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Fourier Transform Measurement of NO_2 Absorption Cross-Section in the Visible Range at Room Temperature

A. C. VANDAELE, C. HERMANS, P. C. SIMON and M. VAN ROOZENDAEL
Institut d'Aéronomie Spatiale de Belgique, 3 av. Circulaire, B-1180 Brussels, Belgium

J. M. GUILMOT, M. CARLEER and R. COLIN
Université Libre de Bruxelles, Laboratoire de Chimie Physique, CP 160/09, 50 av F. D. Roosevelt, B-1050 Brussels, Belgium

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Abstract. New laboratory measurements of NO_2 absorption cross-section were performed using a Fourier transform spectrometer at 2 and 16 cm^{-1} (0.03 and 0.26 nm at 400 nm) in the visible range (380–830 nm) and at room temperature. The use of a Fourier transform spectrometer leads to a very accurate wavenumber scale (0.005 cm^{-1}, 8×10^{-5} nm at 400 nm). The uncertainty on the new measurements is better than 4%. Absolute and differential cross-sections are compared with published data, giving an agreement ranging from 2 to 5% for the absolute values. The discrepancies in the differential cross-sections can however reach 18%. The influence of the cross-sections on the ground-based measurement of the stratospheric NO_2 total amount is also investigated.

Key words: Fourier transform spectroscopy, NO_2, absorption cross-sections, differential absorption cross-sections, visible, stratospheric and tropospheric measurements.

1. Introduction

Nitrogen dioxide plays an important role in the chemistry of the troposphere and the stratosphere. It is produced from the oxidation of NO in the troposphere, where it acts as the main source of tropospheric ozone, and is a precursor to species, such as nitric acid, which play a role in the acidification of the environment. Its role in stratospheric photochemistry has been pointed out by Crutzen (1970). Beside its catalytic interaction in the control of ozone, it regulates the amounts of ClO, which in turn controls the ozone loss due to the chlorine catalytic cycle, and of $ClONO_2$, which is an important stratospheric reservoir of chlorine. It plays thus an important role in the coupling of the NO_x and ClO_x families.

Molecular absorption in the UV-Visible region has been widely used to measure the concentrations of gases in the atmosphere, either in the troposphere or in the stratosphere. The instruments used range from ground-based spectrometers measuring tropospheric or stratospheric concentrations by the Differential Optical Absorption Spectroscopy (DOAS) technique (see, for example, Platt and Perner, 1980; Solomon *et al.*, 1987; Edner *et al.*, 1993; Vandaele *et al.*, 1992; Envagelisti *et* *al.*, 1995; Camy-Peyret *et al.*, 1996), to spectrometers on board satellites such as the GOME (Global Ozone Monitoring Equipment) launched in April 1995 on board ERS-2 satellite, and to SCIAMACHY and GOMOS instruments to be launched in 1999 on board ENVISAT-1. All these instruments require absorption cross-sections of the observed molecules, measured at a resolution of 0.02 nm or better and with an accuracy better than 5% (Chance *et al.*, 1990). Accurate cross-sections are also needed for the chemical-dynamical-radiative modelling of the atmosphere.

The measurement of the NO_2 absorption cross-section is complicated by the presence of its dimer N_2O_4. Several studies have attempted to measure the NO_2 cross-section. Hall and Blacet (1952) measured absorption spectra of NO_2–N_2O_4 mixtures at 298 K and deduced the contribution of N_2O_4. Johnston and Graham (1974) measured the NO_2 cross-section in the 185–420 nm spectral region at room temperature. Bass *et al.* (1976) investigated the 185–410 nm range at 298 K. They corrected their data for the presence of N_2O_4. Leroy *et al.* (1987) reported values from 427 to 450 at 298 K. Schneider *et al.* (1987) obtained the NO_2 absorption cross-section between 200 and 700 nm, at 298 K and determined the absorption cross-section of N_2O_4 between 200 and 255 nm. Koffend *et al.* (1987) used a pulsed dye laser to perform high resolution measurement of NO_2 absorption structures in the 392–395 nm and 411–414 nm. Davidson *et al.* (1988) investigated the dependence of the NO_2 cross-section on temperature and the influence of this dependence on the determination of the photolysis rate of NO_2 in the atmosphere. Harwood and Jones (1994) studied the temperature dependence of the ultraviolet-visible absorption cross-section of NO_2. The cross-section of N_2O_4 were also derived by the latter, as well as new values for the equilibrium constant. Mérienne *et al.* (1995) measured the NO_2 absorption cross-section in the 300–500 nm region at 293 K. The use of an absorption path length of 61 m allowed them to work at very low pressure (< 0.04 torr) and to minimise the influence of the dimer. Discrepancies of the order of 20% or sometimes more are found between all the measurements.

This work presents new absolute absorption cross-section values for NO_2 between 12 000 and 26 000 cm^{-1} (380–830 nm) at 294 K. The absorption cross-section has been measured at two resolutions: 2 and 16 cm^{-1} (0.03 and 0.26 nm at 400 nm). Cross-sections obtained in this work have been measured with a Fourier Transform Spectrometer (FTS), which combines the advantages of a great sensitivity and a built-in wavenumber calibration. This last advantage is achieved by the presence of a He-Ne laser, which allows the interferogram to be digitised at equal intervals. This leads to a highly accurate and reproducible wavenumber calibration. With the Fourier Transform Spectrometer described below, an accuracy of about 0.005 cm^{-1} (8×10^{-5} nm at 400 nm) on the wavenumbers is achieved.

