Excitation of the O I (^3S) and N I (^4P) Resonance States by Electron Impact on O and N†

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The absolute cross sections for the excitation of the O I (^3S) and N I (^4P) resonance states by electron impact on atomic oxygen and nitrogen have been measured over the aeronomically important energy range from threshold to 150 eV. The peak excitation cross sections for these states were found to be 1.2×10^{-16} and 6.2×10^{-16} cm^2, respectively. At low energies, the total O I (^3S) and N I (^4P) cross sections exhibited well-developed peaks near 15 and 25 eV, respectively, indicating that cascade processes probably play an important role in exciting the O I(^3S) and N I(^4P) states.

INTRODUCTION

The resonance multiplet [O I ($3s\,^3S - 2p\,^3P$)] emitted by atomic oxygen at approximatley 1304 Å is a prominent feature in the vacuum ultraviolet spectrum of the aurora, [1,2] the normal terrestial dayglow, [3,4] and the enhanced equatorial airglow[5,6]; O I resonance radiation has also been observed in the vacuum ultraviolet (VUV) spectrum of Mars. [7] A large body of data on the intensity, altitude, and geographical distribution of this emission feature in the Earth's atmosphere has now been obtained by satellite and sounding rocket experiments. Similar information[2] is also available for the resonance triplet [N I ($3s\,^4P - 2p\,^4S$)] emitted by atomic nitrogen at 1200 Å. Unfortunately, an analysis of these data has been hampered by a lack of information on the absolute magnitude and shape of the cross sections for exciting the O I (^3S) and N I (^4P) resonance states by electron impact on atomic oxygen and nitrogen. This situation has existed until now because it is difficult to produce and measure the density of these reactive species under conditions suitable for an electron excitation experiment. These technical problems have now been solved and we present here what we believe to be the first experimental measurements of cross sections for electron impact excitation of atomic nitrogen and oxygen.

EXPERIMENTAL TECHNIQUES

Figure 1 shows a block diagram of the apparatus. The experiment involved passing an electron beam through a flow of gas that had been previously dissociated by a microwave discharge, and observing the resulting resonance radiation. A 90° bend was incorporated in the flow system to eliminate background radiation from the microwave discharge. The collision chamber was constructed of aluminum and the interior walls were painted with a graphite suspension. The total pressure in the collision chamber was usually about 1×10^{-3} Torr with an atomic oxygen density of approximately 7×10^{11} atoms/cm^3. An electrostatically focussed electron gun produced a beam of nearly monochromatic electrons whose energy could be varied from 5 to 150 eV. A Helmholtz coil was mounted inside the large vacuum chamber, and aligned so as to null out the horizontal component of the Earth's magnetic field, and provide a collimating field of approximately 12 G. Checks were made to verify that any undesirable side effects due to backscattered or secondary electrons were negligble. The resonance radiation was observed at right angles to the electron beam by a 1-m normal-incidence monochromator. The photons transmitted by the monochromator were detected by an EMR 541GX solar-blind photomultiplier tube operated in a pulse-counting mode. Windowless apertures were used throughout the system and coherent summing techniques were employed to enhance the signal-to-noise ratio in the primary cross-section data.

The atom density in the collision chamber was determined by measuring the absorption of O I and N I resonance radiation from an external helium discharge as this light passed through the collision chamber. The absorption light source was excited by an rf oscillator of variable power output, and it was possible to produce an optically thin light source by varying the helium pressure and the rf power level. The mean residence time of an atom or molecule in the chamber was determined from the dimensions of the chamber, the temperature of the gas, and an estimate of the atomic wall recombination rate. The total atom densities implied by our absorption measurements indicated that the probability of destroying an atom at the walls of the collision chamber was less that 0.2; the magnitude of this coefficient was small enough to insure a uniform spatial distribution of the ambient O I and N I atoms.

