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GEOPHYSICAL RESEARCH LETTERS, VOL. 11, NO. 12, PAGES 1199-1202, DECEMBER 1984

NEW IN-SITU MEASUREMENTS OF THE ABSORPTION CROSS-SECTIONS OF O_2 IN THE HERZBERG CONTINUUM

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Abstract. The absorption cross-sections of both O_2, from 200 to 220 nm, and O_3 from 220 to 235 nm have been deduced from measurements of the atmospheric absorption performed at night aboard a stratospheric balloon launched from Aire sur l'Adour (France).

The ozone column content was previously determined using the absorption measured from 278 to 289 nm, assuming that the ozone absorption cross sections are well known in this wavelength interval. The O_2 and O_3 cross sections have been found to meet most of the laboratory measurements. From 200 to 210 nm the results concerning the O_2 cross-sections do not confirm the low values measured recently in the stratosphere and in the laboratory.

Introduction

The atmospheric absorption in the Herzberg continuum of O_2 (200 - 242 nm) is of utmost importance for the atmospheric chemistry, but owing to their low values in this continuum, the molecular oxygen absorption cross-sections are extremely difficult to measure accurately in the laboratory. Measurements have been given first by Ditchburn and Young (1962), Hasson and Nicholls (1971), Ogawa (1971) and Shardanand and Prasad Rao (1977). All these results were consistent within ± 20 % from 200 nm to 230 nm. Nevertheless very recent measurements give values 30 to 45 percent smaller than the smallest previous ones (Chueng et al., 1984) from 200 to 204 nm. A reduction of these cross-sections seems confirmed by stratospheric measurements (Frederick and Mentall, 1982), (Herman and Mentall, 1982), (Anderson and Hall, 1983). Nevertheless the reduction percentages are somewhat different ranging from 8 % (Frederick and Mentall, 1982) to 25 % (Herman and Mentall, 1982) in this wavelength interval. The problem is therefore not yet solved. The present work reports on new measurements of the O_2 absorption cross-sections performed from a 330,000 m^3 stratospheric balloon with gas-release valve, over Aire sur l'Adour (43° 42' N, 0° 15' W), in very different experimental conditions from the previous ones. Indeed the measurements have been made at night instead of the day, moreover the oblique column densities crossed by the light was smaller than in the other experiments and the altitude range was different (37 to 38 km instead of 32 to 38 km).

Paper number 4L6276.
0094-8276/84/004L-6276 $03.00.

Experiment and Data Description

The balloon borne spectrophotometer used is described elsewhere (Rigaud et al., 1983). The light collector is a 20 cm Cassegrain telescope with a 1 meter focal length. The dispersion element is a double grating monochromator Jobin-Yvon DH 10 controlled by a stepping motor. In this experiment a spectral span of 102.4 nm (187 - 289.4 nm) is swept cyclically in 0.2 nm increments at the speed of 1 nm sec^{-1} with a final resolution of 1 nm. The detector is a bialkali photomultiplier with a quartz-window, used in the photon counting-mode. The flight took place on the night of May 13-14, 1983. The useful measurements have been performed from 2114 : 51 UT to 2400 : 40 UT ; 91 scans (102.4 s each) have been recorded. The balloon was at an almost constant ceiling from 2114 :51 up to 2230 : 00 at a pressure ranging from 3.66 to 3.85 mb (∿ 38 km). Then, it was slowly descending up to 4.28 mb (∿ 37 km). The star α Lyr has been used as the light source. Its zenith angle was decreasing from 63° to 34°. The experiment was performed with a high resolution barometer (Crouzet 44) to determine exactly the measurement altitude.

Data Analysis

The light flux $F_i(P)$ measured at the altitude at which the pressure is P and at the step i of the scan in wavelength may be written with a good accuracy above 200 nm

$$\text{Log } F_i(P) = \text{Log } F_{oi} - \left(\sum_{s=1}^{2} N(s,P)\, \sigma_{is} + N(M,P)\sigma_{iR} \right) Ch(X) \quad (1)$$

where F_{oi} is the flux above the atmosphere, σ_{is} is the absorption cross-section of the species s (s may be O_3 or O_2), σ_{iR} is the single Rayleigh scattering cross-section, N(s,P) is the vertical column content of the species s from the altitude at which the pressure is P to the top of the atmosphere, N(M,P) is the vertical total column content above the altitude at which the

