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Abstract

The absolute cross sections for the excitation of the OI(^3S) and NI(^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 $1.2 \times 10^{-16} cm^2$ and $6.2 \times 10^{-16} cm^2$ respectively. At low energies the total OI(^3S) and NI(^4P) cross sections exhibited well-developed peaks near 15 eV and 25 eV respectively indicating that cascade processes play an important role in exciting the OI(^3S) and NI(^4P) states.

INTRODUCTION

The resonance multiplet [OI($3s^3S$ - $2p^3P$)] emitted by atomic oxygen at approximately 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] OI resonance radiation has also been observed in the 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 [NI($3s^4P$ - $2p^4S$)] 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 OI(^3S) and NI(^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 degree 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 electron volts. 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 gauss. Checks were made to verify that any undesirable side effects due to backscattered or secondary electrons were negligible. The resonance radiation was observed at right angles to the electron beam by a one-meter 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 OI and NI 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 OI and NI atoms.

Results

The electron excitation functions for the OI(^3S) and NI(^4P) states were obtained first with the microwave discharge turned on. Under these conditions the excitation function included contribution due (1) to the dissociative excitation of ground-state N_2 and O_2 molecules present in the collision chamber, (2) to the direct excitation of free OI and NI atoms, and possibly (3) 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 Figure 2, and that for atomic nitrogen in Figure 3.

The magnitude of the scaling factors used in our analysis of the primary OI 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 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 Figure 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 re-absorption 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(^{3}P) and 3p(^{3}P) states. To illustrate the plausibility of this hypothesis we have taken a theoretical excitation function for electron impact excitation of the ^{3}S 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 Figure 4. If this analysis is taken as approximately correct, the absolute magnitude of the total cross section for direct excitation of the 3p(^{3}P) and 4p(^{3}P) states is about 1.2 x 10^{-16} cm^2 at its peak near 17 eV while the cross section for the direct excitation of the 3s(^{3}S) state is approximately 2.1 x 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(^{4}P) 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(^{3}S) and NI(^{4}P) excitation cross sections is $\pm$ 40%. The relative shapes of the excitation functions are more accurate.

Acknowledgement

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References

1. C. A. Barth, Ann. Geophys. 24, 167 (1968).
2. H. M. Peek, J. Geophys. Res. 75, 6209 (1970).
3. W. G. Fastie, H. M. Crosswhite, and D. F. Heath, J. Geophys. Res. 69, 4129 (1964).
4. R. R. Meier, J. Geophys. Res. 75, 6218 (1970).
5. G. T. Hicks and T. A. Chubb, J. Geophys. Res. 75, 28 (1970).
6. C. A. Barth and S. Schaffner, J. Geophys. Res. 75, 4299 (1970).
7. C. A. Barth, W. G. Fastie, C. W. Hord, J. B. Pearce, K. K. Kelly, A. I. Stewart, G. E. Thomas, G. P. Anderson and O. F. Raper, Science 165, 1004, 1969.
8. W. L. Borst and E. C. Zipf, Bull. Am. Phys. Soc. 16, 205 (1971); also Phys. Rev. (1971), to be published.
9. M. J. Mumma and E. C. Zipf, Bull. Am. Phys. Soc. 15, 422 (1970); also J. Chem. Phys., to be published (1971).
10. G. M. Lawrence, Phys. Rev. A 2, 397 (1970).
11. J. M. Ajello, J. Chem. Phys. 53, 1156 (1970).
12. J. F. M. Aarts, F. J. de Heer, and L. Vriens, Proc. VIth ICPEAC 1969, MIT Press, Cambridge, Mass. 02142, p. 423.
13. A. D. Stauffer and M. R. C. McDowell, Proc. Phys. Soc. 89, 289 (1966).
14. M. J. Mumma and E. C. Zipf, J. Chem. Phys., submitted for publication (1971).
15. C. L. Lin, D. A. Parkes, and F. Kaufman, J. Chem. Phys., 53, 3896 (1970).
16. G. M. Lawrence, Can. J. Chem. 47, 1856 (1969).
17. G. M. Lawrence and B. D. Savage, Phys. Rev. 141, 67 (1966).

