

DETECTION OF SO₂ IN THE UV SPECTRUM OF VENUS

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Abstract. The broad absorption feature below 3300Å in the Venus *uv* spectrum previously reported by Barker is identified as primarily due to SO₂ absorption based on new higher resolution spectra of the 3000-3400Å region showing broad (10Å), unresolved absorptions in the regions at all SO₂ band origins between 3000 and 3300Å. SO₂ mixing ratios vary from 5 X 10⁻⁷ down to an upper limit of 2 X 10⁻⁸ at a phase angle of 138°. Previous observational determinations of the SO₂ mixing ratio were biased toward large phase angles, and consequently did not detect any SO₂ absorption at the 10⁻⁸ level. The upper limit derived from the CS₂ band head at 3206Å is <5 X 10⁻⁸. The observed range of SO₂ mixing ratios (<2 X 10⁻⁸ to 5 X 10⁻⁷) is consistent with model predictions based on the sulfur photo-chemistry at the cloud tops. Ground-based observations of SO₂ mixing ratio will provide constraints on models and check on the Venera and Pioneer Venus measurements of the mixing ratios of SO₂ and other sulfur-bearing gases with altitude.

Introduction

Observations of the ultraviolet SO₂ absorption between 1800-3400Å have been made since 1964 using a variety of techniques from satellites and rockets to conventional ground-based spectrographs. Nearly all attempts shown in Table 1 have been at large phase angles, due to instrumental observing constraints. With the exception of the 10⁻⁶ value of Anderson at 76°, all other upper limits are on the order of 10⁻⁸ and at phase angles of near 90°.

The shape of the relative spectral reflectivity from 3067-5960Å for the integrated disk of Venus (Barker et al., 1975) was explained in terms of a model with two sulfur-containing cloud layers (Hapke and Nelson, 1975). One layer was composed of a mixture of elemental sulfur particles and sulfuric acid droplets, while the other contained larger sulfur particles, some of which were not completely polymerized with the source of the elemental sulfur being photodissociation of COS. Young (1977) pointed out that the shape of the long wavelength end of the sulfur absorption could be more straightforwardly explained by the effect of a temperature gradient within the clouds. Neither initial explanation attempted to account for the absorption feature below 3300Å, although it was present in all spectra. Subsequently, Young (1978) attributed the absorption feature to the "V-Band" absorption of CS₂. The negative "noise spikes" below 3300Å in Fig 1a match fairly well with CS₂ band heads at 3150, 3190, and 3250Å. Similar resolution spectra (Fig. 2) taken in February 1977 at a phase angle of 115° show absorption dips at these wavelengths

but not the broader absorption feature present at 74° shown in Fig. 1. Identification of the molecular species responsible for the broad absorption feature required higher resolution to resolve rotational lines or individual bands within the 3-3300Å region. In particular, the Cl⁻ ion has a continuous band centered at 3000Å. There is a better correlation between SO₂ band origins and the low-resolution absorption dips than there is for CS₂ band heads.

Observations

Higher-resolution spectra (0.1Å and 0.2Å FWHM) covering 50-100Å band passes were obtained on several dates between March and October 1978 using both a linear 1024 Reticon array and the normal coude scanner system of the 2.7-m reflector at McDonald Observatory. Similar spectra of the integrated solar disk were obtained on the same date with the same instrumental setup. Ratio spectra (Venus/Solar) were created after shifting the solar spectrum in wavelength to match the reflected solar spectrum from Venus and then producing an interpolated solar spectrum at the proper shift by using a spline interpolation on the observed solar spectrum. All high signal to-noise ratio spectra (Table 2) show broad, unresolved absorptions near all SO₂ band origins between 3000 and 3300Å. The tabulated spectrograph slit orientation is given with respect to the intensity equator of Venus.

