

Ozone UV Spectroscopy I: Absorption Cross-Sections at Room Temperature

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Abstract. Because of the importance of the absorption cross-sections of ozone in the atmosphere, we give a new set of data at ambient temperature for the whole spectral region within the 195–345 nm range. Two new methods have been investigated for the experiments to measure the ozone pressures. Our results are compared with all of the previous data. The agreement between the more recent works is relatively good and can be improved by making some corrections in the WMO set. The new reference value at 254 nm proposed by Mauersberger *et al.* is confirmed and we suggest taking it as a new standard.

Key words: Ozone, Huggins and Hartley bands, absorption cross-sections, concentration measurements.

1. Introduction

Ozone is indisputably a minor atmospheric constituent which plays a major role in the physico-chemistry of the atmosphere.

It is involved in the direct attenuation of solar irradiance, especially in the UV wavelength range where the Huggins and Hartley bands are located. In this region ($\lambda < 350$ nm), the absorption cross-section values are so great that the major part of the abiotic solar radiation is absorbed.

Ozone is also involved in different photodissociation processes related to the production of atomic oxygen, such as



This photolysis reaction performed with short wavelength radiations ($\lambda < 310$ nm) is particularly important because of the production of O(¹D) radicals. These radicals interact themselves with such molecules as H₂O, CH₄, hydrocarbons, and produce OH radicals which influence all the atmospheric chemistry.

In order to study these processes, the knowledge of the absorption cross-section values is of major importance. Indeed, these parameters are directly used to determine the rate of the photodissociation and to estimate the solar fluxes at various altitudes by atmospheric transmittance calculations (Nicolet *et al.*, 1985). They are also used by the ground-based and satellite remote sensing networks to measure the total amount of atmospheric ozone as well as its concentration profiles.

In each case, an accurate knowledge of the absorption cross-sections in all tropospheric and stratospheric temperature ranges is essential. For these reasons, a large number of experimental determinations of the ozone absorption cross-sections have been performed by different groups. The first were those realised by Inn and Tanaka (1953), Vigroux (1953, 1967), Hearn (1961), Griggs (1968). A comparison of the results shows that discrepancies exist between these sets of measurements; the major reason for the differences is due to the difficulty in measuring the ozone concentration with accuracy.

Two other sets of measurements with better accuracy have been published more recently: Bass and Paur (1984) determined the relative absorption cross-sections in the 245–340 nm range and estimated the absolute values by means of the reference proposed by Hearn (1961): ($\sigma = 114.7 \times 10^{-19} \text{ cm}^2$ at 254 nm and 295 K). These values are now recommended by WMO/NASA. Molina and Molina (1986) proposed absolute absorption cross-sections in the 190–350 nm range. In the overlap wavelength region, these measurements show a relatively good agreement (within 2 or 3%). Nevertheless, recent mass spectroscopy measurements by Mauersberger *et al.* (1987) showed that the reference value chosen by Bass and Paur (1984) is about 1% too high.

Moreover, some small shifts in the wavelengths are observed between the two sets of data in the range of the Huggins bands where the vibrational structure is observed.

In addition, Yoshino *et al.* (1988) gave measurements at several discrete wavelengths corresponding to the mercury lines in the 238–335 nm region. Therefore, we have decided to begin new work on this study in order to extend the comparison with Molina's data down to 195 nm and to give some answers to the two problems mentioned above.

2. Experimental Techniques

In this paper, a critical analysis of the experimental techniques used in the previous studies is made and we describe two new experimental techniques to measure ozone absorption cross-sections.

2.1. Determination of the Ozone Concentration

As stated in the first section, the analysis of the discrepancies between the available sets of data shows that the major reason for these differences results from the difficulty in measuring the ozone concentration in the absorption cell. This difficulty is mostly imputable to the unstable nature of ozone which decomposes into molecular oxygen by thermal or photochemical processes. It must be pointed out that the differences between the temperatures used by different authors (Vigroux: 18 °C, Molina and Molina, Bass and Paur: 25 °C, Inn and Tanaka: 27 °C and Griggs: 30 °C) are of minor impact.