This new cross-section will then be compared with published data sets, measured at similar resolutions. A comparison of cross-sections smoothed to a resolution of 1.0 nm will also be shown. Finally, the importance to dispose of cross-sections

Table I. Experimental conditions

Res cm^{-1}	P_t hPa	Nb of scans	Source[a]	Filter[b]	Detector	Spectral region cm^{-1}
16	10.18	8 × 256	W	b	Si-diode	9500–26000 (380–1050 nm)
16	29.50	14 × 256	W	b	Si-diode	9500–26000
16	29.90	4 × 1024	W	b	Si-diode	9500–26000
16	50.50	4 × 1024	W	b	Si-diode	9500–26000
16	67.70	3 × 1024	W	b	Si-diode	9500–26000
16	10.70	4 × 1024	W	Cu^{++}	Si-diode	15000–30000 (330–670 nm)
16	15.18	4 × 1024	W	Cu^{++}	Si-diode	15000–30000
16	20.02	4 × 1024	W	Cu^{++}	Si-diode	15000–30000
16	30.27	4 × 1024	W	Cu^{++}	Si-diode	15000–30000
16	39.30	4 × 1024	W	Cu^{++}	Si-diode	15000–30000
16	48.65	4 × 1024	W	Cu^{++}	Si-diode	15000–30000
2	13.85	4 × 1024	X	b	UV-diode	15000–30000

[a] W = Tungsten filament lamp, X = High pressure Xenon lamp.
[b] b = Blue filter, Cu^{++} = Copper solution.

of high quality will be stressed, by investigating their influence on ground-based stratospheric NO_2 measurements in the visible range.

2. Experimental Details

The experimental set-up consists of a light source, the spectrometer, and the gas handling system. The choice of the light source, beamsplitter and detector is determined by the spectral region to be investigated. Combinations of a high pressure O_3 free Xenon source (USHIO, 450 W), a Tungsten filament lamp, a Quartz Suprasil beamsplitter with a Si diode or a UV vacuum solar blind diode have been used in order to cover the entire spectral region from 12 000 to 26 000 cm^{-1}. A blue filter provided by BRUKER or a copper sulphate solution filter have been used. The experimental conditions are reported in Table I. A photofeedback system allowed the lamp intensity to be stabilised within 1% throughout the experiments.

The absorption spectra were recorded using either a BRUKER IFS120HR or a BRUKER 120M Fourier Transform Spectrometer. The theoretical resolving power attainable with these spectrometers is 10^6. However, the resolution is essentially limited in the UV by the quality of the mirrors and beamsplitter, leading to a maximum resolution of the order of 10^{-2} cm^{-1} in this region. Following some recommendations concerning the measurements of absorption cross-sections (Chance, 1990), spectra have been recorded with resolutions of 2 and 16 cm^{-1}, corresponding respectively to 0.03 and 0.26 nm at 400 nm.

NO_2 gas (UCAR, stated purity of 99.5%) used without further purification, was introduced in a 5.15 cm absorption cell located in the sample compartment of the Fourier Spectrometer. The partial pressure of the gas was then monitored with a 100 torr full scale Baratron gauge. We waited until the stabilisation of the partial pressure (10 to 30 min, without any lamp illumination) before filling with oxygen in order to obtain a total pressure of 1 atm. The presence of oxygen is of great importance as it induces the reconversion of any NO into NO_2, maintaining the NO_2 concentration constant. NO can be present in the cell as an initial impurity or produced by the photodissociation of NO_2 during the experiment. The cell has been described in an earlier publication (Hurtmans *et al.*, 1993). Its characteristics will be briefly summarised here: the cell is made of anodised aluminium and has quartz windows; the temperature of the gas is monitored inside the cell with a temperature transducer characterised by an accuracy of 0.2 K in the temperature range used in the present work. The temperature in the cell was stabilised with a liquid circulating around the cell. Finally, the whole experimental set-up was located in a temperature stabilised room.

Adsorption of NO_2 on the inner surface of the cell is inevitable. To limit this effect on the pressure measurement, we waited before and after filling the cell with oxygen. This is however not enough to guarantee a stable NO_2 partial pressure throughout the experiment. Each spectrum was therefore the average of a number of scans (see Table I) which have been recorded by sequential blocks of either 256 or 1024 scans. Only the blocks of scans whose absorption did not differ from the first block by more than 1% were retained. We thus checked that the gradual decrease of the NO_2 pressure inside the cell was small. Moreover it proved that photochemical degradation of the sample due to the irradiation by the lamp was not important during the experiment.

Spectra have been obtained using a double sided recording mode, during the forward movement only of the mobile mirror and no apodization function was used. Blank spectra, i.e. with an empty cell, were recorded before and after each measurement.

3. Determination of the Absorption Cross-Section

Absorption cross-sections $\sigma(\lambda)$ are derived from the experimental data using the Beer–Lambert law:

$$I(\lambda) = I_0(\lambda)\exp(-nl\sigma(\lambda)),$$

where n is the gas concentration in the cell; l the absorption path length; $I_0(\lambda)$ and $I(\lambda)$ the intensities of the signal with an empty cell and a filled cell.

The $NO_2 \Leftrightarrow N_2O_4$ equilibrium implies that N_2O_4 is always present in the cell. Absorption of N_2O_4 occurs at wavenumbers greater than 25000 cm^{-1} (Hall and Blacet, 1952; Schneider *et al.*, 1987), but not in the spectral region investigated

Table II. Estimate of the accuracy of cross-section measurements

	Error (%)
Sample impurities	2
Adsorption inside the cell	1
Absorbance on individual spectra	1
Absorption path length	0.5
Pressure	0.1
Temperature	0.1
Cumulative error	< 4

in this work. N_2O_4 should not therefore interfere with the absorption structures of NO_2 studied here.

However the presence of N_2O_4 must be considered when determining the partial pressure of NO_2. This was done by considering the following equations:

$$P_t = P_{N_2O_4} + P_{NO_2} ,$$

where P_t is the total partial pressure in the cell and the partial pressures $P_{N_2O_4}$ and P_{NO_2} are related through the equilibrium constant K_P :

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} ,$$

where K_P is the equilibrium constant.

