UV – Visible Absorption Cross-Sections of Relevant Atmospheric Trace Species

A contribution to subproject TOPAS

M. Carleer[1], R. Colin[1], J.M. Guilmot[1], P.C. Simon[2] and A.C. Vandaele[2]

[1]*Laboratoire de Chimie Physique Moléculaire, C.P. 160/09 Université Libre de Bruxelles, 50 av. F.D. Roosevelt, 1050 Brussels, Belgium*
[2]*Institut d'Aeronomie Spatiale, 3 av. Circulaire, 1180 Brussels, Belgium*

The use of a Fourier transform spectrometer for the measurement of absorption cross-sections combines the advantages of great sensitivity, great spectral interval investigated in a single mirror scan, and wavenumber accuracy due to the built-in wavenumber calibration (He-Ne laser). A Bruker IFS120M Fourier transform spectrometer was used to measure the absorption cross section of atmospheric molecules in the UV-visible spectral range at two resolutions (2 and 16 cm^{-1}). We present here absorption cross sections for SO_2 and CS_2 at room temperature, and for NO_2 at temperatures ranging from 230 to 300 K. Some of these results improve the measurements presented previously [1].

The experimental set-up used allows measurement of the absorption cross sections with great accuracy (up to 1%). The Fourier transform spectrometer is designed to work in the 10000 to 45000 cm^{-1} spectral range. The optical elements used were a quartz Suprasil beamsplitter, visible or UV filters and a Si diode or a solar blind UV diode detector. The light sources were a thungsten halogen lamp for the visible range and a xenon arc lamp for the UV. The latter presents important light drifts during the time of an experiment, due to arc instabilities. To avoid this problem, a feedback system was installed in order to stabilise the Xe lamp light intensity by controlling the power supply output. The absorption cell, made of anodised aluminium and fitted with quartz windows, was located between the lamp and the interferometer. Two different cells of path lengths 5.15 and 21.1 cm were available. The gas pressure was measured using a 100 torr full scale MKS Baratron capacitance gauge model 390HA, stabilised at 45 °C. The cell temperature could be stabilised anywhere between 230 and 360 K with liquid circulating in the double wall within the body of the cell. Water is used with a thermostat at the higher temperatures, and methanol with a cryostat at the lower temperatures. A temperature stability of 0.02 K was achieved. The gas temperature was measured inside the cell with a calibrated temperature transducer of 0.2 K accuracy. Finally, the whole experimental set-up was located in a temperature stabilised room.

Spectra were recorded in the wavenumber ranges 25000–40000 cm^{-1} (400–250 nm) and 10000–30000 cm^{-1} (1000–330 nm). They were measured during the forward movement of the mobile mirror, in single sided mode. Each spectrum was obtained from the average of 4000 interferograms. Samples were prepared by

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introducing first the desired quantity of gas (1 to 50 mb), then oxygen was added to the SO_2 and NO_2 samples and air to the CS_2 samples, to reach 1 atm pressure. Absorption cross sections are derived from the experimental data using Beer-Lambert law:

$$\sigma(\nu) = \ln[I(\nu)/I_0(\nu)]/(n.l)$$

where
- n denotes the concentration of the gas deduced from its partial pressure in the cell
- l the length of the cell (5.15 or 21.1 cm)
- $I_0(\nu)$ the intensity of the spectrum obtained with an empty cell, e.g. the average of two blanks taken before and after the absorption spectrum measurement
- $I(\nu)$ the intensity of the spectrum obtained with the filled cell

Absorption cross sections are presented in Figs. 1 and 2 for SO_2 and CS_2 respectively. They compare well – less than 5% difference – with previous literature data [2, 3] although some local discrepancies can reach up to 20%. These could be due to wavelength calibration errors in the previous measurements. Error limits on the absorption cross sections have been evaluated, taking into account the uncertainties on pressure, temperature and absorption path length. The presence of impurities in the samples, the error on the absorbance and the fluctuations of the source were all included in these error estimates. In the 31800–37000 cm^{-1} interval, the accuracy on the cross sections of SO_2 is of 2%.

In order to obtain the NO_2 absorption cross sections, it was necessary to derive the NO_2 partial pressure from the measured pressure of the $NO_2 - N_2O_4$ mixture. From the known values of the equilibrium constant $K_p = (P_{NO_2})^2/P_{N_2O_4}$ given in the literature [4] for temperatures ranging from 230 to 400 K, values at the temperatures of our experiments were determined by fitting these data to a fourth degree polynomial expansion in the temperature T [5]. Observed absorptions cross sections depend on the pressure according the following relation

$$\sigma_{obs}(\nu) = \sigma_{NO_2}(\nu) + (P_{NO_2}/K_p).\sigma_{N_2O_4}(\nu)$$

By recording spectra at several pressures of the $NO_2 - N_2O_4$ mixture, it was possible to obtain σ_{NO_2} from the plot of σ_{obs} against P_{NO_2}. Fig. 3 shows NO_2 cross sections at several temperatures. These results present errors of the order of a few percent (3% to 10%) mainly due to errors in the equilibrium constant and, at lower temperatures, to absorption of the cell walls.

