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# The temperature and pressure dependence of the absorption cross-sections of NO<sub>2</sub> in the 250–800 nm region measured by Fourier-transform spectroscopy

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## Abstract

The absorption cross-sections of NO<sub>2</sub> at atmospheric temperatures (223–293 K) and pressures (100 and 1000 mbar) were measured in the 250–800 nm (12500–40000 cm<sup>-1</sup>) region using Fourier-transform spectroscopy, at spectral resolutions of 0.5 cm<sup>-1</sup> above 435 nm and 1.0 cm<sup>-1</sup> below 435 nm (corresponding to about 8 and 16 pm at this wavelength). The wavenumber accuracy of the new cross-sections is better than 0.1 cm<sup>-1</sup> (about 0.5 pm at 250 nm and about 6.4 pm at 800 nm), validated by recording of I<sub>2</sub> absorption spectra in the visible using the same experimental set-up (light source, beam splitter, interferometer optics). The NO<sub>2</sub> absorption spectra were recorded at five different sample temperatures between 223 and 293 K, and at each temperature at two total pressures (100 and 1000 mbar) using pure N<sub>2</sub> as buffer gas. Despite the weakness of this effect compared to the density of the NO<sub>2</sub> absorption structures, pressure-broadening was clearly observed at all temperatures. The pressure-broadening was partially modeled using a convolution of the low-pressure NO<sub>2</sub> absorption spectra with a Lorentzian lineshape. The pressure-broadening coefficient increases significantly with decreasing temperature, as already observed in the mid- and near-infrared vibration–rotation spectra of NO<sub>2</sub>. This effect is of importance for high-resolution spectroscopy of the earth's atmosphere in the UV–visible region. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** NO<sub>2</sub>; Atmospheric remote-sensing; Photochemical modelling

## 1. Introduction

Nitrogen dioxide, NO<sub>2</sub>, is an important minor constituent of the earth's atmosphere that is formed by both natural and anthropogenic processes. It plays a significant role in the cycles of stratospheric and tropospheric chemistry, for instance in the catalytic destruction of stratospheric ozone and in the formation of tropospheric ozone smog [1–3]. NO<sub>2</sub> is photolyzed by sunlight and its atmospheric concentrations present strong diurnal and seasonal variations.

In order to measure atmospheric concentrations of NO<sub>2</sub>, remote-sensing by UV–visible absorption spectroscopy is a well-established technique [4]. In particular, for monitoring of the global distribution of O<sub>3</sub>, NO<sub>2</sub> and other important atmospheric trace gases, a new generation of multi-channel satellite-borne spectrometers (pioneered by the Global Ozone Monitoring Experiment, GOME, instrument in orbit

since 1995 onboard ERS-2) has been developed in the past decade [5]. For these experiments, new accurate reference data from laboratory measurements are required. These measurements must cover all relevant atmospheric temperatures and pressures, and have to be performed at a spectral resolution that is adequate for using the reference data in atmospheric retrieval. In addition, an accurate wavelength calibration is crucial in order to reduce systematic uncertainties in the retrieval procedure.

Fourier-transform spectroscopy (FTS) combines the advantages of high spectral resolution, a well-known instrumental line shape, and a linear wavenumber scale [6]. A number of different studies of the UV–visible absorption spectrum of NO<sub>2</sub> has therefore been carried out using FTS in the past few years [7–10]. In two of these studies [8,10], self- and foreign-gas induced pressure-broadening of the NO<sub>2</sub> structures was observed, but in limited spectral regions and at room temperature only.

In order to investigate in more detail the pressure dependence of the absorption cross-sections of NO<sub>2</sub> at all atmospheric temperatures, we have therefore made new FTS measurements of the NO<sub>2</sub> absorption at total pressures of 100 and 1000 mbar and at five different temperatures

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between 223 and 293 K, covering the spectral region between 250 and 800 nm at a resolution between 8 and 16 pm.

