Pergamon

ATMOSPHERIC REMOTE-SENSING REFERENCE DATA FROM GOME: PART 1. TEMPERATURE-DEPENDENT ABSORPTION CROSS-SECTIONS OF NO_2 IN THE 231–794 nm RANGE

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Abstract—Absorption cross-sections of NO_2 between 231–794 nm have been measured in the 221–293 K temperature range, using the global ozone monitoring experiment (GOME) flight-model (FM) satellite spectrometer. The spectra have a resolution of about 0.2 nm below 400 nm and of about 0.3 nm above 400 nm. These are the first reference spectra of NO_2 covering at the same time the entire UV–visible–NIR spectral range and a broad range of relevant atmospheric temperatures. The new absorption cross-sections are important as accurate reference data for atmospheric remote-sensing of NO_2 and other minor trace gases. © 1998 Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

NO_2 is amongst the most important trace gases in the Earth's atmosphere.[1] The chemistry of NO_2 is closely linked to the O_3 cycle, and its atmospheric concentrations vary significantly as a function of altitude, latitude, and season.[2] These variations, partially due to man-made gaseous emissions, need to be monitored in order to provide accurate input for political decisions on environmental protection and the preservation of the stratospheric ozone layer.[3]

For these reasons, the global ozone monitoring experiment (GOME) satellite spectrometer was launched in 1995 onboard the ERS-2 satellite. This instrument measures back-scattered solar radiation for the determination of atmospheric column densities of O_3, NO_2, and other trace gases on a global scale within three days.[4] For the retrieval procedures, absorption characteristics of these gases in the spectral range 231–794 nm are used.

Before launch, laboratory reference spectra of NO_2, O_3, and SO_2 were measured using the GOME FM spectrometer. One important advantage of these spectra is that they cover the entire UV–visible–NIR spectral range and a relevant range of atmospheric temperatures. Furthermore, the GOME FM spectrometer is a well-calibrated instrument, including spectral and radiometric calibration and an accurate determination of its instrumental line shape.[5] Therefore, the new absorption cross-sections measured using the GOME FM spectrometer are essential as reference data for the retrieval of atmospheric NO_2 and other trace gases, not only for GOME but also for medium-resolution zenith sky differential optical absorption spectroscopy (DOAS) observations taken on ground, or from balloon and aircraft platforms.

2. EXPERIMENTAL

2.1. The gome instrument

The GOME instrument is a four-channel Si-diode array grating spectrometer, observing between 231 and 794 nm at a resolution of about 0.2 nm below 405 nm and of about 0.3 nm above 405 nm

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Table 1. Spectral coverage and resolution of the GOME instrument

Channel	1A	1B	2	3	4
Coverage (nm)	231–307	307–316	311–405	405–611	595–794
Resolution (nm)	0.20	0.20	0.17	0.29	0.33

(see Table 1). Three identical instruments were built by an industrial consortium in frame 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 carried out using the GOME FM model.

Light is brought into the GOME spectrometer by a scan mirror and focused onto the entrance aperture by a telescope. A predisperser prism is then used to create a first spectrum, which is separated into the four detection channels (Table 1) by means of a directed prism which picks off and separates channels 1 and 2, and a dichroic mirror which directs light either towards channel 3 or 4. Each channel comprises a high-precision grating and a Peltier-cooled 1024-pixel Si-diode array detector. One advantage of this concept is that the pixel exposure times (PET) can be selected independently for every channel.

The wavelength calibration of the GOME instrument is performed with a built-in Pt–Cr/Ne hollow-cathode lamp. This lamp was spectrally calibrated by high-resolution Fourier-transform spectra in 1994.[6] The radiometric calibration of GOME was performed by the industry, providing accurate key data concerning dark current, pixel-to-pixel gain, stray light, and polarization corrections.[7]

During the measurements described here, the GOME instrument was installed in a White-room at the Institute of Technical Physics (TPD/TNO) in Delft, The Netherlands. In a laboratory room near this White-room, a transportable experimental set-up was installed in order to measure accurate reference spectra using the GOME spectrometer. This set-up, called CATGAS (see below), was linked optically to the GOME instrument by a Quartz glass fiber.