Identification of SO₂ as the absorbing molecule is definite, particularly when the 3000-3150 Å region is observed. SO₂ band origins do not exactly correspond to the position of maximum absorption in Fig. 3, but they are shifted in exactly the same manner in the SO₂ laboratory data of (Warneck et al., 1964). Relative intensities of the bands are indicated by the length of bars and refer to relative room temperature intensities tabulated by (Brand and Nanes, 1973). Mixing ratios were calculated using only depth of the band and absorption intensities of (Warneck et al., 1964) which were scaled by relative room temperature intensities of (Brand and Nanes, 1973) (3048Å, 19 cm⁻¹, 3131Å, 4 cm⁻¹, 3210Å, 0.63 cm⁻¹). For accurate conversion to SO₂ amounts, the SO₂ absorption intensities are being measured in the laboratory under Venus atmospheric conditions of 240°K and 0.1 atm pressure, but there should not be a large relative change between bands under these conditions. In published laboratory data, regular SO₂ bands are superimposed on a broad continuous SO₂ absorption in this region of 2400 to 3400Å. In higher resolution observational data, the exact continuum level is not determinable for ratio spectra because each spectrum corresponds to a 50 or 100Å region and the continuum is never reached except for the few spectra in the 3400Å region. Absorption intensities used to

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TABLE 1. Previous SO₂ Mixing Ratio Upper Limits

Source	Spectra	Phase (°)	[SO ₂]
Cruikshank and Kuiper, 1967	ground	101	<2-5x10 ⁻⁸
Jenkins, et al., 1969	Rocket	93	<1 x10 ⁻⁸
Anderson, et al., 1969	Rocket	76	<2.2x10 ⁻⁶
Owen and Sagan, 1972	OAO-2	103	<1 x10 ⁻⁸
Shaya and Caldwell, 1976	OAO-2	87	<2 x10 ⁻⁹

calculate mixing ratios in Table 2 were not corrected for this background continuum absorption. An integrated band intensity under Venus conditions is necessary for conversion of the broad absorption noted in Fig. 1b into an amount of SO₂. A crude calculation yields a SO₂ mixing ratio of 2 X 10⁻⁷ based on laboratory intensities given by (Thompson et al., 1963).

The question whether there is any additional absorption due to CS₂ can be partially answered by the data presented in Fig. 4. Laboratory data (lower spectrum) taken with the same instrument at room temperature and about 0.1 atm with a 15 cm path length of CS₂ show clearly that SO₂ is

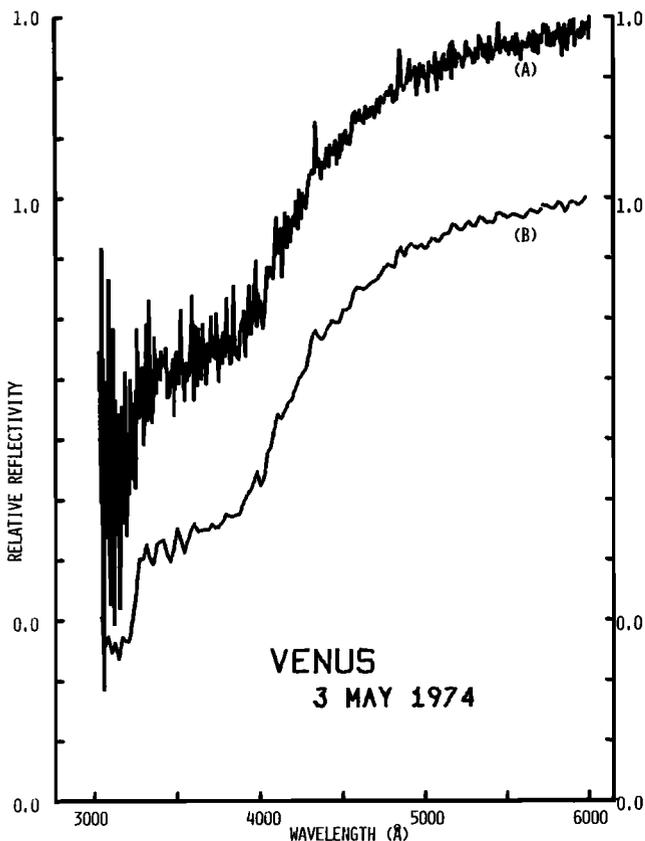


Fig. 1. Venus/Sun ratio spectrum: (a) raw 10Å resolution and (b) resolution smoothed to 40Å. Zero level is vertically displaced for clarity. The phase angle is 74°.

