On the direct and dissociative excitation of the O (3s ³S°) state by electron impact on atomic and molecular oxygen

E C Zipf

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, USA

Abstract. The excitation of the O $(3s\,^3S° \rightarrow 2p\,^3P;\ \lambda\ 1304\ \text{Å})$ resonance transition by electron impact on atomic and molecular oxygen has been studied. The ratio of the cross sections for the specific atomic and dissociative processes, σ_A/σ_D, has been measured accurately from 60 to 300 eV by direct normalisation to the ratio of the specific O^+ and O_2^+ ionisation cross sections. At 100 eV, $\sigma_A/\sigma_D = 3.00 \pm 9\%$. The experiment was carried out using an apparatus that combined a high-density diffuse gas source ($n(O) \sim 10^{12}\ \text{cm}^{-3}$), an electrostatically focused electron gun, a vacuum-ultraviolet monochromator and a quadrupole mass spectrometer for simultaneous optical and composition measurements. The present σ_A/σ_D values are smaller by a factor of 2.1 than the original results of Stone and Zipf and Mumma and Zipf. When revised $\sigma_A(1304\ \text{Å})$ values are calculated from these new data using contemporary calibration standards, it is found that the shape of the cross section for the excitation of the O $(3s\,^3S°)$ state by electron impact on atomic oxygen agrees well with the earlier work but the absolute magnitude of $\sigma_A(1304\ \text{Å})$ must be reduced by a factor of 2.8. The revised cross section values are in good agreement with recent quantum calculations when cascade excitation of the $3s\,^3S°$ state is taken into account.

1. Introduction

The atomic oxygen resonance transition O I $(3s\,^3S° \rightarrow 2p\,^3P;\ \lambda\ 1304\ \text{Å})$ is a prominent emission feature in the vacuum-ultraviolet (VUV) spectrum of the aurora and dayglow (Crosswhite *et al* 1962, Donahue and Strickland 1970, Gentieu *et al* 1981, 1984, Chakrabarti *et al* 1983). Over the past two decades, satellite and sounding rocket studies have amassed a wealth of *in situ* data that suggest that the excitation of atomic oxygen by electron impact

$$e + O\ (2p\,^3P) \xrightarrow{\ \sigma_A\ } O\ (3s\,^3S°) + e \tag{1}$$

$$O\ (3s\,^3S°) \rightarrow O\ (2p\,^3P) + h\nu(\lambda\ 1304\ \text{Å}) \tag{2}$$

is an important source of this (VUV) multiplet in the thermosphere and that dissociative excitation

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

is also a factor in auroral substorms (Strickland and Donahue 1970, Meier *et al* 1982, Meier and Lee 1982, Meier 1982). Much of the interest in the $3s\,^3S°$–$2p\,^3P$ transition arises because its excitation in the upper atmosphere provides a unique opportunity to study two- and three-level optical entrapment problems in a wall-less medium with

an optical depth of the order of 10^5 (Donahue and Fastie 1964, Strickland and Donahue 1970, Meier 1982, Zipf *et al* 1979). The analysis of λ 1304 Å airglow and auroral data has also yielded new insights into the nature and solar cycle variability of the terrestrial photoelectron flux (Meier *et al* 1985, Strickland and Anderson 1983, Stamnes and Rees 1983) and into the behaviour of the secondary-electron energy distribution in auroral substorms (Rees 1975, Rees and Jones 1973). The excitation of the family of O I and O II resonance transitions in the airglow also provides an opportunity to study quantitatively the effects of kinetically energetic atoms that have been produced dissociatively on radiation entrapment, on the escape of atoms from a planetary atmosphere and on the thermal economy of the upper atmosphere (Rees *et al* 1983, Zipf and Wells 1980). Ultimately, it is hoped that observation of these EUV and VUV transitions by satellites will serve as a remote-sensing technique for global studies of the chemistry and dynamics of atomic oxygen in the thermosphere.

