



Absorption Spectra Measurements for the Ozone Molecule in the 350–830 nm Region

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Abstract. Absolute absorption cross-sections of ozone have been measured at ambient (295 K) and low temperature (218 K) in the visible region corresponding to the Chappuis bands. The temperature effect has been studied and found to be very small. The minimum of the absorption between the Hartley and the Chappuis bands is observed for the first time at 377,5 nm.

Key words: ozone, absorption cross-sections, Chappuis bands.

1. Introduction

Owing to its ability to filter the solar UV radiation, it is well known that ozone is the most important molecule in the terrestrial atmosphere. To study atmospheric trend, and more specifically to determine the ozone concentrations either by direct *in situ* measurements or by modelling, it is necessary to know the accurate values of its absolute absorption cross-section in the UV-visible wavelength regions. For the last years, work has been made in our laboratory to improve these values. At present, we can propose a large set of accurate values in the range 195–830 nm at different temperatures.

The first results concerned the most intense bands in the UV region (Hartley and Huggins bands located between 195 and 350 nm) and have been the object of several previous papers (Daumont *et al.*, 1992; Malicet *et al.*, 1995). These values have been obtained at different temperatures (218, 228, 243, 273 and 295 K) usually prevailing in the troposphere and in the stratosphere.

In this paper, recent measurements are presented for the Chappuis band between 420 and 830 nm at ambient temperature and between 515 and 650 nm at 218 K and for the low absorption region 350–420 nm between the Huggins band and the Chappuis band at ambient temperature.

The Chappuis band shows a large continuum with two maximum absorptions ($\sigma = 4.83 \times 10^{-21} \text{ cm}^2$ at 575 nm and $\sigma = 5.23 \times 10^{-21} \text{ cm}^2$ at 603 nm) overlapped by diffuse vibrational structure. For this region discrepancies up to 10%

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between the results of previous authors are observed. Disagreements also exist for the temperature effect which can vary from 0 to 12%.

In the spectral region 350–420 nm located between the Huggins and the Chappuis bands, the absorption cross-section values are very weak (10^{-23} – 10^{-24} cm²). Owing to the experimental difficulties in the measurements of low absorption cross-sections, this region was not investigated up to now. It also consists of a continuum overlapped by diffuse vibrational bands belonging to the Huggins system for the wavelengths lower than 375 nm and to the Chappuis system for the higher wavelengths.

Though the 350–800 nm region is hardly concerned with the problem of the solar attenuation, the knowledge of the absorption cross-section values in this region is required for *in situ* concentration measurements of other species in the atmosphere. In fact these measurements based on differential techniques require subtracting the ozone absorption from the recorded spectra to determine their concentration.

2. Experimental

The technique for the measurements of the ozone absorption cross-sections has been described in previous papers (Daumont *et al.*, 1992; Malicet *et al.*, 1995). It will be briefly reviewed in this section.

The absorption cross-section value is determined by the Beer-Lambert law applied to a perfect gas at pressure P and temperature T according to:

$$\sigma = \frac{D}{P_{\text{O}_3} \times \ell} \times \frac{RT}{N},$$

where

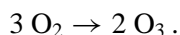
- ℓ = cell optical path
- R = Perfect gas constant
- N = Avogadro number
- P_{O_3} = Ozone partial pressure
- D = $\ln(I_0/I)$ = Optical density

Monochromatic light (0.02 nm FWHM) is obtained with a HR 640 Jobin Yvon monochromator. The emerging beam is split into a working beam passing through the absorption cell and a reference beam, the reference beam measured just after the splitting to take into account the drifts and shifts of the absorption source.