2.2. The CATGAS set-up

The calibration apparatus for trace gas spectra (CATGAS) consists mainly of an optical bench with a 120 cm base-length White-type coolable absorption cell.[8] In this study, the absorption path was varied between 985 and 1465 cm.

The Quartz-cell has a double jacket, with an ethanol–water mixture coolant flow through the inner jacket, the outer jacket being evacuated to provide thermal isolation. In addition, the cell is surrounded by isolating foam (Armaflex). The Ethanol cooling is achieved by a two-stage cryocooler (Haake KT-90). For the measurements described below, temperatures were varied between 221 and 293 K. The temperature stability in the cell was determined to be better than 1 K.

Gaseous mixtures are produced using calibrated flow controllers (MKS). The cell pressure is monitored using capacitive pressure transducers (Baratron). Synthetic air is employed as carrier gas, with typical flow rates of a few hundred ml/min. For this study, NO_2 was taken from a commercial gas bottle (Messer Griesheim) with a certified mixture of 1% NO_2 in N_2. NO_2–air mixing ratios and total flow rates were varied according to the different absorptions of NO_2 between 231 and 794 nm. As broad-band light sources, a D_2 lamp (Heraeus, 200–430 nm) and a quartz–tungsten–halogen lamp (Osram, 340–800 nm) were available.

2.3. Measurement procedure

For all gas mixtures and temperatures (293, 273, 241 and 221 K), the GOME FM measurements were carried out according to the following procedure:[9]

1. Measurement of a spectrum of the GOME internal Pt–Cr/Ne line source, required for spectral calibration.
2. Measurement of a "dark" spectrum without any light source for the selected PET, required for dark current correction.
3. Measurement of a spectrum without any absorber in the CATGAS cell, required as reference for determination of absorption cross-sections.

4. Measurement of a spectrum with the absorber in the CATGAS cell.
5. Measurement of a second spectrum without any absorber in the CATGAS cell, in order to monitor drifts in the lamp reference spectrum.

   Prior to the measurements, optimum PET, gas mixtures, and flow rates were determined in an iterative way. Typical PET for this study were in the range between 1.125 and 36 s.

2.4. Data reduction

All recorded spectra were wavelength-calibrated using a fourth order polynomial and accurate reference line positions of the Pt–Cr/Ne lamp, together with the spectrum recorded in step 1. Then, the dark current (recorded in step 2) was subtracted from every spectrum except for the Pt–Cr/Ne reference spectrum. Thereafter, all spectra were corrected for straylight assuming uniform straylight in all GOME channels, using the signal on the edges of each channel. The latter is a very small correction outside of the edges the overlap regions.

The lamp spectra recorded in steps 3 and 5 were averaged, to obtain a reference spectrum $I_0(\lambda)$. Together with the absorption spectrum $I(\lambda)$ of step 4, the optical densities, $OD(\lambda) = \ln[I_0(\lambda)/I(\lambda)]$, were calculated. These spectra $OD(\lambda)$ were then scaled and concatenated thus obtaining complete coverage of the 240–794 nm range (see Fig. 1).

In order to correct for N$_2$O$_4$ absorption (N$_2$O$_4$ is formed in thermal equilibrium with NO$_2$),[10] a procedure was employed that is based on the fact that this dimer has negligible absorption at wavelengths above 400 nm. To apply these corrections, three spectra $I(\lambda)$ were recorded with different NO$_2$ amounts in the CATGAS cell. An extensive discussion of this approach is given elsewhere.[11] An example for this correction procedure is shown in Fig. 2. Although not the primary focus of this work, the relative shape of the N$_2$O$_4$ absorption is in good agreement with previous studies.[10]

