> 10, where E_e here can stand either for the initial energy of the photon or of the impact electron. Bombardment with ions, however, produces simultaneous ionization in the inner and outer shells that is entirely in variance with photoionization and electron impact.[12]

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Excitation of O_2^+ First Negative Bands by Electron Impact on O_2 †

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Absolute cross sections for the electron-impact excitation of the O_2^+ first negative bands were measured from threshold to 400 eV and extrapolated to 1000 eV by means of a Bethe-Oppenheimer relationship. The peak cross sections for the $(n+1, n)$ and $(n+2, n)$ sequences were found to be 5.30×10^{-18} cm$^2 \pm 10\%$ and 2.10×10^{-18} cm$^2 \pm 10\%$ at 100 eV, respectively. The cross sections for the (0, 0) and (1, 0) bands had a maximum value of 2.14×10^{-18} cm$^2 \pm 15\%$ and 4.33×10^{-18} cm$^2 \pm 15\%$, respectively. The ratio of the total ionization cross section of O_2 to the excitation cross sections of the first negative bands was nearly constant over the energy range 30–1000 eV; it had an average value of 64 for the (1, 0) band. The lifetime of the $\nu' = 1$ level of the $b^4\Sigma_g^-$ state was found to be 1.19 μsec $\pm 5\%$.

I. INTRODUCTION

The first negative bands of O_2^+ appear prominently in the visible spectrum of an aurora,[1–3] where this system is excited principally by electron impact. So far few laboratory studies have been performed on the excitation of the first negative system in the single-collision domain.[4–7] Absolute excitation cross sections can be used together with rocket measurements to determine the primary O_2^+ ionization rate and the total electron flux in auroras.[8,9] We have therefore attempted to measure accurately (10–15%) the absolute cross sections for the most prominent first negative bands. Since most secondary electrons in an aurora have low energies, we have worked in the energy range from threshold to 1000 eV. The existing studies of the first negative system show large discrepancies in the shape and absolute magnitude of the cross sections (by as much as an order of magnitude). These discrepancies are probably due to problems with the complex band structures, which complicate the cross-section evaluation; calibration errors and nonlinear effects due to the type of electron gun used in some of the experiments may also have contributed.

The techniques used in this experiment have been described in detail elsewhere.[10] Both the optical and pressure calibrations were obtained with an absolute accuracy of ±5%, thereby eliminating any need for normalization to other known cross sections. By using an electrostatically focused electron gun and low gas densities, we have avoided any complications due to secondary nonlinear effects.

The excitation cross sections for the (n, n), $(n+1, n)$, and $(n+2, n)$ sequences were measured directly. The cross section for the (0, 0) band was obtained from the (n, n) sequence data and the measured band shape in a straightforward way. The band is relatively free of blending so that there was no need to use Franck-Condon factors in the cross-section evaluation. The opposite is true for the important (2, 0) band, which is strongly blended with several other bands. The (2, 0) cross section was obtained from the $(n+2, n)$ sequence data with the aid of calculated Franck-Condon factors. The cross section for the prominent (1, 0) band was obtained in two ways from the cross section for the $(n+1, n)$ sequence. In the first method, the amount of blending from the (2, 1) band was determined by comparing the structure due to this band with corresponding structure of the (1, 0) band and subsequently substracting the (2, 1) contribution. It was assumed in this method that the individual band shapes for the (1, 0) and (2, 1) are similar. In the second method, calculated Franck-Condon factors were used. Both methods yielded the same cross section for the (1, 0) band. Cross sections for other bands of the first negative system were obtained by using calculated Franck-Condon factors, i.e., relative cross sections, and normalizing to our measured cross section for the (1, 0) band.

The experimental details are summarized in Sec. II. The evaluation of the cross sections is described in detail in Sec. III.

