

**No. 97 SULPHUR COMPOUNDS IN THE ATMOSPHERE OF VENUS
I: AN UPPER LIMIT FOR THE ABUNDANCE OF SO₂**

by D. P. CRUIKSHANK AND G. P. KUIPER

October 20, 1967

ABSTRACT

From the SO₂ electronic bands near 3000 Å an upper limit of 0.05 mm-atm has been derived for the SO₂ content of the Venus atmosphere.

This paper deals with the possible presence of SO₂ on Venus. In the accessible part of the Venus spectrum the most sensitive test by far is through the electronic bands $\tilde{A} \longleftrightarrow \tilde{X}$ near 3000 Å (Herzberg 1966), which in many respects resemble the O₃ bands in the same spectral region and on which they are per force superposed when observed through the terrestrial ozonosphere.

The Venus spectra used in the test were obtained with the 61-in. reflector of the LPL Catalina Observatory (elevation 8260 ft or 2520 m). The spectrograph is autocollimating, with a focal length of 36 in. (91 cm). A wide slit (0.25 mm) corresponding to 2.5 arc sec in the sky was used to smooth out the solar Fraunhofer lines which crowd this region. The grating, with 600 lines per millimeter, was blazed for 6500 Å first order and was used in the second order, giving a dispersion of 8.1 Å/mm. A Corning 9863 filter was used to eliminate the first-order red to which the 103a-O plates used are slightly sensitive.

The most suitable exposure was obtained on 5 July 1967 and is reproduced in Figure 1. At that time Venus was 0.40 illuminated, of phase angle 101°, just past dichotomy, about 3^h from the sun, at declination +13°. The exposure was 15.3 min. At

the end of the exposure the air mass of the sun was 2.77, that of Venus 1.25. The much greater air mass of the sun reduced the contamination by superposed daytime sky radiation in the heaviest part of the ozone absorption, near the cutoff at 2950 Å, as may be seen in Figure 1. This yielded a Venus exposure comparatively undisturbed in the critical area.

Figure 1 also shows four solar spectra taken through different amounts, 2.3, 1.0, 0.5, and 0.1 mm-atm, of SO₂ gas. These spectra were made in the Tucson laboratory with the same spectrograph, grating, slit, and emulsion as used at the telescope. The sunlight recorded was diffusely reflected from a surface of smoked magnesium oxide, and the collimator mirror of the spectrograph was masked to F/13.5 (to match the beam width used on the planet). The SO₂ absorption cell had 2.5 mm path-length, made from two disks of Optosil I (Engelhardt Industries), which has a suitably high transmission in this spectral region. The disks were attached with epoxy to a spacer, with entrance and exit tubes of glass provided for filling the space between the disks with SO₂ gas.

The development of the SO₂ bands with increasing amounts of the gas, from 0.1 to 2.3 mm-atm, is well shown. In each case the gas was mixed with air

