

SO₂ absorption cross section measurement in the UV using a Fourier transform spectrometer

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Abstract. Absorption cross sections of SO₂ have been recorded at 295 K at the resolutions of 2 and 16 cm⁻¹. The 27000- to 40000-cm⁻¹ spectral region has been investigated. The comparison with data available from the literature shows a good agreement between the different data sets (less than 5%). However, local discrepancies, for example at the peaks of absorption, can reach 20%.

Introduction

Sulfur dioxide is a trace species in the Earth's atmosphere mainly present in the troposphere [Möhler and Arnold, 1992; Platt and Perner, 1980; Sandroni and Cerutti, 1977; Vandaele et al., 1993], where it is a primary pollutant emitted by fuel combustion or volcano eruptions. SO₂ is also encountered in the stratosphere [Jaechke et al., 1976; Sagawa and Itoh, 1977; Krueger, 1983] in high concentrations, but only after major volcano eruptions, and is also found in the atmospheres of Io and Venus [Barker, 1979; Bertaux and Belton, 1979] (see Leroy et al. [1983] for a review). SO₂ is chemically important in the Earth's atmosphere as a main source for sulphuric acid aerosols. These last years have seen growing concern for atmospheric pollution in the stratosphere as well as in the troposphere. Several methods have emerged to monitor the concentrations of particularly important trace species such as NO₂, SO₂, or O₃. All methods, based on the recognition of spectroscopic features of these molecules, have in common that they need very accurate laboratory reference spectra.

Absorption cross sections of SO₂ have already been measured at various resolutions and temperature conditions. Warneck et al. [1964] measured the UV absorption spectrum of SO₂ from 185 to 315 nm. Wu and Judge [1981] showed that the previous measurements should be shifted by 0.3 nm. Brassington [1981] investigated the 290- to 317-nm spectral region at relatively high resolution (0.05 nm). More recently, Martinez and Joens [1992] and Hearn and Joens [1991] reported absorption cross-sections of SO₂ from 197 to 240 nm and 228 to 339 nm, respectively. McGee and Burris [1987] presented measurements of the dependence of the cross sections with temperature, showing that cross sections increase at the peak and decrease in the regions between the strong structures for lower temperature. Thomsen [1990] made measurements at high resolution using an excimer laser pumping a pulsed dye laser. These measurements only cover the 265- to 298-nm region. More recently Ahmed and Kumar [1992] reported measurements of the absorption and

fluorescence cross sections of SO₂ in the 188- to 231-nm and 279- to 320-nm ranges. They also derived the fluorescence quantum yields in the two spectral regions. Several discrepancies exist between the literature data, as revealed in a recent compilation [Manatt and Lane, 1993]. These authors report disagreements of the order of 5-10% as well as several wavelength errors. It seems thus worthwhile to measure again SO₂ cross sections with greater accuracy and a reliable wavelength calibration.

Measurements in this work were made with a Fourier transform spectrometer, which combines the advantages of a great sensitivity, a large spectral interval investigated in one scan, and a built-in wavenumber calibration. This last advantage is achieved by the presence of a He-Ne laser, which allows the interferogram to be digitized at equal intervals of retardation. This leads to a very accurate and repeatable wavenumber calibration. With the described spectrometer, an accuracy of about 0.005 cm⁻¹ on the wavenumbers is achievable.

Measurements of SO₂ concentration in the troposphere by the Differential Optical Absorption Spectroscopy (DOAS) technique require the knowledge of the absorption cross sections at resolution of the order of 0.3 to 1.5 nm and on the largest possible spectral interval, typically from 250 to 350 nm [Pommereau and Goutail, 1988; Edner et al., 1993; Plane and Nien, 1992]. Future satellite observations like the Global Ozone Monitoring Experiment (GOME) requires even higher resolution, namely, 0.02 nm (Burrows J., personal communication, 1993). The present work reports absolute absorption cross sections of SO₂ between 27000 and 40000 cm⁻¹ (250-370 nm) at 295 K. The absorption cross sections have been measured at two resolutions (2 and 16 cm⁻¹) corresponding approximately to 0.02 and 0.1 nm at 300 nm.

Description of the Experimental Setup

The absorption spectra were recorded using a BRUKER IFS120HR Fourier transform spectrometer. The theoretical resolving power attainable with this spectrometer is 10⁶. The resolution is essentially limited in the UV by the optical quality of the mirrors and beam splitter, leading to a maximum resolution of the order of 10⁻² cm⁻¹ in this region. However, the absorption features of the studied molecule are large or even

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diffuse in the investigated spectral region, so that no advantage is gained by operating at the best possible resolution offered by the instrument. Furthermore, a higher resolution leads to a higher noise level on the spectra and a much longer recording time. Considering these facts, the resolutions of 2 and 16 cm⁻¹ were chosen.