It will be shown that besides the strong influence of temperature on the NO<sub>2</sub> absorption cross-sections, there is a significant pressure-broadening effect. This latter effect has therefore to be included in the analysis of high-resolution atmospheric measurements of NO<sub>2</sub>, for instance using diode-array or laser spectroscopy in the UV–visible region. At the same time, the pressure-broadening effect increases by more than 30% between 293 and 223 K, which is an important issue for future high-resolution spectroscopic measurements of NO<sub>2</sub> at different altitudes (e.g. in situ measurements using blue diode-lasers or high-resolution LIDAR experiments).

At the same time, the UV–visible absorption spectrum of NO<sub>2</sub> has been a challenge for quantum chemical theory for many years [11]. The new temperature- and pressure-dependent absorption spectra of the present study can assist in reaching a better understanding of the complex nature of the excited electronic states of NO<sub>2</sub>. In particular, the accurate measurement of the temperature dependence of the absorption spectrum contains important information about the potential energy surfaces involved in the transitions. The pressure dependence of the spectrum sets lower limits on the dissociative lifetimes of the upper rovibronic states. In the past, it has been shown for the O<sub>3</sub> molecule that such experimental information is indeed very useful in deriving a detailed picture of the nature of the electronic structure of small polyatomic molecules [12]. It is possible that the UV–visible spectrum of NO<sub>2</sub> will become a benchmark for ab initio methods in the next decade, even though these calculations are extremely difficult due to the presence of a

conical intersection between the ground and the first excited electronic states of NO<sub>2</sub> [13]. Also for this issue, accurate experimental data are indispensable.

## 2. Experimental

### 2.1. Experimental set-up

The experimental set-up used for this study is described in more detail in an internal report for the European Space Agency (ESA-ESTEC) [14], in a Ph.D. thesis [15], and in a recent paper dealing with the temperature dependence of the UV–visible absorption cross-sections of O<sub>3</sub> [16]. For all NO<sub>2</sub> spectra, the high-resolution Fourier-transform spectrometer (Bruker IFS-120 HR) at the University of Bremen was used. The same interferometer configuration was used throughout the study in order to maintain an accurate spectral calibration. The wavenumber accuracy was validated by recording absorption spectra of gaseous I<sub>2</sub> in the visible region at a spectral resolution of 0.6 cm<sup>-1</sup> and found to be better than 0.1 cm<sup>-1</sup> (about 0.5 pm at 250 nm and about 6.4 pm at 800 nm). The light was coupled out of the spectrometer directly after leaving the interferometer chamber, which was evacuated to about 0.03 mbar during recording of the spectra; all wavenumbers and wavelengths in this paper are therefore given for vacuum conditions.

Different combinations of light sources and detectors were needed to cover the entire spectral region (12500–40000 cm<sup>-1</sup>, i.e. 250–800 nm) of this study (see Fig. 1); the QTH lamp was used as broad-band light source for the region below 20000 cm<sup>-1</sup> and the Xe arc lamp for the

