Low-Energy Electron Scattering from Atomic Oxygen*

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The total cross section for the scattering of electrons by atomic oxygen has been measured as a function of electron energy from 2.3 to 11.6 ev. The number of electrons scattered from a region defined by the intersection of an electron beam and a modulated molecular oxygen beam was compared with the number scattered when the oxygen beam was partially dissociated. A radio-frequency discharge dissociated about 30% of the molecules. The degree of dissociation was measured with a mass spectrometer. From the data, the ratios of atomic to molecular scattering cross sections were obtained. The absolute atomic values were calculated by multiplying these ratios by the molecular oxygen cross sections obtained by Brüche. The result is a virtually constant cross section of $(6.2\pm0.5)\pi a_0^2$ in the entire energy range studied. This result is compared with five theoretical estimates.

I. INTRODUCTION

INTEREST in the properties of high-temperature air has produced several theoretical calculations for the total scattering cross section of electrons by atomic oxygen. Recent estimates of its magnitude have yielded divergent results.[1–4]

Electron-neutral scattering cross sections are available for all stable atmospheric constituents.[5] The recent development of the modulated molecular beam technique has made it possible to obtain electron collision cross sections for such unstable species as atomic oxygen.

The ratios of cross sections of atomic to molecular oxygen are obtained from 2.3 ev to the threshold of ionization. The absolute atomic values are calculated from these ratios and the molecular oxygen results obtained by Brüche.[6]

II. EXPERIMENTAL

A. General Description

The measurements of the atomic oxygen cross sections were performed with a modulated molecular beam apparatus. This general experimental approach has been employed in previous investigations of labile atomic species.[7–9]

The basic measurement consisted of comparing the number of electrons scattered from a region defined by the intersection of an electron beam and a molecular oxygen beam, with the number scattered when the oxygen beam was partially dissociated.

A schematic arrangement of the apparatus is presented in Fig. 1. Not shown is the vacuum envelope, made from mild steel (cadmium plated) to minimize stray fields. The partially dissociated oxygen beam is produced in a discharge tube located in the first of three vacuum chambers. The beam passes through a bulkhead slit into an intermediate chamber whose primary purpose is vacuum isolation from the source. Here, also, any charged particles are removed by a set of parallel condenser plates. As the beam emerges into the experimental chamber, it is chopped by a slotted rotating wheel at 101.8 cps, and it is further collimated by a slit just prior to the electron gun mount. It may be interrupted by a beam shutter. The oxygen beam proceeds through the electron gun, where it intersects the electron beam and scatters electrons at the chopping frequency. The attenuation of the electron beam, due to scattering by the neutral beam, is measured as an ac signal. Finally the oxygen beam enters a mass spectrometer which may be employed to determine the degree of dissociation.

B. Atom Source

The source of atomic oxygen was an rf discharge. The oscillator normally operated at a frequency of 15 Mc/sec and an input of about 30 w. The discharge tube was 25-mm diam Pyrex about 150 mm long with a 1.4-mm diam beam exit hole. The oxygen (Liquid Carbonic Medical, 99.7% pure) was mixed with 2 to 3% H_2 to promote dissociation.[10] The discharge, characterized by a reddish pink glow, was operated at about 1.5 mm Hg pressure. Typically, 25 to 35% of the molecules were dissociated.

It was necessary to investigate the temperature of the discharge to ensure that differences between the scattering signal with the discharge on and off were due to atoms rather than velocity changes in beam particles. This was accomplished by adding 1% krypton to the discharge mixture and monitoring its mass peak with the spectrometer. It is unlikely that the Kr changes the discharge characteristics.[10] No change in the magnitude of the Kr mass peak was observed between discharge

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[3] A. Temkin, Phys. Rev. **107**, 1004 (1957).

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[6] E. Brüche, Ann. Physik **83**, 1065 (1927).

[7] R. L. F. Boyd and G. W. Green, Proc. Phys. Soc. (London) **71**, 351 (1958).

[8] B. Bederson, H. Malamud, and J. Hammer, Bull. Am. Phys. Soc. **2**, 172 (1957).

[9] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958). The first of a series of such investigations.

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on and off. A change as small as $\frac{1}{2}\%$ (about 3°C) would have been seen. This indicated that velocity changes could be neglected.

It is unlikely that a significant fraction of electronically or vibrationally excited species reached the interaction region. A review of evidence for this conclusion has been presented by Linnet and Marsden.[11] Subsequently, Fite and Brackmann,[12] who used a partially dissociated oxygen beam similar to that of our experiment, were unable to find excited species. A concentration higher than 3% would have been detected.