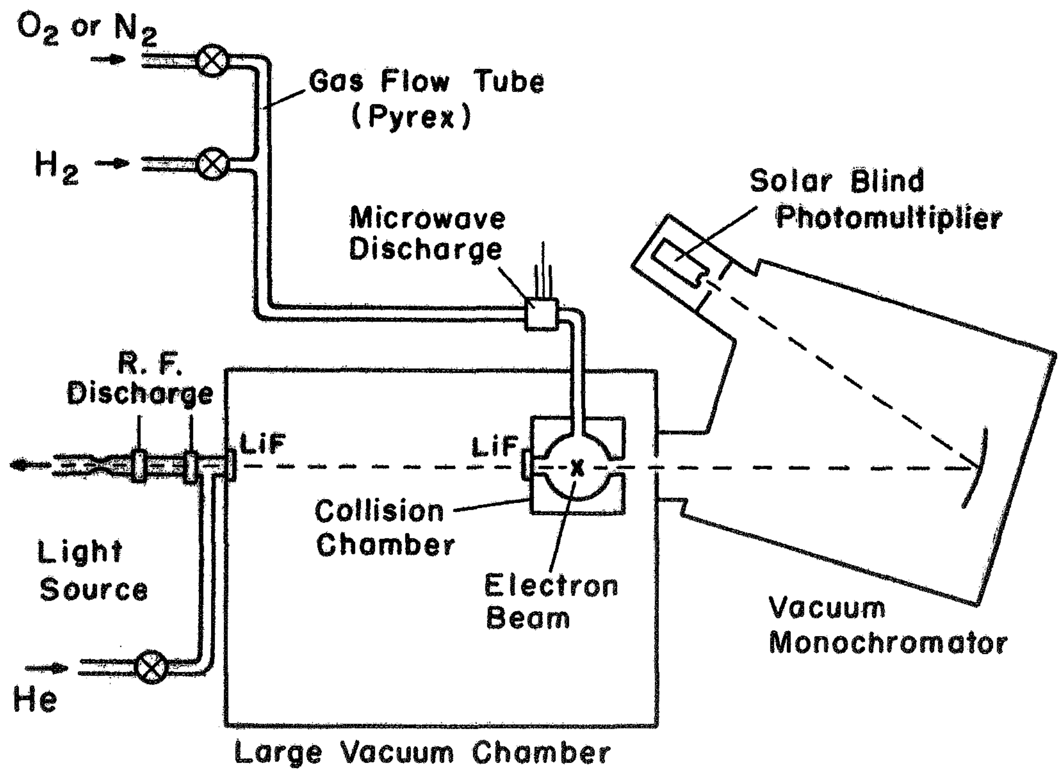
Figure Captions

Figure 1 Diagram of the experimental apparatus.

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

Figure 3 Total cross section for the excitation of the NI($3s^4P$) state by electron impact on atomic nitrogen.

Figure 4 The total OI($3s^3S$) 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.



O2 or N2
Gas Flow Tube
(Pyrex)
H2
Solar Blind
Photomultiplier
Microwave
Discharge
R. F.
Discharge
LiF
LiF
Collision
Chamber
Light
Source
Electron
Beam
Vacuum
Monochromator
He
Large Vacuum Chamber