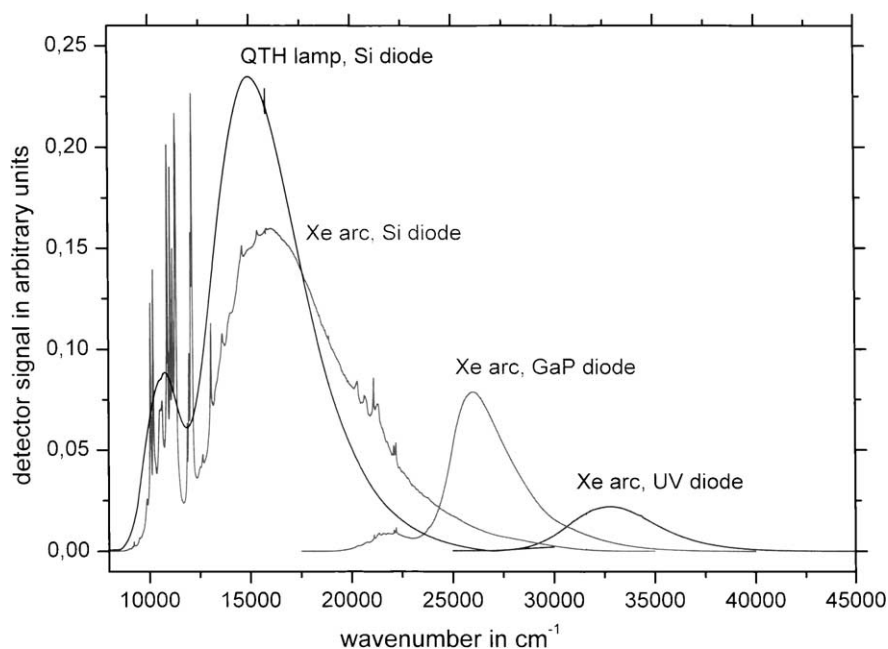


Fig. 1. Spectral distribution obtained using different white-light sources (xenon arc, halogen lamp) and detectors (Si, GaP, and UV diodes) in order to cover the entire spectral region between 10000 and 45000 cm<sup>-1</sup> (225–1000 nm) with the FTS.

region above  $20000\text{ cm}^{-1}$ . Three different detectors were employed: for wavenumbers below  $23000\text{ cm}^{-1}$  a Si diode, for wavenumbers between  $23000$  and  $30000\text{ cm}^{-1}$  a GaP diode, and above  $30000\text{ cm}^{-1}$  a solar-blind UV photodiode. Spectra were recorded at a resolution of  $0.5\text{ cm}^{-1}$  below, and  $1.0\text{ cm}^{-1}$  above  $23000\text{ cm}^{-1}$  ( $435\text{ nm}$ ).

The absorption cell is made of quartz with a total length of  $120\text{ cm}$  and an inner diameter of  $5\text{ cm}$ . It can be equipped with a White-type mirror optics to achieve optical path lengths of up to  $20\text{ m}$ . For the present study, spectra were recorded at optical path lengths of  $120$  and  $505\text{ cm}$ . The cell is surrounded by two envelopes, the inner one being purged with liquid ethanol as a coolant and the outer one being evacuated for thermal insulation. In addition, the absorption cell was completely wrapped into black isolating foam (Armaflex) for optimal thermal stability. The temperature of the cell was controlled by a commercial two-stage cryogenic cooler (Haake KT-90) and calibrated with a Pt-100 temperature element inside the absorption cell before and after the experiments. The stability of the temperature was always better than  $\pm 1\text{ K}$  and the absolute accuracy of the temperature is estimated to be  $\pm 1\text{ K}$  from the calibration of the cell temperature as a function of the temperature of the cooler. The  $\text{NO}_2$  absorption spectra were recorded at the following temperatures:  $223$ ,  $246$ ,  $260$ ,  $280$  and  $293\text{ K}$ . At each temperature, measurements were made at total pressures of  $100$  and  $1000\text{ mbar}$  using different  $\text{NO}_2/\text{N}_2$  mixtures. The  $\text{NO}_2$  partial pressure was always much smaller than that of the buffer gas  $\text{N}_2$ . For monitoring the pressure in the absorption cell, calibrated capacitive pressure transducers (MKS Baratron) were used. Furthermore, in order to be able to correct the measurements for the absorption of the dimer  $\text{N}_2\text{O}_4$  (see below), three spectra at significantly different mixing ratios of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  were recorded at each temperature and each total pressure.

Gaseous  $\text{NO}_2$  samples ( $98\%+$ ) mixtures were supplied by Messer Griesheim, Germany, and used without further purification. The sample purity was certified by the supplier as follows:  $\text{NO}_2 > 98\%$ ,  $\text{H}_2\text{O} < 0.5\%$ ,  $\text{HNO}_3 < 1.5\%$ . It is important to note that, although no significant additional absorbance in the  $250$ – $800\text{ nm}$  region is to be expected from the impurities  $\text{H}_2\text{O}$  and  $\text{HNO}_3$ , their possible presence leads to an additional systematic uncertainty concerning the absolute values of the  $\text{NO}_2$  absorption cross-sections in the entire spectral region. However, we estimate the purity of our sample to be better than that stated by the manufacturer, since in the long-wavelength region above  $600\text{ nm}$  where baseline drifts are small (see the error estimation below) our cross-sections at room temperature agree within better than  $1\%$  with those recorded by other authors [8,10].