Partial pressures of NO_2 and N_2O_4 can thus be calculated. Hurtmans *et al.* (1993) reviewed the values of the equilibrium constant found in the literature and determined an empirical relation for its temperature dependence. For temperatures ranging from 233 K to 403 K, the dependence was expressed by a fourth degree polynomial expansion. At 294.15 K, the value of the constant K_P is 105.72 hPa. Using the above equations the partial pressure of NO_2 can be calculated from the various total pressures used.

The NO_2 absorption cross-section at the resolution of 16 cm^{-1} was obtained by taking the mean value of all the spectra, i.e. all the spectra taken at 16 cm^{-1} and the spectrum at 2 cm^{-1} degraded to 16 cm^{-1}. All measurements were found to agree within 2% which is lower than the uncertainty stated in Table II. The results are plotted in Figure 1 for the entire spectral region. Figure 2 shows a detailed region from 22200 to 23200 cm^{-1} of the spectrum at the resolution of 2 cm^{-1}.

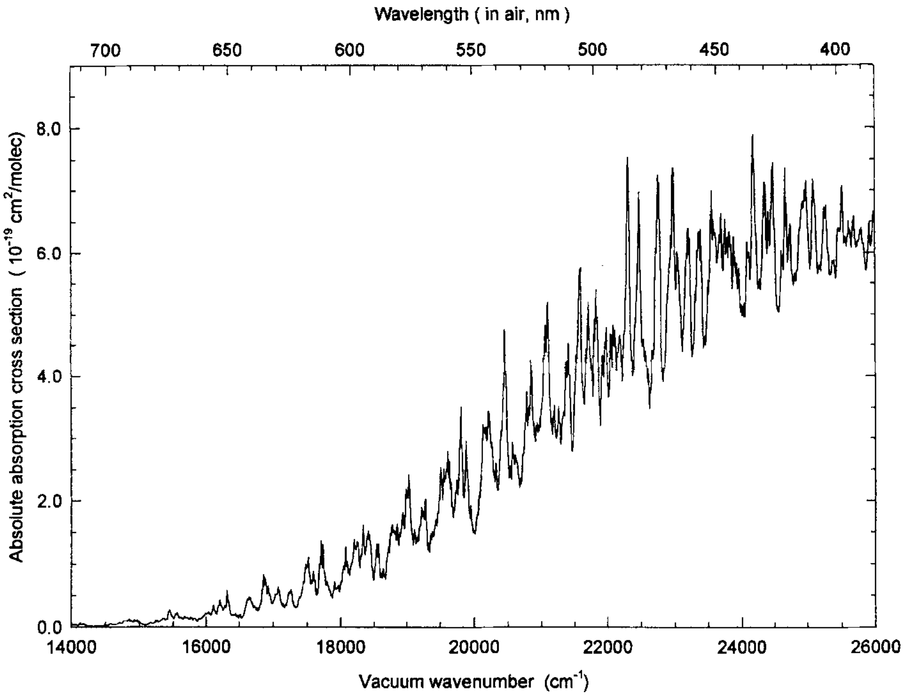

Figure 1. Absolute absorption cross-section of NO_2 at the resolution of 16 cm^{-1} at room temperature.

4. Discussion

4.1. ERROR EVALUATION

The error budget on the absorption cross-section was carefully evaluated, taking into account the errors on the pressure and temperature measurements, on the reaction constant K_P, the uncertainty on the absorption path length, the presence of possible impurities in the samples, the adsorption of NO_2 taking place inside the cell and the absorbance accuracy.

According to the error propagation principle, the uncertainty on the cross-sections can be derived from the following relation:

$$\frac{\delta\sigma}{\sigma} = \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta T}{T}\right)^2 + \left(\frac{\delta l}{l}\right)^2 + \left(\frac{\delta P_{NO_2}}{P_{NO_2}}\right)^2},$$

where A is the absorbance ($A = \ln I_0/I$). From the definition of the partial pressure of NO_2, δP_{NO_2} can be written as:

$$\delta P_{NO_2} = \left(\frac{\partial P_{NO_2}}{\partial K_P}\right)\delta K_P + \left(\frac{\partial P_{NO_2}}{\partial P_t}\right)_{K_P}\delta P_t\,.$$

