

THE ABUNDANCE OF SULFUR DIOXIDE BELOW THE CLOUDS OF VENUS

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*Abstract.* We present a new method for determining the abundance of sulfur dioxide below the clouds of Venus. Absorption by the  $3\nu_3$  band of  $\text{SO}_2$  near  $2.45 \mu\text{m}$  has been detected in high-resolution spectra of the night side of Venus recorded at the Canada-France-Hawaii telescope in 1989 and 1991. The inferred  $\text{SO}_2$  abundance is  $130 \pm 40$  ppm at all observed locations and pertains to the 35–45 km region. These values are comparable to those measured by the Pioneer Venus and Venera 11/12 entry probes in 1978. This stability stands in contrast to the apparent massive decrease in  $\text{SO}_2$  observed at the cloud tops since these space missions. These results are consistent with laboratory and modelling studies of the  $\text{SO}_2$  destruction rates in the lower atmosphere of Venus. The new spectroscopic technique presented here allows a remote monitoring of the  $\text{SO}_2$  abundance below the clouds, a likely tracer of Venusian volcanism.

INTRODUCTION

Sulfur dioxide was first detected above the clouds of Venus by Barker [1979], and later beneath the cloud decks by instruments carried by the Pioneer Venus (PV) and Venera 11/12 entry probes [Oyama *et al.* 1980, Gel'man *et*

*al.* 1979].  $\text{SO}_2$  plays important physical and chemical roles in the Venus atmosphere. It is related to the formation of the planet-wide sulfuric acid clouds, the energy budget of the lower atmosphere and greenhouse effect at the surface, and lithosphere-atmosphere interactions such as surface weathering and volcanism.

Telescopic observations show that the night side of Venus emits significant radiation in narrow near-infrared windows located between regions of strong  $\text{CO}_2$  and  $\text{H}_2\text{O}$  absorption [Allen and Crawford, 1984]. This emission is thermal radiation originating from the hot lower atmosphere, beneath the sulfuric acid cloud decks. It provides a unique opportunity to study the deep atmosphere of Venus from ground-based observatories. In November 1989, Bézard *et al.* [1990] recorded the first high-resolution ( $0.28 \text{ cm}^{-1}$  apodized) spectra of the night side of Venus in the 1.7- and 2.3- $\mu\text{m}$  windows. In the latter window, they were able to identify numerous absorption lines due to the gases  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{HDO}$ ,  $\text{HF}$ , and  $\text{COS}$  and measure their abundances in the altitude range probed (30–50 km). However, Bézard *et al.* could not reproduce the spectra observed between 4020 and 4100  $\text{cm}^{-1}$  (2.44–2.49  $\mu\text{m}$ ), and suggested that this difficulty could be due to absorption by the  $3\nu_3$  band of  $\text{SO}_2$ , which was not included in the models due to a lack of spectroscopic data at that time. We present an analysis of this spectral region using a recent spectroscopic investigation of the  $3\nu_3$  band of  $\text{SO}_2$  [Lafferty *et al.*, 1992], and derive a new measurement of the abundance of sulfur dioxide below the cloud decks of Venus.

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Paper Number 93GL01338  
0094-8534/93/93GL-01338\$03.00

## OBSERVATIONS

Spectroscopic observations of the night side of Venus at wavelengths near 2.3  $\mu\text{m}$  were obtained on 10 November 1989 (UT) with the Fourier Transform Spectrometer at the Canada-France-Hawaii telescope (CFHT) [Bézard *et al.*, 1990]. These spectra were recorded at 0.28  $\text{cm}^{-1}$  resolution (apodized), using a 5-arcsec aperture centered near 30°N latitude and 170° longitude. The angular size of Venus was 25 arcsec. New spectra of the night side were recorded with the same instrument on 28–30 June 1991 UT. The apodized spectral resolution was 0.15  $\text{cm}^{-1}$ . Three regions on the dark side centered at 25°N, 5°N, and 15°S (longitude 200°), were observed using a 5-arcsec circular aperture, while the angular size of Venus was 28 arcsec. Contamination by reflected sunlight from the day side was removed using dayside spectra recorded right after the nightside spectra. Absolute flux calibration was performed by recording spectra of standard stars at similar zenith angles. The available Venus spectra are displayed in Figure 1.

