulation of the stripping background, and off axis signal deflection.

Measurements of the signal count rate were also performed with the electron collector alternately grounded and biased at -10 V. With the collector at -10 V virtually all ions formed from the background gas, or surfaces in the collector, would not be able to reach the interaction region. The ratio between the count rate for S^+ production with the collector biased at -10 V and the count rate for S^+ production with the collector grounded was 1.00 ± 0.01 . This result indicates that ions, formed in the electron collector, do not contribute to the measured signal.

3.2.2 Measurement of the Detection Efficiency

The first step in this measurement is to ensure that D_+ is uniform over the entire area where signal ions may strike the multiplier. This is done by scanning a small ion probe beam, of the same species, charge and energy as the signal, across the entrance to the detection region, while monitoring the count rate. In this way it was found that D_+ was constant for signal ions passing through an area 3.5 cm in diameter, centered on the beam axis, at the entrance to the detection region. At this point a signal ion beam has a diameter of about 1.5 cm. The detection efficiency is determined by centering the ion probe beam

on the beam axis and measuring the count rate, then deflecting it into a deep Faraday cup and measuring its current. As a check this entire procedure is repeated using an ion beam with about the same dimensions as a signal beam. The detection efficiency found with this beam is always the same as that found with the probe beam, to within experimental uncertainty. The detection efficiency, found in this manner, is $D_+ = (25.2 \pm 1.2)\%$. The uncertainty in this measurement essentially comes from the difficulty in measuring the small current of the ion beam (this current, typically about 10^{-14} A, is measured with a Cary model 401 vibrating reed electrometer).

3.2.3 Electron Beam Current Measurement

During a cross section measurement the electron collector is grounded. Both before and after a cross section measurement the electron current, J , is determined, and its waveform monitored, by using an oscilloscope to measure the voltage drop it causes across a 1 K Ω resistor. This method for determining J has a 3% uncertainty, due mostly to the resolution of the oscilloscope screen. Several measurements of J , made directly with a Keithley model 130 digital multimeter, as a consistency check, agree with the former measurements to within experimental uncertainty.

3.2.4 Neutral Beam Flux Measurement

The neutral beam detector consists of a pyroelectric disc 38 mm in diameter with thin silver electrodes deposited

on its surfaces, and with a cylindrical bias ring located just in front of it, through which the beam enters. The detector can be rotated into the neutral beam for a flux measurement, and out of it so the neutral beam is collected in the neutral beam trap for a cross section measurement.

During a flux measurement the bias ring is set to -53 V to collect electrons ejected from the silver surface by the impact of the neutral beam. By measuring the current of electrons leaving the silver surface, I , the neutral flux can be determined if the secondary electron ejection coefficient per incident neutral, γ , is known. In principle γ can be determined by measuring the number of secondary electrons ejected by a given neutral beam, and then measuring the neutral beam current directly via the pyroelectric properties of the detector. Due to a relatively high noise level and low response level, the pyroelectric disc must often be bombarded with the neutral beam for several hours in a single measurement. It was found, however, that beams of heavier atoms, such as argon or sulfur, can change the secondary ejection coefficient of the silver surface within 30 minutes. Therefore it was impossible to measure γ in the way just described, and another method was employed in this experiment.

First it is important to observe that many previous measurements, made with the present neutral detection arrangement, show that the secondary electron ejection coefficient is independent of the charge state of the

impacting particle, to within 20%, for beams of H and He with kinetic energies of 1500 eV and above (cf. Geis et al. 1975). Also, measurements made during the course of this experiment indicate that the same is true for oxygen and argon beams (see Section 3.2.5). These results are generally supported by previous determinations of the secondary electron ejection coefficient of fast beams (cf. Rostagni 1934; Berry 1948; Stier et al. 1954; Hayden and Utterback 1964; Moran and Wilcox 1978; Ray et al. 1979). Therefore, in the present experiment we measure the secondary ejection coefficient for a fast ion beam, γ^+ , to obtain a reasonable estimate for γ .

The parameter γ^+ is measured several times on a day when single ionization cross sections are obtained. The procedure used to measure γ^+ is very similar to that used to measure the signal detection efficiency, D_+ . The first step in this measurement is to ensure that γ^+ is uniform over the entire area where beam particles may strike the detector. This is done by scanning a small ion probe beam across the front of the detector, with the bias ring at its usual setting, while monitoring the current to the front surface I_F . Then by measuring the current of the probe beam, I_+ , in a deep Faraday cup, the current of ejected electrons, I , can be computed for any point on the surface by

$$I = |I_F| - |I_+| \quad (3-5)$$

In this way the current of ejected electrons and thus γ^+ , is always found to be uniform over the surface of the detector to within about 8%. This nonuniformity is always the largest source of error in the determination of γ^+ . The absolute magnitude of γ^+ can then be determined, at any point on the surface from,

$$\gamma^+ = (I_F - I_+)/I_+ \quad (3-6)$$

As a check this entire procedure is always repeated using a full ion beam with about the same dimensions as the neutral beam. In every case the value of γ^+ found by each method always agreed to within experimental uncertainties.

During a measurement of γ^+ and of I , care is always taken to ensure that the detector is only struck by the beam for a total of a few seconds. Very little variation was observed for γ^+ on a given day, and day-to-day variations were on the order of 2%.

3.2.5 Determination of the Geometric Overlap

In the present apparatus there is no way to directly measure the geometric overlap, F , between the electron and neutral beams. It is important to note, however, that F is the only parameter that cannot be obtained, or estimated, from direct measurements. However, it may be deduced, using equation (3-3), from measurements of processes for which the cross section is already known. Such measurements were made using helium, oxygen and argon.

