

Detection of urban O₃, NO₂, H₂CO and SO₂ using Fourier Transform Spectroscopy

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Concentrations of SO₂, NO₂, H₂CO and O₃ have been measured regularly since October 1990 at the urban site of the Campus of the "Université Libre de Bruxelles", using the Differential Optical Absorption Spectroscopy (DOAS) technique associated with a Fourier Transform Spectrometer. The experimental set up has already been described elsewhere (Vandaele et al., 1992). It consists of a source (either a high pressure Xenon lamp or a Tungsten filament) and a 800 m long path system. The spectra are recorded in the 26000 - 38000 cm⁻¹ and 14000 - 30000 cm⁻¹ spectral regions, at the dispersion of 7.7 cm⁻¹.

The analytical method of the DOAS technique is based on the fact that in atmospheric measurements, it is impossible to obtain an experimental blank spectrum. Therefore the Beer-Lambert law has to be rewritten as :

$$I = I'_0 e^{n\Delta\sigma d}$$

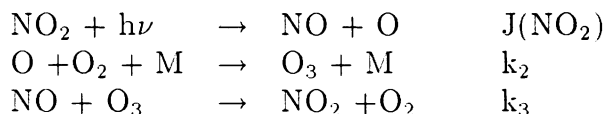
where I is the measured intensity, I₀ the measured intensity from which all absorption structures have been removed, n the concentration, d the optical path length and Δσ the differential absorption cross section of the molecule. Numerous methods for determining I₀' exist. Fourier transform filtering has been used in this work. This method defines I₀' 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. The differential absorption cross sections of SO₂ and NO₂ have been measured in the laboratory (Carleer et al., 1992). Cross sections of O₃ and H₂CO have been taken from the literature (Daumont et al., 1992; Moortgat et al., 1989). Great care has to be taken in order to account for the emission structures of the Xenon lamp. As can be seen in figure 1, these structures are not negligible compared to the absorption features of the atmospheric constituents.

The measured and the calculated optical thickness are compared in figures 1 and 2 respectively in the 26000 - 38000 cm⁻¹ and 14000 - 30000 cm⁻¹ regions. In the first region, NO₂, O₃, SO₂ and H₂CO are detected around 28170 cm⁻¹, 35305 cm⁻¹, 33340 cm⁻¹ and 29515 cm⁻¹ respectively; NO₂ is also detected around 22300 cm⁻¹. The detection limits of these constituents are listed in Table 1. On the few spectra taken during the night in the 14000 - 30000 cm⁻¹, no NO₃ could be detected, in spite the fact that the influence of water was canceled out by dividing the experimental spectrum by a spectrum taken during daytime when no NO₃ was thought to be present.

Table 1 : Detection limits

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

Diurnal variations of SO₂, NO₂, O₃ and H₂CO concentrations measured on the Campus of the "Université Libre de Bruxelles" for February, 27, 1992 are reported in figure 3. SO₂ does not show any clear diurnal cycle and its variation is mostly due to climatic parameters such as the wind force and direction. H₂CO was found to be often below the detection limit. O₃ and NO₂ show strongly anti-correlated cycles, with O₃ increasing between 7 pm and 12 pm, then decreasing till 19 am, increasing again till 2 pm. This cycle has been seen for nearly each day of measurement, however some secondary maximum of O₃ concentration often happens during the late afternoon as can be seen in figure 3. As NO₂ and O₃ seem to be chemically correlated, NO concentrations have been deduced during daytime from the Leighton photochemical reaction scheme :



The NO concentration is given by

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

where $k_3[\text{cm}^3/\text{molec sec}] = 2.0 \cdot 10^{-12} \exp(-\frac{1400}{T})$ (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 3. 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.

Measurements of SO₂, NO₂ and O₃ obtained with the Fourier Transform Spectrometer have been compared to measurements performed by the IHE, which measures these constituents respectively with a photometric method, chemiluminescence and UV absorption. Comparisons of the concentrations are plotted in figure 3. SO₂ profiles are comparable, the shift between the two sets of data can be attributed to the distance between the two sites of measurements. O₃ variations are in good agreement, however the values found in this work are roughly 40 ppb higher. The evolution of NO₂ concentration are similar and present the same position of minimum and maximum, but again the absolute values are quite different (up to 25 % of difference). It is to be reminded that the two measurements are not carried out at the same location, and that the atmosphere composition might be different from one site to another.

