PHOTO-ABSORPTION CROSS SECTIONS OF MOLECULAR OXYGEN BETWEEN 1250 Å AND 2350 Å

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Abstract—Photoelectric methods employing a variety of detectors have been used to determine the photo-absorption cross sections of molecular oxygen in the range 1250–2350 Å. Significant departures from Beer's Law have been observed in a number of wavelength regions. In the Schumann–Runge bands apparent cross sections determined using Beer's Law are found to vary inversely as the square root of the layer thickness of the absorbing gas.

1. INTRODUCTION

THE CROSS sections for the absorption of vacuum ultraviolet radiation by molecular oxygen are of particular interest for atmospheric physics and have been the subject of a number of investigations. An extensive review of work prior to 1956 has been given by WEISSLER,[1] and in 1958 WATANABE,[2] summarized the various measurements which had been made in the wavelength range 100–2000 Å. Subsequently BETHKE,[3] and THOMPSON, HARTECK and REEVES,[4] made further measurements of absorption in Schumann–Runge bands (1750–2010 Å) and DITCHBURN and YOUNG[5] investigated the Herzberg I continuum (1850–2500 Å). HUFFMAN, LARRABEE and TANAKA[6] and COOK and METZGER[7] have made detailed measurements in the region 580–1060 Å and METZGER and COOK[8] have recently reinvestigated the region 1050–1800 Å. SAMSON and CAIRNS[9] have measured photoionization and total absorption cross sections for a number of wavelengths corresponding to intense solar emission lines below 1100 Å.

The present paper reports the use of photoelectric detectors to measure molecular oxygen absorption cross sections in the range 1250–2350 Å with a spectral resolution of 1–2 Å. All the measurements were made using absorption cells fitted with LiF windows at the exit port of the monochromator. At wavelengths exceeding 2350 Å the O_2 absorption was too low to be measured with the longest path length (3 metres) and highest pressure (2 atmospheres) used in these experiments.

The present investigations provide data taken under similar experimental conditions over a range of wavelengths within which the molecular oxygen absorption cross section varies by approximately seven orders of magnitude. Significant departures from Beer's Law have been observed in a number of wavelength regions (for example in the Schumann–Runge bands) and these pressure and path length effects have been carefully studied in order to obtain quantitative results.

2. EXPERIMENTAL METHOD

The dispersing instrument was a half-metre Seya Namioka monochromator manufactured by McPherson and the light source was a windowless discharge lamp of the Hinteregger type which was used to excite either hydrogen or argon spectra[10] at lamp pressures of approximately 4 torr and 200 torr respectively. The argon continuum was used at wavelengths below 1500 Å: the molecular hydrogen spectrum was used at longer wavelengths. A differential pumping system was used to maintain the pressure in the grating chamber at better than 10^{-4} torr with the source running.

Several absorption cells were employed ranging in length from 0.13 cm to 300 cm and the gas pressures used in the absorption cells ranged from 0.1 cm Hg to 150 cm Hg giving a variation in effective path length (or layer thickness) from approximately 2×10^{-4} atm.cm to 600 atm.cm. The gas used was "medical grade" oxygen supplied by Commonwealth Industrial Gases and it was purified by fractional distillation into the absorption cell using suitable cold traps. Pressures were measured with trapped oil or mercury manometers and with a McLeod gauge.

Several types of detection systems were used in these experiments. In the first system a sodium salicylate coated wire grid[11] placed at the exit port of the monochromator was used to monitor the light beam entering the absorption cell. The fluorescence induced by the beam in the sodium salicylate converter was viewed by an EMI type 9514S photomultiplier placed at right angles to the monochromator beam. The radiation transmitted by the absorption cell was measured by a second sodium salicylate sensitized photomultiplier, and a conventional servo-controlled dividing system was used to record the ratio of the intensities entering and leaving the absorption cell. The ratio was normalized by taking measurements with the cell evacuated.

With this detection system, using photomultipliers sensitive to a wide range of wavelengths, it was necessary to make corrections for stray light scattered into the exit beam. The stray light was found to be approximately constant over a wide range of wavelength settings of the monochromator and the results could be corrected by offsetting the zero of the photomultiplier signals by appropriate amounts. The correction was determined by placing filters (such as calcium fluoride, sapphire or quartz) in the beam and zeroing out the signal recorded by the photomultiplier when the monochromator was set for a wavelength shorter than the cut-off of the filter.