## ANALYSIS

Several changes have been made to the radiative transfer model used in Bézard *et al.* [1990]. They are described

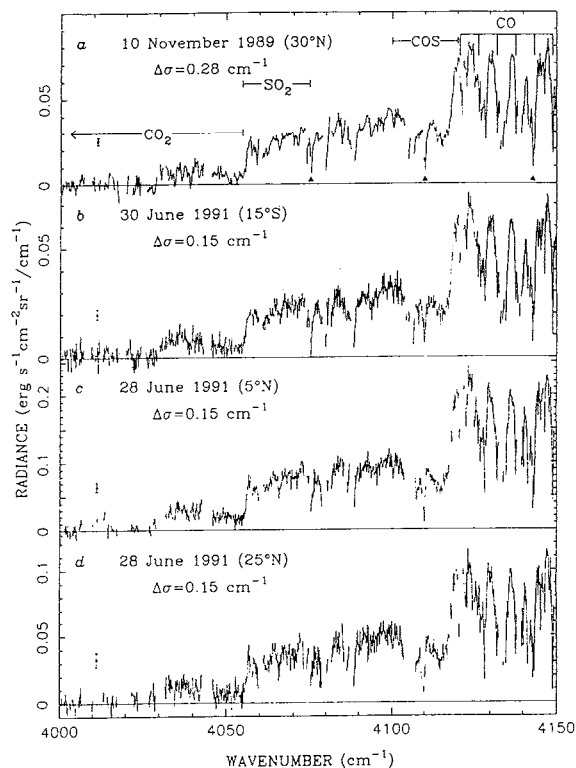


Fig. 1: Spectra of the night side of Venus recorded at 0.28- $\text{cm}^{-1}$  (a) and 0.15- $\text{cm}^{-1}$  (b – d) resolution. Missing data points correspond to spectral regions where the telluric absorption exceeded 50%. The  $\pm 1\sigma$  level is given for each spectrum. Variations in the cloud optical depth are responsible for the large flux differences observed among the spectra. Absorption features due to SO<sub>2</sub>, COS, CO, HF ( $\blacktriangle$ ), and CO<sub>2</sub> are indicated. All the other absorptions are due to H<sub>2</sub>O and HDO.

in detail in Pollack *et al.* [1993], and are summarized here: (1) We used a new high-temperature CO<sub>2</sub> database derived from accurate quantum mechanical calculations. As a result, we can now reproduce the intensity drop observed near 4056  $\text{cm}^{-1}$  due to the head of the weak (01121)–(10002) band of <sup>12</sup>CO<sub>2</sub>. (2) The hot bands of COS associated with the 2 $\nu_3$  fundamental have been added to the model. In contrast, only the fundamental mode was included in the modelling of Bézard *et al.* (3) Following Pollack *et al.*, we have allowed for a variation in the COS mixing ratio with altitude. These improvements lead to a much better overall agreement between the model and the observed nightside spectra than that achieved previously.

However, there still remains a major discrepancy between observed and synthetic spectra near 4070  $\text{cm}^{-1}$ , which is the region of the R-branch of the 3 $\nu_3$  band of SO<sub>2</sub> (Figure 2). Laboratory spectra of this band were recently recorded by two different groups in the U.S. and in France, and line assignments and intensities have been derived [Lafferty *et al.*, 1992]. We used these spectroscopic data to model the SO<sub>2</sub> opacity in our atmospheric calculations. We assumed a constant mixing ratio below 48 km, decreasing at higher altitudes (linearly with logarithm of pressure) down to a value of 0.05 ppm at 70 km [Von Zahn *et al.*, 1983]. Adding SO<sub>2</sub> absorption eliminates the previously existing discrepancy and allows us to adequately reproduce the shape of the Venus spectra. A best fit to all of the observed spectra is obtained for a SO<sub>2</sub> mixing ratio equal to 130 $\pm$ 40 ppm. The error bars encompass instrumental noise as well as uncertainties in the SO<sub>2</sub> band intensity, the cloud model, and the CO<sub>2</sub> continuum opacity with its possible spectral variations. The atmospheric region sounded by these measurements extends from 35 to 45 km, with a maximum sensitivity near the 39-km level. Our data do not constrain the height variation of SO<sub>2</sub>; the inferred mixing ratio thus refers to an average over the range of altitudes probed.