Since the absorption cross-sections of ozone are weak for the wavelengths above 350 nm, we have used a 1 m coolable multiple path cell in stainless steel, this material being well suited for a corrosive gas such as ozone. The alignment of the mirrors at the ends of the cell is achieved by driving motors located outside the cell to avoid contact with ozone. Path lengths up to 92 m can be obtained. To have the best optical density conditions (between 0.5 and 2) the ozone pressure

and the absorption length are adjusted for each scanning region according to the mean cross-section value of ozone in that region. The photoabsorption spectra are then recorded several times and added in order to limit the noise and to increase the accuracy of the measurements. The standard deviation between these scans remains, for the whole spectral region, between 0,9 and 2%.

Ozone is obtained following the procedure previously described by Griggs (1968) from a known initial pressure of molecular oxygen (P_{O_2})_{*i*} using a 400 Hz–15000 V discharge applied between the copper electrodes of an ozonizer according to the global equation:



The ozonizer is cooled in liquid nitrogen and, at the corresponding temperature, ozone is a blue indigo metastable liquid. As soon as the whole amount of oxygen has been transformed, ozone is warmed and spread out in the absorption cell. Then, the pressure of the gas mixture (O_3 , O_2) is measured by a capacitif manometer (MKS-BARATRON) with a relatively accuracy $\Delta P/P$ better than 0,1%.

For experiments lasting several hours, the temperature and the total pressure (P_T) in the cell are measured at steady time intervals. These measurements enable the knowledge of the partial pressure of ozone in the cell at any time, using the equation:

$$P_{O_3} = 2[(P_{O_2})_i - P_T] .$$

This formula takes into account the thermal decomposition and the photolysis of ozone into oxygen. Branching reactions can be neglected, since the concentration of trace gases such as H_2O , CO , CO_2 and N_2O , determined by FTIR, is lower than 0.1%. In this case, the ozone concentration in the absorption cell is determined at any time from the measurement of the total pressure. This method provides an actual improvement for the determination of the cross-section values, as compared to most of the other works.

The experiments have been performed at ambient temperature (295 K) for the whole region, and at 218 K for the 515–650 nm range. A circuit containing methanol and immersed in the tank of a 200 ℓ cryostat is connected to the cell to provide the low temperature. The cell is insulated with an Armaflex foam layer and insulation caps fitted at both ends of the cell are pumped to avoid condensation on the windows for the entrance and exit of the light. The temperature is then measured by several Pt sensors (accuracy 0,05 K). At low temperatures, the temperature deviations between the different parts of the cell remain below 0.3 degree and the stability related to time is better than 0.05 °C.

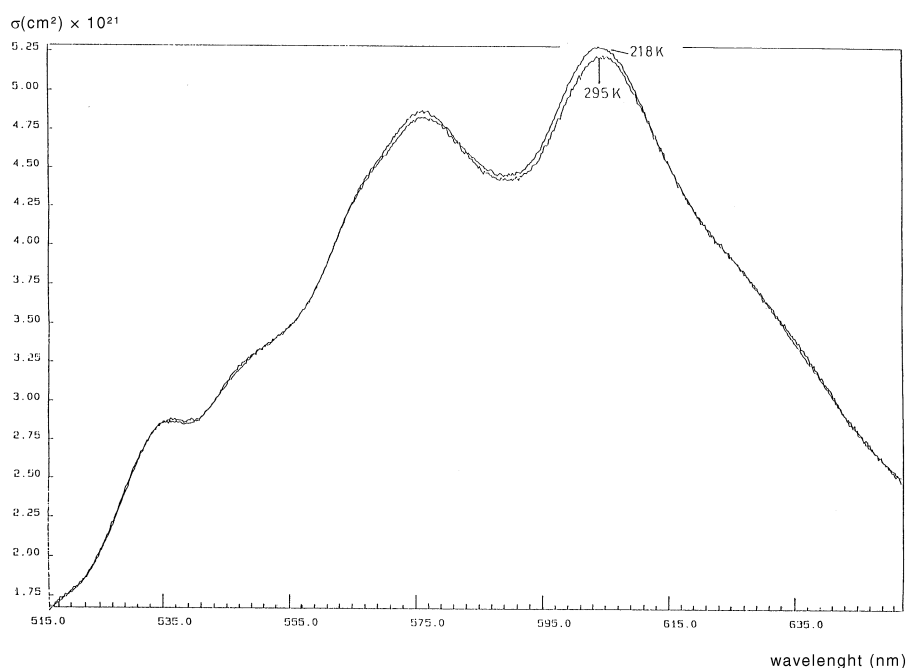


Figure 1. Ozone cross-sections (515–650 nm).

