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THE IONIZATION OF ATOMIC OXYGEN BY ELECTRON IMPACT

E. C. ZIPF
Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.

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Abstract—The single and double ionization of atomic oxygen by electron impact has been studied, and the energy dependence of the specific ionization cross-section, $\sigma(O^+)$ and $\sigma(O^{2+})$, has been measured from 40 to 300 eV using a high-density atomic oxygen source not contaminated by metastable $O(^1D)$ or $O(^1S)$ atoms.

INTRODUCTION

The excitation and ionization of atomic oxygen by electron impact are inelastic processes of major importance in the terrestrial thermosphere. Unfortunately, because high-density sources of atomic oxygen are difficult to prepare in the laboratory under conditions suitable for absolute electron scattering experiments, only a few inelastic OI cross-section measurements have actually been reported over the past 30 years. These include: total scattering (Sunshine *et al.*, 1967), O^+ ionization (Fite and Brackman, 1959; Bokensberg, 1961; Rothe *et al.*, 1962; Brook *et al.*, 1978), O^{2+} ionization (Ziegler *et al.*, 1982), differential inelastic scattering (Khakoo *et al.*, 1983), and $OI(^3S^0, {}^5S^0)$ excitation (Stone and Zipf, 1974). During the same period, satellite and sounding rocket studies have amassed a wealth of airglow and photoelectron flux data whose analysis has been hampered by the scarcity of OI cross-section measurements and by the large probable errors in the published OI excitation cross-section values. The present results developed out of a series of experiments addressing this problem. The initial objective of these experiments was to measure the ratio of the cross-sections for the direct and dissociative excitation of the $OI(3s^3S^0–2p^3P; \lambda 1304\ Å)$ by electron impact, σ_A/σ_D,

$$e + O(^3P) \xrightarrow{\sigma_A} O(3s^3S^0) + e \tag{1}$$

$$e + O_2 \xrightarrow{\sigma_D} O(3s^3S^0) + O + e \tag{2}$$

accurately. The strategy of the experiment was to normalize the σ_A/σ_D ratio directly to the ratio of the O^+ and O_2^+ ionization cross-sections

$$e + O(^3P) \rightarrow O^+ + 2e \tag{3}$$

$$e + O_2(^3\Sigma_g^-) \rightarrow O_2^+ + 2e \tag{4}$$

$\sigma(O^+)/\sigma(O_2^+)$, using an apparatus that combined a high-density, diffuse gas source [$n(O) \sim 10^{12}\,cm^{-3}$], an electrostatically focused electron gun, a vacuum ultraviolet monochromator, and a quadrupole mass spectrometer for simultaneous optical and composition measurements. The σ_A/σ_D ratio is related to the quantities actually measured in the experiment by the following expression,

$$\frac{\sigma_A}{\sigma_D} = \frac{I_A}{I_D} \cdot \frac{S(O_2^+)}{S(O^+)} \cdot \frac{T(O_2^+)}{T(O^+)} \cdot \frac{\sigma(O^+)}{\sigma(O_2^+)} \tag{5}$$

where I_A and I_D are the $\lambda 1304$ Å intensities due to processes (1) and (2), respectively, $S(O_2^+)$ and $S(O^+)$ are the mass spectrometer ion signals, and $T(O_2^+)$ and $T(O^+)$ are the combined transmission and detector sensitivity factors for O_2^+ and O^+ ions. By operating the diffuse gas source under excitation conditions such that the measured counting rates for the $\lambda 1304$ Å intensity, I_A and I_D, and the mass spectrometer ion signals, $S(O_2^+)$ and $S(O^+)$, were in the 100 kHz to 1 mHz range, the statistical errors in the measured I_A/I_D and $\sigma(O^+)/\sigma(O_2^+)$ ratios were reduced to less than 1%. Thus, the overall probable error in the σ_A/σ_D ratio [$\sim \pm 9\%$] was determined chiefly by the precision (repeatability) of the measurement ($\sim 2\%$), the accuracy of the ion transmission–sensitivity ratio, $T(O_2^+)/T(O^+)$, ($\sim 2\%$) and the quadrature error in the published ionization cross-section data for $\sigma(O^+)$ and $\sigma(O_2^+)$, ($\sim 7.5\%$).