Except at  $223\text{ K}$ , all measurements were performed using static mixtures of  $\text{NO}_2$  and  $\text{N}_2$  inside the absorption cell. Particular care was paid to establish that chemical equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  had been achieved by recording low-resolution spectra of the gaseous samples. All spectra were recorded in the dark to avoid photolytic decomposition

of the  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  samples. A typical high-resolution measurement took about  $120\text{ min}$ , the interferograms were recorded block-wise in order to allow for lamp drifts (in particular when using the Xe arc in the UV region above  $30000\text{ cm}^{-1}$ ). At  $223\text{ K}$  only, the measurements were made using constant flows of  $\text{NO}_2$  and of  $\text{N}_2$  (Messer Griesheim,  $5.0$ ) which were maintained by calibrated MKS flow controllers. Although very small flow rates were used, and the  $\text{NO}_2/\text{N}_2$  gaseous mixture passed through a pre-cooler circuit, the flow regime leads to an additional uncertainty in the chemical equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at  $223\text{ K}$  which was however allowed for by the procedure used for the analysis of data (see below).

## 2.2. Experimental procedure, data reduction and error analysis

Reference spectra of the white-light sources were measured (at  $10\text{ cm}^{-1}$  resolution) in order to obtain an accurate zero-absorbance baseline before and after recording  $\text{NO}_2$  absorption spectra at different total pressures, sample temperatures and  $\text{NO}_2$  partial pressures. These spectra were used as a reference to calculate weighted baseline spectra for the  $\text{NO}_2$  absorption spectra which were recorded in up to  $15$  blocks. In this way, the  $\text{NO}_2$  optical densities were obtained with weighted reference spectra before all blocks were averaged. The linearity of the lamp drifts, which reached up to  $20\%$  in the UV region, was carefully validated using spectra of the empty cell recorded under identical conditions.

All  $\text{NO}_2$  spectra were corrected for  $\text{N}_2\text{O}_4$  absorptions using a method described by Eisinger [17]: using three absorption spectra at significantly different  $\text{NO}_2/\text{N}_2\text{O}_4$  mixing ratios, one can separate the spectral contributions of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  under the assumption that the absorption of  $\text{N}_2\text{O}_4$  is negligible compared to that of  $\text{NO}_2$  at wavelengths above  $400\text{ nm}$ . The validity of this approach was already verified during the data analysis of  $\text{NO}_2$  absorption spectra recorded in the laboratory with the GOME Flight Model (FM) in 1994 [18]. However, in particular at low temperatures, the presence of  $\text{N}_2\text{O}_4$  leads to additional uncertainties concerning the absolute absorption cross-sections of  $\text{NO}_2$ . In order to calculate accurate values for the  $\text{NO}_2/\text{N}_2\text{O}_4$  mixing ratios at different temperatures, the well-known constant  $K_p$  for the gaseous  $2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$  equilibrium was taken from the literature [19].

At all temperatures and total pressures, the different  $\text{NO}_2$  optical densities were first scaled to each other in the overlapping regions and then concatenated at three wavenumbers:  $30000\text{ cm}^{-1}$  ( $333\text{ nm}$ ),  $23000\text{ cm}^{-1}$  ( $435\text{ nm}$ ) and  $19850\text{ cm}^{-1}$  ( $504\text{ nm}$ ). The integrated  $\text{NO}_2$  absorption cross-section between  $250$  and  $800\text{ nm}$  was then calculated and found to vary statistically by less than  $3\%$ , in agreement with our previous study using the GOME FM [18]. This quantity—which is proportional to the electronic transition moment—was therefore used to scale the  $\text{NO}_2$  absorption cross-sections at  $223\text{ K}$ , which were recorded in