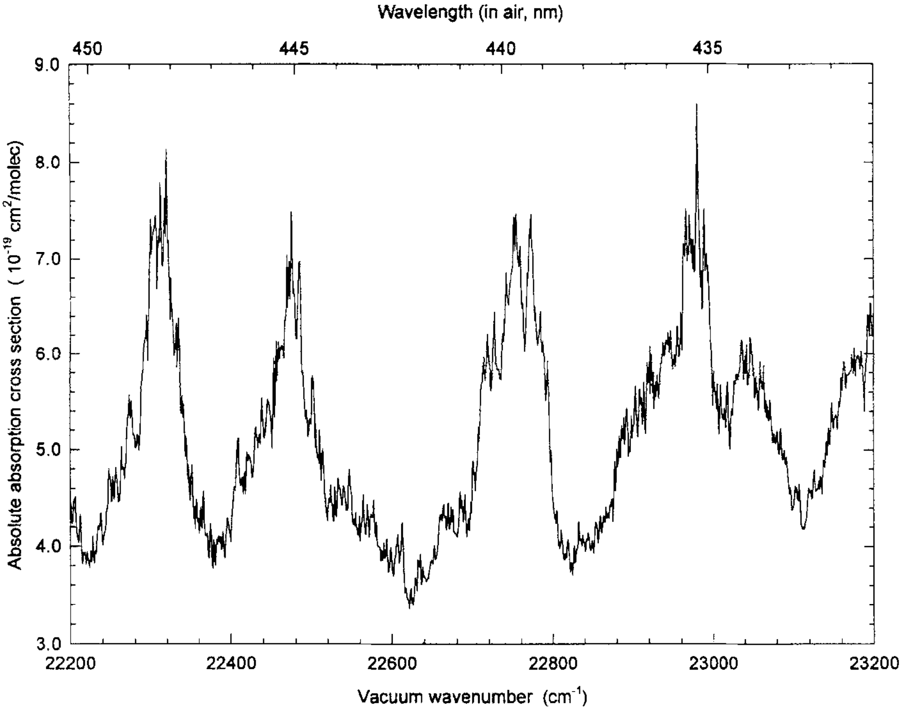

Figure 2. Absolute absorption cross-section of NO_2 at the resolution of 2 cm^{-1} at room temperature from 22200 to 23200 cm^{-1}.

Setting $a = (1 + 4P_t/K_P)^{1/2}$, one obtains

$$\frac{\delta P_{NO_2}}{P_{NO_2}} = \left(\frac{a-1}{2a}\right)\frac{\delta K_P}{K_P} + \left(\frac{4P_t}{2a(a-1)K_P}\right)\frac{\delta P_t}{P_t} .$$

Concerning δK_P, Roscoe and Hind (1993) reviewed different measurements of K_P and came to the conclusion that the error on this constant was of the order of 5% for temperatures ranging from 233 to 300 K. The error on the total pressure arises from the presence of impurities inside the NO_2 bottle, from the adsorption of NO_2 and from the measurement itself (0.1% with the Baratron gauge). The manufacturer states a 99.5% purity NO_2. An infrared study of the sample (Hurtmans *et al.*, 1993; Vander Auwera, personal communication) showed that small amounts of N_2O and CO_2 were present in the sample, as well as negligible amounts of HNO_2 and HNO_3. These species do not interfere with the NO_2 absorption in the visible region but cause an error on the determination of its partial pressure. NO is also present as an impurity in the sample, but the presence of oxygen ensures its conversion into NO_2. An estimated value of 2% is believed to cover the uncertainties due to all impurities. As already explained, the adsorption of NO_2 on the inner walls of the cell causes a decrease of absorption estimated at 1% throughout an experiment. The error on the absorbance for each individual spectrum was less than 1%.

The cumulative error is given in Table II. According to these figures, the accuracy on the present cross-section measurement of NO_2 can be stated to be better than 4%.

4.2. COMPARISON WITH PUBLISHED MEASUREMENTS

The NO_2 absorption cross-section will be compared below with the data from Schneider *et al.* (1987), Johnston and Graham (1974), Harwood and Jones (1994), and Mérienne *et al.* (1995), taking into account the conversion of wavelengths to wavenumbers and the correction of wavelengths from air to vacuum when necessary.

4.2.1. *Comparison of Data at High Resolution*

Data from Schneider *et al.* (298 K, resolution of 0.04 nm), Johnston and Graham (294 K, resolution of 0.1 nm), and Mérienne *et al.* (293 K, resolution of 0.01 nm) have been convolved in order to obtain a resolution equivalent to 16 cm^{-1} and have been compared to our measurement at this resolution. The cross-sections were smoothed using a gaussian function, whose width was given by the desired resolution. Results are plotted in Figures 3 and 4. Figure 3 shows the absolute absorption cross-sections of NO_2 from the four groups of authors in the spectral region from 415 and 465 nm. Figure 4 presents the relative difference (expressed in %) between our data and those of Johnston and Graham and of Mérienne *et al.* The results appear to be 'noisy'. It must be remembered, however, that the necessary conversion of the wavelengths to wavenumbers may introduce artefacts, which could explain some of the noise found in the residuals. Moreover, it is almost impossible to convolve a spectrum so that its new resolution perfectly matches the resolution of another spectrum. This produces yet additional noise in the residual. But the most important source of noise comes from errors in the calibration of the wavelength scale. The wavenumber scale produced by the FTS is linear and absolute, and that wavelength scales produced by grating spectrometers are not and may be shifted or distorted. Moreover, as grating spectrometers usually work on smaller spectral regions, large errors may be introduced when joining two scanned regions. All these errors on the wavelength scale account for most of the noise found in the residuals.

The difference between our data and those of Schneider *et al.* is considerable (10% to 25%) and greatly varies with wavelength. Data from Schneider *et al.* are systematically lower in the 380–426 nm region, as expected if photodissociation of NO_2 was taking place in their experiment. Moreover, a large discrepancy in the wavelength scale is observed in some parts of the spectrum. It seems that errors were introduced in the data set of Schneider *et al.* when merging two contiguous spectral regions.