In the wavelength range 1400–1500 Å a second detection system, which did not require correction for stray light, was used and the results compared with those obtained using the photomultiplier system. In this second arrangement a xylene filled ion chamber[12] with a sapphire window was placed at the end of the absorption cell and the transmission was determined by repeated measurements made with the cell evacuated and filled with oxygen to a measured pressure. Owing to the limited spectral sensitivity of the ion chamber (1400–1500 Å) this detector was insensitive to stray light from the monochromator. The results obtained using the ion chamber for the region round the peak of the Schumann–Runge continuum were in good agreement with those obtained using the photomultiplier system indicating that the corrections applied for stray light in the latter case were adequate. For the region 2000–2350 Å a "solar blind" CBS type CL1064 photomultiplier was used in place of the sodium salicylate sensitized photomultiplier in order to minimize the corrections for stray light. The spectral response of the CBS "solar blind" photomultiplier is limited to the region 1700–2600 Å.

3. BEER'S LAW AND ITS LIMITATIONS

In the simple case in which Beer's law applies the absorption cross section (σ cm^2) can be obtained from the measured transmittance (T) by means of the relation

$$T = \frac{I}{I_0} = e^{-\sigma N} \tag{1}$$

where I_0 and I are the intensities of the radiation entering and leaving the absorption cell and N is the number of absorbing molecules per cm^2 column of the gas. The length of the cell and the gas pressure and temperature determine the value of N. The absorption coefficient (k cm^{-1}) is related to the cross section by

$$k = \sigma n_0 \tag{2}$$

where $n_0 = 2.687 \times 10^{19}$ cm^{-3} is Lochsmidt's number.

The formation of complex molecules (such as O_4) pressure broadening, and the finite resolution of the dispersing instrument are some of the effects which may lead to departures from Beer's Law, i.e. to cross sections determined from equation (1) which are not independent of gas pressure (p) or path length (l).

Finite instrumental resolution is particularly important in the study of band structure (e.g. the Schumann–Runge bands). If the absorption cross section varies significantly over the wavelength band selected by the finite resolution of the measuring instrument, an "effective" absorption cross section evaluated using equation (1) will decrease with increasing layer thickness (N) owing to the hardening of the radiation with increasing thickness of the absorber. In this case we must replace equation (1), which applies only for monochromatic radiation of frequency v, by an equation of the form:

$$T = \int_0^\infty \exp|-\sigma(v) . N| . \phi(v)\, dv \left/ \int_0^\infty \phi(v)\, dv \right. \tag{3}$$

where $\sigma(v)$, is the frequency dependence of the cross section and $\phi(v)$, which is determined by the monochromator resolution, is the frequency distribution of the radiation entering the absorption cell. The evaluation of this integral is complicated[13] and requires detailed information concerning the shape of the cross section curve and the resolution function of the particular instrument. Following the development of NIELSEN et al.[13] we may illustrate the departure from Beer's Law by considering a simple case in which the instrumental resolution has a Gaussian form centred on the frequency v_1,

$$\phi(v) = \exp|-(v-v_1)^2/d^2| \tag{4}$$

where d is a constant for the instrument, and the cross section has a single strong resonance at frequency v_0 so that

$$\sigma(v) = \frac{q^2}{(v-v_0)^2 + \delta^2} \tag{5}$$

where q and δ are constants, characteristic of the particular level. The maximum absorption will be measured when $v_1 = v_0$ in which case, to a sufficiently good approximation, equation (3) gives

$$T = \int_{-\infty}^{\infty} \exp\left(-\frac{q^2 N}{x^2} - \frac{x^2}{d^2}\right) dx \bigg/ \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{d^2}\right) dx \tag{6}$$

where we have written $x = v - v_0$ and neglected the small error involved in extending the lower integration limits from $-v_0$ to $-\infty$. We have also neglected the damping term (δ^2) in the denominator of equation (5) since the contribution to the integral (6) is small for the region $v \simeq v_0$. With these approximations the integrations are straightforward and the minimum transmittance is

$$T = \exp\left[-\frac{2q}{d}(N)^{1/2}\right] \tag{7}$$

under these conditions equation (7) shows that an "effective" absorption cross section evaluated using equation (1) will vary as $N^{-1/2}$ i.e. inversely as the square root of the layer thickness.