II. EXPERIMENTAL

The experimental arrangement is basically the same as that used for the measurement of the emission cross section of the (0, 0) first negative band of N_2^+.[10] The electron-gun collision-chamber electron-collector assembly was mounted in a 200-liter ultra-high vacuum chamber which could reach an ultimate vacuum of better than 5×10^{-11} Torr when mildly baked. The electron gun produced a well-focused beam with a diameter of about 2 mm and current of several microamperes. The gun was electrostatically focused and no collimating magnetic fields were employed. Thoria-coated tridium filaments were used and no deleterious effects of the oxygen gas on the gun's performance were observed. The light emitted from within the collision chamber was detected by a filtered photometer and single-photon counting techniques were used to record the signals. Excitation functions were automatically plotted from threshold to 400 eV on an xy recorder within a few minutes.

The entire vacuum chamber was filled with oxygen to a pressure of about 1×10^{-4} Torr during a measurement. The absolute pressure was measured with an ionization gauge. The calibration procedure is described in detail elsewhere.[10] Care was taken to avoid any problems sometimes encountered in the pressure measurement of relatively reactive gases such as oxygen, in particular in static systems. In our case, the use of the nude ionization gauges with thoria-coated iridium filaments operated at low pressures proved to be very satisfactory. The gauges were mounted within the large 200-liter vacuum vessel which contained the collision chamber and the oxygen gas at a uniform low pressure. The pumping speed at the pump port of the vacuum chamber was kept at a low value of ~100 liter/sec. Under these conditions any pumping effect of the ionization gauges was negligible, and the correct pressure in the collision chamber was that read by the gauge. The gauges were carefully calibrated against a McLeod gauge and an absolute oil manometer as described for the case of nitrogen.[10] It was found that the relative gauge sensitivities for oxygen and nitrogen agreed with those given by the manufacturer to within 2%. The absolute pressure in the collision chamber was known to within ± 5%. The pressure was held constant to within 1% during a measurement by means of a servo leak valve.

The filtered photometer was calibrated absolutely with a standard tungsten lamp and a freshly prepared MgO screen.[10] Both the geometry and the signal levels encountered in the actual experiment were carefully preserved during these measurements. The standard lamp was calibrated by the National Bureau of Standards in terms of the spectral output for a given filament heating current. The brightness temperature of the lamp was monitored periodically with an optical pyrometer to make sure that the original calibration data still applied. During the course of the calibration measurements and throughout the actual experiment, the pulse-height spectrum of the photomultiplier was frequently measured to ensure that the integrated counting efficiency of our apparatus did not change. The absolute error in the optical calibration does not exceed ± 5%.

The transmission functions of the interference filters were measured with a 0.5-m Ebert monochromator; a standard tungsten lamp provided the necessary illumination. The effective filter transmission for the particular band under study had to be determined in order to evaluate the specific band cross section. To obtain this information, the bands were excited in a pulsed microwave discharge in pure O_2 at low pressures and scanned with a 0.5-m Ebert monochromator. An example of a measured band shape is shown in Fig. 1. The effective transmission for a particular filter and band combination was then calculated. The interference filters were carefully chosen in order to cover the main portion of the band under study. For instance, the filter selected for the (1, 0) band had a center wavelength of 5618 Å and a bandwidth of about 20 Å full width at half-maximum (FWHM).

Photon counting rates were about 1000 counts/sec. The background counting rate due to stray light from the gun filament without O_2 in the chamber was about 100 counts/sec. The dark-current counting rate of the cooled photomultiplier tube was about 5 counts/sec.

