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ATMOSPHERIC REMOTE-SENSING REFERENCE DATA FROM GOME—2. TEMPERATURE-DEPENDENT ABSORPTION CROSS SECTIONS OF O₃ IN THE 231–794 NM RANGE

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Abstract—Absorption cross sections of O_3 in the 231–794 nm range have been measured at temperatures between 202 and 293 K using the Global Ozone Monitoring Experiment (GOME) Flight-Model (FM) satellite spectrometer. The GOME FM spectra have a spectral resolution of about 0.2 nm below 400 nm and of about 0.3 nm above 400 nm, and were recorded covering simultaneously the Hartley, Huggins, and Chappuis bands centered around 255, 340, and 610 nm, respectively. The variation of the O_3 absorption cross sections was investigated over the entire spectral range 231–794 nm. The new cross sections are important as reference data for atmospheric remote-sensing of O_3 and other trace gases. © 1999 Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

Many experimental techniques use the characteristic absorption structures of O_3 in the UV and visible spectrum for the determination of the atmospheric ozone. Such measurements are essential for the monitoring of changes in the abundance of stratospheric and tropospheric O_3.

The Global Ozone Monitoring Experiment (GOME) satellite spectrometer, launched in 1995 onboard the ERS-2 satellite, measures back-scattered solar radiation in the nadir-viewing geometry. The data are used for the determination of atmospheric column densities of O_3, NO_2, and other trace gases on a global scale when averaging over a period of about three days. Prior to launch, laboratory reference spectra of NO_2, O_3, and SO_2 were measured using the GOME spectrometer. One important advantage of these spectra is that they cover the entire UV-visible-NIR spectral region and a relevant range of atmospheric temperatures. Furthermore, the GOME FM spectrometer is a well-characterized instrument including both spectral and radiometric calibration, and its instrumental line shape was accurately determined.[1] In a previous communication, temperature-dependent absorption cross sections of NO_2 derived from these measurements have been reported.[2] In the present paper, absorption cross sections of O_3 in the 231–794 nm range at temperatures between 202 and 293 K are presented.

2. EXPERIMENTAL

2.1. Experimental set-up

The GOME instrument is a four-channel Si-diode array grating spectrometer, observing between 231 and 794 nm at a spectral resolution of about 0.2 nm below 400 nm and of about 0.3 nm above 400 nm.[1] Three similar instruments were built in the framework of the GOME project: the bread-board model (BBM), the flight model (FM), and the flight spare model (FSM).‡ All measurements described in this paper were made using the GOME FM model. Optimum pixel exposure

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‡ The spectral resolution of the GOME FM instrument is slightly lower (up to 0.6 nm) in the first part of Channel 2, i.e. in the region between 312 and 321 nm.

times (1.125–36 s), gas mixtures, and flow rates were determined in an iterative way. Details concerning the set-up of GOME and the coolable White-type absorption cell used in this study are given elsewhere.[1−4]

For the measurements described below, the absorption path was varied between 985 and 1465 cm, and cell temperatures were adjusted at 293, 273, 241, 221, and 202 K. Most of the measurements were made using a gas flow of a few hundred ml/min, using synthetic air as the carrier gas mixed with a flow of O_2/O_3, except for a few experiments where the absorption cell was filled up to atmospheric pressure in order to obtain higher absorbance in some spectral regions. O_3 was generated by a silent discharge through a flow of O_2 from a commercial gas cylinder (certified purity 99.99%). O_3 mixing ratios and total flow rates were optimized for absorption in different regions between 231 and 794 nm.

For all gas mixtures and temperatures, the GOME FM measurements were carried out according to the procedure described in Ref. 2, namely, recording of wavelength calibration and of lamp reference spectra followed by an absorption spectrum with O_3 inside the absorption cell. After the silent discharge producing O_3 was switched off, another lamp spectrum was recorded without O_3 in the absorption cell in order to monitor lamp drifts.