This example leads to a simple and explicit mathematical expression (equation 7) for the transmission using instruments of finite resolution. NIELSEN et al.[13] have shown that assuming a triangular resolution function of equivalent width to the Gaussian of equation (4) leads to similar numerical results for the transmission. Thus in most practical cases the square root law for the cross sections may be expected to be a good approximation irrespective of the precise form of the resolution function of the instrument.

In the Schumann–Runge bands the cross section may contain a number of rotational lines within the resolution width of the instrument. ELSASSER[14] has considered the case where the cross section consists of a number of equally spaced resonances whose separation is less than the instrumental resolution. Provided the absorption is not too large Elsasser's results may also be approximated by the simple square root law.

4. RESULTS AND DISCUSSION

The important band system leading to ground state absorption by molecular oxygen in the vacuum ultra-violet region of the spectrum are the Schumann–Runge system $(B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-)$ and the Herzberg systems, the strongest of which is $(A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-)$. It is convenient to discuss the results under the following headings:

(a) The Herzberg system

At wavelengths longer than 2000 Å there is a weak continuum. HERZBERG[15,16] has identified this continuum with the transition: $O_2(^3\Sigma_g^-) \rightarrow O(^3P) + O(^3P)$. The continuum is associated with the band system corresponding to the forbidden transition $^3\Sigma_u^+ \leftarrow ^3\Sigma_g^-$. The $^1\Sigma_u^- \leftarrow ^3\Sigma_g^-$ and $^3\Delta_u \leftarrow ^3\Sigma_g^-$ transitions are much weaker[15,16] and need not be considered in the present discussion. The continuum is probably the main source[5] of oxygen atoms below 80 km in the atmosphere.

Long path lengths (0·5 to 3 metres) and fairly high pressures (0·5 to 2 atm) were needed in order to determine the low absorption cross sections in this region. The measured cross sections (σ) were not independent of the pressure (p) and, in agreement with the results by DITCHBURN and YOUNG,[5] σ was found to increase linearly with p. As suggested by DITCHBURN and YOUNG this departure from Beer's Law probably arises from

the formation, at high pressures, of the complex O_4. The absorption cross sections at a pressure of one atmosphere (σ_1) and the values extrapolated to zero pressure (σ_0) are shown in Fig. 1. The probable error in the cross sections is about 5 per cent. The data in
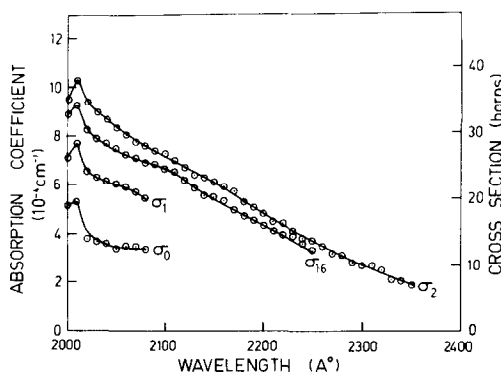

Fig. 1. Absorption cross sections of molecular oxygen in the region 2000–2350 Å. σ_p is the cross section measured at a gas pressure of p atmosphere. σ_0 is the value extrapolated to zero pressure.

this wavelength region were obtained with a monochromator slit width of $60\,\mu$ corresponding to a calculated resolution of 2 Å.

The only experimental results available for comparison are those of DITCHBURN and YOUNG[5] who used photographic recording. The present work, using different experimental techniques, provides general confirmation of the results obtained by DITCHBURN and YOUNG although the cross sections determined in this experiment are about 10–15 per cent higher than their values.