In addition to its primary purpose, the experiment also provided a unique opportunity to determine the energy dependence of the $\sigma(O^+)$ and $\sigma(O^{2+})$ ionization cross-sections

$$e + O(^3P) \rightarrow O^+ + 2e \tag{6}$$

$$e + O(^3P) \rightarrow O^{2+} + 3e \tag{7}$$

with high precision ($\pm 3\%$) and to obtain absolute values with modest accuracy ($\pm 11\%$). The purpose of

this paper is to present our ionization cross-section results and to compare these results with earlier work (Fite and Brackman, 1959; Bokensberg, 1961; Rothe *et al.*, 1962; Brook *et al.*, 1978; Ziegler *et al.*, 1982).

EXPERIMENTAL TECHNIQUES

The basic experimental techniques used in this study have been described in detail previously (Stone and Zipf, 1974). Only a brief summary describing these procedures and the method used to prepare a high-density atomic oxygen source with negligible, metastable $O(^1D)$ and $O(^1S)$ populations will be presented here. Figure 1 shows a schematic diagram of the apparatus. In the present experiment, atomic oxygen was produced by dissociating a gas mixture consisting of 80% O_2 and 20% argon in a microwave discharge. The dissociated gas mixture then flowed into a small collision chamber that was located at the center of a large rapidly pumped UHV vacuum chamber. The flow tube was fabricated out of quartz and passed through a high-efficiency, quarter-wavelength microwave cavity which was resonant at a frequency of 3150 gHz. Microwave energy was supplied to the cavity by a tuneable QK-62 magnetron whose output power level (80 W) was actively controlled. A small constriction in the flow tube just downstream from the microwave cavity facilitated operating the discharge at pressures in the 0.1–1.0 torr range while the collision chamber pressure at a much lower pressure ($\sim$0.2 microns). Beyond the constriction, the flow tube was bent through an angle of 90° before it entered the collision chamber off-axis. This arrangement served several purposes: Firstly, it effectively prevented vacuum ultraviolet [v.u.v.] photons excited in the discharge from reaching the collision region where they would have created an undesirable noise background and might have contributed to the ion signal detected by the quadrupole mass spectrometer by photoionizing the target gases [O, O_2, Ar]. Secondly, it insured that metastable $O(^1S)$ and $O(^1D)$ atoms formed in the discharge would make numerous collisions with the walls of the flow tube and with the metal surfaces of the collision chamber before interacting with the electron beam. Since the efficiency of deactivating these metastable atoms at the walls is essentially unity, the atomic oxygen in the collision chamber was almost entirely in the $O(^3P)$ ground state.

The pressure in the microwave discharge was monitored by an MKS baratron manometer. The flow system was operated in a constant mass mode. Monitoring the partial pressures of the O, O_2, and Ar during the discharge on/off cycles provided a direct check on the performance of the system. These measurements showed that the absolute argon flow rate was indeed constant with no loss of the rare gas in the discharge, but that there was some loss and/or conversion of the O_2 into other species besides atomic oxygen (e.g. H_2O) when the discharge was on. The depletion effect varied with the microwave power level and the pressure in the discharge but was generally less than 5%. The absolute gas pressure in the collision chamber was measured directly by the Extranuclear quadrupole mass spectrometer attached to it.

A collimated electron beam from an electrostatically focused gun (Erdman and Zipf, 1982) passed through the dissociated gas exciting a variety of atomic and molecular states as well as ionizing the target gases. The radiation, which resulted from the relaxation of these states was focused on the entrance slit of a 0.3 m McPherson v.u.v. monochromator by an MgF_2 lens. The slit-height of the monochromator was set at 1 mm

