

STUDY ON ABSORPTION CROSS-SECTIONS IN THE UV AND VISIBLE

EXECUTIVE SUMMARY October 1998

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EXECUTIVE SUMMARY

1 INTRODUCTION

Satellite-based remote sensing methods can be used for quantification of trace gas amounts in the Earth's atmosphere. These methods are used, for example, in connection with studies of ozone depletion chemistry. This type of quantification relies on measurements of electromagnetic radiation at the satellite and subsequent "retrieval" of the desired trace gas amounts from these measurements.

Many techniques have been developed for remote sensing of trace gas amounts in atmospheres, but it is only recently that relatively high resolution visible and absorption spectroscopy in the visible and UV (e.g. using a diffraction grating and a linear detector array), has been used from a space platform. Application of this method involves spectral measurements of solar radiation that has been scattered into the instrument field of view by the molecules and particles in the atmosphere. The measured spectra contain information on trace gases in the atmosphere by virtue of the absorption of radiation by those gases as the radiation travels from the sun to the point of scattering, and from the point of scattering to the spacecraft. The ESA Global Ozone Monitoring Experiment (GOME), which has been in orbit since April 1995, uses this technique.

In order to retrieve trace gas distributions from spectra recorded by instruments such as GOME it is essential to input into the retrieval process quantitative information that describes the interactions between electromagnetic radiation and the trace gases under study. The required information is *absolute* absorption cross-sections for all relevant gases as a function of optical frequency at appropriate physical conditions (e.g. pressure, temperature, mixing ratio) and appropriate instrument conditions (e.g. spectral coverage and resolution). Several approaches can be taken to obtain this information, and the one adopted for this study was to use laboratory-based absorption spectroscopy to measure *absolute* absorption cross-sections directly for the specified molecules at the specified physical and instrument conditions.

2 SCOPE OF THE STUDY

The molecules whose cross-sections were to be measured were specified in the original ITT to be O₂ (and the collision induced 'O₄'), NO₂, O₃, and SO₂. The physical and measurement conditions were specified to be: total pressures of 100 hPa and 1013 hPa, temperatures of 283 K and 223 K (plus 203 K and 246 K in the case of O₃), spectral coverage from 240 nm to 820 nm, spectral resolution better than 0.01 nm (0.02 nm in the region above 400 nm) and wavelength accuracy better than 0.002 nm. The absorption cross-sections were to be measured with an accuracy of 5%.

Although many of these requirements are very demanding, the world-class state-of-the-art facilities available to the study participants meant that in the majority of cases it was possible to meet, or exceed, these specifications. The physical and measurement conditions actually used in the measurements of the absorption cross-sections, and the consortium partner responsible for each part of the programme, are summarised in Table 1 on page VIII.

3 METHODOLOGIES EMPLOYED

The work done at each institute used a high resolution interferometric spectrometer (e.g. a Bruker IFS120HR) coupled optically to absorption cells instrumented with temperature and pressure sensors in which the gases under study could be contained. In all cases, pressure and temperature monitoring was carried out using capacitance manometers and thermistors, thermocouples and platinum resistance thermometers.

At RAL the experimental set-up included a Bruker IFS120HR spectrometer, and an adjustable long path absorption cell (LPAC). The former allowed full coverage of the 800 nm to 455 nm spectral region which includes most of the significant absorptions due to O₂ and O₄ which are required to be quantified in connection with the retrieval of trace gases from GOME data. The LPAC gives variable absorption pathlengths up to a maximum in excess of 512 m at temperatures from room temperature to > 200 K.

The spectrometer used at IC permitted coverage of the 244 nm - 270 nm spectral region where additional O₂ absorptions occur, and also the 233 nm - 345 nm spectral region where SO₂ absorbs. Absorption cells used at IC were a long path cell (61.6 m) at room temperature for the O₂ measurements, and a short path cell coolable to < 200 K for the SO₂ measurements.

The IFE group also used a Bruker IFS120HR and in their set-up. This spectrometer was coupled to an absorption cell, which was coolable to 200 K and which had a maximum pathlength of 19.45 m.

A typical experimental set-up is shown in Figure 1. Radiation from a broadband source of radiation S is collimated and passes through the interferometer. The degree of collimation is defined by the size of the aperture A1. The beam splitter BS divides the radiation such that part travels toward mirror M1 and part toward M2. These are retro-reflectors, which return the radiation to the beam splitter, where interference takes place. The interference depends on the optical path difference (BS to M1 and back minus BS to M2 and back). Linear movement of mirror M1 imposes a sinusoidal amplitude modulation on the intensity of radiation leaving the beam splitter BS in the direction of the detector D. The radiation passes through an optical filter F, which defines the optical band-pass of the spectrometer, a second aperture A2 and an absorption cell in which the vapour under study is contained. The detector converts variations in the incident radiation intensity into an electrical signal. Each optical frequency in the source radiation produces a corresponding electrical frequency in the detector output by virtue of the interference occurring at the beam splitter and the linear movement of mirror M1. The detector output is digitised and processed by application of a Fourier transform. This produces a measurement of the distribution of the intensity of radiation falling on the detector according to its optical frequency. The spectral resolution of the instrument (i.e. its ability to discriminate between optical frequencies in the source) is a function of A1 and the distance the mirror is moved in the interferometer.