(b) *Schumann–Runge bands*

The region between 1750 and 2010 Å is occupied by the Schumann–Runge bands which correspond to the transition $(^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-)$. In the present experiment cell lengths of 143 cm and gas pressures varying between 1 torr and 760 torr have been used to resolve the (1–0) to (16–0) transitions. The cross sections determined using equation (1) show a marked variation with layer thickness which probably arises from the finite resolution of the monochromator in a region where the cross sections are changing rapidly with wavelength. The dependence of the observed cross sections (σ) on layer thickness (N) is shown in Fig. 2 for a number of wavelengths at which the cross sections have either a maximum or a minimum value. It may be seen that σ varies inversely as the square root of n which is the same form as the simple theoretical example considered in Section 3. WATANABE[2] has also found that the observed cross sections in this region decrease with increasing pressure. Because of the strong variation of σ with N it is difficult to display the observed cross sections in an unambiguous way. For the range 1750–1930 Å we have chosen to plot, in Fig. 3 the cross sections (σ_e) evaluated using equation (1) for those values of $N(= N_e)$ for which the transmitted beam was attenuated by a factor $1/e$. These "$1/e$ cross sections", σ_e, were determined by interpolation between a number of absorption curves measured for different values of n. The semi-empirical relation $\sigma \propto N^{-1/2}$
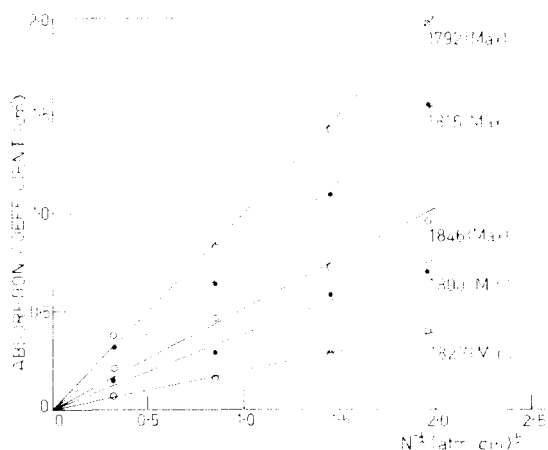
FIG. 2. Absorption coefficients (cm^{-1}) in the Schumann–Runge bands plotted as a function of the inverse square root of the layer thickness $N^{-1/2}$ (atm. cm)$^{-1/2}$. The results are shown for some typical wavelengths where the absorption coefficient has either a maximum or a minimum value.
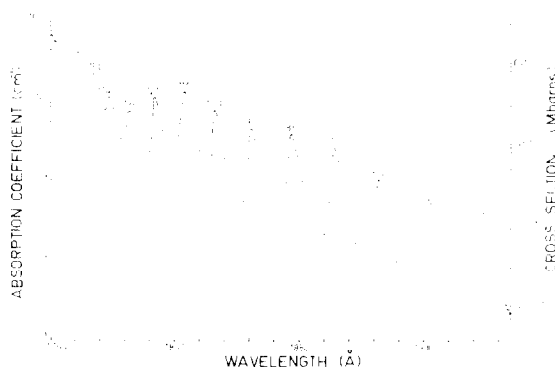

FIG. 3. "$1/e$ absorption cross sections" of molecular oxygen in the region 1750–1930 Å evaluated using Beer's Law and the condition that the transmitted beam at each wavelength was attenuated by a factor e.

illustrated in Fig. 2 and suggested by equation (7) indicates that for a variation in n by a factor of order 10 on either side on N_e we may estimate the appropriate value of σ from the relation $\sigma = (\sigma_e/N)^{1/2}$ (note that $\sigma_e \equiv 1/N_e$). These results were obtained with a monochromator slit width of 60 μ corresponding to a calculated resolution of 2 Å.

The $N^{-1/2}$ relation of equation (7) does not hold at longer wavelengths since, as was noted in the previous section, the cross sections in the Herzberg system contain a term which is proportional to the pressure. For the intermediate region between about 1900 and 2030 Å the observed cross sections were found to have a complicated dependence on pressure and path length. Figure 4 shows the observed cross sections for this intermediate region taken at a pressure of 1 atmosphere with a 1·5 metre absorption cell.
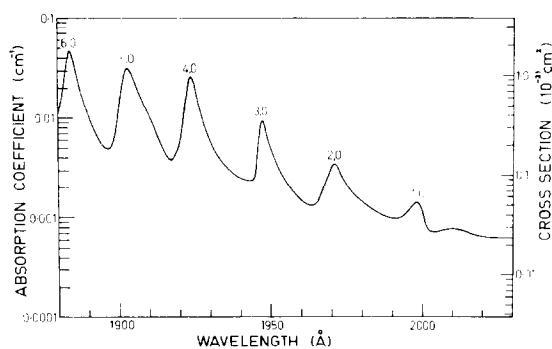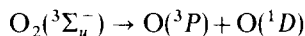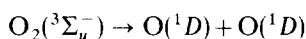
FIG. 4. Absorption cross sections of molecular oxygen in the region 1900–2030 Å measured with a path length of 1·5 metres and a gas pressure of 1 atmosphere.