Another small but interesting background emission was observed with O_2 in the chamber when the electron beam was stopped at the collision-chamber entrance by a suitable retarding potential. This background was not observed in the similar experiments with N_2. It was surmised that this background was due to fast but relatively long-lived O_2^+ ($b^4\Sigma_g^-$) ions entering the chamber. These ions were produced in the gun under the existing biasing conditions whether or not the electron beam was retarded at the collision chamber. To test this hypothesis a system of electrostatic deflection plates was installed between the gun and the collision-chamber entrance. Fast square voltage pulses were applied to these plates. It was found that the background during the on-period of the pulses was completely eliminated. This was a clear indication that the ions were being swept towards the deflection plates and were effectively prevented from entering the collision chamber. In order for the "background ions" from the gun to enter the collision chamber and be detected, their effective lifetime had to be of the order of microseconds. This requirement is only satisfied by ions in the $b^4\Sigma_g^-$ state since, in addition to the time factor, the radiation emitted by the excited species had to be transmitted by the

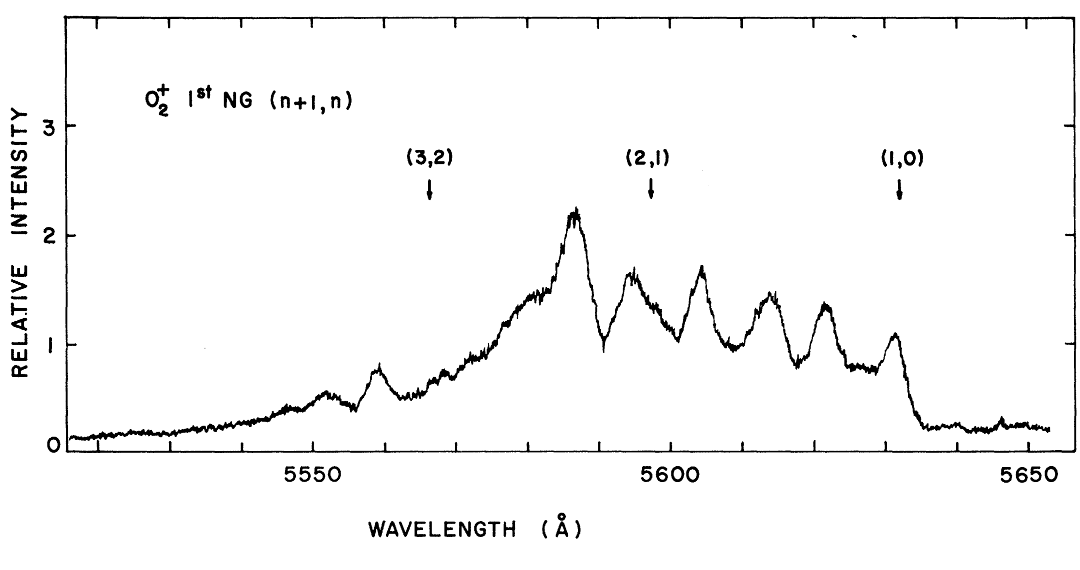

FIG. 1. $(n+1, n)$ sequence of the first negative system of O_2^+ as monitored with an Ebert monochromator with 3 Å resolution. The emission was produced in a low-pressure microwave discharge in pure O_2. The major portion of the entire structure shown belongs to the (1, 0) band. Only the most prominent features in this band can be seen. The actual number of branches and band heads is much larger than the number of detailed features shown. The arrows in the figure indicate the position of the band head of the (1, 0), (2, 1), and (3, 2) bands. The (2, 1) band contributes about 20% to the area under the entire structure. The structure around 5555 Å is also due to the (2, 1) band. The contributions from the (3, 2) band and higher terms in the sequence are negligible. (See also Table III.)

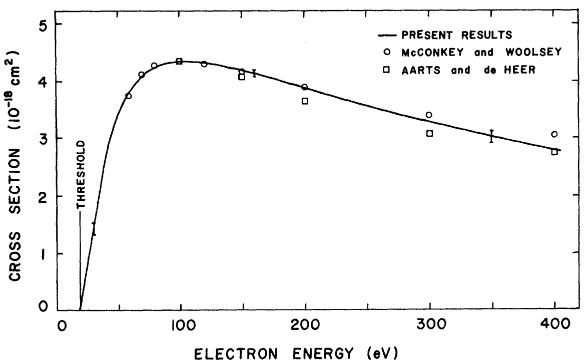

FIG. 2. Excitation cross section for the emission of the (1, 0) first negative band of O_2^+. The curve shown represents an average over 3 runs for each of the (0, 0), (1, 0), and (2, 0) bands. All nine continuous curves thus obtained agreed within the vertical bars shown in the figure, which also indicate the statistical error encountered. For comparison purposes, the excitation functions of McConkey and Woolsey and of Aarts and de Heer (from Ref. 4) have been normalized to the present section at 100 eV.

