

## Absorption Cross Sections of Ozone in the 590- to 610-nm Region at $T = 230$ K and $T = 299$ K

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Measurements of the ozone absorption cross section in the 590- to 610-nm region of the Chappuis bands have been carried out at the temperatures  $T = 230$  K and  $T = 299$  K. Ozone is produced with an electrical discharge and stored cryogenically. Differential absorption measurements are obtained in a slowly evolving mixture of ozone and molecular oxygen. Previous results by other authors indicate a certain disagreement on the temperature dependence of the absorption cross section. Our data at each wavelength show no significant dependence of the absorption coefficient on the temperature, within experimental errors. The statistical consistency of the results is discussed.

### INTRODUCTION

There is interest in the reassessment of the absorption coefficient of ozone in the Chappuis bands because of the applications to remote sensing (in particular, one of the channels of the SAGE II instrument is centered around 600 nm). In general, more precise quantitative information regarding the photodissociation of ozone is useful also in improving the reliability of atmospheric models.

The spectral region 590–610 nm is part of the Chappuis bands. No definitive information on the excited states of ozone had been obtained by studies of the absorption spectrum, and theoretical calculations have to contend with the fact that the bent ground state of the molecule is not well described by only one configuration function [Brand *et al.*, 1977].

From theory it is expected that the Chappuis region is a mixing of transitions to the  $^1B_1$  state and the  $1^1A_1$  state, possibly accompanied by the corresponding triplet-singlet transitions to  $^3B_1$  and  $1^3A_1$ . It would be of interest to establish a possible dependence of the fundamental electronic configuration (and of the absorption cross section) on temperature, particularly over the entire band.

Previous determinations of the temperature dependence of the ozone cross section in the Chappuis bands are few and show a certain disagreement. Chappuis [1880, 1882] and Vassy and Vassy [1948] note an important increase of the absorption coefficient when the temperature is lowered. On the contrary, Lefebvre [1935], Humphrey and Badger [1947], and Vigroux [1953] see a very small dependence of the ozone absorption cross section on temperature. The more recent determinations by Penney [1979] agree with those by Chappuis [1880, 1882] and Vassy and Vassy [1948] but show a weaker dependence on temperature.

Inn and Tanaka [1953] and Griggs [1968] have also carried out measurements of the ozone cross section in the region around 600 nm, but at room temperature only.

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### EXPERIMENTAL SETUP AND PROCEDURE

A description of the method and of the instrumentation has been given already in some detail [Cacciani *et al.*, 1989] and can be summarized as follows.

Radiation from a Xe lamp (Osram XBO 150 W/4) is focused on the entrance slit of a Jobin-Yvon Ramanor U1000 double monochromator with 1800 grooves/mm gratings, and then collimated, partially deviated, and split into two parallel beams. The beams go through two identical stainless steel chambers: one is the reference, and the other is the absorption chamber, which contains the gas to be examined. The absorption chamber is thermally controlled by circulation of ethanol.

The light coming from the two channels is alternately detected by a EMI 9558Q photomultiplier: the detector, cooled to decrease the dark current, is followed by a photon counting system. Pressure and temperature data are acquired and digitized by a 12-bit A/D converter and a multiplexer. The entire acquisition process is computer controlled.

A measurement cycle begins with the ozone production by crown discharge: the absorption chamber is filled with almost 200 torr of ultrahigh-purity  $O_2$ , further purified by passage through a liquid nitrogen trap. The discharge (20 kV, 50 Hz a.c. source) is turned on until the pressure is about 10 torr. The ozone is collected in the liquid state. The chamber is then emptied down to  $10^{-2}$  torr to remove residual  $O_2$ . The ozone is then evaporated to fill the chamber.

The gas is left in the chamber about 10 hours to deactivate the walls by adsorption of ozone molecules. At this point the absorption chamber is emptied down to a vapor pressure of almost  $10^{-2}$  torr, and new ozone for the measurement is produced.