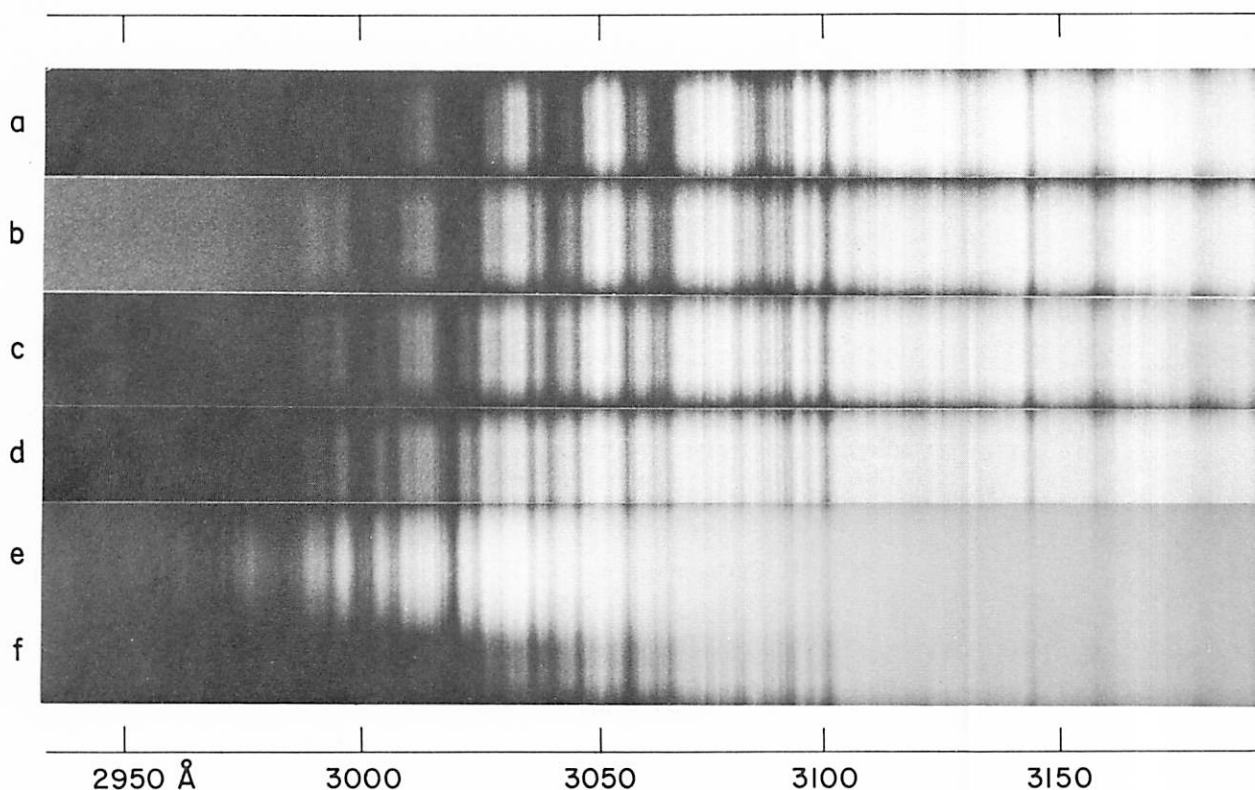


Fig. 1 Comparison of Venus spectrum (e) with sun observed through different amounts of SO_2 : (a) 2.3 mm-atm; (b) 1.0 mm-atm; (c) 0.5 mm-atm; and (d) 0.1 mm-atm. (f) is the sky adjacent to Venus.

so that the total pressure in the cell was always 1 atm. The bands centered at about 3004 and 3020 Å provide sensitive tests for comparison with the Venus spectrum. From an examination of Figure 1, we detect no SO_2 in the Venus atmosphere, and conclude that the upper limit of the abundance of this gas in the complete transmission path through the upper Venus atmosphere is 0.05 mm-atm.

The infrared spectrum of a 10 cm path of SO_2 was also recorded from 0.9 to 2.5 microns for comparison with Venus spectra published by Kuiper (1962) and Kuiper and Forbes (1967). No overtones of the fundamental vibrational bands were noted, in accordance with Herzberg (1945). The first fundamental (ν_3) lies at 7.34 microns.

We shall now examine whether at 3000 Å the optical penetration in the Venus atmosphere is set by Rayleigh scattering by CO_2 , rather than by particles. The extinction coefficient in pure air at 0° C for 1 atm is 1.48×10^{-6} per cm and for CO_2 , 2.28 times this amount (Van de Hulst 1952) or $3.37 \times$

10^{-6} per cm NPT. Optical depth unity is therefore attained by a 3.0 km NPT pathlength of CO_2 , approximately the amount penetrated spectroscopically (two-way transmission) in the 1μ region. Particle scattering rather than Rayleigh scattering will therefore limit the penetration even at 3000 Å. The upper limit of the mixing ratio of SO_2 is therefore somewhat larger than 0.05 mm/3 km or 1.7×10^{-8} (say, 2 to 5×10^{-8}). A sharper limit can probably be set from observations above the ozonosphere, in the 2000–3000 Å region.

Acknowledgment. The planetary program is supported by the National Aeronautics and Space Administration through Grant NsG 161–61.

REFERENCES

- Herzberg, G. 1945, *Infrared and Raman Spectra of Polyatomic Molecules*, Vol. II in *Molecular Spectra and Molecular Structure* (Princeton, N.J.: D. Van Nostrand Co.), p. 285.

- . 1966, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Vol. III in *Molecular Spectra and Molecular Structure* (Princeton, N.J.: D. Van Nostrand Co.).
- Kuiper, G. P. 1962, "Infrared Spectra of Stars and Planets, I: Photometry of the Infrared Spectrum of Venus, 1–2.5 Microns," *Comm. LPL*, 1 (15), 83–117.
- Kuiper, G. P., and Forbes, F. F. 1967, "High-Altitude Spectra from NASA CV 990 Jet. I: Venus, 1–2.5 Microns, Resolution 20 cm^{-1} ," *Comm. LPL*, 6 (95), 117–187.
- Van de Hulst, H. C. 1952, "Scattering in the Atmospheres of the Earth and Planets," *The Atmospheres of the Earth and Planets*, (Chicago: Univ. of Chicago Press), p. 55, Tables 3 and 4.