These elements were chosen because they are some of the few elements for which the cross sections for ionization of the ground state are known. Also, ground state beams of sufficient intensity could easily be obtained for each in our apparatus. Also oxygen, which is in the same periodic group as sulfur, should have similar chemical properties. Furthermore, argon has a larger atomic weight than sulfur while helium and oxygen have smaller atomic weights. Therefore the average overlap obtained from these beams should be representative of that for sulfur.

The procedure used in the single ionization measurements of helium, oxygen, and argon is essentially the same as that described for sulfur. For a helium measurement, an He^+ beam is extracted from He in the source, with the electron arc voltage set at 39 v. It is mass analyzed, and neutralized by charge transfer with He. The resulting neutral beam will be predominantly in the ground state since even excited ions will yield ground state fast neutrals in the resonant reaction,

The helium neutral beam is then crossed with electrons, and the counts are obtained in the usual way. The measurements with argon were done using an identical procedure.

The oxygen atom beam is again formed in the same way, the major difference being that O_2 is used as the source gas and N_2 is used for charge transfer. In this way the

oxygen atom beam should be mostly in the 3P ground state, with a small fraction in the 1D metastable state, as described in detail by Ziegler (1981). Furthermore, theoretical cross sections for single ionization of oxygen atoms in the low lying 3P and 1D states, computed by Peach (1968, 1970, 1971) are the same to within about $\pm 5\%$. Therefore, the cross sections measured using this beam should be appropriate to those of ground state atoms.

The values of the geometric overlap, F , of the electron and atomic beams are shown as a function of electron energy, in Figure 3-3. The values obtained with helium were computed using the total ionization cross sections of Rapp et al. (1965b), with a small correction for double ionization ($\sim 1\%$) using the data of Beakney (1930). The data obtained with oxygen were computed using the absolute single ionization cross sections presented by Brook et al. (1978). The values obtained with argon were normalized to the data of Rapp et al. (1965b), with a small correction for double ionization ($\sim 10\%$) using the data of Gaudin and Hagemann (1967). Since the data of Gaudin and Hagemann do not extend below 100 eV, and there are no other comparable measurements, the argon data below 100 eV were neglected. Triple ionization of argon, which amounts to a correction of about 1%, was neglected.

The data of helium below 50 eV show a great deal of scatter, due to the fact that the cross section for single ionization is changing rapidly at low energies. A

Figure 3-3. Geometric overlap, F , of the electron and atomic beams for atomic beams of: helium - O, oxygen - $\square$, and argon - ∇ . The dotted lines show a linear fit to the data of each beam, as labeled, and the solid line shows the average of the three linear fits.

disagreement in the energy scale, on the order of 1 eV, between the present measurements and the previous measurements causes large oscillations in the values of F . A nearly identical effect was observed in the low energy F values obtained with argon, and thus only a small amount of useful information is lost by neglecting the argon data below 100 eV.

The dotted lines in Figure 3-3 represent fits to the data of each species, as labeled. All data below 47 eV were neglected in these fits. The solid line represents the average of the dotted lines and is taken as the value of the geometric overlap in the analysis of the sulfur cross sections. The resulting value of F as a function of energy is

$$F = (0.792 - 0.000201 E) \text{ cm} \quad (3-7)$$

where E is the electron energy in eV. The overlaps determined with oxygen and helium are both within 17% of the average value, at all energies. Thus, 17% is taken as the uncertainty in this measurement of the geometric overlap.

In employing this method we are in essence measuring the ratio between the cross sections for the ionization of sulfur, and the other elements, so that the value of the geometric overlap cancels out. It is important to note that any systematic error introduced by either the equipment or assumptions employed in the single ionization measurements, will also cancel out. For example, it is no

longer necessary to assume $\gamma = \gamma^+$, it is only important that their ratio be about the same for all four elements used in these measurements. An indication that this is the case is given by the fact that the geometric overlaps determined with helium, oxygen, and argon all show agreement with each other.

3.3 Electron Energy

Since the surfaces surrounding the interaction region are at ground potential the electron beam energy, E , is given by

$$E = eV \quad (3-8)$$

where: e = charge on electron

V = cathode potential

In practice the electron beam energy is about 3 eV less than is predicted by equation 3-8. This is established by examining the measurements of the single ionization of helium around threshold. In Figure 3-4 the presently measured cross sections for the single ionization of helium are plotted, with their energy scale established by equation 3-8, against the cross sections reported by Rapp et al. (1965b). Since Rapp et al. established their energy scale carefully (by plotting electron current as a function of electron energy and extrapolating back to zero current to find the true electron energy zero) and since their measurements show the correct threshold, the

Figure 3-4. Cross sections for single ionization of helium by electron impact versus electron energy. Present data: ●. Data of Rapp and Englander-Golden: ○.

difference in the reported cross sections is attributed to the fact that our electron beam is 2.6 eV less energetic, for energies around 30 eV, than would be expected on the basis of equation 3-8.

This reduction in electron energy is due in part to the work function of the cathode, and in part to the space charge potential of the electron beam. A small contribution comes from field penetration from the source chamber into the interaction region. This effect, estimated by field mapping on resistance paper, amounts to only about a volt at 500 eV.