2.2. Data reduction

Having first subtracted the dark current, the wavelengths for all spectra were calibrated using a fourth-order polynomial. The line positions of the Pt/Cr–Ne hollow cathode emission lamp used for this purpose are known accurately (± 0.0002 nm) from high-resolution Fourier-transform spectra.[1,5] Later, the accuracy of the wavelength calibration was verified using high-resolution absorption spectra of NO_2 and O_3 recorded using a Fourier-transform spectrometer (FTS).[6] The agreement between the spectra recorded using GOME FM and the FTS was found to be better than 0.03 nm.

After wavelength calibration, all spectra were corrected for straylight. This correction was carried out assuming uniform straylight in every GOME channel using the signal on the edges of each channel. The lamp spectra recorded before and after the O_3 absorption spectrum were averaged to obtain a reference spectrum $I_0(\lambda)$. Then, the optical densities, $OD(\lambda) = \ln[I_0(\lambda)/I(\lambda)]$, were calculated, where $I(\lambda)$ is the spectrum with O_3 in the White cell. The optical density spectra $OD(\lambda)$ were scaled and concatenated to obtain complete coverage of the 231–794 nm range (see Fig. 1).

2.3. Determination of absorption cross-sections

The transformation of the spectra $OD(\lambda)$ to absolute absorption cross sections $\sigma(\lambda)$ requires accurate knowledge of the absorption path lengths and the absorber's concentrations in the gas cell. The latter was not determined during the GOME measurements as only limited time was available. Therefore, O_3 cross-section measurements at 293 K in the 300–480 nm range were repeated in Bremen using the same light sources, absorption cell, and gas system, together with a commercial ARC-500 grating spectrometer equipped with a Si-diode array detector. Details of the set-up and measurements are described elsewhere.[4] The same measurement procedure as described above was employed.

To determine absolute O_3 absorption cross sections, NO was added to the gas flow to convert the O_3 into NO_2. By stepwise increasing the NO flow an increase in NO_2 absorption was observed. This increase stopped when the NO amount equaled that of O_3 indicating complete chemical conversion of O_3 into NO_2. The initial O_3 concentration was derived from the NO_2 absorption in this mixture using the absorption cross sections of Ref. 2. The titration cycle was repeated five times and derived O_3 concentrations were averaged. The RMS deviation between the measurements is below 1%. Adding all other experimental uncertainties (cell length, cell pressure, cell temperature) this leads to an overall experimental uncertainty of 2.6% for the O_3 cross sections in the maximums of the Hartley and Chappuis bands. In regions where the O_3 cross sections are the experimental uncertainty becomes larger due to an increasing importance of small lamp drifts, the latter contributing always less than 2% during test measurements.

Using the new room-temperature laboratory cross sections, the GOME optical density spectra at 293 K were scaled to absolute absorption cross sections in the 300–330 nm range. At all other
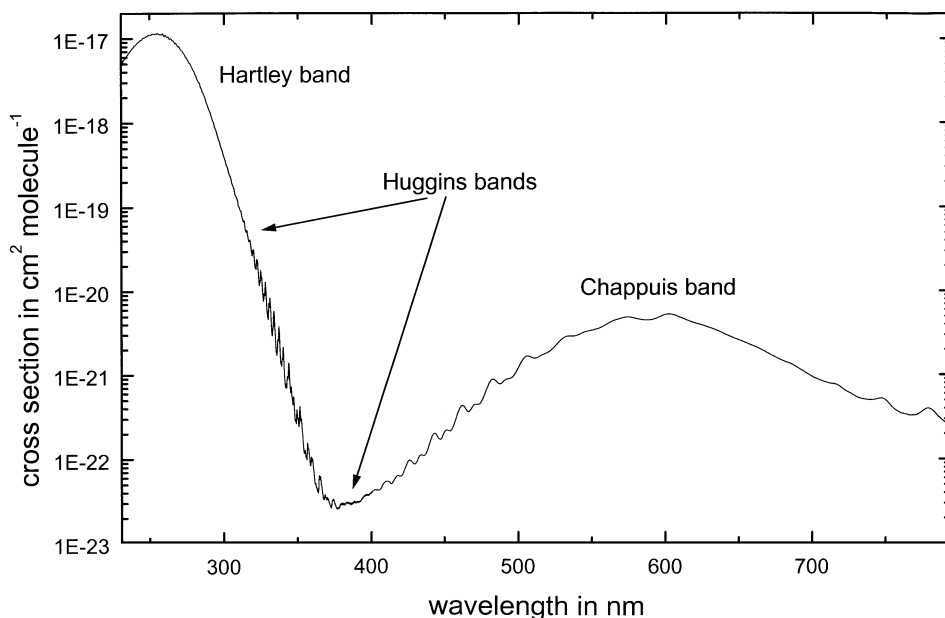
Fig. 1. The O_3 absorption cross section spectrum at 293 K as measured with the GOME FM spectrometer. The spectral resolution is about 0.2 nm at wavelengths below and about 0.3 nm above 400 nm. The different bands discussed in the text are indicated. Note the logarithmic y-scale, and the complete coverage of the 231–794 nm range.