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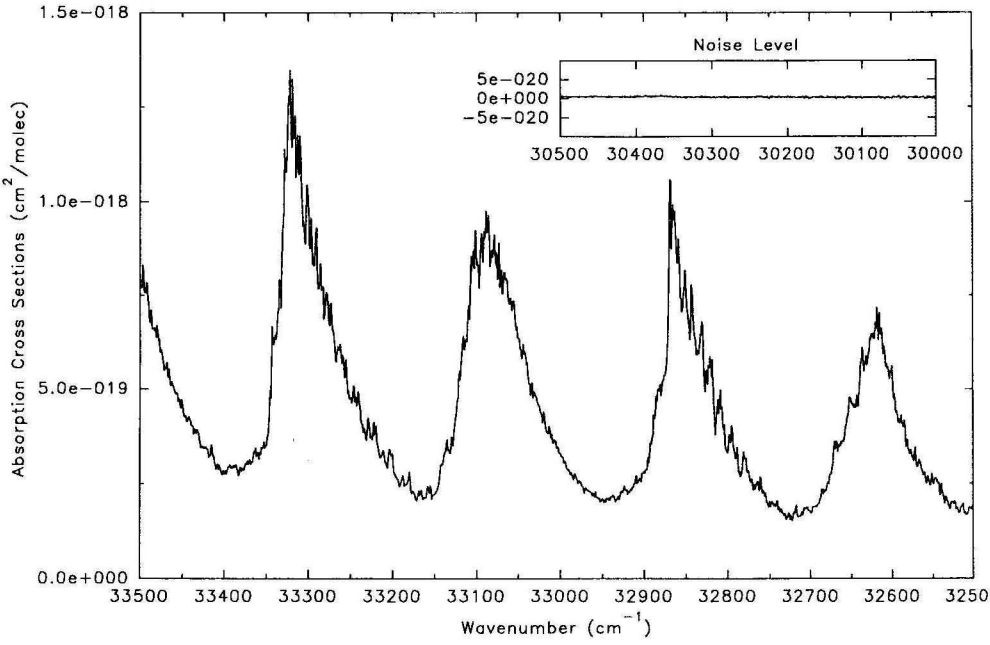

Figure 1. Absorption cross section for SO_2 at 294 K. Spectral resolution: 2 cm^{-1} (~0.02 nm at 300 nm)

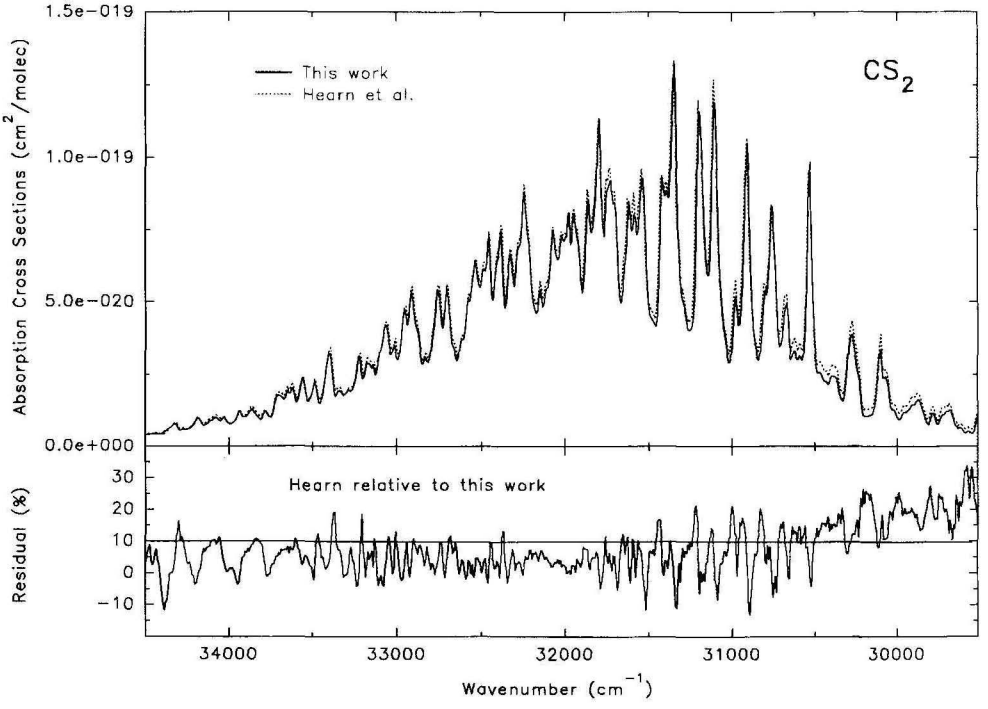

Figure 2. Absorption cross section for CS_2 at 294 K. Spectral resolution: 16 cm^{-1} (~0.1 nm at 300 nm)

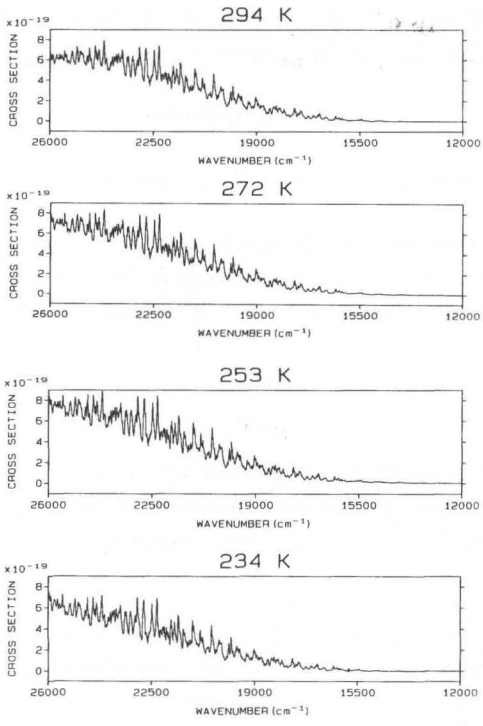

Figure 3. NO_2 absorption cross sections at temperatures between 230 and 300 K. Resolution: 16 cm^{-1}

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