The absorption spectrum of the sample in the absorption cell is typically measured in a two-stage process. Firstly a spectrum is recorded with the cell empty (background spectrum). Secondly the cell is filled with the sample and another spectrum recorded (sample spectrum). On the assumption that the only effect of the sample is to absorb some of the radiation passing through the cell, a transmittance spectrum of the sample can be obtained by ratioing the sample spectrum by the background spectrum.

The procedure for SO₂ was somewhat different because of the stability of the UV sources used. In this case two spectra were recorded simultaneously: a sample spectrum from a light path, which included the absorption cell containing the SO₂ / N₂ mixture, and a background spectrum from a light path, which included a similar absorption cell that was evacuated. This was possible

because the spectrometer used at IC has two outputs. (The spectrometers used at RAL and IFE had only one output.)

For some molecules, notably oxygen, the absorption spectra consist of semi-regular narrow absorption lines with clear regions of zero absorption between them. In this situation it was not necessary to record background spectra separately because the sample spectra also contained sufficient information on the background, which could be readily inferred across the whole spectrum from the regions of zero absorption. Most sample spectra were recorded with the cell filled with gas and then sealed. However, in the case of the O₃ and some of the NO₂ measurements the gases were flowed through the absorption cell.

A very wide range of absorption cross-sections had to be measured for each molecule. This necessitated recording many spectra with different numbers of absorber molecules in the optical path so that optimum photometric conditions could be used. For example, the NO₂ measurements were done in four spectral regions. Adjustment of the absorber amounts was carried out either by adjusting the pathlength or adjusting the absorber partial pressure. In some cases it was not possible to achieve optimum photometry due to, for example, restrictions on maximum achievable pathlength. Consequently it was also necessary to ensure that measurements of the cross-section at a given wavelength, using different measurement conditions, gave consistent results. This was achieved by carefully considering the measurements in the overlaps between adjacent spectral regions.

Once the transmittance has been measured, absorption cross-sections could be derived. The napierian absorbance, $A(\lambda)$, is defined as $-\ln t(\lambda)$ where $t(\lambda)$ is the transmittance at the optical wavelength λ . The absorption cross-section is then given by $\sigma(\lambda) = \frac{A(\lambda)}{nl}$, where n is the number density of absorbing molecules in the cell, and l is the pathlength for radiation passing through the cell.

The number density n is related to the partial pressure of the absorber gas P and the gas temperature T through the relationship $n = \frac{273.13 \times L_0 P}{1013.0 \times T}$, where L_0 is Loschmidt's number. In this report, n is given in molecule cm⁻³, P in hPa, T in Kelvin, l in cm, λ in nm and $\sigma(\lambda)$ in cm² molecule⁻¹. Loschmidt's number has the value of 2.69×10^{19} cm⁻³. The optical frequency unit of wavenumber ($\tilde{\nu}$) in cm⁻¹ is also employed.

4 ASSESSMENT OF ERROR BUDGETS AND DEFINITION OF MEASUREMENT PROCEDURES

Before embarking on the absorption cross-section measurements, each responsible institute carried out a detailed assessment of the equipment to be used in those measurements and the procedures to be adopted to ensure that data of the required quality could be obtained. Many aspects of the experimental set-ups were considered, including:

- Signal to noise ratios.
- Accuracy and repeatability of the "full scale" and "zero" photometric outputs. These aspects of system performance are influenced by factors such as the stability of light sources, and mechanical or thermal deformations of the light path through absorption cells. It is particularly important to ensure that these effects do not affect measurements of very weak broadband absorptions, such as those due to O₄.

- Optical frequency calibration. This was achieved by including a cell of iodine in the optical light path. Iodine has many sharp absorptions in the visible spectral region whose optical frequency are known to an accuracy sufficient for this study.
- absorption pathlength determination
- Determination of total pressure and partial pressure of the absorbing gas. This included accounting for chemical and adsorption effects on surfaces, characterising mixing methods, and correction for the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium.
- determination of sample temperatures

5 SYSTEM DEVELOPMENTS REQUIRED FOR SUCCESSFUL EXECUTION OF THE STUDY

Although the participants had world-class facilities at their disposal for application to the cross-section measurements, each had to develop their systems to some extent to permit a successful outcome to the study.

