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Long Path Monitoring of Tropospheric O<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>CO and SO<sub>2</sub>

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Concentrations of tropospheric O<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>CO and SO<sub>2</sub> have been measured on the Campus of the "Université Libre de Bruxelles" on a routinely basis since October 1990. The long path system (see Figure 1) consists of a source lamp, a first 30 cm f/8 Cassegrain type telescope which collimates the light onto a slightly parabolic mirror placed on the roof of a building situated 394 m away from the laboratory. The light is sent back into a second 30 cm Cassegrain telescope. This telescope has been modified so that the output beam is a 5 cm diameter parallel beam. This beam is then focused onto the entrance aperture of the BRUKER IFS120HR Fourier Transform Spectrometer. The two telescopes are mounted on alignment devices and the external mirror is equipped with a driving system operated from the laboratory. The choice of the light source (either a 1000 W high pressure "ozone free" Xenon lamp or a 250 W Tungsten filament) and of the detector (either a solar blind UV-diode or a Silicon diode) depended on the spectral region studied. These regions lie respectively from 26000 cm<sup>-1</sup> to 30000 cm<sup>-1</sup> (260-380 nm) and from 14000 cm<sup>-1</sup> to 30000 cm<sup>-1</sup> (330-700 nm). The spectra have been recorded at the resolution of 16 cm<sup>-1</sup> and with a dispersion of 7.7 cm<sup>-1</sup>. They have been measured during the forward and the backward movements of the mobile mirror, in double sided mode: each spectrum is an average of 2000 scans. The time required to record a spectrum is about 45 minutes. The shape of the raw spectra in the two investigated regions are represented in Figure 2.

The concentration of the measured constituents are deduced from the experimental spectra using the Beer-Lambert law :

$$I = I_0 e^{-n \Delta \sigma d}$$

where I is the measured intensity, I<sub>0</sub> the measured intensity from which all absorption structures have been

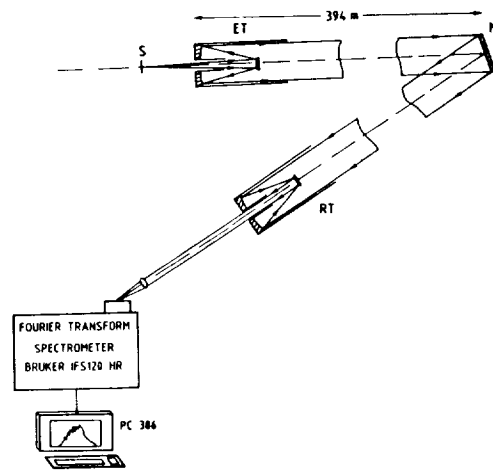


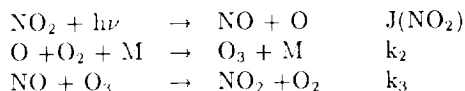
Fig. 1 : Experimental set-up : S = Source Lamp. ET = Emitting Telescope (30 cm  $\phi$ ). RT = Receiving Telescope (30 cm  $\phi$ ). M = Long Focal Retroreflector Mirror

removed, n the concentration, d the optical path length and  $\Delta\sigma$  the differential absorption cross section of the molecule. Numerous methods for determining I<sub>0</sub> exist. Fourier transform filtering has been used in this work. This method defines I<sub>0</sub> as the inverse Fourier transform of the lower frequencies portion of the power spectrum of the experimental data. A least squares procedure is then applied in order to determine the concentration of the desired molecules. Cross sections of O<sub>3</sub> and H<sub>2</sub>CO have been taken from the literature (Daumont et al., 1992; Moortgat et al., 1989). The cross sections of SO<sub>2</sub> and NO<sub>2</sub> have been measured in the laboratory with the same spectrometer (Carleer et al., 1992). These cross sections have been

recorded in the UV and visible regions at different resolutions (2,4,8 and 16 cm<sup>-1</sup>) and at room temperature. The gas is introduced in a 20 cm long absorption cell; the partial pressure of the gas is measured with a Baratron gauge; air is then added to obtain a total pressure of 1 atmosphere. The temperature is measured with a conventional sensor. Two blanks were taken before and after each measurement. The experimental conditions for the measurement of the cross sections are identical to those used for the atmospheric spectra, except that each spectrum is an average of 4000 scans, instead of 2000 scans, in order to improve the signal to noise ratio. Absolute cross sections of SO<sub>2</sub> and NO<sub>2</sub> at the resolution of 16 cm<sup>-1</sup> are plotted in Figures 3 and 4. The accuracy on the cross sections of SO<sub>2</sub> is of the order of ± 2 % and of the order of ± 5 % for NO<sub>2</sub>.