Figure 1

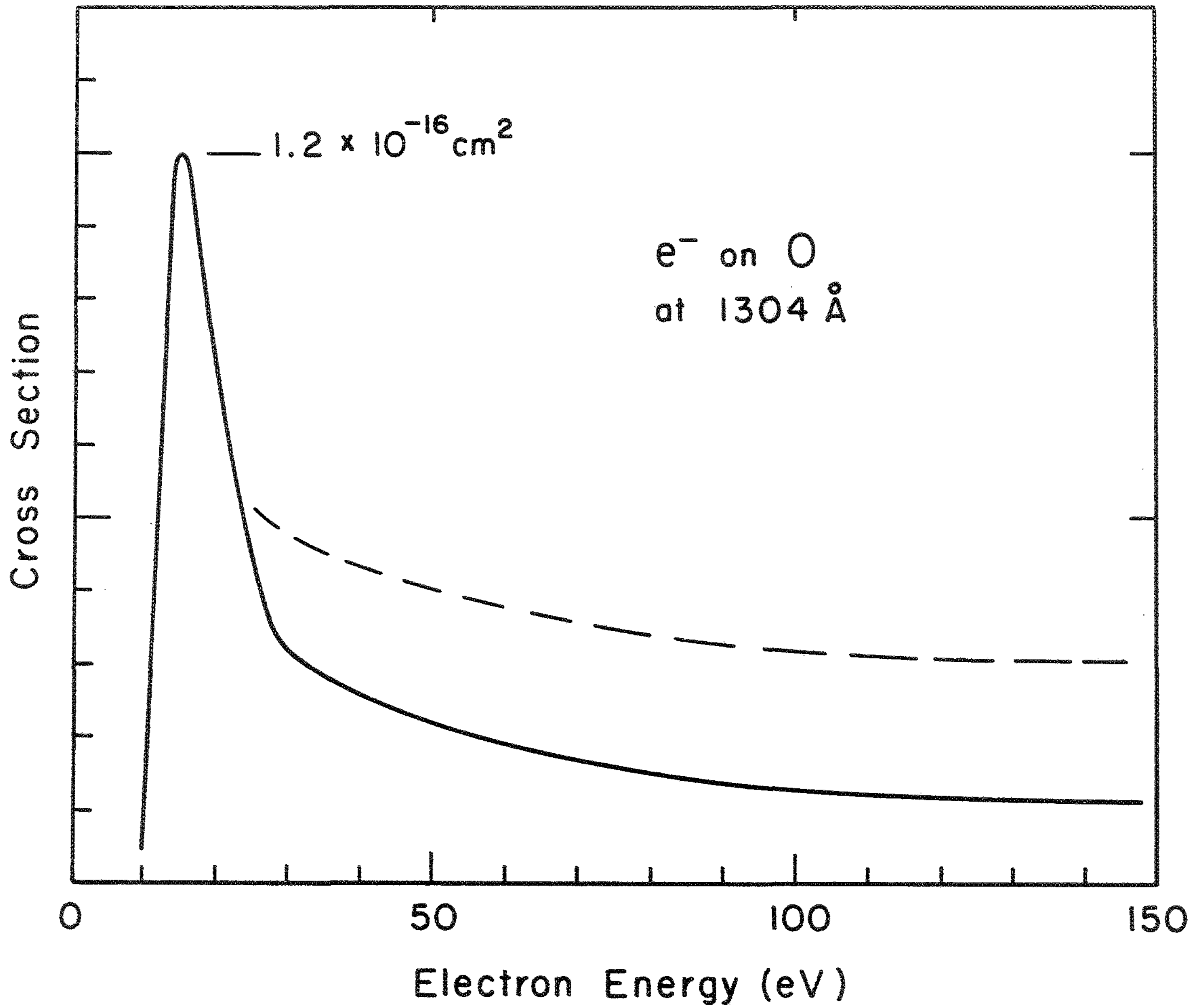

1.2 x 10⁻¹⁶ cm²
e⁻ on O
at 1304 Å
Cross Section
0
50
100
150
Electron Energy (eV)