References

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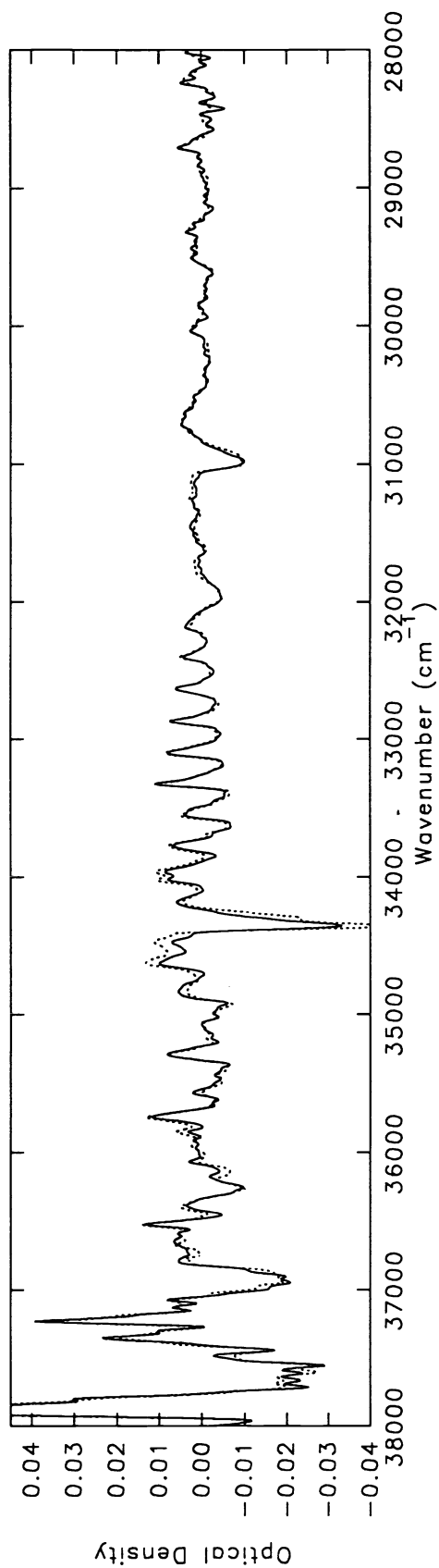


Fig. 1 : Experimental (—) and calculated (.....) optical density in the 28000 – 38000 cm^{-1} region

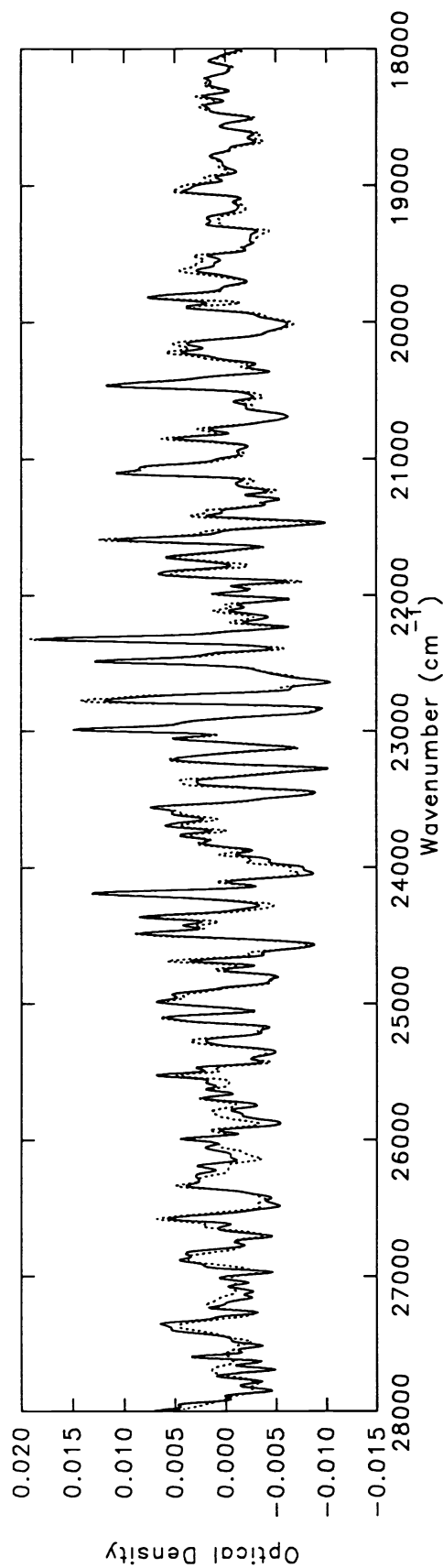


Fig. 2 : Experimental (—) and calculated (.....) optical density in the 18000 – 28000 cm^{-1} region