To measure ozone concentrations, some five different methods have been proposed:

(a) The chemical proportioning used by Vigroux (1953, 1967) which consists in the sampling of iodine (I_2) produced by the reaction:



This kind of determination is imprecise and no longer used today (De More and Patapoff, 1976).

(b) The technique described by Griggs (1968) which is based on the pure preparation of O_3 . Owing to the low variation of pressure in the cell, the ozone decomposition is assumed to be negligible. Measurement of ozone concentration is then a simple measurement of the total pressure.

This technique has also been used by Inn and Tanaka (1953). Nevertheless, they improved this method by introducing a purity coefficient of $92 \pm 3\%$. The mean value of this coefficient is determined by chemical sampling. The questionable point is that it is impossible to confirm the mean purity coefficient by any other technique than the chemical one.

Another version of this method is also proposed by Molina and Molina (1986) and Yoshino *et al.* (1988) who also worked with pure ozone. After ozonization, ozone is trapped at the temperature of liquid nitrogen and the remaining molecular oxygen is pumped out.

For all these methods, the critical point concerns the decomposition of ozone which is not taken into account during the measurements and has to remain low enough to be neglected.

(c) The method used by Hearn (1961) who determined the absorption cross-section by measuring the optical density variation (dD) as a function of the evolution of total pressure (dP_T) according to the relation

$$\sigma = \frac{dD}{dP_T} \times \frac{RT}{2lN} \quad (3)$$

where l is the optical path, N the Avogadro number, R the perfect gas constant, and T the absolute temperature (K).

This technique takes into account the spontaneous decomposition of ozone into molecular oxygen for which the absorption cross-sections (σ_{O_2}) are negligible in the studied wavelength range. As mentioned by Hearn himself, the following assumptions have to be verified:

- the absorption coefficients do not vary with pressure,
- reactions do not occur at the walls of the cell (adsorption or desorption),
- absence of impurities like grease or nitrogen oxides which are immediately oxidized by ozone, and then cause significant errors.

Owing to additional precautions (Quartz cell, pressure range in a ratio 5 to 1), the above-mentioned conditions seem to be verified and the ozone cross-section values determined by this method are probably within the limit of accuracy (0.5 to 2%) given by the author.

However, this method is only applicable for measurements at fixed wavelengths, but not for a large wavelength range. Moreover, it must be used with care because a small deviation from the above conditions induces a large error on the absorption cross-section values.

(d) Bass and Paur (1984) used a technique providing relative values of the cross-sections; it has the advantage of being independent of the determination of the ozone concentration and of its decomposition during the scanning.

In their experiment, the absorbances at each wavelength and at the 254 nm reference wavelength are simultaneously measured and compared. The reference value is a value proposed by Hearn (1961) ($\sigma = 114.7 \pm 2.4 \times 10^{-19} \text{ cm}^2$) at the wavelength of the mercury line ($\lambda = 254 \text{ nm}$). Since then, Mauersberger *et al.* (1987) have shown that this value must be reduced ($\sigma = 113.6 \pm 0.5 \times 10^{-19} \text{ cm}^2$). The major problem of this technique is that it must use an external value in order to calibrate the spectrum.

(e) Mauersberger *et al.* (1987) determined the partial pressure of ozone by simultaneously measuring the composition of the mixture (O_3/O_2) with mass spectroscopy techniques and the total pressure of the gaseous system with a calibrated pressure sensor. The method is precise but involves relatively heavy technology and is limited to measurements at some specified wavelengths.

2.2. New Methods

(a) Continuous pressure measurements (method 1)

In this method, developed in our laboratory, the amount of spontaneously decomposed ozone is continuously controlled and the partial pressure p_{O_3} is known at each time of recording.

According to the decomposition reaction



the partial pressure of ozone at constant temperature and volume is given by the simple expression

$$p_{\text{O}_3} = 2[(p_{\text{O}_2})_i - p_T], \quad (5)$$

where $(p_{\text{O}_2})_i$ is the initial pressure of oxygen used to prepare ozone and p_T is the total pressure of the gaseous system ($\text{O}_3 + \text{O}_2$).

The absorption cross-sections are directly calculated

$$\sigma = \frac{\ln(I_0/I)}{2l[(p_{O_2})_i - p_T]} \times \frac{RT}{\mathcal{N}} \quad (6)$$

The comparison of (6) with expression (3) proposed by Hearn (1961), shows that the two relations are equivalent, Hearn's formulation being deduced from (6) by a derivation.