The experimental setup is shown in Figure 1. It consists of a light source, the spectrometer, the cell, and the pumping and filling system. The choice of the light source, beam splitter and detector is determined by the spectral region to be investigated. A high-pressure xenon ozone-free source and a quartz suprasil beamsplitter combined with a UV vacuum diode, a Silicon diode or a GaAsP diode were used to cover the entire spectral region from 25000 to 40000 cm⁻¹. The experimental conditions used are summarized in Table 1.

The samples were introduced in a cell located in the sample compartment of the spectrometer, between the interferometer and the detector (see Figure 1). The cell has been described earlier [Hurtmans *et al.*, 1993] and its characteristics will be briefly summarized. It is made of anodized aluminium and is fitted with quartz windows. The gas pressure in the cell is measured with a 100-mbar full scale temperature stabilized MKS Baratron capacitance gauge (model 390HA) characterized by a 0.02% error in the 10- to 100-mbar range. In the 1- to 10-mbar region the error can be up to 1%. The temperature of the gas is monitored inside the cell with a temperature transducer. The latter is characterized by an accuracy of 0.2 K in the temperature range used in the present work. The cell temperature could be stabilized with a liquid circulating within the body of the cell; a temperature stability of ±1 K was achieved. Two cells of lengths 21.1 and 5.15 cm were available.

The experimental procedure was as follows: SO₂ (Union Carbide, 99.98% stated purity), used without further purification, was first introduced in the cell and its pressure measured. Then a buffer gas was added to reach 1 atm total pressure. Reference spectra, with the cell filled with 1 atm pure buffer gas, were recorded before and after each sample measurement to compensate for the lamp drift. Spectra were recorded in single-sided mode, during the forward movement of the mobile mirror only and a boxcar apodization function was used. Depending on the detector used, a certain number of mirror scans (interferograms) were to be averaged to get an acceptable signal to noise ratio. This number of scans was recorded in four blocks that were averaged at the end to obtain the spectrum.

During the measurements it was verified that photochemical degradation of the sample was not taking place in the cell due to the irradiation with the Xe lamp. This could be done by checking the sample absorption separately on the different blocks of a spectrum. It should be noted that the lamp used was an ozone-free lamp giving no light below 250 nm and thus preventing the SO₂ from being photolyzed [Finlayson-Pitts and Pitts, 1986]. However, the first samples were prepared using high-purity O₂ as the buffer gas, and photochemical reactions are not excluded because absorption in the 260- to 340-nm range is well known to produce ³SO₂ which can react with O₂ to make SO₃ and O₃ [Finlayson-Pitts and Pitts, 1986]. To control whether a systematic error was present due to oxygen, the cross sections were then measured using high-purity Ar as the buffer gas. Other measurements were also made changing the SO₂ pressure (1- to 13-mbar range) or the irradiation time (15 to 90 min). The different experiments performed are gathered in

