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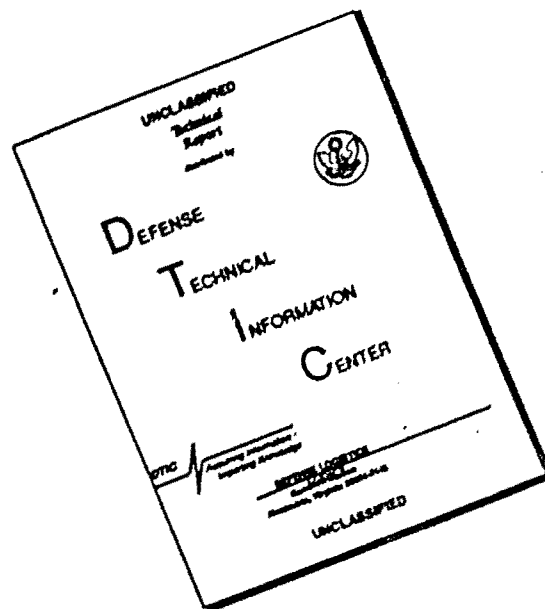
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**Nitrogen and Oxygen Absorption Cross-
Sections in the Vacuum Ultra-Violet**

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Nitrogen and Oxygen Absorption Cross-Sections in the Vacuum Ultra-violet

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The total absorption cross-section (or coefficient) curves of nitrogen and oxygen recently measured in the 580-1050 Å wavelength region using a Hopfield helium continuum background light source are discussed in relation to the absorption of solar radiation in the earth's upper atmosphere. Similar measurements using the hydrogen many-line spectrum background in the 1375-1450 Å region and the 1620-1640 Å region of the oxygen Schumann-Runge continuum are also described. A table listing cross-sections of nitrogen and oxygen at all of the important solar emission lines in the 580-1050 Å region is given. Our measurements are compared with values given by others where possible.

The absorption of solar ultra-violet radiation in the atmosphere produces ions, atoms, and electrons which then generally undergo further reaction with each other and with the ambient atmospheric constituents. In order to understand the numerous reactions that occur in the atmosphere, it thus becomes essential to know the primary photochemical formation rates of these reactive species. For this purpose, it is necessary to know the solar radiation flux incident on the upper atmosphere, the number densities of the atmospheric constituents, the total absorption cross-section, and the cross-section for the specific product of interest.

The purpose of this paper is to make readily available to upper atmosphere theorists recently measured total absorption cross-sections of nitrogen and oxygen, primarily in the 580-1050 Å wavelength region. These measurements were obtained with a continuum background light source, in contrast to most other measurements which were obtained with line emission background light sources and which therefore cannot adequately measure the complicated structure usually present. A general discussion of these measurements and their relation to the molecular structure has been previously given.^{1, 2} In this paper we wish to describe in more detail the measurements at important solar emission lines and also recent measurements in the oxygen Schumann-Runge continuum.

EXPERIMENTAL

The experimental method will not be given in detail here, since it has been previously described.^{1, 2} A repetitive, condensed discharge (0.002 μ F, 5 ke) through helium (38 mm Hg) gives an intense Hopfield continuum³ from 580 to 1100 Å. The radiation then is dispersed with a 2.218 m normal incidence monochromator equipped with differential pumping at the 100 micron entrance slit. A 10 cm long, windowless gas absorption cell is placed directly behind the exit slit. The radiation is detected with a sodium-salicylate-coated glass disc at the end of the cell a few mm from a photomultiplier (EMI 9514B). Pressures were measured with a McLeod gauge. Reagent-grade gas from the Air Reduction Company was used. Wavelengths were located to ± 0.1 Å using impurity lines of known wavelengths, and the bandwidth, as measured from the impurity line half-widths, was slightly less than 0.5 Å.

