

HIGH RESOLUTION FOURIER TRANSFORM MEASUREMENTS OF THE NO₂ VISIBLE ABSORPTION CROSS-SECTION: TEMPERATURE AND PRESSURE INFLUENCES ON ITS ATMOSPHERIC DETECTION

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ABSTRACT

New high-resolution measurements of the NO₂ absorption cross-section have been performed in the near-IR and visible spectral region (10000-25000 cm⁻¹) with a Fourier transform spectrometer coupled to a multiple reflection cell. Spectra were recorded under various pressure conditions (pure NO₂ and NO₂/air mixtures), and at three temperatures (220, 240, and 294 K). The effect of the temperature and pressure dependence on the NO₂ atmospheric determination has been investigated.

1. INTRODUCTION

NO₂ plays an important role in the atmosphere's chemistry, both in the troposphere and in the stratosphere. It is mainly produced from the oxidation of NO in the troposphere, where it acts as the main source of tropospheric ozone, and is a precursor to species, such as nitric acid. In the stratosphere NO₂ is a key species in the control of the ozone concentration and in the coupling of the NO_x and ClO_x families.

Stratospheric and tropospheric NO₂ amounts are routinely measured by the DOAS method (Plane, 1994; Platt and Perner, 1983; Solomon et al., 1987; Vandaele and Carleer, 1999), which makes use of the absorption cross-section of the targeted molecule. Cross-sections need to be recorded under temperature and pressure conditions similar to the one's prevailing in the atmosphere. This work presents new high-resolution measurements of the NO₂ absorption cross-section at three temperatures (220, 240, and 294 K), and under various pressure conditions (pure NO₂, mixtures of NO₂ and air).

2. EXPERIMENTAL DETAILS

The absorption cross-section of NO₂ has been

investigated at high resolution in the visible and near IR region. It has been recorded using a Fourier Transform Spectrometer BRUKER 120M coupled to a multiple reflection cell, which can be cooled down to 220 K. Table 1 summarizes the experimental conditions.

Table 1. Experimental conditions

Region	Spectral Interval (cm ⁻¹)	Path Length (m)	Resolution (cm ⁻¹)
Near IR	10000 - 16000	60.7	0.05
Vis	14000 - 25000	60.7	0.1

Spectra were recorded in a series of successive blocks. This allowed us to verify the reproducibility of the measurements and to correct the absorption for phenomena such as the progressive adsorption of NO₂ on the cell walls. Blank spectra were recorded before and after each NO₂ spectrum.

Measurements have been performed at three distinct temperatures (220, 240, and 294 K) and under different pressure conditions. Pure NO₂ and mixtures of NO₂ and air were used. Table 2 gives a summary of the pressure ranges studied in this work.

3. RESULTS

The absorption cross-section $\sigma(\lambda)$ is derived from the recorded spectra using the Beer-Lambert law:

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

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

Table 2. Pressure conditions

	P_t (torr)		
	T = 220 K	T = 240 K	T = 294 K
Pure NO ₂	0.007 – 1.7	0.006 – 2.0	0.007 – 0.7
965 ppm dilution	7.5 – 760	9.6 – 760	7.6 – 760
92 ppm dilution	79 – 760	79 – 760	235.5 – 760
9.6 ppm dilution	300 – 760	300 – 760	300 – 760

The $2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$ equilibrium implies that N_2O_4 is always present in the cell. Absorption of N_2O_4 occurs at wavenumbers higher than 25000 cm^{-1} , but not in the spectral region investigated here. The presence of the dimer must, however, be considered when determining the NO_2 partial pressure.

The partial pressures of NO_2 and N_2O_4 are related to the equilibrium constant by:

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

and to the total pressure P_t by:

$$P_t = P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4} \quad \text{for pure NO}_2$$

$$\chi P_t = P_{\text{NO}_2} + 2P_{\text{N}_2\text{O}_4} \quad \text{for mixtures } (\chi = \text{dilution factor})$$

Measured pressures were corrected for the thermal transpiration of the capacitance manometer using the formalism described by Poulter et al. (1983).

The high-resolution absorption cross-section obtained with pure NO_2 at 294 K is presented in Figure 1.

4. TEMPERATURE DEPENDENCE

Using the spectra obtained with pure NO_2 at the three temperatures, and assuming the following linear dependence

$$\sigma_{\text{NO}_2}(T) = \sigma_0 + aT$$

where σ_0 represents the absorption cross-section that would be measured at 0 K, the influence of the temperature has been determined. Figure 2 shows the evolution of the σ_0 and α parameters on a small wavenumber interval. The anti-correlation between the two parameters, already mentioned by Davidson et al. (1988), is clearly seen in this Figure.