For RAL this included completion of the optical interface between the spectrometer and the LPAC and the relocation of a filter wheel and silicon detector from their standard positions in the spectrometer optical chain to the output beam from the LPAC. Much time was spent by the RAL group in characterising the baseline stability to a point where accurate measurements of the very weak (<1%) absorptions by O_4 could be measured successfully.

The IFE spectrometer was delivered from the manufacturer only shortly before the start of the study and a complete optical interface to the multi-pass cell had to be designed and built. Furthermore the methodology for determining the amounts of NO_2 in the absorption path had to be developed.

The two-port measurements on SO_2 by the IC group involved significant modifications to the electronics and software that controlled their spectrometer and performed the data acquisition and processing.

On the data analysis, significant effort was required at RAL to develop the software for generating line parameters.

6 MEASUREMENT OF ABSORPTION CROSS-SECTIONS

Spectral measurements of cross-sections for all the molecules and the associated errors are reported. Brief descriptions of the measurements follow.

O_2 and O_4 in the visible spectral region

These measurements were carried out at RAL using zero grade air or pure oxygen in the LPAC at optical pathlengths up to 256.75 m. Figure 2 shows a transmittance spectrum in which the principal absorption features of these molecules can be seen. Note the weakness of some of the absorptions, even at these long pathlengths. Many spectra such as these were recorded to allow O_2 cross-sections over the full range of specified conditions to be determined, with the exception of the γ band which could only be measured at 1000 hPa pressure. It was only possible to determine O_4 cross-sections in 1000 hPa samples of pure oxygen, due to the extreme weakness of these features.

O_2 in the UV spectral region

These measurements were carried out at IC using mixtures of oxygen and nitrogen gases in a multi-pass absorption cell with a pathlength of 61.58 m. Only measurements at room

temperature were possible with this cell. Figure 3 shows a spectrum of absorption cross-sections from this part of the project.

Ozone

The ozone cross-sections were measured at IFE Bremen using a quartz multi-pass absorption cell set to pathlengths up to 9.85 m. The ozone was generated using a silent discharge in oxygen and the flow rate of oxygen adjusted to give a suitable depth of absorption by the ozone. Nitrogen gas was added to give the desired total pressure, and the full range of specified measurement conditions was studied. Figure 7 shows the temperature dependence of measured absorption cross-sections for O₃ in a mixture with O₂ and N₂ at a total pressure of 1000 hPa.

Nitrogen Dioxide

Absorption cross-sections in NO₂ were measured by the IFE Bremen using a quartz multi-pass cell with path lengths up to 5.05 m. Due to the difficulty of correcting for the formation of significant quantities of N₂O₄ at cold temperatures in a static experiment, an arrangement was used in which the NO₂/ N₂O₄ was flowed through the absorption cell in a stream of N₂. Background spectra were recorded with the flow of NO₂/ N₂O₄ turned off, but with the flow of N₂ continued to maintain the total pressure in the cell. Figure 5 shows the measured NO₂ cross-sections and also illustrates the different spectral regions in which measurements were made using different absorber amounts (optical densities).

Sulphur Dioxide

Absorption cross-sections in SO₂ were measured by the group at IC using a two-port interferometer with a short single-pass absorption cell in one beam and a dummy cell in the other. The full range of sample conditions was studied. Figure 6 shows one example of measured cross-sections.

7 MEASUREMENT OF LINE PARAMETERS

The oxygen absorption spectra in the visible region were also analysed at RAL to extract individual line parameters, particularly line centre frequencies, line strengths and pressure broadening parameters. This was done by fitting calculated spectra, which included the instrument line shape function, to the measured spectra. A non-linear least squares method, in which the line frequency, strength and width were adjustable parameters, was used. The calculations proceeded from a first guess spectrum to a final spectrum which was identical to the measured spectrum within pre-determined limits. This procedure is illustrated in Figure 4.

8 AVAILABILITY OF SPECTRAL DATA

All the absorption cross-section data, and the oxygen line parameters, are available on CD-ROM obtainable from ESA (contact Jorg Callies by email at jcallies@jw.estec.esa.nl). At the time of writing the O₂ and O₄ absorption cross-sections are available on-line through the RAL Molecular Spectroscopy Facility Web site (<http://ssdsmsf1.ag.rl.ac.uk/msfdata/>) and the O₃ and NO₂ absorption cross-sections through the IFE Web site (<http://www-iup.physik.uni-bremen.de/gruppen/Data.html>).

9 CONCLUSIONS

New measurements of absorption cross-sections in the UV and visible spectral regions for molecular oxygen and its collision-induced O₄, ozone, sulphur dioxide and nitrogen dioxide have been made over a range of physical conditions.

In the case of the oxygen A and B bands, individual line parameters have been measured. Generally a sufficiently high spectral resolution has been employed to ensure that the derived cross-sections are not affected by spectral saturation effects. A full error analysis has been carried out and the uncertainties in the spectroscopic parameters are also reported. Consequently, major improvements to the knowledge of the spectroscopy of these molecules for application to remote sensing using high visible and UV spectroscopy from space have resulted from this study.

