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Absorption cross-sections of NO₂: simulation of temperature and pressure effects

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Abstract

The measurements of the NO₂ absorption cross sections by several authors have been considered in order to derive its temperature and pressure dependences in the 13 200–42 000 cm⁻¹ spectral range. The temperature dependence is assumed to be linear in the temperature range investigated (217.0–298.5 K), whereas the influence of the total pressure is expressed as a temperature-dependent broadening coefficient. From measurements performed with mixtures of NO₂ in air and in N₂, values of γ_{air}^0 (296 K) and $\gamma_{\text{N}_2}^0$ (296 K) were found to be, respectively, 0.081 ± 0.002 and 0.069 ± 0.003 cm⁻¹ atm⁻¹. The temperature coefficient n obtained in the present work is 0.8 ± 0.1 . The parameterization of the cross sections developed in this work can reproduce measured cross sections within 4%. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The important role of NO₂ in the atmosphere chemistry has motivated many laboratory studies, in order to characterize its complex spectrum. NO₂ is detected by spectroscopic means in the UV-visible and IR regions. The measurement of its concentration in the atmosphere relies on an accurate knowledge of its absorption cross sections. Several measurements have been performed in order to determine this spectroscopic quantity under various temperature and pressure conditions [1–12]. The temperature dependence of the NO₂ absorption cross sections is of major importance. The

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retrieval of the stratospheric NO₂ from ground-based zenith-sky measurements is based nowadays on the use of two or more absorption cross sections obtained under different temperature conditions [13,14]. Pressure also influences the absorption cross sections by broadening the structures. Recent measurements [1,7,8] have investigated this effect on the NO₂ signature. However, no systematic analysis of the pressure dependence has yet been carried out. The pressure effect is quite important for high-resolution spectra, but is completely masked if low resolution is used to record the spectrum.

In this study, selected spectra from the literature have been used to derive a parameterized dependence of the NO₂ cross sections with temperature and pressure. Spectra were selected on the basis of their resolution, spectral interval coverage, temperature and pressure conditions. Most of the recent literature measurements were used to investigate the temperature dependence at the medium resolution of 2 cm⁻¹, corresponding to a resolution of 0.03 nm at 25 000 cm⁻¹ or 400 nm. A second temperature parameterization was developed using the data of Vandaele et al. [1], obtained at a higher resolution (0.05 and 0.1 cm⁻¹). Finally, the air and N₂ pressure broadening coefficients and their temperature dependence have been deduced from all available measurements performed with mixtures of NO₂ with air or N₂.

2. Data description

We have only considered the available data sets, which were obtained at high resolution (<2 cm⁻¹), over a large wavelength range, and under various pressure and temperature conditions. Thus, six sets have been selected. Table 1 summarizes the main experimental conditions relative to these data sets.

The data of Vandaele et al. [1] were measured with a Fourier transform spectrometer Bruker IFS120M at a resolution of 0.1 cm⁻¹ over the 13 800–26 000 cm⁻¹ wavenumber range and of 0.05 cm⁻¹ from 10 800 to 15 100 cm⁻¹. Spectra were obtained under various pressure conditions using pure NO₂ and NO₂/air mixtures with different dilution factors. The partial pressures of NO₂ ranged from 0.9 to 3.2 Pa for the non-diluted samples and the total pressures of the mixtures from 9 to 1013 hPa. The cross sections at three temperatures (220, 240, and 294 K) were investigated.

The data of Vandaele et al. [2] have also been considered. These measurements were performed with the same instrument, but at a resolution of 2 cm⁻¹. The wavenumber range extends from 10 000 to 42 000 cm⁻¹, and two temperatures (220 and 294 K) were studied. Only pure NO₂ samples were investigated.

The data [3–6] of the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA) of the University of Reims (France) have also been selected. These data have been obtained with a Jobin-Yvon THR 1500 spectrometer equipped with a 2400 lines/mm grating. Data are available for the 200–500 nm (20 000–50 000 cm⁻¹) region at two temperatures (220 and 293 K) and between 400 and 500 nm (20 000–25 000 cm⁻¹) at 240 K. The resolution varied from 0.009 nm (0.8 cm⁻¹ at 30 000 cm⁻¹) to 0.05 nm (4.5 cm⁻¹ at 30 000 cm⁻¹) depending on the wavelength region and the temperature (see Table 1 for more details). Pure NO₂ and NO₂/N₂ mixtures were used. In the following, these data will be referenced to as GSMA's data.

Harder et al. [7] measured spectra of NO₂/air mixtures with the Fourier transform spectrometer of the National Solar Observatory, Tucson (Arizona). Spectra were obtained at high (0.15 cm⁻¹) and low (1.5 cm⁻¹) resolutions, at different temperatures (217, 235, 238, and 294 K) over the

Table 1
Experimental conditions of the measurements used in this work

	Wavenumber range	Resolution	Temperature (K)	Pressure	
				Pure NO ₂ (h Pa)	Mixtures (h Pa)
Vandaele et al. [1]	10 800–15 100 cm ⁻¹	0.05 cm ^{-1a}	220, 240, 294	0.4–2.8	400.0, 1013.32 (air)
	13 800–26 000 cm ⁻¹	0.1 cm ^{-1a}	220, 240, 294	0.009–0.32	11.7, 38.0, 133.32, 400.0, 1013.32 (air)
Vandaele et al. [2]	10 000–42 000 cm ⁻¹	2 cm ^{-1a}	220, 294	0.009–2.5	—
Mérianne et al. [6]	300–500 nm	$\lambda > 400$ nm: 0.009 nm ^b $\lambda < 400$ nm: 0.015 nm ^b	293	0.013–0.04	13.32–46.66 (N ₂)
Coquart et al. [3]	400–500 nm	0.01 nm ^b	220, 240	0.013–0.04	13.32–46.66 (N ₂)
Jenouvrier et al. [4]	200–300 nm	0.01 nm ^b	293	< 0.13	—
Mérianne et al. [5]	200–400 nm	0.05 nm ^b	220	0.0027–0.1	—
Harder et al. [7]	17 000–28 570 cm ⁻¹	0.15 cm ^{-1c}	217, 230, 238, 294	—	131.7, 790.3 (air)
Voigt et al. [8]	12 500–23 000 cm ⁻¹	0.5 cm ^{-1c}	223, 246, 260, 280, 293	—	100, 1000 (N ₂)
	23 000–40 000 cm ⁻¹	1.0 cm ^{-1c}	223, 246, 260, 280, 293	—	100, 1000 (N ₂)
Yoshino et al. [9]	360–470 nm	0.005 nm ^b	298.5	0.67–4	—

^aResolution = 0.9/MOPD, with MOPD = maximum optical path difference.

^bResolution = HWHM.

^cResolution = 0.5/MOPD.

17 000–28 600 cm⁻¹ spectral range. Total pressures of the order of 132 and 790 hPa were used. In this study, we have only used their high-resolution data.