The absorption cross-section σ or absorption coefficient k is defined by the expression,

$$I = I_0 \exp[-kx] = I_0 \exp[-\sigma n_0 x], \quad (1)$$

where I_0 and I are the relative intensities without and with gas in the cell, x is the absorption path length reduced to s.t.p., and n_0 is $2.69 \times 10^{19} \text{ cm}^{-3}$, Loschmidt's number. The absorption cross-section is given in units of megabarn (Mb), which is equal to 10^{-18} cm^2 , and the absorption coefficient in units of cm^{-1} . In all cases, a second I_0 scan was made after measuring the absorption to be sure that the light source intensity had remained constant.

A small scattered light correction of from 0.5 to 3% was subtracted from all intensities. At wavelengths less than 661 Å in N₂ and 722 Å in O₂, it was necessary to make small corrections for fluorescence of the gas in the absorption cell. In the 1375-1450 Å region, it was necessary to correct for fluorescence from the lithium fluoride windows.

The measured cell pressures were corrected for the pressure gradient along the light path during windowless operation by measuring the absorption of oxygen around the peak of the Schumann-Runge continuum (1375-1450 Å) both during normal flow operation and with a lithium fluoride windowed cell. From these results, the measured absorption coefficients were increased by the factor 1.15.

ABSORPTION CROSS-SECTIONS, 580-1050 Å

In this section, absorption cross-section curves averaged from at least five scans at different pressures are given. In all cases, the curves agreed well with previous spectra taken in this laboratory with a 6.8 m grazing incidence spectrograph.

Nitrogen absorption cross-sections are shown in fig. 1, covering 1000-800 Å and in fig. 2, covering 800-600 Å. Many sharp molecular bands whose rotational structure are not resolved with the present bandwidth are observed between 1000 and 796 Å, the first ionization threshold. For these unresolved bands, the absorption cross-section increases as

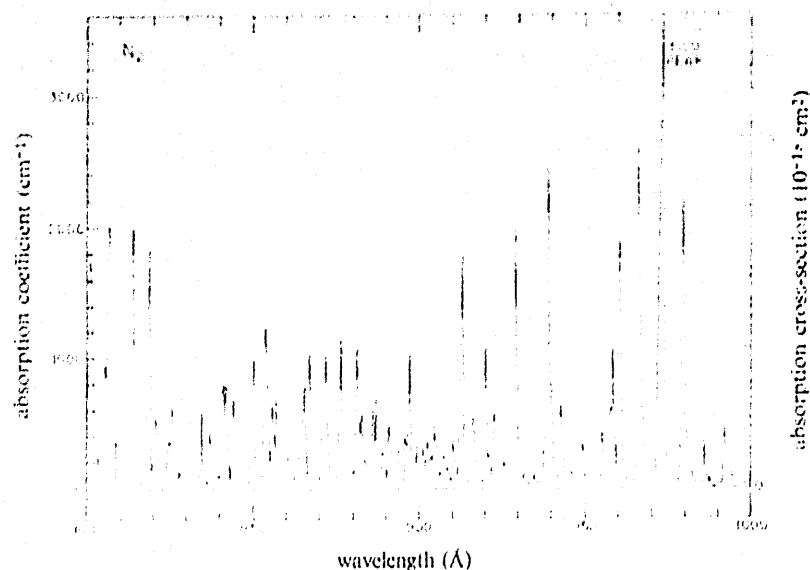


FIG. 1.—Absorption cross-sections of nitrogen in the 1000-800 Å region.

the pressure decreases. This "apparent pressure effect" is probably due to extremely high absorption cross-sections in the sharp rotational lines which generally produce total absorption at the pressures used. In this case, the given band maxima represent a lower limit, and much higher resolution will be needed to study these bands. There is no continuum observable between these bands larger than the approximately one Mb lower limit

for accurate cross-section measurements in these experiments. The significant rise in the continuum beginning near 810 Å is probably due to unresolved Rydberg series members converging to the first ionization threshold at 796 Å. Because of the absence of a continuum and of the sharp appearance of the bands in higher resolution spectra,⁴ it is unlikely that absorption by nitrogen in the 1000-796 Å region will lead to formation of nitrogen atoms by photodissociation in the atmosphere. It is possible that predissociation may occur in some of these bands; however, the necessary high resolution studies have not been done. At wavelengths between 1000 and 1050 Å, the nitrogen absorption bands are much weaker (upper limit about 0.01 Mb) and could not be measured in the present case.

