High-resolution Fourier transform measurement of the NO_2 visible and near-infrared absorption cross sections: Temperature and pressure effects

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[1] High-resolution NO_2 absorption cross sections have been obtained in the near-IR (NIR) and visible regions using a Fourier transform spectrometer coupled to a multiple reflection cell. Spectra were recorded at 0.05 cm^{-1} in the NIR region (10,800–15,100 cm^{-1}) and at 0.1 cm^{-1} in the visible region (13,800–26,000 cm^{-1}), under various pressure conditions (pure NO_2 and NO_2/air mixtures) and at three temperatures (220, 240, and 294 K). The effects of the temperature and the pressure on the NO_2 cross sections have been investigated. As expected, an increase of temperature results in a decrease of the absorption at the maxima of the absorption bands and an increase at the minima. From the measurements performed with pure NO_2 at different temperatures a linear regression of the cross section with temperature has been carried out. This enabled the cross sections to be reproduced within 2% at room temperature and 7% at the lower temperatures. The variation of the cross sections with the total pressure of NO_2/air mixtures has also been investigated at high resolution.   *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* NO_2, absorption, cross section, FT measurements

1. Introduction

[2] The NO_2 radical plays an important role in the chemistry of the Earth's atmosphere. In the troposphere, NO_2 is the main source of ozone and has an active role in the urban photochemical pollution. In the stratosphere, NO_2 is the main constituent that drives the NO_x cycle together with O_3 and is also involved in the coupling of the NO_x, ClO_x, and BrO_x families.

[3] Atmospheric NO_2 has been measured in the UV visible region since the early 1970s [*Noxon*, 1975]. The retrieval of the stratospheric NO_2 is based nowadays on two or more absorption cross sections obtained under different temperature conditions [*Sanders*, 1996; *Richter*, 1997], since several authors have emphasized the importance of using cross sections corresponding to the temperature conditions prevailing in the atmosphere. It was moreover suggested [e.g., *Harder et al.*, 1997; *Vandaele et al.*,

1998] that the pressure dependence of the cross section should be taken into account. For the measurement of weak absorbers such as BrO, OClO, or IO [*Wennberg et al.*, 1997] the accurate removal of the spectral signature of a strong absorber such as NO_2 is a necessity: Small inaccuracies in the NO_2 absorption cross sections impinge on the accuracy of retrieving the weaker concentrations.

[4] Several measurements of the NO_2 absorption cross section have already been performed under different temperature conditions [*Davidson et al.*, 1988; *Coquart et al.*, 1995; *Mérienne et al.*, 1995, 1997; *Jenouvrier et al.*, 1996; *Harder et al.*, 1997; *Yoshino et al.*, 1997; *Burrows et al.*, 1998; *Vandaele et al.*, 1998; *Voigt et al.*, 2002]. The discrepancies between the different sets are rather large, as pointed out by *Orphal* [2001]. They amount to 8% at room temperature but reach 15% at the lower temperatures. NO_2 absorption cross sections of the literature have been obtained at various resolutions. However, none was sufficiently high enough to fully resolve the absorption structures. This may introduce nonlinearities in the cross section,

Table 1. Pressure Ranges Used for the Measurement of the NO$_2$ Cross Section

Temperature, K	Total Pressure, hPa	Dilution Factor, ppm NO$_2$	Spectral Range, cm^{-1}	
			0.05 cm^{-1} Resolution	0.1 cm^{-1} Resolution
294	0.009, 0.037, 0.09	_[a]		13,800−26,000
	0.37, 0.97	_[a]	13,600−15,100	
	10.09	965		13,800−26,000
	38.33	965		13,800−22,200
	105.74	92		14,100−25,500
	399.96	92, 965	11,900−15,100	13,800−23,500
	1013.2	9.6, 92, 965	10,800−15,100	13,800−26,000
240	0.009, 0.033, 0.084	_[a]		13,800−25,000
	0.69, 2.84	_[a]	13,200−14,500	
	12.73	965		13,800−23,600
	38.13	965		13,800−21,500
	133.32	92		13,800−23,600
	399.96	9.6, 92, 965	13,200−15,100	13,800−25,000
	1013.2	9.6, 92, 965	13,200−15,100	13,800−25,000
220	0.012, 0.067, 0.32	_[a]		13,800−26,000
	1.33, 2.40	_[a]	13,200−15,100	
	10.0	965		14,100−23,600
	38.00	965		13,800−22,500
	133.32	92		13,800−23,600
	399.96	9.6, 92, 965	13,800−15,000	13,800−23,600
	1013.2	9.6, 92, 965	13,800−15,000	13,800−24,600

[a] Pure NO$_2$.

as the relation between the amplitude of the absorption structures and the concentration is no longer linear [*Hermans et al.*, 1999; *Vandaele and Carleer*, 1999]. The resolutions used in this work (0.05 and 0.1 cm^{-1}) are probably still not high enough. However, the choice of the resolution is also restricted by some experimental limitations: When using higher resolutions, the acquisition time becomes relatively long and the experiment is more affected by lamp fluctuations or drifts. Moreover, the precision on the measurements and the signal-to-noise ratio are deteriorated when the measurement time increases.

[5] This work presents new measurements of the NO$_2$ absorption cross sections at high resolution (0.05 and 0.1 cm^{-1}) in the near-IR and visible regions (10,800−26,000 cm^{-1}). Measurements have been performed at three temperatures (220, 240, and 294 K) and under various pressure conditions of pure NO$_2$ and NO$_2$/air mixtures. Effects of the temperature and the pressure on the cross section have been investigated.

2. Experimental Conditions

[6] The absorption cross sections of NO$_2$ were investigated at 0.1 cm^{-1} resolution in the visible region and at 0.05 cm^{-1} resolution in the near-IR (NIR) region. Spectra were recorded using a Fourier transform spectrometer BRUKER 120M, characterized by a resolving power better than 10^6. The White-type cell is described in detail elsewhere [*Lux and Coquart*, 1989]. The distance between the mirrors is 5 m; in the visible region the absorption path can be adjusted up to 300 m. The temperature, measured by five platinum sensors regularly placed inside the cell, can be stabilized down to 220 K with the help of a circulating cooling fluid. The pressure is monitored with a MKS Baratron capacitance manometer with 10 torr or 1000 torr heads. For the NO$_2$ absorption measurements a path length of 60.73 m was used. Spectra were recorded from 8000 to 28,000 cm^{-1} with a tungsten lamp source and a silicon diode detector. Recording conditions were optimized in the NIR region by using a filter

(J662a: high-pass filter with 50% cutoff frequency at 662 nm from Métallisations et Traitements Optiques, France).

[7] Measurements were performed at three temperatures (220, 240, and 294 K) under different pressure conditions with pure NO$_2$ and different NO$_2$/air mixtures. Table 1 gives a summary of the pressure ranges studied in this work. The total pressure, the dilution factors, and the spectral intervals for the two resolutions are indicated for each temperature. The NO$_2$ gas was provided by Air Liquide (>99% purity) and was used without any further purification. Mixtures of NO$_2$ and air with predefined dilution factors (9.6, 92, and 965 ppm NO$_2$, respectively) were prepared by Air Liquide (with a stated accuracy of 2% on the dilution factor). Premixed mixtures were used in order to avoid problems when filling the cell with the buffer gas: NO$_2$ could be compressed to one end side of the cell and not well mixed with the added air.