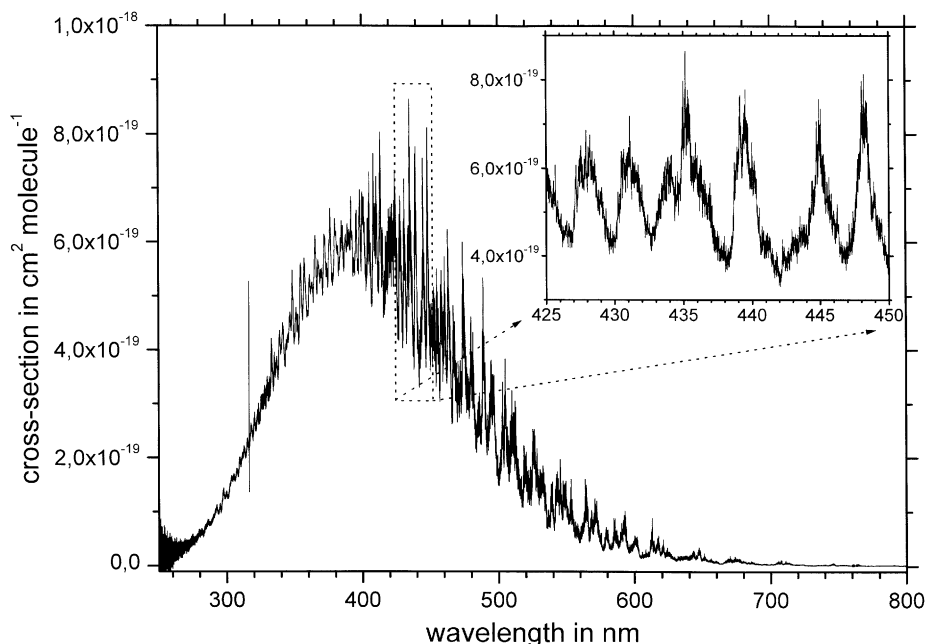


Fig. 2. The new  $\text{NO}_2$  absorption cross-sections of this study at a spectral resolution of  $0.5\text{ cm}^{-1}$  above and  $1.0\text{ cm}^{-1}$  below  $435\text{ nm}$ , at a temperature of  $293\text{ K}$  and a total pressure of  $1000\text{ mbar}$ . The inset shows the  $\text{NO}_2$  cross-sections in the region  $425\text{--}450\text{ nm}$  which is important for atmospheric remote-sensing.

a flow regime leading to a higher uncertainty in the partial pressure of  $\text{NO}_2$ . Together with the systematic uncertainty concerning gaseous impurities in the  $\text{NO}_2$  samples, the total uncertainty of the new cross-sections is estimated to be less than 4% at  $293\text{ K}$  and less than 6% at  $223\text{ K}$ , not including the signal/noise ratio that varies as a function of the spectral region and temperature (decreasing at lower temperatures as a result of the smaller amount of  $\text{NO}_2$  in the  $\text{NO}_2/\text{N}_2\text{O}_4$  mixtures). The total uncertainties of the  $\text{NO}_2$  absorption cross-sections therefore depend both on the spectral region and sample temperature.

Finally, it is possible that the new FTS absorption cross-sections of this study contain additional uncertainties due to residual baseline drifts depending on the spectral region; these drifts are the strongest in regions where the lamp signal is comparatively small (see Fig. 1). It is however important to stress the fact that the advantage of a very accurate wavelength calibration is maintained over the entire spectral region between  $250$  and  $800\text{ nm}$ , and that the error in the differential absorption cross-sections (which are actually used for the analysis of atmospheric data) is smaller in the case of systematic baseline drifts in regions of large absorption cross-sections, e.g. between  $425$  and  $450\text{ nm}$  (see Fig. 2) which is a spectral region typically used in atmospheric remote-sensing of  $\text{NO}_2$  [20].

### 3. Results and discussion

The  $\text{NO}_2$  spectra of this study show clearly the importance of working at high resolution for the determination of