## DISCUSSION

Within the mutual uncertainties, our derived SO<sub>2</sub> mixing ratio is the same as that measured by the PV and Venera 12 gas chromatographs in December 1978. The PV data yielded 185 $\pm$ 43 ppm at 22 km altitude [Oyama *et al.*, 1980], while a SO<sub>2</sub> mixing ratio of 130 $\pm$ 35 ppm was derived below 42 km from the Venera 12 measurements [Gel'man *et al.*, 1979]. A recent reanalysis [Bertaux *et al.*, 1992] of the ultraviolet spectra recorded *in situ* in June 1985 by the scanning spectrophotometers on the Vega 1 and 2 probes yields 120 $\pm$ 20 ppm of SO<sub>2</sub> near 42 km, in good agreement with our results.

However, a few measurements subsequent to the PV and Venera 11/12 encounters tend to indicate lower SO<sub>2</sub> abundances below the cloud deck at  $\sim$ 48 km. In March 1982, the Venera 13/14 gas chromatograph experiment [Mukhin *et al.*, 1983] detected only small (unquantified amounts) of SO<sub>2</sub> and apparently showed that SO<sub>2</sub> was less abundant than the reduced sulfur gases COS and H<sub>2</sub>S; but there was a malfunction with the carrier gas flow from this

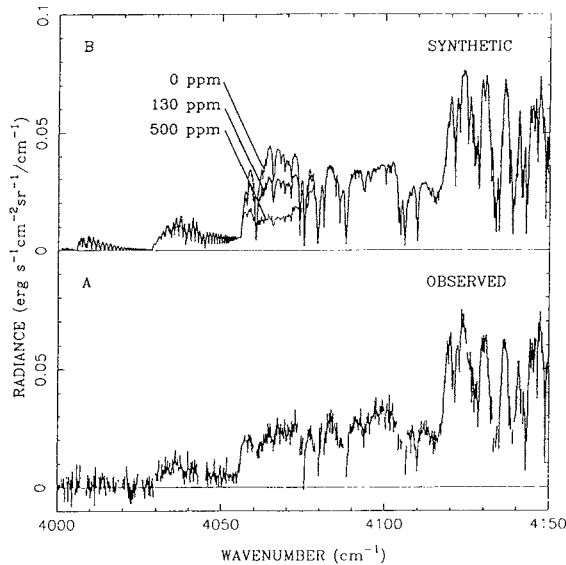


Fig. 2: The observed spectrum *b* (A) is compared with synthetic spectra (B) in which the subcloud (below 48 km) SO<sub>2</sub> mixing ratio has been varied. Spectra were computed with a H<sub>2</sub>O mixing ratio of 30 ppm below the cloud deck and a constant HF mixing ratio of 0.006 ppm. The CO vertical profile is the one deduced by Von Zahn *et al.* [1983] from probe data. The COS concentration is 0.35 ppm at 37 km and increases with depth to a value of 10 ppm at 30 km and below. The model also includes a continuum opacity ( $\alpha = 4 \times 10^{-8} \text{ cm}^{-1} \text{ amagat}^{-2}$ ), needed to reproduce the observed spectrum longward of 4350 cm<sup>-1</sup>, where CO<sub>2</sub> is the only gaseous absorber. The thick curve in B corresponds to the SO<sub>2</sub> abundance (130 ppm) which provides the best overall agreement with the observations.

experiment [Krasnopolsky, 1986], and many of its results are suspect. The SO<sub>2</sub> profiles retrieved from the Vega 1 and 2 measurements in 1985 strongly decrease downwards below the cloud deck reaching 20–25 ppm at 12 km. The mixing ratios derived at 22 km (30–40 ppm) are ~5 times lower than measured by the PV gas chromatograph in 1978. Finally, in March–April 1987, broad-band microwave observations of Venus gave SO<sub>2</sub> upper limits as low as 60 ppm below the clouds [Steffes *et al.*, 1990]. However, the microwave spectrum of Venus is not very sensitive to the SO<sub>2</sub> opacity and the uncertainties related to errors in the absolute calibration were not taken into account in the analysis.