[8] Spectra were recorded in a series of successive blocks, allowing us to control the reproducibility of the measurements and to correct the absorption for phenomena such as the progressive adsorption of NO$_2$ on the cell walls and the photolysis of NO$_2$. Blank spectra were recorded before and after each NO$_2$ experiment. This made it possible to correct for the lamp fluctuations, which took place during the experiments, assuming a linear variation of the lamp intensity with time. In general, the intensity variations between the blank spectra taken before and after the NO$_2$ measurements were <1%.

[9] Spectra were obtained during the forward and backward movements of the mobile mirror, using a single-sided recording mode. The apodization function was a boxcar. Table 2 gives a summary of the experimental conditions for the two spectral regions investigated. The detector type, the spectral range, the resolution used for each region, the number of coadded scans per block, the number of blocks, the measurement time, and the iris diameter are given. Figure 1 shows an example of blank and NO$_2$ spectra corresponding to the two experimental configurations investigated in this work. They depend on the combination of the chosen optics (essentially the beam splitter), the detector,

Table 2. Experimental Conditions

	Near-IR Region	Visible Region
Lamp	tungsten	tungsten and J662a filter
Detector	silicon diode	silicon diode
Spectral range, cm^{-1}	8,000–17,000	13,000–28,000
Resolution, cm^{-1}	0.05	0.1
Scans/block	64	64
Number of blocks	8	8
Measurement time,[a] h	6	3.5
Iris diameter, mm	0.85	1.1

[a] For the NO$_2$ measurements only, thus excluding the blank spectra recordings.

and the filter used. The two bands systems appearing $\sim$11,000 and 9000 cm^{-1} are due to the water vapor present in the absorption path outside the cell. The signal-to-noise ratio (SNR) reaches 2600 at the maximum of the NIR spectrum (10,000 cm^{-1}), but is of the order of 200 in the 12,000–14,500 cm^{-1} region. Values of the SNR for the visible light spectrometer (VIS) configuration peak at 17,000 cm^{-1} with a value of 1100 and are of the order of 500 at 15,000 cm^{-1} and 260 at 22,000 cm^{-1}. Values of the cross sections determined in this work are given for wave numbers up to 26,000 cm^{-1}. However, from Figure 1 and from the values of the SNR, it can easily be inferred that values for wave numbers >22,000 cm^{-1} are strongly affected by noise. Most of the structures appearing in this region are most probably noise structures and should not be attributed to NO$_2$ absorption signatures.

[10] The spectrometer was not operated under vacuum so that all wave numbers given in this work are expressed in air and are therefore defined as $1/\lambda_{air}$. The conversion to wave number in vacuum, using the Edlén [1996] formula, for example, requires the knowledge of the temperature, pressure, and relative humidity in the laboratory. The temperature and pressure corresponding to the path external to the cell did not vary strongly during the measurement

campaign, but the relative humidity varied more, from 42% to 59%. The reproducibility of the wave number scale was tested by comparing the position of some lines belonging to the atmospheric A band of O$_2$ $\sim$13,200 cm^{-1}, corresponding to the absorption of O$_2$ in the part of the path outside the cell. Forty-four well-defined lines were selected for the calibration. Considering all spectra obtained with the NIR configuration, the mean standard deviation on the position of the chosen lines was 0.002 cm^{-1}. The wave number scale was recalibrated by use of a spectrum with both lines of the O$_2$ atmospheric bands and I$_2$ bands present (see Coheur et al. [2002] for a description of the calibration procedure).

3. Results

[11] The absorption cross sections $\sigma(\lambda)$ are derived from the recorded spectra using the Beer-Lambert law:

$$I(\lambda) = I_o(\lambda)\exp[-nl/\sigma(\lambda)], \qquad (1)$$

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

[12] The 2NO$_2$ $\Longleftrightarrow$ N$_2$O$_4$ equilibrium implies that N$_2$O$_4$ is always present in the cell. Absorption of N$_2$O$_4$ occurs at wave numbers >25,000 cm^{-1} but not in the spectral region investigated here [Vandaele et al., 1998]. The presence of the dimer must, however, be considered when determining the NO$_2$ partial pressure. The partial pressures of NO$_2$ (P_{NO_2}) and N$_2$O$_4$ ($P_{NO_2O_4}$) are related to the total pressure Pt by

$$P_t = P_{NO_2} + P_{N_2O_4} \qquad (2a)$$

for pure NO$_2$,

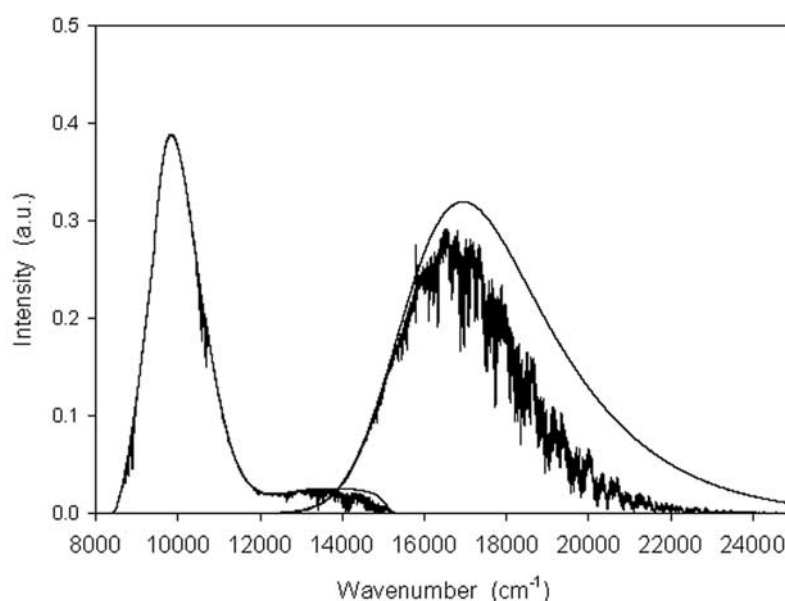$$\chi P_t = P_{NO_2} + 2P_{N_2O_4} \qquad (2b)$$

