

## **Supplementary material for**

### **“Simultaneous satellite observations of IO and BrO over Antarctica”**

#### **On the temperature dependence of the absolute and differential IO absorption cross sections in the 400-470 nm spectral range**

##### **1. Experimental methods**

The experimental set up has been described in detail in previous publications (Gómez Martín et al., 2005; Gómez Martín et al., 2007). Iodine oxides were generated in a double-jacketed 120 cm long and 5 cm diameter quartz reaction vessel, by flash photolysis of I<sub>2</sub>/O<sub>3</sub> mixtures carried in a stable, laminar, slow flow of N<sub>2</sub> and O<sub>2</sub>. The outer jacket of the reactor was evacuated for thermal isolation, while a cooling fluid (ethanol) was pumped through the inner jacket by a cryocooler (Haake KT90). A stable flow of I<sub>2</sub> was produced by passing N<sub>2</sub> through a thermostated and pressure stabilised glass trap containing I<sub>2</sub> crystals. This flow could be diluted by an additional flow of pure N<sub>2</sub>. Care was taken to keep the I<sub>2</sub> partial pressure in the reactor well below the vapour pressure at the corresponding temperature, in order to prevent condensation on reactor surfaces and optics. O<sub>3</sub> was produced by passing a stream of O<sub>2</sub> through a home made silent discharge ozonizer. The flows were controlled by using calibrated mass flow controllers (MKS instruments) ranging from 100 to 10000 standard cm<sup>3</sup> per minute (sccm).

The I<sub>2</sub>+N<sub>2</sub> and O<sub>3</sub>+O<sub>2</sub> gas flows were mixed and pre-cooled before entering the reactor. A cooling thermostat (Haake KT90) was used to cool the gas mixtures down to the target temperature (233 K to 298 K). Temperature was monitored by two resistance temperature detectors (PT100) situated inside the reactor. The temperature inside the

reactor was stable within  $\pm 2$  K. Calibrated capacitance barometers (MKS instruments) in the range of 100 and 1000 hPa were used to monitor the pressure, which was varied between 10 and 600 hPa for each target temperature.

IO and OIO were monitored by optical absorption spectroscopy, by combining a multipath white optic system inside the reactor with a 500 cm spectrometer and a CCD camera operating in kinetic mode (Rowley et al., 1996; Gómez Martín et al., 2005). A 150 grooves/mm grating was used in order to cover a wide spectral range (300-600 nm) containing absorption features of all relevant chemical species (FWHM=1.3 nm at 546 nm). The approach for spectral deconvolution of IO, I<sub>2</sub>, OIO and higher iodine oxides was the same followed by Spietz et al. (Spietz et al., 2005) at room temperature

## **2. Results**

No pressure dependence of the IO spectrum was observed between 10 and 600 hPa, apart from the well know pressure effect on the highly structured (2-0) band. Therefore, a spectrum for each temperature was calculated by averaging the spectra taken at different pressures. These relative spectra were scaled to absolute absorption cross sections by normalising them to the area under the curve and multiplying by the area under the absorption cross sections measured at 298 K, based on the fact that the overall probability of transition between two electronic states does not depend on the particular occupation of ro-vibronic energy levels (i.e. on temperature) (Fleischmann et al., 2004). The IO bands narrow down and grow higher as temperature decreases (see Fig. S1). The peak values of the relevant bands for DOAS retrieval change significantly with temperature in the range between 298K and 273K. Between 273 K and 233 K changes in the (4-0) band height are small, which could be a scaling problem due to the higher level of noise in the 233 K and 243 K spectra. The peak values of the differential

absorption cross sections IO(5-0), IO(4-0) and IO(3-0) increase by 17%, 29% and 39% respectively from 298 K to 233 K. The valleys tend to be deeper as temperature decreases, implying a further increase in the differential cross section. On the other hand, the hot bands with  $v'=1$  become smaller with decreasing temperature.

A discussion of the OIO spectrum is beyond the scope of this paper. However, it is worth mentioning that it does not show any significant temperature dependence in the range of atmospheric temperatures.

