

High-resolution laboratory absorption cross section of O₃. Temperature effect

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Ozone (O₃) is one of the most important minor components of the troposphere and stratosphere. It is involved in the attenuation of the solar flux in the visible and ultraviolet regions and in many photochemical processes. Accurate calculations of the atmospheric transmission and photolysis frequencies require laboratory values of the absorption cross sections σ_{O_3} in the temperature range 200–300 K; such values are reported.

Measurements of the absorption cross sections of O₃ have been made at four temperatures 218, 228, 243 and 295 K in the range 195–345 nm and at 273 K in the range 300–345 nm. The absorption spec-

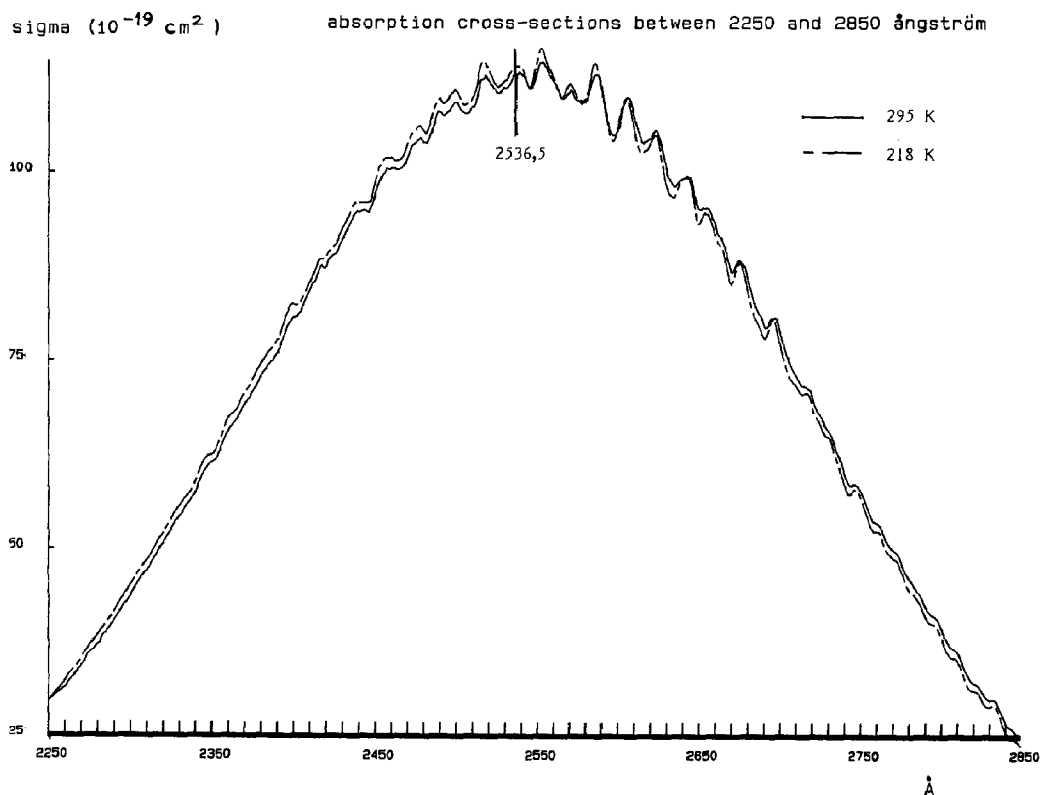


Fig. 1. Hartley band in the region of the maximum.