Unfortunately, the investigation of these interesting problems has been hampered by a lack of accurate cross section data. Until recently, the excitation cross sections for only two transitions, O I $(3s\,^3S^\circ \rightarrow 2p\,^3P;\ \lambda\,1304\,\text{Å})$ and O I $(3s\,^5S^\circ \rightarrow 2p\,^3P;\ \lambda\,1356\,\text{Å})$, had been measured. Stone and Zipf (1974) found peak cross section values of $5.3 \times 10^{-17}\,\text{cm}^2$ and about $2.5 \times 10^{-17}\,\text{cm}^2$, respectively, for these features with an uncertainty of about a factor of 2. This experimental work has now been extended by Kao and Zipf (1985) to include electron impact excitation of atomic oxygen to the entire triplet manifold of states $(ns\,^3S^\circ,\ np\,^3P$ and $nd\,^3D^\circ)$ up to $n=6$ with limited data to $n=8$. However, since these data were normalised to the original $\sigma(1304\,\text{Å})$ values of Stone and Zipf (1974), they also share the uncertainty of the original work.

The experimental O I cross section values are quite large, and this in itself has been a matter of considerable concern, since the experimental values and the results of recent quantum scattering calculations differ by a factor of about 2.5 or more (e.g. Smith 1976, Rountree 1977). However, since the calculated $3s\,^3S^\circ$ oscillator strength used in the theoretical studies had a probable error of 25 to 50%, the experimental and theoretical results were just barely compatible when cascade was included. Attempts to derive a more accurate $\sigma(1304\,\text{Å})$ value from airglow data have yielded mixed results. Julienne and Davis (1976) recommended that the $\sigma(1304\,\text{Å})$ values of Stone and Zipf be reduced by a factor of 2 while Meier and Lee (1982) found little evidence for this suggestion. More recent appraisals (Meier *et al* 1985) support a 40% reduction. Unfortunately, these estimates depend heavily on the choice of a photoelectron flux model and an atomic oxygen density profile, and since both of these are also beset by factor-of-2 differences of opinion (Hernandez *et al* 1983, Conway 1983, Richards and Torr 1984, Walton *et al* 1984), the airglow values for $\sigma(1304\,\text{Å})$ have uncertainties at least as large as the laboratory results of Stone and Zipf (1974).

The present results developed out of a series of experiments addressing these problems. In this paper, we describe an experiment in which we have measured the ratio of the cross sections for the direct and dissociative excitation of the O I $(3s\,^3S^\circ-2p\,^3P;\ \lambda\,1304\,\text{Å})$ by electron impact, σ_A/σ_D, accurately. The strategy of the experiment was to normalise the σ_A/σ_D ratio directly to the ratio of the O^+ and O_2^+ ionisation cross sections $\sigma(O^+)/\sigma(O_2^+)$

$$e + O(^3P) \rightarrow O^+ + 2e \tag{4}$$

$$e + O_2(X\,^3\Sigma_g^-) \rightarrow O_2^+ + 2e \tag{5}$$

using an apparatus that combined a high-density diffuse gas source $(n(O) \sim 10^{12}\,\text{cm}^{-3})$,

an electrostatically focused electron gun, a vacuum-ultraviolet monochromator and a quadrupole mass spectrometer for simultaneous optical and composition measurements. The experiment was designed to yield ion and photon data with statistical uncertainties of less than 1%, so that the probable error in the final σ_A/σ_D ratio values would be due mostly to the quadrature error in the ratio of the ionisation cross sections, $\sigma(O^+)/\sigma(O_2^+)$. The total cross section for process (1), $\sigma_A(1304\ \text{Å})$, was then calculated as a function of energy from the dissociative excitation cross section data of Mumma and Zipf (1971) and Gorman and Zipf (1986), $\sigma_D(1304\ \text{Å})$, which were first scaled downward by 34% as a result of new studies by Shemansky *et al* (1985), Van Zyl *et al* (1985) and Risley (1985) which have revised the absolute calibration standard used in the earlier work. The new $\sigma_A(1304\ \text{Å})$ cross section values are smaller than the results of Stone and Zipf (1974) by a factor of 2.8. The results presented here are in good agreement with recent quantum calculations (Smith 1976) when cascade excitation of the $3s\ ^3S^o$ state is taken into account.