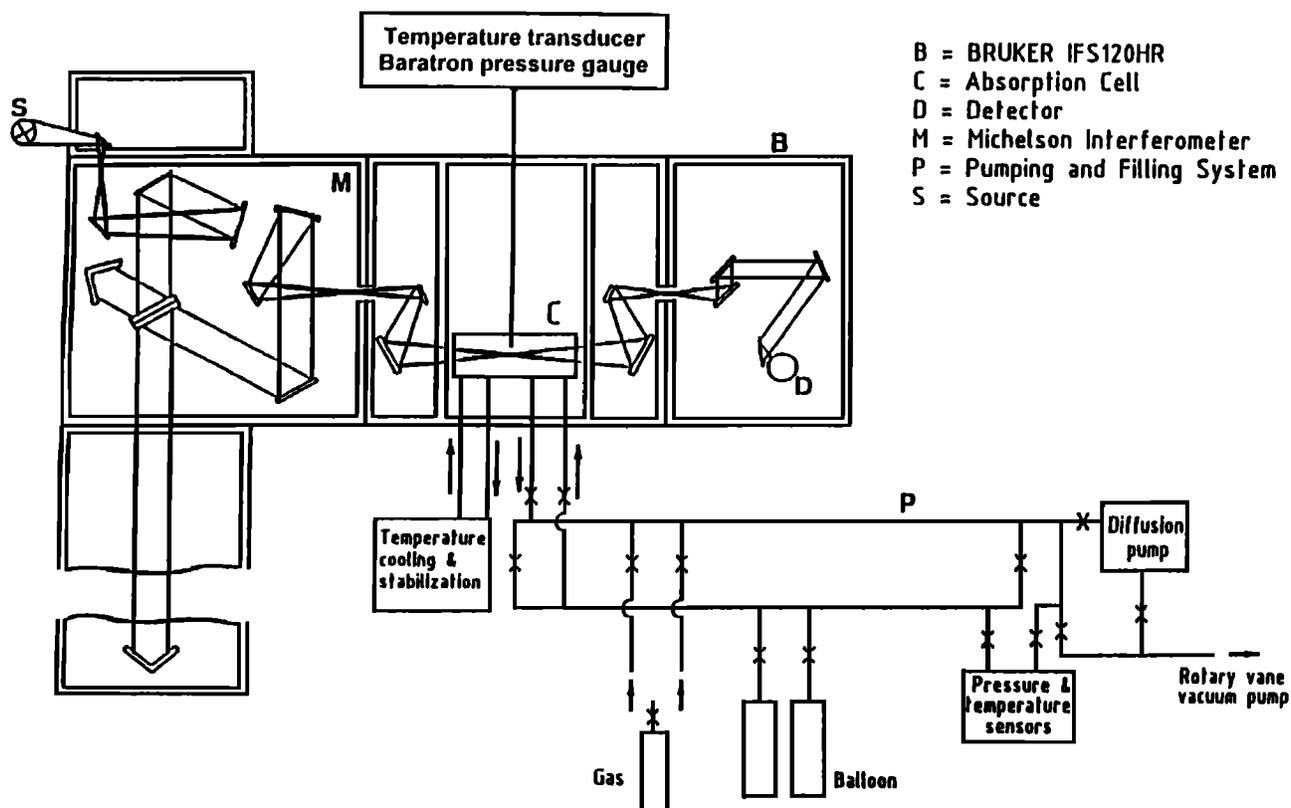


Figure 1. Experimental setup.

Table 1. Experimental Conditions

Resolution cm ⁻¹	Temperature K	Pressure hPa	Pathlength cm	Buffer Gas l atm	Number of Scans	Recording Time, min	Detector	Spectral Region, cm ⁻¹
16	296	1.96	21.1	O ₂	1024	15	GaAsP diode	25000-35000
16	295	1.65	21.1	O ₂	4096	90	UV diode	30000-40000
16	294	1.99	21.1	Ar	1024	15	Si diode	20000-37000
16	294	8.36	5.15	Ar	1024	15	Si diode	20000-37000
16	294	12.45	5.15	Ar	4096	90	UV diode	30000-40000
16	294	10.63	5.15	Ar	2048	45	UV diode	30000-40000
2	295	1.02	21.1	O ₂	4096	180	UV diode	30000-40000

Table 1. The various experimental conditions used allowed us to control the reproducibility of our measurements (see next paragraph) and to state that no photochemical processes were present or at least detectable within our experimental uncertainty.

To check the SO₂ purity, a high-resolution (0.005 cm⁻¹) Fourier Transform Infrared (FTIR) spectrum (from 500 to 5000 cm⁻¹) of a sample was also recorded. Several infrared absorbing impurities were found: NO₂ (<0.4%), N₂O (<0.1%), and CO₂ (<0.005%). The proportion of each impurity was estimated by comparing line intensities measured on the infrared spectrum with the literature line intensities (HITRAN molecular database, [Rothman et al., 1992]).

Determination of the Absorption Cross Sections

Absorption cross sections $\sigma(\lambda)$ are derived from the experimental data using the Beer-Lambert law:

$$I(\lambda) = I_0(\lambda) \exp(-n l \sigma(\lambda))$$

where n denotes the concentration of the gas deduced from its partial pressure in the cell; l is the length of the cell (21.1 or 5.15 cm); $I_0(\lambda)$ is the spectrum obtained with an empty cell,

e.g., the average of blanks taken before and after the absorption spectrum measurement; and $I(\lambda)$ is the spectrum obtained with the filled cell.

Absorption cross sections of SO₂ over the 27000- to 40000-cm⁻¹ spectral range have been compiled using the different spectra recorded and described in Table 1. The absorption cross sections at the resolution of 16 cm⁻¹ are plotted in Figure 2. These cross sections are of great interest for atmospheric monitoring, as most of the grating spectrometers working in the UV-visible region use a resolution between 0.3 and 1.5 nm [Platt and Perner, 1980; Pommereau and Goutail, 1988; Edner et al., 1993; Plane and Nien, 1992]. However, some atmospheric applications may want to use absorption cross sections measured at higher resolutions, e.g., 0.02 nm, in order to make an accurate convolution of the absorption spectrum with the instrument response function. Figure 3 presents a part of the SO₂ absorption cross sections at 2 cm⁻¹. The noise level found in this spectrum is also shown. It can be seen that this level is lower than the fine structures existing in the spectrum.