UV–visible absorption cross-sections of  $\text{NO}_2$  (see Fig. 2), as already pointed out previously by Harder et al. [8] and Vandaele et al. [9,10]. The variation of the  $\text{NO}_2$  absorption cross-sections with temperature consists mainly in an increase of the differential absorption cross-sections with decreasing temperature (see Fig. 3). However, due to the high resolution employed in this study one can also observe shifts and changes in the shape of the spectral features. Apparently, these effects become significantly smaller at wavelengths below  $400\text{ nm}$  (corresponding to the dissociation limit of  $\text{NO}_2$ ) [21]. This indicates that, at energies below  $25000\text{ cm}^{-1}$ , the temperature-dependent changes in the  $\text{NO}_2$  absorption cross-sections are essentially due to the variation as a function of temperature of the rotational and vibrational state distribution of the  $\text{NO}_2$  molecules in their electronic ground state. It is important to note that the spectra of this study were recorded at five different temperatures ( $293$ ,  $280$ ,  $260$ ,  $246$  and  $223\text{ K}$ ) so that these temperature effects can be easily included in the analysis of data from atmospheric remote-sensing experiments. Furthermore, a theoretical investigation to interpret the temperature dependence of the UV–visible  $\text{NO}_2$  absorption cross-sections in terms of ground state populations and rovibronic transition moments based on the spectra obtained in this study is currently in progress [22].

There is a clear indication of pressure-broadening effects in the UV–visible spectrum of  $\text{NO}_2$  (see Fig. 4) which can be partly modeled using a convolution of the low-pressure spectra with a Lorentzian lineshape. However, the pressure effect is not completely reproduced by this approach, probably due to line-mixing effects and also to the fact that the

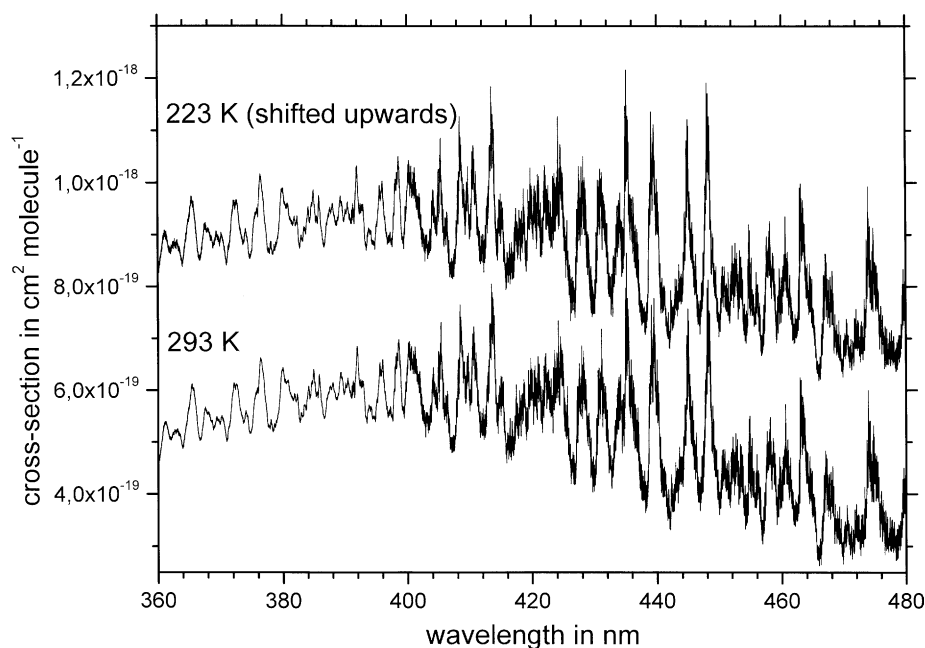


Fig. 3. The temperature dependence of the  $\text{NO}_2$  absorption cross-sections in the region 360–480 nm, at a total pressure of 1000 mbar (the spectrum at 223 K was shifted upwards by  $4.0 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$  for the sake of clarity). Note that, at both temperatures, the rotational structure disappears as the energy approaches  $25000 \text{ cm}^{-1}$  (400 nm) which corresponds to the dissociation energy of the  $\text{NO}_2$  molecule. There is a clear increase in the differential cross-sections with decreasing temperature, in good agreement with previous studies.