2. 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 techniques 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 centre of a large rapidly pumped ultra-high vacuum chamber. The flow tube was constructed out of quartz and passed through a high-efficiency quarter-wavelength microwave cavity which was resonant at a frequency of 3150 MHz. Microwave energy was supplied to the cavity by a tunable 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 was at a much lower pressure (about 0.2 μm). Beyond the constriction, the flow tube was bent
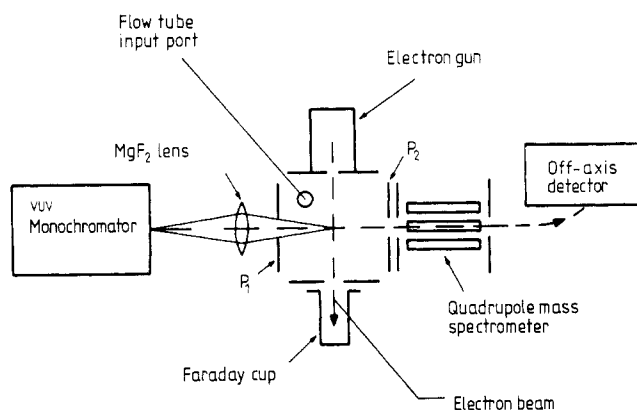

Figure 1. Simplified diagram of the experimental apparatus.

through an angle of 90° before it entered the collision chamber off-axis. This arrangement served several purposes. First, it effectively prevented vacuum-ultraviolet 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 signals detected by the quadrupole mass spectrometer by photoionising the target gases (O, O_2, Ar). Secondly, it ensured 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 ionising the target gases. The radiation that resulted from the relaxation of these states was focused on the entrance slit of an 0.3 m McPherson vuv monochromator by an MgF_2 lens. The slit height of the monochromator was set at 1 mm 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 collinear, and the electron beam was at right angles to this common axis. The vuv detector used in this experiment consisted of a caesium 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 vuv detector, which had a large surface area (about $10\ cm^2$), was negligible (being less than 1 count/s).

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 figure 1 was kept at ground potential. The back plate 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 (diameter 2 mm) on the optical axis of the experiment through which ions were extracted and focused 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^+ ionisation cross sections for electron impact on argon and

molecular oxygen, respectively, duplicated the recent work of Stephan and Mark (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 was essentially independent of the mass below 50 amu. 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 ionisation 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 electron multiplier was operated as an event detector in order to minimise the mass-dependent discrimination effects which are likely when these devices are used as simple current amplifiers. In the event-detector mode, the multiplier is operated at a very high gain (about 2×10^7) so that an average anode pulse produced by an incident positive ion contains a charge of approximately -3.2×10^{-12} C. The actual amount of charge varies with the mass of the incident ion that impacts the multiplier with an energy of 4.5 keV. Pulse height distribution studies of the detector used in this work indicate that the difference in the average pulse height over the O^+ to O_2^+ mass range is less than 30%. Since the threshold sensitivity of the pulse-amplifier discriminator in the mass spectrometer was -1.0×10^{-14} C, the small variation in the pulse height (gain) with ion mass did not affect the performance of the MM-1 multiplier as a mass-independent event detector. 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 analyser from which they were transferred to a VAX-750 computer for detailed analysis using IDL software.

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 excitation cross section since we could not calibrate the vuv monochromator independently with comparable absolute accuracy. The σ_A/σ_D ratio is related to the quantities actually measured in the experiment by

$$\frac{\sigma_A}{\sigma_D} = \frac{I_A}{I_D} \frac{n(O_2)}{n(O)} = \frac{I_A}{I_D} \frac{S(O_2^+)}{S(O^+)} \frac{T(O_2^+)}{T(O^+)} \frac{\sigma(O^+)}{\sigma(O_2^+)} \tag{6}$$

where I_A and I_D are the λ 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. In equation (6), $S(O^+)$ is the mass-16 ion signal due to electron impact ionisation of atomic oxygen (process (4)). $S(O^+)$ is determined by subtracting the O^+ ion signal due to dissociative ionisation