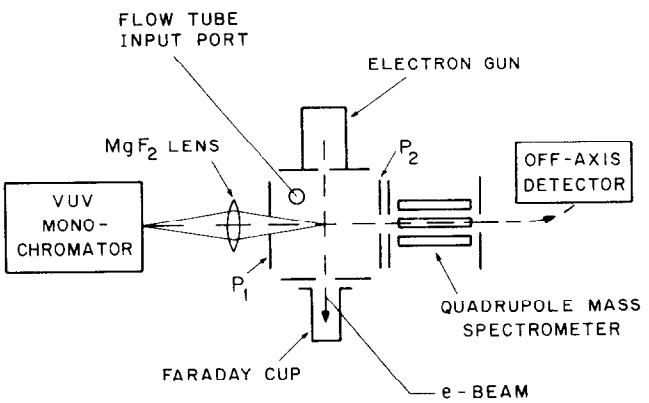

FIG. 1. SIMPLIFIED DIAGRAM OF THE EXPERIMENTAL APPARATUS.

so that the volume from which the photons were emitted was the same volume sampled by the mass spectrometer. The optical axis of the monochromator and the geometric axis of the quadrupole lens were co-linear; the electron beam was at right angles to this common axis. The v.u.v. detector used in this experiment consisted of a cesium iodide-coated plate, which served as a photocathode, and a Johnston Laboratories MM-1 multiplier, which collected the ejected photoelectrons. The background counting rate (equivalent dark current) of the v.u.v. detector, which has a large surface area (~ 10 cm^2), was negligible (< 1 ct s^{-1}).

The collision chamber was built in the form of a rectangular box with each wall electrically isolated so that the magnitude of the stray currents could be monitored. In normal operation, the end plate on which the electron gun was mounted as well as the cover plates parallel to the plane of Fig. 1 was kept at ground potential. The backplate on which the insulated Faraday cup was mounted was slightly negative with respect to ground due to the small voltage-drop across the electrometer measuring the current to this plate which provided important diagnostic data on the focusing of the beam as the beam energy varied. Plate P_1 contained a small slit, which along with the slit on the monochromator, defined the beam volume from which photons were collected. Plate P_2 contained a hole (dia. 2 mm) on the optical axis of the experiment through which ions were extracted and focussed into the mass spectrometer. Plates P_1 and P_2 were operated at elevated potentials so that there was an electric field which accelerated ions from the collision region towards the exit aperture. V_1-V_2 was adjusted so that for a fixed electron beam current and target gas pressure, the shape of the Ar^+ and O_2^+ ionization cross-sections for electron impact and argon and molecular oxygen, respectively, duplicated the recent work of Stephen *et al.* (1980a,b) and Mark (1975). The potential difference was of the order of 10 V.

The quadrupole mass spectrometer was operated at very low resolution ($M/\Delta m \sim 15$) so that the mass peaks were flat-topped and the transmission of the mass spectrometer essentially independent of the mass below 50 a.m.u. This was verified by making comparative measurements on gas mixtures containing H_2, He, CH_4, Ne, N_2, O_2, Ar, and Kr and using literature values for their specific ionization cross-sections. The detector for the mass spectrometer was a Johnston Laboratories MM-1 multiplier, which was located off-axis so that photons or metastable species produced in the interaction region would not reach it. The detector was operated in the pulse counting mode with sufficient gain to insure virtually 100% collection efficiency. This was independently checked for each ion (mass) in order to eliminate discrimination effects which are quite likely when these devices are used as simple current amplifiers. Coherent summing techniques were also used to enhance the quality of the data and to average out small drifts ($< 1\%$) in such parameters as the beam current, target density, etc. The data were initially stored in a multichannel analyzer from which they were transferred to a VAX-750 for detailed analysis using IDL softwear.

The intent of the primary experiment was to compare σ_A/σ_D with $\sigma(O^+)/\sigma(O_2^+)$ accurately and not to make an absolute determination of either specific cross-section since we could not calibrate the v.u.v. monochromator with comparable absolute accuracy. The ratio of the ionization cross-sections enters the analysis because it is necessary to know the density ratio, $n(O)/n(O_2)$. This ratio was deduced from the measured ion signals using literature values for $\sigma(O^+)$ and $\sigma(O_2^+)$. The experiment then yields σ_A/σ_D, $\sigma(O^{2+})/\sigma(O^+)$, and the energy dependence of $\sigma(O^+)$ and $\sigma(O^{2+})$. Alternatively, the analysis of the target composition for constant mass flow provides an independent means for estimating the $n(O)/n(O_2)$ ratio with some additional uncertainty due to the complications of wall losses, and thus to determine $\sigma(O^+)/\sigma(O_2^+)$ independently. These absolute results indicate that the $\sigma(O^+)/\sigma(O_2^+)$ ratio obtained from the data of Brook *et al.* (1978) and Mark (1975) are accurate to within $\sim 11\%$. Viewed from this perspective, the present experiment provides absolute cross-section values and is quite similar in technique to the earlier work of Fite and Brackman (1959).