### 3. Discussion

The effect of temperature on the IO absorption cross section is analogous and comparable in magnitude to the effect observed on the BrO spectrum (Fleischmann et al., 2004). Spectral simulations with the computer program PGOPHER (Western, 2009) show that the cause of the change in shape and height of the IO bands with temperature is a shift in the population of rotational levels within the ground vibrational state. By decreasing the temperature, the lines of both the P and the Q branches with larger rotational number  $J$  become weaker and the lines with lower  $J$  become stronger, indicating a reduction of the population of rotational levels of  $v''=0$  with higher  $J$  (see fig. S2). As a result of strong pre-dissociation, Lorentz line broadening washes out the rotational structure of the more prominent bands (Newman et al., 1998).

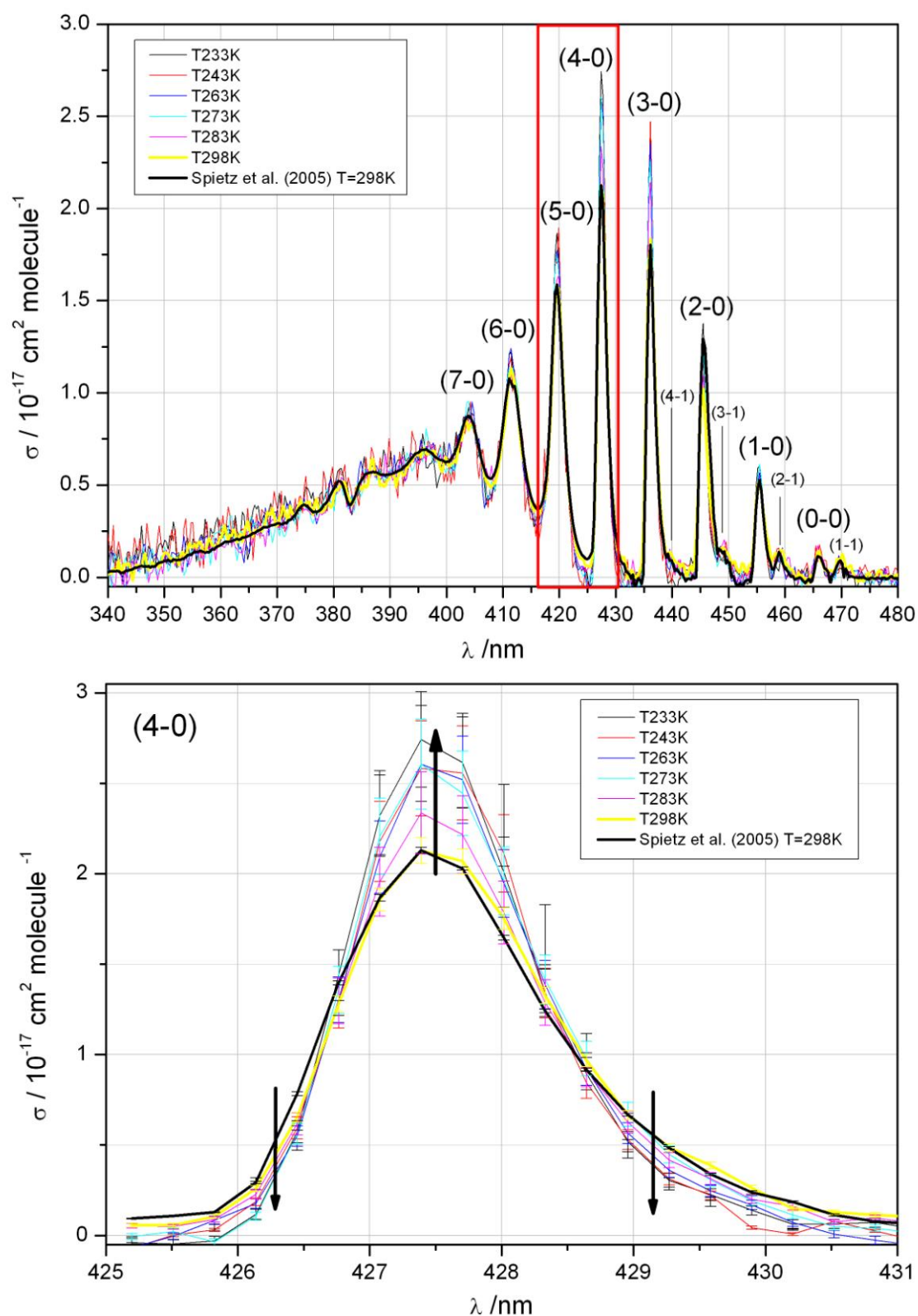
Changes in the population of vibrational levels, although implying a change in  $v''=1$  bands, do not contribute significantly to the temperature dependence observed for the  $v''=0$ . The occupation of the 1<sup>st</sup> vibrational excited state of the ground electronic state goes from ~4% at 298 K down to ~2% at 233 K, and this slightly increases the integrated cross section of the  $v''=0$  band system, but not the band shapes.