$$e + O_2 \rightarrow O^+ + O + 2e \tag{7}$$

from the total mass spectrometer signal at 16 amu. The dissociative ionisation signal is derived from measurements of the O_2 density in the collision chamber and from a knowledge of the cracking characteristics of the ioniser. Depending on the energy of the electron beam, the dissociative ionisation signal can be large (e.g. at 60 eV, process (7) accounts for about 20% of the total mass-16 signal). Thus, the accuracy of the difference signal $S(O^+)$ depends critically on the statistical quality and precision of the primary mass spectrometer data. By operating the diffuse gas source under excitation conditions such that the measured counting rates for the λ 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 $S(O^+)/S(O_2^+)$ ratios were reduced to less than 1%. Errors due to drifts in the electron beam current or target gas pressure were kept below 1% by the use of regulators and coherent summing techniques.

The atomic oxygen density could also be determined independently from measurements on doubly ionised atomic oxygen, $S(O^{2+})$,

$$e + O \xrightarrow{\sigma(O^{2+})} O^{2+} + 3e \tag{8}$$

relying on the cross section data of Ziegler *et al* (1982) for absolute values. For this species, the correction for O^{2+} ions produced dissociatively was very small (<1%) so that the potential subtraction error was negligible. The $n(O)$ results obtained by either method agreed closely. The experiment also provided an opportunity to measure the energy dependence of the ratio of the cross section for double and single ionisation of atomic oxygen, $\sigma(O^{2+})/\sigma(O^+)$ by electron impact as an additional test of the technique. These results are shown in figure 2; the agreement with the data of Ziegler *et al* (1982) is excellent. Absolute values for $\sigma(O^+)$ were also obtained during this study. The results agree closely with the earlier work of Brook *et al* (1978) and have been described elsewhere (Zipf 1985).
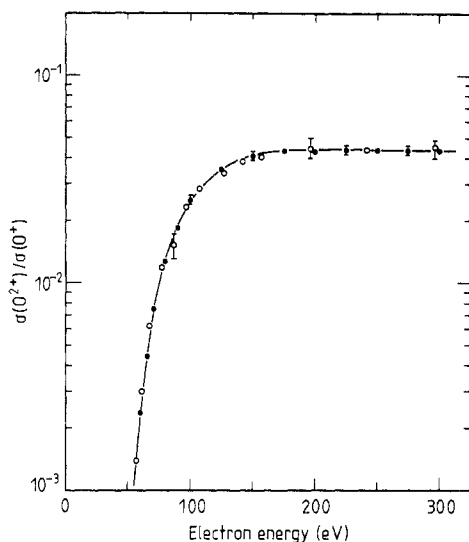

Figure 2. The ratio of the cross sections for double and single ionisation of atomic oxygen, $\sigma(O^{2+})/\sigma(O^+)$, by electron impact against energy: O, data points from Ziegler *et al* (1982); ●, present results, which have an uncertainty of ±5%.

3. Results

The ratio of the cross sections for the direct and dissociative excitation of the O I $(3s\ ^3S^\circ - 2p\ ^3P;\ \lambda\ 1304\ \text{Å})$ multiplet, σ_A/σ_D, by electron impact on atomic and molecular oxygen has been measured from 60 to 300 eV. The results of this study are presented

in table 1. The final values were obtained by averaging data from ten experimental runs. The standard deviation, which reflects the statistical quality and precision of the individual measurements, is also given in the table for each ratio value. The probable absolute error in the σ_A/σ_D ratio values includes contributions, summed in quadrature, from the following sources: the standard deviation, the uncertainty in the transmission-sensitivity ratio of the mass spectrometer, $T(O^+)/T(O_2^+)$ (approximately $\pm 3\%$) and the probable error in the literature values for the ratio of the ionisation cross sections, $\sigma(O^+)/\sigma(O_2^+)$ (approximately ± 7–11%). At 100 eV, these errors result in an estimated overall uncertainty in the σ_A/σ_D ratio of about $\pm 9\%$.

The present σ_A/σ_D values are smaller than earlier ratio results based on the cross section data of Stone and Zipf (1974) and Mumma and Zipf (1971) by a factor of 2.1. However, because of the large uncertainties in the earlier cross section data ($\pm 40\%$ and $\pm 18\%$, respectively), the two sets of σ_A/σ_D values actually agree within their quoted probable errors. The measured energy dependence of σ_A/σ_D is the same in both experiments. This agreement is illustrated in figure 3.