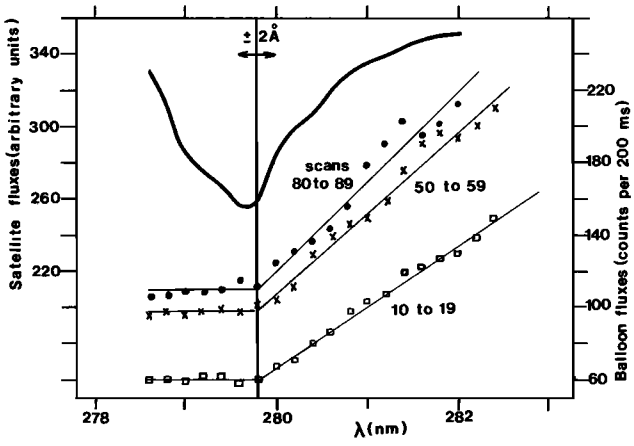

Fig. 1. Comparison of light fluxes from the star α Lyr measured by satellite (full line) and at different balloon levels (symbols, see below). The resolution is 1 nm for both set of measurements. The balloon measurements have been averaged over 10 scans to reduce the statistical fluctuations. The averaged values over the scans 10 to 19 (squares), 50 to 59 (crosses) and 80 to 89 (dots) are shown.

pressure is P, χ is the zenith angle and Ch(X) is the Chapman function.

At each wavelength we have recorded 91 values (one per scan) of the light fluxes as a function of the pressure and of the zenithal angle of the star. The O_2 absorption cross-section may therefore be computed solving the 91 equations (1) using a weighted linear least squares method with 2 unknown parameters : F_{oi} and σ_{O2}. The other parameters are either known or may be computed previously. Since the pressure is measured, $N(O_2,P)$ and $N(M,P)$ are known. The following relations have been used : $N(O_2,P)_{22} = 4.44 \times 10^{21} \times P(mb)$ cm^2 ; $N(M,P) = 2.12 \times 10^{22} \times P$ (mb) cm^2. The Rayleigh scattering cross-sections given by Bates (1984) and the O_3 absorption cross-sections given by Inn and Tanaka (1959) have been assumed to be exact. The ozone column content alone has to be determined previously.

Determination of the Vertical Ozone Column Content

To this end the light fluxes measured from 278 to 289 nm have been used. In this wavelength interval indeed, the molecular oxygen is not absorbing and the O_3 cross-sections are relatively well known. The means of the cross-sections given by Inn and Tanaka (1959) and by Bass and Paur (1981) have been used. Relation (1) may therefore be used to compute the vertical ozone column content. A good accuracy can be obtained because the ratios of the minimum fluxes over the maximum ones are very adequate ranging from 0.7 at 289 nm and 0.3 at 278 nm. Nevertheless in this interval the O_3 cross-sections are varying somewhat fastly as a function of the wavelength. So, small errors in the calibration in wavelength could lead to errors in the column content which are not negligible. As seen on Figure 1 a rapid increase of the fluxes measured over the atmosphere by satellite (Lamers et al., 1981), above 279.8 nm is also seen at the balloon levels above the same wavelength. This warrants that the calibration in wavelength performed in the laboratory was not changing during the flight or at least that the shift if it exists is lower than ± 2 A. We can nevertheless remark that the same increase of the satellite fluxes below 279.6 nm is not observable at the ballon level but such a feature is expected because the absorption cross- sections are increasing as the wavelength decreases. We may also notice on the figure that the flux increase is seen at the same wavelength whatever the scans are. We can therefore warrant moreover that the calibration was not changing as a function of the time, or at least that the shift is lower than ± 2 A. It has been shown nevertheless that the uncertainties in the calibration have to be taken into account.

Assuming the mean pressure scale height H_p given by the U.S. Standard Atmosphere (1976), the ozone column content may be written :

$$N(O_3, P) = N(O_3, P_o) \times (P/P_o)^{H_p/HO_3} \qquad (2)$$

where HO_3 is the unknown ozone scale height which is assumed to be constant over the altitude range of the measurements (37 - 38 km) and $N(O_3, P_o)$ is the ozone column content at a pressure P_o.