(c) *Schumann–Runge continuum*

The region between 1250 and 1750 Å is occupied by the Schumann–Runge continuum peaking at 1425 Å with three diffuse bands or narrow continua peaking at 1294, 1334 and 1354 Å. The Schumann–Runge continuum is the principal source of oxygen atoms above 80 km in the atmosphere by means of the process

$$O_2(^3\Sigma_u^-) \rightarrow O(^3P) + O(^1D)$$

The subsidiary bands or narrow continua probably involve the processes

$$O_2(^3\Sigma_u^-) \rightarrow O(^1D) + O(^1D)$$

and

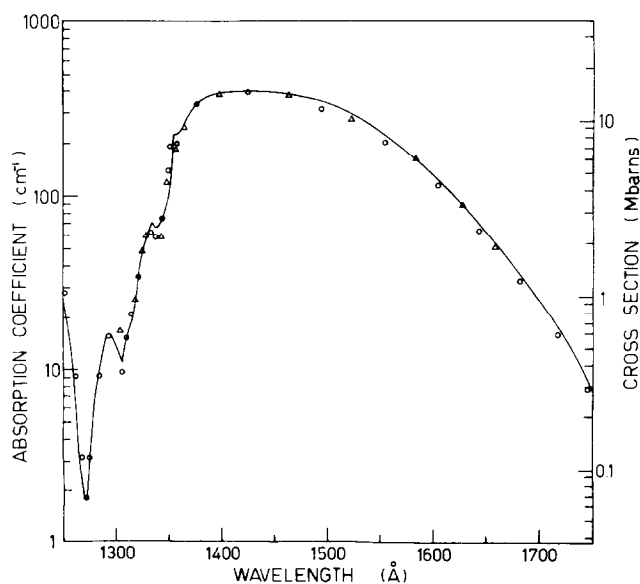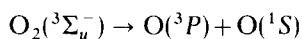$$O_2(^3\Sigma_u^-) \rightarrow O(^3P) + O(^1S)$$

FIG. 5. Absorption cross sections of molecular oxygen in the region 1250–1750 Å. The solid line represents the present results, the circles (○) those of WATANABE,[2] and the triangles (△) those of METZGER and COOK.[8]

The present data in this region were obtained using a 5 cm and 10 cm long absorption cell and pressures in the range 2 torr to 50 torr with a monochromator slit width of 30 μ corresponding to a resolution of 1 Å. The results are shown in Figs. 5 and 6 where they are compared with those of Watanabe[2] and Metzger and Cook.[8]
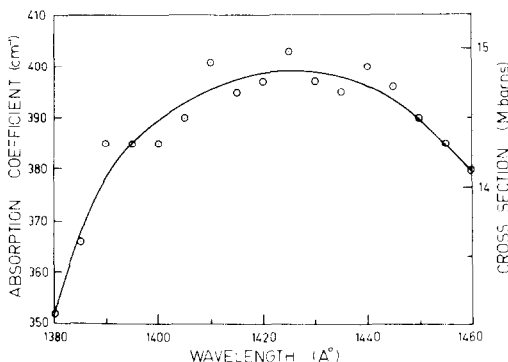

Fig. 6. Absorption cross section of molecular oxygen near the maximum of the Schumann–Runge continuum.

The main continuum has a rather flat maximum at 1425 Å where the absorption cross section is $(1.48 \pm 0.07) \times 10^{-17}$ cm^2. This result is in very good agreement with the values determined by Metzger and Cook[8] and by Huffman et al.[17] The cross sections at a number of wavelengths corresponding to strong lines in the ultra-violet spectrum[18] of the sun are listed in Table I. The estimated error in these cross sections is ± 5 per cent except for the OI lines at 1302,4,6 Å where the error is ± 10 per cent.

Table 1. O$_2$ Absorption cross section (σ) at solar lines

Wavelength	Solar line	Cross section
1302,4,6 Å	OI	4.6×10^{-19} cm^2
1334,5	CII	2.7×10^{-18}
1394	SiII	1.4×10^{-17}
1403	SiIV	1.45×10^{-17}
1548,51	CIV	8.7×10^{-18}
1656	CI	1.9×10^{-18}
1670	AlII, FeII	1.55×10^{-18}

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