C. Electron Gun

The source of low-energy electrons (Fig. 2) was constructed from cylindrical stainless steel electron gun parts. All components except the filament were at ground potential. The filament was placed at the appropriate accelerating potential. The gun was surrounded by a stainless steel oven which allowed it to be outgassed at 250°C.

The relative cross section at each voltage was obtained from a ratio of electron currents which were measured at the collector. This ratio is the ac scattering signal to direct current. In principle, the two intersecting beams should be the same size. The electron beam, by definition, consists only of electrons reaching the collector. If any part of the electron beam fails to pass through the neutral beam, the currents will not be appropriate for the calculation of this ratio. If the neutral beam is too large, then some electrons may be deflected into the collector, decreasing the angular resolution. Alignment difficulties necessitated the use of a molecular beam height larger than the electron beam diameter. Variation of the neutral beam height from 1.8 to 2.4 times greater than the electron beam produced no observable change in the relative cross section obtained.

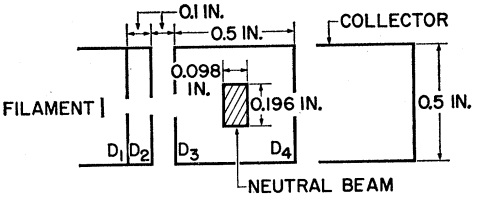

FIG. 2. Diagram of low-energy electron gun. The ac attenuation of the electron beam is measured at the collector. The electron beam holes D_1, D_2, D_3, and D_4 are 0.08, 0.08, 0.100, and 0.120 in. in diameter, respectively.

Calculation of the angular resolution of the gun, by using a method similar to that of Kusch,[13] yielded a value of about 25°. This angle is defined as the scattering angle for which the efficiency of detection of scattering is 50%. Although the effect of the nondetectable scattering upon the total atomic cross section must await angular distribution measurements, the present method of obtaining the cross section by measuring a ratio of cross sections reduces the error.

The filament was thoriated tungsten. Since the limit of accuracy is determined by the ac signal-to-noise ratio, and noise from the filament was far greater than from any other source, considerable attention was given to filament selection.

The energy of the electrons, as well as the energy spread, was determined by applying retarding potentials (E) to the collector and observing the collector currents (I). The energy spread (defined as the width at half-maximum of dI/dE vs E) was 0.45 v at 11 v and 0.33 v at 2.3 v.

D. Mass Spectrometer

The mass spectrometer used to monitor the degree of dissociation was a 60-deg sector instrument with 10-cm radius of curvature. Mass analysis was performed at a constant ion energy (about 275 ev) by varying the magnet current. The magnet, inside the vacuum, was surrounded by a magnetic shield of soft iron to minimize the effect of stray fields upon the low-energy electrons. This shield also functioned as a vacuum-tight container which prevented outgassing of the magnet coils.

The ion source was a Bayard-Alpert inverted type. Three cylindrical electrodes focused the ions into the magnetic field. A collimator in front of the ionizer permitted the neutral beam to pass cleanly through it, which made surface recombination negligible.

Since the temperature of the gas remained constant (within 3°C) when the discharge was struck, the degree of dissociation was measured primarily by the decrease in the mass 32 peak. No mass peaks other than 32, 16, 2, and 1 (the latter two from the H_2 impurity) were seen.

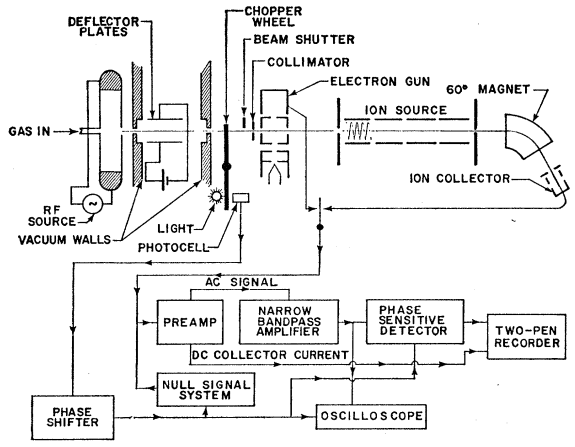

FIG. 1. Experimental arrangement for the scattering of electrons by atomic oxygen. The scattering occurs in the electron gun. The distance from the rf source to the electron gun is 21 cm.