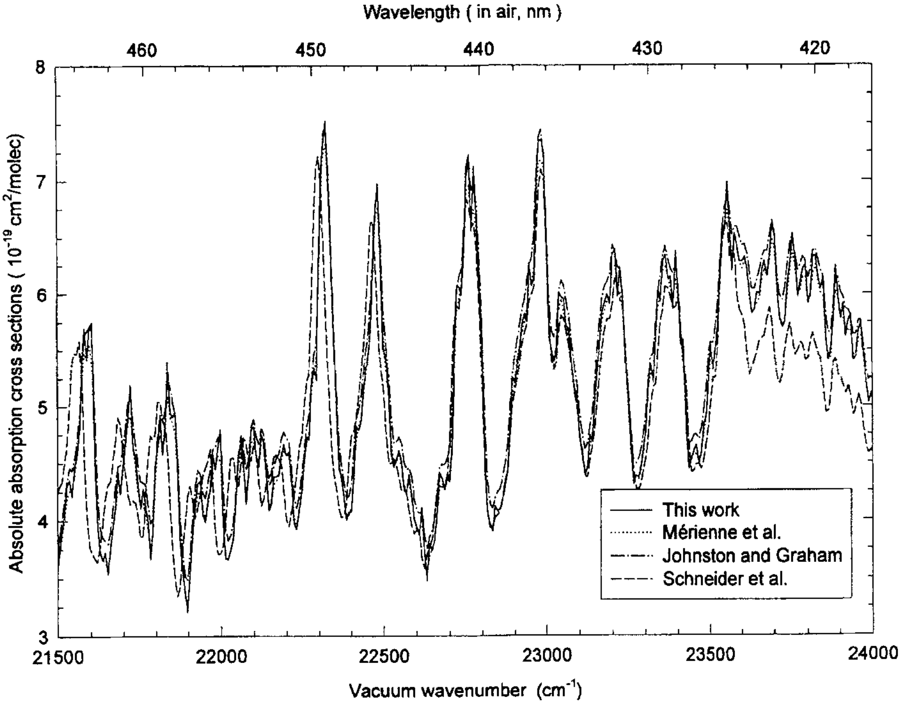

Figure 3. Comparison of absolute cross-sections of this work (——), Mérienne *et al.* (1995) (......), Johnston and Graham (1974) (-·-), and Schneider *et al.* (1987) (- - -). All data from the literature have been convolved to correspond to the resolution of 16 cm^{-1}. The wavenumber scale of Johnston and Graham has been shifted by 5 cm^{-1}. No shift in the wavenumber scale of Schneider *et al.* has been applied as it is not constant on the entire spectral range.

The comparison with the results of Johnston and Graham shows that values found in our work are systematically 5% lower between 415 and 500 nm. For wavelengths higher than 525 nm, data from Johnston and Graham are lower by 5%. Attention should be paid to the fact that a wavelength shift of the complete data set of Johnston and Graham of 0.25 nm has been applied in order to make the absorption structures coincide.

The comparison of our data with the data of Mérienne *et al.* shows a very good agreement (less than 2%). This result is noteworthy as it must be pointed out that the two sets of data were obtained with completely different spectrometers and instrumental set-ups. Moreover, a comparison of the two sets at the higher resolution (2 cm^{-1}) has been made showing (Figure 5) again a difference of only 2% between the two sets of data.

4.2.2. *Comparison of Data at Low Resolution*

In order to compare the NO_2 absorption cross-section obtained in this work with the data from Harwood and Jones (1994) (298 K, resolution of 0.54 nm), all data

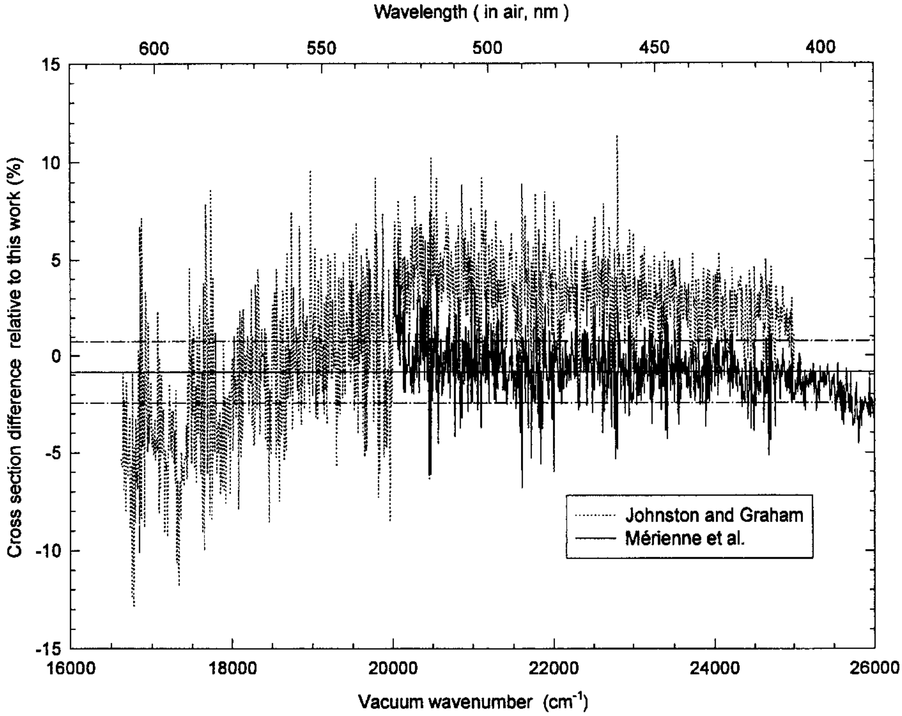

Figure 4. Relative differences between the absolute cross-sections of Mérienne *et al.* (1995) (—), Johnston and Graham (1974) (......), convolved to 16 cm^{-1}, and the cross-section of this work. The wavenumber scale of Johnston and Graham has been shifted by 5 cm^{-1}. The mean value and the 1σ deviation for the data of Mérienne *et al.* are also presented.

sets have been convolved to a chosen resolution of 1.0 nm using a gaussian function (see 4.2.1). The resolution of most of DOAS grating instruments lies usually in the range between 0.5 and 1.2 nm; a resolution of 1.0 nm is therefore representative for that kind of instruments.

The convolved absolute cross-section of Harwood and Jones is systematically lower by 5% than the convolved data measured in this work. The differences reach, however, 15 % in the 430 to 440 nm region.

As the DOAS technique is based on the differential cross-section of the absorbing molecules rather than their absolute cross-section, differential cross-sections derived from the measurements of the various groups were also compared. The differential cross-section is obtained by smoothing the absolute cross-section to remove all the absorption structures from the spectrum, and by subtracting this smoothed curve from the absolute cross-section. The data have been smoothed with a running average over a number of points corresponding to a spectral interval of 25 nm.