temperatures (273, 241, 221, and 202 K), the integrated optical density $\int OD(\lambda)d\lambda$ between 231 and 794 nm was calculated and scaled to the integrated absorption cross section $\int \sigma(\lambda)d\lambda$ at 293 K. The same procedure was already applied to the NO_2 spectrum recorded with GOME.[2] This approach is possible because the integrated absorption cross section is independent of temperature when the electronic transition moment is independent of the nuclear coordinates (Franck–Condon principle). The influence of temperature on the spectrum is therefore only produced by the different populations of the lower vibrational–rotational states, all of which are accounted for by integrating over a broad absorption region.

The new approach has the advantage that an experimental determination of the O_3 concentration at only one reference temperature (e.g. 293 K) is sufficient to scale optical densities at other temperatures to absolute absorption cross sections. This significantly reduces experimental uncertainties when comparing spectra at different temperatures, since there is no additional uncertainty due to the different O_3 concentration determinations. Therefore, the overall uncertainties of the new O_3 absorption cross sections are given by the experimental uncertainties and the systematic errors introduced by the assumption of temperature-independent integrated absorption cross sections. The latter contributions are not accurately known but are estimated to be smaller than 2% on comparison with other measurements of temperature-dependent absorption cross sections of O_3 and other molecules (NO_2, OClO) in the UV-visible range.

A comparison between the new O_3 absorption cross sections and their temperature dependence measured with the GOME FM spectrometer and earlier work is presented below.

3. DISCUSSION

The O_3 absorption cross sections and their temperature dependence are of importance for both the physics and chemistry of the atmosphere. For example, they determine atmospheric photolysis rates of O_3 and the contribution of O_3 to the atmospheric heat balance.[7] Also, an accurate knowledge of the temperature dependence of the absorption cross sections in the Huggins bands (300–370 nm) is potentially of relevance for the retrieval of O_3 profiles from nadir-viewing satellite instruments such as GOME.[8-10]
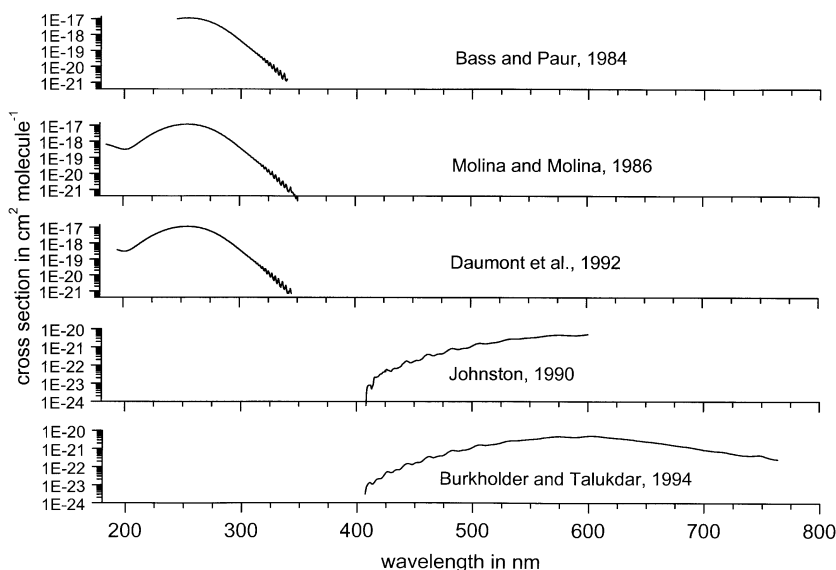
Fig. 2. Overview over some previously published O_3 absorption cross sections at room temperature. Until this study, no simultaneous measurements of the Hartley, Huggins, and Chappuis bands were reported. Note the logarithmic y-scales and the different magnitudes in the upper three and the lower two traces.