Figure 1. Raw spectra obtained with the two configurations NIR and VIS (see Table 2 for the description of the experimental conditions).
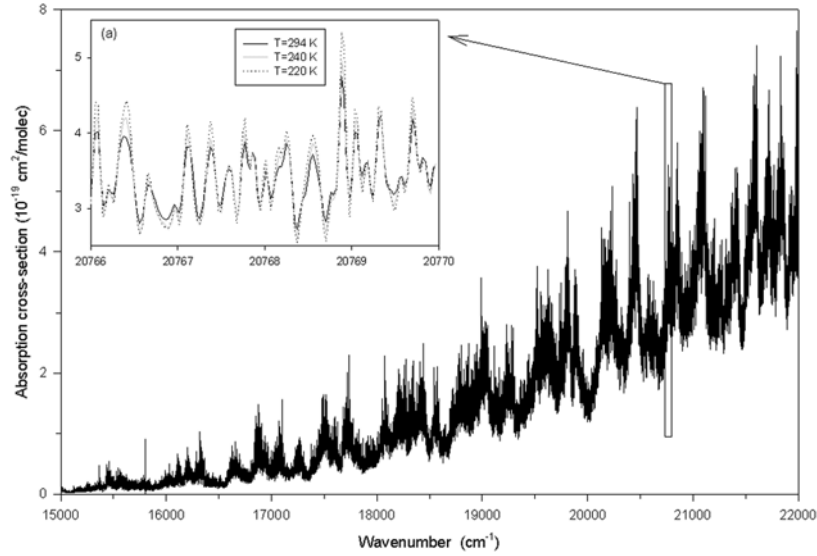
Figure 2. NO$_2$ absorption cross section at 294 K. For clarity the data for wave numbers lower than 15,000 cm^{-1} have been multiplied by a factor of 10. The inset shows the temperature effect for a small part of the spectrum.

for mixtures (χ = dilution factor), and to the equilibrium constant by

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}}. \qquad (3)$$

[13] The value of the equilibrium constant depends only on the temperature. Values of K_P at 294 and 240 K were calculated using the polynomial expansion of $Log_{10}K_P$ derived by *Hurtmans et al.* [1993] from experimental values of K_P (K_P = 104 and 0.58 hPa, respectively, at 294 and 240 K). The value of K_P at 220 K was calculated using the formula given by *Chao et al.* [1974] (K_P = 0.042 hPa).

[14] The absorption cross section values obtained at 294 K are plotted in Figure 2 for the whole spectral region. Figure 2 illustrates the presence of high-resolution structures in the NO$_2$ spectrum. The temperature effect is also shown on a small part of the spectrum.

3.1. Accuracy

[15] The accuracy of the NO$_2$ absorption cross sections obtained in this work has been estimated from the uncertainties on the various experimental parameters, using

$$\frac{\delta\sigma_{NO_2}}{\sigma_{NO_2}} = \frac{\delta A}{A} + \frac{\delta T}{T} + \frac{\delta l}{l} + \frac{\delta P_{NO_2}}{P_{NO_2}}. \qquad (4)$$

In this expression, $\delta T/T$ and $\delta l/l$ represent the error on the temperature (0.5%) and the cell length (0.05%, l = 60.73 m), respectively. The error on the temperature is estimated from the statistical error resulting from the reading given by the five temperature sensors for each experiment, on the one hand, and from the combination of all the experiments at the temperature considered, on the other hand. The error on the NO$_2$ partial pressure arises from different sources: reading error, error on the K_P value, presence of impurities, error on the dilution factor, and adsorption of NO$_2$ on the cell walls.

It can be written as [*Mérienne et al.*, 1995; *Vandaele et al.*, 1998]

$$\frac{\delta P_{NO_2}}{P_{NO_2}} = \left(\frac{a-1}{2a}\right)\frac{\delta K_P}{K_P} + \frac{2P_t}{aK_P(a-1)}\frac{\delta P_t}{P_t} \qquad (5)$$

for pure NO$_2$ experiments with a = $[1 + (4P_t/K_p)]^{1/2}$, and

$$\frac{\delta P_{NO_2}}{P_{NO_2}} = \left(\frac{a-1}{2a}\right)\frac{\delta K_P}{K_P} + \frac{4P_{eq}}{aK_P(a-1)}\left(\frac{\delta P_t}{P_t} + \frac{\delta\chi}{\chi}\right) \qquad (6)$$

for NO$_2$/air mixtures with a = $[1 + (8P_{eq}/K_p)]^{1/2}$ and P_{eq} = χP_t, χ being the dilution factor. The global error on the measured pressure is represented by $\delta P_t/P_t$, which includes the error due to the reading (0.1%), the presence of impurities, and the error on the dilution factor (certified by the manufacturer to be of the order of 2% for the tank), as well as the adsorption of NO$_2$ on the cell walls and the photolysis inside the cell (<1%). The last term was obtained by comparing the amplitude of the NO$_2$ absorption of each block to that of the first block for a given experiment. The readout error on the pressure takes into account the linearity of the Baratron head, which is specified to be 0.08% on the whole pressure scale. The 1000 torr head was calibrated with a high precision barometer: An error of 27 Pa at 1013.25 hPa was obtained. No calibration of the 10 torr head was done, and the specifications of the manufacturer were taken into account. We did not take into account the effect of the NO$_2$ gas on the Baratron heads. The error on the K_P values was estimated at 5% on the basis of the study of *Roscoe and Hind* [1993]. The error on the absorbance is $\delta A/A$ (1% above 16,000 cm^{-1}). Below 16,000 cm^{-1} the cross-section values are very small, and it is no longer adequate to express the error in percents. For these data the absolute error due to the absorption was estimated to be <1.0 $\times$ 10^{-22} cm^2 molecule^{-1}. The error estimates in the two spectral regions at the different temperatures are detailed in Table 3. For the $\delta P_{NO_2}/P_{NO_2}$ term the values given in Table 3 are the averages

Table 3. Error Estimates (in Percent) on the Various Parameters and on the Absorption Cross Section

Parameter	Temperature, K	Near-IR Region	Visible Region
$\delta A/A$		see text	1.0
$\delta l/l$		0.05	
$\delta T/T$		0.5	
$\delta P_t/P_t$		3.0	
$\delta K_P/K_P$		5.0	
$\delta P_{NO_2}/P_{NO_2}$[a]	294	3.0	3.0
	240	3.6	3.1
	220	3.9	3.5
$\delta\sigma/\sigma$[b]	294	3.6	4.6
	240	4.2	4.7
	220	4.5	5.0
$\delta\sigma/\sigma$ RMS[c]	294	3.0	3.2
	240	3.7	3.3
	220	3.9	3.7

  [a] Averages of the errors for all the spectra (with pure NO$_2$ and mixtures) measured at one temperature.
  [b] Parameters are $\delta\sigma/\sigma = \delta l/l + \delta T/T + \delta P_{NO_2}/P_{NO_2}$ for the near-IR data and $\delta\sigma/\sigma = \delta A/A + \delta l/l + \delta T/T + \delta P_{NO_2}/P_{NO_2}$ for the visible data.
  [c] Parameters are $\delta\sigma/\sigma = \sqrt{(\delta l/l)^2 + (\delta T/T)^2 + (\delta P_{NO_2}/P_{NO_2})^2}$ for the near-IR data and $\delta\sigma/\sigma = \sqrt{(\delta A/A)^2 + (\delta l/l)^2 + (\delta T/T)^2 + (\delta P_{NO_2}/P_{NO_2})^2}$ for the visible data.

of the errors obtained by using equations (5) and (6) for all the spectra measured at a given temperature. This error did not vary very much from spectra obtained with pure NO$_2$ to spectra obtained with NO$_2$/air mixtures. The total error on the absorption cross-section values above 16,000 cm^{-1} varies from 4% to 5%, depending on the temperature. The total error (all terms, except $\delta A/A$) on the near-IR data varies from 3.5%

to 4.5%. The total RMS error is also given in Table 3, in order to make a comparison with literature data easier.