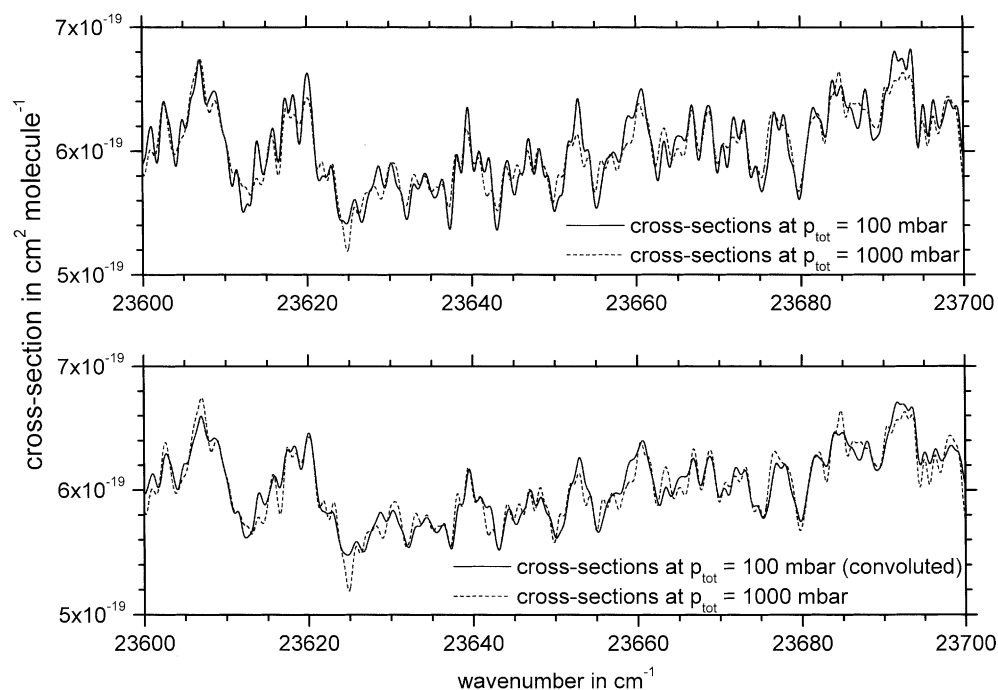


Fig. 4. Example for the pressure dependence of the  $\text{NO}_2$  absorption cross-sections in the region between  $23600$  and  $23700 \text{ cm}^{-1}$  ( $421.9$ – $423.7 \text{ nm}$ ), at a spectral resolution of  $1.0 \text{ cm}^{-1}$  (sampling interval  $0.5 \text{ cm}^{-1}$ ), at a temperature of 293 K. The upper trace shows the cross-sections at total pressures of 100 and 1000 mbar, the lower trace shows the same cross-sections but the 100 mbar data being folded with a Lorentzian profile to better reproduce the data at 1000 mbar. There is clear pressure-broadening in the entire spectral range between 400 and 800 nm. Note that the 1000 mbar is not entirely reproduced by the convolution of the 100 mbar data, probably due to non-linear effects such as line-mixing.