The absolute cross sections measured in this work have been compared to data from the literature (Schneider et al., 1987; Thomsen, 1990). The absolute cross sections of NO<sub>2</sub> are in good agreement in the wavenumber range 30800 - 34000 cm<sup>-1</sup> (better than 5%), however discrepancies of about 10% appear in the 23800 - 30800 cm<sup>-1</sup> range. Below 23500 cm<sup>-1</sup> the cross sections measured by Schneider et al. present some anomalies regarding the wavelength calibration. The comparison between the cross sections of SO<sub>2</sub> of this work and of Thomsen, shows that the data are in good agreement (better than 5%).

Diurnal variations of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>CO concentrations measured on the Campus of the "Université Libre de Bruxelles" for February, 27, 1992 and April 29, 1992 are reported in Figure 5. SO<sub>2</sub> does not show any clear diurnal cycle and its variation is mostly due to climatic parameters such as the wind velocity and direction. H<sub>2</sub>CO was found to be often below the detection limit. O<sub>3</sub> and NO<sub>2</sub> show strongly anti-correlated cycles, with O<sub>3</sub> increasing between 7 pm and 12 pm, then decreasing till 19 am, increasing again till 2 pm. As NO<sub>2</sub> and O<sub>3</sub> seem to be chemically correlated, NO concentrations have been deduced from the Leighton photochemical reaction scheme, which is only valid when photochemical equilibrium has been reached (daytime conditions, except at sunrise or sunset) :



The NO concentration is given by

$$[\text{NO}] = \frac{J(\text{NO}_2)}{k_3} \frac{[\text{NO}_2]}{[\text{O}_3]}$$

where  $k_3$  [cm<sup>3</sup>/molec sec] = 2.0 · 10<sup>-12</sup> exp(- $\frac{1400}{T}$ ) (DeMore et al., 1990) and the photodissociation rate  $J(\text{NO}_2)$  is calculated using the empirical relation given by Parrish (Parrish et al., 1986).

Results for February 27, 1992 are plotted in Figure 6. NO concentrations measured by the Institute for Hygiene and Epidemiology (IHE, Brussels) are also reported. The station of the IHE is located at Uccle, 3 km away from the Campus of the ULB and uses a chemical technique to measure NO.

The detection limits of these constituents are listed in Table 1.

Table 1 : Detection limits

	$\bar{\nu}$ (cm <sup>-1</sup> )	S/N	Detection Limit (ppb)
SO <sub>2</sub>	33340	3200	0.1
NO <sub>2</sub>	28710	500	5.8
	22300	4000	0.3
O <sub>3</sub>	35305	1700	1.6
H <sub>2</sub> CO	29514	1000	5.2

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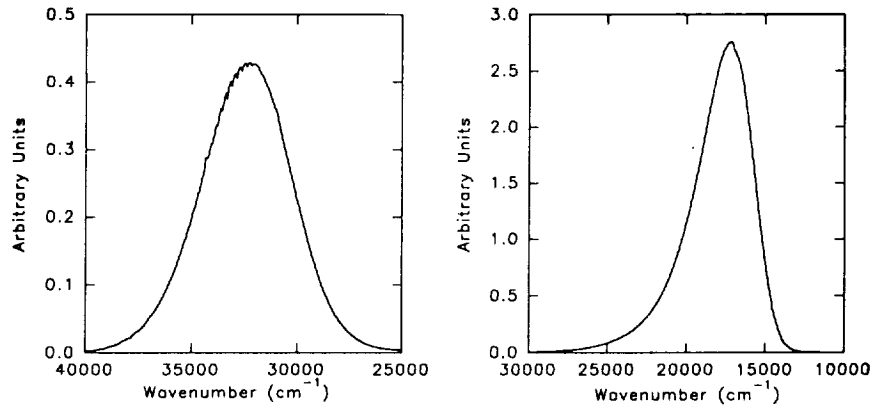