In order to extrapolate the energy correction to other beam currents and energies used in this experiment, it is necessary to obtain an estimate of the space charge potential of the electron beam. The value of this potential at the center of the interaction region is computed by means of the integral

$$U = \int_{Vol} \rho / (4\pi\epsilon_0 r) dV \quad (3-9)$$

where: ρ = charge density of electron beam

ϵ_0 = permittivity of free space

r = distance between volume of integration and point at which potential is computed

Vol = representative volume for electron beam

The value of the space charge potential at the edges of the electron beam should be about $\frac{1}{2}$ the value at the center, and thus the mean space charge potential should

be about 3/4 the value obtained in equation (3-9).

Values for the mean space charge potential of the electron beam, computed for typical electron energies and currents used in these measurements are shown in Table 3-1. Since the space charge potential at 24 volts is 0.5 V the contact potential of the cathode, V_c , is given by

$$V_c = 2.6 \text{ V} - 0.5 \text{ V} = 2.1 \text{ V} \quad (3-10)$$

The correction to the electron energy due to space charge potential, contact potential, and field penetration is also shown in Table 3-1. Since the energy scale is not critical at higher energies where the cross sections are not changing, a correction of 3 eV is used to compute the energy scale for all cross sections reported in this thesis.

It is important to note here that the kinetic energy of the signal ions will be affected by the space charge potential and field penetration in the interaction region. The S^+ signal ions will lose up to 3 eV and the S^{++} signal ions will lose up to 6 eV of kinetic energy as they leave the potential well, centered in the interaction region. Evidence for this effect can be found in the signal energy analyses of Figure 2-2. In these analyses it can be clearly seen that the energy of the S^+ signal ions is as much as 3 eV less than that of the S^+ parent beam, and the energy of the S^{++} signal ions is as much as 6 eV less than that of the S^+ parent beam.

Table 3-1. Computed mean space charge potential, and correction to the electron energy due to space charge potential, cathode contact potential and field penetration, for various beam energies and currents used in the cross section measurements.

Electron Energy (eV)	Electron Current (mA)	Space Charge Potential (V)	Electron Energy Correction (eV)
5	0.02	-0.2	-2.3
25	0.08	-0.5	-2.7
50	0.25	-1.2	-3.4
100	0.60	-2.0	-4.3
180	1.00	-2.5	-4.9
300	1.00	-1.9	-4.6
500	1.00	-1.7	-4.4

CHAPTER 4

MULTIPLE IONIZATION MEASUREMENTS

Once the absolute cross sections for single ionization have been measured, cross sections for each multiple ionization process can most easily be determined by measuring the ratio of the cross sections for each multiple ionization process to those for single ionization. In this chapter these ratios are defined in terms of measurable quantities. Then the actual procedures used to determine these quantities are described.

4.1 Derivation of Cross Section Ratios

The absolute cross section for double ionization of atomic sulfur by electron impact can be written in terms of the parameters

$$\sigma_{++} = \frac{R_{++}}{D_{++}} \cdot \frac{e}{J} \cdot \frac{ey}{I} \cdot \frac{vV}{(v^2+V^2)^{\frac{1}{2}}} \cdot F \quad (4-1)$$

where R_{++} and D_{++} are the measured count rate and detection efficiency, respectively, for double ions. The other parameters are as defined for equation (3-1).

By taking the ratio of equations (4-1) and (3-1) we find the ratio of the cross sections for double and single ionization to be

$$\frac{\sigma_{++}}{\sigma_{+}} = \frac{R_{++}}{R_{+}} \cdot \frac{D_{+}}{D_{++}} \quad (4-2)$$

given that the beam intensities and geometric overlap do not change between the determination of R_{++} and R_{+} . Similarly the ratio of the cross sections for each multiple ionization process and single ionization is given by

$$\frac{\sigma_{n+}}{\sigma_{+}} = \frac{R_{n+}}{R_{+}} \cdot \frac{D_{+}}{D_{n+}} \quad (4-3)$$

4.2 Measurement of Parameters for Double Ionization

During the actual data acquisition the beam intensities and the count rates are observed to be constant to within about 1%, and the rates R_{++} and R_{+} are measured alternately several times, so that the small effects due to beam drifts cancel out in the measurement of the ratio. Typically, counts are recorded until the statistical uncertainties in the measurements of R_{+} and R_{++} are 1% and 3% respectively. It is important to note that when alternating between measurements of R_{++} and R_{+} only the signal collection optics in the detection region are changed; nothing is changed in the interaction region where the product ions are formed.

4.2.1 Measurement of the Count Rates

As in the single ionization measurements, about 5% of the count rate observed during S^{+} signal acquisition is due to processes other than electron impact. As before this background is caused by secondary particles produced when stripping ions are rejected by the energy analyzer,

and by secondary particles ejected from the neutral beam trap. About 20% of the counts received during a measurement of S^{++} signal are background counts, which in this case, are due almost entirely to the impact of the neutral beam in its collector. Electron beam backgrounds contribute negligibly to the observed count rates in both cases.

In order to separate the signal from these backgrounds the beam modulation scheme described in Chapter 3 was used. This scheme is susceptible to the same problems for a measurement of R_{++} as were described for a measurement of R_+ . Therefore, several tests were performed to ensure that the double ionization measurements were free from spurious sources of signal.

In one of these tests, the ratio of the count rates for double and single ionization were measured as a function of electron beam current. The results of these measurements, made at a collision energy of 177 eV, are displayed in Figure 4-1. As one can see, to within experimental uncertainties, the ratio is constant for electron beam currents from 0.25 to 1.2 mA.

Measurements of the count rate for S^{++} production were also performed with the electron collector alternately grounded and biased at -10 V. The ratio between the count rate for S^{++} production with the collector biased at -10 V and the count rate for S^{++} production with the collector grounded was 1.01 ± 0.04 . This result indicates that ions, formed in the electron collector, do not

Figure 4-1. Ratio of observed count rates for double and single ionization of sulfur, R_{++}/R_+ , as a function of electron beam current, at an electron energy of 177eV.

contribute to the measured signal.

