



## MEASUREMENTS OF THE NO<sub>2</sub> ABSORPTION CROSS-SECTION FROM 42 000 cm<sup>-1</sup> TO 10 000 cm<sup>-1</sup> (238–1000 nm) AT 220 K AND 294 K

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**Abstract**—The NO<sub>2</sub> absorption cross-section has been measured from 42 000 to 10 000 cm<sup>-1</sup> (238–1000 nm) with a Fourier transform spectrometer (at the resolution of 2 cm<sup>-1</sup>, 0.01 nm at 240 nm to 0.2 nm at 1000 nm) and a 5 m temperature controlled multiple reflection cell. The uncertainty on the cross-section is estimated to be less than 3% below 40 000 cm<sup>-1</sup> ( $\lambda > 250$  nm) at 294 K, 3% below 30 000 cm<sup>-1</sup> ( $\lambda > 333$  nm) at 220 K, but reaches 10% for higher wavenumbers. Temperature and pressure effects have been observed. Comparison with data from the literature generally shows a good agreement for wavenumbers between 37 500 and 20 000 cm<sup>-1</sup> (267–500 nm). Outside these limits, the difference can reach several percent.  
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### 1. INTRODUCTION

NO<sub>2</sub> plays an important role in the photochemistry of the Earth's atmosphere. In the troposphere, it acts as the main source of ozone and is a precursor to the nitric acid, which influences the acidification of the environment. It participates in the stratospheric chemistry by controlling the amounts of ozone and ClO.<sup>1</sup> It plays thus an important role in the coupling of the NO<sub>x</sub> and ClO<sub>x</sub> families.

Since the development of spectroscopic instruments capable of measuring atmospheric pollution by means of the absorption of visible and u.v. light, NO<sub>2</sub> has been intensively measured in the stratosphere and in the troposphere.<sup>2–4</sup> To determine the NO<sub>2</sub> amount in the atmosphere, the widely used DOAS technique (Differential Optical Absorption Spectroscopy) requires the knowledge of a precise absorption cross-section, measured in the laboratory. Since generally the resolving power of the spectrometers used for the atmospheric measurements is rather low, the DOAS procedure involves a convolution of the laboratory data with the appropriate instrumental function. Previous studies of the NO<sub>2</sub> absorption cross-section<sup>5,6</sup> have pointed out discrepancies in the literature of the order of 10–20% between data determined at room temperature. The discrepancies arise as differences in the absolute values of the cross-section, but also as differences in the amplitude of the absorption structures and in the wavelength scales. Recently, it was shown<sup>7</sup> that many of the residual structures found after the removal of the NO<sub>2</sub> signature from the atmospheric spectra could be attributed to the temperature dependence of the NO<sub>2</sub> cross-section.

Therefore to analyse the atmospheric spectra and to obtain accurate NO<sub>2</sub> amounts, it is necessary to have a precise cross-section at high resolution and to know its temperature dependence.

Laboratory measurements of the NO<sub>2</sub> cross-section are complicated by the presence of the dimer N<sub>2</sub>O<sub>4</sub> through the reaction 2NO<sub>2</sub> ⇌ N<sub>2</sub>O<sub>4</sub>. Unfortunately the value of the equilibrium constant is not well defined, particularly at low temperature. In addition, N<sub>2</sub>O<sub>4</sub>, which is more abundant at low temperature, also shows an absorption spectrum above 25 000 cm<sup>-1</sup> ( $\lambda < 400$  nm).

The three groups involved in this work have already contributed to the study of the NO<sub>2</sub> cross-section. The Groupe de Spectrométrie Moléculaire et Atmosphérique of Reims (GSMA) built a 5 m multipass absorption cell<sup>8</sup> which can be temperature regulated down to 220 K. They used it in conjunction with a grating monochromator to measure the NO<sub>2</sub> absorption cross-section in

the UV/visible region at 220, 240, and 294 K<sup>6,9-11</sup> This cell allowed them to operate at very low pressures, thus minimizing the influence of N<sub>2</sub>O<sub>4</sub>. Using a Fourier transform spectrometer (FTS), the Laboratoire de Chimie Physique Moléculaire of the Université Libre de Bruxelles (CPM) in collaboration with the Institut d'Aéronomie Spatiale de Belgique (IASB) investigated<sup>5</sup> the NO<sub>2</sub> absorption cross-section under more atmospheric-like conditions (NO<sub>2</sub> diluted in 1 atm of O<sub>2</sub>). They recorded the NO<sub>2</sub> absorption in the visible region at room temperature. The results were in good agreement (2%) with those of the GSMA. This agreement is lower than the estimated errors on the separate measurements.

In order to extend the study of the NO<sub>2</sub> cross-section to a larger wavenumber region and to combine the advantages of high resolution measurements to those of low pressure experiments, the groups quoted above have undertaken new measurements coupling the FTS of the CPM group and the multiple reflection cell of the GSMA group. An additional motivation for the CPM group is to record the NO<sub>2</sub> absorption cross-section at the same resolution used by its FTS while measuring atmospheric spectra. This avoids the otherwise necessary step of the convolution procedure.

This work presents new values for the NO<sub>2</sub> absorption cross-section in the spectral interval from 42 000 to 10 000 cm<sup>-1</sup> (238–1000 nm) at the resolution of 2 cm<sup>-1</sup> (0.01 nm at 240 nm to 0.2 nm at 1000 nm) and at two temperatures (220 and 294 K).

According to the criteria discussed above, the experimental conditions were defined as follows:

1. The gas pressures were low to minimize the formation of N<sub>2</sub>O<sub>4</sub>. Then long optical absorption paths were needed to obtain a good signal to noise ratio.
2. Different pressures were used to determine the N<sub>2</sub>O<sub>4</sub> contribution in the UV spectral region.
3. The spectra were recorded at high resolution in order to resolve the structures of the bands lying at wavenumbers smaller than 25000 cm<sup>-1</sup> ( $\lambda > 400$  nm).
4. The good accuracy and reproducibility of the wavelength scale was ensured by the presence of the frequency stabilized He–Ne laser controlling the FTS.

From the measurements, complete sets of data at 294 and 220 K have been obtained and comparisons have been made with data available in the literature. In addition to the temperature dependence of the NO<sub>2</sub> absorption cross-section, a pressure effect has been observed in the visible region of the spectrum. The absorption cross-section of N<sub>2</sub>O<sub>4</sub> has also been deduced from the measurements made at 220 K. Finally a reanalysis of previously recorded stratospheric spectra was performed with the new absorption cross-section of NO<sub>2</sub> to confirm the impact of the temperature dependence in the determination of NO<sub>2</sub> amounts.

## 2. EXPERIMENTAL

All the measurements were performed with a Bruker 120M FT spectrometer, characterized by a maximum resolution of 0.008 cm<sup>-1</sup> and a resolving power better than 10<sup>6</sup>. It is capable of recording spectra from the MIR to the UV regions with a wavenumber accuracy of 0.005 cm<sup>-1</sup>.

The cell,<sup>8</sup> whose temperature can be stabilized down to 220 K owing to a circulating cooling fluid, is 6 m long with a base distance of 5 m between the mirrors. The total absorption path can be adjusted up to 300 m in the visible region. The temperature is measured by 5 platinum sensors regularly distributed inside the cell and the temperature variation from end to end never exceeds  $\pm 0.2$  K at 220 K. The pressure is monitored by a MKS Baratron capacitance manometer with a 1 torr and a 10 torr heads.

In this work two light sources were used: a high pressure non-ozone-free xenon arc lamp (450 W) for the region extending from 42 000 to 20 000 cm<sup>-1</sup> (238–500 nm), a tungsten–halogen lamp (200 W) for the visible region below 20 000 cm<sup>-1</sup> ( $\lambda > 500$  nm). The absorption path length was 60.7 m with the tungsten lamp as the source and was reduced to 20.8 m with the xenon lamp, in order to minimize the photodissociation occurring inside the cell. Three different detectors were used to cover the entire spectral region: a u.v.-, a GaP- and a Si-diode.