Error limits on the absorption cross sections have been evaluated, taking into account several points: error on the pressure (the maximum estimated error of 1% is taken) and temperature measurements, uncertainty on the absorption

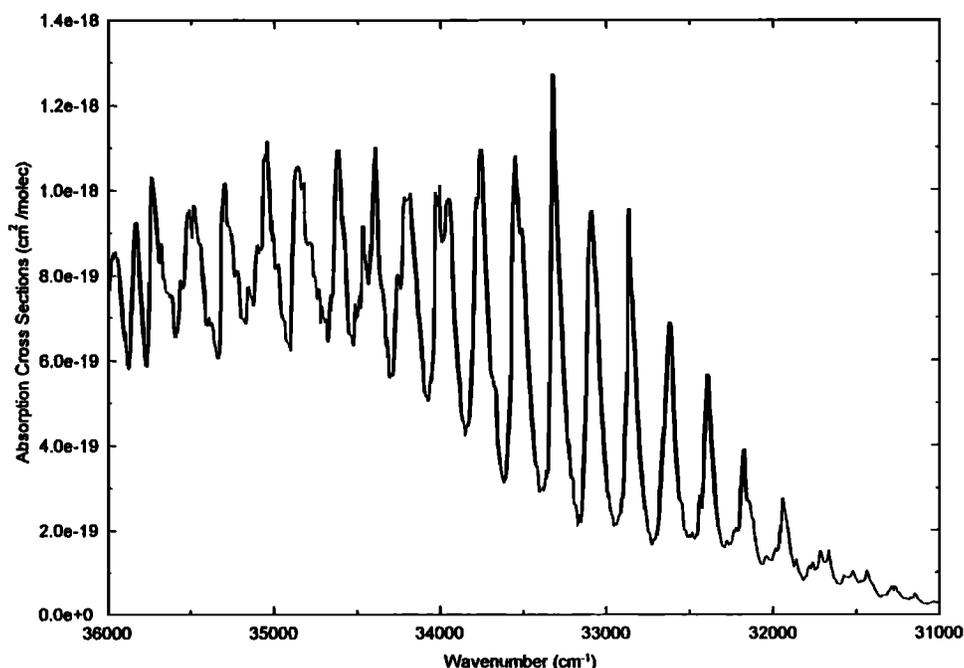


Figure 2. Absorption cross sections of SO₂ at the resolution of 16 cm⁻¹.

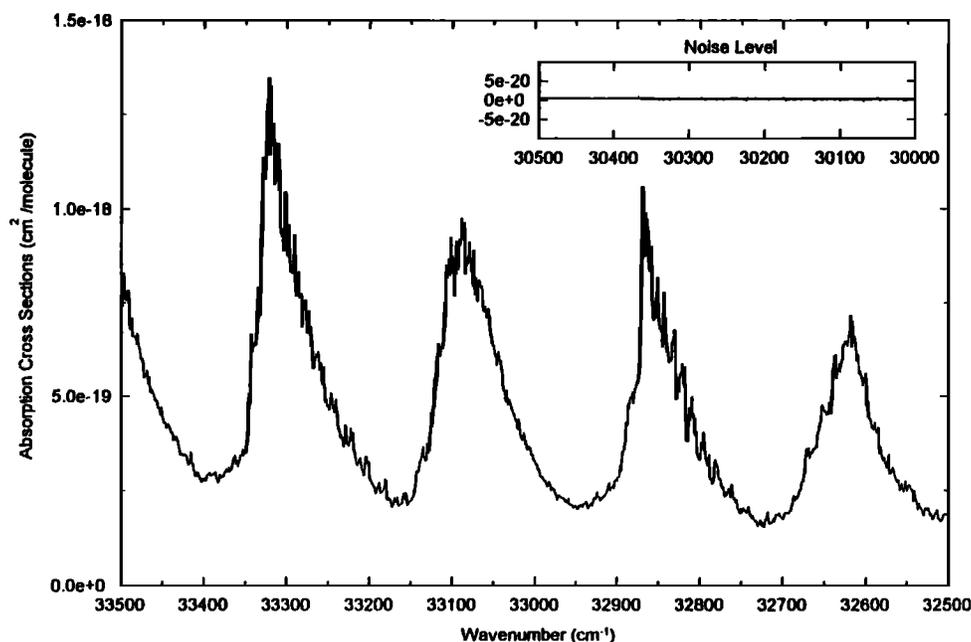


Figure 3. Absorption cross sections of SO₂ at the resolution of 2 cm⁻¹.