Although a relatively large number of studies on the absorption cross sections of O_3 has been published, no previous study has measured both the spectral window and the temperature range of the present work. As a result, the present work can be compared with earlier studies only in selected spectral and temperature regions. Some published O_3 absorption cross sections at room temperature are shown in Fig. 2.

As the new O_3 absorption cross sections at different temperatures were calibrated by applying the assumption that the integrated cross sections are temperature-independent, relevant features of the temperature dependence of the O_3 spectrum require further discussion.

3.1. Hartley band (231–300 nm)

The absolute value and the temperature dependence of the absorption cross sections in the Hartley band was studied by several authors; see Ref. 11 and references therein. The most recent measurements of the absolute value of the O_3 cross sections at 293 K vary at 253.65 nm (Hg emission line, see Table 1) between 1130.5 and 1157×10^{-20} cm^2 molecule^{-1}, i.e. they agree within 2.3%. The value recommended by NASA is 1147×10^{-20} cm^2 molecule^{-1} (Ref. 11). The new GOME data, calibrated using laboratory measurements in the 300–330 nm region, provide a cross section of 1150×10^{-20} cm^2 molecule^{-1} at 253.65 nm, which is in good agreement with the other studies (see Table 1).

Table 1. Room-temperature absorption cross sections of O_3 in the Hartley band at 253.65 nm (in 10^{-20} cm^2 molecule^{-1})

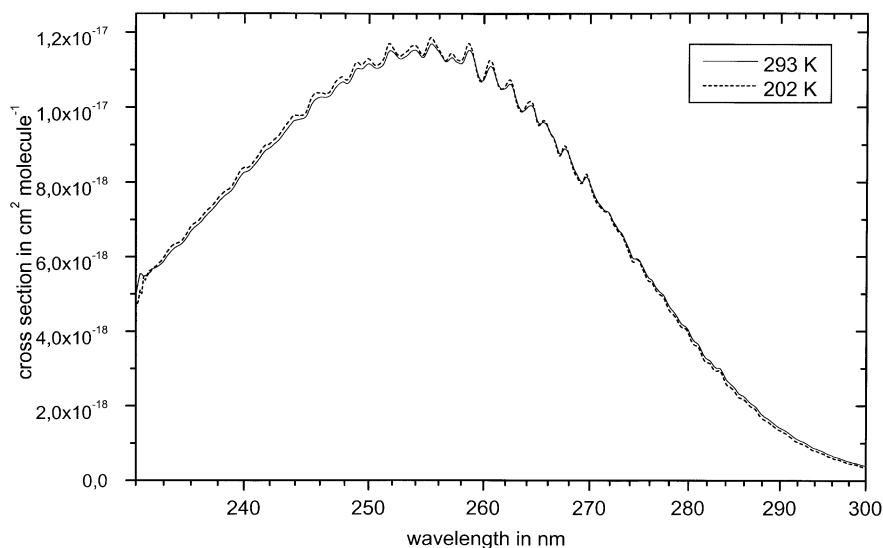| Source	T (K)	σ_{O3}
Hearn[12]	295	1147
Bass and Paur[13]	298	1145
Molina and Molina[14]	298	1157
Mauersberger et al[15]	297	1136
Yoshino et al[16]	295	1143
Daumont et al[17]	295	1130.5
This work	293	1150

Fig. 3. The new absorption cross sections of O_3 at 293 K (solid line) and 202 K in the Hartley band (dotted line). An increase in the differential absorption cross sections with decreasing temperature is obvious, see text for more details. The overall shape of the Hartley band also changes slightly with temperature.