The measurement is based on the application of the Beer-Lambert law:

$$K = \frac{P_0 T}{L P T_0} \log \left( \frac{I_0}{I} \right) \quad (1)$$

where  $P$  and  $T$  are the partial pressure and temperature of ozone;  $P_0$  and  $T_0$  are the standard values ( $P_0 = 760$  torr,  $T_0 = 273.16$  K),  $L$  is the optical path of the incident radiation (111.5 cm, the length of the absorption chamber),  $I_0$  and  $I$  are

the emitted and the transmitted light intensities, respectively.

The measurement cycle includes the acquisition of the emitted and transmitted radiation intensities and of the pressure and temperature of the gas. The scan proceeds at steps of 0.1 nm with the resolution of the monochromator kept at 0.05 nm. For each cycle, two complete spectral scans are carried out, first with the chamber filled with gas and then with it evacuated. The determination of the partial pressure of ozone in the absorption chamber constitutes one important part of the measurement procedure: during the experiment the O<sub>3</sub> progressively undergoes a slow transformation back to O<sub>2</sub> while the total pressure of the gas mixture changes. The asymptotic value attained at the end is related to the reactions taking place in the chamber.

The ozone decay is principally due to a first-order heterogeneous reaction:



which is catalyzed by the presence of the walls; the slower thermal reaction can be neglected as well as the adsorption of gas molecules by the walls. For details, see *Cacciani et al.* [1989].

The evolution of the gas mixture from O<sub>3</sub> to O<sub>2</sub> is well fitted by the law

$$P_t = P_i [1 - (1/3) \exp(-t/\tau)] \quad (3)$$

where  $P_t$  is the total pressure,  $P_i$  is the asymptotic pressure, and  $\tau$  is the time constant of the order of  $10^5$ – $10^6$  s. As a result the partial pressure of O<sub>3</sub> can be obtained by

$$P = 2(P_i - P_t) \quad (4)$$

where  $P_i$  is obtained from (3). By knowing  $P_t$ ,  $P_i$ , the optical density, and the temperature, the absorption coefficient value at the desired wavelength is determined. A full measurement cycle takes about 300 min, during which the change in pressure inside the chamber is less than 2%.

## RESULTS

The spectral scans cover the 590- to 610-nm interval. The cross-section determinations at each temperature and wavelength are the result of averaging over six scans. To check the independence of the results with pressure, each scan has been obtained at a different initial pressure.

The results of the averaging are shown in Figures 1 and 2. The reproducibility of the results is high, and the error on each datum can be estimated to be nearly 1% on the pressure and nearly 0.5% on the temperature and the optical path length. In addition, since the standard deviation on the determination of the optical density is about 0.7%, the error on this variable is estimated to be about 2% (3 times the standard deviation value).

Comparing at each wavelength the magnitude of the error to the difference between the averaged values, the results show no significant dependence of the absorption coefficient on temperature: the mean ratio of low- and high-temperature values is less than 1.01, which is within the expected experimental error of the measurements.

To clarify further a possible temperature dependence, the experimental absorption data have been fitted, in the interval 590–610 nm, by different analytical functions, e.g., para-

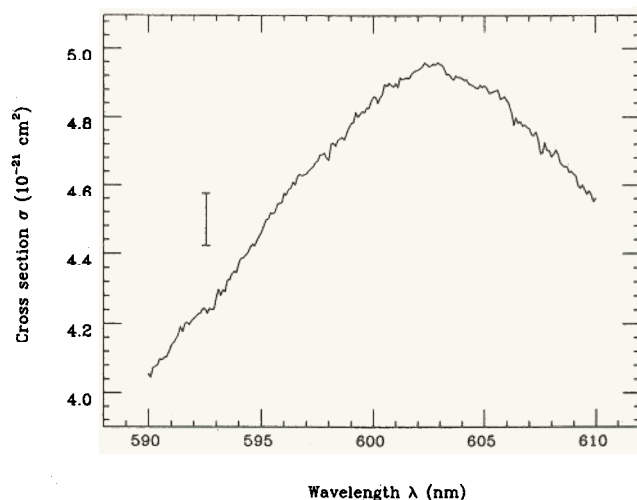


Fig. 1. Absorption spectrum in the region 590–610 nm at 299 K averaged over 0.5 nm. The error bar indicates the standard deviation of the average over six scans.