The next set [8] to be considered has been compiled by the Institut für Umweltp Physik of the University of Bremen (Germany). NO₂ absorption cross sections were obtained using a Fourier transform spectrometer from 12 500 to 23 000 cm⁻¹ at a resolution of 0.5 cm⁻¹ and from 23 000 to 40 000 cm⁻¹ at a resolution of 1.0 cm⁻¹. Five temperatures were investigated (223, 246, 260, 280, and 294 K) with mixtures of NO₂ and N₂. Two series of spectra were obtained with total pressures of 100 or 1000 hPa.

Finally, the data of Yoshino et al. [9] have also been selected. They were obtained with a 6.65 m McPherson spectrometer and with NO₂ pressures ranging from 66.6 to 400 Pa. Measurements were

performed at 298.5 K and at a resolution of 0.005 nm (0.3 at 25 000 cm⁻¹) in the 360–470 nm (21 275–27 700 cm⁻¹) spectral range.

All these data have been extensively compared in Refs. [1,2,15], so that only a summary of these comparisons, pertinent to this study, will be given here. The comparisons were made by convolving all spectra to a lower resolution, in order to eliminate differences in high-resolution structures and to reduce the pressure effect on the cross sections. The conclusions were the following:

- The data of Refs. [1,2] agree to within 2.5% and 1.8% at, respectively, 294 and 220 K.
- The GSMA data [3–6] agree to within 1.9%, 1% and 0.2% with those of Ref. [1] at, respectively, 294, 240, and 220 K, and to within 1.5% and 2.5% with the data of Ref. [2] at 294 and 220 K.
- The data of Harder et al. [7] at 294 K are in good agreement (3%) with the data of Ref. [1] for wavenumbers higher than 20 000 cm⁻¹. Below this limit, both data sets diverge, data of Ref. [1] being 5% higher. Harder et al. [7] estimated a larger error on their measurements in this region mainly due to lamp drifts. At 240 K, the difference between the two data sets reaches 3.7%.
- The comparison between data of Ref. [1] and those obtained by Voigt et al. [8] shows a larger disagreement, different for each temperature set. Orphal [15] showed that data of Voigt et al. [8] at 223 K were 22% lower than the corresponding cross sections measured by Vandaele et al. [2]. The former attributed this difference to an important base line error. Moreover, from Ref. [8], it is inferred that the data at 223 K were obtained in a slightly different manner than the cross sections at the other temperatures. The latter were obtained from spectra recorded using a cell with NO₂/N₂ mixtures, while the data at 223 K were obtained in flow regime and were thereafter calibrated using the data at other temperatures. This could also explain the observed discrepancies.
- The data of Yoshino et al. [9] are 2% lower than those of Ref. [2]. Small wavelength shifts are observed. They are due to the concatenation of data from several regions (7.5 nm large) measured separately in [9].

Orphal [15] pointed out that the data of Refs. [1,2] show small but systematic wavelength differences compared to most of the literature data, but agree very well between each other with respect to wavelength calibration. This shift in wavelength was estimated to be 0.0012 nm in the 390–460 nm region (about 0.07 cm⁻¹ at 25 000 cm⁻¹). Two remarks have to be made: Firstly, the data of Ref. [1] used in Ref. [15] were not wavelength calibrated. They were calibrated later, using the A band of O₂ present in most of the spectra of Ref. [1]. Secondly, when all data were used in the present work to derive a temperature dependence, they were convolved to a resolution of 2 cm⁻¹ and interpolated on a grid with 0.5 cm⁻¹ spacing. After this treatment, such discrepancies in the wavenumber scale are not observed.

3. Temperature effect

A linear dependence of the NO₂ cross sections with temperature was assumed. The choice of this simple model has been dictated by its rapid and easy implementation. Moreover, a previous study of the temperature dependence of the NO₂ cross sections [15] showed that using more complicated models, such as a quadratic polynomial or an exponential function, did not give better results. The following expression was considered:

$$\sigma(\bar{\nu}, T) = \sigma_{273 \text{ K}}(\bar{\nu}) + \alpha(\bar{\nu})(T - 273), \quad (1)$$

in which $\sigma_{273\text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ represent, respectively, the NO_2 absorption cross sections as would be obtained at 0°C and the linear temperature coefficient. Values of $\sigma_{273\text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ have been deduced from the selected NO_2 cross sections, as a function of wavenumber.

Two cases have been investigated. First, only the most recent literature measurements have been taken into account to derive a temperature dependence at the medium resolution of 2 cm^{-1} . Then the data of Ref. [1] have been considered separately to derive temperature dependence parameters at a higher resolution.

3.1. Temperature effect at medium resolution

The resolution of 2 cm^{-1} was chosen for two main reasons: This value is higher than the resolution used by most UV-visible atmospheric instruments, and at this resolution, no pressure effect is detectable [1]. All the data mentioned above, obtained either with pure NO_2 samples or mixtures of NO_2 and a buffer gas have been taken into account. First of all, air wavelengths were converted, if necessary, into vacuum wavenumbers using the Edlén's formula [16]. When no indication of pressure or temperature of the instrument or the experimental room was given, the values of 15°C and 1 atm were used. The data were then convolved to the resolution of 2 cm^{-1} . As pointed out in [17], the convolution was not applied directly to the cross sections themselves, but to 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. The latter correction is needed when comparing spectra obtained with a grating spectrometer with those obtained with a Fourier transform spectrometer. All convolved data were finally interpolated on a wavenumber grid covering the $13\,200\text{--}42\,000\text{ cm}^{-1}$ spectral range, with a 0.5 cm^{-1} spacing. The lower spectral limit was chosen on the basis of the scarcity of high-quality measurements below this limit and because of the presence of the atmospheric A band of O_2 between $13\,040$ and $13\,180\text{ cm}^{-1}$ in some of the spectra.

Fifty-three literature measurements were taken into account for the determination of the temperature dependence. They cover the temperature range extending from 217 to 298.5 K. Fig. 1 shows the number of spectra taken into account as a function of the spectral region. From this figure, it can clearly be seen where measurements are mostly needed. The region extending from $15\,000$ to $25\,000\text{ cm}^{-1}$ has been extensively investigated by several authors. However, above $25\,000\text{ cm}^{-1}$ and below $15\,000\text{ cm}^{-1}$, measurements of high quality are scarce. In Table 2 are indicated the limits between which each measurement was taken into account. These limits were chosen considering the noise levels or the presence of large discrepancies with respect to the other measurements. In some cases, it was preferred to correct the data, in order to take them into account. These corrections are also indicated in Table 2. As already discussed, the spectra of Voigt et al. [8] obtained at 223 K showed large differences with the other data obtained at roughly the same temperature. They were therefore not retained.

Fig. 2 shows the values of $\sigma_{273\text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ derived for the whole spectral interval investigated in this work. Below $25\,000\text{ cm}^{-1}$, both $\sigma_{273\text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ show anti-correlated behaviors: when the temperature increases, the value of $\sigma_{273\text{ K}}(\bar{\nu})$ at the peaks decreases, while that in the valleys increases. An increase in the temperature increases the rotational temperature, which results in an increase of the number of lines in each band and consequently the blending of the absorption structures.