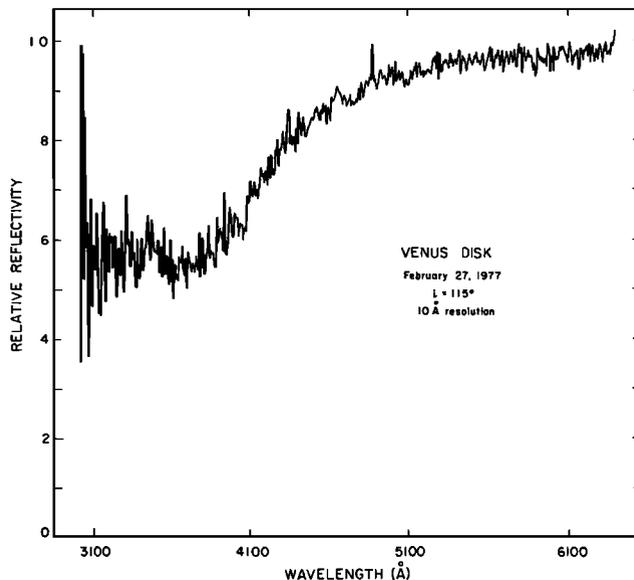


Fig. 2. Venus/Sun ratio spectrum.

the major absorber. If the small minima in the upper spectrum at the positions marked for maximum CS₂ absorption in Fig. 4 are converted into an amount of CS₂ with total band strength of 2.7 X 10⁻⁴ (Rabalais et al., 1971), we obtain a CS₂ mixing ratio of 5 X 10⁻⁸. Several other ratio spectra have small noise features similar to those shown in Fig. 4. This mixing ratio of 5 X 10⁻⁸ is 10X smaller than proposed by (Young 1978). Although the measured mixing ratio is much smaller, Young's arguments are still valid and CS₂ at the 10⁻⁸ level is chemically plausible, but observational evidence for a clean detection is marginal at best.

Discussion

The prime reason for determining the SO₂ mixing ratio at cloud tops is to set realistic constraints on photochemical reactions involving photodissociation of COS and formation of H₂SO₄ acid cloud droplets. The range of values (<2 X 10⁻⁸ to 5 X 10⁻⁷) for the observed SO₂ mixing ratio is compatible with the 10⁻⁷ predicted by (Prinn, 1973). But observation of an actual amount of SO₂ or mixing ratios is a more severe model constraint than just an upper limit to the SO₂ mixing ratio. One of the consequences of an observed mixing ratio for SO₂ is to set limits on the eddy diffusion coefficient in the H₂SO₄ cloud (Prinn, 1978). Since this detection of SO₂ is the only direct measurement of a sulfur-bearing gas in the Venus atmosphere, atmospheric models proposed by (Turco et al., 1978 and others can be based on firm observations.

Observed strengths of the SO₂ features under an equatorial slit do vary on a daily time scale, which is what one would expect from the long-observed variability in *w* cloud contrasts and positions. Phase angle effect is apparent when one considers that the only detections occur at phase angles between 30° and 74° (Figs. 3, 4) and