3. Results

The cross-section values have been determined for the whole 350–830 spectral region by steps of 0.01 nm and are available on request to the authors either by e-mail, or on floppy disk.

The photoabsorption spectrum (Figures 1 and 2) appears as a broad continuum, covering the whole visible spectral range with two maxima located at 575 and 603 nm. Important vibrational structure, superimposed on the continuum, belongs to the Chappuis bands (Spectral region: 375–603 nm), to the Huggins bands (below 375 nm) and to the Wulf System (beyond 700 nm) which continues fairly far into the near I.R.

A deep minimum is shown, for the first time at 377,5 nm ($\sigma = 4,4 \times 10^{-24} \text{ cm}^2$), between the Huggins Bands and the Chappuis System.

3.1. ERROR BUDGET

The uncertainty on the cross-sections has been estimated from the accuracy on the measurements of the different parameters involved (see Part 2 – Experimental and Table I).

The error $\Delta\sigma/\sigma$, in connection with the uncertainty in wavelength ($\Delta\lambda = 0.01$ nm) has been determined for each spectral region. In the Chappuis Band, where the vibrational structure is smooth, this error is small (0,1%). On the contrary in

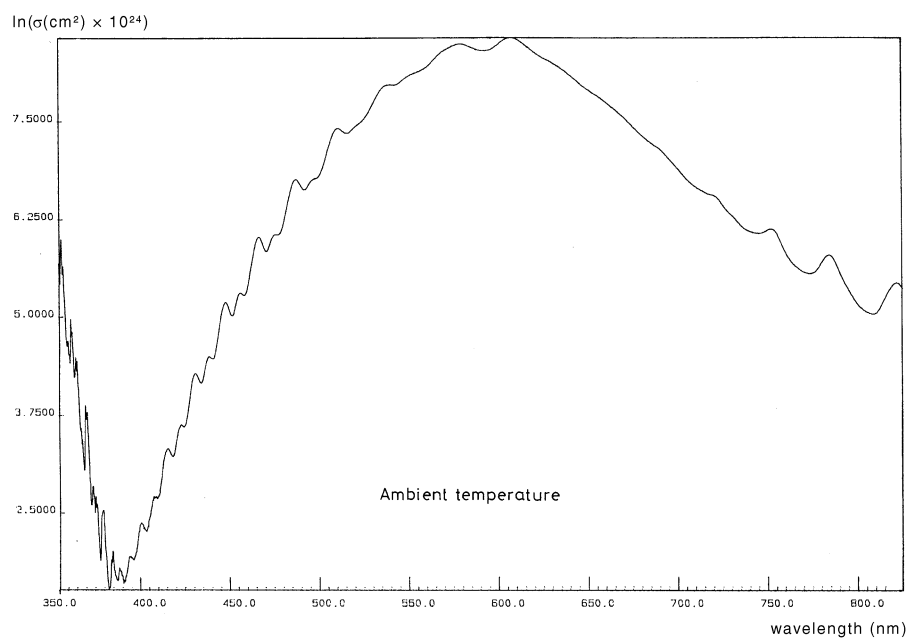


Figure 2. Ozone cross-sections (350–820 nm).