Table 2
Description of the literature data considered for the determination of the temperature dependence at medium resolution. The comparisons between the modeled and experimental cross sections in two separate spectral regions are also indicated

Ref.	T (K)	P (hPa)	Wavenumber limits (cm^{-1})	Correction	Comparison between the modeled and the experimental cross sections				
					16 500–36 000 cm^{-1}		13 200–15 500 cm^{-1}		
					Mean relative difference (%)	SD (%)	Mean relative difference (%)	SD (%)	
[9]	298.5	Pure	21 200	—	27 834	0.0	0.9	—	—
[1]	294	Pure	14 700	—	26 000	-0.2	1.0	0.0	2.4
[1]	294	12	16 000	—	26 000	0.0	1.6	—	—
[1]	294	38	15 000	—	22 200	0.3	0.8	11.5	5.5
[1]	294	133	14 700	—	25 500	0.6	1.8	0.4	5.3
[1]	294	400	14 700	—	23 500	-1.7	1.3	-7.6	4.2
[1]	294	1013	14 700	—	26 000	-1.9	2.0	-29.4	19.0
[1]	294	Pure	13 200	—	15 100	—	—	-1.2	2.4
[1]	294	400	13 160	—	15 100	—	—	-5.0	2.8
[1]	294	1013	13 160	—	15 100	—	—	-3.3	2.9
[1]	294	Pure	15 002	—	39 000	1.6	0.7	—	—
[3–6]	293	Pure	20 000	—	41 980	0.8	1.1	—	—
[7]	294	800	18 182	—	28 985	2.4	1.7	—	—
[8]	293	1000	13 200	-0.12×10^{-20}	23 000	—	—	4.6	3.0
[8]	293	1000	23 000	—	26 100	0.5	1.2	—	—
[8]	293	100	13 200	-0.12×10^{-20}	23 000	—	—	-1.1	3.8
[8]	293	100	23 000	—	26 100	0.8	1.9	—	—
[8]	280	1000	14 700	—	23 000	—	—	8.6	5.5
[8]	280	1000	23 000	—	31 500	-2.5	2.0	—	—
[8]	280	100	14 700	—	23 000	—	—	4.6	3.7
[8]	280	100	23 000	—	31 500	-2.7	1.4	—	—
[8]	260	1000	13 200	$+0.1 \times 10^{-20}$	23 000	—	—	10.5	8.3

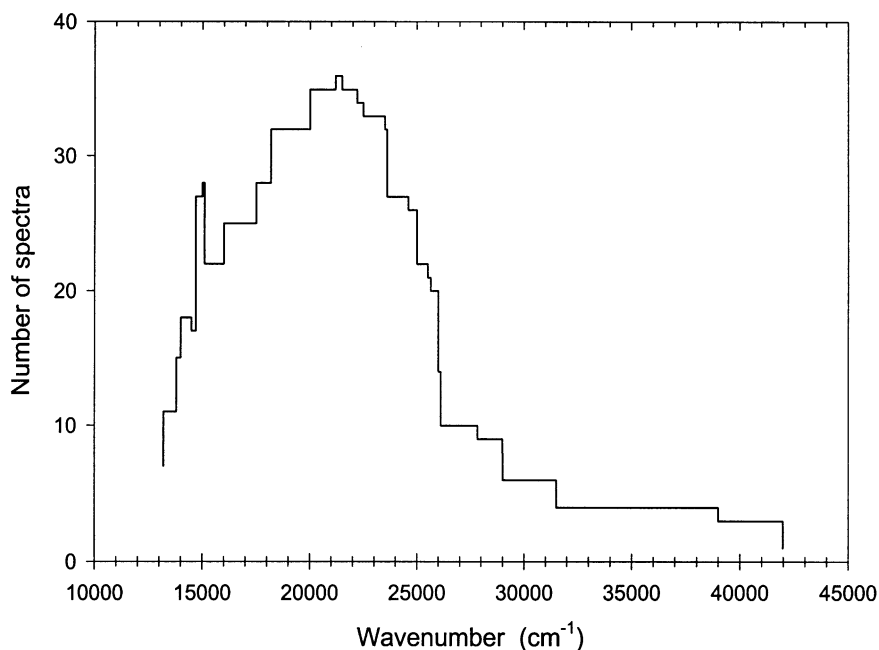


Fig. 1. Number of measurements at medium resolution (2 cm^{-1}) taken into account for the determination of the temperature dependence of the NO_2 absorption cross sections.

The evolution of the temperature coefficient in the $25\,000\text{--}33\,000 \text{ cm}^{-1}$ spectral region has been explained [10,18] as resulting from the displacement and broadening of the bell curve of the cross sections. The envelope of the absorption cross sections generated by vibrationally excited NO_2 molecules is larger than that of NO_2 in the ground state. It is moreover displaced toward lower wavenumbers. As the temperature increases, the relative intensities of the hot and cold bands are modified, and the bell shape is broadened and displaced. Liévin et al. [19] have calculated the absorption cross sections using the reflection method applied on ab initio data. They could derive the envelope of the photoabsorption cross sections of NO_2 by considering the two electronic transitions originating from the ground state \tilde{X}^2A_1 to the excited states \tilde{A}^2B_2 and \tilde{B}^2B_1 . They moreover took into account the fact that the transitions could originate from the $|0\,1\,0\rangle$ vibrational level of \tilde{X}^2A_1 . From the calculations at 220 and 300 K, we derived a temperature coefficient α ($\alpha = (\sigma_{220 \text{ K}} - \sigma_{300 \text{ K}})/(220 - 300)$). It is compared in Fig. 3 to its corresponding value obtained from cross sections calculated using the linear regression (Eq. (1)). These cross sections were smoothed to eliminate all the fine structures, which are not reproduced by theory. The theoretical curve has been shifted by 600 cm^{-1} , as proposed in [19] to take into account a systematic error introduced by the reflection method itself. The ab initio curve does explain some of the features of α , such as the two bumps and their relative positions. However, it does not reproduce the relative intensity observed for the two large structures. A residual N_2O_4 contribution cannot therefore be ruled out, as the structure observed at $30\,000 \text{ cm}^{-1}$ corresponds to the main feature of the N_2O_4 absorption cross sections. No significant temperature dependence is observed between $33\,000$ and $38\,000 \text{ cm}^{-1}$.