The new FTS absorption cross-section spectra of O₃ and NO₂ are a unique set of reference data for atmospheric remote sensing. These data cover a broad spectral range with very high wavelength accuracy. This is important in order to evaluate previous reference data recorded using grating spectrographs. The fact that O₃ and NO₂ cross-section spectra are now available for nearly all atmospheric temperatures and pressures is important for the spectroscopic retrieval of stratospheric and tropospheric O₃ and NO₂ column densities. The high resolution of the new spectra will be used for atmospheric remote sensing of O₃ and NO₂ by ground-based Fourier transform spectroscopy and laser absorption spectroscopy.

This work includes the most comprehensive study to date of the visible bands of oxygen. The cross-section data reported here are the first measurements at the specified range of conditions of pressure, temperature and mixing ratio. These data are of improved accuracy when compared to the few literature values at similar conditions for which an error analysis is available. Significant improvements have been made to line parameters in the A and B bands, particularly air broadening coefficients and pressure shifts, for which very little room temperature data and virtually no low temperature data existed previously.

For SO₂ a new two-beam method of observation that avoids errors due to source instability has been used.

The data acquired during this study are available either on CD-ROM through ESA, or, in most cases, through the consortium partners' Web sites.

10 PUBLICATION OF RESULTS

Absorption Cross-sections: O₂/ O₄ in the Visible

"Visible Absorption cross-sections and integrated absorption intensities of molecular oxygen (O₂ and O₄)"

D A Newnham, W J Reburn and J Ballard

J Geophys Res, submitted 1998

Absorption Cross-sections: NO₂ in the UV and Visible

"The Near-Infrared Bands of NO₂ observed by High-Resolution Fourier-Transform Spectroscopy"

J. Orphal, S. Dreher, S. Voigt, J. P. Burrows, R. Jost, A. Delon

Accepted for publication J. Chem. Phys. (1998)

"Absorption Cross-Sections of NO₂ in the 230-790 nm range at Atmospheric Temperatures and Pressures"

S. Voigt, J. Orphal and J. P. Burrows,

To be submitted to Chem. Phys. Lett. (1998)

Absorption Cross-sections: O₃ in the UV and Visible

"Absorption Cross-Sections of O₃ in the 230-790 nm range at Atmospheric Temperatures and Pressures"

S. Voigt, J. Orphal and J. P. Burrows,

To be submitted to Chem. Phys. Lett. (1998)

Absorption Cross-sections: SO₂ in the UV

"Upgrading the atomic and molecular database for astrophysics and atmospheric physics by Fourier transform spectroscopy."

J. C. Pickering, R. Schermaul, G. Cox, A. P. Thorne, R. C. M. Learner and P. Smith

In press, NIST Special Publication, 1998.

Molecule (Target gas/buffer gas)	Responsible Institute ¹	Spectral region ²	Nominal Pressures hPa (Target gas / Total)	Nominal Temperature K	Spectral resolution nm
O ₂	RAL	A Band	20/100	283, 223	<0.002
/zero grade air			200/1000	283, 223	
		B Band	20/100	283, 223	
			200/1000	283, 223	
		γ Band	200/1000	283, 223	
O ₂ /O ₂		γ Band	1000/1000	283	
O ₂ / N ₂	RAL / IC	270.2 - 243.9	200/400	296	<0.0004
		nm	200/600		
			200/800		
			200/1000		
O ₄ / O ₂	RAL	Visible bands	/1000 see note 3	283, 223	<0.2
SO ₂ / N ₂	IC	300 nm	3.5/100	280, 223	<0.02
		band system	3.5/1000		
			8/100		
			8/1000		
NO ₂ /N ₂	IFE	230 - 833 nm	/ 100 see note 4	293, 280, 260, 246,223	0.03 - 0.005
			/ 1000 see note 4		
O ₃ /O ₂ /N ₂	IFE	220 – 800 nm	/100 see note 5	293, 280, 246, 223,203	0.02 – 0.3
			/1000 see note 5		

Table 1: Summary of physical and measurement conditions employed for the study

Notes:

¹ RAL = Rutherford Appleton Laboratory, IC = Imperial College, IFE = Institute of Remote Sensing, University of Bremen.

² Regions of significant absorption by the target molecule

³ The O₄ absorptions measured here are more properly described as absorptions that are induced when two O₂ molecules collide. They are expressed in terms of the number density of O₂ molecules, so the only pressure of relevance is the total pressure.

⁴ NO₂ exists in equilibrium with its dimer N₂O₄. The partial pressure of NO₂/ N₂O₄ in N₂ was determined by a volumetric method, and the NO₂ amount deduced using the known equilibrium constant for the dimer formation.

