Communications of the
LUNAR AND PLANETARY LABORATORY

Communications Nos. 93–99

Volume 6 Part 3

THE UNIVERSITY OF ARIZONA

AGA-03-007-002

Communications of the
LUNAR AND PLANETARY LABORATORY

Communications Nos. 93–99

Volume 6 Part 3

THE UNIVERSITY OF ARIZONA

1967

Communications of the Lunar and Planetary Laboratory

These *Communications* contain the shorter publications and reports by the staff of the Lunar and Planetary Laboratory. They may be either original contributions, reprints of articles published in professional journals, preliminary reports, or announcements. Tabular material too bulky or specialized for regular journals is included if future use of such material appears to warrant it. The *Communications* are issued as separate numbers, but they are paged and indexed by volumes.

The *Communications* are mailed to observatories and to laboratories known to be engaged in planetary, interplanetary or geophysical research in exchange for their reports and publications. The University of Arizona Press can supply at cost copies to other libraries and interested persons.

The University of Arizona	GERARD P. KUIPER, *Director*
Tucson, Arizona	*Lunar and Planetary Laboratory*

Editor, G. P. Kuiper; Associate Editor, W. K. Hartmann;
Assistant Editor, Barbara Vigil

Published with the support of the National Aeronautics and Space Administration and the University Space Sciences Committee.

Library of Congress Catalog Number 62-63619

No. 93 A PROGRAM OF ASTRONOMICAL INFRARED SPECTROSCOPY FROM AIRCRAFT

by G. P. Kuiper, F. F. Forbes, and H. L. Johnson

June 30, 1967

ABSTRACT

A program of astronomical infrared spectroscopy from aircraft is developed based on the facilities offered by the NASA CV 990 Jet, with its 65° window ports and its gyrostatically controlled heliostats. A 12-in. horizontal telescope on shock mounts was added, equipped with standard astronomical attachments for spectral observation of the PbS region of the infrared. Table 1 summarizes the vertical distribution of water vapor in the atmosphere in the middle latitudes which determines the relative efficiency of flight operations from different heights. A description is given of the NASA-developed procedures for observation of planets and stars of different declinations. Table 4 summarizes the eight operational flights that took place in the spring of 1967. The efficiency of this approach was much increased when it was shown that a medium-resolution Block interferometer could be used in spite of aircraft vibrations or expected scintillation effects.

1. *Introduction*

Ground-based astronomical spectroscopy has well-known serious barriers. At jetcraft altitudes (10–20 km), the ozone absorptions still prohibit useful work at $\lambda < 3000$ A; but the peculiar distribution of atmospheric water vapor (scale height in troposphere about 1.6 km versus 8.0 km for air generally) makes possible at these altitudes a very large reduction of the infrared telluric bands, most of which are due to H_2O. This is most important because the infrared spectrum contains the fundamental molecular vibrations and their lower overtones. Thus, at these altitudes basic information on the composition, temperature, and stratification of planetary atmospheres may be derived, as well as properties of the exposed planetary surface.

The development of large commercial jets cruising safely at altitudes of at least 40,000 ft (12 km) makes their ceiling altitude a convenient stepping stone. Large instruments can be carried to this altitude and operated under laboratory conditions; yet no special safety devices (pressure suits or oxygen helmets) are needed, as even sudden partial decompression of the cabin does not pose fatal risks. For operations above 45,000–50,000 ft (14–15 km), aircraft with limited space and much smaller payloads must be used and observers must operate in pressure suits. This limits these higher altitudes at present to special projects. Supersonic transports will in time provide larger capabilities above the present 40,000–45,000-ft level.