This analogy implies that the conditions mentioned by Hearn should be also verified in our technique. For that reason, we have used an absorption cell in quartz, well known for its chemical stability. In addition, we have performed our measurements with monochromatic light in order to limit the photodissociation and then the production of the extremely reactive O¹D radicals. To control the absence of secondary reactions, the total pressure was measured after the entire decomposition of ozone; after several days, it was verified that this pressure was exactly the same as the initial pressure of the oxygen introduced before ozonization. Moreover, Fourier transform infrared measurements have shown that impurities such as H₂O, CO, CO₂, and N₂O, in our case, are negligible.

The main advantage of this method is to know continuously the partial pressure of ozone, separately from its decomposition ratio during the time of a wavelength scanning. This simple method was used to allow recordings over the whole wavelength range. We also point out that a slightly variant version of our method has been used since then by Cacciani *et al.* (1989). These authors used a similar expression for the determination of the partial ozone pressure, but in their calculations, the initial pressure is deduced by extrapolation at the time $t = 0$ from the kinetics equation.

(b) *Limit vapor pressure or Dew point method (method 2)*

To confirm the results obtained by the above method, we have used a second method involving a completely independent procedure (Malicet *et al.*, 1989). It is based on the determination by Mauersberger *et al.* (1985) of the ozone vapor pressure near the normal boiling temperature of liquid argon (−185.9 °C). For this experiment, a reservoir of liquid ozone is kept at the temperature of liquid argon during the measurements. The liquid argon bath is continuously shaken and the device is carefully insulated to avoid any temperature gradient. Thus, the vapor pressure depends only on the temperature of the bath.

Because of the very high variation of the vapor pressure with respect to temperature, a very precise determination of the temperature is requested. Therefore, for the temperature measurements, a Pt 100 sensor, sensitive up to 1/100 °C, has been calibrated with a primary standard. Moreover, we have controlled, with precision, the temperature of the bath so that it was exactly the same as that of boiling argon at atmospheric pressure in the laboratory. Under these conditions, the precision of the temperature measurement is estimated to be within 0.02 °C, leading to an uncertainty on the ozone pressure $\Delta \ln p_{O_3} = 0.6\%$. Since the difference of the temperatures in the ozonisor (87 K) and in the cell (295 K) is large, we also verified

that the thermodynamic conditions for the pressure equilibrium (Poulter *et al.*, 1983) was satisfied. For this, calculations over the whole range of temperature and pressure showed that the mean free path of the ozone molecules is smaller than the diameter of the tube connecting the reservoir and the cell.

Under these conditions, the pressure of the ozone is constant during the experiment and independent of the temperature of the cell. The disadvantage of the method is that the vapor pressure of ozone is low ($\approx 4.05 \times 10^{-2}$ Torr) so that this method can be only used for measurements of high-value absorption cross-sections ($\sigma \approx 10^{-17}$ cm² for an optical path of 1 m). Thus, the comparison between the results of the two new methods was restricted to a range near the maximum of the Hartley band at 254 nm.

2.3. *Experimental Device*

As mentioned above, monochromatic light has been used in the two types of experiments, in order to limit the photodissociation process producing very active O(¹D) radicals which can affect the chemical budget.

The spectrometer is a 1.5 m Czerny Turner type monochromator (THR 1500 Jobin-Yvon) equipped with a 2400 lines/mm grating. According to the spectral range, it is coupled with either a premonochromator (Amici Prism – REOSC) or an interferential narrow band filter. Under these conditions, diffusion light is negligible.

Measurements are performed by a Hamamatsu R929 photomultiplier tube connected to a microcomputer for the acquisition of the data.

For the wavelengths below 300 nm, a stabilized deuterium lamp is used as the continuous source; for the higher wavelengths, the continuum is provided by a controlled tungsten lamp.

The wavelength calibration in air is obtained by the reference lines of an iron hollow cathode and mercury and cadmium lamps. The precision is better than 0.005 nm.

The temperature of the cell is controlled by a regulation system involving the circulation of methanol around the cell at a fixed value (295 K). The stability is of the order of 0.05 degree and the temperature control unit gives a precision of 0.02 degree on the measurements.