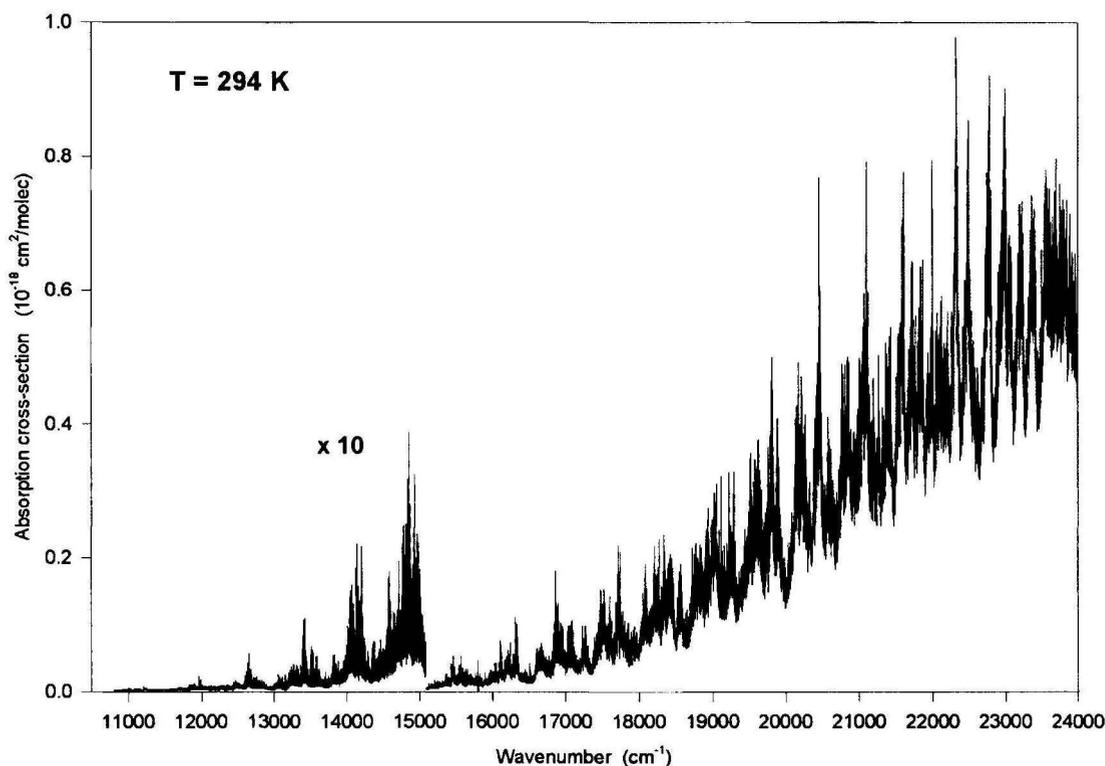


Figure 1: NO_2 absorption cross-section at 294 K.

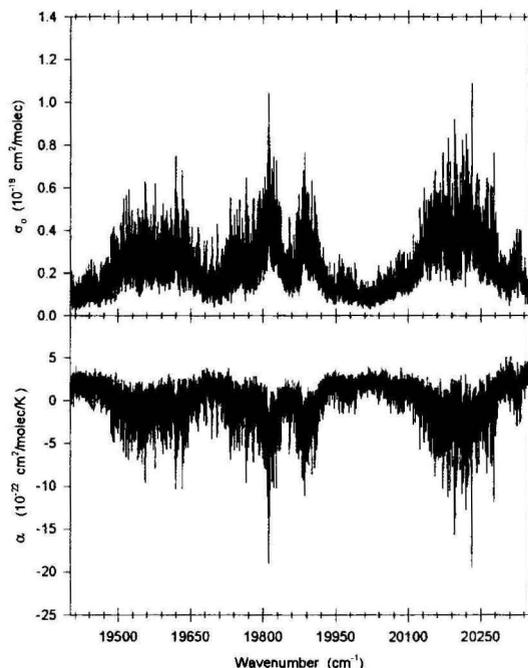


Figure 2: Parameters α and σ_0 for a linear temperature dependence.

A comparison between measured and recalculated cross-sections is presented in Figure 3, which shows the relative difference (in %) for the three temperatures. Differences are lower than 3% at 294K, but reach 10% at the lower temperatures.

5. PRESSURE EFFECT

The effect of the pressure on the NO_2 absorption cross-section has been investigated by analyzing the spectra recorded under the different pressure conditions described in Table 2. In Figure 4 is reproduced a small section of the spectra obtained at 294K and at different total pressures.