Some excellent work has been done at still higher altitudes, up to 120,000 ft (36 km), using unmanned balloons. The potentialities of this approach have recently been summarized in several articles in *Applied Optics* (see Supplementary References). The logistics of balloon operations are much more complex than those of aircraft, and special atmospheric conditions must be awaited for launch. Also, failure rates are not negligible, and telescope and accessories may be damaged or lost at launch or during landing. No such problems exist with aircraft, where two or three missions per week are feasible and the astronomical program can be planned beforehand to the minute. Of cardinal importance is the ability in aircraft to check out in flight the complex recording equipment and to make quick repairs or substitutions with backup units when called for. Also, one has complete certainty as to the circumstances under which the observations were made. The equipment and attachments, as well as the scientific and technical staff, can be readily adapted to the requirements of each flight. The relative merits of the unmanned-balloon approach versus the use of manned operations from aircraft therefore involve numerous factors, scientific and logistic, that must be carefully weighed.

2. *Atmospheric Conditions and Available Equipment at 40,000 ft (12 km)*

The average tropospheric scale height for water vapor (~ 1.6 km) indicates that in the middle latitudes (30°–50°), where the tropopause is about 11–12 km high, a reduction of some 2000 times in the ambient atmospheric water-vapor content will be attained over sea level and of some 600 times over a typical mountain observatory (2 km, 6600 ft). Above the tropopause, the water-vapor content is nearly constant up to an elevation of about 20 km. Above this level there is still some uncertainty. Earlier measures, made from balloons, showed a steady increase with a broad maximum indicated near 30 km. It was found, however, that balloons often exude considerable quantities of water vapor at high altitude. In a compilation of all available data up to 1962, Junge (1963) therefore included only such series in which measures made during the balloon ascent agreed with those made on the descent. In Table 1 we have used Junge's data up to 25 km, and in turn averaged these with the results of a very thorough study extended over a year made by Sissenwine, *et al.* (1966) over north-central California (lat. 40° N, long. 122° W) up to elevations of 32 km. These latter are of special interest here because our spectral observations are made from nearly the same geographic position. The averages so derived in Table 1 still indicate a water-vapor maximum in the middle stratosphere, but less pronounced than in Junge's (1963) compilation and now centered around 25 km. Table 1 gives, in addition, an alternative distribution for altitudes above 18 km based on the assumption of a constant mixing ratio as advocated by English observers and recently by Calfee and Gates (1966). These authors, reviewing much recent work, some from high-altitude aircraft, conclude, "the stratosphere is dry and the distribution, although slightly variable, is well fitted by a constant mixing ratio throughout the stratosphere" (2 or 3 parts per million).

On either model it is apparent from Table 1 that the 12–13-km level is very well suited for operations, not merely logistically because of available aircraft, but also scientifically. Full advantage is then taken of being above the relatively wet troposphere and just below the level (13 km) at which observers must wear safety devices in the aircraft. Only a further reduction of other atmospheric components (CO_2, N_2O, CH_4), as well as of the strongest water-vapor bands, will make supplementary observations at much higher altitudes necessary. Spectroscopic observation at the 12–14-km level cannot easily distinguish between the two models (Houghton 1963).

The intensity of the telluric water-vapor bands depends not merely on the integrated abundance along the atmospheric path but also on the pressure.

TABLE 1

AVERAGE VERTICAL DISTRIBUTION OF WATER VAPOR (MIDDLE LATITUDES)*

Altitude								
(KM)	(1000 FT)	log R		log ρ	log W		W (μ)	
0	0	−2.4:		−2.9	−0.3:		5000:	
2	6	−2.8		−3.0	−0.8		1600.	
4	13	−3.1		−3.1	−1.2		600.	
6	20	−3.5		−3.2	−1.7		200.	
8	26	−3.9		−3.3	−2.2		60.	
10	33	-4.4^5		−3.4	-2.8^5		14.	
12	39	−5.1		−3.5	−3.6		2.5	
14	46	−5.5		−3.6	−4.1		0.8	
16	52	−5.5		−3.8	−4.3		0.5	
18	59	−5.5	−5.6	−3.9	−4.4	−4.5	0.4	0.3
20	66	−5.3	−5.6	-4.0^5	-4.3^5	-4.6^5	0.5	0.2
25	82	−4.8	−5.6	−4.4	−4.2	−5.0	0.6	0.1
30	98	−4.8:	−5.6	−4.7	−4.5:	−5.3	0.3:	0.05

*R = average mixing ratio, H_2O/air, by weight; ρ atmospheric density; average W water vapor, weight in grams per 1 km path length in clear air; W (μ) same, in microns liquid equivalent.