Table 1 indicates the spectral regions investigated using different combinations of lamps and detectors. A blue filter was used to optimise the sensitivity at wavenumbers greater than 15 000 cm<sup>-1</sup> ( $\lambda < 667$  nm). The absorption path length used for each region is also given in Table 1.

The NO<sub>2</sub> gas was provided by Air Liquide (99% purity) and was used without further purification at the pressure indicated in Table 1.

The experimental procedure was the following:

1. Before a set of measurements, the light source was left in operation for several days to stabilize its intensity.

2. A blank spectrum was recorded with the cell empty.

3. The light beam was deviated from the entrance of the cell while the NO<sub>2</sub> was introduced. After a time long enough (a few minutes) to allow most of the gas adsorption on the inner wall of the cell to take place, the light was admitted into the cell and spectra were recorded. The pressure was monitored throughout the experiment. The continuous decrease of the pressure due to the gas adsorption on the walls of the cell was found to be about 3% for an experiment at 294 K and up to 8% at 220 K. A time dependent correction was then applied for this pressure variation. With the xenon lamp, the pressure correction also included the pressure variation due to the NO<sub>2</sub> photodissociation. This variation could be determined by difference with the correction applied for an experiment with the tungsten lamp under the same initial pressure conditions.

4. The gas was pumped out and a new blank spectrum was recorded.

5. All the spectra were obtained at the resolution of 2 cm<sup>-1</sup> during the forward and backward scans of the mobile mirror, using a single sided recording mode. Table 2 gives the number of scans co-added to record a spectrum and the corresponding time.

### 3. RESULTS

$P_{\text{NO}_2}$  and  $P_{\text{N}_2\text{O}_4}$  are the partial pressures of the two species, which are related to the total pressure  $P_{\text{tot}}$  and to the equilibrium constant  $K_p$  by:

$$P_{\text{tot}} = P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4}$$

and

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

The value of the equilibrium constant depends only on the temperature. From experimental values of  $K_p$ , Hurtmans et al<sup>12</sup> derived a temperature dependent polynomial expansion of  $\text{Log}_{10}K_p$ . This equation is only valid in the temperature range in which measurements of  $K_p$  were performed (233–404 K). At 294 K, the value of  $K_p$  is 78.38 torr according to these authors. At 220 K, the value has been calculated using the formula given by Chao et al<sup>13</sup> ( $K_p = 0.03178$  torr).

The absorption cross-sections of NO<sub>2</sub> and of N<sub>2</sub>O<sub>4</sub> are deduced from the experimental spectra using the Beer–Lambert's law:

$$A'(\lambda) = \frac{P_0 T}{N_0 T_0 d} \cdot \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sigma_{\text{NO}_2}(\lambda) \cdot P_{\text{NO}_2} + \sigma_{\text{N}_2\text{O}_4}(\lambda) \cdot P_{\text{N}_2\text{O}_4} \quad (1)$$

where  $I(\lambda)$  and  $I_0(\lambda)$  are the intensities recorded with and without the gas,  $N_0$  is the number of molecules per cm<sup>3</sup> in the normal conditions of temperature and pressure ( $T_0, P_0$ ),  $T$  is the temperature and  $d$  the absorption path length;  $\sigma_{\text{NO}_2}(\lambda)$  and  $\sigma_{\text{N}_2\text{O}_4}(\lambda)$  are the absorption cross-section of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>.

Eq. (1) can be rewritten as

$$\frac{A'(\lambda)}{P_{\text{NO}_2}} = \sigma_{\text{NO}_2}(\lambda) + \sigma_{\text{N}_2\text{O}_4}(\lambda) \cdot \frac{P_{\text{N}_2\text{O}_4}}{K_p} \quad (2)$$

From measurements at various pressures, the NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> contributions can be separated. Plotting the  $A'(\lambda)/P_{\text{NO}_2}$  values vs  $P_{\text{N}_2\text{O}_4}/K_p$  allows us to determine the  $\sigma_{\text{NO}_2}(\lambda)$  values by the slope and the  $\sigma_{\text{N}_2\text{O}_4}(\lambda)$  values by the intercept at zero pressure. These parameters were determined using a linear least squares fitting procedure.

Table 1. Experimental conditions for the absorption measurements

Region	Lamp	Detector	Spectral interval in $\text{cm}^{-1}$ (in nm)	Absorption path length (m)	Total pressures (torr)	
					220 K	294 K
1a	Tungsten	Si-diode	17000-10000 (588-1000)	60.7	1 to 2 (2 spectra)	0.5 to 1.0 (3 spectra)
1b	Tungsten + blue filter	Si-diode	23000-15000 (435-666)	60.7	0.01 to 1 (9 spectra)	0.01 to 0.5 (16 spectra)
2	Xenon	GaP-diode	32000-20000 (312-500)	20.8	0.007 to 0.03 (15 spectra)	0.02 to 0.06 (7 spectra)
3	Xenon	solar blind u.v.-vacuum diode	42000-30000 (238-333)	20.8	0.01 to 0.06 (21 spectra)	0.01 to 0.2 (25 spectra)

Table 2. Number of blocks, number of scans per block and recording time for each spectrum

Region 1b	Number of blocks	Number of scans	Measurement time (min)
Region 1a	8	64	30
Region 1b	8	128	60
Region 2	4	128	30
Region 3	10	128	30

### 3.1. NO<sub>2</sub> cross-section at 294 K

**3.1.1. Values.** At 294 K and at the pressures used in this work, the N<sub>2</sub>O<sub>4</sub> concentration in the cell is small: 1.2% for the highest pressure (1.0 torr). Since at the maximum absorption of N<sub>2</sub>O<sub>4</sub> (at 29 500 cm<sup>-1</sup>, 340 nm) its contribution to the total absorption is less than 0.1%, we have neglected the N<sub>2</sub>O<sub>4</sub> absorption on the whole wavelength range. The NO<sub>2</sub> absorption cross-section was therefore directly determined from the reduced Eq. (3).

$$A'(\lambda) = \sigma_{\text{NO}_2}(\lambda) \cdot P_{\text{NO}_2} \quad (3)$$

The final cross-section given in this work results from the averaged values obtained with several measurements: 2 spectra recorded with a NO<sub>2</sub> partial pressure of 1.0 torr for the wavenumber region below 15 000 cm<sup>-1</sup> ( $\lambda > 667$  nm); 6 spectra at partial pressures of 0.01 and 0.02 torr for the region between 22 000 and 15 000 cm<sup>-1</sup> (455–667 nm) and 26 spectra at pressures lower than 0.2 torr for the region above 22 000 cm<sup>-1</sup> ( $\lambda < 455$  nm). The restriction to the indicated pressures, particularly for the 22 000–15 000 cm<sup>-1</sup> region (455–667 nm), was necessary because a pressure dependence was observed for the cross-section calculated at higher pressures. This effect will be discussed in a next section but is not clearly detected (in the limit of our precision) at wavenumbers greater than 22 000 cm<sup>-1</sup> ( $\lambda < 455$  nm).

The absorption cross-section of NO<sub>2</sub> at 294 K is represented in Fig. 1 for the entire spectral region (Fig. 1a: 42 000–25 000 cm<sup>-1</sup>, 238–400 nm; Fig. 1b: 25 000–15 000 cm<sup>-1</sup>, 400–666 nm and Fig. 1c: 15 000–10 000 cm<sup>-1</sup>, 666–1000 nm).