The more accurate σ_A/σ_D values presented in this paper do require a substantial reduction in the σ_A(1304 Å) cross section with important consequences to the aeronomy community (Zipf and Erdman 1985). Revised values for the excitation cross section of the O I ($3s\ ^3S^o$–$2p\ ^3P$; λ 1034 Å) resonance transition by electron impact on atomic oxygen have been calculated from the excitation function data of Stone and Zipf (1974), the σ_A/σ_D ratio values given in table 1 and the σ_D(1304 Å) data of Mumma and Zipf (1971) renormalised to reflect the recent H_2 dissociative excitation work of Shemansky *et al* (1985), Van Zyl *et al* (1985) and Risley (1985). These workers have obtained new values for the cross section for the dissociative excitation of Lyman alpha (λ 1215 Å) by electron impact on H_2

$$e + H_2 \rightarrow H(2p) + H + e \tag{9}$$

$$H(2p) \rightarrow H(1s) + h\nu(\lambda\ 1215\ \text{Å}) \tag{10}$$

which had been used as a calibration standard by Mumma and Zipf (1971). The new

Table 1. Ratio of the cross sections of the direct and dissociative excitation of the O I ($3s\ ^3S^o$–$2p\ ^3P$; λ 1304 Å) multiplet by electron impact on atomic and molecular oxygen.

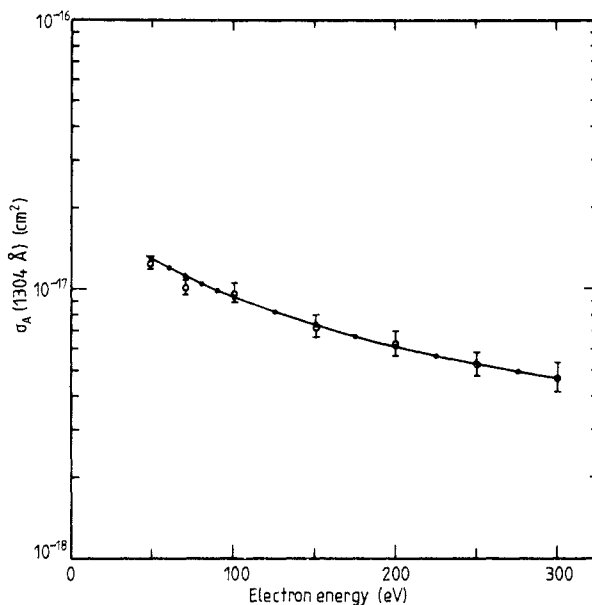| Electron energy (eV)	σ_A/σ_D	Standard deviation
60	3.75	± 0.08
70	3.52	0.04
80	3.28	0.05
90	3.11	0.08
100	3.00	0.05
125	2.93	0.03
150	2.88	0.03
175	2.86	0.03
200	2.82	0.04
225	2.78	0.03
250	2.75	0.03
275	2.71	0.04
300	2.70	0.04

Figure 3. A comparison of the energy dependence of $\sigma_A(\lambda\ 1304\ \text{Å})$ based on the present results (●) and the earlier work of Stone and Zipf (1974) (○) reduced by a factor of 2.8.
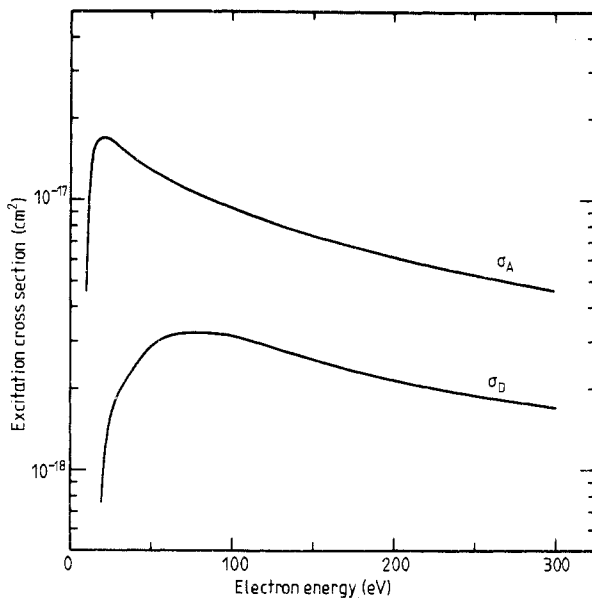