Since for strong bands the product $\sqrt{NP}$ is relevant, the contribution to the stronger bands would decrease with altitude even for the left-hand column in Table 1.

In an important pioneering effort, a series of high-altitude solar spectra between 1.0–6.5 μ was obtained from a Canberra jet with an open port by Houghton. *et al.* (1957, 1961) at the Royal Aircraft Establishment, Farnborough, England. The altitudes ranged up to 48,000 ft (14.6 km), and the spectra show the need of reaching at least 40,000 ft (12 km) in astronomical IR spectroscopy. We have obtained a series of solar calibration spectra for 1.0–2.5 μ from altitudes of 1.5–12.5 km (5,000–41,000 ft), with the equipment used on the planets Venus and Mars. The resolution is 20 cm^{-1}, less than the 2 cm^{-1} (at 2.4 μ) to 11 cm^{-1} (at 1.1 μ) used by Houghton, *et al.* (1961), but with more accurately controlled levels of the continuum. These spectra are reproduced in *Comm. LPL* No. 94 and will in their range, 1.0–2.5 μ, serve as references in medium- to low-resolution astronomical spectroscopy.

The moisture distribution of Table 1 is representative of only the middle latitudes where the tropopause lies near the 11–12-km level instead of 7–8 km as in the polar areas, or 18 km as in the tropics. The boundary between the tropical and the middle-latitude circulation zones varies with the seasons, being around 30° in winter and 45° in summer. Near the boundary, the tropopause may be double, often accompanied by a jet stream. This region is likely to be turbulent and is best avoided in observing runs. Since the tropopause is normally well above the upper boundary of cloud formations (only thunderstorm cumuli may penetrate the lower stratosphere), the 12–14-km zone in the middle latitudes is seen to be remarkably suited to astronomical observations in the infrared.

Our first concrete application of high-altitude aircraft to planetary astronomy was a program developed by Dr. Kuiper with Dr. P. St. Amand at the Naval Ordnance Test Station, China Lake, California, in April 1965. It used an A-3B Jet, having a ceiling of about 44,000 ft (13.4 km) which, without major modifications, could accommodate refracting telescopes up to 3- or 4-in. aperture, fastened in a window through a swivel vacuum junction. Mr. Carl Gillespie, our high-altitude observer, found that hand-guiding had sufficient precision (1–2 arc min) for certain integrated measures in the far infrared. The program was developed further by Dr. Frank Low and Mr. Carl Gillespie, and three groups of flights took place in 1966. The results relate mostly to the sun and the sky brightness at 1 mm and will be published elsewhere. The sky radiation attributable to water vapor dropped sharply to inappreciable amounts at an altitude somewhere between 37,000–44,000 ft (11.3–13.4 km) depending on conditions, confirming the general picture of Table 1. The observations were suspended early in 1967 through the tragic loss of the competent crew and the aircraft, on a flight not connected with the IR program.

Planetary and stellar spectroscopy in the near infrared in practice requires a telescope of at least 12-in. aperture on which observations can be made at least over an hour with a guiding precision of 1 arc min or better. Exploratory discussions with Dr. Michel Bader and Mr. Robert Cameron of the NASA-Ames Laboratories early in 1966 led to the formulation of such a program with the NASA Convair 990 Jet. In this aircraft a row of 12 × 14 in. clear-aperture windows was available at 65° above the horizon and also facilities for mounting a telescope with attachments and supporting electronics; further, a gyro-controlled heliostat, allowing continuous guiding with a precision of 10–20 arc sec for at least an hour; while the astronomical operations could be performed with the convenience of a physical laboratory, no pressure suit being required. Formal proposals for a flight program were made in December 1966, and through support by both NASA Hq., and NASA-Ames the authors were assigned time during April-June 1967 in a schedule that was already nearly filled. The aircraft is based at Moffett Field, California (30 mi SE of San Francisco). The relevant features are described below.