RESULTS

The electron excitation functions for the O I (^3S) and N I (^4P) states were obtained first with the microwave discharge turned on. Under these conditions the excitation function included contributions
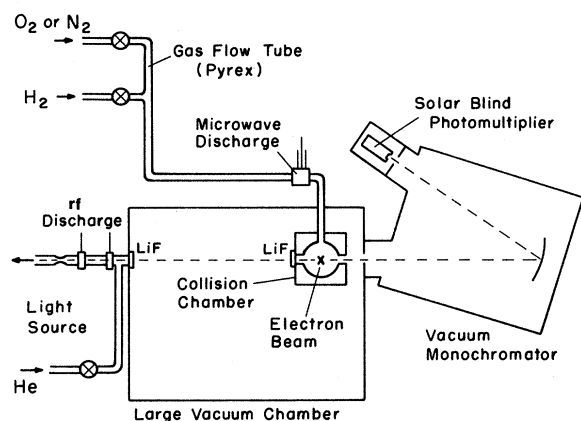
FIG. 1. Diagram of the experimental apparatus.

FIG. 3. Total cross section for the excitation of the N I (3s ⁴P) state by electron impact on atomic nitrogen.

due (i) to the dissociative excitation of ground-state N_2 and O_2 molecules present in the collision chamber, (ii) to the direct excitation of free O I and N I atoms, and possibly (iii) to the dissociative excitation of unwanted metastable molecular states. The microwave discharge was then turned off and the measurement was repeated. In this case the resulting excitation function was due entirely to the dissociative excitation of ground-state N_2 and O_2 molecules. The discharge-on and discharge-off measurements were then compared.

At electron energies below the threshold for dissociative excitation, the atomic signal was large and uncontaminated. At higher energies the situation was less favorable, since at some energies dissociative excitation contributed as much as 96% (for oxygen) to the composite signal. In this case the
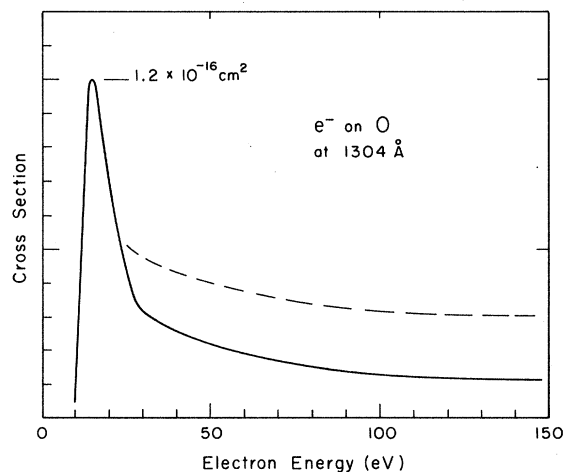
two excitation functions were multiplied by appropriate scaling factors and subtracted. The resulting difference function was assumed to be characteristic of the direct atomic excitation channel. The final result for atomic oxygen is shown in Fig. 2, and that for atomic nitrogen in Fig. 3.

The magnitude of the scaling factors used in our analysis of the primary O I cross-section data above 25 eV depended critically on an assessment of the probability that a resonance photon produced by dissociative excitation would be absorbed by ambient

FIG. 2. Total cross section for the excitation of the O I (3s ³S) state by electron impact on atomic oxygen. The dashed line represents a rejected alternative in the interpretation of the data.
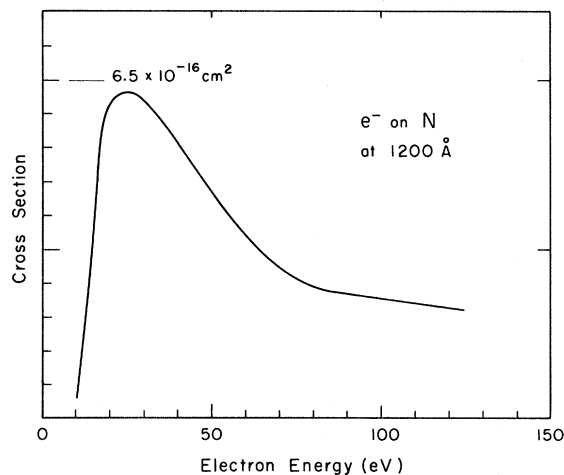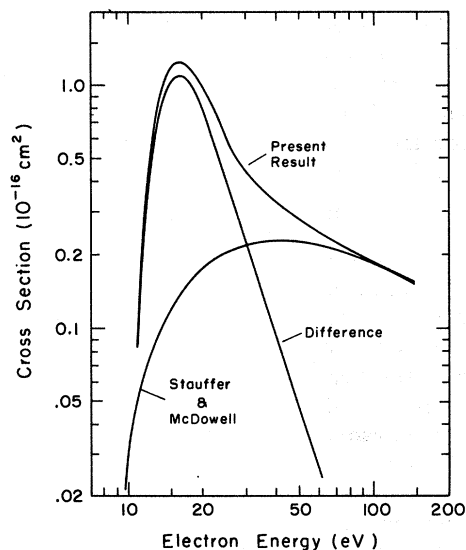