Figure 2

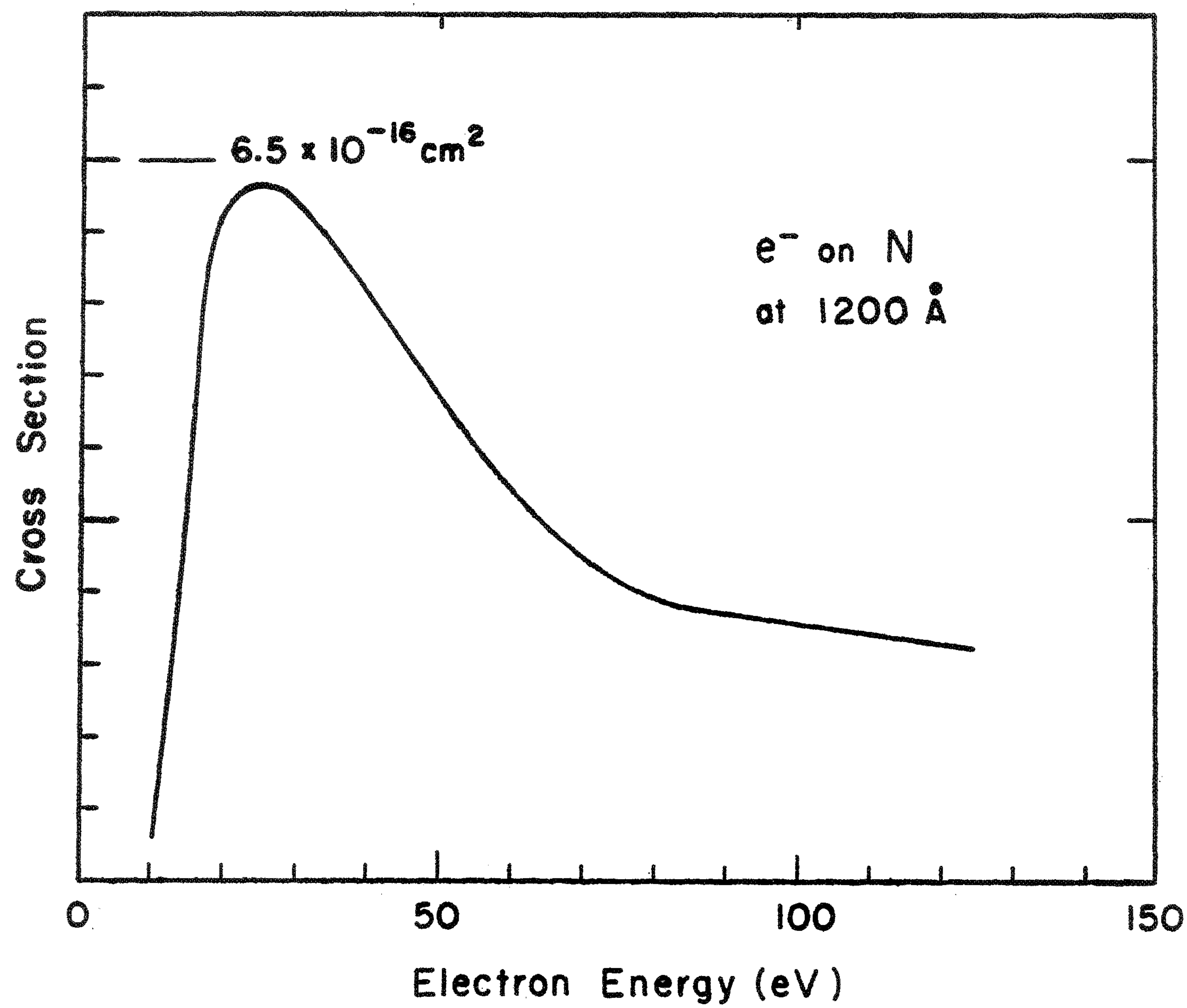

6.5 x 10^-16 cm^2
e^- on N
at 1200 Å
Cross Section
0
50
100
150
Electron Energy (eV)