⁵ Derivation of cross-sections was made by scaling to previous measurements made with the GOME Flight Model Instrument. The determination of cross-sections from the GOME FM measurements was based on titration to NO₂ and used the NO₂ absorption cross-sections at room temperature obtained in this study

⁶ Checks against "known" positions of iodine spectral lines showed that the FTS wavenumber measurements differed by less than the stated accuracy of the iodine atlas (0.006 cm⁻¹). Thus the FTS measurements were well within the 0.002 nm accuracy required for the study.

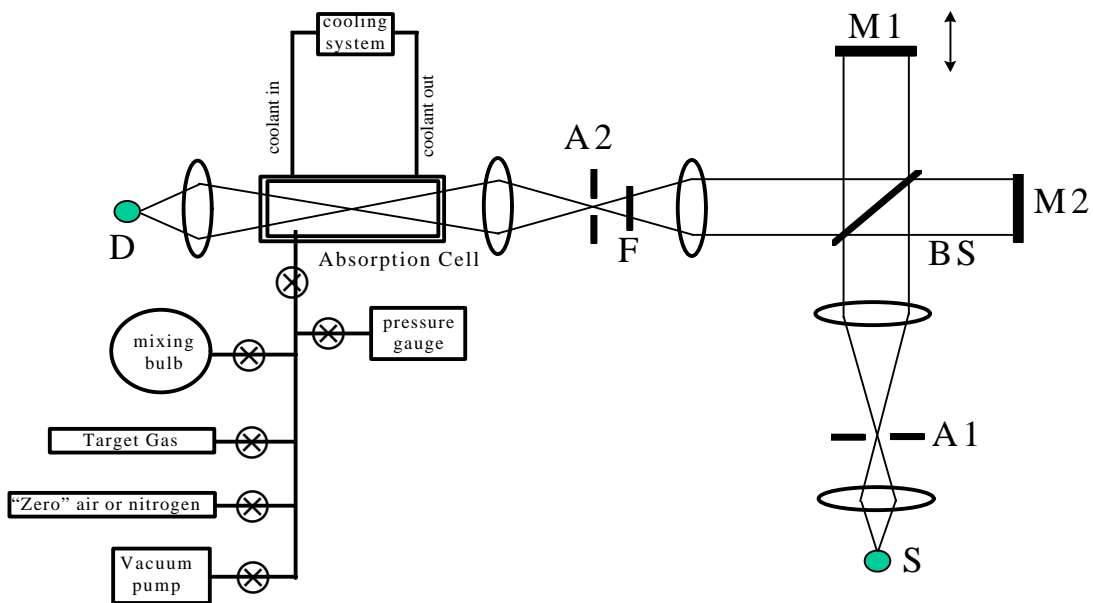


Figure 1: Typical experimental set-up in schematic form.

In practice most optical components are mirrors. The set-up at IC used a two-port interferometer with a reference cell in the second port.