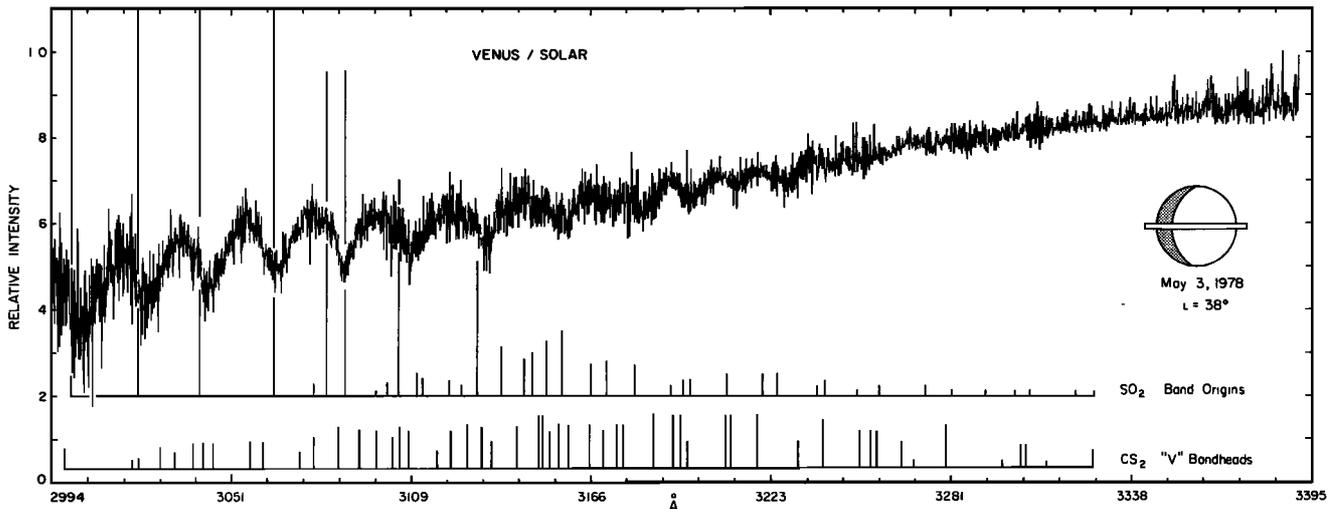


Fig. 3. Venus Solar ratio spectrum consisting of 4 overlapping Reticon spectra each covering 106Å. Positions and relative strengths of SO₂ and CS₂ bands indicated by vertical bars.

upper limits of 10^{-8} have been recorded for phase angles greater than about 90° (Figs. 2, 5). A similar phase effect for another minor constituent is seen in the variation by a factor of 10 in H₂O abundance above the clouds between moderate (~ 60) and large phase angles (>120) (Barker, 1975). Both effects are readily explained by the fact we are seeing deeper into cloud tops at 60° than we are at 140° , since the total CO₂ path length increases by a factor of 3.5 between phase angles of 140° and 60° (Barker, 1978, Young, 1972).

It is interesting to note that an equatorial *w* feature was visible on photographs taken along with scans in Fig. 3 which show the strongest SO₂ features observed. Further studies are under way using monochromatic area scanner techniques in and out of SO₂, sulfur, CO₂ and H₂O absorption features to determine any spacial correlations. Venera and Pioneer Venus Entry Probes will provide measurements of mixing ratios of various sulfur gases as a function of altitude starting near cloud tops (65 km). Ground-based measurement of the SO₂ mixing ratio above the clouds at that time will provide a valuable check on those measurements, as well as an overlap into the atmosphere above the clouds.

TABLE 2. SO₂ Mixing Ratios [3 km-atm CO₂]

Date 1978	Slit Orientation	Phase (°)	λ (SO ₂) Band	[SO ₂]
3/13	~ PP@CD	17	3210Å	3.4×10^{-7}
4/30	~ EQ@EQ	35	3210Å	5.3×10^{-7}
5/3	~ EQ@EQ	36	3210Å	2.6×10^{-7}
5/4	//EQ@EQ	37	3048Å	5.6×10^{-8}
	//EQ@EQ		3131Å	1.4×10^{-7}
	//EQ@EQ		3210Å	5.0×10^{-7}
6/3	//EQ@EQ	49	3210Å	3.3×10^{-7}
	//EQ@EQ		3210Å	3.7×10^{-7}
6/4	//EQ@EQ	49	3210Å	5.7×10^{-7}
7/9	//EQ@EQ	65	3210Å	2.2×10^{-7}
10/17	CC@EQ	138	3131Å	$< 2.3 \times 10^{-8}$