Figure 4. Revised cross sections for the excitation of the O I $(3s\ ^3S^\circ$-$2p\ ^3P;\ \lambda\ 1304\ \text{Å})$ transition by electron impact on atomic and molecular oxygen, σ_A and σ_D, respectively.

$\sigma(1215\ \text{Å})$ values $(8.18\times10^{-18}\ \text{cm}^2\pm15\%;\ \ 7.5\times10^{-18}\ \text{cm}^2\pm10\%;\ \ 7.22\times10^{-18}\ \text{cm}^2\pm$ 19%) indicate that the original results of Mumma and Zipf (1971) are too large by about 34% and that $\sigma(1304\ \text{Å})$ needs to be decreased proportionally. The revised cross section values for $\sigma_A(1304\ \text{Å})$ and $\sigma_D(1304\ \text{Å})$ are shown in figure 4 and listed

Table 2. Revised cross section values for the excitation of the O I (3s $^3S^\circ$-2p ^3P; λ 1304 Å) transition by electron impact on atomic (σ_A) and molecular (σ_D) oxygen.

Electron energy (eV)	$\sigma_A(\lambda$ 1304 Å) (10^{-17} cm^2)	$\sigma_D(\lambda$ 1304 Å) (10^{-18} cm^2)
11	0.46	—
12.5	1.03	—
15	1.56	—
20	1.69	0.78
25	1.67	1.53
30	1.56	1.90
35	1.48	2.19
40	1.40	2.36
45	1.33	2.64
50	1.27	2.88
60	1.19	3.16
70	1.12	3.19
80	1.05	3.20
90	0.994	3.20
100	0.948	3.16
125	0.835	2.85
150	0.741	2.58
175	0.665	2.33
200	0.611	2.16
225	0.563	2.02
250	0.522	1.90
275	0.491	1.81
300	0.463	1.71

in table 2. The $\sigma(1215$ Å) value of Risley (1985) (7.5×10^{-18} cm$^2 \pm 10\%$) was adopted in the renormalisation calculation. We estimate that the uncertainty in the $\sigma_D(1304$ Å) values is approximately $\pm 15\%$ and in the $\sigma_A(1304$ Å) values is approximately $\pm 18\%$.

4. Discussion

The total cross sections given in table 2 for the excitation of the O I (3s $^3S^\circ$-2p ^3P; λ 1304 Å) transition by electron impact on atomic oxygen are in good agreement in both magnitude and energy dependence with the theoretical work of Smith (1976). The best fit between theory and experiment is obtained by using a two-configuration ground-state representation with exchange to calculate the cross section for direct excitation of the 3s $^3S^\circ$ state (no cascade) $Q(^3P$-3s $^3S^\circ$) (Smith 1976, figure 2a) and a single-configuration ground-state representation with exchange for $Q(^3P$-3p ^3P) (Smith 1976, figure 5a). Cascade contributions from higher ns $^3S^\circ$ and nd $^3D^\circ$ levels must also be included. In a separate study, Kao and Zipf (1985) have found that the O I (3d $^3D^\circ$-3p ^3P; λ 1.12 μm), O I (4d $^3D^\circ$-3p ^3P, λ 7200 Å) and O I (4s $^3S^\circ$-3p ^3P; λ 1.31 μm) account for about 19% of the O I (3s $^3S^\circ$) excitation rate at 100 eV under optically thin conditions. These results are in general agreement with the cascade estimates of Smith and we find that the measured and calculated total cross section, $\sigma_A(1304$ Å), differ by less than 10% from 20 to 300 eV.

