ABSORPTION CROSS SECTIONS OF THE SCHUMANN–RUNGE BANDS OF MOLECULAR OXYGEN

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Abstract—A new study of the absorption bands of the Schumann–Runge system of molecular oxygen, which overlap the Herzberg continuum is made in order to improve the aeronomic calculations in the mesosphere and stratosphere. After a complete analysis performed at high resolution of the rotational structure from the (0–0) band at 2050 Å to the dissociation limit at 1750 Å, absorption cross section values for various rotational lines are measured from 2011·63 to 1763·66 Å using emission silicon lines of which wavelengths are known with high precision. The absorption cross sections are obtained with a 0·5 cm^{-1} resolution taking into account the rotational line shape due to predissociation, Franck–Condon factors and electronic absorption oscillator strengths.

1. INTRODUCTION

Absorption cross sections* of the Schumann–Runge band system ($B\,^3\Sigma_u^-\, -\, X\,^3\Sigma_g^-$) of O_2 have been measured for more than fifty years (see Fig. 1). The first investigations were undertaken in the laboratory or in the open air using arcs or sparks as light sources, and the measurements were made at specific wavelengths of various emission lines. This procedure was followed by Kreusler (1901), Granath (1929) and by Buisson et al. (1933). The large variation of absorption cross section with wavelength observed by these authors was not understood before the investigation of the fine structure of the various bands by Curry and Herzberg (1934), by Knauss and Ballard (1935) and by Brix and Herzberg (1954).

Using hydrogen continuum light sources, Watanabe et al. (1953) measured absorption cross sections. However, since their measurements were made at low resolution and without sufficient pressure broadening, they lead only to a qualitative indication of the cross sectional structure and they cannot be used to obtain oscillator strengths. See also Thompson et al. (1963) and Blake et al. (1966). Ditchburn and Heddle (1954) have measured the absorption cross section with an improved resolution and have obtained oscillator strengths under the assumption of a Doppler line half width. Their results have been shown to be considerably in error first by Bethke (1959b) and more recently by Hudson et al. (1968, 1969a, 1969b) who have indicated a line width much larger than would be expected from Doppler effects.

Predissociation in the oxygen molecule increasing the line width in the Schumann–Runge bands has been proposed by Flory (1936) to explain on one hand the absence of emission bands having $v' > 2$ or according to Feast (1949) $v' > 3$, and on the other hand the different photochemical effects due to the irradiation of oxygen in two different wavelength regions, namely those of the Schumann continuum and of the Schumann–Runge bands (Smith and Kistiakowsky, 1935). Wilkinson and Mulliken (1957) have given spectrographic evidence for line broadening and have come to the conclusion that predissociation occurs in some of the bands. From absorption measurements at 1781 and 1796 Å they also have inferred the probable existence of a continuum lying under the bands. From the study of his photographic spectra, Carroll (1959) observed important line broadening for $v' = 4$ and