3.2. Comparison With the Literature

[16] The absorption cross-section values obtained with pure NO$_2$ have been compared with recent data from the literature. To avoid the problem due to the different resolutions, all the data have been convolved at a resolution of 2 cm^{-1}. The choice of this resolution ensures that the pressure effect is removed from the comparison (see section 5). As pointed out by *Vandaele and Carleer* [1999], the convolution has not been applied directly on the cross sections themselves but on a synthetic spectrum calculated using the Beer-Lambert law, with a Gaussian I_0 spectrum and an arbitrary absorber density. The convolution process takes into account the initial and desired resolution and the variation of the resolution on the whole spectral interval. This latter correction is needed when convolving spectra obtained with a grating spectrometer. The results of the comparison for the cross section obtained at room temperature are presented in Figure 3, where the relative differences (given as percentages)

$$\frac{(\sigma_{literature} - \sigma_{this\,work})}{\sigma_{this\,work}} \qquad (7)$$

are plotted for the 16,000–25,000 cm^{-1} interval.

[17] In Figure 3a the data of this work are compared with those of *Vandaele et al.* [1998]. The latter were obtained with the same experimental setup as that used in this work, with pure NO$_2$ but at a resolution of 2 cm^{-1}. They were
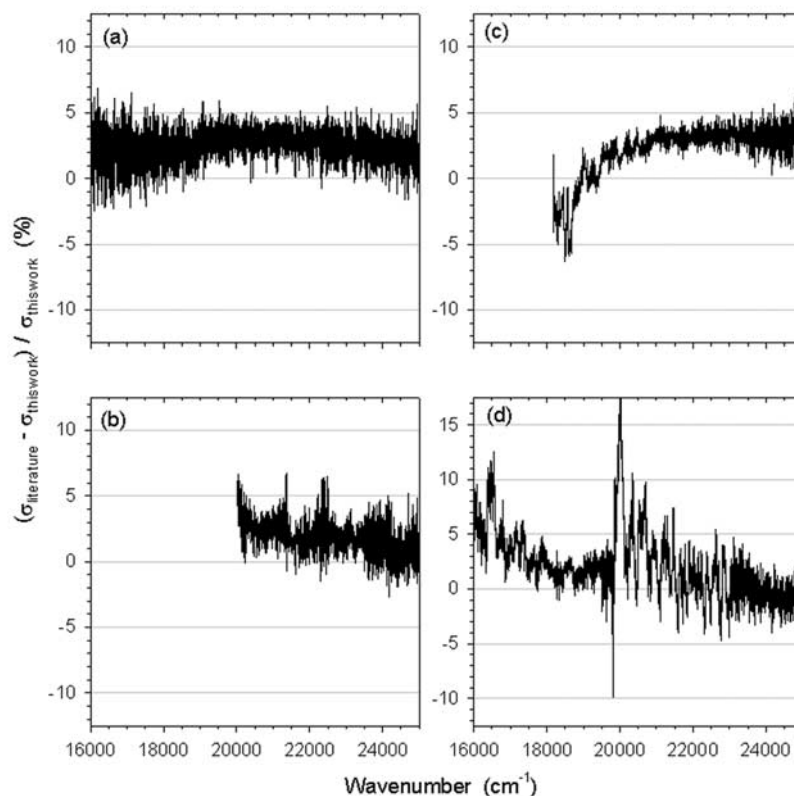

Figure 3. Comparison of the NO$_2$ absorption cross section at 294 K with data of the literature: (a) *Vandaele et al.* [1998], (b) *Mérienne et al.* [1995], (c) *Harder et al.* [1997], and (d) *Voigt et al.* [2002].
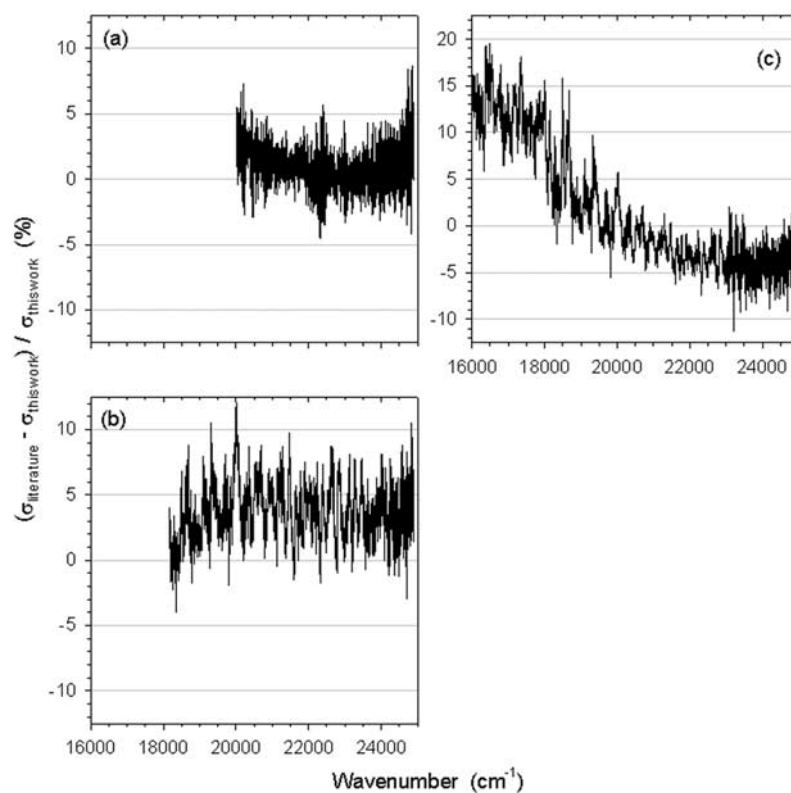
Figure 4. Comparison of the NO$_2$ absorption cross section at 240 K with data of the literature: (a) *Coquart et al.* [1995], (b) *Harder et al.* [1997], and (c) *Voigt et al.* [2002].
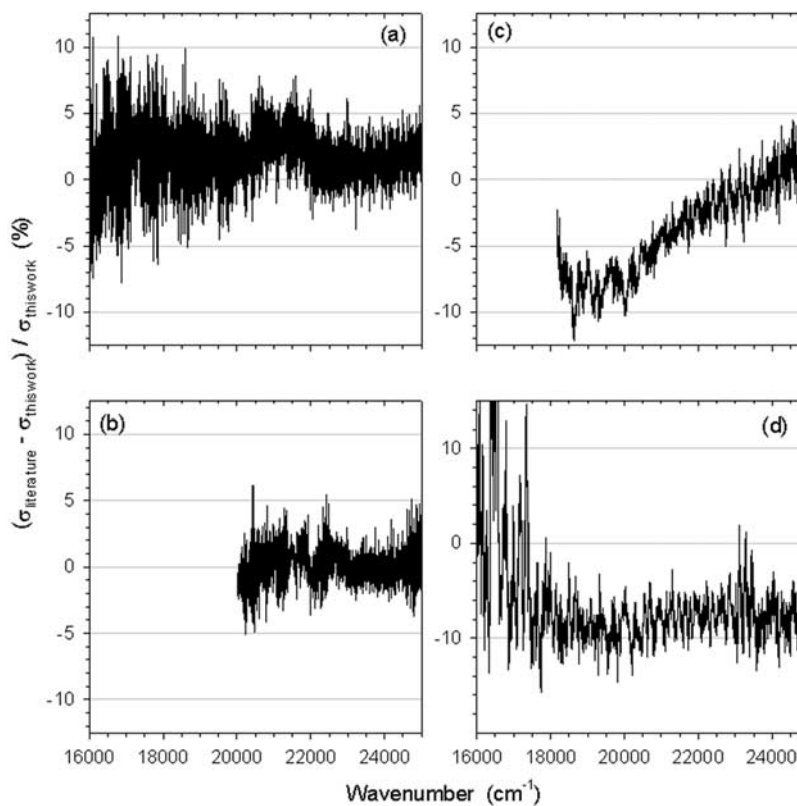