The total error results from the separate errors on the different parameters (Table 3): temperature, pressure, length of the absorption path, impurities in the sample, drift of the lamp, measured absorbance defined as  $A = \ln(I_0(\lambda)/I(\lambda))$  and  $K_p$  value. The total error on the NO<sub>2</sub> cross-section was determined using the following expressions (see for example Ref. 5):

$$\frac{\delta\sigma}{\sigma} = \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta T}{T}\right)^2 + \left(\frac{\delta d}{d}\right)^2 + \left(\frac{\delta P_{\text{NO}_2}}{P_{\text{NO}_2}}\right)^2} \quad (4)$$

with

$$\frac{\delta P_{\text{NO}_2}}{P_{\text{NO}_2}} = \left(\frac{a-1}{2a}\right) \frac{\delta K_p}{K_p} + \left(\frac{4P_{\text{tot}}}{2a(a-1)K_p}\right) \frac{\delta P_{\text{tot}}}{P_{\text{tot}}} \quad (5)$$

where  $a = (1 + 4P_{\text{tot}}/K_p)^{1/2}$ .

The total uncertainty is of the order of 3% below 40 000 cm<sup>-1</sup> ( $\lambda > 250$  nm) and reaches 6% between 42 000 and 40 000 cm<sup>-1</sup> (238–250 nm).

**3.1.2. Comparisons.** The NO<sub>2</sub> cross-section obtained in this work at 294 K has been compared with the following data: Vandaele et al<sup>5</sup> (293 K, 2 cm<sup>-1</sup> resolution), Mérienne et al<sup>6</sup> and Jenouvrier et al<sup>9</sup> (294 K, 0.01 nm resolution), Bass et al<sup>14</sup> (235 and 298 K, 0.015 nm resolution), Yoshino<sup>15</sup> (293 K, 0.005 nm resolution), Harder et al<sup>16</sup> (298 K, 0.15 cm<sup>-1</sup> resolution), Corcoran et al<sup>17</sup> (295 K, 0.075 nm resolution), Johnston and Graham<sup>18</sup> (293 K, 0.1 nm resolution), and Harwood and Jones<sup>19</sup> (293 K, 0.54 nm resolution). All the data listed above, except those of Johnston and Graham<sup>18</sup> and Harwood and Jones<sup>19</sup>, are considered as high resolution data.

To make comparisons at a resolution equivalent to that of this work (2 cm<sup>-1</sup>), all the high resolution data from the literature were convolved with a gaussian function and were interpolated to correspond to the present wavenumber scale. Similarly, when our data were compared with data obtained at a lower resolution (Johnston and Graham<sup>18</sup> and Harwood and Jones<sup>19</sup>), our values were convolved to achieve an equivalent resolution.

Figure 2 compares the relative differences

$$\left( \frac{\sigma_{\text{other}} - \sigma_{\text{this work}}}{\sigma_{\text{this work}}} \times 100 \right)$$

for the high resolution data at room temperature. The mean value of the differences as well as their standard deviation are indicated by the horizontal lines.

The data of Vandaele et al<sup>5</sup> shows discrepancies up to 10% (Fig. 2a) for wavenumbers lower than  $18\,000\text{ cm}^{-1}$  ( $\lambda > 555\text{ nm}$ ). The mean and standard deviations of the differences plotted in Fig. 2(a) have been calculated for wavenumbers higher than this limit. The large differences observed at the limits of the spectrum (4% at  $26\,000\text{ cm}^{-1}$ , 385 nm and 10% below  $18\,000\text{ cm}^{-1}$  ( $\lambda > 555\text{ nm}$ )) can be attributed to an uncertainty in the data of Vandaele et al due to the experimental conditions. In these regions, the detector combined with the xenon lamp leads to very

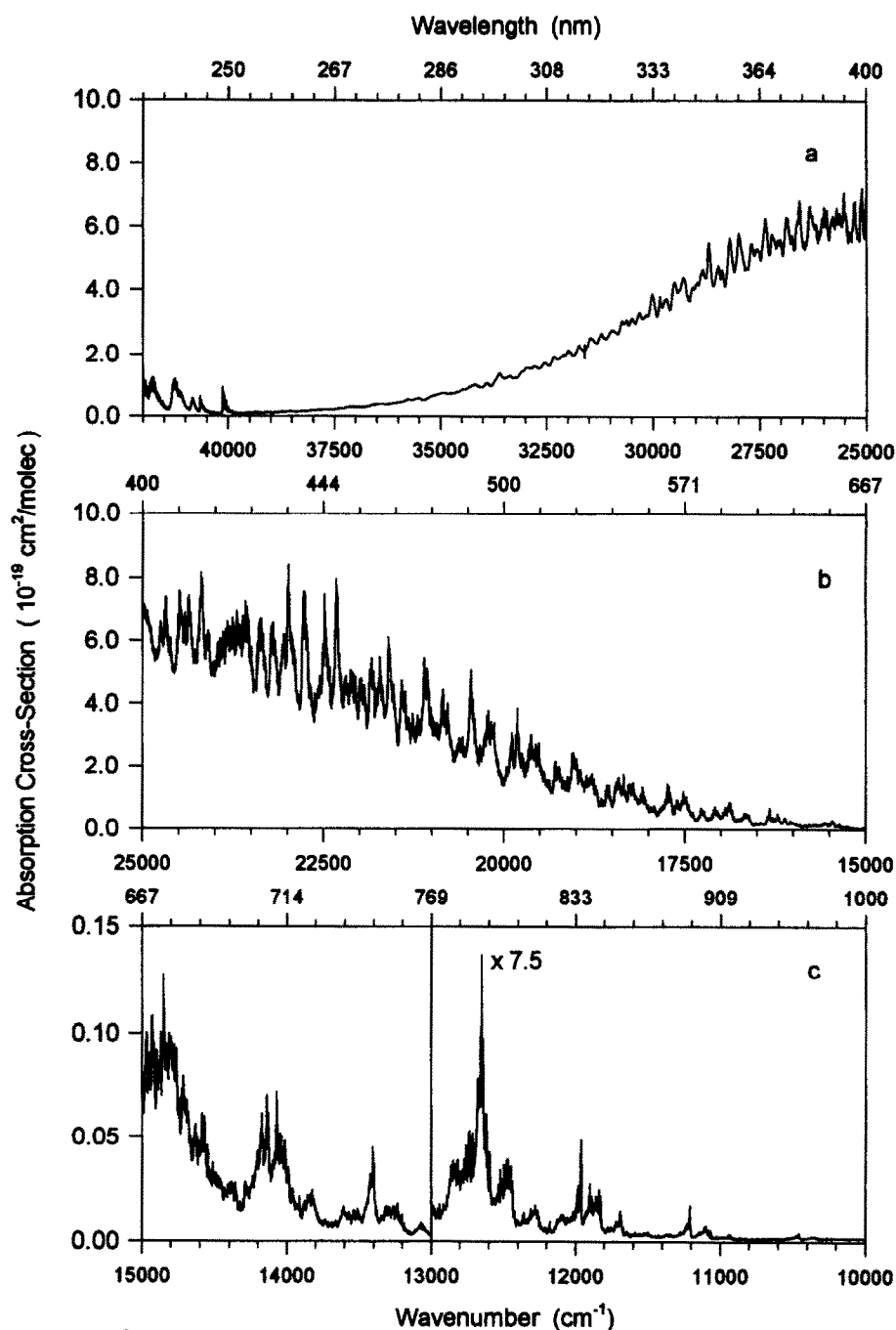


Fig. 1. Absorption cross-section of NO<sub>2</sub> at the resolution of  $2\text{ cm}^{-1}$  and at 294 K (a) from  $42\,000$  to  $25\,000\text{ cm}^{-1}$  (238–400 nm), (b) from  $25\,000$  to  $15\,000\text{ cm}^{-1}$  (400–666 nm), and (c) from  $15\,000$  to  $10\,000\text{ cm}^{-1}$  (666–1000 nm). Below  $13\,000\text{ cm}^{-1}$  (769 nm), the cross-section has been expanded by a factor of 7.5.