The cross sections of the O_3 Hartley band and their temperature dependence were studied by Hearn,[12] Bass and Paur,[13] Molina and Molina,[14] Mauersberger et al,[15] Yoshino et al,[16] and Daumont et al.[17] The studies of Bass and Paur, Molina and Molina, and Daumont et al report a 0.9–1.0% increase of the cross sections between room (293–298 K) and low temperatures (202–218 K), while Yoshino et al conclude that the temperature effect is negligible. In this study, a clear temperature effect is observed, showing a systematic increase in the differential cross sections in the structured absorption between 240 and 270 nm with decreasing temperature (see Fig. 3). The increase at 253.65 nm is 1.6% between 293 and 202 K. Although the integrated absorption cross sections were assumed to be constant over the studied temperature range, the increase of differential structures in the Hartley band is independent of this assumption. Note also the effect of an increase of the O_3 cross sections below 260 nm with temperature, while they decrease with temperature at wavelengths above 260 nm. This observation is in good agreement with the earlier study of Molina and Molina.[14]

3.2. Huggins bands (300–370 nm)

The absorption cross sections in the Huggins bands of O_3 show a strong temperature dependence. There are several previous studies of this region, in particular the work of Bass and Paur[13] (203–293 K, 245–340 nm), of Brion et al[18] (218–295 K, 195–345 nm), and of Cacciani et al[19] (220 and 293 K, 339–355 nm). A comparison of the new GOME FM data with previous work shows reasonable agreement both in the magnitude and in the temperature dependence of the cross sections, see Fig. 4. Figure 5 shows a part of the Huggins bands between 327 and 360 nm at temperatures from 202 to 293 K. The temperature dependence of the spectrum is explained by changing rotational and vibrational distributions in the electronic ground state. In the long-wavelength tail of the Huggins bands, hot bands arising from excited vibrational levels of O_3 can clearly be distinguished from cold bands (see Fig. 5). Vibrational assignments of the Huggins bands were given by Katayama[20,21] and by Joens.[22] A more detailed theoretical analysis of the spectrum is currently in progress.

3.3. Chappuis band (370–794 nm)

The absorption cross sections of O_3 in the Chappuis band have been studied by several authors.[23–27] However, the only investigation of temperature effects in the 400–480 nm region was published by Burkholder and Talukdar.[27] Using a double-absorption cell set-up, these authors
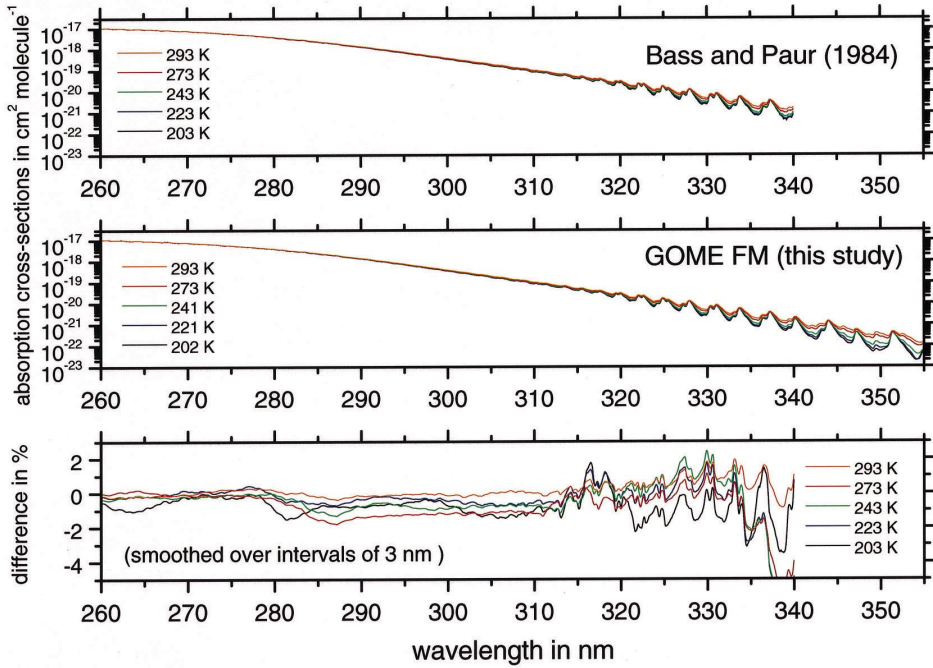
Fig. 4. Comparison between the absorption cross sections of O_3 recorded with GOME FM and from Bass and Paur (1984). The differences between GOME FM and the reference spectra (lowest trace) were smoothed over intervals of 3 nm to account for the different instrumental functions and other effects (wavelength uncertainties etc). The overall agreement is better than 2% up to 310 nm. The sharper features in the Huggins bands show stronger deviations, partly due to different instrumental functions.
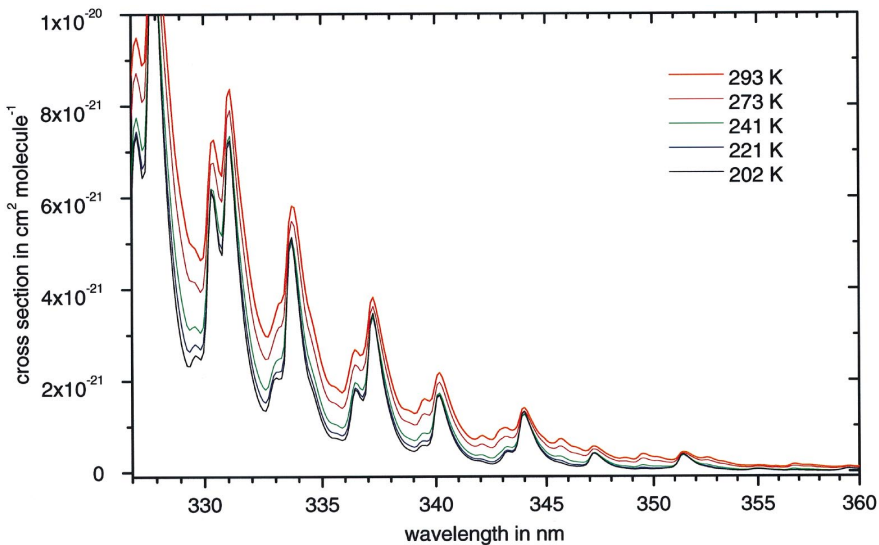