FIG. 4. The total O I (3s ³S) cross section is interpreted as the sum of a theoretical cross section for direct excitation of the ³S state (normalized to the experimental data at 150 eV) and cascade contributions from high-lying ³P states indicated by the difference curve.

and thermalized oxygen atoms present in the collision chamber when the microwave discharge was turned on. Borst and Zipf[8] have shown recently that in dissociative excitation the atomic fragments can have high velocities at least when oxygen atoms in Rydberg or metastable states are produced. If we assume that this is a general characteristic of dissociative excitation, then the radiation produced by this process will exhibit a broadened line profile and little of this radiation will be absorbed by the ambient thermal atoms. The result of this assumption is indicated by the solid line in Fig. 2. On the other hand, if we assume that the dissociated fragments have a thermal velocity distribution, the resulting cross section is indicated by the dashed line. We prefer the first assumption on the basis of the experiments of Borst and Zipf. In the nitrogen resonance-line experiment the reabsorption question made only a small difference because the primary atomic light signal was very large so that only modest corrections were required.

The shape of each excitation function shows a relatively rapid rise to a peak value, below 20 eV in oxygen, and below 40 eV in nitrogen. These shapes are not characteristic of dissociative excitation functions, indicating that any contamination of the atomic signal by excited molecular states was minimal. Examples of dissociative excitation functions in nitrogen and oxygen can be found in the work of Mumma and Zipf,[9] Lawrence,[10] Ajello,[11] and Aarts et al.[12] Furthermore, the absolute magnitude of the atomic excitation cross sections is more than one order of magnitude larger than the corresponding dissociative excitation cross section; again this makes it unlikely that the excitation of minor contaminants such as $O_2(^1\Delta_g)$ or $N_2(A^3\Sigma_u^+)$ contributes in a significant way to the measured OI and NI signals.

The sharp rise and early peak of the OI (^3S) cross section is unexpected. The shape of the excitation function is suggestive of an optically forbidden transition. In all likelihood the ^3S state is populated efficiently by cascade radiation from the $4p(^3P)$ and $3p(^3P)$ states. To illustrate the plausibility of this hypothesis we have taken a theoretical excitation

function for electron impact excitation of the ^3S state from the work of Stauffer and McDowell[13] and normalized it to our result near 140 eV. The difference between the two curves has a shape which is characteristic of an optically forbidden transition. These curves are shown in Fig. 4. If this analysis is taken as approximately correct, the absolute magnitude of the total cross section for direct excitation of the $3p(^3P)$ and $4p(^3P)$ states is about 1.2×10^{-16} cm^2 at its peak near 17 eV while the cross section for the direct excitation of the $3s(^3S)$ state is approximately 2.1×10^{-17} cm^2 at its peak near 50 eV. Cascade radiation also appears to play an important role in the excitation of the NI(^4P) resonance state below 40 eV.