In the wavelength interval under consideration in this section (278 - 289 nm) Rayleigh scattering is negligible so the relation (1) may be written, taking (2) into account :

$$\text{Log } F_i(P) = \text{Log } F_{oi} - N(O_3, P_o) \times (P/P_o)^{H_p/HO_3} \, Ch(X) \, \sigma_{iO3} \qquad (3)$$

The unknown parameters are F_{oi}, $N(O_3, P_o)$ and HO_3. At each wavelength (between 278 and 289 nm), 91 values (one per scan) of $F_i(P)$ have been recorded. The unknown parameters may therefore be computed at each wavelength solving the set of 91 equations using a weighted least squares method. The results show that $N(O_3, P_o)$ and HO_3 are not functions of the wavelength as expected although owing to the statistical fluctuations in the measurements they fluctuate slightly around means which are respectively $HO_3 = 4.85$ km and $N(O_3,P_o) = 3.93 \times 10^{17}$ cm^2 at $P_o = 3.77$ mb. The random uncertainties in both parameters are ± 2 %. We have to point out that, if the pressure scale height that we have assumed is not exact, this leads to a systematic error in HO_3 but not in the ozone column content. On the contrary, the uncertainties in the calibration in wavelength discussed previously lead to systematic errors in the column content. These errors are ± 2 % in $N(O_3,P_o)$ and ± 7 % in HO_3. The uncertainties in the O_3 absorption cross-sections also lead to systematic errors in $N(O_3, P_o)$. Assuming first Inn and Tanaka cross-sections then Bass and Paur ones leads to an uncertainty of ± 2 % on this parameter. Finally we have adopted $HO_3 = 4.85$ km ± 6 % and $N(O_3,P_o) = 3.93 \times 10^{17}$ cm^2 ± 9 % at 3.77 mb.

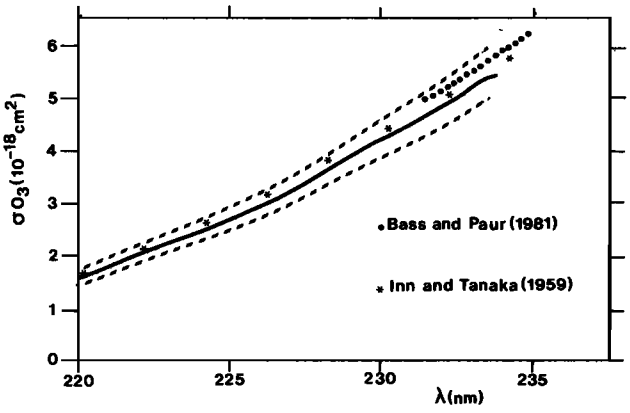

Fig. 2 The O_3 absorption cross-sections as a function of the wavelength from 220 to 235 nm. The solid line joins the values of σ_{i03} averaged over 10 steps of the scan. The dashed lines show the minimum and maximum possible averaged values due to the systematic errors in the ozone column content and in the calibration in wavelength.

Molecular Oxygen Absorption Cross-Sections From 200 nm to 220 nm

Stratospheric measurements do not allow the determination of the O_2 absorption cross-sections above about 220 nm because the ozone absorption is largely prevailing over the O_2 absorption.

On the contrary, assuming approximate values of the O_2 cross-sections it is possible to compute the O_3 cross-sections with a good accuracy solving, at each wavelength above 220 nm, the set of 91 equations (1) by a linear least squares method. The results are shown on Figure 2 up to 235 nm. O_2 cross-sections given by Nicolet (1978) have been used. Our values are about 2 % lower than those given by Inn and Tanaka and 4 % lower than those given by Bass and Paur above 230 nm. These difference can be easily explained either by systematic errors on the ozone column content as discussed above (see Figure 2) or by uncertainties in the laboratory measurements. This result proves that the ozone column content has been well determined assuming the possible systematic errors already discussed.

As the wavelength decreases from 220 nm the O_2 absorption increases and becomes comparable with the O_3 absorption. Assuming that the O_3 cross-sections are known it is possible to compute the O_2 cross-sections from 200 to 220 nm as seen previously. In this interval the ratios of the minimum fluxes over the maximum ones are about 0.75. The random uncertainties infered from the least squares method are relatively important because these ratios are somewhat large but they are still reasonnable because the number of measurements is important. These random uncertainties have been found to be about 10 %. These ones have been reduced to 3 % in averaging the O_2 cross-sections over 10 steps of the scan.