4.2.2 Measurement of the Detection Efficiency

The procedure used to measure the detection efficiency for S^{++} is essentially the same as that used for S^+ . The first step in the measurement is to ensure that D_{++} is uniform over the entire area where signal ions may strike the multiplier. This is done by scanning a small S^{++} ion probe beam, with the same kinetic energy as the signal, over the entrance to the detection region. Next the absolute detection efficiency is measured by centering the ion probe beam on the beam axis and measuring the count rate, and then deflecting it into a deep Faraday cup and measuring its current. With the knowledge that each ion is doubly charged the ion beam flux can be computed directly from the current measurement. By dividing the observed count rate by the S^{++} beam flux, the detection efficiency, in counts per impinging S^{++} ion, is determined.

A problem arose in that D_{++} varied from day to day, and was between one and two times the value that would normally be expected. This was attributed to the fact that the S^{++} ion probe beam, produced in the source, contained varying amounts of O^+ ions (both have $e/m = 16$). Since these ions are singly charged, and in the flux computations they are assumed to be doubly charged, their flux would be underestimated by a factor of two. Thus, given that the detection efficiency for S^{++} and O^+ is

approximately equal, the detection efficiency for this beam could be overestimated by as much as a factor of two.

The presence of O^+ in the S^{++} beam might seem unexpected in that the S beam contains less than 1% O_2 . It is important to note, however, that the S^{++} beam is generally only 1% or less as intense as the S^+ beam, and therefore a small flux of O^+ ions would be significant. It is also important to note that O_2^+ is not observed in the ion beam when O_2 is not in the source. On the other hand, O^+ is always observed in conjunction with OH^+ and H_2O^+ , and with currents comparable to typical S^{++} beam currents. Furthermore, a possible component in the 1% impurity in the CS_2 is SO_2 . Since in SO_2 the two oxygen atoms are separated by the larger sulfur atom, with a 120 degree bond angle, one is more likely to obtain O^+ than O_2^+ . A similar argument holds for a possible CO_2 contaminant. Also, when O_2 is in the source, the O^+ beam has been observed to be as much as 50% as large as the O_2^+ beam. Therefore, even if the impurity in the source were O_2 , which is unlikely, the S^+ beam could be pure to within 1%, while the S^{++} beam, which is itself only 1% as large as the S^+ beam, could contain significant amounts of O^+ . Therefore, it is not surprising that an O^+ impurity is present in an S^{++} beam produced in the source.

In order to eliminate the O^+ ions, the ion beam is passed through a gas cell which contains Krypton. Since the majority of the O^+ ions are likely to be in the 4S

and 2D states, given the likely sources (Hughes and Tiernan 1971), they will efficiently become neutralized in the reactions

Thus they will neither be deflected into the multiplier during the count rate measurement, nor into the deep Faraday cup during the current measurement. At a sufficiently high pressure of Kr in the gas cell the O^+ flux will be insignificant, and D_{++} will assume the value for S^{++} , which will not change as the Kr pressure is increased.

A plot of D_{++} versus gas cell pressure is shown in Figure 4-2. As one can see, when the Kr pressure reaches 2 mT, D_{++} reaches a constant value of about 35%, as would be expected for double ions in this apparatus. The value for the detection efficiency computed from calibrations both before and after data acquisition is $D_{++} = (35.1 \pm 2.0)\%$. The principal source of error comes from the difficulty in measuring the small current of the ion probe beam.

The value for the detection efficiency for single ions, measured both before and after data acquisition, is $D_+ = (27.5 \pm 1.3)\%$. This yields the ratio $D_+/D_{++} = 0.783 \pm 0.058$. The ratios and cross sections for double ionization thus determined are shown in Figures 7-2 and 7-3.

Figure 4-2. Observed detection efficiency for beam with $e/m = 16$ versus the pressure of Kr in a gas cell through which the beam passes.

4.3 Measurement of Parameters for Triple and Quadruple Ionization

The procedure for measurement of the parameters in triple and quadruple ionization is very similar to the procedure used in double ionization. The detection efficiency for triple ions, measured in the manner described in Chapter 3, is $D_{+++} = (36.4 \pm 5.1)\%$, giving a ratio $D_{+}/D_{+++} = 0.755 \pm 0.112$. The detection efficiency for quadruple ions was not measured due to the fact that a detectable beam of quadruply charged sulfur ions could not be obtained from the source. Therefore, the detection efficiency for quadruple ionization was assumed to be the same as that for triple ionization. This assumption is valid given the large statistical uncertainty in the measurement of the count rate for the production of quadruple ions. In fact, the principal source of experimental uncertainty in the triple and quadruple ionization measurements comes from the statistical uncertainty in the measurement of R_{n+} . The measured ratios and absolute cross sections for triple and quadruple ionization are displayed in Figures 7-4 and 7-5.

CHAPTER 5

NEUTRAL BEAM STATE ANALYSIS

The sulfur ion beam is neutralized in the charge transfer cell by charge exchange collisions with O_2 and NO. These gases are used since they have small energy defects for charge transfer from the low lying states of S^+ to the low lying states of S. Neutralization of the beam in this manner can lead to excited sulfur atoms, and so it is important to take steps to determine what effect, if any, excited atoms have on the measurements.