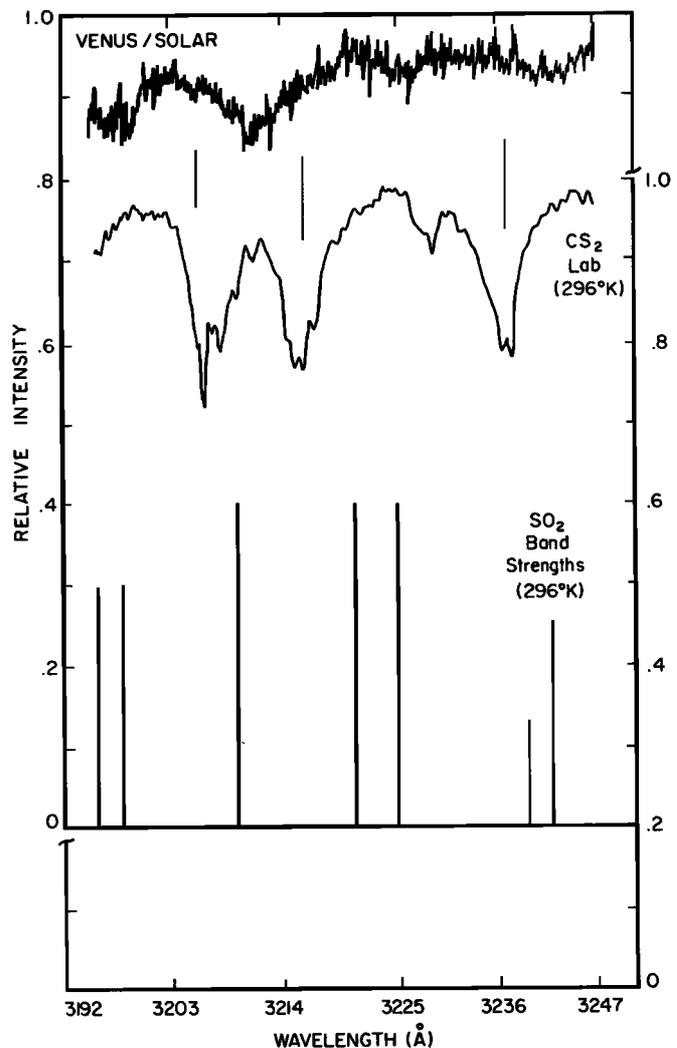


Fig. 4. Venus/Solar ratio spectrum with 0.1Å resolution. The scale of the relative SO₂ band strength bars are 10X those in Fig. 3.

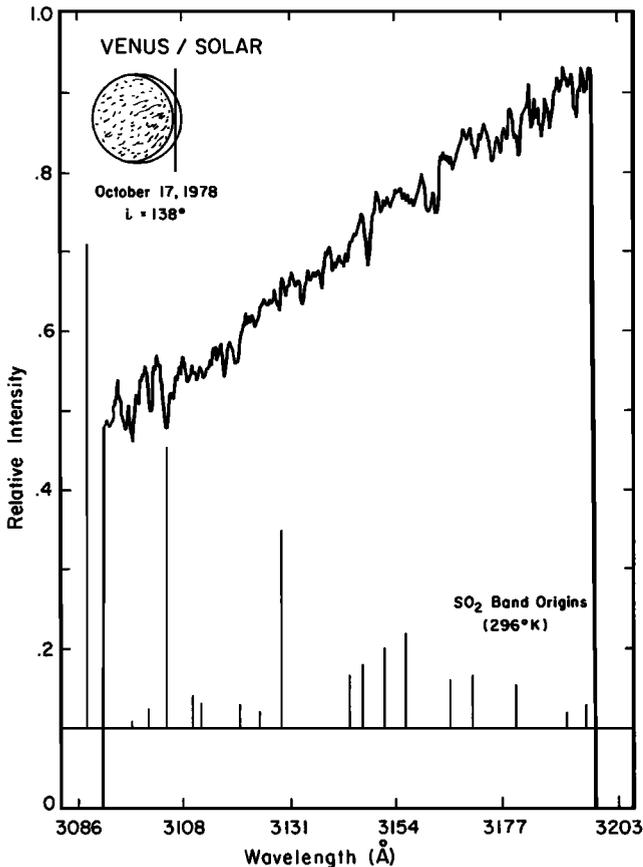


Fig. 5. Venus/Solar ratio spectrum with 0.2 resolution lack of measurable absorption at the 3131Å SO₂ band origin yields an upper limit of 2×10^{-8} for the SO₂ mixing ratio. Narrow lines present in the ratio spectrum are residual solar lines that were not completely subtracted out by the real time sky subtraction.

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