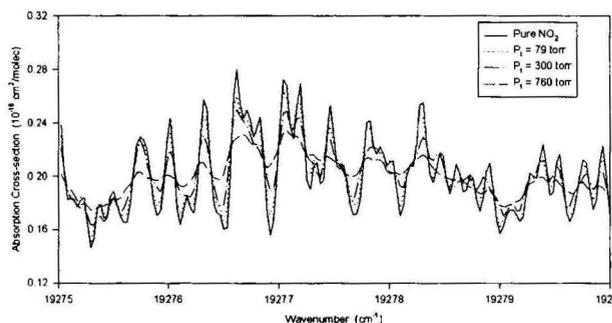


Figure 4: Pressure effect on the NO_2 absorption cross-section at 294 K

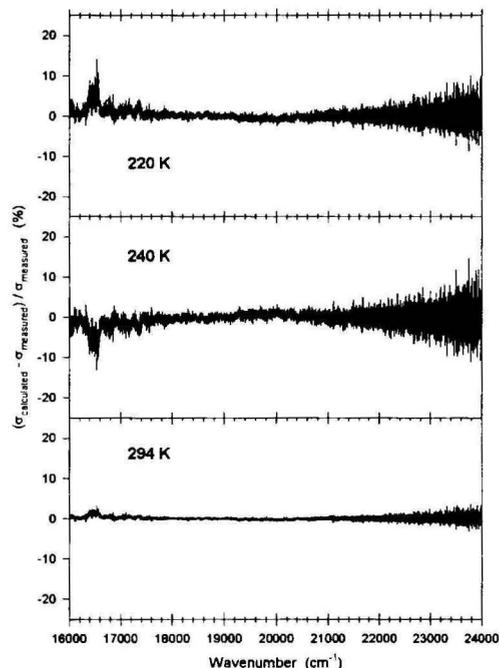


Figure 3: Comparison between the measured and simulated cross-sections assuming a linear temperature dependence.

A very simple model has been developed in order to express the absorption cross-sections of diluted NO_2 in terms of the cross-section obtained with pure NO_2 . This latter spectrum has been chosen as a reference and was then convolved by a gaussian function to reproduce the spectra measured under the other pressure conditions. The width of the gaussian was held constant on the whole spectral interval and was adjusted using a non linear least-squares fit. At room temperature, the convolved and measured spectra were in good agreement. At the lower temperatures, the simple assumption of a constant width was not satisfactory and a more sophisticated model should be used. Figure 5 illustrates the linear variation of the gaussian width with the total pressure at 294 K.

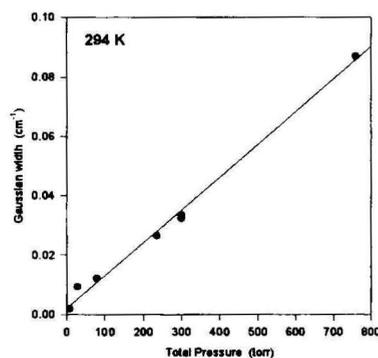


Figure 5: Variation of the width of the gaussian function representing the pressure effect with total pressure.

6. APPLICATION TO ATMOSPHERIC SPECTRA

The analysis of the temperature dependence and the possible influence of the pressure effect on the atmospheric observation of NO₂ has been performed using the retrieval program WinDOAS for UV/VIS spectra analysis. Stratospheric NO₂ amounts were determined from zenith-sky UV/VIS observations obtained at the NDSC station of Harestua (Norway, 60°N) with a grating spectrometer operating at a resolution of 1 nm (Van Roozendael et al., 1995). The amounts of NO₂, O₃, O₄, and H₂O were fitted simultaneously on the 454-514 nm (22026-19455 cm⁻¹) spectral range. Different sets of cross-sections were used in the case of NO₂ in order to evaluate their influence on the retrieved NO₂ amount:

Case a: pure NO₂ at 220 and 294 K

Case b: pure NO₂ at 220, 240 and 294 K

Case c: pure NO₂ at 220 K + diluted NO₂ (268 torr total pressure) at 240 K + diluted NO₂ (760 torr total pressure) at 294 K

The pressure and dilution factors used in case c have been chosen to represent as closely as possible the temperature and pressure vertical profiles of the atmosphere. The use of three cross-sections (cases b and c), instead of two (case a) did not improve significantly the quality of the NO₂ results. However, the low resolution of the instrument used to record the atmospheric spectra prevents any attempt to deduce any precise information concerning the vertical profile of NO₂. Further analysis of this effect will be undertaken using FT-UV measurements performed at higher resolution.

7. CONCLUSIONS

The NO₂ absorption cross-section has been measured from 10000 cm⁻¹ to 25000 cm⁻¹ at high resolution (0.05 and 0.1 cm⁻¹), at three temperatures (220, 240, and 294 K). Data have been obtained under different pressure conditions: pure NO₂ and mixtures of NO₂ and air, with three different dilution factors (9.6, 92, and 965 ppm of NO₂).

From the measurements performed at the three temperatures and with pure NO₂, a temperature dependence has been deduced. Recalculated cross-sections using the linear regression equation are in good agreement with the measured ones (below 3% at 294K, and 10% at the lower temperatures). Analysis of the spectra obtained with diluted NO₂ has demonstrated the presence of a pressure effect on the absorption cross-section. This effect has been well reproduced at 294 K by broadening the spectra obtained with pure NO₂ with a gaussian function whose width is linearly dependent on the total pressure.

ACKNOWLEDGMENTS

This project was supported by the Belgian State- Prime Minister's Service - Federal Office for Scientific, Technical and Cultural Affairs and the Fonds National de la Recherche (Belgium). We are grateful for support provided by the Centre national de la Recherche Scientifique (France) and Institut National des Sciences de l'Univers (France) through the Programme National de Chimie Atmosphérique.

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