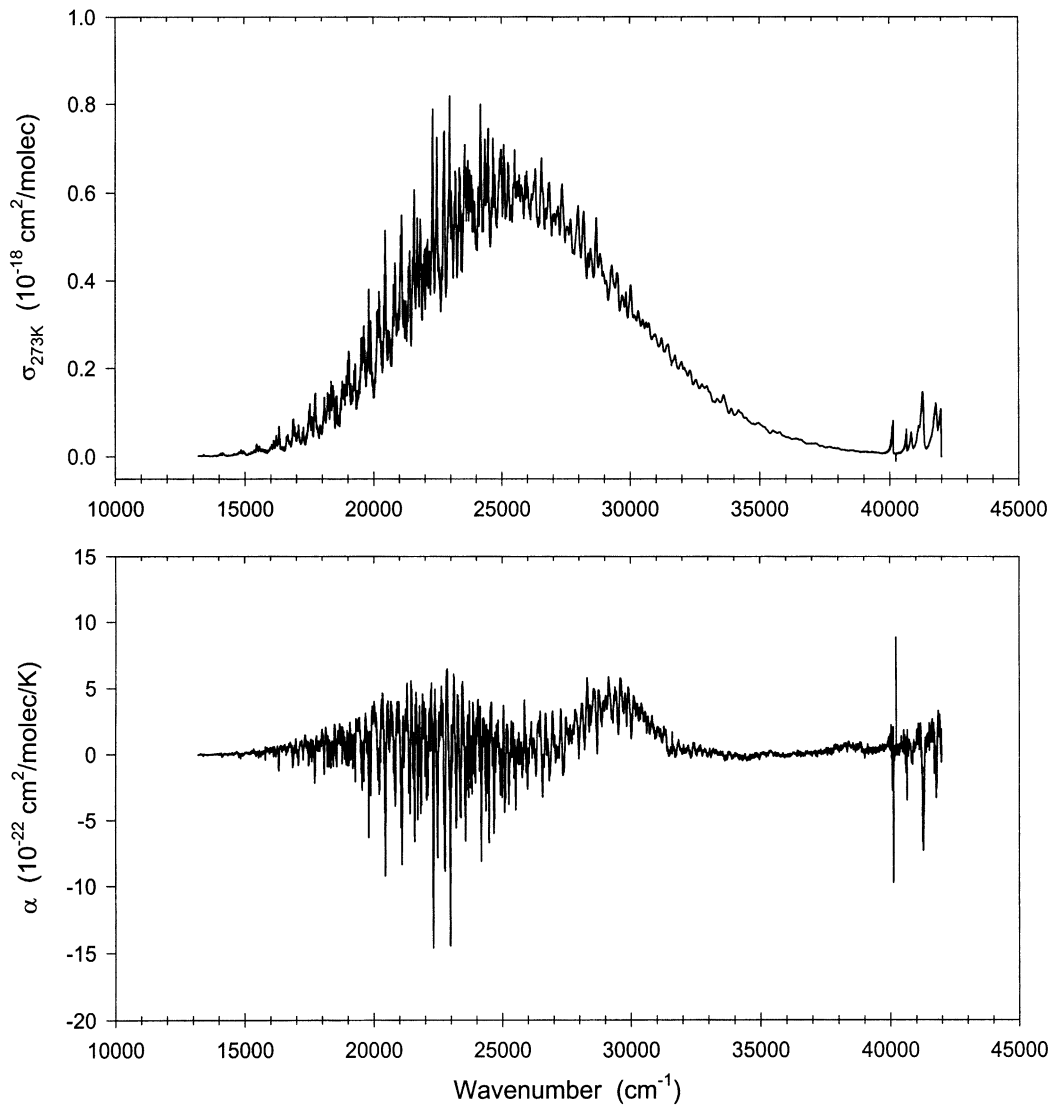


Fig. 2. Temperature dependence of the NO₂ absorption cross sections at the resolution of 2 cm⁻¹. $\sigma_{273 \text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ represent, respectively, the NO₂ absorption cross sections as would be obtained at 0°C and the linear temperature coefficient.

3.2. Temperature effect at high resolution

For some atmospheric applications, the medium resolution of 2 cm⁻¹ might not be adequate. The temperature dependence has therefore been determined using data of Ref. [1] which were obtained at a higher resolution. Two regions were defined:

1. 13 200–14 500 cm⁻¹, where data of Ref. [1] at 0.05 cm⁻¹ resolution were considered. Data are given at three distinct temperatures (220, 240, and 294 K). Only the spectra obtained with pure NO₂ were considered.

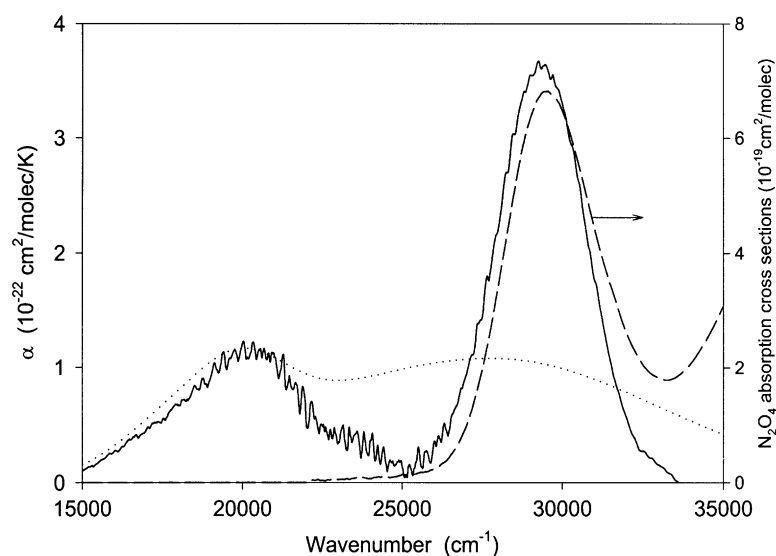


Fig. 3. Temperature coefficient calculated from the absorption cross sections at 220 and 300 K (—) using cross sections calculated with the linear regression model developed in this work, (---) using cross sections obtained by the reflection method applied on ab initio data. The absorption cross sections of N_2O_4 [2] are also shown.

- 14 000–25 000 cm^{-1} , where data of Ref. [1] at the resolution of 0.1 cm^{-1} were used. Again only the cross sections obtained at three temperatures and with pure NO_2 were retained.

In each region, a linear relation between the NO_2 cross sections and the temperature was assumed. Using Eq. (1), values of $\sigma_{273\text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ have been determined for the two regions. These parameters show a similar trend as those at lower resolution (see Fig. 4).

4. Pressure effect

Harder et al. [7] and Vandaele et al. [2] showed that pressure affects the NO_2 absorption cross sections. However, because of their experimental conditions (no pressure range for Ref. [7] and low resolution for Ref. [2]) they could only suspect this effect, but not investigate it in detail. Voigt et al. [8] and Vandaele et al. [1] performed measurements under more various total pressure conditions. Voigt et al. [8] used mixtures of NO_2 and N_2 with total pressures of 100 and 1000 h Pa. With only two total pressures, no systematic study of the pressure effect could be carried out. However, by convolving their low-pressure spectra with a Lorentzian function to reproduce their higher pressure data, these authors deduced a pressure broadening coefficient for the UV-vis part of the NO_2 spectrum. Their absolute value of the N_2 pressure broadening coefficient at 293 K being larger than those found in the mid- and near-IR, they attributed this difference to their low resolution, which was not high enough to fully resolve the NO_2 structures. Using all the spectra obtained with mixtures of NO_2 in air (Refs. [1,7]) and in N_2 (Ref. [8]), new values of the air and N_2 broadening coefficients and their temperature dependence were determined.