pathlength, presence of impurities in the samples (0.5% as estimated from the FTIR spectra), error on the absorbance due to the noise on the spectra, and fluctuations of the source which are unavoidable in the UV domain. The error on the absorbance for the spectra at 16 cm⁻¹ is lower than 0.1% in the 31800- to 37000-cm⁻¹ interval and is still lower than 1% between 30000 and 31800 cm⁻¹. It reaches 2.5% in the 27500- to 30000-cm⁻¹ and 37000- to 40000-cm⁻¹ regions. For the spectra at 2 cm⁻¹ this error remains lower than 0.2% between 31800 and 37000 cm⁻¹. The error due to the lamp drift can be estimated by looking at the intensity variation between the two reference spectra in each measurement and is of the order of 2% on the absorbance. The error budget is given in Table 2. A total rms value is also given which represents the square root of the sum of the squares of the individual errors. According to these figures the accuracy on the cross sections of SO₂ is of the order of 2.4%.

The reproducibility of our measurements was also checked by comparing all the cross sections obtained at 16 cm⁻¹ resolution (see Table 1) as well as the 2 cm⁻¹ resolution cross-section degraded to 16 cm⁻¹. All the measurements were found to agree well within the experimental uncertainty and no systematic

error, due to photochemical processes for instance, could be detected. The reproducibility is 2.5%, which compares well with the error stated in Table 2.

Discussion and Conclusion

The absorption cross sections measured in this work were compared to the data available from the literature.

A preliminary remark has to be made on the wavelength-wavenumber conversion which was necessary to apply in order to compare data from this work with data measured with grating spectrometers. With such instruments, wavelengths are usually reported in air (λ_{air}). Wavelength in vacuum (λ_{vac}) and wavenumber ν are related by

$$\nu = 1 / \lambda_{\text{vac}}$$

where λ_{vac} is determined from λ_{air} using the empirical relation,

$$\lambda_{\text{vac}} = 1.000\,273\,250 \times \lambda_{\text{air}} - 0.010\,7 + 196.24 / \lambda_{\text{air}} \quad [\lambda] = \text{\AA}$$

Table 2. Error Budget on Cross Section Measurements

	Error, %	
	Resolution, 16 cm ⁻¹	Resolution, 2 cm ⁻¹
Wavenumber Interval, cm ⁻¹	[31800-37000]	[31800-37000]
Optical path	0.5	0.5
Pressure	1	1
Temperature	0.4	0.4
Impurities in the sample	0.5	0.5
Source Drift	2	2
Absorbance	0.1	0.2
Total rms	±2.4%	±2.4%

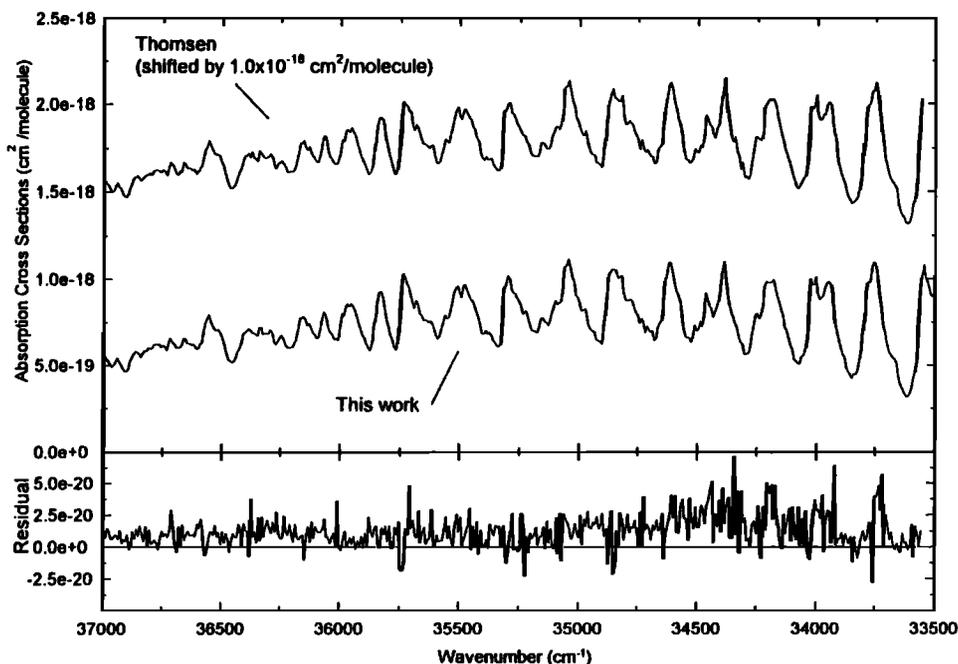


Figure 4. Comparison with the data of *Thomsen* [1990]. Values of *Thomsen* have been shifted by 1.0×10^{-18} $\text{cm}^2/\text{molecule}$ to make the comparison easier. Absolute residuals are also represented.