Table 3. Error estimate on the NO<sub>2</sub> cross-section measurements at 294 K

	Error (%)	
	Region 40000–10000 cm <sup>-1</sup> (250–1000 nm)	Region 42000–40000 cm <sup>-1</sup> (238–250 nm)
Absorption path length	0.05	0.05
Temperature	0.1	0.1
Lamp drift	1	1
Absorbance	0.1	5
Sample impurities	1	1
$K_p$	5	5
Pressure	0.1	0.1

small signals so that the relative error increases rapidly. At lower wavenumbers, the differences can also result from the pressure effect (see Section 3.4), since the measurements were obtained with higher pressures ( $\approx 10$  mbar of NO<sub>2</sub> diluted in 1 atm of O<sub>2</sub>). We cannot explain the sudden change observed in the noise level near 22 200 cm<sup>-1</sup> (450.5 nm).

The comparison with the data of Mérienne et al<sup>6</sup> and Jenouvrier et al<sup>9</sup> (Fig. 2b) indicates the regions where the mergings of their data were performed. Small shifts in wavenumbers between the two sets of data are observed over the spectral range up to 39 000 cm<sup>-1</sup> (256 nm) but they are within the limit of the precision given by these authors (0.01 nm). For wavenumbers lower than 37 500 cm<sup>-1</sup> ( $\lambda > 267$  nm), the data of Mérienne et al<sup>6</sup> agree within  $\pm 1.5\%$  with the present data.

Figure 2(c) shows the comparison with the unpublished data of Yoshino<sup>15</sup>, obtained from spectra recorded at a resolution of 0.005 nm with a 6.65 m McPherson spectrometer and with NO<sub>2</sub> pressures ranging from 0.5 to 3 torr. A very small shift (0.1 to 0.25 cm<sup>-1</sup>) was observed in some of the regions. The data of Yoshino<sup>15</sup> are 2% lower than ours.

In Fig. 2(d) are plotted the results of the comparison with the data of Harder et al<sup>16</sup>. The agreement seems quite good ( $< \pm 2\%$ ) for wavenumbers higher than 20 000 cm<sup>-1</sup> ( $\lambda < 500$  nm). Below this limit their cross-section values are up to 8% smaller than the present data. However it can be noted that Harder et al have estimated a larger error in this region, mainly due to a lamp drift; the effect is to shift downwards the whole set of values. Adding a value of  $0.8 \times 10^{-20}$  cm<sup>2</sup>/mole to the data of Harder et al, the relative difference is constant over the whole region and the corrected values are 2.5% higher than ours.

The mean of the relative differences for the data of Bass et al<sup>14</sup> (Fig. 2e) is about 3%. However larger differences are observed above 37 000 cm<sup>-1</sup> ( $\lambda < 270$  nm): they result mainly from a shift in the wavenumber scale. The mean value and the standard deviation plotted in Fig. 2(e) have been calculated for wavenumbers lower than 37 000 cm<sup>-1</sup> ( $\lambda > 270$  nm).

The discrepancies with the data of Corcoran et al<sup>17</sup> are very large (Fig. 2f); they are mostly due to a systematic difference in the amplitude ( $0.14 \times 10^{-19}$  cm<sup>2</sup>/mole) and a wavenumber shift of 2.3 cm<sup>-1</sup>.

Figure 3(a) and (b) show the relative differences at 294 K with the low resolution data of Harwood and Jones<sup>19</sup> and Johnston and Graham<sup>18</sup> respectively. The data of Harwood and Jones<sup>19</sup> are 6% lower than ours, and those of Johnston and Graham<sup>18</sup> are 2% higher. A wavenumber shift ( $-12$  cm<sup>-1</sup> below 22 000 cm<sup>-1</sup> ( $\lambda > 455$  nm), and  $-1$  cm<sup>-1</sup> at higher wavenumbers) is also observed for the data of Johnston and Graham.<sup>13</sup>

### 3.2. N<sub>2</sub>O<sub>4</sub> cross-section at 220 K

**3.2.1. Values.** The absorption cross-section of N<sub>2</sub>O<sub>4</sub> has been obtained using Eq. (2), applied on all the spectra measured with the GaP- and u.v.-diodes (respectively, 15 and 21 spectra for total pressures from 0.007 to 0.03 torr for the GaP-diode and 0.01 to 0.2 torr for the u.v.-diode). The cross-section values, smoothed to remove the noise, are plotted in Fig. 4 with previous data<sup>11, 14, 19</sup> from 40 000 to 22 000 cm<sup>-1</sup> (250–455 nm) but are significant only above 25 000 cm<sup>-1</sup> ( $\lambda < 400$  nm).

The error on the N<sub>2</sub>O<sub>4</sub> cross-section has been deduced from the least squares fitting method and varies from 2% to 20%.

**3.2.2. Comparisons.** Bass et al<sup>14</sup> reported values of the N<sub>2</sub>O<sub>4</sub> cross-section determined at 250 and 298 K from spectra recorded under high pressure conditions, so that the NO<sub>2</sub> absorption became negligible. They did not observe a temperature dependence. In their calculations they used  $K_p$  values

determined from the previous formula of Chao et al<sup>20</sup> giving higher values than their latest expression<sup>13</sup> (2% at 250 K). As a result they overestimated the  $\text{N}_2\text{O}_4$  cross-section. However this cannot explain the difference (21% at  $29\,000\text{ cm}^{-1}$ , 345 nm) with our results. Their spectrum is very noisy and consists of the juxtaposition of intervals with discontinuities in the cross-section values.

Harwood and Jones<sup>19</sup> obtained the cross-section at various temperatures; only the results of their measurements made at 253 and 225 K are plotted in Fig. 2. They observed a clear dependence of the cross-section with the temperature and determined the  $K_p$  values from their measurements. These values are systematically larger than those determined from Chao et al<sup>13</sup> for temperatures