interference filter. In the measurements of the relative excitation functions and the absolute cross sections the small O_2^+ background described above could be easily subtracted. With the modified gun the lifetimes of the *slow* O_2^+ ($b^4\Sigma_g^-$) ions produced in the collision chamber could be measured. To this end the beam was allowed to enter the collision chamber by removing the retarding potential, but

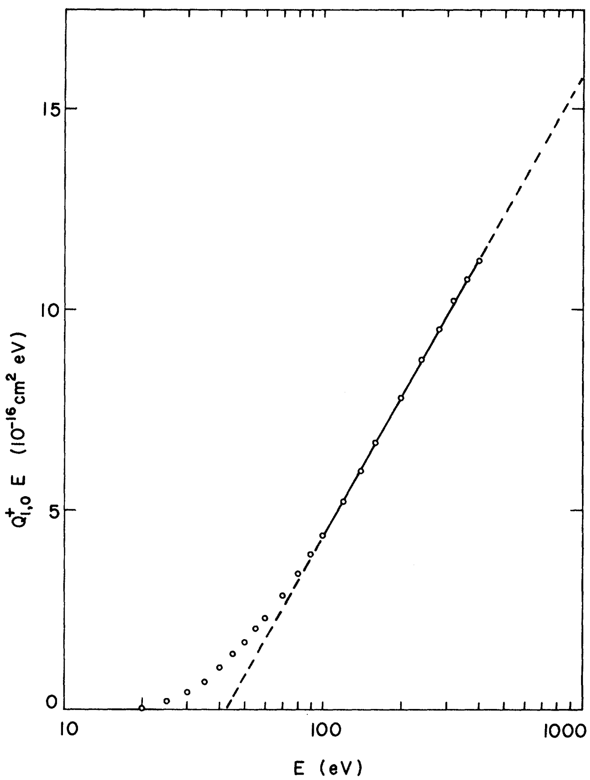

FIG. 3. Bethe plot of the emission cross section of the (1, 0) first negative band of O_2^+. The constants A and B in the Bethe-Oppenheimer relation $Q = AE^{-1}\ln(BE)$ were obtained from a least-square fit to the present data over the energy range 100–400 eV. They are $A = 5.15\times10^{-16}$ cm^2 eV and $B = 2.37\times10^{-2}$ eV^{-1}.

still pulsing it with the deflection plates. The resulting exponential decay of radiation during the time when the beam was deflected yielded an accurate lifetime measurement (see below).

TABLE I. Emission cross section of the 5632 Å (1, 0) band of O_2^+ in units of 10^{-18} cm^2.[a]

Energy (eV)	Cross section	Energy (eV)	Cross section
20	0.17	120	4.31
25	0.80	140	4.23
30	1.41	160	4.12
35	2.02	200	3.87
40	2.63	240	3.61
45	3.05	280	3.38
50	3.36	320	3.17
55	3.62	360	2.97
60	3.81	400	2.77
70	4.06	500	2.48
80	4.22	600	2.22
90	4.30	800	1.85
100	4.33	1000	1.59

[a]Values above 400 eV were calculated from a Bethe-Oppenheimer relation which was fitted to the data between 100 and 400 eV (see also Fig. 3).

III. RESULTS AND DISCUSSION

The results of the cross-section measurements are shown in Figs. 2 and 3 and in Tables I and II. The quantities that could be measured directly were the cross sections for the (n, n), $(n+1, n)$, and $(n+2, n)$ sequences of the O_2^+ first negative system. The three corresponding excitation functions ex-

TABLE II. Measured maximum cross section of O_2^+ first negative bands at 100 eV in units of 10^{-18} cm^2.