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* The absorption cross section (σ) used here is defined by the relation $\sigma = [1/nd] \ln I_0/I$, where n is the number density in cm^{-3} of the absorbing gas in the optical path of length d in cm. I_0 and I respectively represent the incident and transmitted radiation intensities.
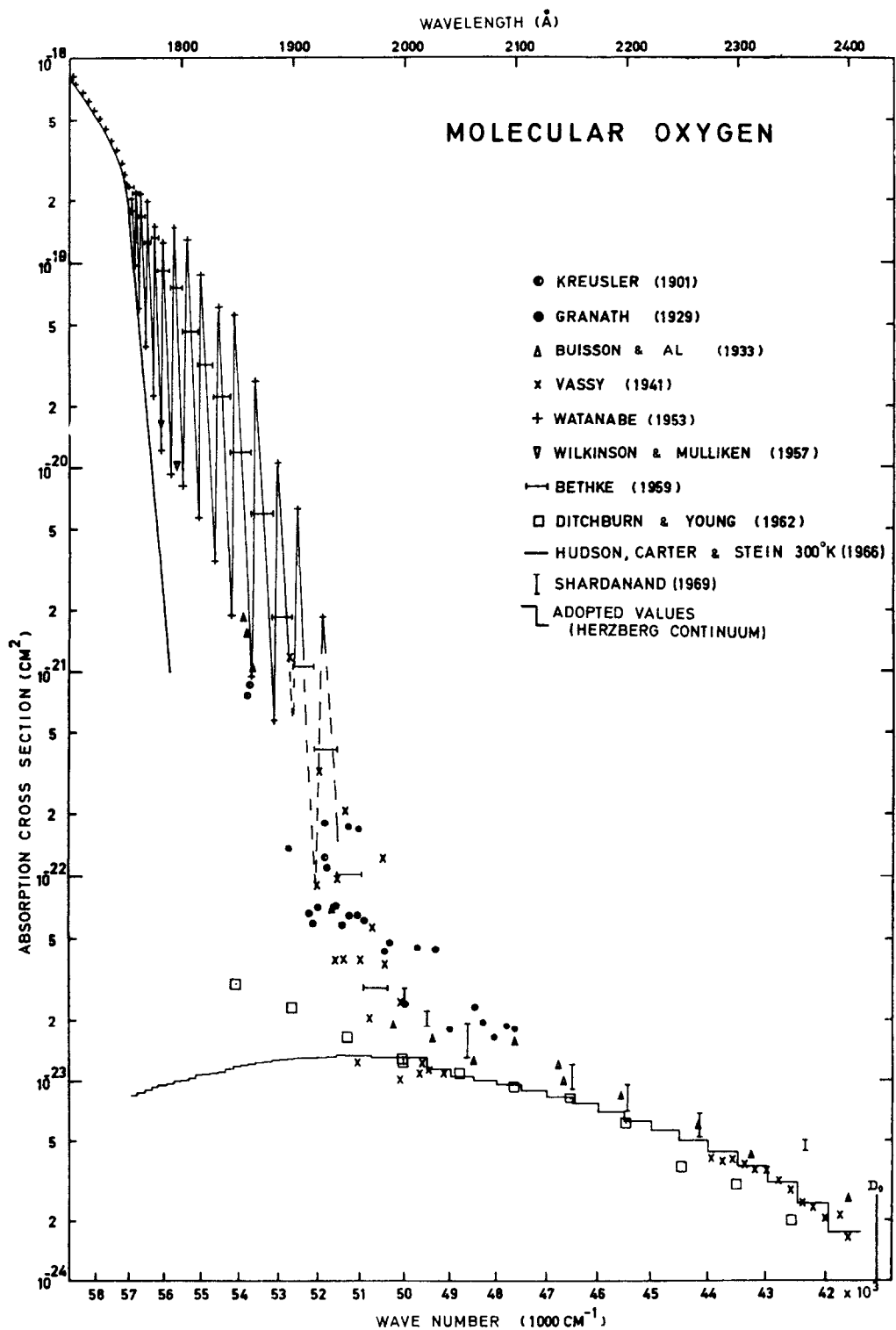
FIG. 1. EXPERIMENTAL ABSORPTION CROSS SECTIONS OF THE SCHUMANN–RUNGE BANDS OF
MOLECULAR OXYGEN.
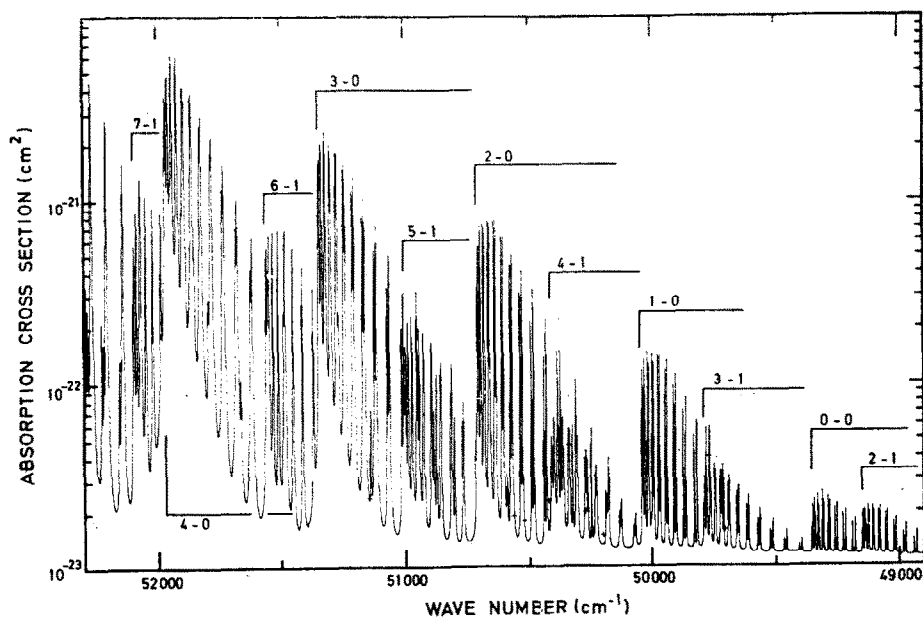Adopted values for the Herzberg continuum are also shown.

FIG. 2a. COMPUTED CROSS SECTION VS. WAVENUMBER FOR A 300°K TEMPERATURE FROM THE 2–1 to 7–1 BANDS.
Experimental values are represented by crosses. For wavenumbers less than 51,000 cm⁻¹, the effect of the Herzberg continuum is apparent.
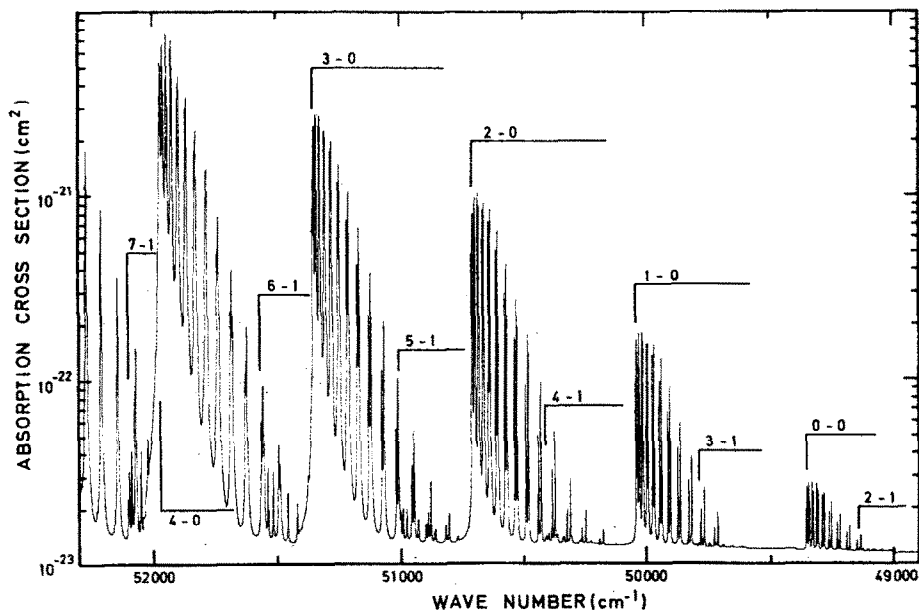