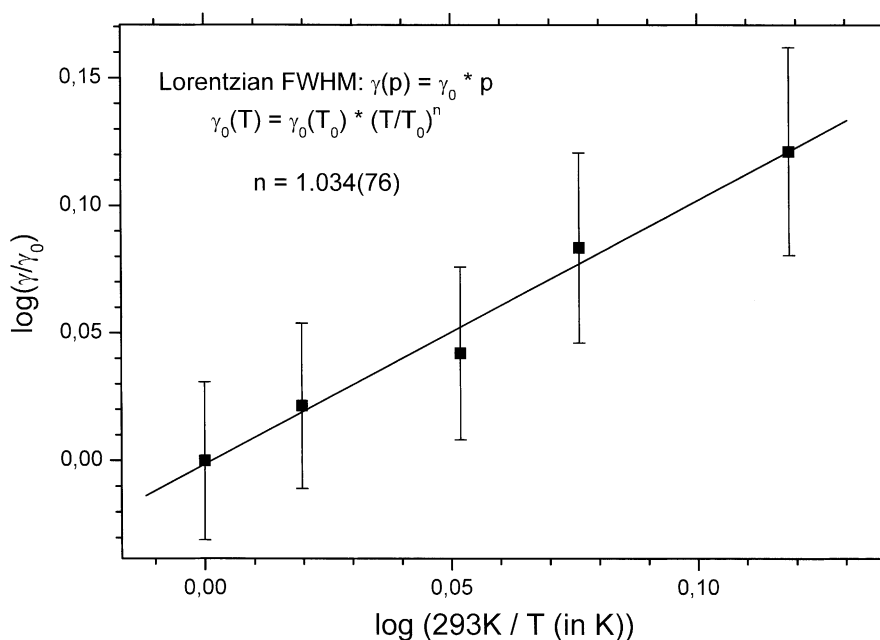


Fig. 5. Temperature dependence of the pressure-broadening of NO<sub>2</sub> by N<sub>2</sub> from least-squares fitting of the Lorentzian lineshape used for convolution of the data at 100 mbar to minimize the difference between the convoluted cross-sections at 100 mbar and the measured cross-sections at 1000 mbar, for 20 spectral windows between 400 and 800 nm. Note the increase of pressure-broadening (more than 30%) with decreasing temperature and the good agreement with the power law expected from pressure-broadening theory.

spectral resolution is still limited by the spectrometer and not by the spectral linewidth of the NO<sub>2</sub> absorption features (the Doppler width for NO<sub>2</sub> at 25000 cm<sup>-1</sup> is about 0.04 cm<sup>-1</sup>). It would therefore be interesting to validate the observations of this study at higher resolution, at least in parts of the spectrum. Such a study is presently in progress [23].

In order to obtain the best agreement between the observed spectra at 1000 mbar and the spectra at 100 mbar convoluted with a Lorentzian lineshape, the halfwidth of the Lorentzian function was varied with a least-squares program to minimize the differences between the spectrum at 1000 mbar and the convoluted spectrum (at 100 mbar). This fitting procedure was carried out at all five temperatures and in 20 spectral windows between 400 and 800 nm. It is important to note that, at each temperature, the agreement between the Lorentzian halfwidths from the 20 spectral windows was excellent (variations of less than 5%), and that there is also clear observation of the temperature dependence of the pressure-broadening. In Fig. 5, the increase of the N<sub>2</sub> pressure-broadening coefficients with decreasing temperature is shown, which is as much as 30% between 293 and 223 K. Furthermore, the linear slope is in good agreement with line-broadening theory [24]. The slope of 1.03(8) is, to the best of our knowledge, the first experimental determination of this quantity using UV–visible spectroscopy, in very good agreement with the value obtained from diode-laser measurements by Malathy-Devi et al. [25] in the mid-infrared (IR), 1.03(1). Note that in the present HITRAN edition [26] the standard value of 0.5 (from hard-collision theory) is given for the temperature

dependence of the pressure-broadening coefficient, which is probably too low by about a factor of 2. However, the absolute value of the N<sub>2</sub> pressure-broadening coefficient at 293 K from the present study, 0.134(10) cm<sup>-1</sup>/atm (HWHM), is higher than the values determined by mid- and near-IR spectroscopy (varying between 0.061 and 0.112 cm<sup>-1</sup>/atm at 293 K [27–31]), probably due to the above mentioned problems of line-mixing and spectral resolution. Nevertheless, the agreement between this study and those carried out using isolated NO<sub>2</sub> lines in the mid- and near-IR is surprisingly good, keeping in mind the limited spectral resolution of this study (0.5 cm<sup>-1</sup>) and the high congestion of the UV–visible absorption spectrum of NO<sub>2</sub>.

#### 4. Conclusion

The temperature and pressure dependence of the absorption cross-sections studied in this paper are important data for atmospheric remote-sensing applications and for our understanding of the electronic spectrum of NO<sub>2</sub>. Comparisons with previous studies show good agreement concerning the temperature dependence of the NO<sub>2</sub> cross-sections, while the systematic study of pressure-broadening in the UV–visible is made for the first time in the present work, to the best of our knowledge. These variations of the NO<sub>2</sub> cross-sections with temperature and total pressure clearly need to be included in the analysis of high-resolution spectra of the earth's atmosphere, for present and future applications (in particular when working at higher resolution

from ground, airborne or satellite platforms). The NO<sub>2</sub> cross-sections of the present study at all five temperatures (223–293 K) and at 1000 and 100 mbar, respectively, are available in digital form upon request to one of the authors and on <http://www.iup.physik.uni-bremen.de/gruppen/molspec/index.html>.

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