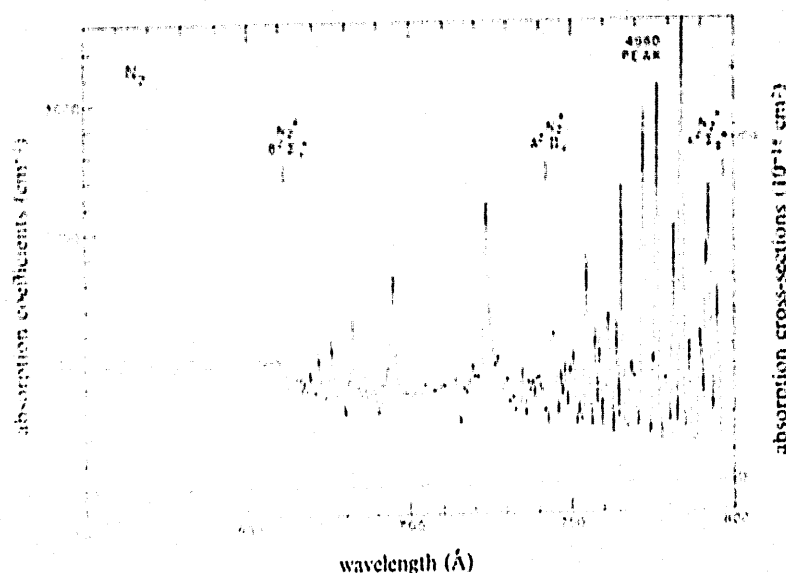


Fig. 2. Absorption cross-sections of nitrogen in the 800-600 Å region.

At wavelengths less than 796 Å, nitrogen can be ionized to the $X^2\Sigma_g^+$ ground state of N_2^+ , and fig. 2 shows the presence of the expected continuum in this region. There are also many bands, especially in the 796-725 Å region, which have been found to be extensively pre-ionized.⁶ Around the $N_2^+ A^2\Pi_u$ threshold at 743 Å, there is a gradual rise in the continuum towards shorter wavelengths. However, at the $N_2^+ B^2\Sigma_g^+$ state threshold at 661 Å, there is a step-like threshold and then a relatively featureless continuum down to the lower wavelength limit of 580 Å. In the region below 661 Å, fluorescence from N_2^+ has been observed.⁶ This radiation is probably the first negative bands of N_2^+ , $B^2\Sigma_g^+ \rightarrow X^2\Sigma_g^+$.

Oxygen absorption cross-sections are shown in the 1060-830 Å region in fig. 3 and in the 830-600 Å region in fig. 4. The observed continuum increases very slowly below the first ionization threshold at 1026.7 Å ($X^2\Pi_u$ state of O_2^+), probably because of large differences in equilibrium internuclear distances between the ground states of O_2 and O_2^+ . At the other ionization thresholds shown, the continuum also rises gradually. In addition, dissociation continua² may contribute to the observed continuum.

All of the bands at wavelengths less than the ionization threshold of 1026.7 Å are diffuse and have been found to be pre-ionized.⁷ At wavelengths less than about 722 Å, fluorescence from O_2^+ was observed.⁶ This was probably due largely to the second negative bands of O_2^+ , $A^2\Pi_u \rightarrow X^2\Pi_u$. In general, the oxygen curve is much better known than the nitrogen curve. The bands are more diffuse due to pre-ionization.

In fig. 1-4, the experimental error is estimated to be $\pm 10\%$ under the most favourable conditions. This error applies for absorption cross-sections between about 2 and 150 Mb, and becomes larger outside these limits. Where necessary in later discussions, specific estimated errors will be given.