given by *Neckel and Labs* [1984]. The conversion of the energy scale may introduce artefacts, which could explain some of the spikes found in the residual between a spectrum obtained with the Fourier Transform Spectrometer (FTS) and a spectrum taken with a grating spectrometer. Moreover, it is almost impossible to degrade a spectrum, so that its new resolution perfectly matches the resolution of another spectrum. This produces yet other spikes in the residual. But the most important source of spikes comes from errors of calibration of the wavelength scale. It should be remembered that the wavenumber scale produced by

the FTS is more accurate and reproducible. However, wavelength scales produced by grating spectrometers may be shifted, stretched, or distorted. Moreover, as grating spectrometers usually work on smaller spectral regions, errors may be introduced when merging two scanned spectral regions. All these errors on the wavelength scale account for most of the spikes found in the residual.

Thomsen [1990] has measured SO₂ absorption cross sections between 265 and 298 nm. The stated resolution of these data is 0.03 nm. However, when compared to the values obtained at the

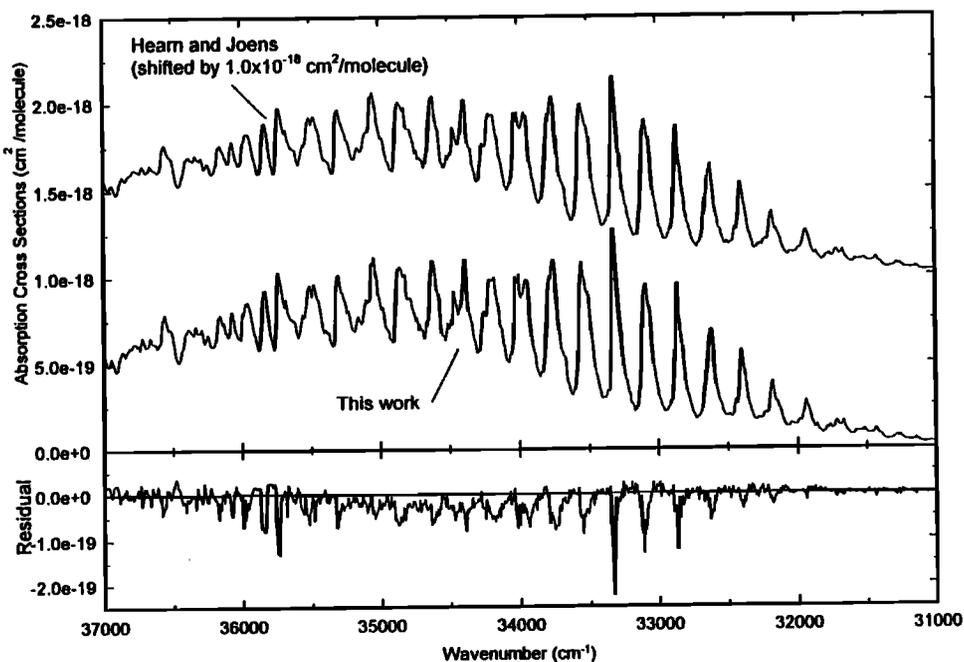


Figure 5. Comparison with the data of *Hearn and Joens* [1991]. Values of *Hearn and Joens* have been shifted by 1.0×10^{-18} $\text{cm}^2/\text{molecule}$ to make the comparison easier. Absolute residuals are also represented.