bolic, Gaussian, and Lorentzian. The best fit for the high-temperature data has been obtained for a Lorentzian curve:

$$\Sigma = (ab)/[(\Lambda - \Lambda_0)^2 + b^2]$$

where  $\Sigma$  is the cross-section value,  $\Lambda$  is the wavelength,  $a = 130.230 \times 10^{-20} \text{ cm}^3$ ,  $b = 267.350 \text{ cm}$ , and  $\Lambda_0 = 6028.52 \times 10^{-8} \text{ cm}$ .

The 230 K averaged values are best fitted by the Gaussian law

$$\Sigma = c \exp[-(\Lambda - \Lambda_0)^2/(2d^2)] + e$$

where  $c = 0.102 \times 10^{-20} \text{ cm}^2$ ,  $d^2 = 4109.96 \text{ cm}^2$ ,  $\Lambda_0 = 6028.41 \times 10^{-8} \text{ cm}$ ,  $e = 4 \times 10^{-21} \text{ cm}^2$ . The results of the  $\chi^2$  test are shown in Table 1.

We have also computed the average difference between the sets of data at the two temperatures: by subtracting the set at 299 K from the set at 230 K we obtained an average difference of  $-5.16 \times 10^{-23} \text{ cm}^2$  (standard deviation,  $5.60 \times 10^{-23} \text{ cm}^2$ ).

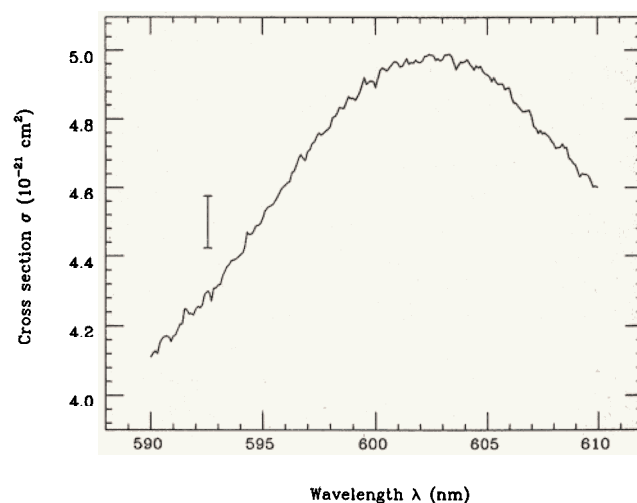


Fig. 2. Absorption spectrum in the region 590–610 nm at 230 K averaged over 0.5 nm. The error bar indicates the standard deviation of the average over six scans.

TABLE 1 Results of the  $\chi^2$  Test

	299 K	230 K
Parabolic curve	72.47	70.94
Gaussian curve	44.95	21.57
Lorenzian curve	38.72	36.77

The cross correlation between the two sets of values, at low and high temperature, has also been evaluated. The maximum value of the normalized cross correlation is 0.99723, obtained for a relative shift toward shorter wavelengths of the low-temperature curve of 0.13 nm. At no shift the cross correlation is 0.99667. The value of the cross correlation is reduced to 0.99575 for a positive shift equal to 0.1 nm.

The average difference between the two sets of data, after shifting the high-temperature data toward longer wavelengths by 0.1 nm, is  $-4.91 \times 10^{-23} \text{ cm}^2$  (standard deviation,  $5.31 \times 10^{-23} \text{ cm}^2$ ).

These considerations could lead to the statement that at each wavelength the two measurements are temperature

independent within the experimental error. However, the two curves taken as a whole show a displacement that amounts to about 0.1 nm. This should qualify the previous statement concerning the temperature dependence.

The limited extent of the spectral region considered prevents us from further conclusions about the absolute independence of the entire Chappuis band on the temperature.