FIG. 2(b). COMPUTED CROSS SECTION VS. WAVENUMBER FOR A 200°K TEMPERATURE FROM THE 2–1 to 7–1 BANDS.
At such a low temperature the effect of the $v'' = 1$ bands becomes very small while the Herzberg continuum plays a role up to 52,000 cm⁻¹.

5 and, from an examination of absorption plates taken by Brix and Herzberg (1954), concluded that broadening was evident for bands having v' values from 8 through 13. Recently, Ackerman and Biaumé (1970) have systematically measured line half widths from the 0–0 to the 15–0 band. A rather good agreement has been found between the trend of observed line width vs. v' and the trend of the predissociation probability computed by Murrell and Taylor (1969) who have been able to characterize precisely the repulsive electronic state which is responsible for the predissociation.
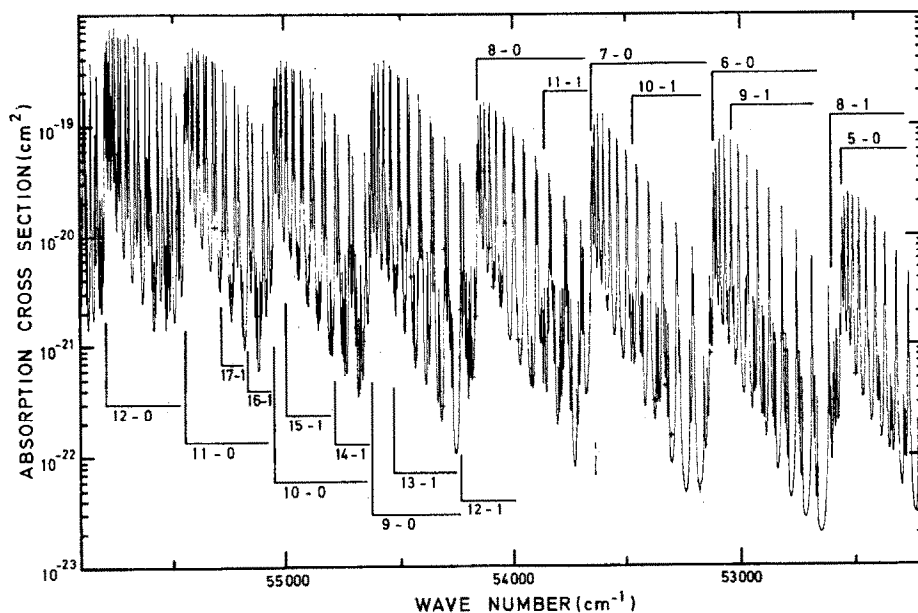

FIG. 3(a). COMPUTED CROSS SECTIONS VS. WAVENUMBER FOR A 300°K TEMPERATURE FROM THE 5–0 to 12–0 BANDS.
Experimental values are represented by crosses. The increase of the absorption cross section with the wavenumber is due to the greater overlapping of rotational lines in addition to the change in Franck–Condon factors.

From an aeronomical point of view, the Schumann–Runge bands of O_2 present a special interest due to the important role that they play in the stratosphere and mesosphere. They control almost completely the penetration of the solar radiation from roughly 2000 to 1750 Å i.e. from the 0–0 band to the second dissociation limit of the molecule at 7·08 eV. Since their absorption cross sections vary approximately between 10^{-19} cm^2 and 10^{-23} cm^2, it appears that the penetration of the vacuum ultraviolet solar radiation is affected from 15 km at the bottom of the stratosphere to above the mesosphere where the total molecular oxygen contents are respectively of the order of 5×10^{23} cm^{-2} and 1×10^{19} cm^{-2}. As already pointed out by Nicolet and Mange (1954), a precise knowledge of the absorption cross sections in the Schumann–Runge bands is required for the study of the chemosphere. A few authors have attempted to solve this specific problem. For example, values have been obtained at wavelengths greater than 1850 Å by Ditchburn and Young (1962) and by Hudson *et al.* (1966) at wavelengths smaller than 1800 Å. The association of these two sets of data would lead to the conclusion that the Schumann–Runge bands have a very low absorption cross section and play a role in the atmosphere in a narrow altitude region located in the low stratosphere. The straightforward contradiction between these results