On the left side of the aircraft a series of extra window ports allow observation from 65° ± 10° elevation. The window port assigned to this program is located over the wing, for maximum stability and minimum vibration. Its position with respect to the various control points is shown in Figure 1. The dimensions and construction of the window port itself are shown in Figure 2. An outside metal shield, flush with the aircraft skin, protects the optical surface during takeoff and landing. When not in operation a pane of safety glass protects the optical window from the inside. The cross section of the fuselage is shown in Figure 3, which indicates also the position of the two seat rails to which the telescope is fastened. The incoming beam from the 65° window is intercepted by a gyrostatically controlled

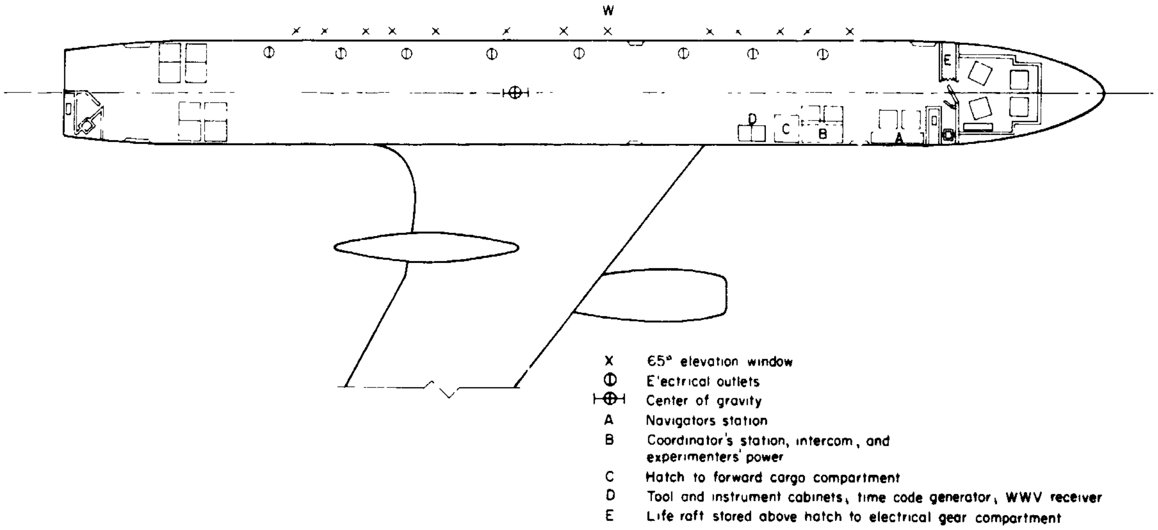


Fig. 1 Floor plan of control points in NASA 990 Jet. *W* gives position of window used in planetary observations.