2.5. Determination of absolute absorption cross-sections

The direct 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. However, the latter was not determined during the GOME measurements in Delft, as only limited time was available.
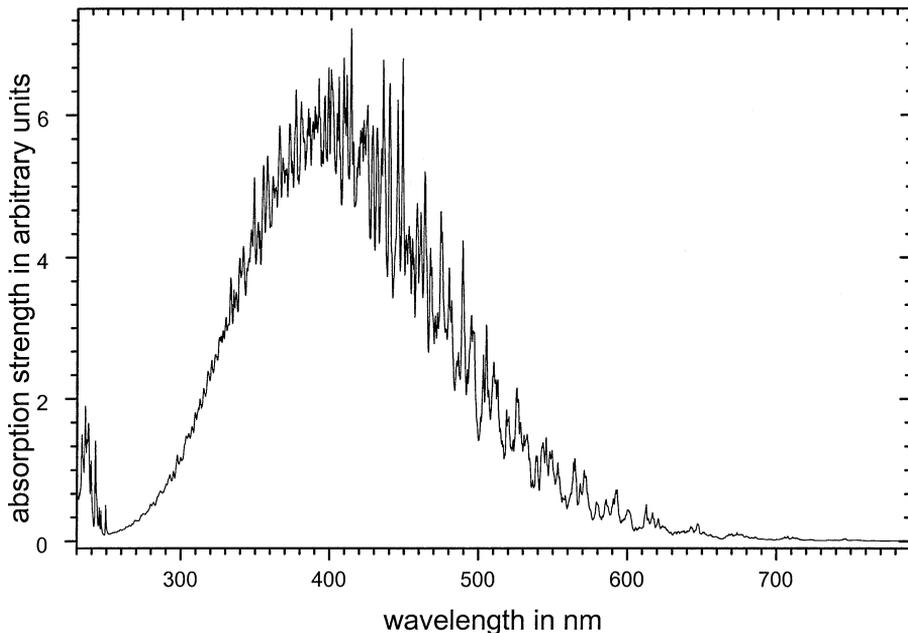
Fig. 1. Relative NO$_2$ spectrum at 293 K measured by GOME FM between 231–794 nm. The spectral resolution is 0.2 nm at wavelengths below and 0.3 nm above 400 nm.
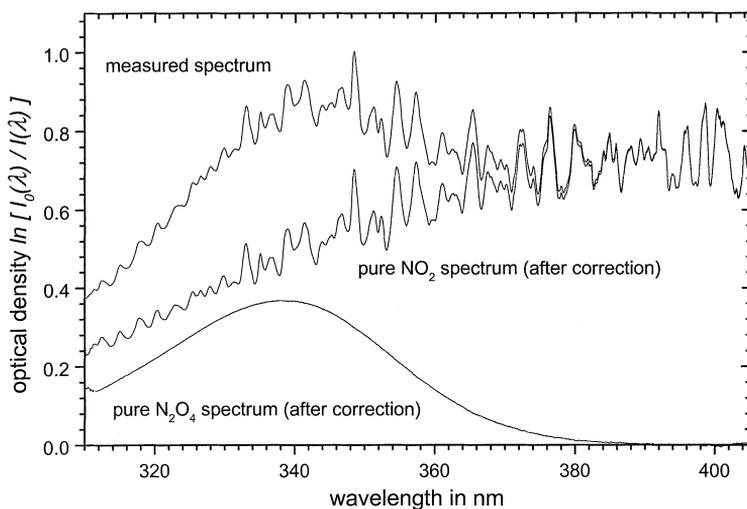
Fig. 2. Spectral separation of the NO_2 and N_2O_4 absorption (temperature of 221 K) in the 300–400 nm region. For the spectral correction procedure, absorption spectra of three different NO_2/N_2O_4 mixtures at the same temperature are required.

Therefore, NO_2 cross-sections $\sigma(\lambda)$ at 293 K were measured in Bremen after completion of the GOME FM experiments, using the CATGAS set-up and a Bruker 120-HR Fourier-transform spectrometer in the 400–550 nm range. Details of the set-up and measurements are described elsewhere.[12] Briefly, the same measurement procedure as described above was employed. The only difference is that NO_2 was taken from a lecture bottle with a very pure sample (98% stated purity). In this case, absolute NO_2 concentrations were determined accurately from the pressure in the gas mixing system. Several experiments were performed to reduce the influence of statistical errors, such as lamp drifts, etc. Together with other uncertainties (cell length, cell pressure, cell temperature) this leads to an experimental uncertainty of the reference NO_2 cross-sections of 4%.