State analysis was particularly difficult in the case of sulfur, in that no method could be found to positively identify the abundance of excited S^+ ions in the parent ion beam. Furthermore, little work has been done with sulfur beams, and there are no published accounts of attempts to characterize the proportion of excited ions, or atoms, in fast sulfur beams. Because of these difficulties the exact proportion of atoms in excited states could not be determined. However, several tests and observations indicate the measured cross sections are characteristic of those of ground state atoms. The low lying states of S and S^+ are shown in Figure 5-1.

Figure 5-1. Low lying states of S° and S^{+} . Each state is shown with the configuration of it's outer electron, spectroscopic designation, and potential energy in eV.

5.1 Effect of Excited Atoms on the Single Ionization Measurements

First it is important to note that the cross sections for single ionization of sulfur, measured in the present experiment, show a threshold at 10 eV. Also, the cross sections measured at electron energies of 5 and 7 eV are zero, to within experimental uncertainty. Since the threshold for single ionization of sulfur atoms in the 5S excited state, or more highly excited states, is 3.9 eV or less, these results indicate that either atoms in these excited states have a negligible cross section for electron impact ionization, or their flux in the beam is negligible. Since it is unlikely that their cross sections are negligible, these results are an indication that the neutral beam used in these measurements did not contain significant fluxes of sulfur atoms in the 5S state or above.

The observed threshold is not sufficiently definite to rule out the presence of atoms in the low lying 1D and 1S metastable states. It is important to note however, that Peach (1968, 1970, 1971) calculates that the cross sections for electron impact ionization of the 3P ground and 1D and 1S metastable states are all within 5% of each other for electron energies from threshold to 500 eV. Since the uncertainty in the single ionization measurements is already about 20%, unless the calculations of Peach are significantly in error, the cross sections for single ionization, determined in this experiment, should be

characteristic of those for ^3P ground state atoms. (In fact, the primary data were taken with O_2 in the charge transfer cell, for which the likely channels for neutralization yield only ^3P and ^1D atoms.)

5.2 Effect of Excited Atoms on the Multiple Ionization Measurements

In the case of double ionization there are no theoretical calculations which give the relative values of the cross sections for the ^3P , ^1D and ^1S states. Therefore, tests were conducted that indicate excited atoms either are not present in the neutral beam, or if present, do not affect the measured ratio of double to single ionization. These tests consisted of measuring this ratio with O_2 , and with NO , as the charge transfer gas, and with the source electron arc potential raised from the typical 8 volts to 16 volts, in an attempt to vary the proportion of excited atoms in the beam and observe the effects. As it is evident in Figure 7-2, the data obtained with the different source conditions all agree, to within experimental uncertainty, indicating that excited atoms, if present, do not change the value of the measured ratios. Thus, the cross sections for double ionization, computed with these ratios and the single ionization measurements, should be characteristic of those for ground state atoms.

The uncertainty in the triple and quadruple ionization measurements is quite large, and thus no measurements

were made to determine the effect of excited atoms. However, the above tests show that these measurements should at least be characteristic of atoms in the 3P , 1D or 1S low lying states. These results should be quite adequate, considering the uncertainties encountered in the aeronomic work for which they will be useful.

CHAPTER 6

THEORY

In this chapter theoretical calculations of the cross sections for single and multiple ionization of sulfur atoms by electrons are discussed. Single ionization cross sections have been obtained from both quantum calculations and empirical parameterizations. Cross sections for double ionization have been computed using an empirical approach only. Triple and quadruple ionization has not been treated theoretically.

6.1 Quantum Calculations for Single Ionization

Cross sections for single ionization of sulfur atoms by electron impact have been computed using the first Born approximation by Peach (1968, 1970, 1971), and using the simpler Bethe approximation by Gaudin et al. (1968a,b,c). The cross sections computed using each method show acceptable agreement with the present measurements.

6.1.1 The Born Calculation

The basic assumption in the Born approximation is that the impacting electron is moving fast enough that it is not significantly perturbed in the interaction, and thus can be represented as a plane wave in both the initial and final state wave functions. This greatly simplifies the integrals to be solved in the expression for the

scattering amplitude, however, it limits the accuracy of the cross sections obtained for low energy collisions. The cross sections obtained in this approximation are generally greater than experiment for collision energies below 1 KeV.

Peach computes cross sections for the single ionization process in which a fast projectile electron strikes and singly ionizes a sulfur atom,

Let $\underline{k}''$ denote the initial momentum of the projectile electron and let $\underline{k}'$ and $\underline{k}$ denote the final momentum of the projectile and ejected electron respectively. (All vectors in this analysis are underlined, and atomic units are used throughout.) The energy of the impacting electron, E , can be expressed as

$$E = \underline{k}''^2 = \underline{k}'^2 + \underline{k}^2 + IP \quad (6-2)$$

where IP is the ionization potential of the sulfur atom. Also, the change in momentum of the projectile electron is denoted

$$\underline{K} = \underline{k}'' - \underline{k}' \quad (6-3)$$

The wave function for the target atom is a properly antisymmetrized set of one electron Hartree-Fock wave functions, $\psi(x_1, x_2, \dots, x_{16})$, where $x = (r_j, s_j)$ is the space and spin coordinate of electron j . The choice of a wave function to represent the ionized system, $S^+ + e$, in

the final state is particularly difficult in ionization processes, in that the ejected electron may move slowly away from the ionic core, and interact strongly with the core electrons. This will be particularly true in low energy collisions. The wave function chosen to represent the $S^+ + e$ system, $\psi(x_1, x_2, \dots, x_{16}, k)$ is an antisymmetrized product of the wave function $\psi(k, x)$, which describes the ejected electron, and a set of one electron wave functions, which describe the residual S^+ ion. The wave function for the ejected electron is taken to be an undistorted Coulomb function of effective charge unity

$$\psi(k, r) = \left(\frac{1}{2\pi}\right)^{3/2} \exp(\pi/2k) \Gamma(1-i/k) \exp(ik \cdot \underline{r})$$

$$\times \sum_{n=0}^{\infty} \frac{[(i/k) + n] [(kr - \underline{k} \cdot \underline{r})]}{2\Gamma[i/k] \Gamma[n+1]} \quad (6-4)$$