Table I. Error budget

Error origin	$\frac{\Delta\sigma}{\sigma}$ (%)
Optical density	1% (420–830 nm) 1–3% (350–420 nm)
Optical path	0.1%
Ozone pressure	0.1%
Temperature	0.02% ($T = 295$ K) 0.15% ($T = 218$ K)
Impurities	< 0.1%
Wavelength	0.1% (420–830 nm) 0.1–0.7% (350–420 nm)
Total systematic error	≈ 1.5% (420–830 nm) 1.5–4% (350–420 nm)
Random error (RMS)	0.9–2%

the Huggins bands, this error is fairly strong (0.7%) on account of the important vibrational structure and the strong variation of σ with wavelengths.

Finally, the uncertainty on the optical density $\Delta D/D$ has been calculated from signal/noise ratios of different scans and is about 1% for the whole spectrum, except in the 360–420 nm region where the σ values are very small and the noise important ($\Delta D/D$ from 1 to 3%).

In these conditions, the total uncertainty is about 1.5% for the Chappuis band region and about 4% near the absorption minimum.

3.2. COMPARISONS

For the visible region, there are numerous references about experimental measurements; some of them are very old since the first absorption spectrum (between 520 and 650 nm) was observed by Chappuis (1880) at the end of last century. Then, measurements were made by Humphrey and Badger (1947 and 1953), Vassy (1948) and Vigroux (1953 and 1969). More recently Inn and Tanaka (1968), Griggs (1968), Penney (1979), Amoruso (1990), and Anderson and Mauersberger (1992 and 1993) at a few wavelengths, and Burkholder and Talukdar (1994) have reconsidered these works to propose more precise data sets.

The comparison between the previous works shows important discrepancies. The data of Vigroux, Griggs, Penney and Anderson are in good agreement (within the limit of 1%), but they are 10% larger than those of Tanaka, and 4–5% larger than those of Amoruso. The results of Vigroux, Tanaka, Amoruso are in good agreement concerning the location of the two maxima at 575 and 603 nm while a systematic shift towards lower wavelengths is observed in the spectrum of Griggs as compared to the others.

A comparison of our results (Table II) with the more precise data provided by Anderson and Mauersberger (1992) and Hearn (1961) at 6 discrete wavelengths located near the maxima shows a very good agreement except at 594.096 nm where the deviation is about 2.5%. Nevertheless (Figure 3) it should be noted that the error bars for the sets of measurements are overlapping, thus showing the consistency of these values. In addition, our measurements have the advantage of providing a large set of values for the overall spectrum, compared to the data of the other authors given only at the lines of a helium-neon laser and the mercury lamp.

For longer wavelengths, in the region of the Wulf Band, we have been able to extend the comparison of our values with those of Anderson and Mauersberger (1993). In general, these values are from 2 to 5% below ours. Nevertheless, it can be noted that the comparison is difficult because of a lack of precision in wavelength in the measurements of these authors related to a lower resolution (3.1 nm FWHM).

Table II. Comparison of the ozone cross-sections ($\sigma_{O_3} \times 10^{21} \text{ cm}^2$) at six discrete wavelengths

λ (nm)	Anderson and Mauersberger	Hearn	Present work	Deviation (%)
543,516	$3,075 \pm 0,027$		$3,122 \pm 0,047$	-1,53
576,96		$4,76 \pm 0,09$	$4,766 \pm 0,071$	-0,13
594,096	$4,569 \pm 0,037$		$4,682 \pm 0,070$	-2,47
604,613	$5,125 \pm 0,036$		$5,180 \pm 0,078$	-1,07
611,971	$4,633 \pm 0,033$		$4,634 \pm 0,070$	-0,00
632,816	$3,383 \pm 0,024$		$3,388 \pm 0,051$	-0,15