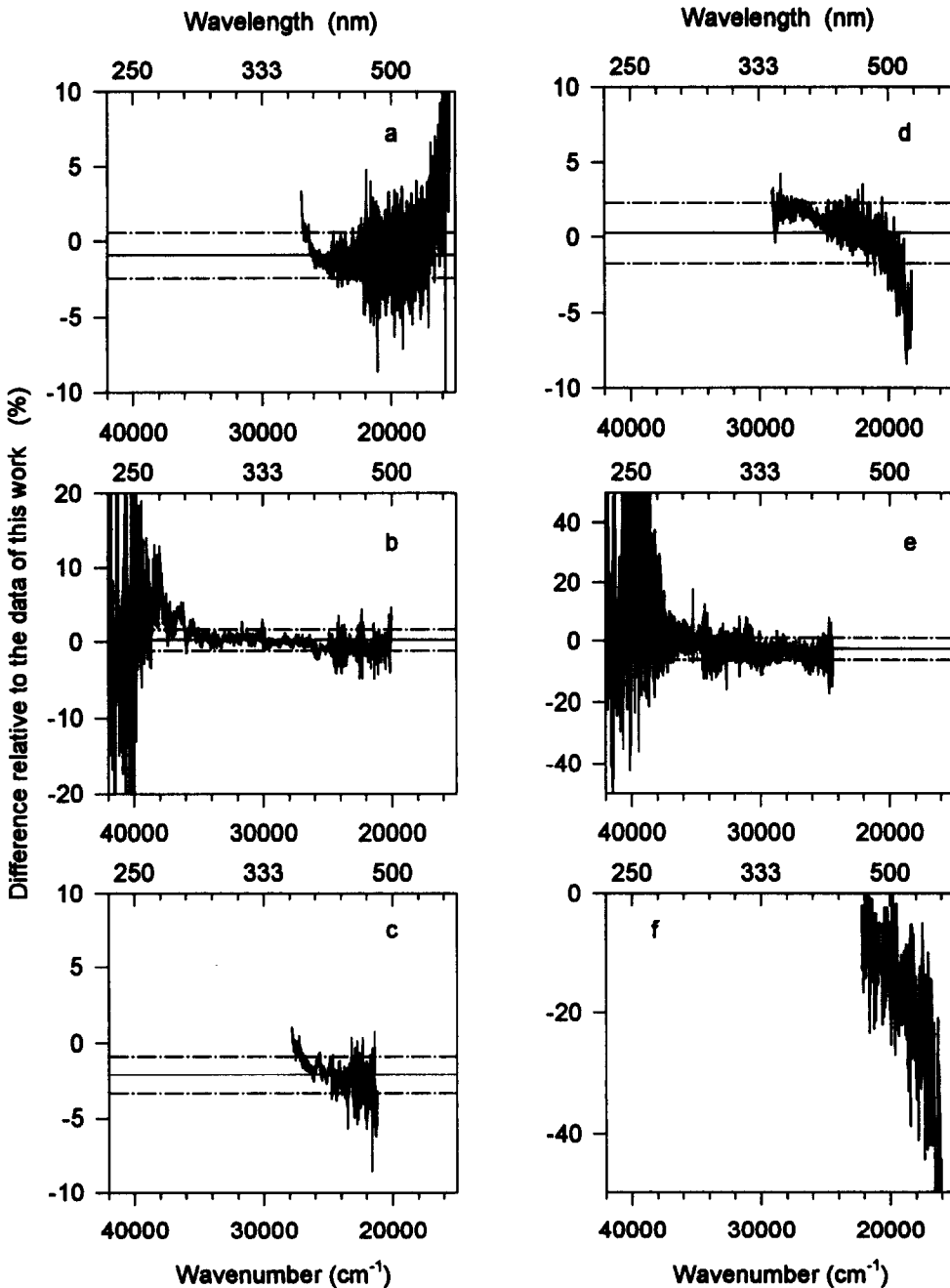


Fig. 2. Comparison of the new  $\text{NO}_2$  absorption cross-section at 294 K with the high resolution data of: (a) Vandaele et al<sup>5</sup>, (b) Mérianne et al<sup>6</sup>, (c) Yoshino<sup>15</sup>, (d) Harder et al<sup>16</sup>, (e) Bass et al<sup>9</sup>, and (f) Corcoran et al<sup>17</sup>.

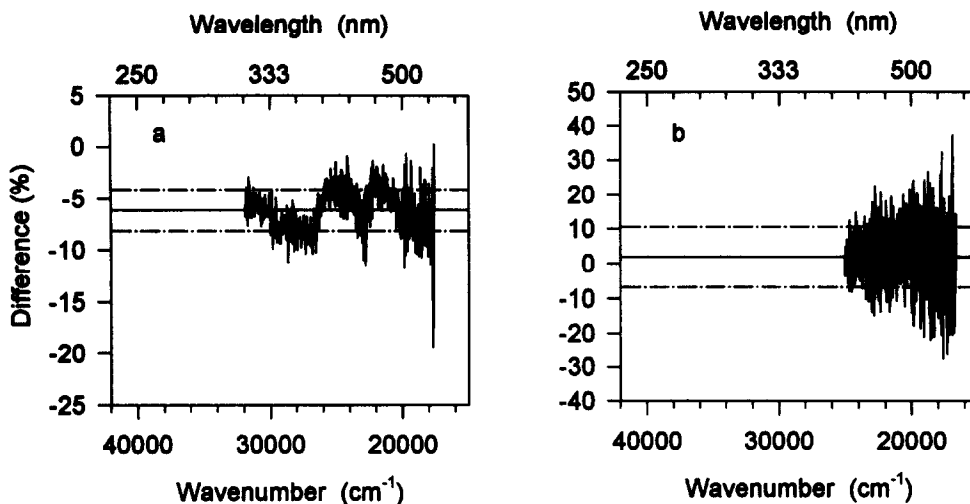


Fig. 3. Comparison of the new NO<sub>2</sub> absorption cross-section with the low resolution data of: (a) Harwood and Jones<sup>19</sup> (298 K), (b) Johnston and Graham<sup>18</sup> (293 K).

lower than 243 K. The value of  $K_p$  interpolated at 220 K from the values of Harwood and Jones<sup>19</sup> is 0.038 torr. This value yields an underestimation of the concentration of N<sub>2</sub>O<sub>4</sub> (10% at their lowest pressure), and in turn implies an overestimation of its cross-section. However the cross-section values of Harwood and Jones<sup>19</sup> are lower than ours. So that the difference cannot be explained by the difference in the  $K_p$  values.

Finally our data are compared to those of Mérienne et al<sup>11</sup> obtained at 220 K with pressure conditions similar to those of this work, and with  $K_p$  values also derived from Chao et al<sup>13</sup> Therefore

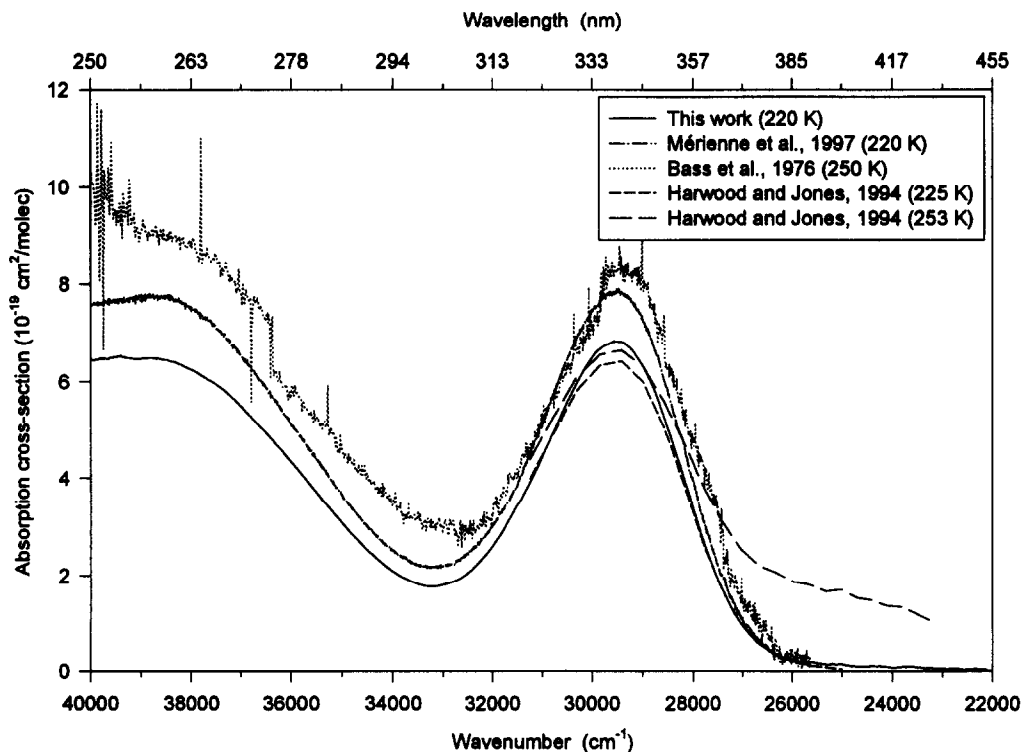


Fig. 4. The N<sub>2</sub>O<sub>4</sub> absorption cross-section: this work at 220 K (—); Bass et al<sup>14</sup> (-·-·-); Mérienne et al<sup>11</sup> (·····); Harwood and Jones<sup>19</sup> at 253 K (- - -) and at 225 K (- · - ·).