The comparison has been limited to the 410–460 nm region, where the DOAS stratospheric NO_2 measurements are usually performed (Hofmann *et al.*, 1995).

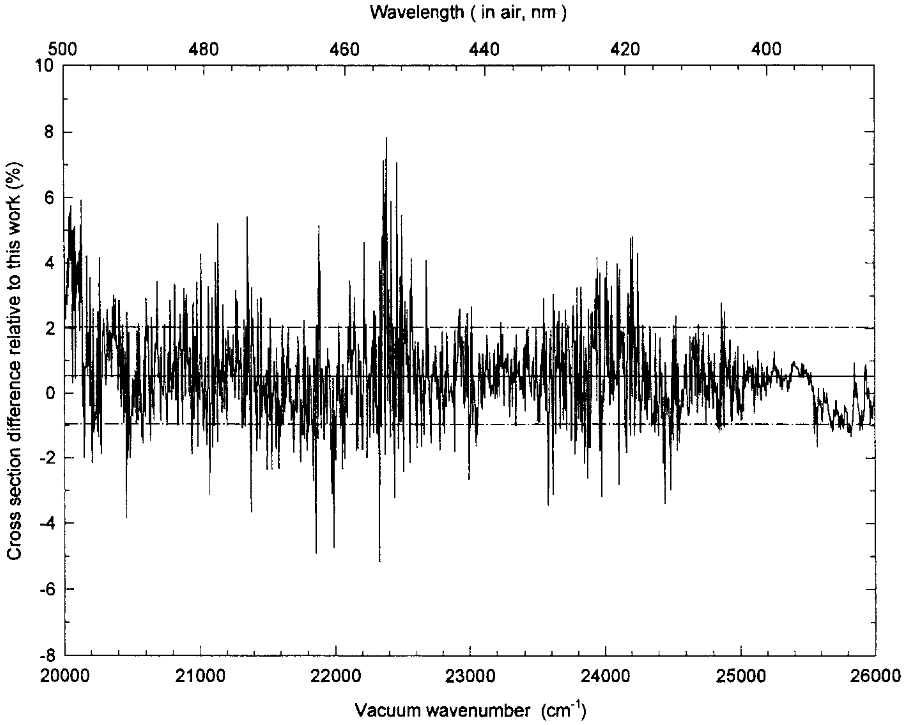

Figure 5. Relative differences between the absolute cross-section of Mérienne *et al.* (1995) convolved to 2 cm^{-1}, and the cross-section of this work. The mean value and the 1σ deviation are also presented.

Results are reported in Figure 6, where differential cross-sections and their differences relative to our data are presented. Shifts in the wavelength scales in the data of Schneider *et al.* and of Johnston and Graham have not been corrected. The good agreement between the data of this work and those of Mérienne *et al.* is again confirmed. Once the shift in the data of Johnston and Graham is taken into account, their differential absorption structures appear to agree very well (less than 2%). A shift in the data of Schneider *et al.* clearly visible above 425 nm could not be corrected as it is not constant over the entire range; differences up to 70% are therefore present.

Table III shows more clearly the differences existing between the various data sets. Each differential cross-section has been compared to the differential cross-section of this work. Shifts in the wavelength scale and correction factor of the amplitude were thus determined. The fitted region ranged from 410 to 460 nm when possible. For values of Schneider *et al.*, two regions were chosen, as their shift is highly dependent on the wavelength region. In the 410–420 nm region they do not present any significant shift compared to the data of Mérienne *et al.* In the 450–460 nm region, a shift of 0.58 nm relative to our data is present. However, once this shift has been taken into account, differential cross-sections agree well.