The statistical errors in our laboratory results were small since coherent summing techniques were used in obtaining our primary data. The absolute magnitudes of the cross sections were determined by comparing the optical signal for the atomic excitation, taken just below the threshold for dissociative excitation, with the signal from pure dissociative excitation at 100 eV. Known absolute cross sections for dissociative excitation were used as standards. For nitrogen, these cross sections have been measured by Mumma and Zipf,[9] Ajello,[11] and Aarts et al.[12] and for oxygen by Mumma and Zipf,[14] and Lawrence.[10] The optical oscillator strengths which were used to calculate the atomic densities were taken from the work of Lin et al.,[15] Lawrence,[16] and Lawrence and Savage.[17] Most of these results are quoted with a probable error of about ± 20%. In order to make ample allowance for these probable errors, for the statistical errors in our own experiment, and for possible systematic errors in our calculation techniques, we conclude that the total probable error in the absolute magnitude of our OI(^3S) and NI(^4P) excitation cross sections is ± 40%. The relative shapes of the excitation functions are more accurate.

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Dissociative Electron Attachment in Br₂ at 296°K*

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Dissociative electron attachment frequencies have been determined for bromine in the presence of helium using microwave cavity techniques. Initial ionization was produced by a single light pulse from a hydrogen flash lamp. The value for the electron attachment coefficient k determined from the attachment frequency data is $k = 0.82 \times 10^{-12}$ cm³ sec⁻¹ ±10% at 296 °K. The electron-ion ambipolar diffusion coefficient $(D_{a+}p)$ for Br_2^+ in helium was found to be 795 cm² Torr sec⁻¹ ±10% at 296 °K. The positive-ion–negative-ion ambipolar diffusion coefficient for this ion was found to be 380 cm² Torr sec⁻¹ ±10% at 296 °K under the conditions where the only significant negative ion present was Br⁻.

I. INTRODUCTION

Although measurements of dissociative electron attachment in bromine have been carried out previously for electron energies in the eV region[1] little information is available concerning the rate constant for this process at thermal energies. Frost and McDowell,[2] however, established that electrons with an energy of approximately 0.03 eV can become attached to bromine by the reaction

$$Br_2 + e \rightarrow Br^- + Br. \tag{1}$$

The present study has been carried out to determine the magnitude of the rate constant related to process (1) for the case in which the electrons and bromine molecules are in thermal equilibrium at room temperature (296 °K).

Initial ionization was created using a hydrogen flash lamp adjacent to a microwave cavity which contained the bromine vapor. The time dependence of the electron number density within the microwave cavity was measured using a microwave resonant frequency shift technique.

The equations describing the time dependence of the electron and ion densities in the afterglow are given when electron attachment and ambipolar diffusion are the main collision processes. In addition to results pertaining to electron attachment frequencies determined as a function of Br₂ pressure, data concerning positive-ion diffusion are also presented. These latter data have been obtained in order that the contribution of diffusion loss of electrons to the total electron loss frequency could be assessed separately. An examination of both

positive and negative ions has also been carried out in the afterglow after the transition from electron–positive-ion ambipolar diffusion to positive-ion–negative-ion ambipolar diffusion has occurred. As will be discussed, it is only after this transition has occurred that significant negative-ion wall currents are observed. In the Discussion (Sec. V) a comparison is made between the results for the dissociative attachment coefficient obtained in the present study and the results of Bailey *et al.*,[1] which were obtained at higher electron energies.

II. EXPERIMENTAL APPARATUS

The apparatus used for the current study has been previously described.[3,4] Included are a microwave cavity which acts as the plasma container, and a hydrogen flash lamp adjacent to the cavity which produces the initial ionization of the bromine within the cavity. Microwave and associated equipment used in conjunction with the cavity allows the determination of the time dependence of the electron number density within the cavity after a single photoionization pulse. In addition to the measurements of the time dependence of the electron density, a quadrupole mass filter has been used to obtain the time dependence of the ion wall currents. In the present experiment the ions pass from the cavity into the quadrupole mass filter through an orifice having a 0.0076-cm diam which was drilled in a 0.0025-cm-thick nickel foil mounted between the cavity and quadrupole chamber. Collection of the ions is assisted by means of a grid located 0.14 cm from the orifice between the orifice and the quadrupole mass-filter assembly.