This complex wave function, which is typically used in electron impact ionization calculations (Rudge 1968), does not take into account the interactions between the core electrons and the free electron. It simply represents the free electron in the presence of a positively charged particle, that is, an $H^+ + e$ system. The use of this wave function constitutes the major approximation made in Peach's calculations, other than the Born approximation itself. A primary reason no quantum calculations have been done for the double ionization of sulfur by electrons is the difficulty in finding a wave function that accurately represents the two ejected electrons.

In order to derive the formula for the scattering amplitude presented by Peach we begin with its basic form in the first Born approximation (c.f. Mertzbacher 1970)

$$f(k, k') = - \frac{1}{2\pi} \iint \psi_f^*(x_1, x_2, \dots, x_{16}, k) \exp(-i\mathbf{k}' \cdot \mathbf{R}) V(R, r) \\ \times \psi_i(x_1, x_2, \dots, x_{16}) \exp(i\mathbf{k}'' \cdot \mathbf{R}) dR dr_1 dr_2 \dots dr_{16} \quad (6-5)$$

where the projectile electron is represented by plane waves, with special coordinate R , both before and after the collision. The interaction potential, $V(R, r)$, is simply the electrostatic potential between the atomic electrons and the projectile electron (in atomic units)

$$V(R, r) = \sum_{s=1}^{16} \frac{1}{|\mathbf{R} - \mathbf{r}_s|}$$

This yields:

$$f(k, k') = - \frac{1}{2} \int \psi_f^*(x_1, x_2, \dots, x_{16}, k) \sum_{s=1}^{16} \int \frac{\exp(i\mathbf{K} \cdot \mathbf{R})}{|\mathbf{R} - \mathbf{r}_s|} dR \\ \times \psi_i(x_1, x_2, \dots, x_{16}) dr_1 dr_2 \dots dr_{16} \quad (6-6)$$

We now employ the very useful identity

$$\int \frac{\exp(i\mathbf{K} \cdot \mathbf{R})}{|\mathbf{R} - \mathbf{r}_s|} dR = \frac{4\pi}{K^2} \exp(i\mathbf{K} \cdot \mathbf{r}_s)$$

which yields,

$$f(k, k') = - \frac{2}{K^2} \int \psi_f^*(x_1, x_2, \dots, x_{16}, k) \sum_{s=1}^{16} \exp(i\mathbf{K} \cdot \mathbf{r}_s) \\ \times \psi_i(x_1, x_2, \dots, x_{16}) \, dr_1 dr_2 \dots dr_{16} \quad (6-7)$$

This is exactly the form of the scattering amplitude in the Born approximation used by Peach (1968, 1970, 1971).

A small correction for the effects of exchange, between the projectile and scattered electron, is made by use of the Ochkur approximation as derived by Peach (1966). This correction makes about a 5 to 10% difference in the value of the computed cross sections, and should yield more accurate values.

Cross sections are obtained by integrating $|f(k, k')|^2$ over all possible values of the final momenta k and k' . Peach computes and tabulates cross sections of sulfur atoms in the 3P , 1D , and 1S states for both outer shell, and first inner shell single ionization. The computed cross sections for each of these low lying states are the same, to within about $\pm 5\%$, in the energy range from threshold to 500 eV. The cross sections for ionization of the 3P ground state are plotted in Figure 7-1, along with the measured cross sections. Cross sections computed using the Born approximation almost always exceed measurements, and often by as much as a factor of two (cf. Peach 1971, Brook et al. 1978). Thus, the agreement between these computed cross sections, and the present

measurements, is considered to be satisfactory (Peach 1981).

6.1.2 The Bethe Approximation

The Bethe (1930) approximation essentially carries the Born approximation one step further. That is, it is assumed that the projectile electron moves fast enough that the change in its wave vector, $\underline{K} = \underline{k}'' - \underline{k}'$, is small. Thus, the exponential in the scattering amplitude formula (6-7) may be expanded

$$\exp(i\underline{K} \cdot \underline{r}) = 1 + i\underline{K} \cdot \underline{r} + \dots \quad (6-8)$$

and only the first two terms retained. The first term gives zero due to orthogonality, and so, the second term in this expansion replaces the exponential in equation (6-7). The Bethe approximation generally makes poor predictions at low energies, however, leads to a $(\ln E)/E$ dependence in the cross sections at high energies, which generally agrees fairly well with experiment.

Gaudin uses Slater wave functions to represent the atomic states, and like Peach, uses a totally screened Coloumb function of effective charge unity to represent the ejected electron. The cross sections thus obtained are plotted in Figure 7-1, along with the measured cross sections. As one can see, the agreement is best at the highest energies, as expected. The agreement between this theory and experiment is actually quite good given its predictions for other elements (Gaudin 1968b,c).

6.2 Empirical Theories for Single Ionization

An empirical formula presented by Lotz (1967) is based on the functional form for single ionization cross sections predicted by the Bethe approximation at high energies,

$$Q = a \cdot n \cdot \frac{\ln(E/U)}{EU}$$

where Q is the cross section for ionization of a particular atomic subshell, n is the number of electrons in the subshell, and U is the ionization potential of the subshell. The collision energy is given by E , and " a " is a parameter to be determined experimentally.