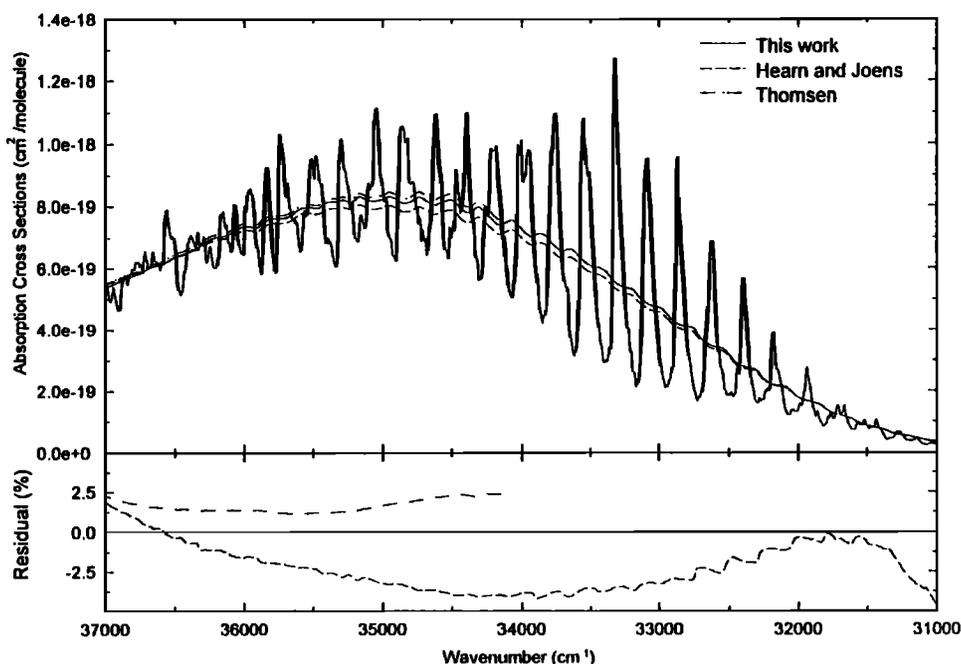


Figure 6. Comparison of the smoothed absorption cross sections with data of *Hearn and Joens* [1991] and *Thomsen* [1990].

resolution of 16 cm^{-1} , resolutions were found to be very similar. The data of *Thomsen* [1990] were therefore not convoluted and used directly without reduction of their resolution. Results are shown in Figure 4. Values of *Thomsen* [1990] have been artificially shifted, to make the comparison easier. Absolute differences between the two sets of data are also reported. The values of *Thomsen* [1990] are in good agreement (discrepancies less than 3%). They seem to be generally higher at the peaks and lower in the regions in-between.

The SO₂ cross sections have also been compared to the results of *Hearn and Joens* [1991]. This set of data, which extends from 230 to 340 nm and is given at the resolution of 0.06 nm, has been compared to the spectrum at 16 cm^{-1} without any correction for the resolution. As can be seen from Figure 5, the values of *Hearn and Joens* [1991] seem to agree well in the region between the absorption peaks but are systematically lower at the peaks (up to 20%). This could be due to the fact that our resolution seems better than the resolution at which the values of *Hearn and Joens* [1991] are given.

To eliminate the problems due to the wavelength-wavenumber conversion and differences in resolution, the smoothed cross sections have been compared. This technique, which is illustrated in Figure 6, consists in smoothing out all the absorption structures by using a running average over a large number of points, in order to calculate the mean cross sections. From Figure 6 it can be seen that the discrepancies between the data of *Thomsen* [1990] and the present data are constant over all the reported region and that differences with *Hearn and Joens* [1991] vary considerably over the same region. In the 31000- to 36500- cm^{-1} region, values of *Hearn and Joens* [1991] are lower than those found in this work, but the differences never exceed 5%. In the spectral range from 36500 to 37000 cm^{-1} , values of *Hearn and Joens* [1991] are greater than ours and the differences reach 2.5%.

This work provides new SO₂ absolute absorption cross sections measured at room temperature at the resolutions of 2 and 16 cm^{-1} . The comparison with other data sets shows important discrepancies. The use of a Fourier transform spectrometer does eliminate wavelength errors, and according to the error budget reported in this work, these new absorption cross sections are more accurate. They are also given at different resolutions making them very useful for various DOAS instruments measuring SO₂ either in the troposphere or from the satellites.

Upon request to the authors all spectra are available on floppy disks, either in wavenumber or in wavelength scales.

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References

- Ahmed, S. M., and V Kumar, Quantitative photoabsorption and fluorescence of SO₂ at 188-231 and 278.7-320 nm, *J. Quant. Spectrosc. Radiat. Transfer*, *47*(5), 359, 1992.
- Barke, E. S., Detection of SO₂ in the UV spectrum of Venus, *Geophys. Res. Lett.*, *6*, 117, 1979.
- Bertaux, J. L., and M. J. S. Belton, Evidence of SO₂ on Io from UV observations, *Nature*, *282*, 813, 1979.
- Brassington, D., Sulfur dioxide absorption cross-section measurements from 290 nm to 317 nm, *Applied Optics*, *20*, 3774, 1981.
- Edner, H., P. Ragnarson, S. Spännare, and S. Svanberg, Differential optical absorption spectroscopy (DOAS) system for urban atmospheric pollution monitoring, *Appl. Opt.*, *32*(3), 327, 1993.
- Finlayson-Pitts, B. J., and J. N. Pitts Jr., *Atmospheric Chemistry*, John Wiley, New York, 1986.
- Hearn, C., and J. A. Joens, The near UV absorption spectrum of CS₂