These spacecraft *in situ* measurements and ground-based microwave observations show a wide range of values, and have been interpreted to show a monotonic decrease in the SO<sub>2</sub> mixing ratio below the clouds since 1978. Our observations clearly contradict the latter conclusion, as well as the proposal by Wood and Hashimoto [1991] that the 185 ppm of SO<sub>2</sub> observed in 1978 was the result of a transient volcanic effusion.

In contrast, UV spectroscopic measurements [Esposito 1984, Esposito *et al.* 1988, Na *et al.* 1990], which probe the Venusian cloud tops, show as much as an order of

magnitude decrease in the abundance of SO<sub>2</sub> from 1978 to 1988. The higher SO<sub>2</sub> abundance in 1978 was hypothesized to be the result of a major volcanic eruption prior to the PV and Venera missions [Esposito, 1984]. The subsequent drop off would then be due to the conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> aerosols. Another possibility is that the observed variation results from dynamical and/or photochemical processes in the upper atmosphere. In any case, our observations show that this drop off has no connection to what is happening below the clouds.

In addition, a rapid decline in the SO<sub>2</sub> abundance below the clouds is difficult to explain in the framework of existing thermochemical models of the deep atmosphere of Venus. Chemical reactions with surface minerals advocated by some workers [e.g., Wood and Hashimoto, 1991] cannot buffer SO<sub>2</sub> at low levels because of the extremely slow reaction rates involved. Laboratory studies of the SO<sub>2</sub> reaction rate with Ca-bearing minerals such as calcite, diopside, and anorthite, which are believed to be present on the surface of Venus [Fegley and Treiman 1992, and references therein], show that millions of years are required to remove SO<sub>2</sub> from the atmosphere by anhydrite (CaSO<sub>4</sub>) formation [Fegley and Prinn 1989, Fegley and Treiman 1992]. During the intervening 14 years, since the discovery of enhanced cloud-top SO<sub>2</sub> abundances, the fastest anhydrite formation reaction (SO<sub>2</sub> + calcite) would have removed only 0.009% of the ~150 ppm SO<sub>2</sub> observed by PV and Venera 12 in 1978.

We cannot either find any plausible atmospheric sink which could have consumed a large fraction of the SO<sub>2</sub> observed in 1978. Calculations of buffering by minerals [Fegley and Treiman, 1992] and of thermochemical equilibrium in the deep atmosphere [Krasnopolsky and Parshv, 1979] do predict COS mixing ratios of a few tens of ppm near the surface, but show that SO<sub>2</sub> is still by far the dominant sulfur-bearing gas at low altitudes. COS formation could thus neither have removed much of the ~150 ppm SO<sub>2</sub>, nor produce a strong vertical gradient in the SO<sub>2</sub> profile as derived from the Vega 1 and 2 spectrophotometers [Bertaux *et al.*, 1992].

Hence, both our observations, and existing models cast doubts on the validity of the SO<sub>2</sub> measurements below the clouds taken during the 1980's that indicated monotonically decreasing amounts. They suggest that the SO<sub>2</sub> abundance in the deep atmosphere has changed little, if any, since the PV and Venera 12 encounters in 1978.

Spectroscopic observations of the nightside provide a unique means of remotely monitoring the SO<sub>2</sub> abundance below the clouds of Venus. These capabilities are crucial for a better understanding of the origin and distribution of SO<sub>2</sub> and of the sulfur chemistry on Venus.

*Acknowledgments.* We are indebted to W.J. Lafferty *et al.* for diligently carrying out measurements and spectral analysis of the 3ν<sub>3</sub> band of SO<sub>2</sub>. B.F. was supported by grants from the NASA Planetary Atmospheres and Venus Data Analysis Programs. The Canada–France–Hawaii Telescope is operated by the National Research

Council of Canada, the Centre National de la Recherche Scientifique de France, and the University of Hawaii.

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(Received December 21, 1992;

Revised May 5, 1993;

Accepted May 21, 1993)