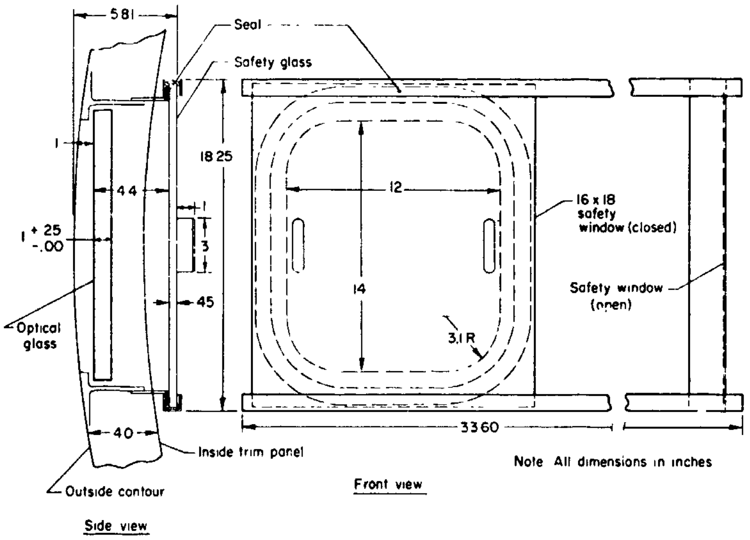


Fig. 2 Construction and dimensions of window port.