Figure 5. Comparison of the NO$_2$ absorption cross section at 220 K with data of the literature: (a) *Vandaele et al.* [1998], (b) *Coquart et al.* [1995], (c) *Harder et al.* [1997], and (d) *Voigt et al.* [2002].
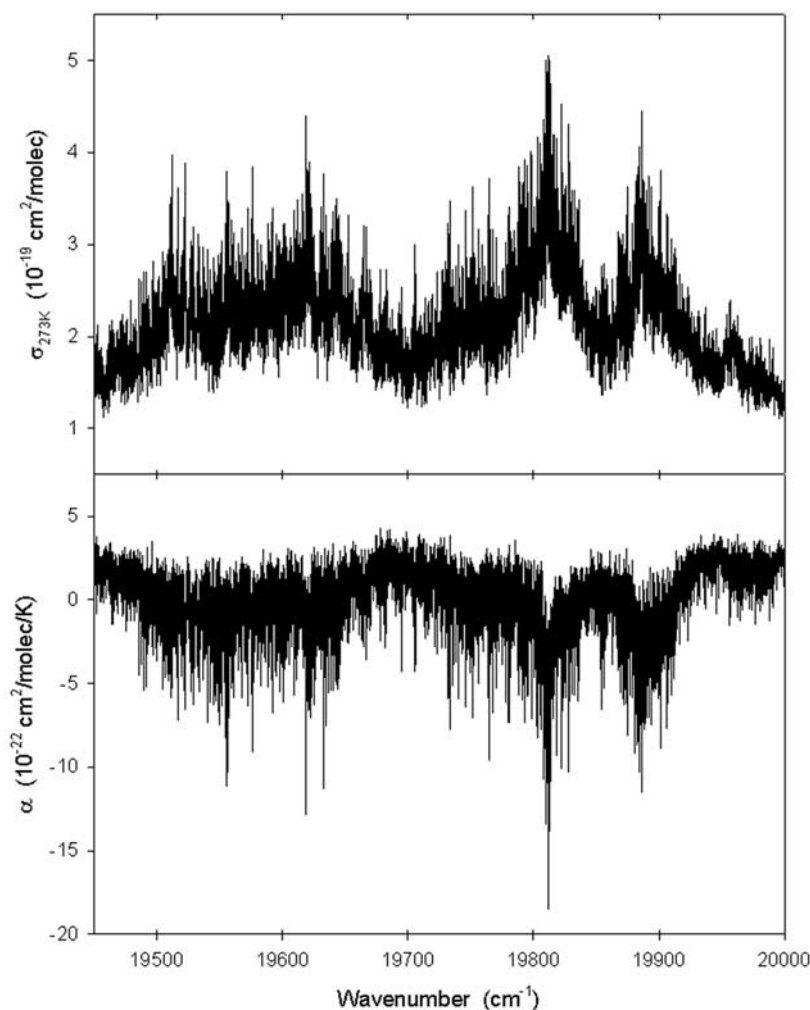
Figure 6. Temperature dependence of the NO$_2$ absorption cross section. The variables $\sigma_{273K}(\overline{\nu})$ and $\alpha(\overline{\nu})$ represent the cross section as would be measured at 0°C and the linear temperature coefficient, respectively.

therefore not convolved. The agreement is good: The mean difference is of 2.5% (±1.1%). The relative difference appears noisy, but this is an artifact introduced by the convolution process. A small step is observed ~18,800 cm^{-1}, which corresponds to a concatenation limit of the data obtained in this work.

[18] Figure 3b presents the comparison between our data and those of *Mérienne et al.* [1995] obtained from measurements at room temperature (293 K) and at a resolution of 0.009 nm with pure and diluted NO$_2$. The agreement is once again good (mean difference is 1.9% and standard deviation is 1.2%). However, as the measurements of *Mérienne et al.* [1995] were performed on successive limited intervals, discontinuities are observed in the regions of the merging of their data.

[19] The data of *Harder et al.* [1997], obtained with a Fourier transform (FT) spectrometer at a resolution of 0.5 cm^{-1} and at 298 K, are in agreement (3.0%) for wave numbers >20,000 cm^{-1} (see Figure 3c). Below this limit both data sets diverge, ours being larger by 5%. *Harder et al.* [1997] estimated a larger error for their measurements in this region, mainly owing to a lamp drift.

[20] The data of this work have also been compared with those of *Voigt et al.* [2002], who measured the NO$_2$ absorption cross section at various temperatures and with NO$_2$/N$_2$ mixtures at two different total pressures (100 and 1000 hPa). These data are given at a resolution of 0.5 cm^{-1} for wave numbers lower than 23,000 cm^{-1} and at 1.0 cm^{-1} for higher wave numbers. For the comparison their data at 293 K and 100 hPa were convolved to a resolution of 2 cm^{-1}. Figure 3d readily shows the concatenation limits in the data of *Voigt et al.* [2002] with three distinct regions linked at 19,800 and 23,000 cm^{-1}. Below 19,000 cm^{-1} the agreement becomes very good (mean difference is 0.3% and standard deviation is 0.6%) if their values are lowered by a constant value of 1.5×10^{-21} cm^2 molecule^{-1}. Between 19,800 and 23,000 cm^{-1} the amplitude of the structures of the cross section of *Voigt et al.* [2002] is systematically lower.