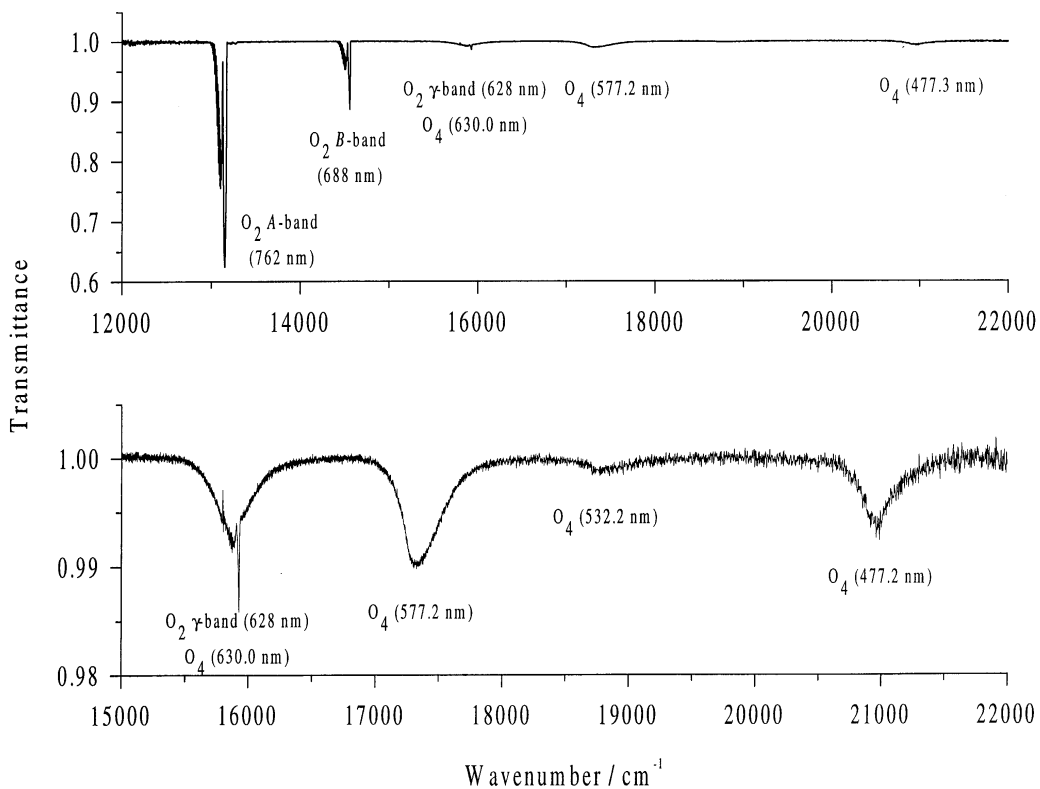


Figure 2: Transmittance spectrum of molecular oxygen and the collision-induced O_4 in the visible spectral region