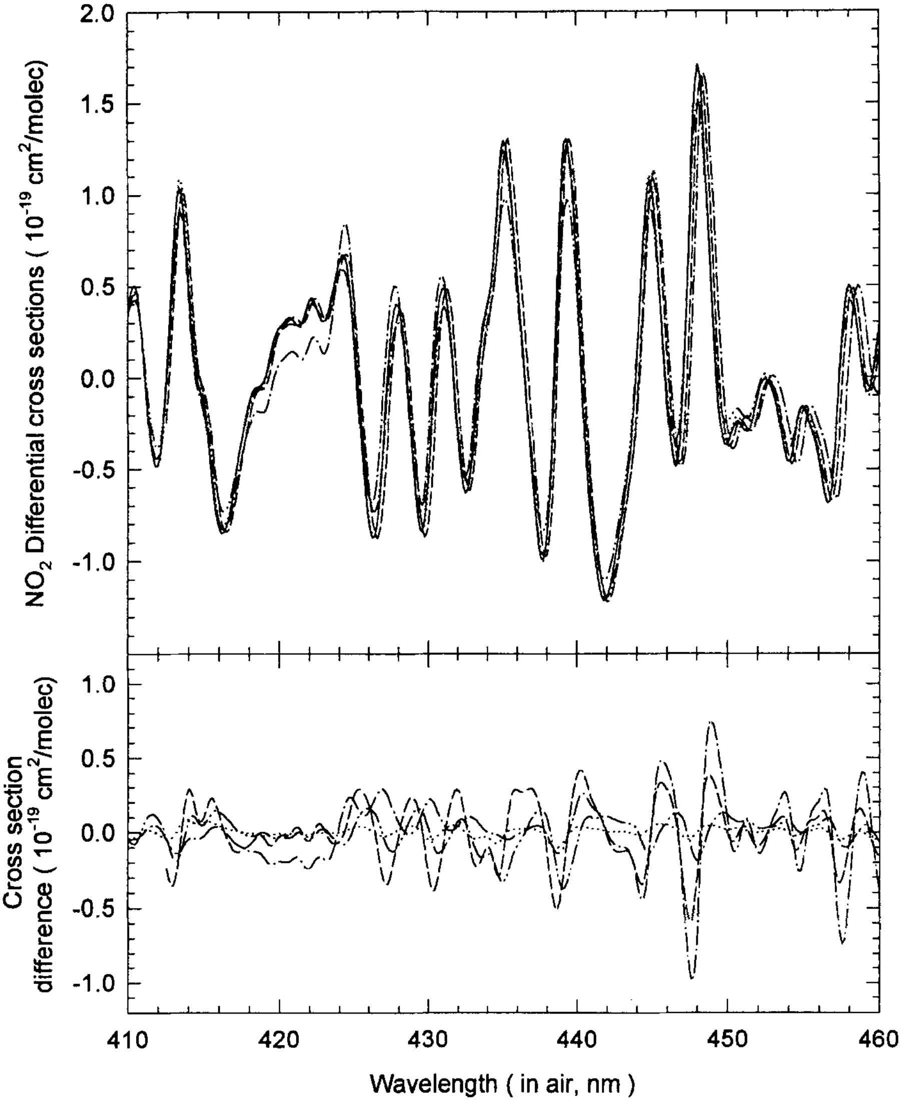

Figure 6. (a) Comparison of the NO_2 differential cross-sections in the 410–460 nm spectral range: (——) this work, (......) Mérienne *et al.*) (1995), (- - -) Johnston and Graham (1974), (- · -) Schneider *et al.* (1987), and (- · · · -) Harwood and Jones (1994). Shifts in the wavelength scales of Johnston and Graham and Schneider *et al.* have not been corrected. (b) Differences in the NO_2 differential cross-sections with respect to the data of this work.

Altogether differential cross-sections agree within 1.5% in amplitude except for the data of Harwood and Jones.

Table III. Comparison of the differential cross-sections

	Fit range (nm)	Shift (nm)	Correction factor
This work		0	1
Mérienne *et al.*	410–460	0.03	1.003
Harwood and Jones	410–460	0.04	1.160
Johnston and Graham	415–460	0.24	1.002
Schneider *et al.*	410–420	0.03	1.017
Schneider *et al.*	450–460	0.58	1.018

5. Influence of the Cross-Sections on Stratospheric NO_2 Measurements

The measurements of the NO_2 concentration in the atmosphere, either the stratosphere or the troposphere, mostly rely today on the use of the spectroscopic signature of the molecule. The NO_2 amount is usually determined using the intense absorption structures located between 400 and 600 nm, but its spectrum must be taken into account on the whole UV/visible range in order to eliminate its interference with the absorption of other molecules.

The need for NO_2 cross-section values of high quality has recently been illustrated in a NDSC (Network for the Detection of Stratospheric Change) campaign, focused on the measurements of stratospheric NO_2 using various UV/Visible spectrometers (Hofmann *et al.*, 1995). Seven instruments participated in the campaign. Each instrument worked with a different NO_2 cross-section more suited to its instrumental function. It was decided to calibrate all the instruments by the use of NO_2 cell measurements. The participants thus derived a correction factor lying between 0.96 to 1.08 to apply on their NO_2 data. This means that based on the choice of the NO_2 absorption cross-sections, a discrepancy of 12% on the NO_2 concentration was avoided.

The Institute for Space Aeronomy participated in this campaign with a ground based instrument developed for stratospheric studies. This instrument has already been described in a previous paper (Van Roozendael *et al.*, 1994) and will only be briefly summarised here. The instrument records spectra of the zenith scattered sunlight and is optimised for the detection of NO_2 and O_3 in the visible. The detector used is an EG&G Reticon photodiode array (1024 pixels). The spectral range extends from 400 to 560 nm, with a resolution of 1.0 nm corresponding to a sampling ratio of 6.6 pixels/FWHM. The software permits a shift and a stretch of the wavelength scale of the cross-section with respect to the analysed spectrum.

Zenith sky spectra recorded at Harestua (Norway) on day number 218, 1995 have been analysed with the different absorption cross-sections mentioned above, convolved with the instrumental function of the instrument. The relative differences in NO_2 column abundance are plotted in Figure 7a. Column abundances calculated with our cross-section have been chosen as references. The scatter of points at lower NO_2 slant amount is due to the increase of the noise relative to the NO_2 differential signature. Results calculated with the differential cross-section obtained in this work, that of Johnston and Graham, and that of Mérienne *et al.* do agree well (within less than 1%). Results derived from Harwood and Jones are about 18% higher. These results mainly reproduce the differences observed between the differential cross-sections themselves. More interesting are the results plotted in Figure 7b, where the standard deviations on the NO_2 slant amount have been represented as a function of the NO_2 slant column. This is representative of how well the absorption cross-sections compare with the absorption signatures found in the atmospheric spectra. Except at high NO_2 slant amounts, corresponding to very high zenith angles and thus very low signal to noise ratio, the standard deviation should be independent of the NO_2 slant amount if no instrumental factor interferes. The fact that the evolution is linear reflects the crucial effect of the shape of the differential structures of the absorption cross-sections. Cross-sections of this work, Mérienne *et al.* and Johnston and Graham lead to similar standard deviations, although the cross-section of Harwood and Jones leads to a higher dependence in the NO_2 amount.