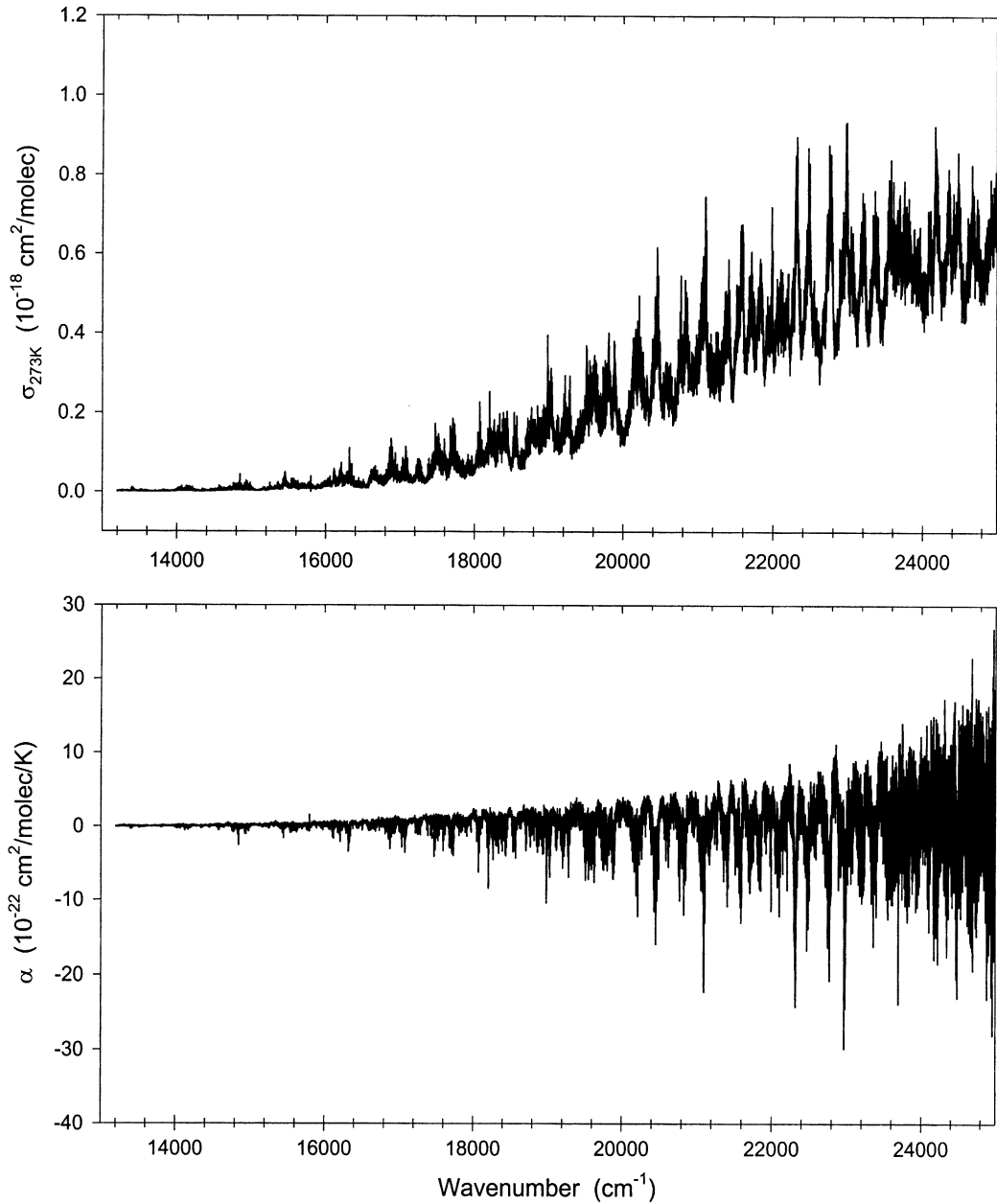


Fig. 4. Temperature dependence of the NO₂ absorption cross sections at high resolution. $\sigma_{273\text{ K}}(\bar{\nu})$ and $\alpha(\bar{\nu})$ represent, respectively, the NO₂ absorption cross sections at 0 °C and the linear temperature coefficient.

The broadened profile of a spectral line is a Lorentzian profile, whose mathematical representation is

$$G(\bar{\nu} - \bar{\nu}_0) = \frac{2\gamma_L}{2\pi} \frac{1}{(\bar{\nu} - \bar{\nu}_0)^2 + (2\gamma_L/2)^2}. \quad (2)$$

The pressure broadening parameter γ_L (half-width at half-maximum) can be expressed as a function of temperature (T) and total pressure (P) using

$$\gamma_L = \gamma_{\text{buffergas}}^0(T_0) \left(\frac{T_0}{T} \right)^n P, \quad (3)$$

where γ_L is expressed in cm^{-1} , $\gamma_{\text{buffergas}}^0(T_0)$ in $\text{cm}^{-1} \text{atm}^{-1}$, and P in atm; T_0 has been chosen to be 296 K. By convolving the spectra obtained at the highest resolution with pure NO_2 , with a Lorentzian function to fit spectra of mixtures of NO_2 in air or N_2 , values of $\gamma_{\text{air}}^0(T_0)$, $\gamma_{\text{N}_2}^0(T_0)$, and n are then deduced. The treatment of the spectra of Vandaele et al. [1] on the one hand and of Harder et al. [7] and Voigt et al. [8], on the other is slightly different, because of the different resolutions used in these studies. We will first describe the analysis performed on the spectra of Vandaele et al. [1] and then explain how the spectra of Harder et al. [7] and Voigt et al. [8] can be used to validate the results.

4.1. Spectra of Vandaele et al. [1]

At each temperature, the spectrum obtained with pure NO_2 was selected as a reference. This spectrum was then convolved with a Lorentzian function whose width γ_L could be varied using a Levenberg–Marquardt procedure to best reproduce the chosen high-pressure spectrum. Two spectral regions were selected: 18 200–22 800 cm^{-1} in the visible region and 13 950–14 250 cm^{-1} in the near-IR region. The smaller spectral region used in the case of the NIR spectra was chosen in order to select the $\tilde{A}^2B_2 - \tilde{X}^2A_1$ ($\Delta v_2 = 6$) absorption band [20]. The results are summarized in Table 3, where γ_L values are given in regard to their corresponding temperature and total pressure. Values deduced from the visible ($\gamma_{L,\text{VIS}}$) and near-IR ($\gamma_{L,\text{NIR}}$) parts of the spectrum are indicated separately. The two parameters $\gamma_{\text{air}}^0(T_0)$ and n have been deduced from the data of Table 3. The usual way of determining these parameters is to apply a linear regression between the quantities $\ln(\gamma_L/P)$ and $\ln(T_0/T)$. However, using this technique, the parameters were determined with large uncertainties. We preferred the use of a non-linear least-squares method to directly deduce $\gamma_{\text{air}}^0(T_0)$ and n from the γ_L , P , and T data. Our choice was also based on the χ^2 values derived from each of the methods. With the linear regression method applied on both $\gamma_{L,\text{VIS}}$ and $\gamma_{L,\text{NIR}}$, a value of 7.3×10^{-3} is found, which has to be compared with the value of 5.0×10^{-4} obtained using the non-linear procedure. In Table 4, values of these two parameters obtained using values of $\gamma_{L,\text{VIS}}$ and $\gamma_{L,\text{NIR}}$ separately and from both series combined are given. When using both series of γ_L values, the following expression is obtained:

$$\gamma_L(\text{cm}^{-1}) = 0.081(2)(\text{cm}^{-1} \text{atm}^{-1}) \left(\frac{296}{T} \right)^{0.8(1)} P(\text{atm}), \quad (4)$$

where the numbers in brackets represent 1σ uncertainties.