$Q_{0,0}$	2.14 ± 15%
$\sum Q_{n+1,n}$	5.30 ± 10%
$Q_{1,0}$	4.33 ± 15%
$\sum Q_{n+2,n}$	2.10 ± 10%

hibited the same shape within the statistical noise (1% rms) present in the measurements. Therefore, only one curve is shown in Fig. 2. It is seen in Fig. 3 that the cross sections accurately satisfy a Bethe-Oppenheimer relationship above 100 eV. The cross section was extrapolated to 1000 eV (Table I) because of the excellent fit in Fig. 3.

In arriving at the cross section for the individual bands, certain difficulties were encountered due to the complex band structures of the first negative system. Apparently, no laboratory measurements exist for the band shapes which would correspond to the present experimental conditions of low pressure and beam current. To our knowledge, no synthetic spectra have been calculated for the first negative system. These calculations would be difficult indeed in view of the fact that the transitions involve quartet states and intermediate coupling. It was possible, however, to arrive at absolute cross sections for the (0, 0) and (1, 0) bands with a minimum of assumptions and within the errors quoted in Table II. On the other hand, it is difficult to extract the cross section for the (2, 0) band directly from the total cross section for the $(n+2, n)$ sequence because of the strong blending of this band with other bands. We obtained a value for the (2, 0) cross section by resorting to calculated Franck-Condon factors (see below).

The method adopted in determining the cross sections for the individual bands was as follows: The band shapes resulting from the microwave discharge were assumed to be the same as those from the beam experiment. Further, the amount of blending was estimated by assuming that the band shapes for the individual bands in a sequence are similar. For instance, this works well for the (1, 0) band where the main portion of blending comes from the (2, 1) band and the higher bands can be neglected. The structure around 5555 Å in Fig. 1 which is due to the (2, 1) band was scaled to the corresponding peak heights of the (1, 0) band and subsequently subtracted. As a result, the area to be subtracted was about 20% of the total area under the curve in Fig. 1.

In an independent estimate of the blending in this band, the recent transition probabilities of Shemansky and Vallance Jones[2] for the first negative system were used together with the calculated Franck-Condon factors[11,12] for the transition from the O_2 ground state. The resulting relative excitation cross sections (relative band intensities) are listed in Table III which also contains the known wavelengths for the first band head[13] in the bands. It is seen from Table III that the amount of blending from the (2, 1) band in the $(n, n+1)$ sequence is about 20% which is the same correction obtained directly.

TABLE III. Relative excitation cross sections for O_2^+ first negative bands (first entry) and wavelengths of the first band head (second entry).[a]

v' \ v''	0	1	2	3	4	5
0	72.6	75.5	48.5	24.6	10.9	4.4
	6026.4	6418.7	6856.3	7348	7891	...
1	100.0	5.0	9.7	25.7	25.1	16.7
	5631.9	5973.4	6351.0	...	...	...
2	25.9	21.6	16.4	0.6	2.9	7.8
	5295.7	5597.5	5925.6	...	...	...
3	1.7	15.3	1.4	7.2	2.6	...
	5005.6	5274.7	5566.6	5883.4	...	...
4	...	1.6	5.6	0.02	1.7	1.6
	...	4998	5259	5540.7	5847.3	...

[a]Relative intensities were obtained from Shemansky's transition probabilities and the calculated Franck-Condon factors of Wacks. The wavelengths listed are from Pearse and Gaydon.