Using the new laboratory cross-sections at 293 K, the GOME spectra $OD(\lambda)$ at 293 K were then scaled to absolute absorption cross-sections. For all other temperatures (273, 241 and 221 K), the integrated optical density $\int OD(\lambda)$ between 252–794 nm was calculated and scaled to the integrated absorption cross-section $\int \sigma(\lambda)$ at 293 K. This procedure is justified by the fact that the NO_2 spectrum in this range arises from transitions to three electronic states ($\tilde{A}^2B_2$, $\tilde{B}^2B_1$, and $\tilde{C}^2A_2$) with small absorption at 252 and 794 nm.[13] Therefore, the integrated absorption cross-section $\int \sigma(\lambda)$ is only determined by the overlap integral between the electronic wave functions of the upper and lower states, and this quantity is independent of temperature.[14] The only influence of temperature is given by the different populations of the lower vibrational–rotational states, which is accounted for by integrating over the whole electronic absorption region. This approach was in part validated by comparison of absolute absorption cross-sections determined at 273 K using GOME spectra calibrated by IUP absorption cross-sections (obtained using pure NO_2 samples).

This new approach has the advantage that only one experimental determination of the NO_2 concentration, namely at 293 K, is required to scale all optical densities at different temperatures to absolute absorption cross-sections, therefore reducing experimental uncertainties significantly when comparing spectra at different temperatures. However, this procedure requires complete coverage of the NO_2 absorption spectrum between 252 and 794 nm, which has never been undertaken prior to this study. A comparison of the new NO_2 absorption cross-sections with previously published data is presented below.

3. DISCUSSION

As the new NO_2 absorption cross-sections at different temperatures were calibrated by a self-consistent approach, relevant features of the temperature dependence of the NO_2 spectrum (see Fig. 3) require further discussion. The overall differential absorption cross-sections clearly increase
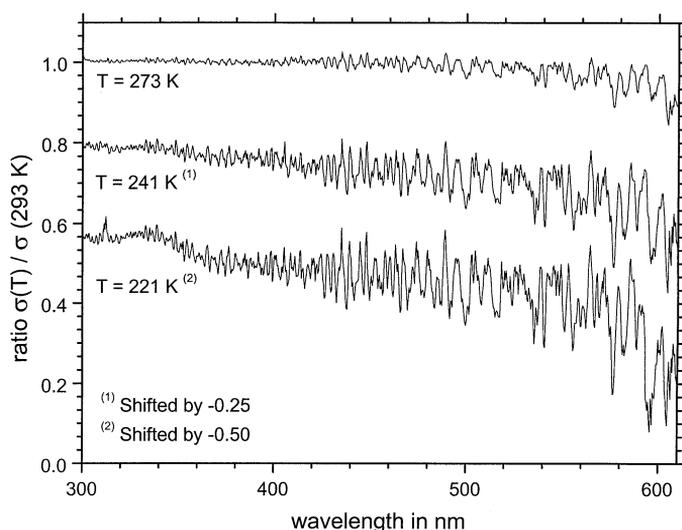
Fig. 3. Ratio of the new absorption cross-sections of NO$_2$ at 273 K, 241 K and 221 K, to those at 293 K in the 300–610 nm region. The spectra at 241 and 221 K were shifted downwards by 0.25 and 0.50 for the sake of clarity. See text for a detailed discussion of the temperature effects.

with decreasing temperature. At the same time, this effect becomes more significant at longer wavelengths.

The first observation (increasing differential structure with decreasing temperature) is explained by the lower state's rotational population which changes significantly with temperature, leading to sharper vibrational bands. The second observation, an overall increased sensitivity towards temperature at longer wavelengths, is explained by an increasing contribution of "hot" bands at the long-wavelength side of the NO$_2$ spectrum, in good agreement with recent theoretical studies.[15,16] An additional feature explaining this observation is the reduced lifetime of excited NO$_2$ states below 400 nm (dissociation threshold) leading to a significant broadening towards shorter wavelengths and thereby reducing the temperature effect. These temperature effects are most important since they can significantly reduce the residual errors in atmospheric trace gas retrievals[17] and since they provide an opportunity for detection of tropospheric NO$_2$ by DOAS methods.[18]

Although a relatively large number of studies on the absorption cross-sections of NO$_2$ have been performed, no previous study has measured both the spectral window and temperature range of the present work. As a result, the present work can be compared with previous studies only in selected spectral and temperature regions. A selection of the published NO$_2$ absorption cross-sections at room temperature is given in Fig. 4.