4.2. Spectra of Harder et al. [7] and Voigt et al. [8]

The difficulty in using these spectra is twofold: firstly, the resolution at which they were obtained (respectively, 0.15 and 0.5 cm^{-1}) is higher than that of Vandaele et al. [1], which are used as references and this could partly mask the pressure effect. Secondly, these spectra were recorded

Table 3
Lorentzian half-widths deduced from the absorption cross sections of diluted NO₂

T (K)	P (h Pa)	$\gamma_{L,VIS}$ (cm ⁻¹)	$\gamma_{L,NIR}$ (cm ⁻¹)	$\gamma_{L,Harder}$ (cm ⁻¹)	$\gamma_{L,Voigt}$ (cm ⁻¹)
294	10	0.00417(4)	—	—	—
	38	0.00672(3)	—	—	—
	100	—	—	—	0.0133(3)
	106	0.01264(3)	—	—	—
	400	0.02888(7)	0.03160(7)	—	—
	800	—	—	0.0626(1)	—
	1000	—	—	—	0.0870(3)
	1013	0.0928(2)	0.0791(2)	—	—
280	100	—	—	—	0.0034(3)
	1000	—	—	—	0.0710(2)
260	100	—	—	—	0.0054(2)
	1000	—	—	—	0.0770(2)
246	100	—	—	—	—
	1000	—	—	—	0.0686(2)
240	13	0.00360(4)	—	—	—
	38	0.00649(2)	—	—	—
	133	0.01518(3)	—	—	—
	400	0.0438(1)	0.0353(1)	—	—
	1013	0.1047(2)	0.0881(3)	—	—
238.6	790	—	—	0.08093(2)	—
230	790	—	—	0.0759(1)	—
223	100	—	—	—	0.0088(2)
	1000	—	—	—	0.0870(3)
220	10	0.00273(5)	—	—	—
	38	0.00687(3)	—	—	—
	133	0.01565(3)	—	—	—
	400	0.04389(9)	0.0381(2)	—	—
	1013	0.1106(3)	0.0983(4)	—	—
217	133	—	—	0.01537(8)	—

under temperature conditions different from those of Vandaele et al. [1], which can therefore not be used in a direct way as references.

The following procedure was then carried out: considering the NO₂ absorption cross sections obtained at the temperature T , total pressure P , and resolution r ($\sigma_{T,P,r}(\bar{\nu})$), a high-resolution reference cross section ($\sigma_{ref,T}$) is calculated at temperature T using the linear temperature dependence (Eq. (1)). This reference cross section is then convolved with a Lorentzian function whose width

Table 4

Values of $\gamma_{\text{air}}^0(T_0)$, $\gamma_{\text{N}_2}^0(T_0)$, and n obtained in this work and in the literature

		γ_{air}^0 (296 K) ($\text{cm}^{-1} \text{atm}^{-1}$)	$\gamma_{\text{N}_2}^0$ (296 K) ($\text{cm}^{-1} \text{atm}^{-1}$)	n
This work	Using all $\gamma_{\text{L,VIS}}$	0.085(2)		0.8(1)
	Using all $\gamma_{\text{L,NIR}}$	0.078(2)		0.7(1)
	Using all $\gamma_{\text{L,VIS}}$ and $\gamma_{\text{L,NIR}}$	0.081(2)		0.8(1)
	Using all $\gamma_{\text{L,Harder}}$	0.082(3)		0.8 ^a
	Using all data in air ($\gamma_{\text{L,VIS}}, \gamma_{\text{L,NIR}}, \gamma_{\text{L,Harder}}$)	0.8(1)		0.8(1)
	Using all $\gamma_{\text{L,Voigt}}$		0.069(3)	0.8 ^a
Dana et al. [22]		0.0704	0.0723	—
Gianfrani et al. [23]		0.0671	0.0705	—
HITRAN database [24]		0.067		0.5
May and Webster [25]		0.071(4)	—	0.99(19)
Voigt et al. [8]		—	0.134(10) ^b	1.02(4)
Malathy Devi et al. [26]		—	0.0659 ^c	0.968(31)
Malathy Devi et al. [27]			0.066(2)	0.99(3)

^aThe value of n is imposed.^b $T_0 = 293$ K.^c $T_0 = 300$ K.Figures in brackets represent the 1σ standard error.

can be varied ($\tilde{\sigma}_{\text{ref},T,\gamma_{\text{L}}}$) and a synthetic spectrum is constructed using the Beer–Lambert law

$$I(\bar{\nu}) = I_0(\bar{\nu}) \exp(-n d \tilde{\sigma}_{\text{ref},T,\gamma_{\text{L}}}(\bar{\nu})). \quad (5)$$

This spectrum is then convolved with a Gaussian function whose width is chosen to correspond to the resolution r of the high-pressure cross sections. The latter convolution has to be applied to a spectrum and not directly to the cross sections themselves, as discussed in Ref. [21]. The convolved cross sections $\tilde{\sigma}_{\text{ref},T,\gamma_{\text{L}}}$ are finally determined by inverting Eq. (5). The air broadening coefficient γ_{L} is varied in a non-linear least-squares manner so as to find the best fit between the convolved cross sections $\tilde{\sigma}_{\text{ref},T,\gamma_{\text{L}}}(\bar{\nu})$ and the measured one $\sigma_{T,P,r}(\bar{\nu})$. The fit has been limited to the 18 200–22 800 cm^{-1} region. Values obtained by this method using the data of Harder et al. [7] ($\gamma_{\text{L,Harder}}$) and of Voigt et al. [8] ($\gamma_{\text{L,Voigt}}$) are given in Table 3.

Values of $\gamma_{\text{air}}^0(T_0)$ and $\gamma_{\text{N}_2}^0(T_0)$ were obtained using, respectively, the γ_{L} values found from Refs. [7,8] data. In both cases, two fits were performed: with and without imposing the value of n . Fitted values of this parameter were, respectively, 0.4(5) and 1.0(5), the figure inside brackets representing 1σ uncertainty on the last digit given. These are quite large and can be explained by the fact that for Ref. [7] only 4 γ_{L} values are available and in the case of Ref. [8], spectra have been recorded only at 2 total pressures. If the value of n is fixed to 0.8, which is the value obtained using Ref. [1] data, $\gamma_{\text{air}}^0(T_0)$ and $\gamma_{\text{N}_2}^0(T_0)$ are, respectively, found to be 0.082(3) and 0.069(3) $\text{cm}^{-1} \text{atm}^{-1}$.