ABSORPTION CROSS-SECTIONS, 1050-2000 Å

Nitrogen has a number of absorption band systems in this wavelength region. However, all of these are quite weak and are optically forbidden. No accurate cross-sections have

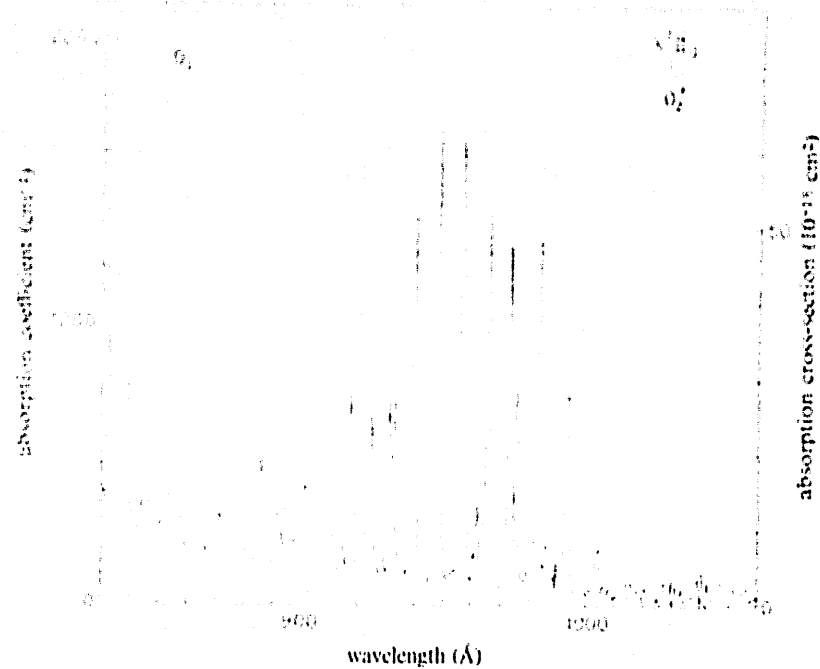


Fig. 3.—Absorption cross-sections of oxygen in the 1060-830 Å region.

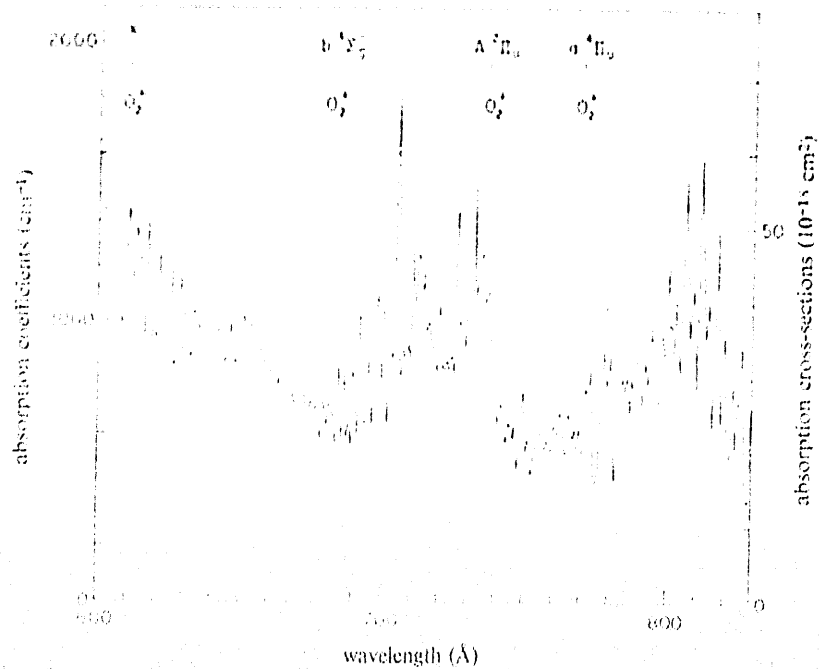


Fig. 4.—Absorption cross-sections of oxygen in the 830-600 Å region.

been measured, and the strongest bands have generally been estimated to be no larger than 0.01 Mb.⁷ Predissociation has been found in some of the Lyman-Birge-Hopfield bands in this region.⁸

On the other hand, oxygen has an intense, complicated absorption spectrum in this region.⁹ The Schumann-Runge (SR) continuum between roughly 1300 and 1750 Å is generally believed to be responsible for most of the atomic oxygen found above 90 km in the atmosphere. Absorption in this continuum yields one ¹P ground state atom and one ¹D excited state atom per photon absorbed. Predissociation can occur in the SR bands.⁹ In this case, two ¹P ground state atoms are formed in the dissociation.