Through many trials Lotz found that the modification of this formula,

$$Q = a \cdot n \cdot \frac{\ln(E/U)}{EU} \{1 - b \exp[-c(E/U - 1)]\} \quad (6-10)$$

gave good agreement with measured cross sections. The free parameters a , b , and c must be determined for each element "by experiment, theory, or reasonable guesswork" (Lotz 1968).

The cross sections for single ionization of sulfur by electrons, computed by Lotz (1968) using this formula, are displayed in Figure 7-1, with the present measurements. As one can see, the best agreement is at the higher energies, which might be expected since that is where the

Bethe approximation gives the best results.

An empirical formula presented by Mann (1967) is essentially a simple parameterization of the Bethe result. For s electrons the cross section for ionization of a given shell is given by,

$$Q = \frac{AR^2}{U} \cdot \frac{\ln(E/U)}{E/U} \quad (6-11)$$

where R is the atomic radius, E is the collision energy and U is the ionization potential of the shell. For p electrons the formula

$$Q = \frac{AR^2}{U} \cdot \frac{\ln(E/U)^{3/4}}{(E/U)^{3/4}} \quad (6-12)$$

was empirically found to give the best results, for moderately low energies (< 200 eV). Using the atomic radii given by Mann, the cross section for single ionization of the outer, and first inner, shell of sulfur was computed. These cross sections are shown in Figure 7-1. It is interesting to note that this theory gives the best fit to the data, even though a major part of it (equation 6-12) has the least physical justification.

6.3 Classical Theories for Ionization

A classical theory presented by Gryzinski (1965a,b,c) can be used to obtain quantitative cross sections for single ionization of sulfur. The formula is essentially derived from a classical calculation for inelastic scattering of the projectile electron by an atomic electron.

First, he assumes an initial velocity distribution for the bound, atomic electron. Then he computes the cross section for collisions in which the projectile electron transfers an amount of energy, to the atomic electron, greater than or equal to its ionization potential.

In the calculations Gryzinski makes three rather crude approximations in the derivation of a cross section formula. First, since in a classical formulation the single ionization process is an insoluble many body problem, the reaction is approximated as a two body interaction. That is, the interactions between the electrons involved in the ionization process and the spectator electrons are neglected. Clearly, this will lead to poor results for low energy collisions. Further, he models the initial state of the bound electron classically. He assumes the bound electron is in a spherically symmetric state, which is probably not a good approximation for the outer p electrons of sulfur. Also, the velocity distribution of the bound electron, $f(v)$, is assumed to be,

$$f(v) = (\bar{v}/v)^3 \exp(-\bar{v}/v)$$

where $\bar{v}$ is the mean electron velocity. This distribution was chosen simply because it gives cross sections with the Bethe energy dependence, $(\ln E)/E$, which agree well with experiment at high energies. In this respect the formulas presented by Gryzinski are actually empirical parameterizations. Finally, he neglects the wave nature

of the particles in the collision.

The cross sections derived by Gryzinski are plotted in Figure 7-1. As one can see, the agreement is good, considering the assumptions made in the theory.

Gryzinski (1965c) also develops an approximate formula for double ionization, based on the single ionization formula. He computes the cross sections for two processes: One in which the projectile ejects two electrons directly, and another in which the projectile electron imparts enough energy to a bound electron that it ejects a second electron as it leaves the atom. In this calculation it is necessary to know the relative positions of the electrons in the atom. Gryzinski assumes that the density of electrons is uniform and spherically symmetric with mean electron separation r . This mean separation is approximated by

$$r = n \cdot R^3$$

where n is the number of target electrons and R is the atomic radius. The rather complex formula thus derived is a function of the atomic radius R .

The cross sections computed using this theory often disagree with observations by more than an order of magnitude (Roy 1971), and are generally only useful when an order of magnitude estimate is needed. The cross sections for the double ionization of sulfur, derived with this formula, with the value of R taken from Mann (1967), are

about a factor of two larger than the present measurements,
and are thus not plotted.

CHAPTER 7

RESULTS AND DISCUSSION

The cross sections for single ionization of atomic sulfur by electron impact are shown in Figure 7-1. Also shown are theoretical cross sections as discussed in Chapter 6 by Peach (1968, 1970, 1971), Gaudin (1968a,b,c), Lotz (1968), Gryzinski (1965), and Mann (1967). The agreement seen here between experiment and theory is typical, and is quite satisfactory considering the fairly crude assumptions made in the theoretical calculations. It is particularly important to note that the theories based on the Born approximation agree with experiment best at the highest energies, as one would expect. The measured cross sections for single ionization of atomic sulfur are tabulated in Table 7-1.

The ratio of the cross sections for double and single ionization of atomic sulfur by electron impact are shown in Figure 7-2. Also shown are the ratios measured to test for excited states as described in Chapter 5. Absolute cross sections for double ionization are obtained by multiplying these ratios by the absolute cross sections for single ionization. The absolute cross sections for double ionization of sulfur atoms by electrons are shown in Figure 7-3. Both the measured ratios and absolute cross sections for double ionization are tabulated in Table 7-2.

Figure 7-1. Cross sections for single ionization of sulfur atoms by electron impact: •. The curves represent theoretical cross sections, as discussed in the text.

Table 7-1. Absolute cross sections for single ionization of sulfur atoms by electron impact. The numbers in parentheses give the experimental uncertainties in the last two places of the numbers they follow.