Taking into account all the values of γ_{L} obtained from spectra recorded with air as buffer gas ($\gamma_{\text{L,VIS}}$, $\gamma_{\text{L,NIR}}$, and $\gamma_{\text{L,Harder}}$), $\gamma_{\text{air}}^0(T_0)$ is found to be 0.081(1) $\text{cm}^{-1} \text{atm}^{-1}$ with $n = 0.8(1)$. The same value of $\gamma_{\text{air}}^0(T_0)$ is found whether the value of n is imposed or not.

4.3. Comparison with literature values

Few literature values are available concerning the air-broadening coefficient. Dana et al. [22] report values of $\gamma_{\text{O}_2}^0$ and $\gamma_{\text{N}_2}^0$ for a series of lines around 3.4 μm . A mean value for γ_{air}^0 of $0.0704 \text{ cm}^{-1} \text{ atm}^{-1}$ was estimated from these results considering only the lines for which both $\gamma_{\text{O}_2}^0$ and $\gamma_{\text{N}_2}^0$ are given. Individual values of γ_{air}^0 and $\gamma_{\text{N}_2}^0$ varied, respectively, from 0.056 to $0.085 \text{ cm}^{-1} \text{ atm}^{-1}$ and from 0.057 to $0.087 \text{ cm}^{-1} \text{ atm}^{-1}$. The mean values of γ_{air}^0 and $\gamma_{\text{N}_2}^0$ are given in Table 4 with some other literature values. Gianfrani et al. [23] investigated the pressure broadening of some NO_2 lines in the near infrared. They found values of γ_{air}^0 ranging from 0.0583 to $0.0785 \text{ cm}^{-1} \text{ atm}^{-1}$ and values of $\gamma_{\text{N}_2}^0$ ranging from 0.0608 to $0.0823 \text{ cm}^{-1} \text{ atm}^{-1}$. The respective mean values (0.0671 and $0.0705 \text{ cm}^{-1} \text{ atm}^{-1}$) are indicated in Table 4. The HITRAN database [24] recommends the use of $\gamma_{\text{air}}^0 = 0.067 \text{ cm}^{-1} \text{ atm}^{-1}$ in combination with $n = 0.5$. May and Webster [25] obtained values of γ_{air}^0 and n from the analysis of spectra measured at two different temperatures (214 and 293 K). From mixtures of NO_2 in N_2 , Malathy Devi et al. [26,27] determined the temperature dependence of the Lorentz half-width for 10 lines of NO_2 around 1580 cm^{-1} . They found similar values for $\gamma_{\text{N}_2}^0$ in both their studies: $0.066(2) \text{ cm}^{-1} \text{ atm}^{-1}$ at 296 K [27] and $0.0659 \text{ cm}^{-1} \text{ atm}^{-1}$ at 300 K [26], which corresponds to $0.0668 \text{ cm}^{-1} \text{ atm}^{-1}$ at 296 K using their mean value of n (0.968). From the data in [27], we deduced a value of 0.99(3) for n . Voigt et al. [8] deduced values of $\gamma_{\text{N}_2}^0$ at 293 K and n from the comparison of low- and high-pressure spectra. Their values are larger than those found in this work and in most of the literature. Strangely, their value of $\gamma_{\text{N}_2}^0$ corresponds to twice the value found in this work and others. This could be due to a problem in the definition of the half-width.

Our value for $\gamma_{\text{N}_2}^0$ (296 K) ($0.069(3) \text{ cm}^{-1} \text{ atm}^{-1}$) compares very well with the data of the literature. The value γ_{air}^0 (296 K) deduced in this work is higher than most of the literature data. However, such high values of this parameter were found for individual lines by several authors. It must be noted that the value deduced from the NIR part of the NO_2 cross sections is lower than the value found in the visible region. We have further investigated this phenomenon by determining the broadening coefficient on successive 500 cm^{-1} wide windows extending from the NIR to the visible region. We have only used the diluted spectra of Ref. [1]. For each of these spectral intervals, values of γ_{air}^0 (296 K) and n were calculated. The value of n was found to be relatively constant (0.85) in the $15\,000\text{--}21\,500 \text{ cm}^{-1}$ interval (see Fig. 5) and decreases outside these limits. The values of γ_{air}^0 (296 K), obtained when imposing or not the value of n , are plotted in Fig. 5b. They slowly increase from the NIR to the visible.

5. Simulation of spectra

The validity of the temperature dependence formula at the resolution of 2 cm^{-1} was tested by comparing the values resulting from the measurements with the calculated cross sections. The mean values and the standard deviations of the relative differences between the modeled and experimental cross sections are reported in Table 2. Values are given in %. In the $13\,200\text{--}15\,500 \text{ cm}^{-1}$ interval, cross sections values are small (of the order of $1.0 \times 10^{-21} \text{ cm}^2/\text{mol}$) and small relative difference result in large percentage deviations. For the $16\,500\text{--}36\,000 \text{ cm}^{-1}$ region, the mean difference is smaller than 3.6%.

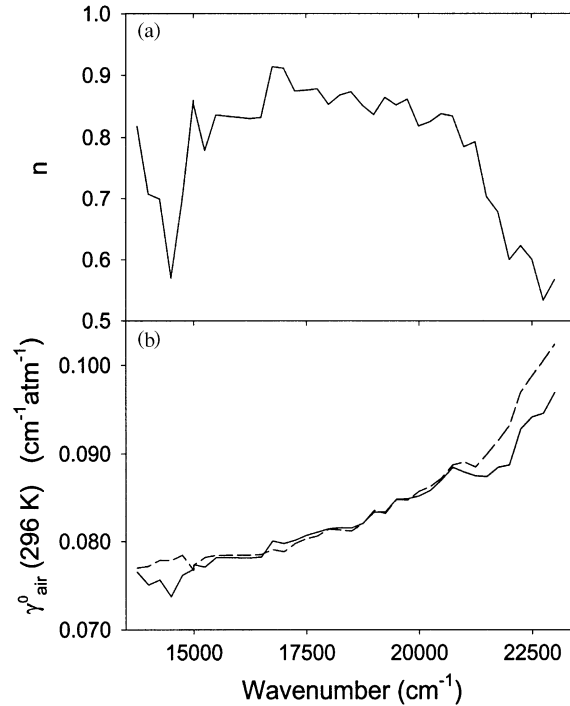


Fig. 5. Temperature dependence coefficient n (a) and air broadening coefficient γ_{air}^0 (b) as a function of the wavenumber. In (b), the solid line represents the values of γ_{air}^0 obtained when imposing the value of n to 0.8, while the dashed line represents values obtained when fitting both n and γ_{air}^0 .