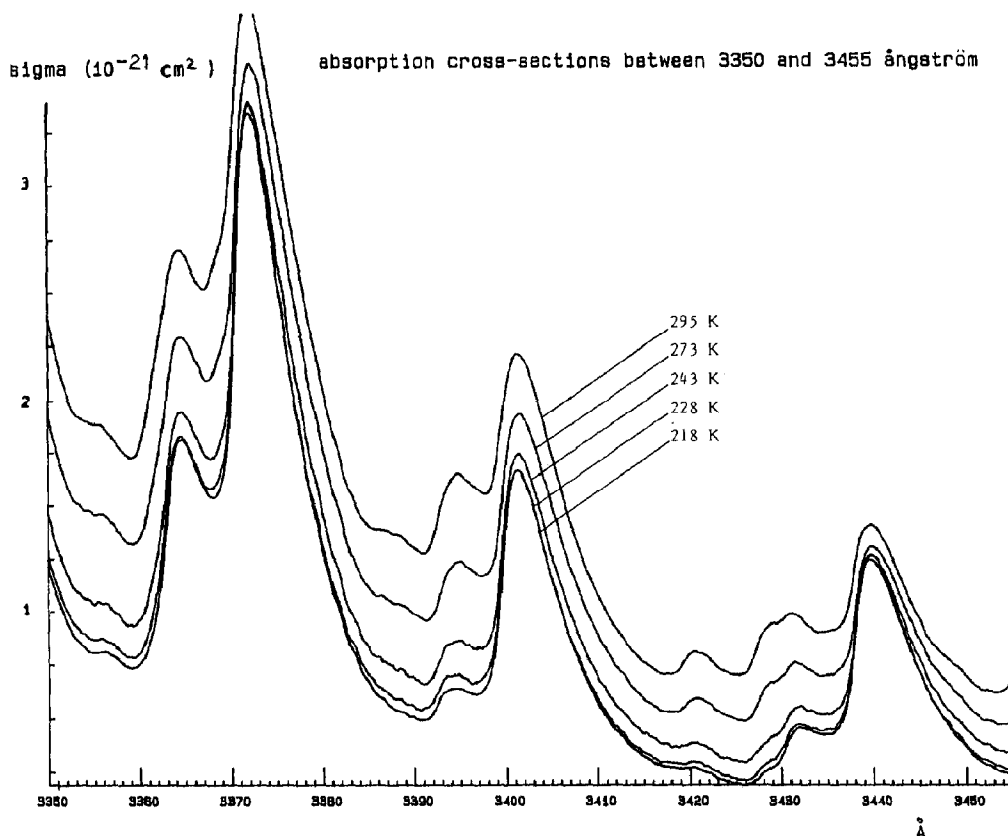


Fig. 2. Temperature effect in the Huggins bands.

trum consists of a strong continuum (Hartley band) with a maximum near 250 nm which is overlapped in the higher wavelength region ($\lambda > 310$ nm) by diffuse vibrational structures corresponding to the Huggins bands. In the Hartley band the temperature effect is found to be weak. At the mercury line wavelength ($\lambda = 253.65$ nm), near the maximum of the absorption (fig. 1), the cross section increases by about 1% when the temperature decreases from 295 to 218 K. At ambient temperature, our σ value $(113.0 \pm 1.1) \times 10^{-19} \text{ cm}^2$ is close to the new value determined by Mauersberger et al.: $(113.6 \pm 0.5) \times 10^{-19} \text{ cm}^2$ [1]; this agreement confirms the validity of our absolute measurements.

In the optical window centered at 210 nm, the observed cross sections exhibit a negligible temperature dependence.

On the other hand, in the Huggins bands, there is a strong variation of the values with temperature,

particularly in the regions of low absorption between the peaks (fig. 2). Moreover, the whole structure of the bands is slightly shifted (0.05 nm) towards lower wavelengths when the temperature decreases to 218 K.

A comparison with other data shows relatively good agreement with

- the absolute value of Molina and Molina [2]: better than 1% in the optical window near 210 nm, 2%–3% for $\lambda > 230$ nm;
- the relative values of Bass and Paur [3] which have recently been adopted by the IOC as a reference: 1%–2%, after calibration to the new value of Mauersberger et al. [1] and shifting their wavelength scale by about 0.05 nm towards the UV. Note that a similar shift in wavelength is also observed in the NO_2 spectrum of Bass and Paur as shown by Koffend et al. [4], Davidson et al. [5] and our group.

The present results obtained at five temperatures

between 295 and 218 K in the spectral range 190–350 nm (273 K: 300–345 nm) in steps of 0.01 nm are now available on floppy disks. They have been obtained with an experimental device described previously [6]. Two absorption tubes have been used for the measurements. They are made from quartz and are 32.85 and 815.0 mm long. The range of the ozone partial pressure is about 1–600 Torr, in order to provide optical densities close to unity. Two spectrometers THR 1500 and HR 640 (Jobin Yvon) have been used. In both cases the spectral bandwidth is about 0.01 nm.

For low-temperature measurements the absorption cell has been connected to a cryostat with a cooled methanol flow. Fluctuation of the temperature is within 0.1° and the difference between different parts of the cell remains below 0.3°.

The absorption cross section σ is given by

$$\sigma = \frac{D}{2l[(p_{\text{O}_2})_i - p_{\text{T}}]} \frac{RT}{\mathcal{N}}$$

where $(p_{\text{O}_2})_i$ is the initial oxygen pressure and p_{T} the total pressure of the mixture. \mathcal{N} is Avogadro's number, T the temperature (K), D the optical density and l the optical length.

Under these experimental conditions, the total er-

ror has been estimated [6] as 1.3% in the Hartley band and 1.3% to 2.5% in the Huggins bands, the difference being related to the strong variation of the cross section with wavelength in the latter spectral range.

At present, determination of cross sections is in progress at 218 and 295 K in the visible absorption band (Chappuis band) where some uncertainties remain. In addition, a cooled multipass cell is in the course of construction for very low absorption cross-section measurements in the 350–500 nm region between the Chappuis and Huggins bands.

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