- and SO₂ at 300 K, *J. Quant. Spectrosc. Radiat. Transfer*, *45*(2), 69, 1991.
- Hurtmans, D., M. Herman, and J. Vander Auwera, Integrated band intensities in N₂O₄ in the infrared range, *J. Quant. Spectrosc. Radiat. Transfer*, *50*(6), 595, 1993.
- Jaechke, W., R. Schmitt, and H. W. Georgii, Preliminary results of stratospheric SO₂ measurements, *Geophys. Res. Lett.*, *3*, 517, 1976.
- Krueger, A. J., Sighting of El Chichon sulfur dioxide clouds with the Nimbus 7 Total Ozone Mapping spectrometer, *Science*, *220*, 1377, 1983.
- Leroy, B., P. Rigaud, J. L. Jourdain, and G. Le Bras, Spectres d'absorption dans le proche ultraviolet de CS₂ et SO₂ entre 200 et 300 K, *Moon Planets*, *29*, 177, 1983.
- Manatt, S. L., and A. L. Lane, A compilation of the absorption cross-sections of SO₂ from 106 to 403 nm, *J. Quant. Spectrosc. Radiat. Transfer*, *50*(3), 267, 1993.
- Martinez, R. D., and J. A. Joens, SO₂ absorption cross-section measurements from 197 nm to 240 nm, *Geo. Phys. Res. Lett.*, *19*(3), 277, 1992.
- McGee, T. and J. Burris Jr., SO₂ absorption cross-sections in the near UV, *J. Quant. Spectrosc. Radiat. Transfer*, *37*(2), 165, 1987.
- Möhler, O., and F. Arnold, Gaseous sulfuric acid and sulfur dioxide measurements in the arctic troposphere and lower stratosphere: Implications for hydroxyl radical abundances, *Geo. Phys. Res. Lett.*, *19*(17), 1763, 1992.
- Neckel, H., and D. Labs, The solar radiation between 3300 and 12500 Å, *Sol. Phys.*, *90*, 205, 1984.
- Plane, J. M., and C. Nien, Differential optical absorption spectrometer for measuring atmospheric trace gases, *Rev. Sci. Instrum.*, *63*(3), 1867, 1992.
- Platt, U., and D. Perner, Direct measurement of atmospheric CH₂O, HNO₂, O₃, and SO₂ by differential absorption in the near UV, *J. Geophys. Res.*, *85*, 7453, 1980.
- Pommereau, J. P., and F. Goutail, O₃ and NO₂ ground based measurements by visible spectrometry during arctic winter and spring 1988, *Geophys. Res. Lett.*, *15*(8), 891, 1988.
- Rothman, L. S. et al., HITRAN molecular database edition of 1991 and 1992, *J. Quant. Spectrosc. Radiat. Transfer*, *48*, 469, 1992.
- Sagawa, E., and T. Itoh, Mass spectrometric observations of SO₂ in the stratosphere, *Geophys. Res. Lett.*, *4*, 29, 1977.
- Sandroni, S., and C. Cerutti, Long path measurements of atmospheric sulfur dioxide by a Barringer Cospec III, *Atmos. Environ.*, *11*, 1225, 1977.
- Thomsen, O., Messung des Absorptionswirkungsquerschnitts von Schwefeldioxid im Wellenlängenbereich von 265 bis 298 nm, Diplomarbeit, GKSS 90/E/36 Forschungszentrum, Geesthacht, Germany, 1990.
- Vandaele, A. C., P. C. Simon, M. Carleer, and R. Colin, Detection of minor tropospheric constituents in the near UV by Fourier Transform Spectroscopy, in *Proceedings of the EUROTRAC Symposium 1992*, edited by P.M. Borell et al., 234 pp., SPB Academic Publishing, The Hague, Netherlands, 1993.
- Warneck, P., F. Marmo, and J. Sullivan, Ultraviolet absorption of SO₂: Dissociation energies of SO₂ and SO, *J. Chem. Phys.*, *40*, 1132, 1964.
- Wu, C., and D. Judge, SO₂ and CS₂ cross section data in the ultraviolet region, *Geophys. Res. Lett.*, *8*, 769, 1981.
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