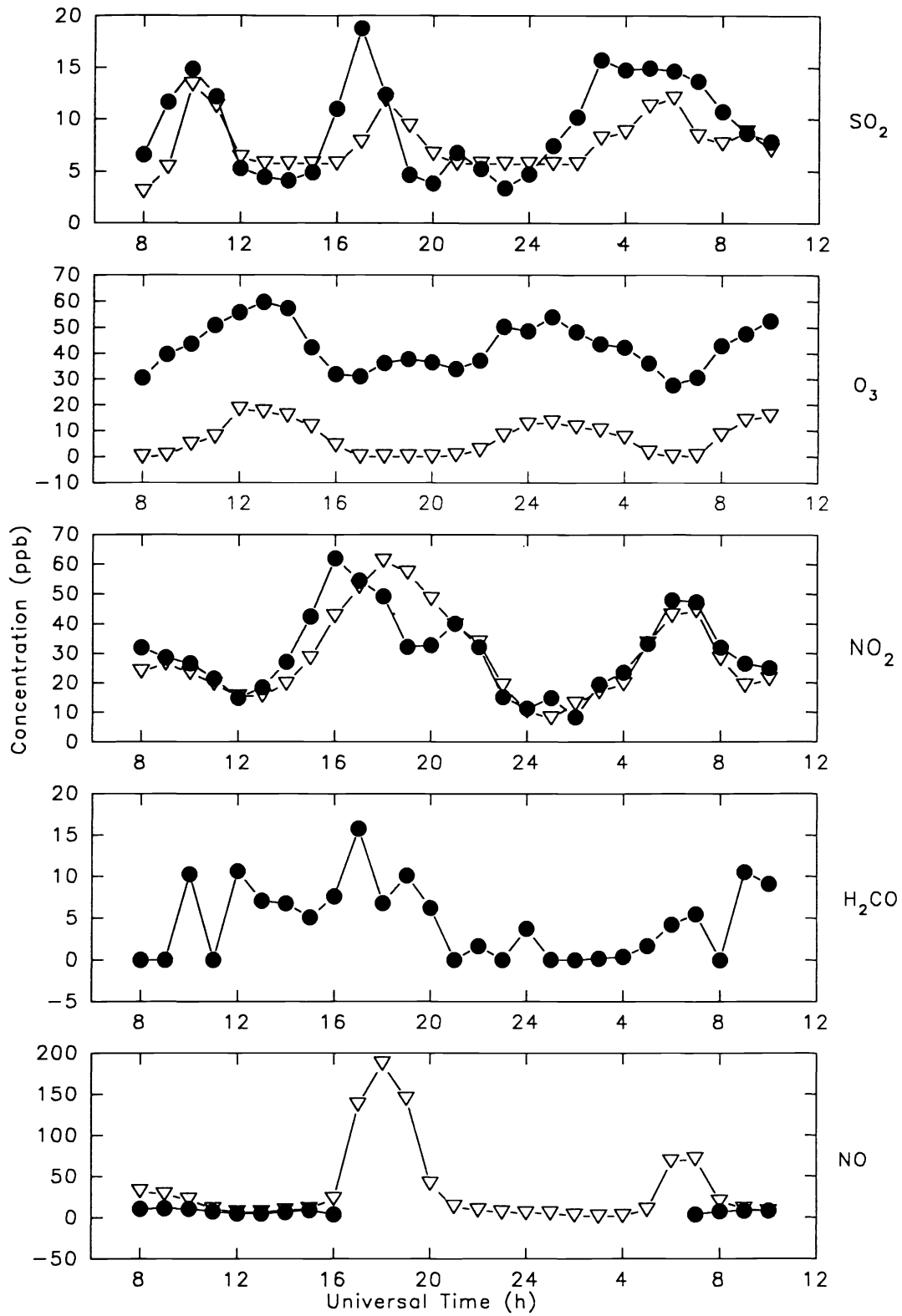


Fig. 3 : Diurnal variation of SO₂, O₃, NO₂, H₂CO and NO measured on the February 27, 1992 at the ULB (●) and the IHE station (▽)