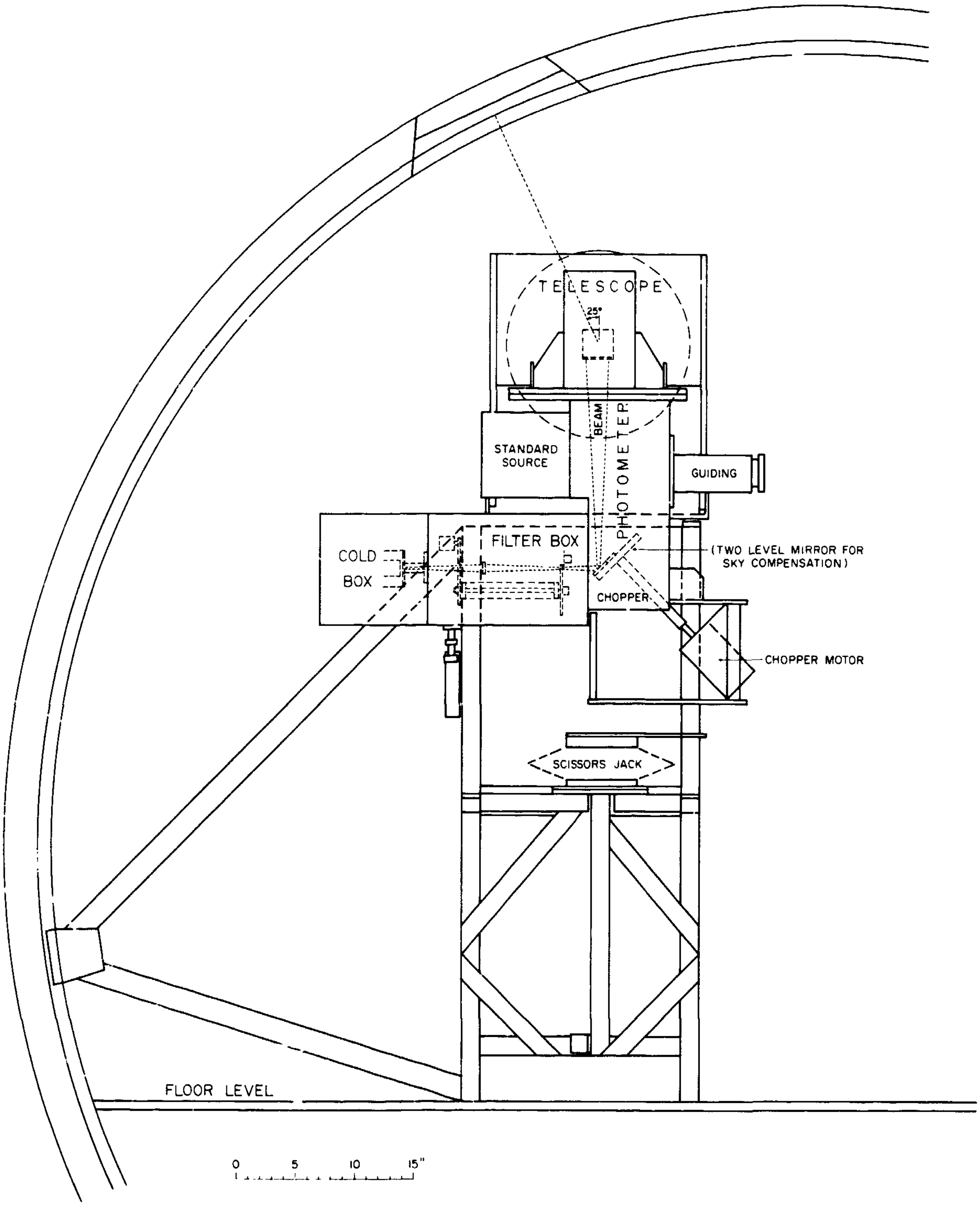


Fig. 3 Cross section of telescope, support, and window normal to aircraft axis. Cf. Fig. 4