For convenience, Table 2 gives the absorption cross-section values at the two temperatures: in the table, however, the data, as presented in Figures 1 and 2, have been additionally subjected to a running average over 0.5-nm intervals.

Comparisons with the results of other authors indicate a certain disagreement on the temperature dependence of the absorption cross section.

At room temperature, *Vigroux's* [1953] spectrograms suggest values that agree well with *Grigg's* [1968] data; the mean ratio between *Vigroux's* and the present work is 1.1. This work is in good agreement with the results by *Inn and Tanaka* [1953]. The mean ratio from the more recent work by *Penney* [1979], as obtained by reading graphs, is 1.04.

TABLE 2. Absorption Cross Sections of O<sub>3</sub> at 299 K and 230 K (Running Average Over 0.5-nm Intervals)

Wavelength, nm	Cross Section T = 299 K ( $10^{-20} \text{ cm}^2$ )	Standard Deviation, %	Cross Section T = 230 K ( $10^{-20} \text{ cm}^2$ )	Standard Deviation, %
590.0	0.4067	0.75	0.4126	0.90
590.5	0.4091	0.75	0.4155	0.83
591.0	0.4133	0.78	0.4172	0.92
591.5	0.4188	0.82	0.4229	0.87
592.0	0.4214	0.76	0.4245	0.95
592.5	0.4239	0.81	0.4284	0.90
593.0	0.4268	0.75	0.4319	0.85
593.5	0.4317	0.89	0.4376	0.83
594.0	0.4368	0.79	0.4407	0.88
594.5	0.4413	0.85	0.4472	0.84
595.0	0.4466	0.87	0.4514	0.85
595.5	0.4520	0.81	0.4559	0.85
596.0	0.4566	0.78	0.4607	0.91
596.5	0.4612	1.10	0.4668	0.85
597.0	0.4637	0.82	0.4702	0.87
597.5	0.4674	0.85	0.4751	0.84
598.0	0.4698	1.01	0.4785	0.93
598.5	0.4731	1.75	0.4833	0.85
599.0	0.4781	0.81	0.4862	0.75
599.5	0.4814	0.88	0.4902	0.95
600.0	0.4847	0.83	0.4915	0.85
600.5	0.4883	0.92	0.4948	0.89
601.0	0.4897	0.78	0.4961	0.82
601.5	0.4915	0.84	0.4966	0.85
602.0	0.4940	0.93	0.4972	0.86
602.5	0.4954	0.85	0.4984	0.89
603.0	0.4952	0.85	0.4980	0.85
603.5	0.4919	0.84	0.4968	0.93
604.0	0.4913	0.85	0.4967	0.89
604.5	0.4891	0.80	0.4951	0.92
605.0	0.4886	0.85	0.4927	0.95
605.5	0.4871	0.78	0.4907	0.85
606.0	0.4843	0.85	0.4876	0.90
606.5	0.4783	0.83	0.4832	0.81
607.0	0.4762	0.79	0.4803	0.85
607.5	0.4721	0.81	0.4760	0.84
608.0	0.4697	0.86	0.4729	0.85
608.5	0.4664	0.83	0.4713	0.89
609.0	0.4628	0.85	0.4660	0.90
609.5	0.4587	0.87	0.4635	0.83
610.0	0.4574	0.85	0.4621	0.91

At low temperature, it should be mentioned that Vigroux's [1953] and Humphrey and Badger's [1947] results are almost temperature independent: in fact, the ratio between low- and high-temperature values is nearly unity (1.01) in Vigroux's case, while Humphrey and Badger see little increase (+3%) in the absorption coefficient when temperature is lowered. On the contrary, Chappuis [1880, 1882] qualitatively and Vassy and Vassy [1948] and Penny [1979] quantitatively obtain higher values (+18.8% and +12%, respectively) for the cross section at low temperature. In a note added in proof, Penney [1979] lessens the dependence of the absorption coefficient on temperature, its corrected value being 2.5%.

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