[11] J. W. Linnet and D. G. H. Marsden, Proc. Roy Soc. (London) **A234**, 489 (1956).

[12] W. L. Fite and R. T. Brackmann, Phys. Rev. **113**, 815 (1959).

[13] P. Kusch, "Notes on resolution in scattering measurements," Physics Department, Columbia University (private communication).

The rise of the mass 16 peak was also measured at intervals. The results were consistent with ionization cross sections measured by Fite and Brackmann,[12] although precise comparison was precluded by the electron energy spread of the ionizer. The spectrometer was further used in a search for degassed water vapor. This test was conducted with an argon discharge and negative results were obtained.

E. Circuitry

The present circuitry consisted of conventional phase-sensitive, narrow-bandpass amplification.[9] Two modifications are noted.

A preamplifier with a tuned *L-C* circuit was used. The circuit had an ac input impedance of approximately 10^7 ohms at the chopping frequency, but only 3000 ohms dc resistance. Since the collected direct current was typically 1–3 μa, it was not necessary to compensate for a dc voltage drop across an input resistor to maintain the collector at ground potential. A secondary advantage was the ability to conduct the signal through long shielded cables and to use its capacitance as part of the tuned circuit, which obviated the need to place the preamplifier inside the vacuum.

The scattering signal at the collector was not uniformly amplified at all energies. This was attributed to an energy-dependent ac impedance (comparable in magnitude to the preamplifier input impedance) characteristic of the gun. This led to the introduction of a null system. The circuit employed a fraction of the ac current from the photocell, shifted its phase, and converted it to an adjustable, accurately known, constant current source. This provided a calibrated source of alternating current 180° out of phase with the scattering signal, which could be applied to just cancel the scattering signal. This eliminated the need for linearity in the amplification system.

Although the sensitivity of the electronics was about 10^{-14} amp, electron gun noise limited detection to about 10^{-13} amp.

F. Apparatus Tests

The need for the greatest possible beam intensity led to source pressures greater than those satisfying effusive flow. This leads to two possible sources of error. First, a gas cloud probably forms near the source which might preferentially scatter either atoms or molecules. Second, the partially hydrodynamic flow may lead to atomic velocities that differ from the expected $\sqrt{2}$ factor of the molecular velocities. The combined effect of these two sources of error was measured by an ionization experiment. The electron impact ionizer (Fig. 3) was designed to collect all ions, including those energetic ones formed in the dissociative ionization of molecular oxygen. The total ion collection was verified experimentally by the constancy of the ion signal despite large variations of extraction and focusing conditions. The electron energy

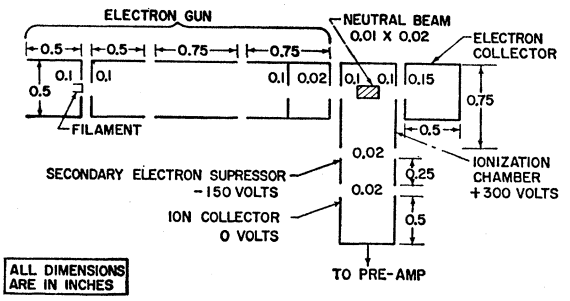

FIG. 3. Arrangement of ionization experiment. The molecular beam goes into the paper. All ions formed in the interaction region, including dissociatively ionized oxygen, are collected, Cylindrical components and circular electron beam apertures are used.

was 200 ev. The ion signal was measured with the discharge on (J') and off (J). The fraction of molecules dissociated (D) was separately measured with the spectrometer.

If velocity and scattering effects did not exist, these data would give the following ratio of the total ionization cross section of atomic oxygen (Q_a) to that of molecular oxygen (Q_m):

$$\frac{Q_a}{Q_m}=\frac{(J'/J)-1+D}{D\sqrt{2}}.$$

Q_m has been measured by Tate and Smith.[14] The deviation of our ionization result from the correct value yielded a correction factor which was applied to the scattering results.

The correct value of Q_a was obtained by replacing the exit hole of the discharge tube with a 0.02-mm slit and repeating the measurements. The source pressure was about 1 mm Hg (the oxygen mean free path is about 0.04 mm), thereby satisfying Knudsen conditions. The degree of dissociation was measured as before. The measurement of Q_a at 200 ev yielded 1.42 πa_0^2. Neglecting multiple ionization of atomic oxygen, we may compare this value with results for single ionization. It is in good agreement with an experimental value of Fite and Brackmann[12] ($1.46\pi a_0^2$) and with a theoretical value of Seaton[15] ($1.61\pi a_0^2$) but in disagreement with the more recent work ($2.42\pi a_0^2$) of Boksenberg.[16] The apparatus was also tested by the use of hydrogen. We obtained good agreement with a previous measurement[9] of the ionization cross section of atomic hydrogen. These determinations will be discussed in a subsequent paper. The correction applied to the scattering cross sections of atomic oxygen is about minus 20%.