Electron Energy (eV)	$\sigma + (\text{\AA}^2)$
5	0.03 (08)
7	0.02 (05)
12	0.54 (16)
17	1.80 (36)
22	2.81 (56)
27	3.28 (65)
37	3.23 (64)
47	3.17 (63)
57	3.14 (62)
67	3.30 (65)
77	3.29 (65)
87	3.16 (63)
97	3.22 (64)
107	3.09 (62)
117	3.02 (60)
127	2.89 (58)
142	2.83 (56)
157	2.82 (53)
177	2.67 (53)
197	2.71 (54)
242	2.27 (45)
297	1.98 (39)
347	1.87 (37)
497	1.44 (27)

Figure 7-2. Ratio of the cross sections for double and single ionization of sulfur atoms by electron impact. Source electron arc potential 8 V and sulfur atom beam formed by charge transfer with NO - O, O₂ - V. Source electron arc potential 16 V and sulfur atom beam formed by charge transfer with NO - S. Where not shown error bars are approximately equal to those of nearby points.

Figure 7-3. Cross sections for double ionization of sulfur atoms by electrons.

Table 7-2. Ratio of the cross sections for double and single ionization of atomic sulfur by electron impact and absolute double ionization cross sections. The numbers in parentheses give the experimental uncertainties in the last two places of the numbers they follow.

Electron Energy (eV)	σ_{++}/σ_{+}	$\sigma_{++} (\text{\AA}^2)$
17	-0.0005 (34)	-0.001 (06)
27	-0.0003 (13)	-0.001 (04)
37	0.0049 (09)	0.016 (04)
42	0.0168 (21)	0.054 (13)
47	0.0305 (29)	0.097 (21)
57	0.0411 (34)	0.129 (28)
67	0.0479 (39)	0.158 (34)
77	0.0521 (42)	0.171 (37)
87	0.0524 (44)	0.166 (36)
97	0.0511 (40)	0.165 (35)
107	0.0534 (44)	0.165 (36)
117	0.0505 (41)	0.153 (33)
127	0.0503 (43)	0.145 (32)
142	0.0467 (36)	0.132 (28)
157	0.0454 (39)	0.128 (28)
177	0.0441 (35)	0.118 (25)
197	0.0427 (33)	0.116 (25)
242	0.0420 (34)	0.097 (21)
272	0.0415 (33)	0.089 (19)
297	0.0421 (33)	0.083 (18)
347	0.0391 (31)	0.073 (16)
397	0.0373 (30)	0.063 (14)
497	0.0386 (36)	0.056 (12)

The ratio of the cross sections for triple and single, and also, quadruple and single ionization of sulfur atoms by electron impact are shown in Figure 7-4. The absolute cross sections, computed by multiplying the ratios by the cross sections for single ionization, are shown in Figure 7-5. These data for triple and quadruple ionization are tabulated in Tables 7-3 and 7-4, respectively.

These measured cross sections will be of aid to the space scientists attempting to model the Io torus. For example, Shemansky (1980a) estimates the rate coefficient for ionization of sulfur atoms by electrons in the outer portion of the Io torus to be 5×10^{-8} cc/sec, based on the calculated cross sections of Peach (1968, 1970). Given the electron concentration there is $\sim 2000/\text{cc}$, he concludes the lifetime of neutral sulfur in that portion of the Io torus is about 2.5 hours. Since the present measurements indicate that the cross sections for electron impact ionization of sulfur atoms are about a factor of two lower than those computed by Peach, at all energies, the lifetime of a neutral particle in the Io torus is likely to be closer to 5 hours. Considering that a particle ejected from Io at escape velocity will leave the torus in about 8 hours, this result may lower the current estimates of the probability of capture of sulfur atoms into the Io torus. This may lead to either increased estimates of the particle fluxes into the torus, from the volcanoes or other sources on Io, or lower estimates of

the ion diffusion rates out of the torus (cf. Shemansky 1980b).

Figure 7-4. Ratio of the cross sections for triple and single: ●, and quadruple and single: □, ionization of sulfur atoms by electron impact.

Figure 7-5. Cross sections for triple: $\bullet$, and quadruple: $\square$, ionization of sulfur atoms by electron impact.

Table 7-3. Ratio of the cross sections for triple and single ionization of atomic sulfur by electron impact and absolute triple ionization cross sections. The numbers in parentheses give the experimental uncertainties in the last two places of the numbers they follow.

Electron Energy (eV)	σ_{+++}/σ_{+} (x 100)	σ_{+++} (10^{-18} cm)
72	-0.016 (40)	-0.051 (13)
97	0.090 (29)	0.29 (11)
147	0.139 (30)	0.39 (12)
197	0.155 (28)	0.42 (11)
247	0.247 (42)	0.57 (15)
272	0.350 (57)	0.75 (19)
297	0.397 (64)	0.79 (20)
347	0.569 (89)	1.06 (27)
397	0.64 (10)	1.10 (27)
447	0.67 (11)	1.06 (27)
497	0.74 (14)	1.06 (28)

Table 7-4. Ratio of the cross sections for quadruple and single ionization of atomic sulfur by electron impact and absolute quadruple ionization cross sections. The numbers in parentheses give the experimental uncertainties in the last two places of the numbers they follow.

Electron Energy (eV)	σ_{4+}/σ_+ (x 100)	σ_{4+} (10^{-18} cm)
147	0.010 (10)	0.028 (28)
247	0.037 (19)	0.085 (47)
327	0.060 (12)	0.116 (33)
397	0.124 (26)	0.211 (61)
497	0.176 (36)	0.253 (72)

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