Figure 3

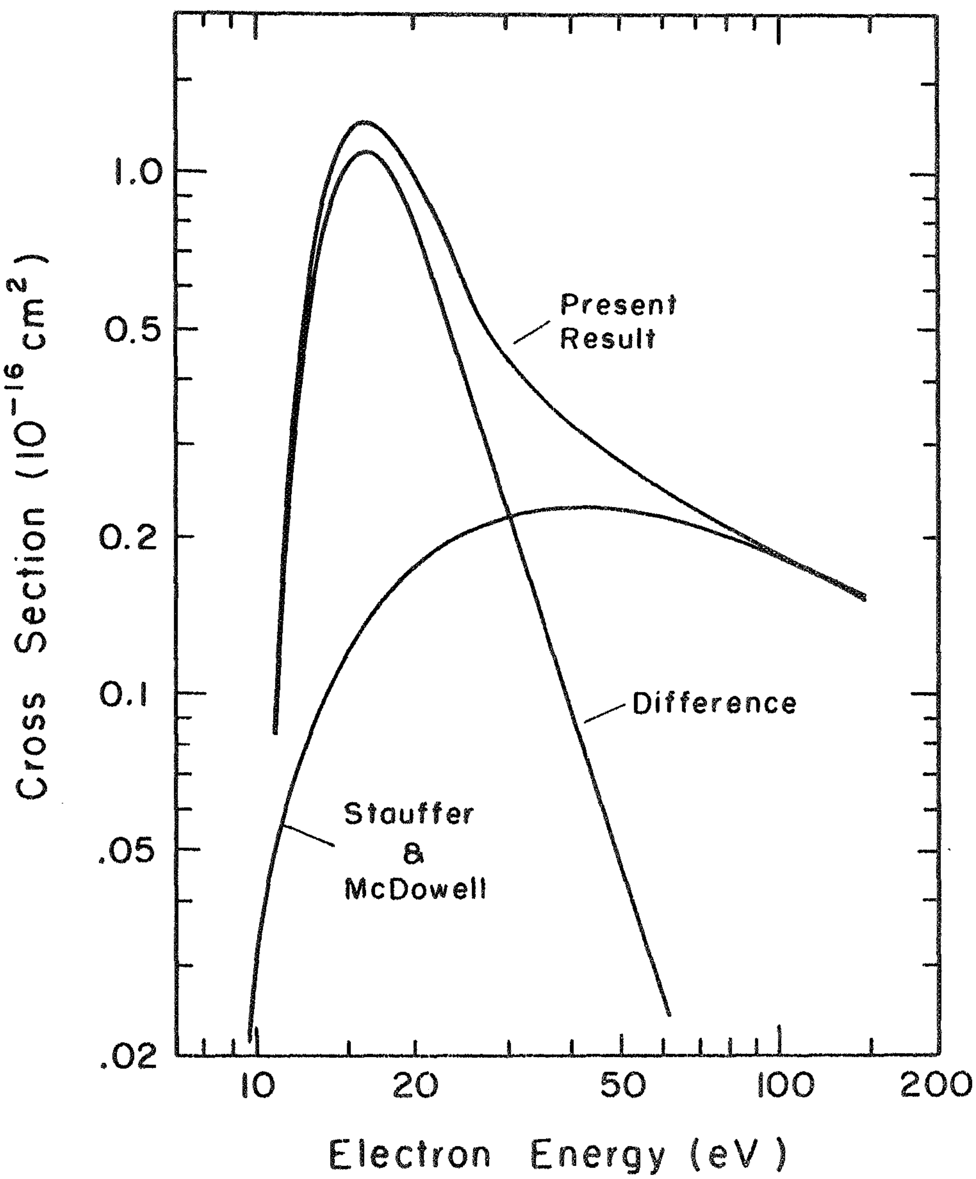

Cross Section (10^{-16} cm^2)
1.0
0.5
0.2
0.1
.05
.02
10
20
50
100
200
Electron Energy (eV)
Present Result
Difference
Stauffer & McDowell

Figure 4

The Space Research Coordination Center, established in May, 1963, has the following functions: (1) it administers predoctoral and postdoctoral fellowships in space-related science and engineering programs; (2) it makes available, on application and after review, allocations to assist new faculty members in the Division of the Natural Sciences and the School of Engineering to initiate research programs or to permit established faculty members to do preliminary; work on research ideas of a novel character; (3) in the Division of the Natural Sciences it makes an annual allocation of funds to the interdisciplinary Laboratory for Atmospheric and Space Sciences; (4) in the School of Engineering it makes a similar allocation of funds to the Department of Metallurgical and Materials Engineering and to the program in Engineering Systems Management of the Department of Industrial Engineering; and (5) in concert with the University's Knowledge Availability Systems Center, it seeks to assist in the orderly transfer of new space-generated knowledge in industrial application. The Center also issues periodic reports of space-oriented research and a comprehensive annual report.

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