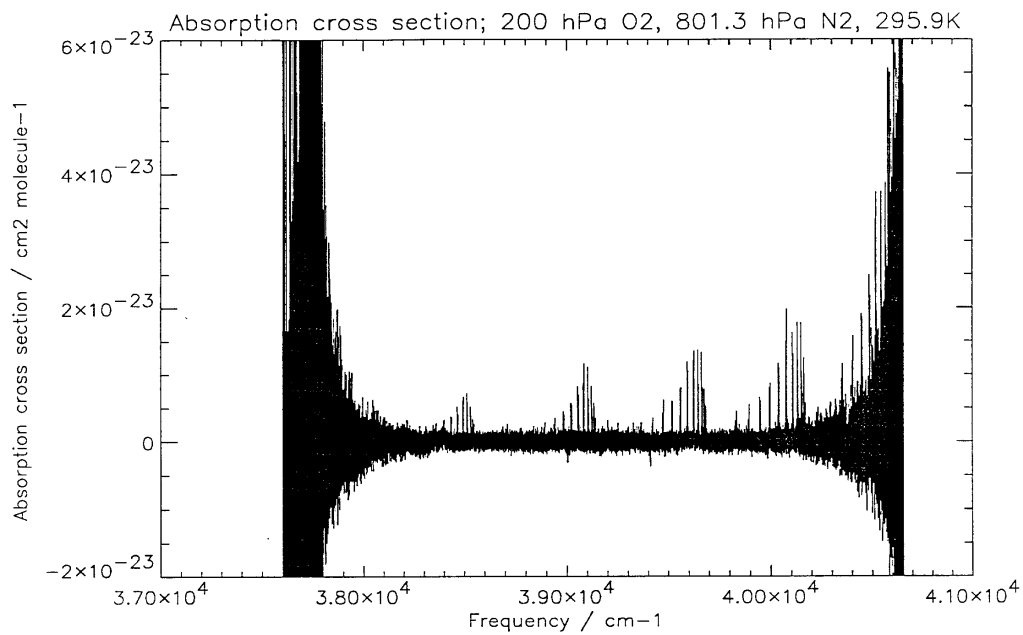


Figure 3: Molecular oxygen cross-sections in the UV spectral region

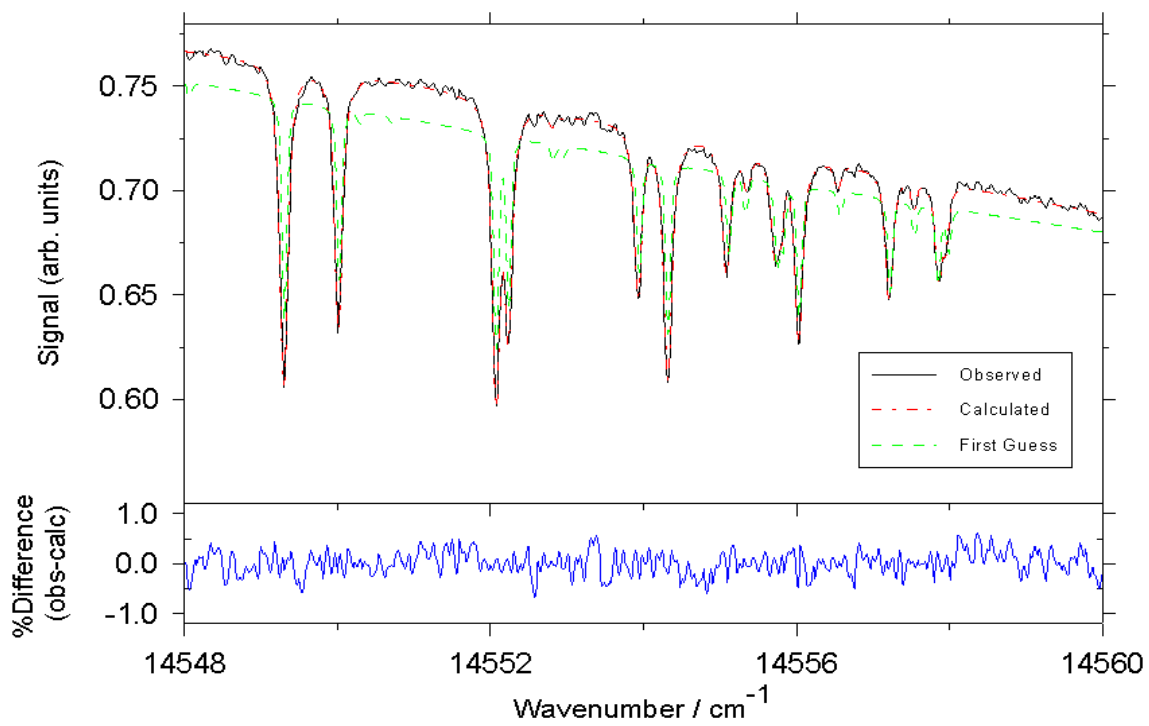


Figure 4: Non-linear least squares fit of a calculated spectrum to a measured spectrum of molecular oxygen in the visible spectral region

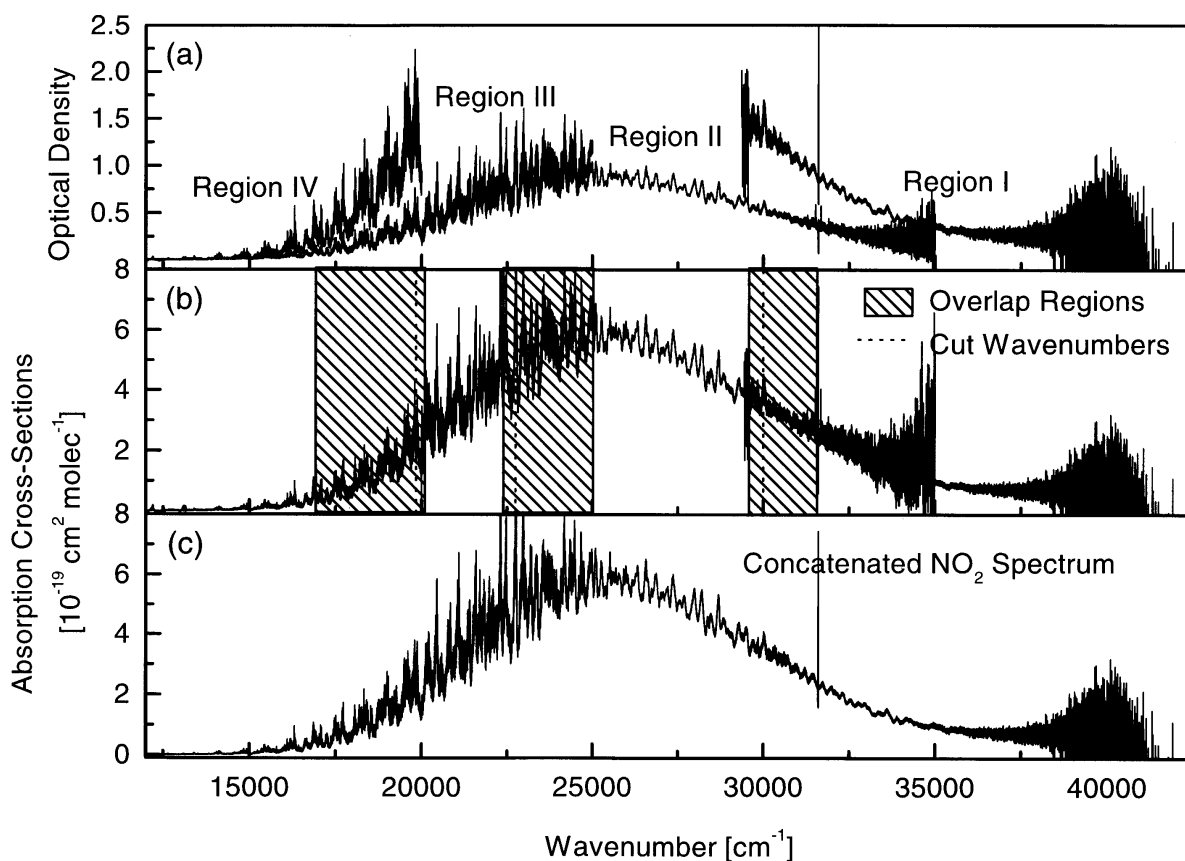


Figure 5 Measured nitrogen dioxide cross-sections

This illustrates the four spectral regions in which measurements were made at different absorber amounts (optical densities) and the overlap regions that were used to ensure consistency of the measurements.