and the previous ones, some of which having been reanalysed (Ackerman, 1970), has prompted the investigation reported here which is based on different types of data. First of all, absorption cross sections have been measured for 41 silicon emission lines from 1763·66 to 2011·63 Å of which the wavelengths are very accurately known. A preliminary interpretation (Ackerman et al., 1969) of the results has shown the need for more accurate spectroscopic data for the bands having v' values smaller than 12. Such new data have been obtained by Ackerman and Biaumé (1970) using spectra taken in the Physics Division of the
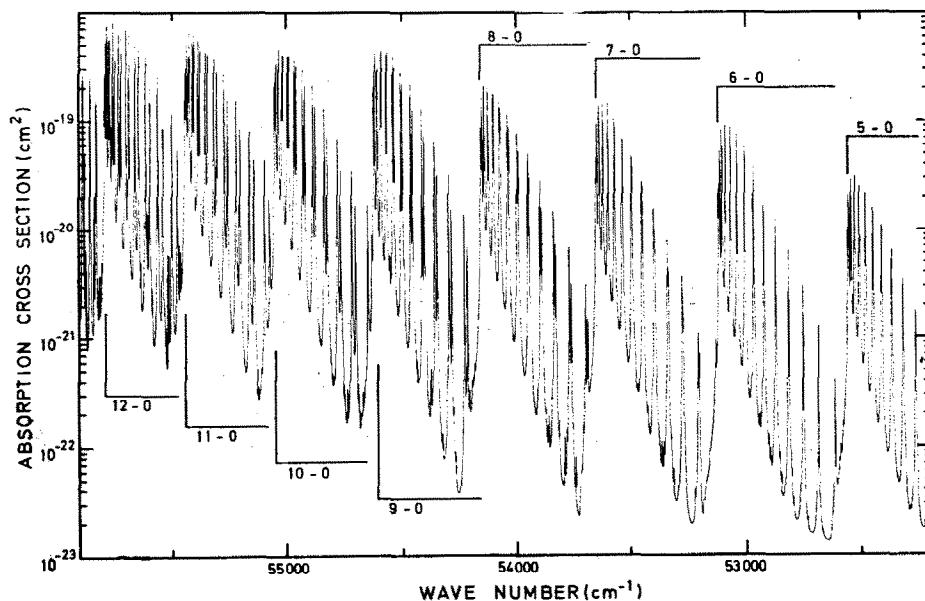

FIG. 3(b). COMPUTED CROSS SECTION VS. WAVENUMBER FOR A 200°K TEMPERATURE FROM THE 5–0 TO 12–0 BANDS.
Note the increasing importance of atmospheric windows when the temperature is lowered.

National Research Council of Canada (Ottawa). Simultaneously, line width values have been determined. In this paper we present a model for the absolute cross sections in the Schumann–Runge bands. This theoretical model will be shown to fit the experimental data.

2. EXPERIMENTAL DETAILS

The light source used for the measurements is a microwave discharge lamp. A vertical pyrex tube (20 cm length, 11 mm inside dia.) containing silicon tetrachloride is kept at dry ice temperature in a Dewar flask. An horizontal quartz tube is attached to it by means of a graded seal and is sealed at the end by a 'suprasil' plane window. The lamp attached to a gas manifold, is first thoroughly cleaned by successive microwave discharges in helium at a pressure of the order of 1 mm followed by evacuation. The emitted light is observed through a spectroscope and the cleaning process is stopped when the spectrum does not change from one discharge to the next one. $SiCl_4$ is then distilled under vacuum and subsequently trapped in the lamp at liquid nitrogen temperature. Helium at a pressure of 0·5 mm Hg is introduced and the lamp is sealed off. A similar device has been described by Kaufman et al. (1966). The emitted atomic spectrum has been analysed in detail (Radziemski et al., 1967). This lamp emits practically no continuous radiation.

The lamp is then placed so that the plane 'suprasil' window is in front of the entrance slit of a 50 cm focal length Bausch and Lomb grating monochromator adapted for vacuum operation and used in the first and in the third orders. After the exit slit, the light of proper wavelength enters a 401 cm length pyrex tube closed at each end with a 'suprasil' lens. The light intensity is monitored by an EMI 6255 Cd photomultiplier. The output is recorded for various O_2 pressures measured by using mercury manometers and MacLeod gauges. The measured cross sections are presented in Table 1. For most of the measurements Beer's
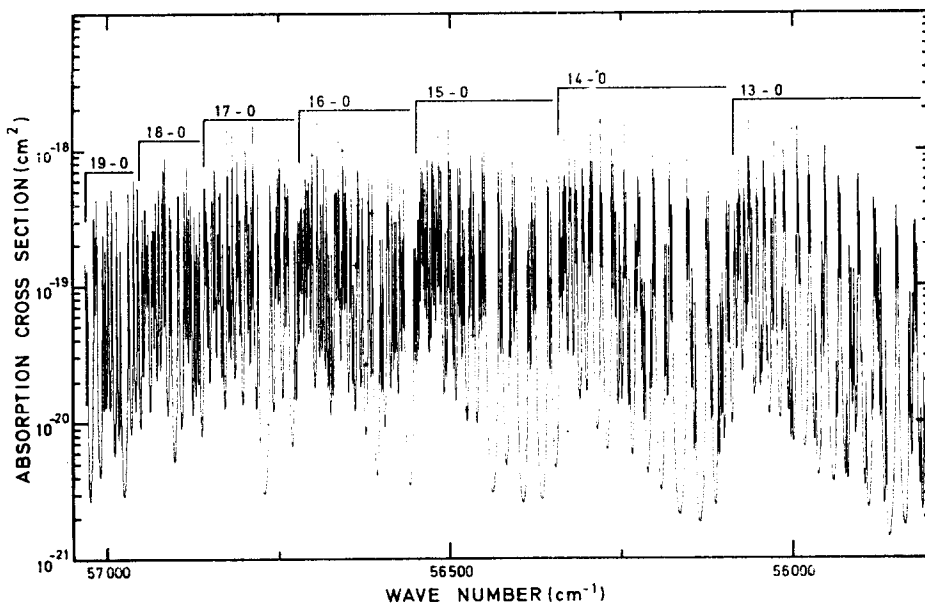