[21] Comparisons of our data at 240 and 220 K with those of the literature are shown in Figures 4 and 5, respectively. Figure 4a shows the comparison with the data of *Coquart et al.* [1995], performed at 240 K. Both data sets differ by 1% (±1.5%). The mean difference between our
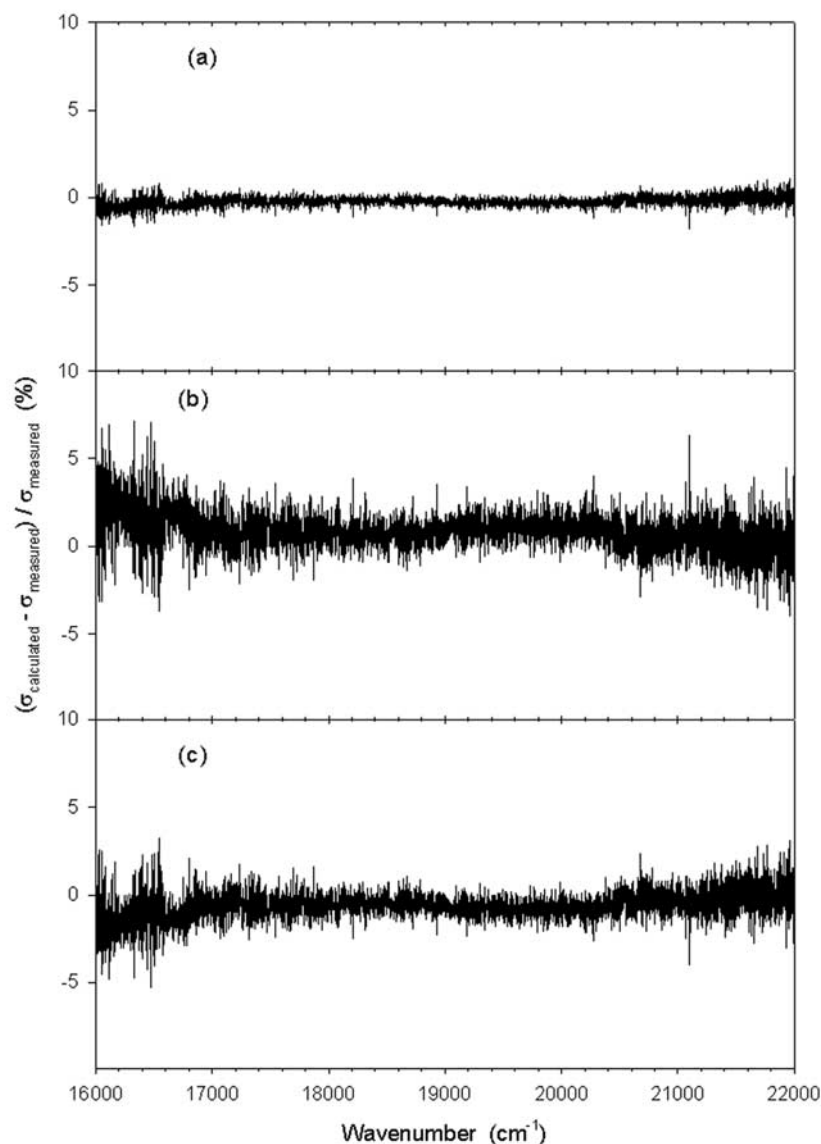
Figure 7. Comparison between the measured cross sections and their corresponding cross section obtained using a linear temperature regression at (a) 294 K, (b) 240 K, and (c) 220 K.

data and those of *Harder et al.* [1997] at 238 K (Figure 4b) is 3.7% (±2.1%). A large disagreement with the data of *Voigt et al.* [2002] at 246 K is clearly apparent in Figure 4c, where differences up to 15% are observed. A constant offset could not explain the observed discrepancy. A possible explanation could be a drift in the lamp intensity during the measurements of one of the groups, since the stability of the source is particularly crucial for the measurements in the region below 18,000 cm^{-1}, in which the cross-section values become small.

[22] In Figure 5a the data of this work at 220 K and those of *Vandaele et al.* [1998] at 2 cm^{-1} resolution are compared. The mean difference is 1.8% (±1.9%). Two concatenation limits clearly appear: The first one, at 20,500 cm^{-1}, corresponds to the limit for one of the regions recorded in this work; and the second, at ~22,000 cm^{-1}, arises from the merging of two measurement intervals in the work of *Vandaele et al.* [1998]. The

comparison with the data of *Coquart et al.* [1995] at 220 K (Figure 5b) shows a very good agreement (mean difference is 0.2% and standard deviation is 1.2%). Figure 5c compares our data with those of *Harder et al.* [1997] at 230 K. Their data are systematically lower than ours. The observed difference cannot be totally explained by a constant offset, since increasing differences are observed from 25,000 to 18,500 cm^{-1}. In contrast, most of the data of *Voigt et al.* [2002] at 223 K are lower than ours, particularly for wave numbers >18,000 cm^{-1}, for which the relative difference is ~8% (Figure 5d).

4. Temperature Dependence

[23] The temperature effect on the NO₂ absorption cross section has already been studied by several authors [*Davidson et al.*, 1988; *Coquart et al.*, 1995; *Mérienne et al.*, 1995; *Harder et al.*, 1997; *Kirmse and Jost*, 1997; *Vandaele et al.*,
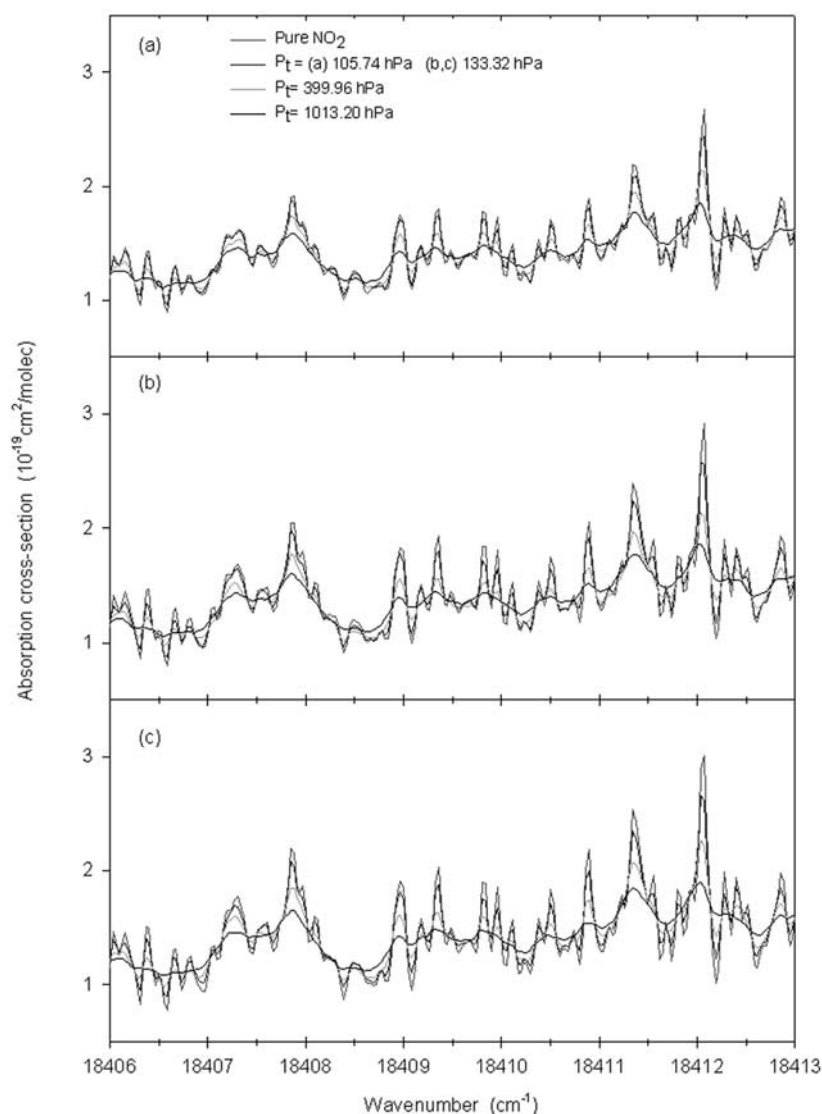
Figure 8. Pressure effect on the NO₂ absorption cross section at (a) 294 K, (b) 240 K, and (c) 220 K. See color version of this figure at back of this issue.