Fig. 2 : Experimental spectra in the two investigated regions

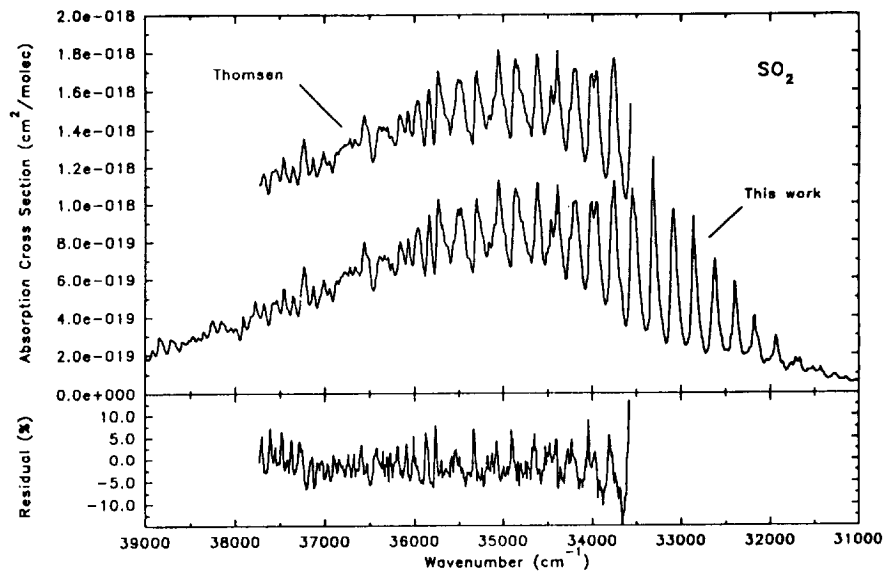


Fig. 3 : Absolute absorption cross sections of  $\text{SO}_2$  between  $31000$  and  $39000 \text{ cm}^{-1}$ . The values of Thomsen (1990) have been displaced by  $7 \cdot 10^{-19} \text{ cm}^2/\text{molec}$  for comparison purposes.

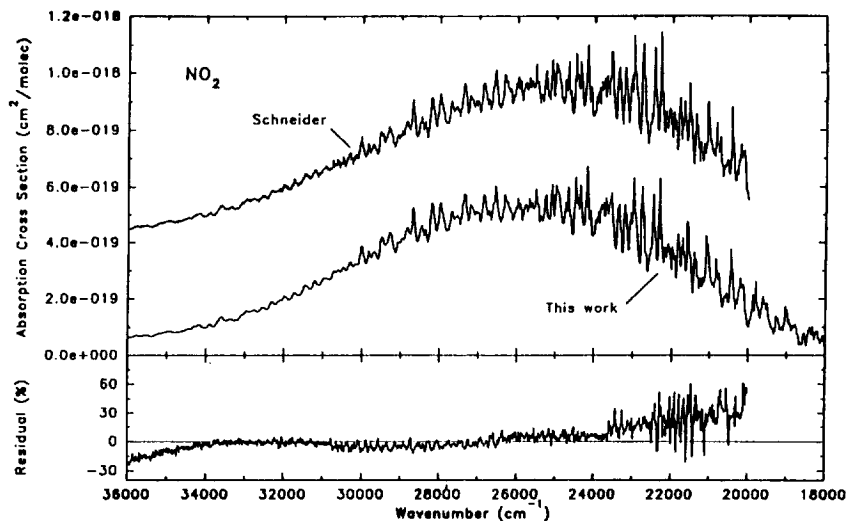


Fig. 4 : Absolute absorption cross sections of  $\text{NO}_2$  between  $18000$  and  $36000 \text{ cm}^{-1}$ . The values of Schneider et al. (1987) have been displaced by  $4 \cdot 10^{-19} \text{ cm}^2/\text{molec}$  for comparison purposes.

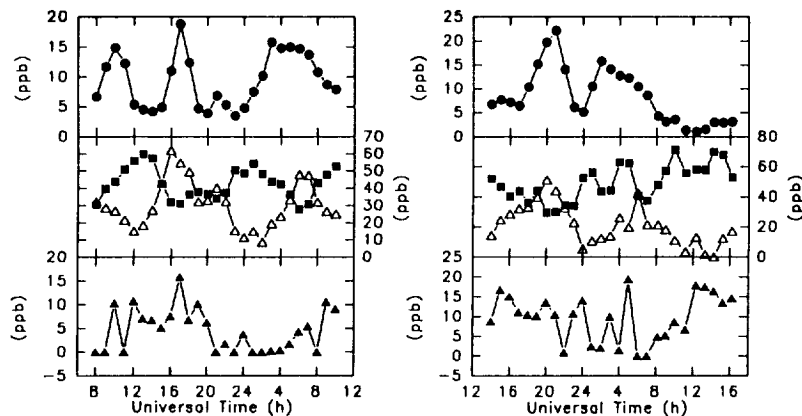


Fig. 5 : Diurnal variations of  $\text{SO}_2$  (●),  $\text{O}_3$  (■),  $\text{NO}_2$  (△) and  $\text{H}_2\text{CO}$  (▲) measured at the ULB on the February 27, 1992 and April 29, 1992.

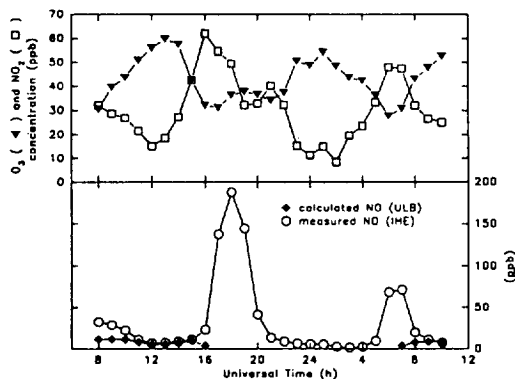


Fig. 6 : Comparison between calculated NO and measured NO for February 27, 1992.