RESULTS

The primary quantities measured in this experiment were the relative ionization cross-sections, $\sigma(O^+)$ and $\sigma(O^{2+})$, for the specific production of O^+ and O^{2+} ions by electron impact on atomic oxygen. The measurements were carried out over an energy range from 40 to 300 eV. The ratio, $\sigma(O^{2+})/\sigma(O^+)$, was obtained as an immediate result without the need for normalization. These results are shown in Fig. 2 where they are compared with the data presented by Ziegler *et al.* (1982); the agreement between the two studies is very good. Numerical values for the $\sigma(O^{2+})/\sigma(O^+)$ ratio, which has a probable error of $\pm 5\%$, are listed in Table 1.

Single ionization of atomic oxygen by electron impact has been studied by several workers using different techniques. Both Fite and Brackman (1959) and Rothe *et al.* (1962) deduced $\sigma(O^+)$ values from direct measurements of the $\sigma(O^+)/\sigma(O_2^+)$ ratio using the total ionization cross-section data of Tate and Smith (1932) for absolute normalization. Recent work by

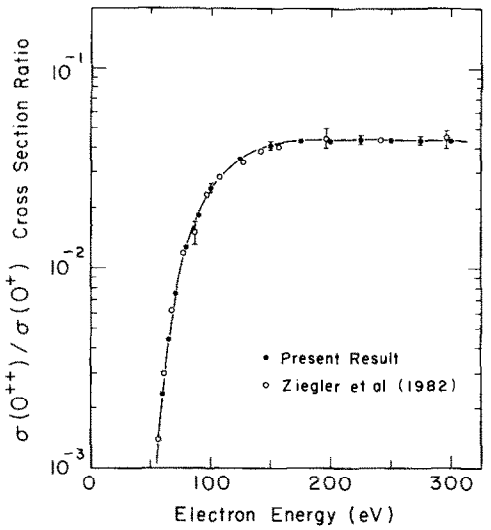

FIG. 2. THE RATIO OF THE CROSS-SECTION FOR DOUBLE AND SINGLE IONIZATION OF ATOMIC OXYGEN, $\sigma(O^{2+})/\sigma(O^+)$, BY ELECTRON IMPACT VS ENERGY.
The open circles are data points from Ziegler *et al.* (1982). The solid dots show the present results which have an uncertainty of $\pm 5\%$.

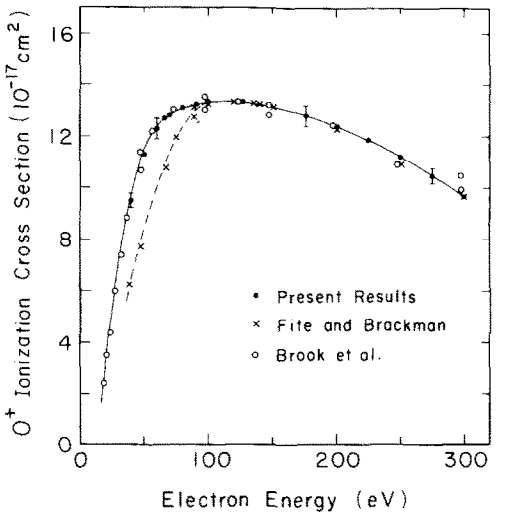

FIG. 3. THE CROSS-SECTION FOR SINGLE IONIZATION OF ATOMIC OXYGEN BY ELECTRON IMPACT.
The revised values of Fite and Brackman (1959) and the results of Brook *et al.* (1978) are shown along with the present results. The estimated probable error in these data are indicated by the bars.