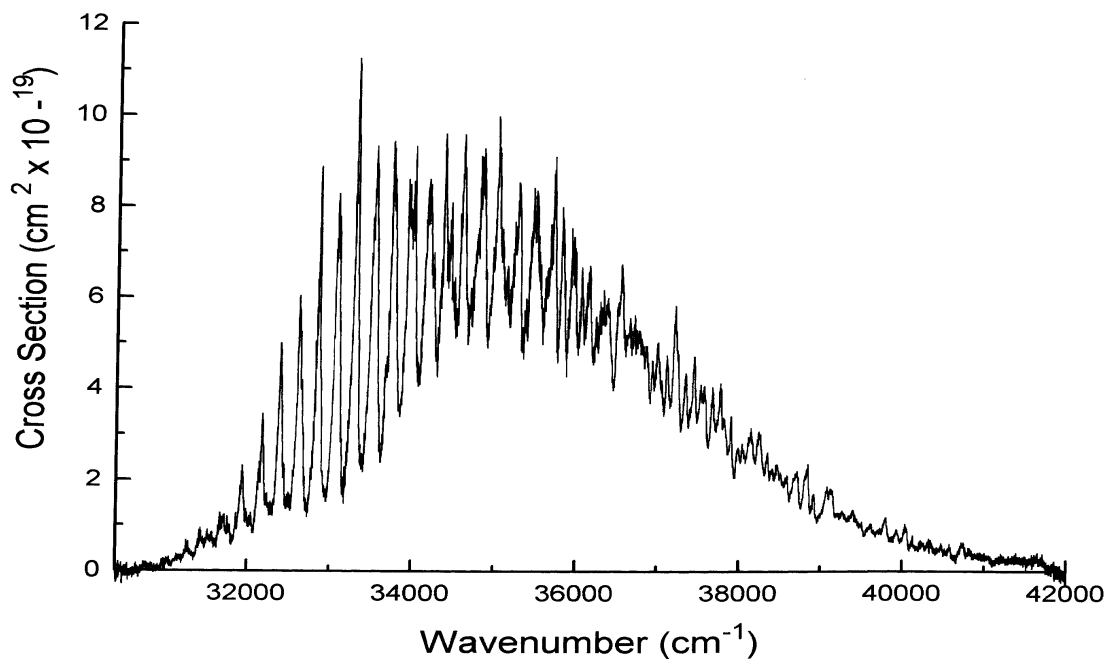


Figure 6: Measured sulphur dioxide cross-sections

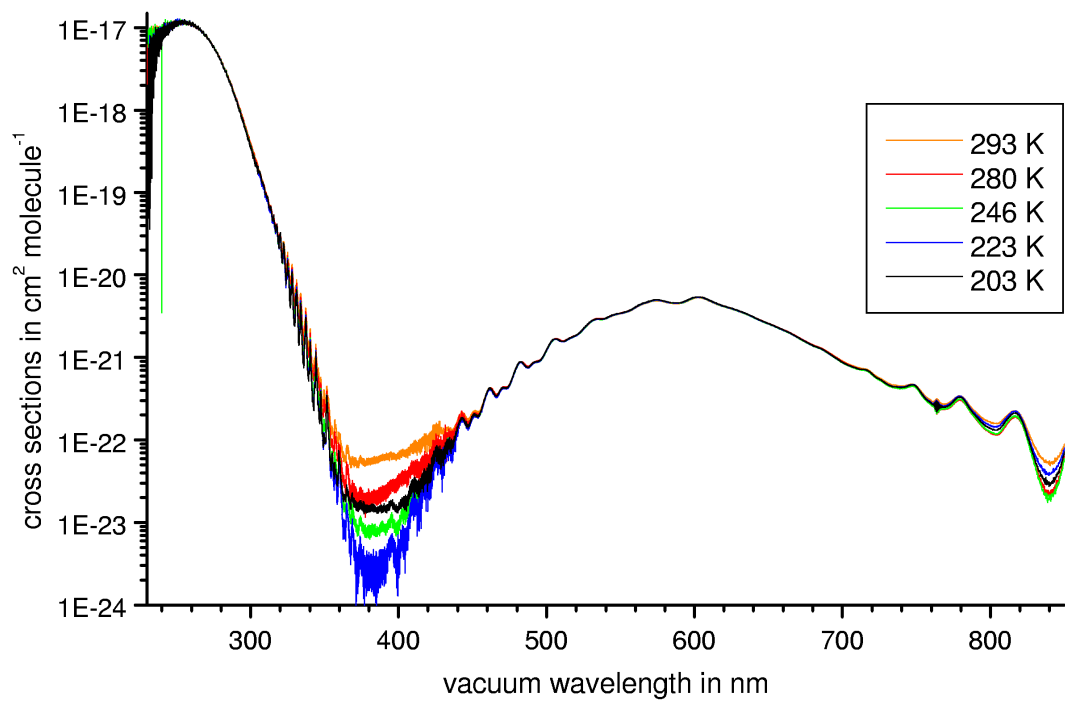


Figure 7: Temperature dependence of ozone absorption cross-sections