The pressures which need to be measured with a high degree of accuracy, since they allow the determination of the ozone concentrations, are obtained by a capacitance manometer (MKS Baratron) precalibrated and regularly compared with a high precision mercury barometer.

Cross-sections have been measured in a serie of 15 nm adjacent regions with a 5 nm overlap. For each region, 10 scans have been made under the experimental conditions summarized in Table I.

Table I. Summary of the experimental conditions

T(K)	Spectral range (nm)	Tube length (cm)	Ozone pressure (Torr)
295	195–335	3.285 ± 0.001	(1–600)
295	320–350	81.50 ± 0.05	(20–200)

3. Results and Discussion

3.1. Shape of the Spectrum

The absorption spectrum of ozone in the UV region (Figure 1) shows a large continuum from 200 to 350 with a maximum near 250 nm (Hartley band) on which some small diffuse undulations spaced by approximately 200 cm^{-1} can be seen. At the higher wavelengths (310–350 nm), the spectrum is dominated by more intense but also diffuse vibrational bands corresponding to the Huggins bands.

New measurements based on the method of the continuous pressure measurements (method I) have been obtained at room temperature for the entire 195–345 nm range, by steps of 0.01 nm. They extend and slightly change the values of a preliminary work (Malicet *et al.*, 1984). A complete set of data containing all the values is available on floppy disk in MS-DOS format and can be obtained on request from the authors.

According to Table II, given the detailed error budget, the accuracy of the measurements is about 1–1.5% in the Hartley band and 1–3% in the Huggins bands.

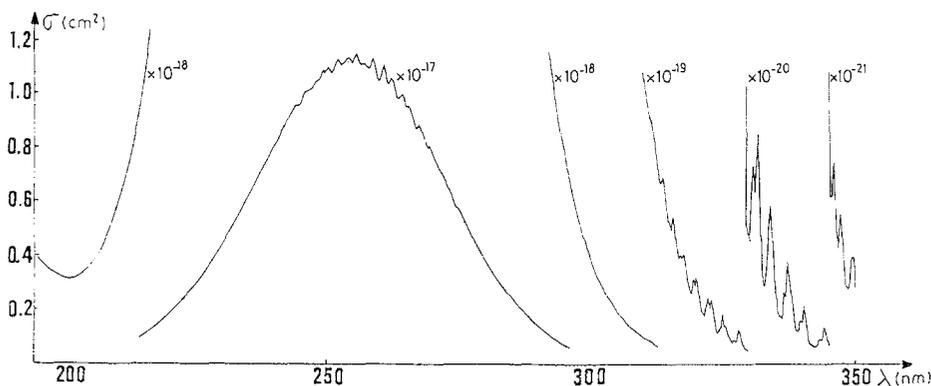


Fig. 1. Absorption cross-sections of O_3 in the Hartley and Huggins bands.

Table II. Analysis of the errors

Optical path	0.05%	
Ozone pressure	0.1%	
Temperature	0.02%	
Absorbance ($\lambda < 335$ nm)	1%	
Impurities	<0.1%	
Wavelength	0–0.05%	Hartley Band
($\Delta\lambda = 0.005$ nm)	0–0.8%	Huggins Band
Total error	1.3%	Hartley Band
	1.3–2.5%	Huggins Band
Random errors (RMS)	0.9–2.2%	

3.2. Comparison of the Results

Before comparing our results with those of other authors, we critically controlled the internal consistency of our results. For this, experimental conditions were varied, such as the partial pressures of ozone (within the ratio 1 to 20) and the optical path (3.3 and 80 cm). Under these different conditions, the results were shown to be in good agreement, the difference remaining below the uncertainty values (1 to 2%).

But the major test to verify the quality of our values was to compare the results obtained near the maximum of absorption by methods 1 and 2.