We have measured the absorption cross-section of the SR continuum around its maximum using a lithium fluoride windowed absorption cell and the hydrogen molecular spectrum as background. Measurements in the broad maximum (1375-1450 Å) of the continuum and at a few wavelengths near 1630 Å are given in table 1. At the observed peak of the

TABLE 1. ABSORPTION COEFFICIENTS OF OXYGEN IN THE SCHUMANN-RUNGE CONTINUUM. AT THE MAXIMUM OF THE BEST CURVE THROUGH THE MEASUREMENTS GIVEN, THE k -VALUE IS 403 CM⁻¹ AND THE WAVELENGTH IS 1415.5 Å. SHORTER WAVELENGTH RANGE VALUES AVERAGES OF 9 TO 7 MEASUREMENTS. LONGER WAVELENGTH RANGE VALUES AVERAGES OF 3 MEASUREMENTS. ESTIMATED ERROR IS LESS THAN $\pm 10\%$.

λ (Å)	k (cm ⁻¹)	λ (Å)	k (cm ⁻¹)
1376.6	369	1434.2	398
1379.5	375	1435.6	399
1393.3	393	1436.7	397
1395.5	395	1437.2	398
1396.7	395	1438.1	394
1398.2	393	1440.1	396
1401.3	400	1442.6	394
1401.8	401	1445.2	396
1406.5	397	1622.2	90
1409.5	402	1627.6	89
1412.0	406	1627.7	85
1426.8	401	1627.5	80
1429.1	400	1632.8	76
1430.2	400	1633.2	75
1431.8	398	1634.3	74
1432.1	401	1635.5	72
1433.3	400	1638.0	70
		1639.4	68

continuum, the cross-section was 15.0 $\pm$ 1.5 Mb or 403 $\pm$ 40 cm⁻¹. This value is in good agreement with several other photoelectric measurements.^{5, 7, 10} However, it is roughly 20% lower than several early photographic technique measurements.¹¹ The problem of reconciling these measurements has been discussed,^{7, 12} and it is apparent that precise measurements by several independent techniques must be carried out in an attempt to fix the best value of this important cross-section.

We have not measured cross-sections with comparable accuracy at any other wavelengths in this region. It is planned to study this entire region with continuum background light sources in the future. In particular, the region 1050-1350 Å will be studied, since it has not been possible to interpret the cross-section curves well in this region.

UPPER ATMOSPHERE ABSORPTION

The solar radiation flux $\Phi(h, \lambda)$ in photon/cm² sec at any altitude h is given by the expression

$$\Phi(h, \lambda) = \Phi_0(\lambda) \exp \left(- \sum_j \sigma_j(\lambda) N_j h \right) \quad (2)$$

where $\Phi_0(z)$ is the flux incident on the earth's atmosphere, σ is the total absorption cross-section for the j th constituent, and N_j is the number of atoms in a vertical or slant cm² column along the path of the incident radiation. The production rate of a new species by absorption of solar radiation is given by

$$R_{jk}(h) = \sum_i \sigma_{ji}(z) n_j(h) \Phi_0(z) \exp(-\sum_i \sigma_i N_i) \quad (3)$$

where σ_{jk} is the cross-section for absorption by the j th constituent leading to process k and $n_j(h)$ is the number density of the j th constituent. The cross-section σ_{jk} is the fraction of the total absorption cross-section which yields the product of interest. This cross-section may describe ionization, dissociation, dissociative ionization, fluorescence, product excitation or other processes. It will be observed in (3) that both the specific process cross-section σ_{jk} and the total absorption cross-sections for all atmospheric constituents are necessary before accurate production rates at a given wavelength can be calculated.