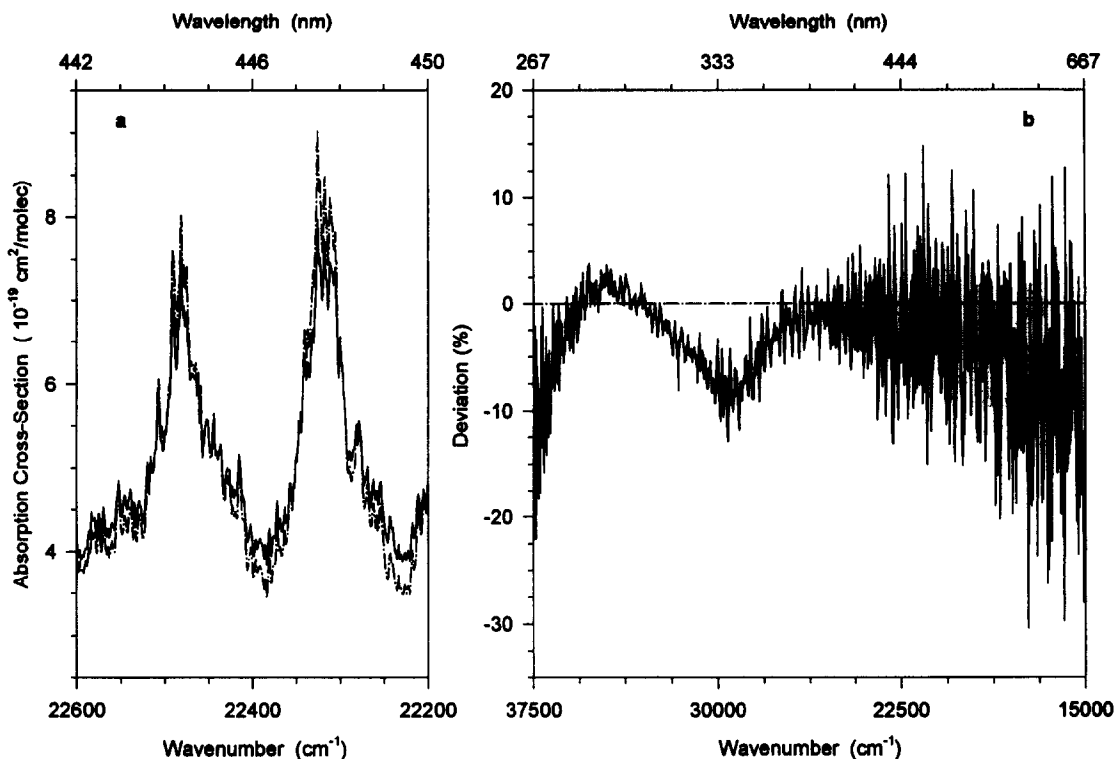


Fig. 5. (a) Temperature dependence of the  $\text{NO}_2$  absorption cross-section between  $22\,600$  and  $22\,200\text{ cm}^{-1}$  ( $442.5$  and  $450.5\text{ nm}$ ):  $T = 294\text{ K}$  (—) and  $T = 220\text{ K}$  (---). (b) the deviation (in %) of the absorption cross-section at  $220\text{ K}$  relative to that at  $294\text{ K}$  between  $37\,500$  and  $15\,000\text{ cm}^{-1}$  ( $270$  and  $670\text{ nm}$ ).

the results from the two works should be very close. However, our data are systematically lower by a factor of  $0.85$ . We cannot explain this discrepancy.

### 3.3. $\text{NO}_2$ cross-section at $220\text{ K}$

**3.3.1. Values.** In the region below  $22\,000\text{ cm}^{-1}$  ( $\lambda > 455\text{ nm}$ ), where there is no  $\text{N}_2\text{O}_4$  absorption, the  $\text{NO}_2$  cross-section has been directly deduced using Eq. (3). From  $22\,000$  to  $15\,000\text{ cm}^{-1}$  ( $455$ – $666\text{ nm}$ ), only 4 spectra obtained for  $\text{NO}_2$  partial pressures lower than  $0.014$  torr were used, since a pressure dependence was observed for higher pressures. For wavenumbers higher than  $25\,000\text{ cm}^{-1}$  ( $\lambda < 400\text{ nm}$ ), the absorption of the dimer must be taken into account through Eq. (2).

The error on the  $\text{NO}_2$  cross-section in the region below  $25\,000\text{ cm}^{-1}$  ( $\lambda > 400\text{ nm}$ ) can be obtained from Eq. (4) and Eq. (5) and can be estimated to be  $5\%$ . Above  $25\,000\text{ cm}^{-1}$  ( $\lambda < 400\text{ nm}$ ), Eq. (4) and Eq. (5) also allow to calculate the error on the  $A'(\lambda)$  values determined from Eq. (2). However the errors on the  $\text{NO}_2$  cross-section and the  $\text{N}_2\text{O}_4$  cross-section are correlated. The standard error on the  $\text{NO}_2$  cross-section obtained from the least squares fits of Eq. (2) increases from  $2\%$  near  $25\,000\text{ cm}^{-1}$  ( $400\text{ nm}$ ) to  $5\%$  near  $30\,000\text{ cm}^{-1}$  ( $333\text{ nm}$ ) and to more than  $10\%$  above  $34\,000\text{ cm}^{-1}$  ( $\lambda < 295\text{ nm}$ ).

**3.3.2. Temperature effect.** Fig. 5(a) compares the  $\text{NO}_2$  cross-section at  $294$  and  $220\text{ K}$  in the  $22\,600$ – $22\,200\text{ cm}^{-1}$  region ( $442.5$ – $455\text{ nm}$ ). They show a similar structure with changes in the amplitude of the peaks. The absorption increases at the peak maxima and decreases at the peak minima when the temperature decreases. Such a dependence is expected, since the population of the higher energy rotational levels increases when the temperature increases. The structures are also smeared. Figure 5(b) shows the deviation (%) of the cross-section determined at  $220\text{ K}$  compared to that at  $294\text{ K}$  on the  $37\,500$ – $15\,000\text{ cm}^{-1}$  ( $267$ – $667\text{ nm}$ ) spectral interval. For wavenumbers higher than  $37\,500\text{ cm}^{-1}$  ( $\lambda < 267\text{ nm}$ ), this deviation is higher, but this can be the result of the higher uncertainty on our data in this region. For wavenumbers lower than

15 000 cm<sup>-1</sup> ( $\lambda > 667$  nm), both pressure and temperature effects have to be taken into account: for this reason this region is not represented in Fig. 5.

**3.3.3. Comparisons with previous data.** The cross-section determined at 220 K is compared to the data of Coquart et al<sup>10</sup>, Mérienne et al<sup>11</sup> (220 K), Harder et al<sup>16</sup> (217 K) and Harwood and Jones<sup>19</sup> (225 K) in Fig. 6. The agreement with the data of Coquart et al<sup>10</sup> and Mérienne et al<sup>11</sup> is within  $\pm 2.5\%$ . The present cross-section values are 2% lower in the u.v. region. The comparison with the data of Harder et al<sup>16</sup> shows again larger differences at smaller wavenumbers. The mean difference is about 5%; this cannot be explained by the small temperature difference. In Fig. 6(c) the relative differences between the data of Harwood and Jones<sup>19</sup> at 225 K and ours at 220 K are presented. Discrepancies up to 20% are observed. Figure 2(a) and Fig. 6(c), both comparing the cross-section of Harwood and Jones<sup>19</sup> with the present ones, show a similar periodic pattern. Harder et al<sup>16</sup> already mentioned that this effect resulted from the juxtaposition of successive spectra. As these spectra were recorded with a diode array (Harwood and Jones<sup>19</sup>), Harder et al<sup>16</sup> suggested that the resolution, the illumination and the focusing of the light were different on the edges of the detector providing differences at the limits of the recorded regions.