$$\text{Deviation} = (\sigma - \sigma_{PW}) / \sigma_{PW} .$$

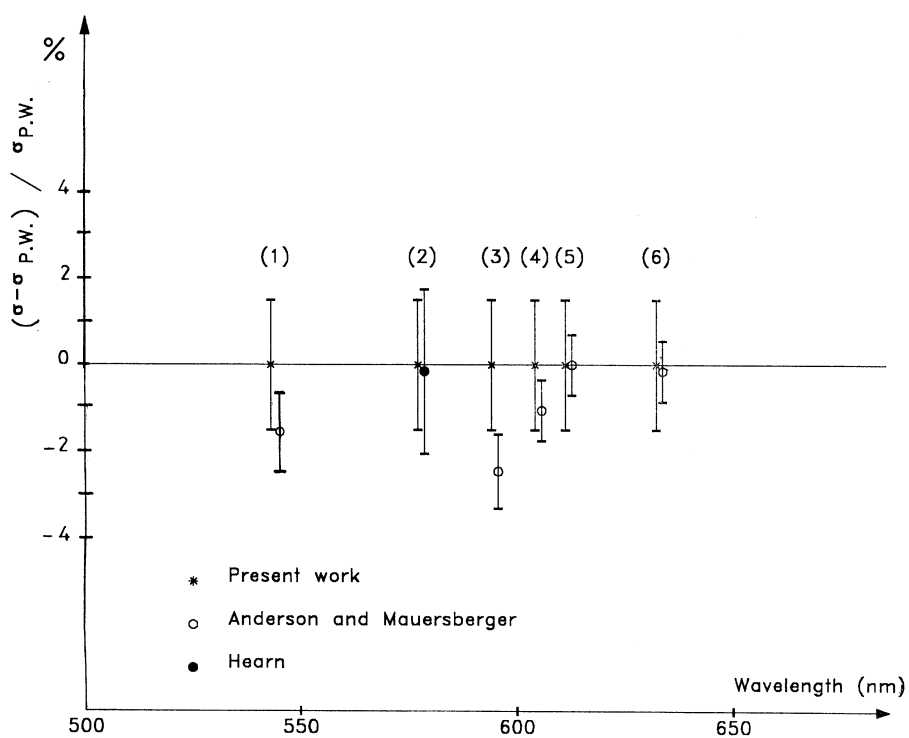


Figure 3. Comparison of the ozone cross-sections.

3.3. TEMPERATURE EFFECT

The knowledge of the variation of the cross-section values with temperature is particularly important in this spectral region since it must be taken into account for the calculation of the ozone profile in the atmosphere as well as for the determination of other trace gases by differential techniques subtracting the ozone contribution.

Large disagreements are observed for the temperature effect. While the data of Humphrey seem to show that the temperature effect is negligible in the Chappuis band, the values of Chappuis, Vassy and Penney differ from 12 to 20% for the two extreme temperatures.

Our results at 218 and 295 K show that for the 515–650 nm region the temperature effect is very weak: the two spectra overlap except near the two maximum absorptions for which the cross-section values increase by about 1% as the temperature decreases. From these new results, it is evident that the measurements of Chappuis, Vassy and Penney at low temperature display significant errors.

Recently, Burkholder and Talukdar (1994) reported cross-section variations with temperature from 4% (at 520 nm) to 40% (at 420 nm) between 298 and 220 K. Unfortunately, we cannot confirm the importance of the variation at 420 nm, having no measurements at this wavelength at low temperature. Nevertheless, our value at 520 nm and 218 K display a temperature effect below 1% and so suggest that the variations observed by this authors are perhaps less important than reported.

4. Conclusion

As regards atmosphere models or the ozone concentration measurements in the atmosphere, we can now recommend a set of absolute cross-section values of ozone on the whole UV-Visible region (200–830 nm) corresponding to the Hartley, Huggins and Chappuis Bands.

These values have been measured with high resolution ($\Delta\lambda \leq 0,02$ nm FWHM) and in very controlled experimental conditions. Contrary to the Huggins Bands, where the temperature effect is very large, we confirm, that in the region of the Chappuis Bands the variation of the cross-section is very weak and remains below 1% for measurements at 218 and 295 K.

In addition, the minimum of absorption between the UV and Visible band is observed for the first time and located precisely at 377,5 nm.

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