In optically thick environments, the infrared cascade transitions are enhanced considerably (as much as an order of magnitude) as the result of the entrapment of the numerous O I EUV resonance multiplets that originate from the same upper state (Julienne and Davis 1976). Under these conditions, the effective λ 1304 Å excitation cross section depends sensitively on the degree of opacity and on the nature of the electron energy distribution, and may be three times larger than the values given in table 1.

Acknowledgments

References

Brook E, Harrison M F A and Smith A C H 1978 *J. Phys. B: At. Mol. Phys.* **11** 3115
Chakrabarti S, Paresce F, Bowyer S, Kimble R and Kumar S 1983 *J. Geophys. Res.* **88** 4898
Conway R R 1983 *Planet. Space Sci.* **31** 1223
Crosswhite H M, Zipf E C and Fastie W G 1962 *J. Opt. Soc. Am.* **52** 643
Donahue T M and Fastie W G 1964 *Space Research* vol IV (Amsterdam: North-Holland) p 304
Donahue T M and Strickland D J 1970 *Planet. Space Sci.* **18** 691
Erdman P W and Zipf E C 1982 *Rev. Sci. Instrum.* **53** 225
Gentieu E P, Feldman P D, Estes R W and Christensen A B 1984 *J. Geophys. Res.* **89** 11053
Gentieu E P, Feldman P D and Meier R R 1981 *J. Geophys. Res.* **86** 3583
Gorman M R and Zipf E C 1986 *J. Chem. Phys.* to be published
Hernandez S P, Doering J P, Abreu V J and Victor G A 1983 *Planet. Space Sci.* **31** 221
Julienne P S and Davis J 1976 *J. Geophys. Res.* **81** 1397
Kao W W and Zipf E C 1985 unpublished
Mark T D 1975 *J. Chem. Phys.* **63** 3731
Meier R R 1982 *J. Geophys. Res.* **87** 6307
Meier R R, Conway R R, Anderson D E, Feldman P D, Estes R W, Gentieu E P and Christensen A B 1985
    J. Geophys. Res. **90** 6608
Meier R R, Conway R R, Feldman P D, Strickland D J and Gentieu E P 1982 *J. Geophys. Res.* **87** 2444
Meier R R and Lee J-S 1982 *Planet. Space Sci.* **30** 439
Mumma M J and Zipf E C 1971 *J. Chem. Phys.* **55** 1661
Rees M H 1975 *Planet. Space Sci.* **23** 1589
Rees M H, Emery B A, Roble R G and Stamnes K 1983. *J. Geophys. Res.* **88** 6289
Rees M H and Jones R A 1973 *Planet. Space Sci.* **21** 1213
Richards P G and Torr D G 1984 *J. Geophys. Res.* **89** 5625
Risley J 1985 Personal communication
Rountree S P 1977 *J. Phys. B: At. Mol. Phys.* **10** 2719
Shemansky D E, Ajello J M and Hall D T 1985 *Astrophys. J.* **296** 756
Smith E R 1976 *Phys. Rev.* A **13** 65
Stamnes K and Rees M H 1983 *J. Geophys. Res.* **88** 6301
Stephan K and Mark T D 1980a *Adv. Mass Spectrom.* **8A** 122
—— 1980b *J. Chem. Phys.* **73** 3763
Stone E J and Zipf E C 1974 *J. Chem. Phys.* **60** 4237
Strickland D J and Anderson D E 1983 *J. Geophys. Res.* **88** 9260
Strickland D J and Donahue T M 1970 *Planet. Space Sci.* **18** 661

Van Zyl B, Gealy M W and Neumann H 1985 *Phys. Rev.* A **31** 2922
Walton M R, Carrington T, Shepherd G G and Young R A 1984 *Planet. Space Sci.* **32** 771
Ziegler D L, Newman J H, Smith K and Stebbings R F 1982 *Planet. Space Sci.* **30** 451
Zipf E C 1985 *Planet. Space Sci.* **33** 1303
Zipf E C and Erdman P W 1985 *J. Geophys. Res.* **136** 11087
Zipf E C, McLaughlin R W and Gorman M R 1979 *Planet. Space Sci.* **27** 719
Zipf E C and Wells W C 1980 *Planet. Space Sci.* **28** 859