The studies of Schneider et al (1987),[19] Vandaele et al (1996),[20] and Voigt et al (1997)[12] can be compared with the new GOME FM spectra over a broad spectral range. Comparisons of this work with the studies of Harder et al (1997),[21] Mérienne et al (1995)[22] and Harwood and Jones (1994)[10] are confined to smaller spectral regions.

A detailed discussion of instrumental effects due to the use of different spectrometers is given by Harder et al. Two important conclusions they derive are that the data of Schneider et al suffer from inaccurate wavelength calibration, and that the cross-sections of Merienne et al, although very accurate with respect to wavelength calibration, show problems due to an undersampling of the data.

The spectra of Harder et al, Vandaele et al, and Voigt et al were recorded using high-resolution Fourier-transform spectrometers, therefore the wavelength accuracy or sampling problems are significantly smaller in these studies. However, the data of Harder et al show large deviations in the absorption cross-sections due to lamp stability problems at longer wavelengths, and the data of Vandaele et al show deviations at wavelengths below 330 nm.

The amplitude of the new absolute absorption cross-sections in the important 400–500 nm range agrees very well with previous studies. The average difference of the new data to the studies of
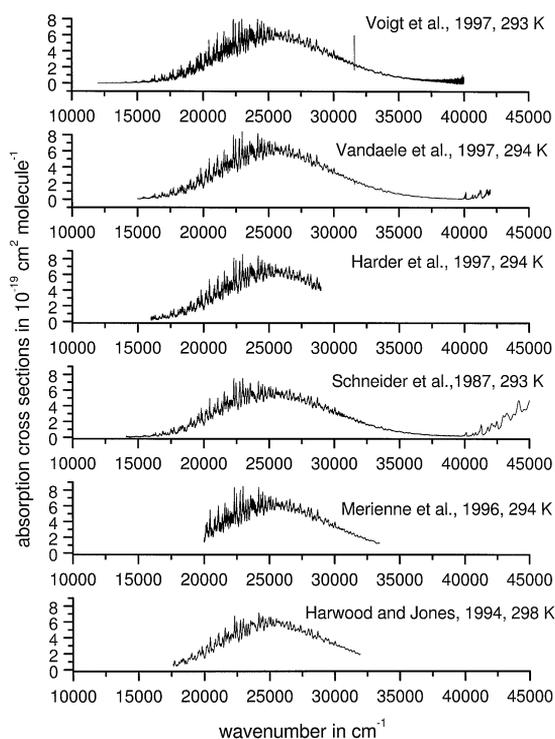
Fig. 4. Selection of previously published absorption cross-sections of NO_2 at ambient temperature, in the $10\,000$–$45\,000$ cm^{-1} range (0.2–1.0 μm). The spectra of Voigt et al, Vandaele et al and Harder et al were recorded using Fourier-transform spectrometers. The spectra of Schneider et al, Merienne et al and Hardwood and Jones were recorded using grating spectrometers.

Merienne et al, Vandaele et al and Voigt et al is smaller than 2%, while the cross-sections of Harder et al are on average 5–7% larger compared to the present work. The cross-sections of Harwood and Jones in this range are about 2–5% smaller than the new GOME FM data, while the data of Schneider et al are on average 1–4% smaller, but show significant local differences due to the lower wavelength accuracy.

In conclusion, the results of this study using GOME FM data can be regarded as an accurate medium-resolution reference standard for NO_2 absorption cross sections in the UV–visible–NIR spectral region. The new temperature-dependent NO_2 absorption cross-sections are currently used in the data processing of the GOME FM spectra recorded from space. They show the smallest residual errors between observed and predicted spectra when included in the DOAS data analysis. All data can be obtained as ASCII files upon request to the authors.

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