#### 3.4. Pressure effect on the NO<sub>2</sub> absorption cross-section

Important pressure effects on the NO<sub>2</sub> absorption cross-section were detected in the visible part of the spectrum at both temperatures. These effects seem to be restricted to some absorption bands

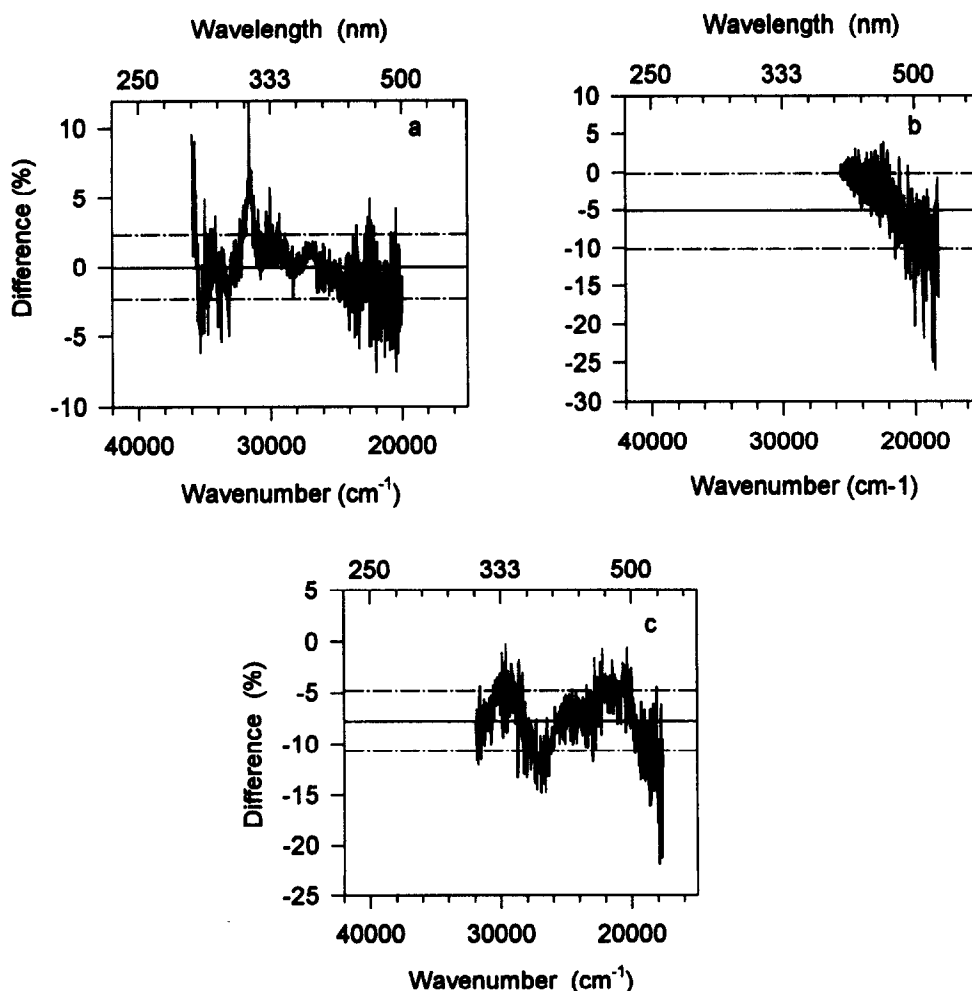


Fig. 6. Comparison of the new NO<sub>2</sub> absorption cross-section at 220 K with the data of: (a) Coquart et al<sup>10</sup> (220 K); (b) Harder et al<sup>16</sup> (217 K) and (c) Harwood and Jones<sup>19</sup> (225 K).

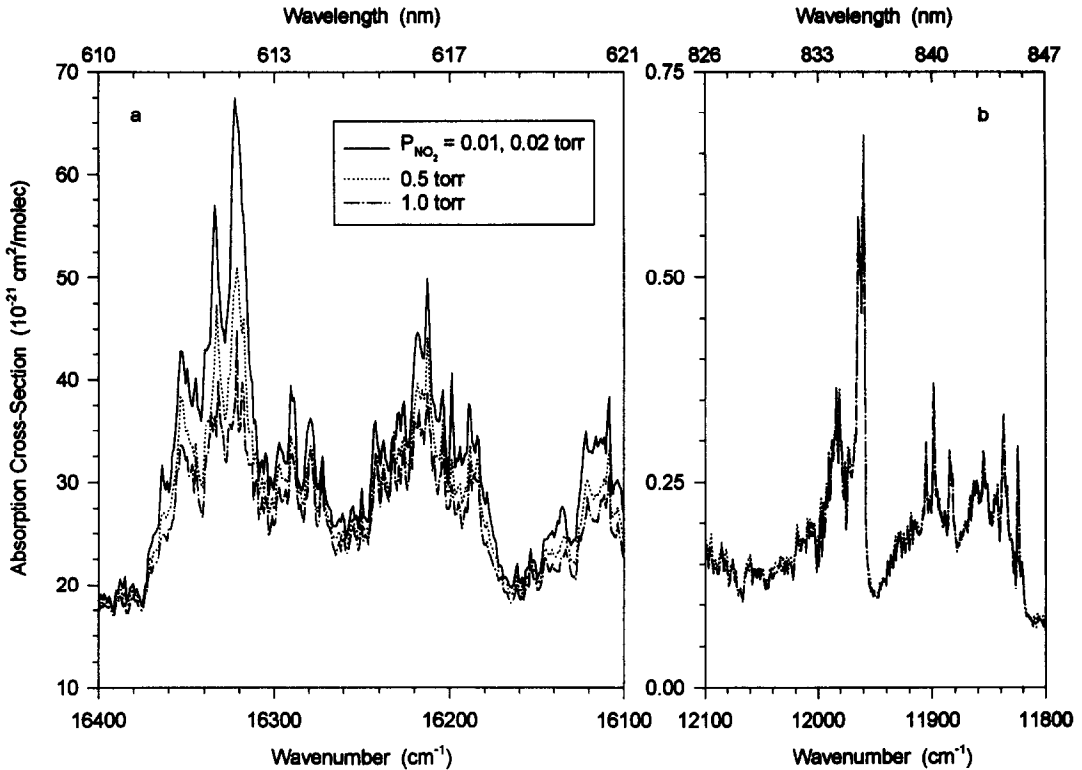


Fig. 7. Pressure effect on the absorption cross-section of  $\text{NO}_2$  at 294 K: (a)  $16\,400\text{--}16\,100\text{ cm}^{-1}$  region ( $610\text{--}621\text{ nm}$ ); (b)  $12\,100\text{--}11\,800\text{ cm}^{-1}$  region ( $825\text{--}850\text{ nm}$ ). ———  $P_{\text{NO}_2} = 0.01$  and  $0.02$  torr; .....  $P_{\text{NO}_2} = 0.5$  torr; - · - ·  $P_{\text{NO}_2} = 1.0$  torr.

in the  $20\,000\text{--}12\,000\text{ cm}^{-1}$  ( $500\text{--}833\text{ nm}$ ) spectral range. However it must be noted that the pressures used for the spectra recorded in the  $42\,000\text{--}22\,000\text{ cm}^{-1}$  ( $238\text{--}455\text{ nm}$ ) range never exceeded 0.06 torr. Thus a pressure effect in these regions cannot be totally ruled out. Indeed Harder et al<sup>16</sup> reported a pressure dependence in the  $22\,676\text{--}22\,125\text{ cm}^{-1}$  ( $441\text{--}452\text{ nm}$ ) region.

As shown by Fig. 7(a), the intensity of the bands at 294 K in the  $16\,400\text{--}16\,100\text{ cm}^{-1}$  ( $610\text{--}621\text{ nm}$ ) range depends strongly on the pressure; Fig. 7(b) shows another region of the spectrum where no pressure effect is observed. The relative difference between the cross-section obtained with  $\text{NO}_2$  partial pressures varying from 0.02 to 1.0 torr, reaches 40% at the peaks of the structures.

No simple quantitative expression can be found to describe this pressure dependence from the present experiments. Further measurements are required with various buffer gases and  $\text{NO}_2$  mixtures. More complete experiments are also necessary for the region extending from  $25\,000$  to  $16\,600\text{ cm}^{-1}$  ( $400\text{--}602\text{ nm}$ ) where measurements of stratospheric  $\text{NO}_2$  are performed, in order to assess the presence of a possible pressure dependence in this region.