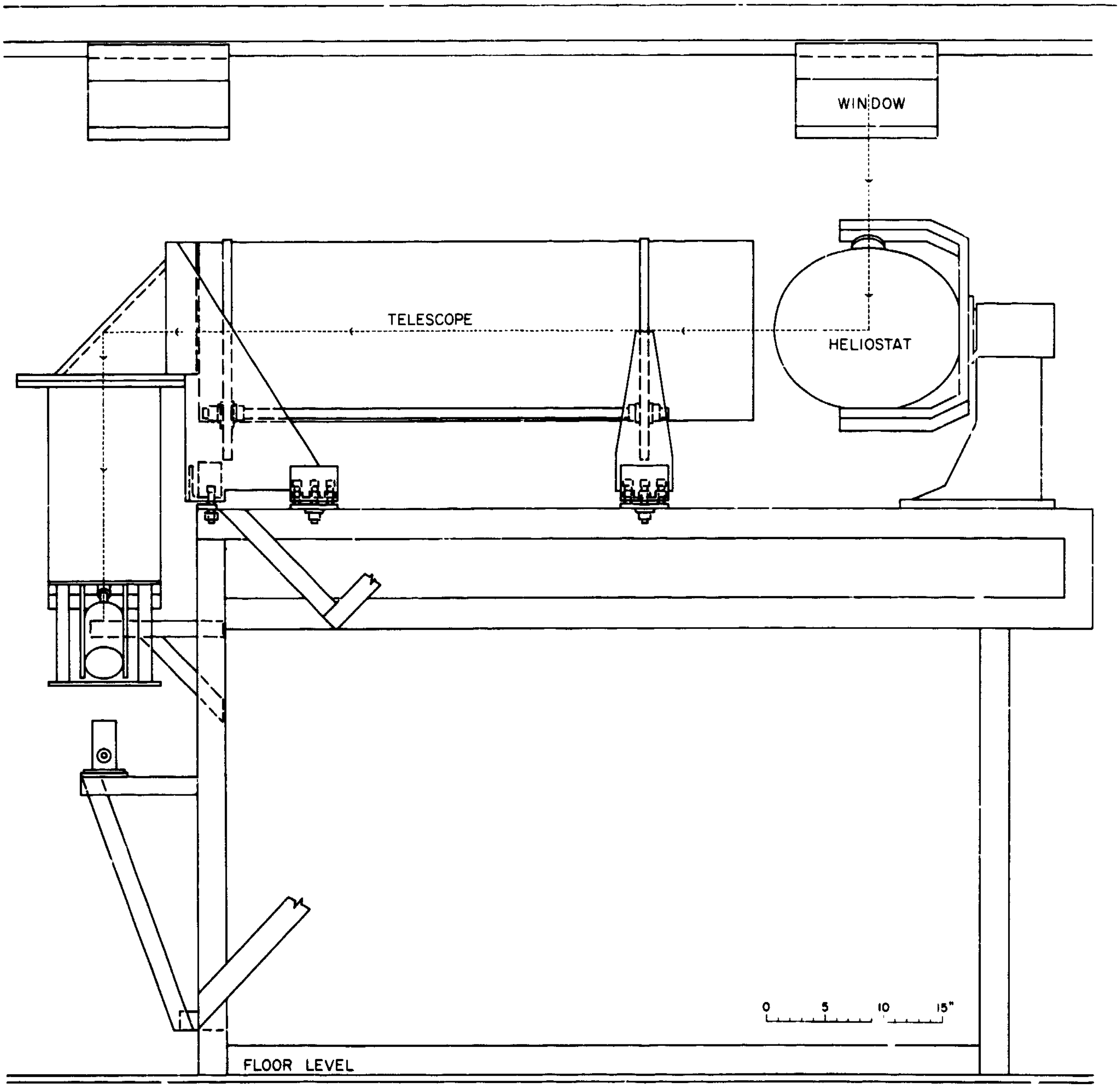


Fig. 4 Longitudinal projection of telescope and accessories.

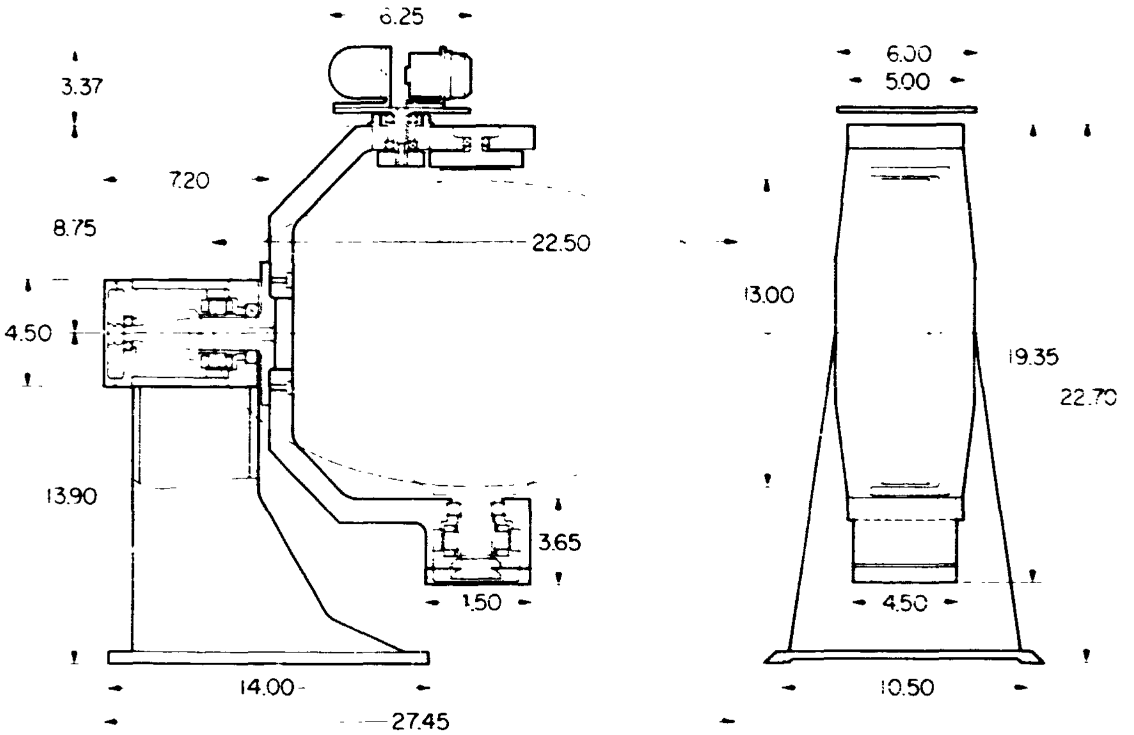


Fig. 5 Dimensions and controls of heliostat mirror. Cf. Fig. 4.

heliostat, the overall dimensions and construction of which are seen in Figures 4 and 5. During operations, the heliostat mirror is not kept parallel to itself as the plane rolls or pitches; instead it is corrected by *half* the angular amounts, which causes the reflected beam of a stationary object to remain parallel to the plane's fuselage. As a result, the image of a planet would be stationary in a telescope attached to the aircraft structure if its azimuth and elevation were stationary. Normally, the observations are made when the planet is in transit, and the plane flies west. Since the heliostat has drives with adjustable rates in both coordinates, the altazimuth drifts can be compensated for. In addition, there are manual overrides for small erratic motions resulting from uncompensated motions of the aircraft. The assemblage of telescope, heliostat, and window port is seen in Figures 4 and 6.