The (0, 0) band is relatively free of blending due to the small cross section for the (1, 1) band, and furthermore, the other bands in the (n, n) sequence are fairly well separated in wavelength from the (0, 0) band. On the other hand, the (2, 0) band is strongly blended with several other bands. This makes it difficult to extract the cross section for this band from the measured band shape of the $(n+2, n)$ sequence. From Table III and the value for $Q_{1,0}$ (Table II) we obtain $Q_{2,0} = 1.12\times10^{-18}$ cm^2. With the measured value for $Q_{0,0}$ (Table II) we find a value of 1.20 for the ratio $Q_{0,0}/(Q_{2,0}+Q_{3,1})$. This can be compared with a value of 1.1 to 1.9 for this ratio as obtained by Hunten (see Ref. 2) in an auroral measurement.

The measured cross sections $\sum Q_{n+1,n}$, $Q_{1,0}$, and $\sum Q_{n+2,n}$ (Table II) are consistent with the relative values in Table III. If $Q_{1,0}$ from Table II is used to normalize the values in Table III, then we obtain $\sum Q_{n+1,n} = 5.3\times10^{-18}$ cm^2 and $\sum Q_{n+2,n} = 2.1\times10^{-18}$ cm^2 which agrees very well with our measured values in Table II.[14] Our results are to be compared with values of 8.8×10^{-18} cm^2 and 3.8×10^{-18} cm^2 as measured by McConkey and Woolsey[4] for the above two cross sections, respectively. It is interesting to note, however, that the ratios of the two cross sections, which are 2.5 in our case and 2.3 in McConkey's case, agree well. The discrepancy in the absolute values may be due to a difference in the absolute calibrations. These authors also deduced a value of $Q_{1,0} = 7.3\times10^{-18}$ cm^2 which again is consistently larger than ours (Table II). Nishimura[5] obtained a value $Q_{1,0} = 1.3\times10^{-18}$ cm^2 by normalizing to the cross section of the 3914 Å first negative band of N_2^+. However, recent cross-section measurements for this band are about 3 times larger than that used by Nishimura. If we take our recently measured cross section[10] of $Q_{3914}=1.74\times10^{-17}$ cm^2, then Nishimura's measurement yields $Q_{1,0}=3.7\times10^{-18}$ cm^2. This is in good agreement with our cross section for the (1, 0) band (Table II).

The cross section for the (0, 0) band in Table II is smaller than a value of 3.16×10^{-18} cm^2 obtained from Table III. We have not been able to trace this discrepancy to a calibration error. It appears that the Franck-Condon factor for the $\nu'=1$ level is larger than that for the $\nu'=0$ level in discord with the theoretical predictions.[11,12] The electron-impact results of Aarts and de Heer (see Ref. 4) also indicate that the $\nu'=1$ level is more efficiently populated than the $\nu'=0$ level.

Not enough experimental information exists to decide on a set of reliable Franck-Condon factors for the transition from the ground state. Franck-Condon factors obtained by Berkowitz, Ehrhardt, and Tekaat[15] with photoelectron spectroscopy show a strong deviation from the calculated values, whereas Turner and May[16] using similar techniques claim good agreement with the calculated values. As far as the present cross-section measurements can indicate, there is good general agreement with the calculated values. The transition probabilities for the first negative bands[2] themselves seem to be rather accurate. This is corroborated by our lifetime measurements (see Sec. II). For instance, the lifetime of the $\nu'=1$ level was found to be 1.19 μsec ± 5% which is in good agreement with a value of 1.16 μsec listed in Shemansky's paper.

The measured cross sections accurately follow a Bethe-Oppenheimer relationship $Q=AE^{-1}\ln(BE)$ for energies above 100 eV. The constants A and B determined from a least-square fit to the present data are listed in Fig. 3. The cross sections can be safely extrapolated to 1000 eV (Fig. 3 and Table I). Thus the energy range of greatest significance in auroral physics is covered by our measurements, particularly the region below 100 eV.

The geophysically important ratio of the total ionization cross section of oxygen[17] to the emission cross sections of the first negative bands was also determined. It was found that this ratio is nearly constant from 30 eV to 1 keV and had an average value of about 64 in this energy range. Correspondingly, values for the other bands can be obtained from the present cross-section measurements and Table III. Details concerning the geophysical applications of the present work will be presented elsewhere.

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