Fig. 5. The absorption cross sections of O_3 in the Huggins bands, showing a strong temperature dependence. The differential absorption cross sections increase in a non-linear way with temperature, probably due to the presence of hot bands at higher temperatures and to congestion by rotational depopulation of the lower states. Several hot bands appear at wavelengths above 340 nm.

employed the room-temperature cross sections at selected laser wavelengths from Anderson and Mauersberger[26] to determine the absolute absorption cross sections at lower temperatures.

In the 370–500 nm region, the new GOME absorption cross sections show the same temperature effect as observed in Ref. 27, i.e. a decrease with decreasing temperature. At wavelengths above
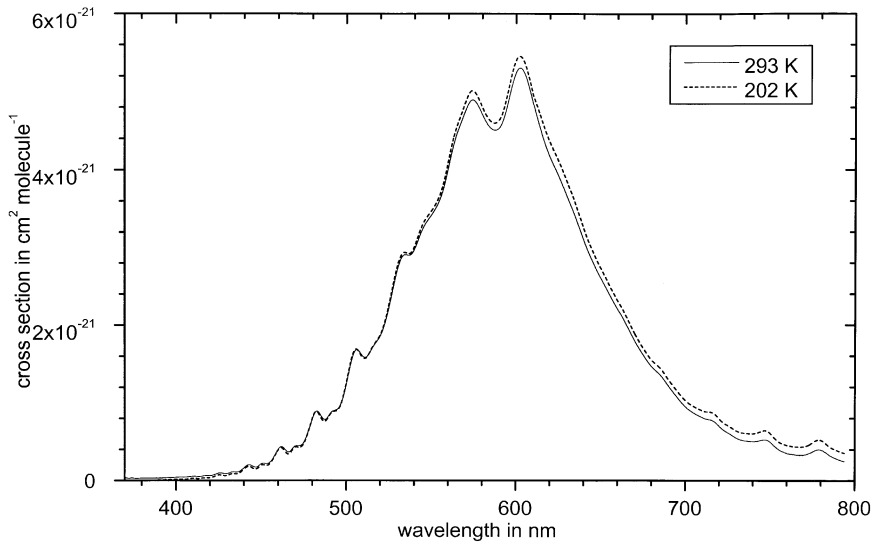
Fig. 6. The new GOME FM absorption cross sections of O_3 in the Chappuis band at temperatures of 293 K (solid line) and 202 K (dotted line), see text for more details.