At certain wavelengths and altitudes there are effectively only one or two absorbing constituents.¹³ In addition, from measurements of the solar flux at a number of wavelengths as a function of altitude, the number densities, and total absorption cross-sections in some cases, can be found.¹³

The solar flux below about 1300 Å consists almost entirely of emission lines, although the hydrogen Lyman continuum does extend throughout the region 913-800 Å. In order to calculate production rates, it is essential to know the cross sections at these lines. Our measurements of the total absorption cross-sections are given for nitrogen and oxygen in table 2 together with the proposed classification and the general type of absorption occurring at the solar line. We have selected these lines from recent photoelectric intensity measurements.¹⁴ A number of other lines have been found by several investigators,^{15, 16} but they are weaker.

The hydrogen Lyman continuum can be readily observed in the upper atmosphere solar spectra extending from 913 to about 800 Å. With some improvement in noise levels, it will probably be possible to observe the absorption spectra of nitrogen and perhaps oxygen superimposed on the continuum. For identification of spectra and possible number density measurements, the appropriate sections of fig. 1 and fig. 3 may be utilized.

The estimated errors in table 2 are in several cases larger than the estimates previously given. This is in order to take into account special factors which increase the error estimates, such as impurity lines in the region, low background light intensity at the edges of the continuum background, "apparent pressure effect" in unresolved bands, and cross-sections outside the range of most accurate measurement. The values are considerably better relative to each other than absolutely.

Several intense lines in table 2 deserve special discussion. At 1025.7 Å, H I γ , we find oxygen has a moderate cross-section of 1.5 Mb. Other values have been 2.0,¹⁷ 1.6,¹⁸ 1.6,¹⁷ 1.9,¹⁹ and 2.2 Mb.²⁰ There does not appear to be any reason to place less weight on any of these results. The average of 1.8 Mb is probably the best value at this time, and all measurements are within $\pm 15\%$, which is the smallest error claimed.

The nitrogen cross-section at 972.5 Å, H I γ , is very large. We find the cross-section to be 300 Mb, and other measurements are 370,²¹ 150,¹⁷ 11,¹⁷ and 190.²⁰ There is a large "apparent pressure effect" because of insufficient resolution, and the measured values should be considered to be lower limits. With this consideration and also because special low pressure measurements were done, the most reliable value is probably the largest one, or 370 Mb. This value is within the estimated error of our measurement. Our oxygen-cross-section at H I γ is 31 Mb, which is identical with another recent measurement.¹⁹ A higher value of 50 Mb has also been obtained.¹⁷

The He I line at 584.3 Å is one of the most intense lines in this wavelength region, but unfortunately it is relatively weak and also partially self-absorbed in our light source. Therefore the $\pm$ error shown in table 2 is larger than for most of our measurements. For nitrogen, our measurement is 36 Mb. Other measurements are 18,¹⁷ 26,²² 15,²³ 19,²⁴ and 30.²⁰ As mentioned earlier, we corrected for fluorescence, which may have affected some earlier measurements. For oxygen, we find the cross-section to be 23 Mb. Other

investigators find values of 16,¹⁷ 20,¹⁸ and 21.¹⁹ It is apparent that the differences between all these measurements is larger than desirable, but it is not possible to rule out any of these at this time. It is probably significant that the photographic technique measurements,^{16, 17, 20, 21} in which the gas is placed in the spectrograph itself, are generally lower than the photoelectric technique measurements,^{19, 22, 23} in which the gas is confined to a cell. The average of all values is 24 Mb for nitrogen and 20 Mb for oxygen.

TABLE 2.—ABSORPTION CROSS-SECTIONS AT IMPORTANT SOLAR EMISSION LINES. CROSS-SECTIONS σ IN UNITS OF MEGABARS, OR 10^{17} CM². FOR MEANING OF SYMBOLS, SEE NOTE BELOW.