In order to estimate the effect of using 298 K reference cross sections for atmospheric

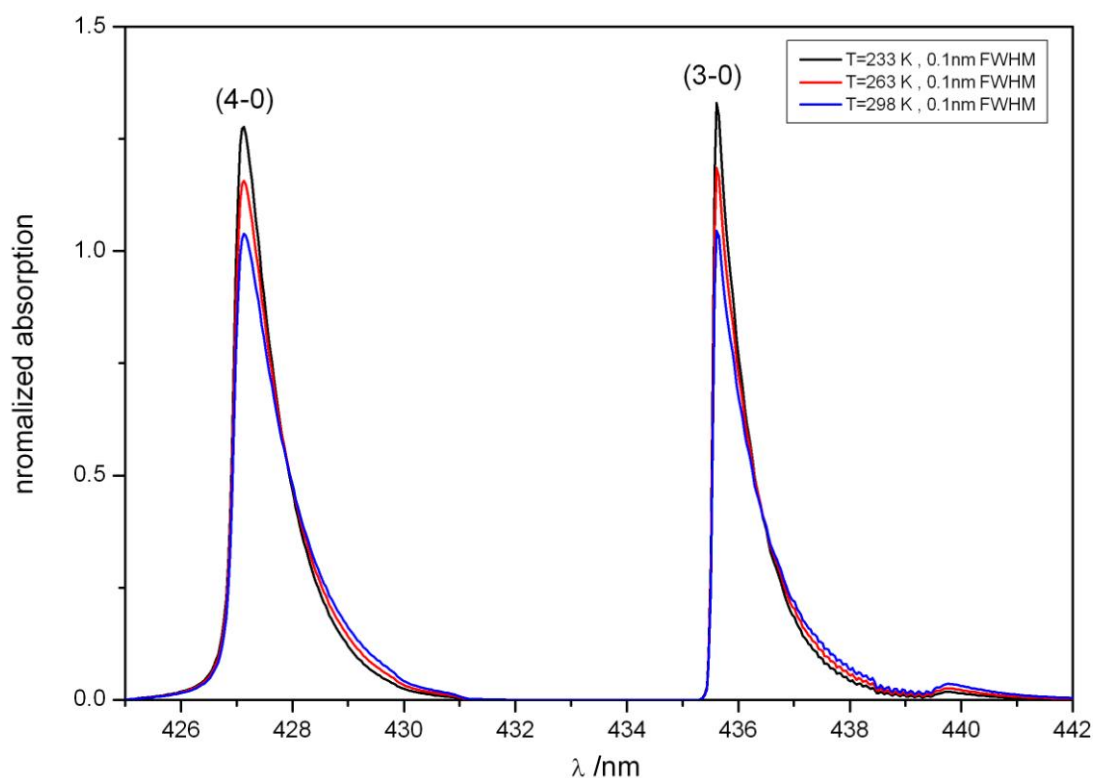
retrieval at lower temperatures, the scaling factor between the 298 K and the 243 K differential spectra has been calculated by linear regression (Figure S3). From this analysis a factor of 1.2 is obtained, implying that concentrations or column densities over Polar Regions are overestimated by ~20% when using the room temperature reference spectrum. Also the quality of the fit is affected as result of the band shape differences.

The temperature dependence of the (4-0) peak cross sections reported in the literature are summarised in Fig. S4 (Sander, 1986;Harwood et al., 1997;Bloss et al., 2001). The possible reasons for the observed discrepancies have been discussed by Bloss et al. (Bloss et al., 2001), who found a temperature dependence in reasonable agreement with the results presented here.