By combining the temperature dependence (Eq. (1)) and the total pressure broadening coefficients ($\gamma_{\text{air}}^0(T_0)$ or $\gamma_{\text{N}_2}^0(T_0)$ and n), the NO_2 absorption cross sections can be calculated for any temperature between 220 and 294 K and any pressure condition. Fig. 6 shows for example the comparison between the observed cross sections obtained at 220 K and $P = 400$ hPa by Vandaele et al. [1] and the recalculated cross sections using the parameterization developed in this work. In Section 4.1 are plotted the cross sections values for a small spectral interval and Section 4.2 shows the relative difference between the two spectra. The mean value of this difference is -0.2% ($\pm 3\%$) for the $17\,000\text{--}25\,000\text{ cm}^{-1}$ spectral range. As can be seen in Fig. 6(b), the structures appearing in the difference spectrum may be attributed to noise as no absorption structure remains. The systematic comparison of the diluted spectra of Vandaele et al. [1] with their parameterized correspondents in the $17\,000\text{--}25\,000\text{ cm}^{-1}$ spectral interval, indicates that at 294 K, the mean difference reaches 1.5% at the total pressure of 1013 hPa, with a residual noise amplitude of 3% (1σ SD). At 240 K, the mean differences lie between 1.3% and 3.8% ($\pm 4\%$, 1σ SD) and at 220 K between 0.3% and 2.5% ($\pm 3\%$, 1σ SD). It should be pointed out that the values of the residual noise (defined as the 1σ SD of the difference spectrum) and of the mean differences are of the order of the uncertainty of the NO_2 absorption cross sections mentioned in the literature.

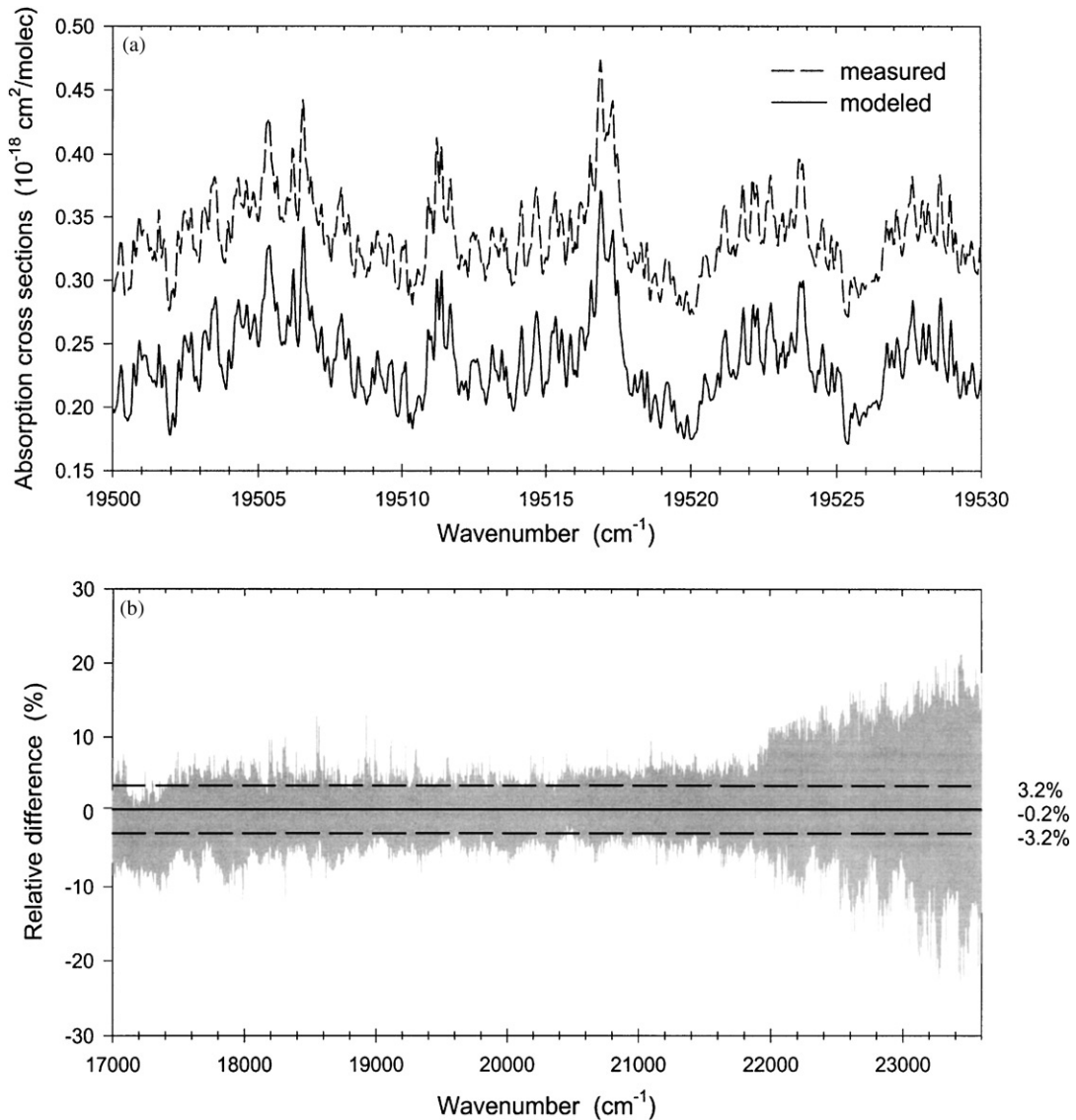


Fig. 6. (a) Comparison of a measured and modeled NO₂ absorption cross sections ($T = 220$ K, $P = 400$ hPa). Values of the model have been arbitrary displaced by 1.0×10^{-19} cm²/mol for clarity. (b) Relative difference between the measured and model cross sections. The mean difference and the standard deviation (1σ) are also indicated.

As already discussed in Orphal [15], one clear advantage of using the parameterization of the NO₂ cross sections is the limitation of the noise level in the simulated spectrum. This can be explained by the fact that the temperature dependence parameters have been deduced from several spectra at different temperatures, improving the signal to noise ratio.

6. Conclusions

The temperature and pressure dependences of the NO₂ absorption cross sections have been investigated using measurements performed by many authors. The modeling of the temperature dependence makes use of a linear relation between the cross sections and the temperature. Although no physical interpretation can be given for such a relation, it has been chosen because of its simplicity and rapidity of implementation. Moreover, a previous study [15] showed that no better results were obtained if using more complicated models, such as a quadratic polynomial or an exponential function.

Using all recent high-resolution measurements of the NO₂ cross sections convolved to a resolution of 2 cm⁻¹, temperature parameters were determined. More than 50 individual spectra obtained at temperatures ranging from 217.0 to 298.5 K were used to characterize the linear dependence. The temperature dependence at higher resolution (0.05 and 0.1 cm⁻¹) has been deduced from spectra obtained with pure NO₂ samples by Vandaele et al. [1].

Using cross sections of NO₂ diluted in a buffer gas (air or N₂), the pressure broadening coefficients and their temperature dependence have been determined. Values of γ_{air}^0 ($T_0=296$ K), $\gamma_{\text{N}_2}^0$ ($T_0=296$ K), and n have been found to be, respectively, 0.081(1), 0.069(3) cm⁻¹ atm⁻¹ and 0.8(1) by combining data of Harder et al. [7], Voigt et al. [8], and Vandaele et al. [1].

According to the present model, the combination of the temperature and pressure dependences allows to reproduce the observed cross sections within 4%, which is of the order of the uncertainty given in most of the literature data.

All the data derived in this work are available at the Web site of the Belgian Institute for Space Aeronomy (<http://www.oma.be/BIRA-IASB/Scientific/Data/CrossSections.html>) or upon request to the authors.

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