FIG. 4(a). COMPUTED CROSS SECTIONS VS. WAVENUMBER FOR A 300°K TEMPERATURE FROM THE 13–0 to 19–0 BANDS.
Experimental values are represented by crosses.

law was obeyed. In a few cases where an Si emission line was very close in wavelength to an O_2 absorption line, a negative pressure effect appeared. This is due to the absorption of the wing of one line in the steep wing of the other one. In some other cases, in the 3–0, 2–0 and 1–0 bands, a positive pressure effect was observed which is probably due to the absorption by O_4 which has been reported for instance by Heilpern (1941) and has now been more extensively studied by Shardanand (1969). When either one or other of these two effects has been encountered, the absorption cross section is marked by an asterisk in Table 1 and has been obtained by extrapolation to zero pressure.

3. INTEPRETATION OF THE DATA

(a) *Preliminary analysis*

A first study of the results showed a systematic decrease of the measured absorption cross sections for increasing differences between the wavenumbers of silicon atomic lines and oxygen rotational lines. A systematic correlation was then made which has been presented by Ackerman *et al.* (1969). An O_2 Schumann–Runge rotational line profile was deduced for some bands and was found to be of Lorentz type with an average width value equal to 1·4 cm^{-1}. This value had to be tentatively assigned and by its combination with values of

TABLE 1. EXPERIMENTAL ABSORPTION CROSS SECTIONS FOR O_2 IN THE SCHUMANN–RUNGE BANDS AT $T = 300°K$

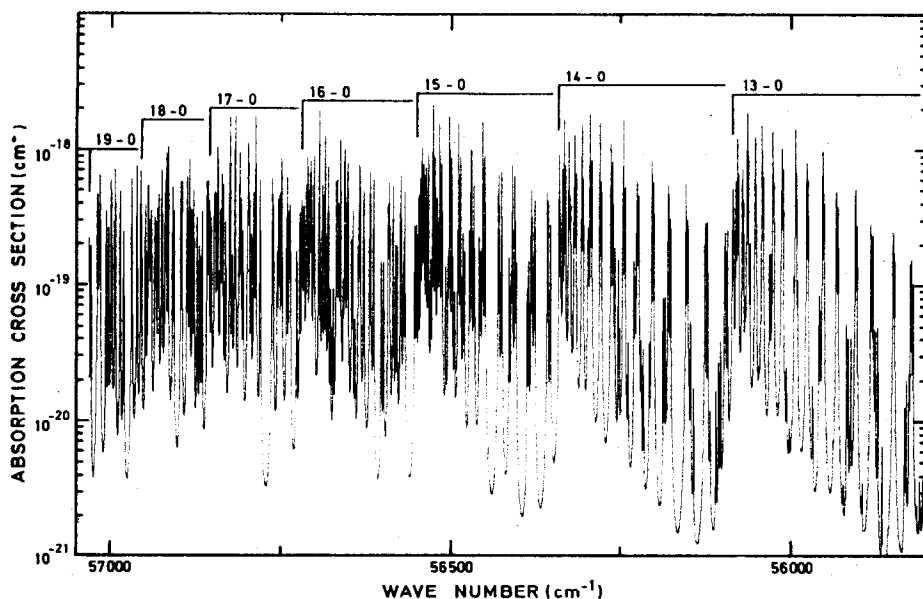| ν (cm⁻¹)	λ (Å)	σ (cm²)	ν (cm⁻¹)	λ (Å)	σ (cm²)
56700·25	1763·66	$9·25 \times 10^{-19}$*	54034·40	1850·67	$1·31 \times 10^{-20}$
56656·27	1765·03	$1·00 \times 10^{-18}$	53981·90	1852·47	$1·11 \times 10^{-21}$
56637·28	1765·62	$1·42 \times 10^{-19}$	53387·30	1873·10	$3·14 \times 10^{-22}$
56623·13	1766·06	$2·65 \times 10^{-20}$	53337·80	1874·84	$4·28 \times 10^{-22}$
56613·79	1766·35	$3·46 \times 10^{-19}$*	53310·20	1875·81	$1·50 \times 10^{-22}$
56477·09	1770·62	$1·23 \times 10^{-20}$	53139·10	1881·85	$8·28 \times 10^{-22}$
56467·75	1770·92	$4·24 \times 10^{-20}$	52974·70	1887·69	$1·71 \times 10^{-20}$
56280·19	1776·82	$1·58 \times 10^{-18}$	52819·20	1893·25	$1·23 \times 10^{-21}$
55309·40	1808·01	$1·21 \times 10^{-20}$	52594·50	1901·33	$3·06 \times 10^{-22}$
55276·00	1809·10	$1·15 \times 10^{-20}$	52502·70	1904·66	$5·26 \times 10^{-22}$
55124·40	1814·07	$1·90 \times 10^{-21}$	51151·70	1954·96	$2·40 \times 10^{-23}$*
55038·00	1816·92	$1·60 \times 10^{-19}$	50566·40	1977·59	$1·90 \times 10^{-23}$*
54451·00	1836·51	$4·24 \times 10^{-21}$	50525·30	1979·20	$1·80 \times 10^{-23}$*
54313·80	1841·15	$2·87 \times 10^{-22}$	50489·30	1980·61	$2·50 \times 10^{-23}$*
54305·10	1841·44	$7·54 \times 10^{-21}$	50422·70	1983·23	$2·30 \times 10^{-23}$*
54236·70	1843·76	$2·11 \times 10^{-21}$	50343·20	1986·36	$4·60 \times 10^{-23}$*
54185·30	1845·51	$5·12 \times 10^{-22}$	50276·70	1988·99	$2·00 \times 10^{-23}$*
54167·90	1846·11	$1·85 \times 10^{-21}$	50204·50	1991·85	$1·50 \times 10^{-23}$*
54128·00	1847·47	$3·83 \times 10^{-20}$	49773·70	2009·09	$4·00 \times 10^{-23}$*
54108·15	1848·15	$7·71 \times 10^{-21}$	49710·60	2011·64	$1·60 \times 10^{-23}$*
54090·70	1848·74	$3·39 \times 10^{-21}$			