WAVELENGTH	IDENTIFICATION	N_2	REMARKS	O_2	REMARKS
1037.6	O VI	cont.	cont.	0.4	cont.
1031.9	O VI	cont.	cont.	0.6	cont.
1025.7	H Ly β	cont.	cont.	1.5 $\pm$ 0.3	cont.
991.5	N III	1.9 $\pm$ 0.4	β -band	1.7 $\pm$ 0.3	cont.
989.8	N III	1.1 $\pm$ 0.4	cont.	6.0 $\pm$ 2.0	band
977.0	C III	0.6 $\pm$ 0.3	cont.	4.7 $\pm$ 0.7	cont.
972.5	H Ly γ	300 $\pm$ 70	P , k -band	31 $\pm$ 5	H -band
949.7	H Ly δ	5.2 $\pm$ 1.0	m -band edge	6.3 $\pm$ 1.0	M -band edge
937.8	H Ly ϵ	10 $\pm$ 4	P , n -band	5.0 $\pm$ 0.7	cont.
930.7	H Ly ζ	4.8 $\pm$ 1.9	P , Ryd; A , 2_1	27 $\pm$ 4	M -band
904	C II	6.3 $\pm$ 1.0	cont.	11 $\pm$ 1.5	band
835.3	O III	15 $\pm$ 5	P , Ryd; A , 4_0	13 $\pm$ 1.5	cont.
835.1	O III	26 $\pm$ 10	P , Ryd; A , 4_1	12 $\pm$ 1.5	cont.
834.5	O III	3.3 $\pm$ 0.5	cont.	13 $\pm$ 1.5	cont.
790.2	O IV	25 $\pm$ 4	Ryd; A , 3_1	32 $\pm$ 4	band
790.1	O IV	29 $\pm$ 5	Ryd; A , 3_1	32 $\pm$ 4	band
787.7	O IV	12 $\pm$ 2	cont.	29 $\pm$ 4	band
780.3	Ne VIII	19 $\pm$ 3	cont.	31 $\pm$ 4	band
770.4	Ne VIII	15 $\pm$ 2	cont.	22 $\pm$ 3	cont.
765.1	N IV	78 $\pm$ 20	P , band	24 $\pm$ 3	band
703.8	O III	26 $\pm$ 3	cont.	32 $\pm$ 6	F , cont.
702.3	O III	26 $\pm$ 3	cont.	24 $\pm$ 5	F , cont.
686.3	N III	27 $\pm$ 3	cont.	24 $\pm$ 5	F , cont.
685.8	N III	27 $\pm$ 4	cont.	23 $\pm$ 5	F , cont.
685.5	N III	25 $\pm$ 4	cont.	24 $\pm$ 5	F , cont.
685.0	N III	26 $\pm$ 4	cont.	30 $\pm$ 6	F , r -band
629.7	O V	35 $\pm$ 7	F , cont.	41 $\pm$ 8	F , Ryd; x , 4_1
625	MgX	36 $\pm$ 7	F , cont.	35 $\pm$ 7	F , cont.
610	MgX	34 $\pm$ 7	F , cont.	44 $\pm$ 12	F , cont.
599.6	O III	35 $\pm$ 10	F , cont.	36 $\pm$ 12	F , cont.
584.3	He I	36 $\pm$ 12	F , cont.	23 $\pm$ 8	F , cont.

NOTE.—The following symbols are used to indicate region of the absorption spectrum of the solar line: cont., is continuum; band, band showing designation previously given; Ryd, A 3_0 Rydberg band, member of series having apparent quantum number λ and converging to the $r = 0$ level of the A state of the molecule (or); P , band shows apparent pressure effect, F means fluorescence correction applied.

CONCLUSION

Total absorption cross-sections of molecular oxygen and nitrogen have been given for the wavelength region 580-1050 Å. Cross-sections for oxygen have also been given in the Schumann-Runge continuum. These cross-sections can be used for calculation of formation rates of reactive species and of particle concentrations in the atmosphere. They can also be used to interpret solar flux measurements as a function of altitude. Comparison with other measurements has been made where possible.

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