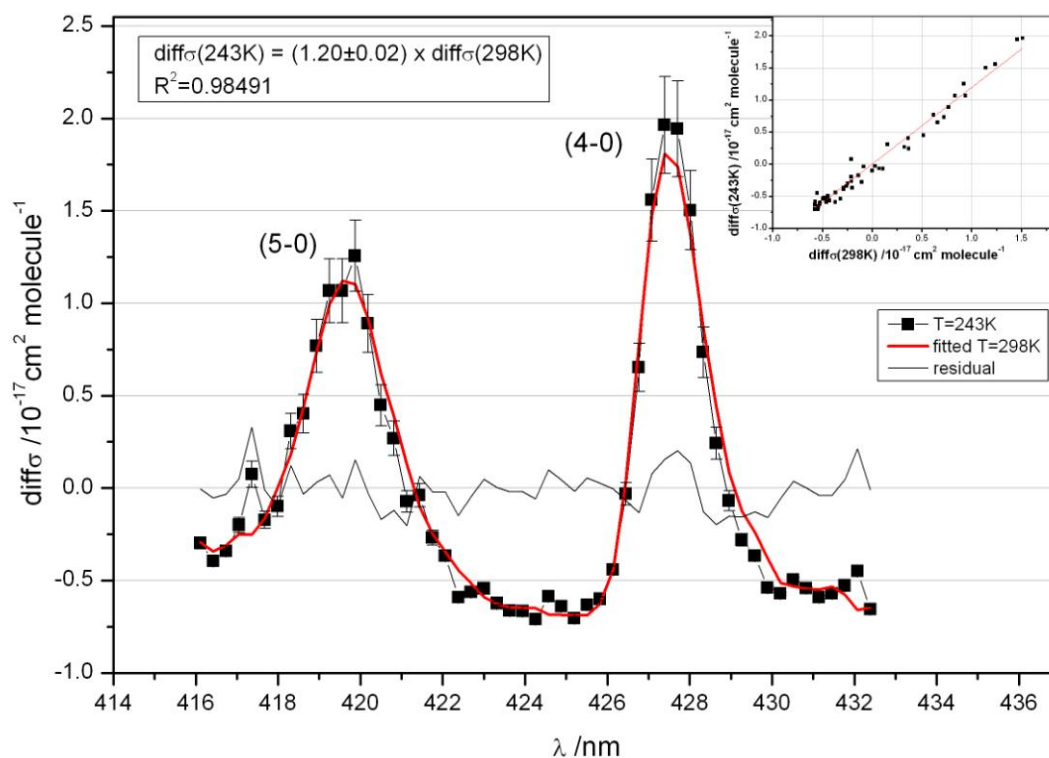
## 4. Figures



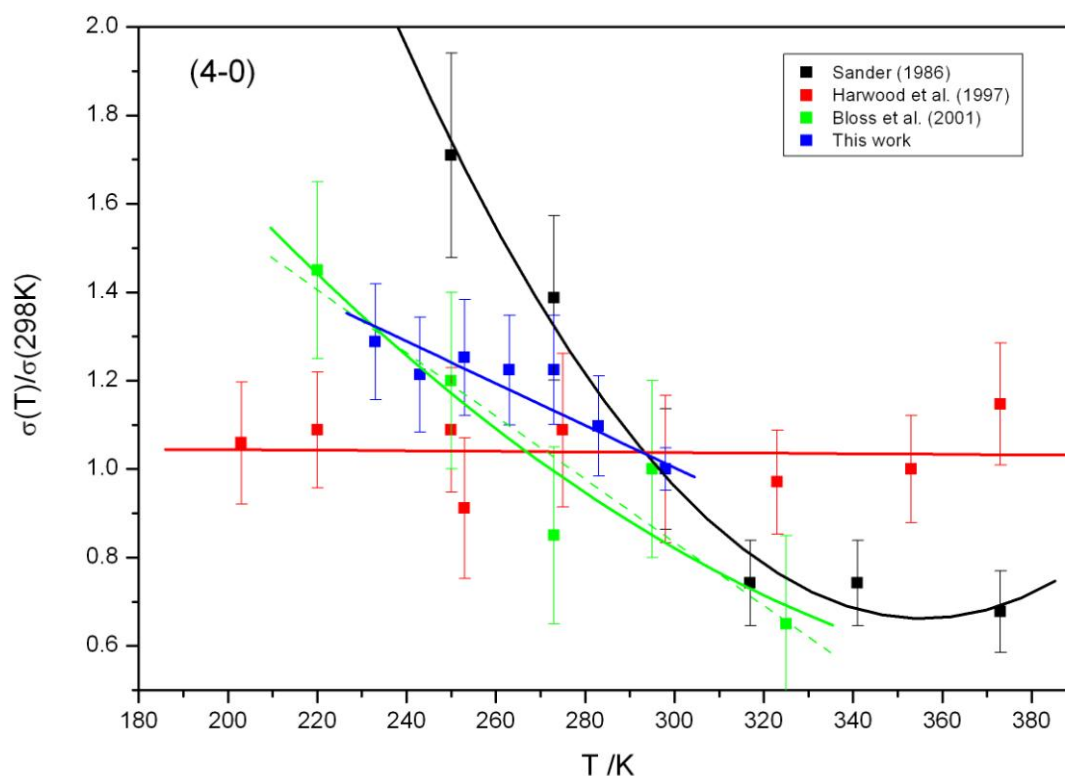
**Figure S1.** Upper panel: Temperature dependence of the full UV-Vis IO spectrum (air wavelengths). The DOAS retrieval window is marked in red. Lower panel: zoom on the 4-0 band. Arrows indicate the effect of decreasing temperature.