FIG. 4(b). COMPUTED CROSS SECTION VS. WAVENUMBER FOR A 200°K TEMPERATURE FROM THE 13–0 to 19–0 BANDS.

band oscillator strengths the best fit to the experimental data could be reached by a rather empirical trial and error process. This demonstrated however that the natural shape, and moreover the Doppler shape of the lines, were overshadowed by a Lorentz profile of such a large width that only predissociation could explain it.

To improve the interpretation of the experimental results it appeared necessary to represent the absorption cross section in the Schumann–Runge bands by a large number of overlapping rotational lines, each having long wavenumber range effects. Since the line centre can be precisely located, a computation can be made provided that band integrated absorption cross sections are distributed over the rotational lines having a Lorentz profile with a definite half width and relative intensities within a band governed by the temperature of the gas.

(b) *Wavenumbers of rotational lines*

For the $v'' = 0$ sequence, a sufficient number of measured rotational wavenumbers are available so that experimental values have been taken from Brix and Herzberg (1954) for the 13–0 to the 19–0 bands and from Ackerman and Biaumé (1970) for the 0–0 to 12–0 bands. The 20–0 and 21–0 bands have not been directly considered. They have a small practical influence since the wavenumber interval that they cover is only of the order of 100 cm⁻¹ and an extrapolation of Schumann–Runge continuum can reasonably be used in this spectral region.

Since for the $v'' = 1$ sequence too few experimental values are available, the rotational wavenumbers, v_i, have been determined from the relation (Herzberg, 1950),

$$v_i = v_0 + (B_v' + B_v'')m + (B_v' - B_v'' - D_v' + D_v'')m^2$$
$$-2(D_v' + D_v'')m^3 - (D_v' - D_v'')m^4 \tag{1}$$

which is applicable to P and R branches corresponding to allowed transitions in the case of a $\Sigma - \Sigma$ system. In Equation (1) v_0 is the band origin available from the $v'' = 0$ bands since the energy difference (1556·39 cm⁻¹) between the $v'' = 0$ and the $v'' = 1$ vibrational levels is precisely known from the work of Babcock and Herzberg (1948). The values of the rotational constants B_v and D_v have been taken from Brix and Herzberg (1954) and from Ackerman and Biaumé (1970) for the upper state, and from Babcock and Herzberg (1948) for the lower state. The triplet splitting has been taken into account for the bands in which it can play a role, namely for v' values larger than 12 by using the triplet constants given by Brix and Herzberg (1954) for the upper states and by Babcock and Herzberg (1948) for the lower ones.

All rotational lines contributing significantly to the absorption cross section have been taken into account. For the $v'' = 1$ sequence, lines of the bands from 2–1 to 17–1 contribute to the absorption under aeronomic conditions.

(c) *Band integrated absorption cross sections*

If $\sigma(v)$ (cm²) represents the absorption cross section of a line as a function of wavenumber v(cm⁻¹), the band integrated absorption cross section K(cm) can be written (Bethke, 1959a; Herzberg, 1950).

$$K = \int \sigma(v) \, dv = \frac{\pi e^2}{mc^2} f(v', v'')F(v'') = 8\cdot853 \times 10^{-13} f((v', v'')F(v''). \tag{2}$$

In Equation (2), m and e are the mass and charge of the electron respectively, $F(v'')$ is the fraction of molecules in the lower vibrational state and $f(v', v'')$ is the total band absorption oscillator strength. As will be shown later, the effect of the temperature dependent term $F(v'')$ can be very important under aeronomic conditions.