Table 2. Room-temperature absorption cross sections of O_3 at selected wavelengths (in nm) in the Chappuis band (in $10^{-24} cm^2 molecule^{-1}$)

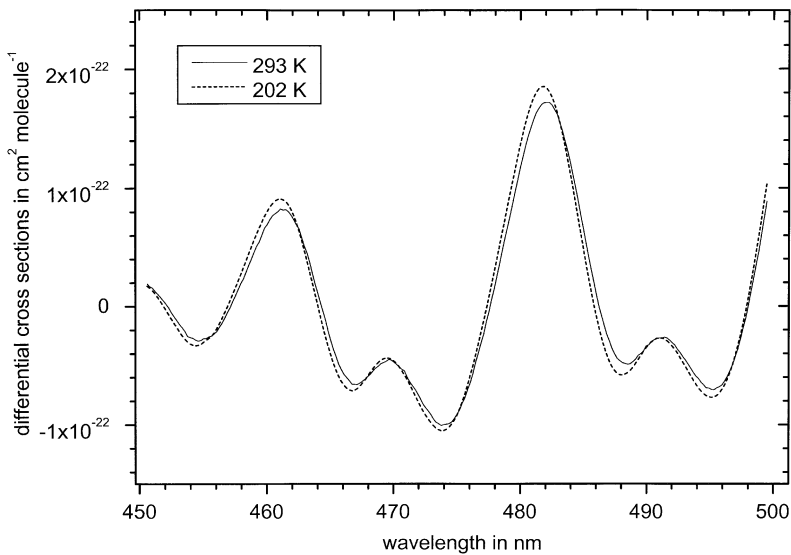| Source	T (K)	543.516	594.096	611.971	632.816
Ref. 26	298	3092	4674	4427	3313
Ref. 27	298	3075	4569	4633	3383
This work	293	3167	4756	4700	3505

Fig. 7. The differential absorption cross sections O_3 in the Chappuis band at temperatures of 293 K (solid line) and 202 K (dotted line), obviously increasing with decreasing temperature. Note that the positions of the maxima and minima shift towards smaller wavelengths with decreasing temperature. These temperature effects are of importance in DOAS retrievals of atmospheric O_3, NO_2, and $OClO$ column densities.

650 nm, the new GOME cross sections increase with decreasing temperature (see Fig. 6), in discrepancy with Burkholder and Talukdar. Note that these authors observed a decrease in the integrated absorption cross section of the Chappuis band (400–750 nm) with decreasing temperature (1.2% at 220 K). In this study, the integrated cross sections of the Chappuis band systematically increase with decreasing temperature (up to 3.6% at 202 K), except for 241 K where the integrated cross sections are 1.0% smaller compared to 293 K. It is possible that small lamp drifts are the origin of the latter deviation. Further work is in progress in order to determine the temperature dependence of the O_3 cross sections in the NIR region.[28]

The magnitude of the absorption cross sections around the peak of the Chappuis band at 612 nm is in reasonable agreement with previous work (see Table 2) and shows only little variation with temperature. Vigroux,[23] Amoruso et al,[24] and Burkholder and Talukdar[27] measured a small increase of up to 1%, while the new GOME data show an increase of 3% between 298 and 202 K. The differential cross sections between 460 and 500 nm show an important temperature dependence, see Fig. 7. The latter effect is of major importance for ground-based DOAS and is included in recent atmospheric studies.[29–31]

4. CONCLUSION

The absolute absorption cross sections of O_3 measured with the GOME FM spectrometer are an accurate medium-resolution reference standard for O_3 absorption cross sections in the UV–visible–NIR spectral region. The temperature-dependent O_3 absorption cross sections determined in this study are currently used in the data processing of the backscattered and reflected earthshine radiance recorded from space with the GOME FM. When applied to ground-based atmospheric spectra the new O_3 cross sections show very small residual errors in the DOAS analysis.[30] Tables of the O_3 cross sections recorded with the GOME FM can be obtained as ASCII files upon request to the authors.

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