TABLE 1. O_2 Absorption cross-sections

Wavelength (nm)	Averaged O_3 cross-sections (10^{-24} cm^2)	Uncertainties
202.1	10.2	9 %
204.	9.8	10 %
206.	9.8	12 %
208.	8.8	14 %
209.9	8.5	16 %
211.9	8.0	24 %
213.9	8.0	30 %
215.8	7.1	41 %
217.8	6.7	52 %
219.8	4.8	85 %

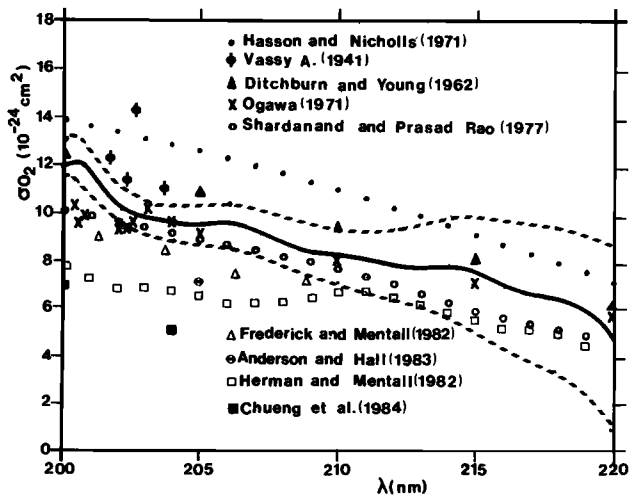

Fig. 3 The O_2 absorption cross-sections as a function of the wavelength from 200 to 220 nm. The solid line joins the values of σ_{i02} averaged over 10 steps of the scan. The dashed lines show the minimum and maximum possible values of σ_{i02} averaged over 10 steps of the scan due to the systematic errors in the ozone column content and in the calibration in wavelength. Earlier measurements are indicated with different symbols.

Other errors are systematic and are due to the errors in the ozone column content and in the calibration in wavelength. Table 1 gives some numerical results. The uncertainties include random and systematic ones. These results are also shown on Figure 3 and compared with earlier measurements. We have to point out that from 200 to 205 nm our absorption cross-sections obviously include the absorption which comes from both the Herzberg continuum and the Schumann Runge bands (1,0), (0,0), (2,1), and (3,1). The (1,0) band is clearly seen around 200.5 nm. Assuming a small influence of the (0,0), (2,1) and (3,1) bands on the results we may conclude that, above 202 nm our measured values of the O_2 cross-sections are between those given by Ogawa (1971) and by Vassy (1941) or by Ditchburn and Young (1962). The more recent laboratory measurements given by Shardanand and Prasad Rao (1977) and the atmospheric measurements given by Frederick and Mentall (1982) and by Anderson and Hall (1983) are also consistent with our measurements taking into account the relatively large uncertainties. On the contrary Hasson and Nicholls

(1971) give larger values while Herman and Mentall (1982) and Chueng et al. (1984) give smaller values. Let us remark that no uncertainty in the O_3 cross-sections has been taken into account from 200 to 220 nm. We have shown that if uncertainties of ± 5 % are assumed in these cross-sections this leads to uncertainties in the O_2 cross-sections which range from 3 % at 202 nm to 9 % at 210 nm. Such values do not change the main conclusions.

Conclusion

A balloon borne experiment has enabled us to study the stratospheric absorption in the "atmospheric window" near 200 nm. Assuming a good knowledge of the absorption cross-sections of O_3 from 278 to 289 nm, we have deduced the absorption cross-sections of O_2 in the Herzberg continuum from 202 to 220 nm and those of O_3 from 220 to 235 nm. The results are consistent with most of the laboratory values, and do not confirm the recent atmospheric measurements given by Herman and Mentall (1982) or the laboratory results of Chueng et al. (1984). To confirm this very important result we plan to measure again these cross-sections in somewhat different experimental conditions in a near future.

Acknowledgments. We wish to express our gratitude to the French Space Agency C.N.E.S. and to the Swiss Science Foundation for their constant support to this project.

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(Received June 6, 1984 ;
revised October 5, 1984 ;
accepted October 9, 1984.)