The band oscillator strengths are related to the Franck–Condon factors $q(v', v'')$ and to the electronic absorption oscillator strength f_{el} by the relation (Bethke, 1959a)

$$f(v', v'') = f_{el}q(v', v'')\nu_0(v', v'')/\nu_{max} \qquad (3)$$

where $\nu_0(v', v'')$ is the band origin wavenumber and ν_{max} corresponds to the wavenumber at the maximum absorption in the Schumann–Runge continuum, i.e. 68,500 cm^{-1}. Several values of f_{el} deduced from optical measurements are available in the literature for the $^3\Sigma_g^- - \,^3\Sigma_u^-$ transition of O_2 considered here. Watanabe *et al.* (1953), Bethke (1959b), Goldstein and Mastrup (1966) and Farmer *et al.* (1968) have respectively found f_{el} equal to 0·161, 0·163, 0·156 and 0·162. The last value, in good agreement with the others, has been used in the present work.

In the $v'' = 0$ sequence, the Franck–Condon factors $q(v', 0)$ computed by Jarmain (1963) have been used except from the 5–0 to 13–0 bands where unpublished values of Jarmain and Nicholls have been deduced from the work of Hudson and Carter (1968). The values of $K(v'' = 0)$ obtained in this manner are in good agreement with the experimental data of Bethke (1959b) for the bands that he has measured. In the $v'' = 1$ sequence the $q(v', 1)$ factors have been calculated from the $q(v', 0)$ values multiplied by the ratio $q(v', 1)/q(v', 0)$ computed by Harris *et al.* (1969).

The integrated band absorption cross sections finally deduced are listed in Table 2.

(d) *Rotational line shape*

As shown by Rice (1930) the following relation

$$\sigma(\nu) = \frac{2k_0/\pi\Delta\nu}{1 + [(2\nu - \nu_i)/\Delta\nu]^2} \qquad (4)$$

can be used to represent the line absorption cross section $\sigma(\nu)$ as a function of the wavenumber ν in case of predissociation broadening. In Equation (4), k_0 is, for a specific line, the integrated absorption cross section expressed here in cm; ν_i is the wavenumber at the centre of the line determined as already described in paragraph B of this section. The line width is represented by $\Delta\nu$ and the adopted values, listed in Table 2 are practically identical with those measured by Ackerman and Biaumé (1970). For the same v' values, the same line width has been used in both the $v'' = 0$ and $v'' = 1$ sequences. All the lines of a band have been assumed to have the same width. The values of k_0 have been obtained from the integrated band absorption cross sections K, listed in Table 2, by attributing a weight to each line of the band according to the temperature dependent population of the rotational levels of the $X\,^3\Sigma_g^-$ state. The integration of all the k_0 values in one band leads, of course, to the corresponding value of K.

(e) *Computation*

The computation of the absorption cross section spectra, involving a total number of 2622 rotational lines, has been carried out on the IBM 1800 of the Institute of Aeronomy between 57030·5 cm^{-1} and 48767·5 cm^{-1} from the previously described input data. Since the overlap of lines belonging either to the same band or even to different bands is important,

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TABLE 2. BAND INTEGRATED ABSORPTION CROSS SECTIONS, K, IN cm AND ADOPTED LINE
WIDTHS $\Delta\nu$ IN cm^{-1} (SCHUMANN-RUNGE BANDS OF O_2)

v'	$\Delta\nu$	$K(v'' = 0)$	$K(v'' = 1, T = 300°K)$
0	1·00	$3·05 \cdot 10^{-22}$	—
1	1·10	$3·45 \cdot 10^{-21}$	—
2	1·20	$2·10 \cdot 10^{-20}$	$2·72 \cdot 10^{-22}$
3	2·20	$8·75 \cdot 10^{-20}$	$1·06 \cdot 10^{-21}$
4	3·70	$2·84 \cdot 10^{-19}$	$3·13 \cdot 10^{-21}$
5	2·30	$7·53 \cdot 10^{-19}$	$7·78 \cdot 10^{-21}$
6	1·90	$1·69 \cdot 10^{-18}$	$1·60 \cdot 10^{-20}$
7	2·20	$3·37 \cdot 10^{-18}$	$2·94 \cdot 10^{-20}$
8	2·00	$5·91 \cdot 10^{-18}$	$4·78 \cdot 10^{-20}$
9	1·10	$9·39 \cdot 10^{-18}$	$7·00 \cdot 10^{-20}$
10	1·70	$1·39 \cdot 10^{-17}$	$9·72 \cdot 10^{-20}$
11	1·70	$1·85 \cdot 10^{-17}$	$1·21 \cdot 10^{-19}$
12	1·00	$2·24 \cdot 10^{-17}$	$1·39 \cdot 10^{-19}$
13	0·60	$2·55 \cdot 10^{-17}$	$1·49 \cdot 10^{-19}$
14	0·50	$2·68 \cdot 10^{-17}$	$1·50 \cdot 10^{-19}$
15	0·50	$2·58 \cdot 10^{-17}$	$1·41 \cdot 10^{-19}$
16	0·50	$2·29 \cdot 10^{-17}$	$1·23 \cdot 10^{-19}$
17	0·50	$1·97 \cdot 10^{-19}$	$1·02 \cdot 10^{-19}$
18	0·50	$1·62 \cdot 10^{-17}$	—
19	0·50	$1·27 \cdot 10^{-17}$	—