Several sources of erroneous ac scattering signals should be considered. These are 101.8 cps modulation of (a) filament emission, (b) background gas pressure, and (c) photons from the discharge.

[14] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).
[15] M. J. Seaton, Phys. Rev. **113**, 814 (1959).
[16] A. Boksenberg, Physics Department, University College, London (private communication).

A filament modulation signal, unless it had the same phase and energy dependence as a true scattering signal, would have changed the shape of a known energy vs cross-section curve. Such an alteration was initially observed in experiments with molecular oxygen, although the inert gases helium and argon gave the correct energy dependence.[5] The filament modulation was manifested directly in a change of phase from the true scattering signal. More precise alignment of the molecular beam with the gun, which eliminated the possibility of collisions of neutral beam particles with gun surfaces and consequent scattering into the filament, overcame this difficulty. The undesired phase shift vanished and the molecular oxygen cross-section data then agreed with the curve obtained by Brüche.[6] The inert gases still showed an energy dependence consistent with previous results. The cross-section curve of molecular oxygen[6] is shown in Fig. 4 as well as experimental points obtained with the present apparatus. Since only the energy variation of the cross section was measured and not its absolute magnitude, the curve was normalized to Brüche's results at 11.5 ev.

The molecular cross sections obtained with the apparatus could have resulted from sufficiently intense pressure modulation of the background gas, largely composed of beam molecules. For an atomic oxygen beam, recombination would lead to incorrect cross sections. Three independent tests demonstrated that background modulation was not important for oxygen. First, the beam shutter was closed. This presumably blocked the beam without seriously altering the background modulation. No ac signal was observed. Second, 35% of the wall area of the oven was removed and replaced by mesh (of 95% transmission). This would be expected to alter significantly the pressure modulation inside the oven caused by beam particles deflected there by oven and gun surfaces. No change in the ac signal was observed. Finally in the most direct test, a small ionizer was placed in several strategic positions in the apparatus, both in the beam and out. The modulated ion current was 10^3 to 10^4 times as high in the beam as in the background gas, demonstrating that background modulation was negligible.

Because of the low intermediate chamber pressure, chopped background gas, coinciding spatially with the beam, is negligible compared to the beam.

Tests for possible effects from modulated photons, originating in the discharge, showed negative results. No ac signal was observed in a comparison of beam shutters of thin collodion film (transparent to photons) and the normal copper sheet. Finally, with the electron beam off, no ac signal was observed at the collector.

G. Experimental Procedure

The electron gun was normally degassed about two hours at 250°C. The temperature was then lowered to 200°C for normal operation. Typical pressures in the experimental chamber were 6×10^{-7} and 2×10^{-7} mm Hg with gas flow on and off, respectively.

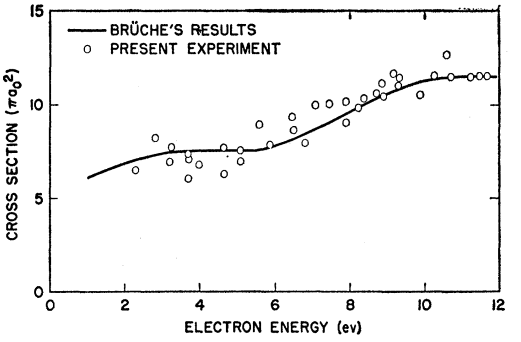

FIG. 4. Total collision cross sections for electrons scattered by molecular oxygen. The spread of data is greater than for the cross sections of atomic oxygen, since the latter are obtained from measurements relative to molecular oxygen at a given energy.

The filament was placed at the appropriate voltage and was heated by direct current to a temperature such that, at the highest accelerating voltage used, the emission was space-charge limited. This procedure minimized the effect of random emission changes.

With the beam flag closed, the recorder reading of ac output was noted. The beam flag was opened then and the resulting ac scattering signal was balanced by means of the null system. The dc collector current was recorded simultaneously. The discharge then was turned on and a new null system current was recorded, as well as the direct current. After these two scattering signals were obtained, the degree of dissociation was measured with the mass spectrometer. Occasionally, the gas into the discharge tube was turned off and the difference in ac signals at the gun collector with flag open and closed was noted. This difference was always zero.