Mark (1975) has yielded revised values for the specific O_2^+ ionization cross-section, $\sigma(O_2^+)$, and these results have been used to recalculate $\sigma(O^+)$ from the original ratio data of Fite and Brackman (1959). The revised Fite and Brackman cross-section values are compared in Fig. 3 with the data of Brook *et al.* (1978) which was obtained in an absolute measurement using atomic beam techniques. The absolute agreement is quite satisfactory for incident electron energies greater than 100 eV. However, at lower energies, the $\sigma(O^+)$ values of Fite and Brackman (1959) are somewhat smaller (10–50%) than the results of Brook *et al.* (1978).

TABLE 1. THE MEASURED RATIO OF THE CROSS SECTIONS FOR DOUBLE AND SINGLE IONIZATION OF ATOMIC OXYGEN BY ELECTRON IMPACT AND THE ABSOLUTE SINGLE AND DOUBLE IONIZATION CROSS-SECTIONS

Electron energy (eV)	$\sigma(O^{2+})/\sigma(O^+)$	$\sigma(O^+)$ (10^{-16} cm^2)	$\sigma(O^{2+})$ (10^{-18} cm^2)
40		0.95	
50		1.13	
60	2.41(−3)*	1.23	0.296
65	4.43(−3)	1.27	0.563
70	7.52(−3)	1.28	0.963
80	1.28(−2)	1.31	1.68
90	1.83(−2)	1.32	2.42
100	2.53(−2)	1.33	3.34
125	3.55(−2)	1.33	4.72
150	4.11(−2)	1.31	5.38
175	4.37(−2)	1.28	5.59
200	4.33(−2)	1.24	5.37
225	4.38(−2)	1.18	5.17
250	4.40(−2)	1.12	4.93
275	4.35(−2)	1.05	4.57
300	4.35(−2)	0.970	4.22

* Read 2.43×10^{-3}.

The results of the present experiment are also shown in Fig. 3. The relative $\sigma(O^+)$ data were normalized to provide a best fit in the 100–300 eV energy range to the composite set of cross-section values obtained by Fite and Brackman (1959) and Brook *et al.* (1978). Below 100 eV our results, which have a precision of $\pm 3\%$, agree well with the low-energy data of Brook *et al.* (1978). Absolute values for $\sigma(O^+)$ and $\sigma(O^{2+})$ can be deduced from our primary data using the mass flow analysis, but the probable uncertainty ($\pm 11\%$) is considerably larger. Nonetheless, the absolute values are in close agreement with the work of Brook *et al.* (1978) over the entire energy range. Numerical values for $\sigma(O^+)$ and for $\sigma(O^{2+})$ are given in Table 1, while Fig. 4 illustrates the energy dependence of the $\sigma(O^{2+})$ cross-section.

DISCUSSION

The present $\sigma(O^+)$ and $\sigma(O^{2+})$ results were obtained using a high-density atomic oxygen source that permitted relative cross-section measurements with small probable errors and absolute values with modest

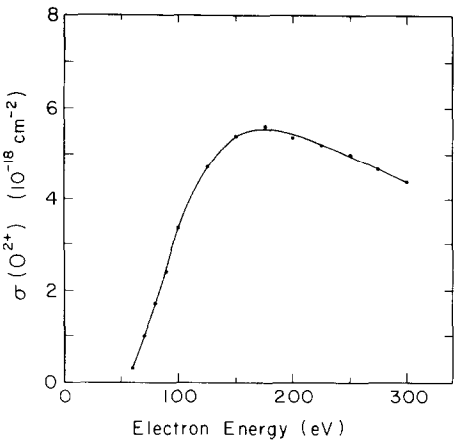

FIG. 4. THE CROSS-SECTION FOR DOUBLE IONIZATION OF ATOMIC OXYGEN BY ELECTRON IMPACT.

uncertainty. Our relative cross-section results are in good agreement with earlier work of Fite and Brackman (1959), Rothe *et al.* (1962) and Brook *et al.* (1978) for single ionization of atomic oxygen by electron impact and with the recent study of Ziegler *et al.* (1982) for double ionization. These are encouraging developments that suggest that the absolute values for $\sigma(O^+)$ and $\sigma(O^{2+})$, which reflect this entire body of work, have an accuracy (± 5–10%) comparable to the specific cross section values for diatomic targets (e.g. O_2, N_2) and thus may be used with confidence in aeronomic calculations.

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