1998]. They all agree in the description of this effect: The absorption increases at the peak maxima and decreases at the peak minima when the temperature decreases. In most of the quoted studies a linear dependence with temperature was observed or assumed. However, *Kirmse and Jost* [1997] gave a more complex relation, separating the variation of the bell-shaped envelope and the superimposed spectral structures. In this study, we only use a linear temperature dependent relation:

$$\sigma_{NO_2}(\overline{\nu}, T) = \sigma_{273K}(\overline{\nu}) + \alpha(\overline{\nu}).(T - 273), \qquad (8)$$

where $\sigma_{273K}(\overline{\nu})$ and $\alpha(\overline{\nu})$ are the cross section that would be measured at 0°C and the temperature coefficient, respectively, at each wave number $\overline{\nu}$. The values of these two parameters are represented for a small spectral interval in Figure 6. As already pointed out by *Davidson et al.* [1988], $\sigma_{273K}(\overline{\nu})$ and $\alpha(\overline{\nu})$ present anticorrelated behaviors.

[24] Figure 7 shows the relative difference ($\sigma_{calc} - \sigma_{meas})/\sigma_{meas}$ (given as a percentage) between the values obtained using equation (8) and the experimental data. The mean differences are lower than 1% (−0.22%, 0.87%, and −0.62% at 294, 240, and 220 K, respectively). However, local peak differences can reach 2% at 294 K and 7% at the lower temperatures.

5. Pressure Effect

[25] Spectra recorded under various pressure conditions (see Table 1) allowed the investigation of the pressure dependence of the NO₂ absorption cross section. A pressure effect in pure NO₂ was observed by *Vandaele et al.* [1998]. It might, however, be attributed to an experimental artifact, as the resolution used in this work was not sufficient to fully resolve the NO₂ structures and as the absorption was high. Both phenomena lead to deviations from the Beer-Lambert
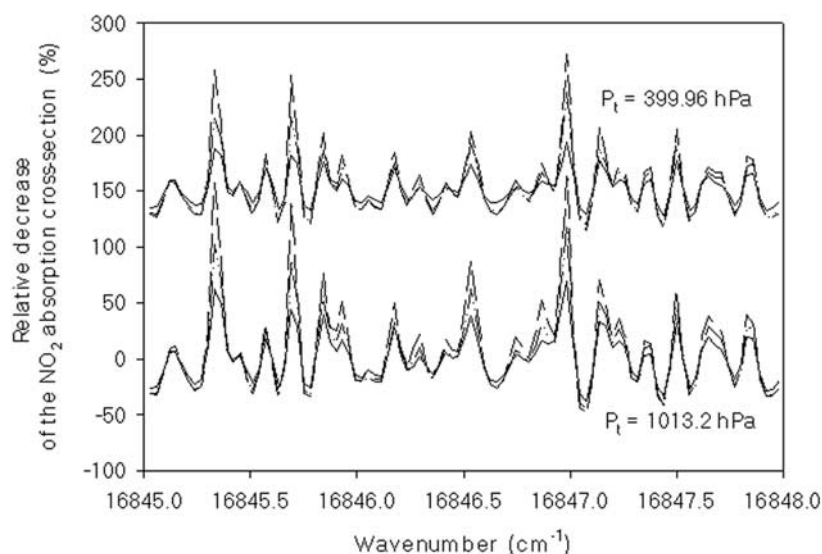
Figure 9. Effect of the temperature on the diluted spectra of NO₂. Two series of spectra are shown corresponding to the total pressures of 399.96 and 1013.2 hPa at the three temperatures (294, 240, and 220 K).

law and introduce nonlinearities in the cross sections [*Hermans et al.*, 1999]. This pressure effect could not be verified in this work owing to the lower pressures used when recording the pure NO₂ spectra.

[26] Important pressure effects have, however, been observed in spectra obtained with diluted NO₂. Figure 8 presents the NO₂ cross sections obtained at the three temperatures under different total pressures on a small spectral interval. The pressure effect is clearly visible: Structures are smoothed out and the amplitudes of the structures decrease with increasing total pressure. The effect is enhanced at the lower temperatures, as can be clearly seen in Figure 9, where the relative decreases of the NO₂ absorption cross section are plotted. These quantities have been calculated using the following expression (given as percentages):

$$\frac{(\sigma_{NO_2}(P_t, T, \lambda) - \sigma_{NO_2}(\text{pure}, T, \lambda))}{\sigma_{NO_2}(\text{pure}, T, \lambda)} \times 100, \qquad (9)$$

and they represent the variations of amplitude of the cross section obtained with diluted NO₂, compared with the amplitude of the cross section measured at the same temperature with pure NO₂. The decrease of the cross-section amplitude is larger at the lowest temperature. It can reach 150% at 220 K, compared with 50% at 294 K at the total pressure of 1013.2 hPa.

[27] Few studies have investigated the pressure effect on the NO₂ absorption cross section. *Harder et al.* [1997] mentioned measurements performed at high resolution (0.028 cm⁻¹) by P. Wennberg and T. Hanisco at the Department of Chemistry, Harvard University, using a fixed number of NO₂ molecules and increasing N₂ pressures. These measurements were complementary to high-resolution visible measurements of IO in the atmosphere [*Wennberg et al.*, 1997]. A large variation (30%–40%) in the differential amplitude with changing pressure was observed.

Voigt et al. [2002] have recorded spectra with NO₂/N₂ mixtures at two different total pressures. Figure 10 illustrates the pressure effect at room temperature. Two sets of data are plotted: Cross sections obtained in the present study with total pressures of 105.74 and 1013.2 hPa (at a resolution of 0.1 cm⁻¹) and cross sections obtained by *Voigt et al.* [2002] at 100 and 1000 hPa (at a resolution of 0.5 cm⁻¹). The data of *Voigt et al.* [2002] have been shifted by a constant value of 1.0×10^{-19} cm² molecule⁻¹ for the clarity of the graph. The effect of the total pressure is clearly visible on our data, while barely perceptible in the data of *Voigt et al.* [2002]. This is due to the lower resolution used by these authors.

[28] *Vandaele et al.* [2001] analyzed the influence of this parameter on UV-visible measurements of NO₂ performed with ground-based grating spectrometers: The low resolution of these instruments completely masks the pressure effect, and no information concerning the NO₂ profile could be extracted from these data. However, measurements performed at higher resolution might provide a rough vertical profile by combining the temperature and pressure dependences.