At the mercury line wavelength ($\lambda = 254$ nm), the value $\sigma(\text{O}_3)$ measured by method 1 was found to be

$$\sigma(\text{O}_3) = (113.0_5 \pm 1.1) \times 10^{-19} \text{ cm}^2.$$

This is in very good agreement (0.4%) with the value determined by means of the dew point technique (method 2):

$$\sigma(\text{O}_3) = (112.6 \pm 2.0) \times 10^{-19} \text{ cm}^2.$$

These values are also in close agreement (<0.5%) with the value recently proposed by Mauersberger *et al.* (1987), at the same reference wavelength, by means of the mass-spectrometry technique:

$$\sigma(\text{O}_3) = (113.6 \pm 0.5) \times 10^{-19} \text{ cm}^2.$$

Table III gives a comparison of the values obtained by different authors at the mercury wavelengths.

Finally, we compared our results over the wavelength range 195–345 nm with the recently published data of Molina and Molina (190–350 nm) (1986) and of Bass and Paur (245–340 nm) (1984). This led to the following conclusions:

Table III. Absorption cross-sections at the mercury wavelengths

λ (Hg I) (nm)	Present work	Molina and Molina	Bass and Paur ^a	Yoshino	Mean values \pm RMS
253.65	113.05	115.7		114.5	
289.36	15.13	15.40	14.87	14.88	15.07 ± 0.25 (1.7%)
296.73	6.146	6.229	6.01	5.97	6.09 ± 0.12 (2.0%)
302.15	2.985	3.027	2.91	2.91	2.958 ± 0.057 (1.9%)
334.15	4.658 $\times 10^{-2}$	4.460 $\times 10^{-2}$	4.66 $\times 10^{-2}$	4.37 $\times 10^{-2}$	4.54 ± 0.14 (3%) $\times 10^{-2}$

^a Renormalized on the Mauersberger Reference at 253.65 ($\sigma = 113.6 \times 10^{-19} \text{ cm}^2$).

1. Comparison with the data of Molina and Molina

- For wavelengths lower than 225 nm, our results and those of Molina and Molina (1986) are within 1%. This agreement shows that the values of Inn and Tanaka (1953), still used in the modelling calculations, and lower by between 3 and 7% than ours, are inaccurate (Figure 2). This is important, since very few measurements are available in this region corresponding to the ‘atmospheric optical window’ centered at 210 nm.
- For longer wavelengths ($\lambda > 225$ nm), small differences are observed, the values proposed by Molina and Molina (1986) being, on average, 1 to 3% greater than ours. Some greater discrepancies (4 to 6%) are locally observed for wavelengths above 325 nm where the absorption cross-section values are very low ($\sigma < 0.1 \times 10^{-19} \text{ cm}^2$) and where the accuracy of the measurements become smaller; however the mean differences remain in the order of 2%.

2. Comparison with the values of Bass and Paur

A first investigation clearly shows a discrepancy in the wavelength calibration between our work and that of Bass and Paur (1984). In the region of the Huggins bands, shifts of up to 0.05 nm are observed in the structure of the bands (Figure 3). This is also confirmed by the data of Molina and Molina which are red shifted (from 0.04 to 0.06 nm) compared to the data of Bass and Paur.

As for the values of the cross-sections, they are compared at the minima and the maxima of absorption. The values of Bass and Paur are slightly higher than ours (0 to 2%). However, these values are relative values, referred to the standard value at 254 nm ($\sigma = 114.7 \times 10^{-19} \text{ cm}^2$). Taking account of the new value obtained by Mauersberger *et al.* (1987) at this wavelength ($\sigma = 113.6 \times 10^{-19} \text{ cm}^2$) to normalize the results of Bass and Paur, the two sets of measurements now agree within 1%; this is in the limit of the experimental uncertainties.