the process consists in computing at a specific wavenumber the contribution to the absorption cross section due to all the lines having their maximum intensity within an interval of 150 cm^{-1} centered on the specific wavenumber. The sum of the different contributions is then made. The same procedure is then reproduced at another specific wavenumber differing from the first one by 0·5 cm^{-1} and so on. Such a small step has been used in order to obtain a worthwhile resolution on the spectra. Since the absorption cross section due to the Herzberg continuum was expected to bring a contribution, mainly at small wavenumbers by underlying the Schumann–Runge bands, its values, shown in Fig. 1 and taken from the work of Jarmain and Nicholls (1967), have been added.

4. RESULTS AND DISCUSSION

Absorption cross section spectra have been plotted directly from the IBM 1800 by means of a data plotter. They are shown in Fig. 2(a), 3(a) and 4(a) for a temperature of 300°K and in Figs. 2(b), 3(b) and 4(b) for 200°K. It has been necessary to split the spectra into three successive portions for each temperature so as to give a complete display of most of the features.

On the 300°K spectra, the experimental values listed in Table 1 have been represented by crosses. The agreement between the calculated and measured absorption cross sections is quite satisfactory. It indicates that the model which represents the absorption in the Schumann–Runge bands is consistent with the results of the measurements. The combination of the adopted values of the band integrated absorption cross section, K, and of the line width, $\Delta\nu$, leads to a perfect agreement with the measurements. For example, the details of the 8–0 and 9–0 bands which are shown in Fig. 5 indicate over an interval of 470 cm^{-1} 11 measured absorption cross sections at different distances from the centre of different rotational lines. There is practically no difference between experimental and computed values of the absolute cross sections.

It can also be pointed out that measurements at 300°K can not be interpreted without introducing the rotational lines belonging to the $v'' = 1$ sequence in addition to the Herzberg
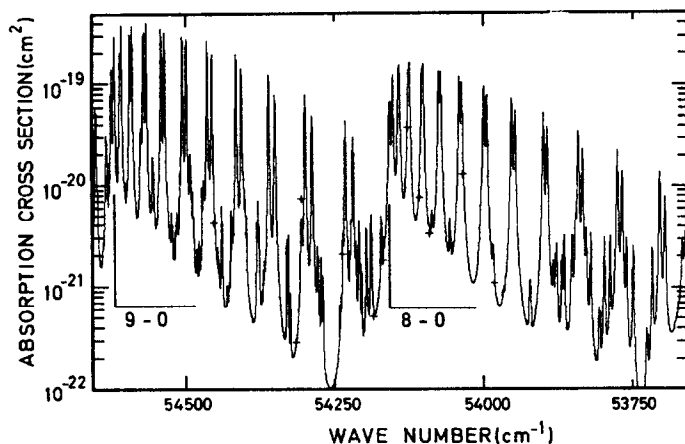
FIG. 5. DETAILED COMPARISON BETWEEN THE CALCULATED VALUES OF THE CROSS SECTION IN THE 8–0 AND 9–0 BANDS AND THE EXPERIMENTAL DATA (CROSSES) OBTAINED (SEE TABLE 1) AT WAVE-LENGTHS OF ATOMIC SILICON LINES.

continuum. In Fig. 2(a), for instance, the experimental points within the 4–1 and 3–1 bands closely fit the theoretical spectrum at 300°K. But, if those measured values had been plotted in Fig. 2(b) for a 200°K spectrum, they would not have matched the theoretical curve. This clearly shows the temperature effect on the absorption cross section. Nevertheless, as shown here, the line spectrum also leads in some way to some kind of continuous absorption even if the cross section varies by several orders of magnitude over small wavelength intervals.

The 200°K spectra of Figs. 2(b), 3(b) and 4(b) show the important impact on the absorption cross section resulting from the change with temperature of both rotational and vibrational populations in the ground electronic state of the molecule. In particular, the effect of the $v'' = 1$ sequence is not important.

5. CONCLUSION

The whole structure of the absolute values of the absorption cross section in the Schumann–Runge bands of O_2 has been obtained with a model which reproduces experimental data. Such a model is based on a predissociation line broadening and can by calculation take into account temperature effects which can be important. In fact the values of the band integrated absorption cross sections and of the rotational line widths which have been adopted determine the cross section values of the model. The uncertainty which may remain is related to the approximations involved in these two parameters.

In any case, for the first time sufficient data are available to permit the evaluation, in the spectral range of the Schumann–Runge bands, of the penetration of the solar ultraviolet radiation in a planetary atmosphere. This penetration is complex since it involves a high spectral resolution and is subject to a temperature effect. In the terrestrial atmosphere the absorption occurs in atmospheric regions where the temperature varies from 160 to 300°K. A complete analysis of the solar radiation absorption in spectral range of the Schumann–Runge bands will be presented in another paper.

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