**Figure S2.** Spectral simulation of the (4-0) and (3-0) bands, showing the effect of decreasing temperature on band shape and height.



**Figure S3.** Differential absorption cross section of IO at 243 K plotted against the reference differential cross section at 298 K in the atmospheric retrieval window (bands (5-0) and (4-0)). The inset shows the linear regression fit.



**Figure S4.** Comparison with temperature dependent cross sections of the IO (4-0) band reported in the literature. All data have been normalised to the value at 298 K.

## References

- Bloss, W. J., Rowley, D. M., Cox, R. A., and Jones, R. L.: Kinetics and Products of the IO Self-Reaction, *The Journal of Physical Chemistry A*, 105, 7840-7854, 2001.
- Fleischmann, O. C., Hartmann, M., Burrows, J. P., and Orphal, J.: New ultraviolet absorption cross-sections of BrO at atmospheric temperatures measured by time-windowing Fourier transform spectroscopy, *Journal of Photochemistry and Photobiology A: Chemistry*, 168, 117-132, 2004.
- Gómez Martín, J. C., Spietz, P., and Burrows, J. P.: Spectroscopic studies of the I<sub>2</sub>/O<sub>3</sub> photochemistry: Part 1: Determination of the absolute absorption cross sections of iodine oxides of atmospheric relevance, *Journal of Photochemistry and Photobiology A: Chemistry*, 176, 15-38, 2005.
- Gómez Martín, J. C., Spietz, P., and Burrows, J. P.: Kinetic and Mechanistic Studies of the I<sub>2</sub>/O<sub>3</sub> Photochemistry, *The Journal of Physical Chemistry A*, 111, 306-320, 2007.
- Harwood, M. H., Burkholder, J. B., Hunter, M., Fox, R. W., and Ravishankara, A. R.: Absorption Cross Sections and Self-Reaction Kinetics of the IO Radical, *The Journal of Physical Chemistry A*, 101, 853-863, 1997.
- Newman, S. M., Howie, W. H., Lane, I. C., Upson, M. R., and Orr-Ewing, A. J.: Predissociation of the A<sub>2</sub>P<sub>3/2</sub> state of IO studied by cavity ring-down spectroscopy, *J. Chem. Soc., Faraday T rans.*, 94, 2681-2688, 1998.
- Rowley, D. M., Harwood, M. H., Freshwater, R. A., and Jones, R. L.: A Novel Flash Photolysis/UV Absorption System Employing Charge-Coupled Device (CCD)

- Detection: A Study of the BrO + BrO Reaction at 298 K, *The Journal of Physical Chemistry*, 100, 3020-3029, 1996.
- Sander, S. P.: Kinetics and mechanism of the IO + IO reaction, *The Journal of Physical Chemistry*, 90(10), 2194-2199, 1986.
- Spietz, P., Gómez Martín, J. C., and Burrows, J. P.: Spectroscopic studies of the I<sub>2</sub>/O<sub>3</sub> photochemistry: Part 2. Improved spectra of iodine oxides and analysis of the IO absorption spectrum, *Journal of Photochemistry and Photobiology A: Chemistry*, 176, 50-67, 2005.

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