We have also used cross-sections measured at lower temperatures by Coquart *et al.* (1995) to determine the NO_2 amount. It should be pointed out that the spectrum of NO_2 is composed of a series of narrow structures, whose width are of the order of or lower than the resolutions used for the laboratory data. Moreover their shape varies with temperature. This effect is of great importance when monitoring the stratospheric NO_2, as temperature in the stratosphere can be as low as 190 K. Residuals of the fitting procedure applied to derive the NO_2 amount were found to be correlated with the temperature dependence of the cross-section (Hoffman *et al.*, 1995). The cross-sections of Coquart *et al.* (1995) measured at 220 and 240 K have also been used to measure the NO_2 amount in the spectra recorded at Harestua, during day number 218. Results are plotted in Figure 7. The NO_2 slant columns are 14% and 20% lower when using absorption cross-sections at 240 K and 220 K respectively, but the standard deviation on these results are lower. This lower error level is consistent with the observation of an absorption arising from NO_2 situated in the stratosphere at altitudes where the temperature is of the order of 220–240 K. The evolutions of the standard deviation with the NO_2 slant column at the two low temperatures are very similar. The residual error level attained is believed to result mainly from errors due to the convolution process or the variation of the resolution in the spectral range studied. These results confirm the necessity to take into account the temperature dependence of the absorption cross-section. This dependence affects not only the amplitude of the differential structures of the cross-section, but also their shape.

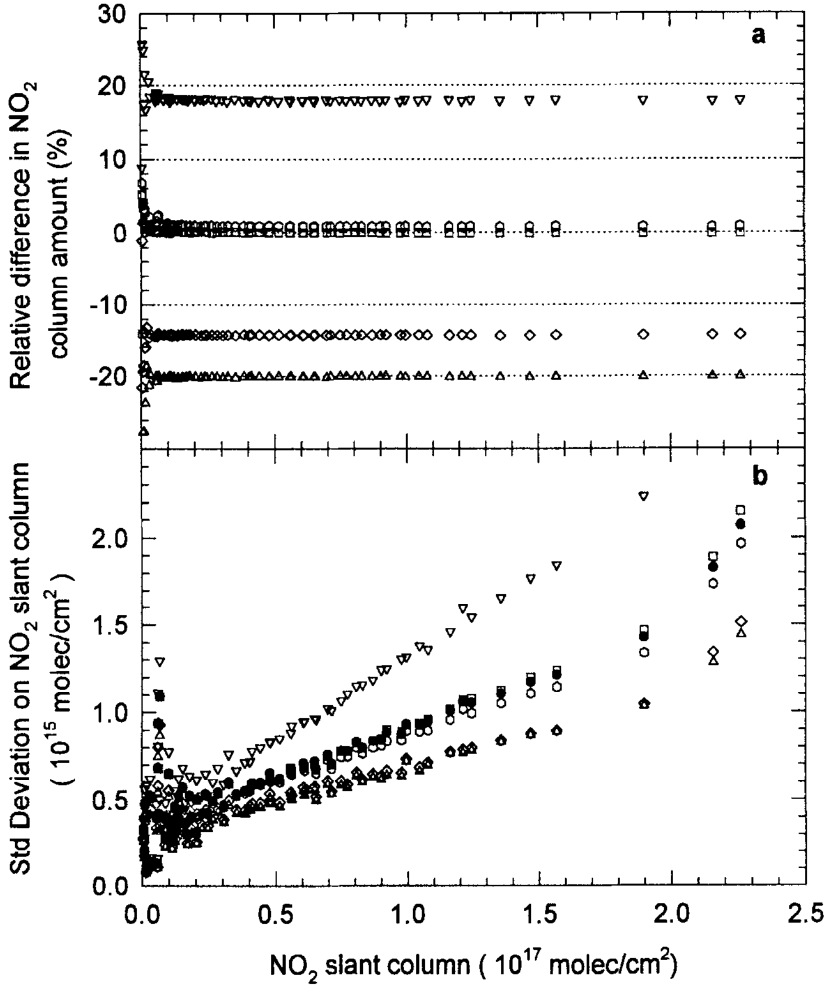

Figure 7. Influence of the absorption cross-section on the determination of stratospheric NO_2 column abundances. Results shown correspond to zenith sky measurements made at Harestua (Norway) on julian day 218, 1995 using the cross-sections of this work (●), Mérienne *et al.* (1995) (○), Johnston and Graham (1974) (□), Harwood and Jones (1994, data at 298 K), (▽), and Coquart *et al.* (1995) at 240 K (◇) and 220 K (△). The differences in NO_2 column amount relative to the NO_2 amounts found with the cross-section of this work are plotted in Figure 7(a), and the standards deviations on the measurements in Figure 7(b).

6. Conclusions

The NO_2 absolute absorption cross-section has been measured at room temperature at resolutions of 2 and 16 cm^{-1} (0.03 nm and 0.26 nm at 400 nm respectively). The accuracy on these new measurements is believed to be better than 4%, with an accuracy on the wavenumber scale of 0.005 cm^{-1} (8×10^{-5} nm at 400 nm). Absolute and differential cross-sections have been compared to other data sets generally used in atmospheric measurements. Our data show good agreement with data of Mérienne *et al.* (1995) (better than 2%). Data from Johnston and Graham (1974) present a difference of 5% in the absolute cross-section, however the differential cross-sections are in better agreement. The wavelength scale of their data shows a systematic shift compared to the scale of the Fourier transform spectrometer. Data from Schneider *et al.* (1987) show large discrepancies in the wavelength scale. The absolute cross-section of Harwood and Jones (1994) is systematically 5% lower, and the differential cross-section is 18% higher.

These cross-sections and those measured at lower temperatures by Coquart *et al.* (1995) have been convolved at a resolution of 1.0 nm and used to derive NO_2 slant amounts measured with a DOAS stratospheric instrument. The results of this comparison show the good quality of the new measurements but demonstrates also the need to take into account the temperature dependence of the cross-section. New measurements of this temperature dependence will be undertaken soon.

All the data obtained during this work are available on floppy disks, either on a wavenumber of a wavelength scale.

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