An integrating circuit in the electronics of 10-sec time constant was used to feed the pen recorder. Observations of signals with the recorder were made normally for a period of 5 to 10 min.

The gas was admitted to the discharge tube through a needle valve from a reservoir held somewhat above an atmosphere of pressure. Since the pressure in the discharge was about 1.5 mm Hg, the mass flow remained constant regardless of discharge conditions. Under these circumstances, the ratio of the atomic to the molecular cross section (Q_A/Q_M) is given[17] by

$$\frac{Q_A}{Q_M}=\frac{(S'/S)-1+D}{D\sqrt{2}},$$

where S' and S are defined as the scattered alternating current per unit dc electron beam current with the discharge on and off, respectively, and D is the fraction of molecules dissociated.

[17] R. T. Brackmann, W. L. Fite, and R. H. Neynaber, Phys. Rev. **112**, 1157 (1958).

III. DISCUSSION OF RESULTS

A partial solution of the electron-atomic oxygen scattering problem was obtained by Bates and Massey[18] who considered only s-wave scattering. They employed Hartree-Fock functions and a variable parameter to account for the effect of polarization of the orbitals upon the scattering. Seaton[19] has calculated a p-wave contribution.

Robinson,[1] who did not include exchange or polarization in his calculations, obtained both s- and p-wave contributions. Hammerling, Shine, and Kivel[2] obtained only an s-wave; polarization and exchange corrections were estimated.

Temkin[3] also computed s-wave scattering. In satisfying the Pauli principle, the exchange polarization is treated more elaborately than by the other theorists. It is not a parameter as in the Bates and Massey treatment. Temkin's method sacrifices some polarizability terms which are classically included by Bates and Massey. Temkin suggests that the s-wave cross section should be bracketed by his results and those of Bates and Massey.

Klein and Brueckner[4] have published results including s- and p-wave caclulations. They determine the polarization (and, implicitly, exchange) parameters by utilizing experimental results on the binding energy of O^-.

The present experimental results consisted of determinations spread over the entire energy range from 2.3 to 11.6 ev. Although the measurements at low energy were inherently less accurate, the spread of points there was not significantly greater than that at the higher energies. We have obtained a least squares fit for our data with the result that the cross section is almost constant at $(6.2\pm0.5)\pi a_0^2$ over the entire energy range studied. The quoted error gives a band of values about the curve in which the half the 64 experimental points lie.

Our results as well as the theoretical estimates, are shown in Fig. 5. Also shown is a point (near 0.5 ev) obtained by a shock tube technique.[20] For purposes of comparison, p-wave cross sections have been added to the s waves of Bates and Massey; Temkin; and Hammerling, Shine, and Kivel. The p-wave results of Seaton and Klein and Brueckner are very similar (surprisingly so, in view of the different computational methods). The latter are used here because of the larger energy range computed.

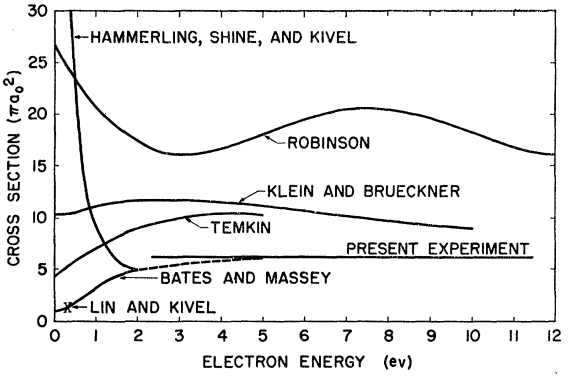

FIG. 5. Total collision cross sections for electrons scattered by atomic oxygen. All theoretical curves, except Robinson's, have the p-wave contribution of Klein and Brueckner added to the original s-wave calculation. Robinson calculates his own p-wave contribution.

The Bates and Massey s-wave result was obtained from Seaton.[19] It was calculated to 2 ev; the dashed line is an extrapolation.

Our results are bracketed by the Bates and Massey and Temkin curves over the range calculated. This is in accord with Temkin's predictions.

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[18] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).
[19] M. J. Seaton, Trans. Roy. Soc. (London) **A245**, 469 (1953).
[20] S. C. Lin and B. Kivel, Phys. Rev. **114**, 1026 (1959).