6. Conclusions

[29] Using a Fourier transform spectrometer and a 5 m multiple reflection cell, high-resolution measurements of the NO₂ absorption cross section have been performed in the NIR visible region (from 10,800 to 26,000 cm⁻¹). Measurements have been carried out at three different temperatures (294, 240, and 220 K) with pure NO₂ and NO₂/air mixtures. The accuracy on the absorption cross sections has been estimated to be between 3.6% and 5.0%, depending essentially on the temperature. The agreement with published data is quite remarkable, as differences between our data and those of *Coquart et al.* [1995], *Mérienne et al.* [1995], and *Vandaele et al.* [1998] are lower than 2.5% at the three
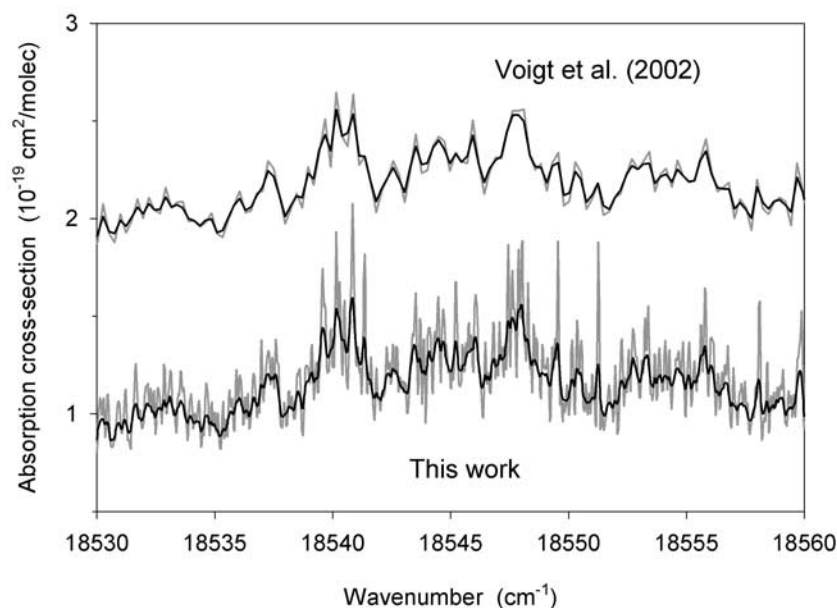
Figure 10. Comparison of the NO$_2$ absorption cross section obtained at a resolution of 0.1 cm^{-1} at 294 K with the total pressures of 105.74 hPa (grey) and 1013.2 hPa (black) with the corresponding data of *Voigt et al.* [2002] obtained at a resolution of 0.5 cm^{-1}. The latter values have been shifted by 1.0 $\times$ 10^{-19} cm^2 molec^{-1} for clarity.

temperatures. Although this new set of measurements does not lead to new or innovative results, it confirms the accuracy of already existing data. This work moreover provides a consistent set of data at high resolution and at three temperatures with a very precise wave number scale.

[30] The temperature effect has been investigated: An increase of the temperature results in a decrease of absorption at the maxima of the cross section and an increase at the minima. The differential amplitude of the cross section is thus significantly reduced. It is necessary to take this behavior into account for NO$_2$ stratospheric measurements, as already mentioned by *Harder et al.* [1997] and *Vandaele et al.* [1998]. A linear temperature-dependent formula has been proposed for the temperature effect.

[31] The use of NO$_2$/air mixtures at different temperatures showed a strong pressure effect. However, this effect is only observed at high resolution and completely disappears at the lower resolution used by ground-based UV visible grating spectrometers. Taking into account the combined effect of the temperature and the pressure should improve the sensitivity of the detection of the stratospheric NO$_2$ and could provide a rough vertical profile if the resolution of the atmospheric instrument is high enough.

[32] All the cross-section values obtained during this study are available upon request to the authors. They can also be downloaded from the Web site of the Belgian Institute for Space Aeronomy (IASB-BIRA) (http://www.oma.be/BIRA-IASB/Scientific/Data/CrossSections/CrossSections.html).

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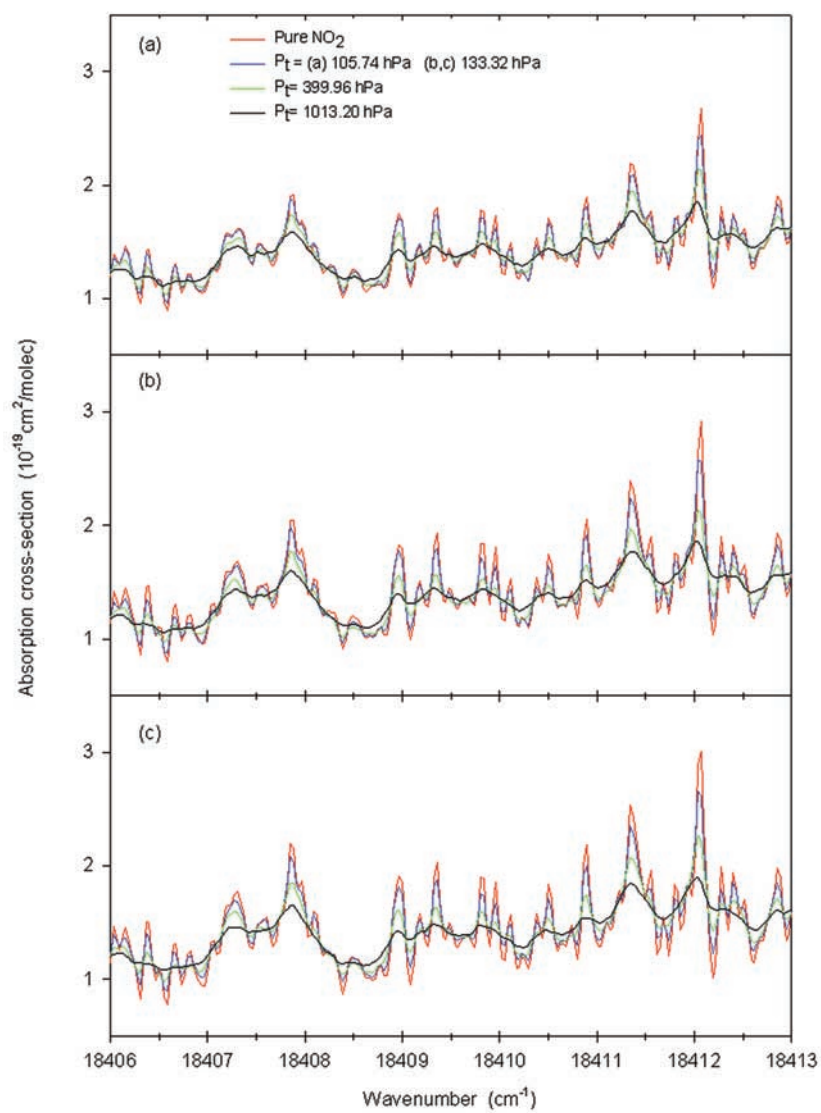
Figure 8. Pressure effect on the NO$_2$ absorption cross section at (a) 294 K, (b) 240 K, and (c) 220 K.