#### 4. INFLUENCE OF THE CROSS-SECTION ON STRATOSPHERIC $\text{NO}_2$ MEASUREMENTS

The measurements of the  $\text{NO}_2$  concentration in the stratosphere are mostly based today on the use of spectroscopic techniques. The  $\text{NO}_2$  amount is usually obtained using intense absorption structures in the  $25\,000\text{--}20\,000\text{ cm}^{-1}$  ( $400\text{--}500\text{ nm}$ ) region, where temperature effects are not negligible. We have therefore investigated the influence of the temperature in using temperature dependent cross-section values for the determination of the  $\text{NO}_2$  content.

The IASB has developed a ground-based instrument for stratospheric studies. This instrument, already described in a previous paper<sup>21</sup>, records spectra of the sunlight scattered at zenith, from  $25\,000$  to  $17\,850\text{ cm}^{-1}$  ( $400\text{--}560\text{ nm}$ ), and operates at a resolution of 1.0 nm. The  $\text{NO}_2$  absorption

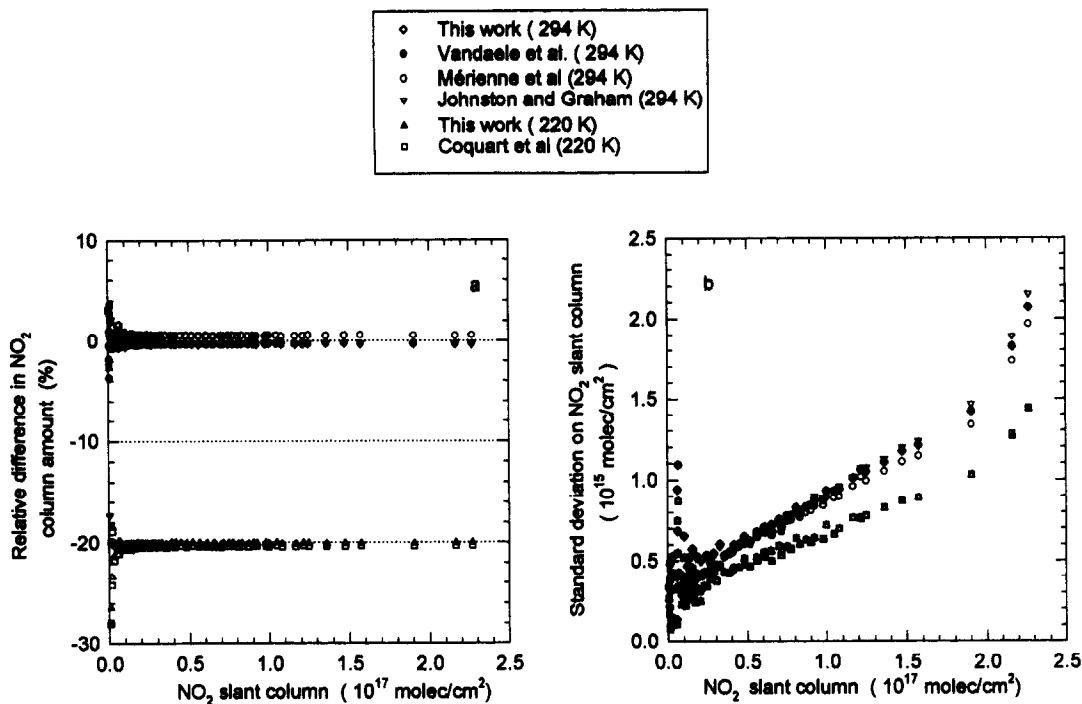


Fig. 8. Influence of the NO<sub>2</sub> cross-section temperature dependence on stratospheric measurements. Zenith sky spectra were analysed using the present cross-section at 294 K (◊) and 220 K (▲), those of Vandaele et al.<sup>5</sup> (●), Mérienne et al.<sup>6</sup> (○), Johnston and Graham<sup>18</sup> (▽) and Coquart et al.<sup>10</sup> (◻). (a) Difference in % in the NO<sub>2</sub> column abundances relative to those obtained using the cross-section of this work at 294 K. (b) Standard deviation on the NO<sub>2</sub> column abundances.

cross-section measured at 220 and 294 K, as well as data of the literature (Mérienne et al.<sup>6</sup> Coquart et al.<sup>10</sup> Johnston and Graham<sup>18</sup>) have been convolved with the instrumental function of the IASB instrument. For each of them, NO<sub>2</sub> column abundances have been calculated from spectra obtained at Harestua (Norway) on day number 218, 1995. Figure 8(a) shows the difference in the NO<sub>2</sub> column abundances relative to the abundances found with the present cross-section at 294 K. If all the cross-section values recorded at room temperature give similar results, it is important to note that the abundances calculated with the cross-sections at 220 K are consistently 20% smaller. Figure 8(b) presents the evolution of the standard deviation of the NO<sub>2</sub> measurements as a function of the NO<sub>2</sub> column content. It should be independent of the NO<sub>2</sub> slant amount, and would be a measure of the noise level of the spectra. Obviously it is not and the standard deviations are all situated on two non-horizontal straight lines, except for the points at the highest slant amounts which correspond to atmospheric spectra recorded at very high zenith angles and thus with very poor signal-to-noise ratios. The linear dependence of the standard deviation on the concentration shows a mismatch between the cross-section and the atmospheric spectra. The line with the greatest slope was determined with all the data calculated with cross-section values at 294 K and the other (with the smaller slope) with all the data at 220 K. The value of the slope being a measure of how well the absorption cross-section used compares with the signature found in the atmospheric spectra, it is clear that the cross-section values recorded at 220 K are better suited for NO<sub>2</sub> stratospheric measurements. This is consistent with the localization of the NO<sub>2</sub> bulk in the stratosphere around 30 km, at a temperature close to 230 K. It emphasizes the absolute necessity to use a cross-section measured at a temperature as close as possible to that prevailing in the region of the atmosphere where the observed constituent lies. As was mentioned above, this changes the measured NO<sub>2</sub> concentrations by 20%. The remaining non-zero slope obtained when using 220 K cross-section values can be explained in different ways: first, it may result from a pressure effect on the cross-section, as the cross-section has been measured using pure NO<sub>2</sub> at very low pressure; it may also indicate that one has to use a weighted sum of cross-section values at different temperatures to account for the vertical distribution of the NO<sub>2</sub>; and finally it may also partly come

from imperfections in the convolution process used to match the spectral resolution of the cross-section to the atmospheric spectra.

## 5. CONCLUSIONS

Using the advantages of a FT-spectrometer and a 5 m temperature controlled multiple reflection cell, the NO<sub>2</sub> absorption cross-section has been determined at 220 and 294 K at a resolution of 2 cm<sup>-1</sup> in the spectral region extending from 42 000 to 10 000 cm<sup>-1</sup> (238–1000 nm). Long absorption paths allowed to use low pressures (NO<sub>2</sub> partial pressures between 0.01 and 2 torr) in order to minimize the absorption due to the dimer N<sub>2</sub>O<sub>4</sub>.

The temperature effect has been analysed in view of the impact on the calculation of the stratospheric NO<sub>2</sub>. The calculation of the NO<sub>2</sub> column abundances with the cross-section at 220 K reduces by 20% the values obtained with the cross-section at 294 K, as well as the standard error (by 25%) on the determination of the abundance.

A significant pressure effect has been observed in the visible region of the spectrum at both temperatures. Differences up to 45% in the absorption cross-section values have been observed with NO<sub>2</sub> partial pressures of 0.02 and 1.0 torr in the 16 400–16 200 cm<sup>-1</sup> region (610–617 nm). The effect in the 25 000–20 000 cm<sup>-1</sup> region (400–500 nm), corresponding to most of the atmospheric NO<sub>2</sub> measurements, could not be firmly detected. Work is in progress to define this effect accurately by using different NO<sub>2</sub> mixtures with different buffer gases.

The NO<sub>2</sub> absorption cross-section at 220 and 294 K has been compared to data of the literature, and it has been shown that there were important differences as well in the amplitude as in the wavenumber scaling of the spectra.

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