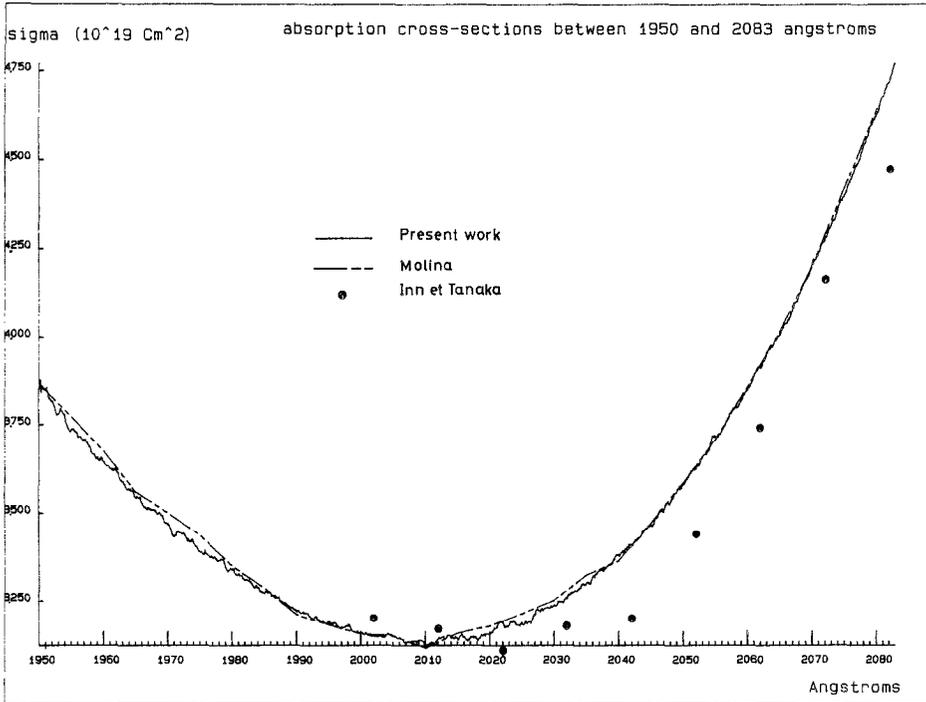


Fig. 2. Comparison of the O₃ cross-section values available in the 210 nm atmospheric window.

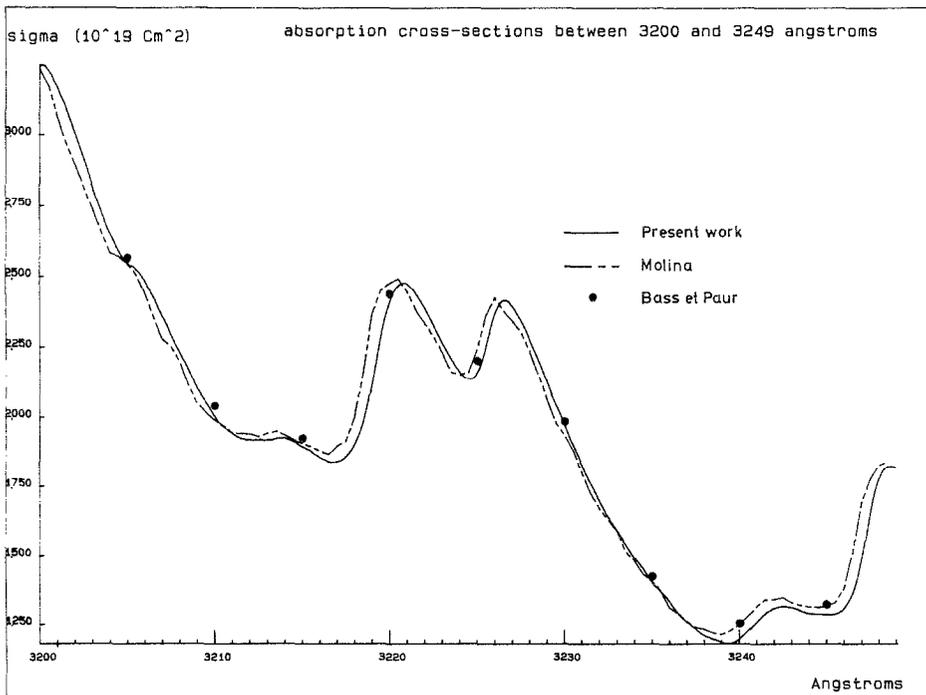


Fig. 3. Observed wavelength shifts in the Huggins bands.

4. Conclusion

Owing to the measurements performed on the basis of our two new methods, a complete and coherent set of data is proposed for the absorption cross-sections of ozone at ambient temperature between 195 and 350 nm.

The agreement between the three sets of data, ours, those of Bass and Paur (1984), and those of Molina and Molina (1986), is relatively good and can be improved by taking into account the new reference value, proposed by Mauersberger *et al.* (1987), at 254 nm and in matching the wavelength calibration of Bass and Paur to that of the two other sets which are in agreement.

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