The telescope used in this program is a cassegrain of 12-in. aperture, F/4 primary and F/13 secondary, provided by this Laboratory. The F-ratio was so chosen that the photometers and other attachments in use at the Catalina Observatory could be used without change.

Two attachments have been used so far: (1) a Block interferometer with resolution of 20 cm^{-1}, using uncooled PbS cells, kindly lent to us by Mr. Lawrence Mertz pending the receipt of a Block interferometer on order; and (2) a Johnson photometer equipped with rotating interference wedge filters covering the region of 1.2–4.2 microns. The photometer has a lead-sulfide cell, ¼ × ¼ mm, liquid-nitrogen cooled (NEP = 1.5×10^{-11} W).

The output of either instrument is recorded on magnetic tape and displayed in parallel on an oscilloscope. The wedge spectra are also recorded on the high-speed (0.01 sec response time) recorder. These extra attachments are used for monitoring purposes. Figures 3, 4, and 7 show the telescope with the photometer and filter-wedge device attached. The electronics equipment is mostly kept in the frame that supports the telescope; cf. Figures 4, 6, and 7.

The telescope is attached to the aircraft by shock mounts so that vibration during takeoff and landing, and in flight, are damped. Except for one flight at ceiling [illegible] when the outside temperature had dro[illegible] C and parts of the wing flow [illegible] velocity of sound, causing a special

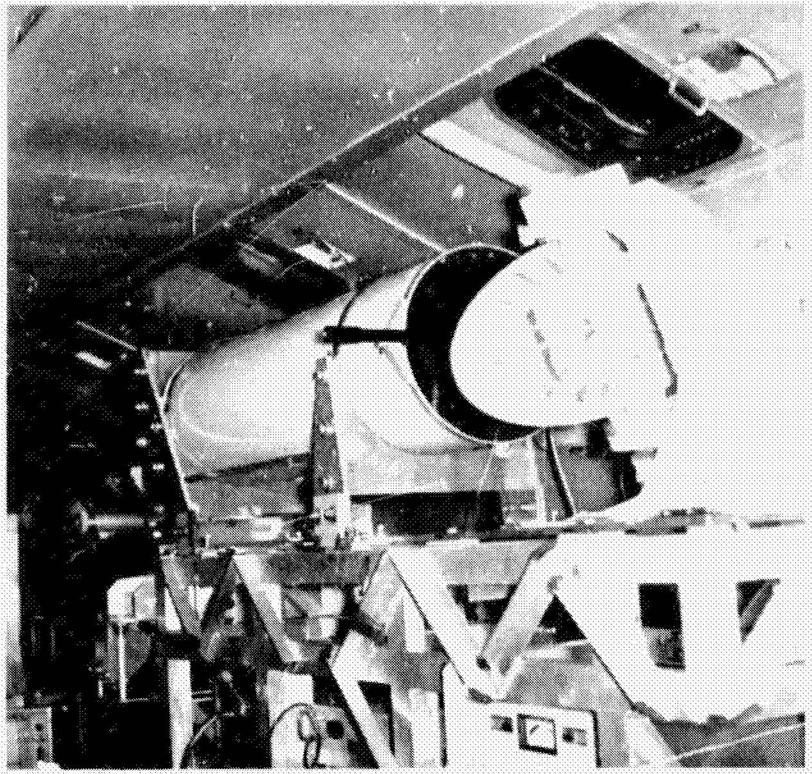


Fig. 6 Photograph of telescope mount and accessories. Cf. Figs. 3–5.

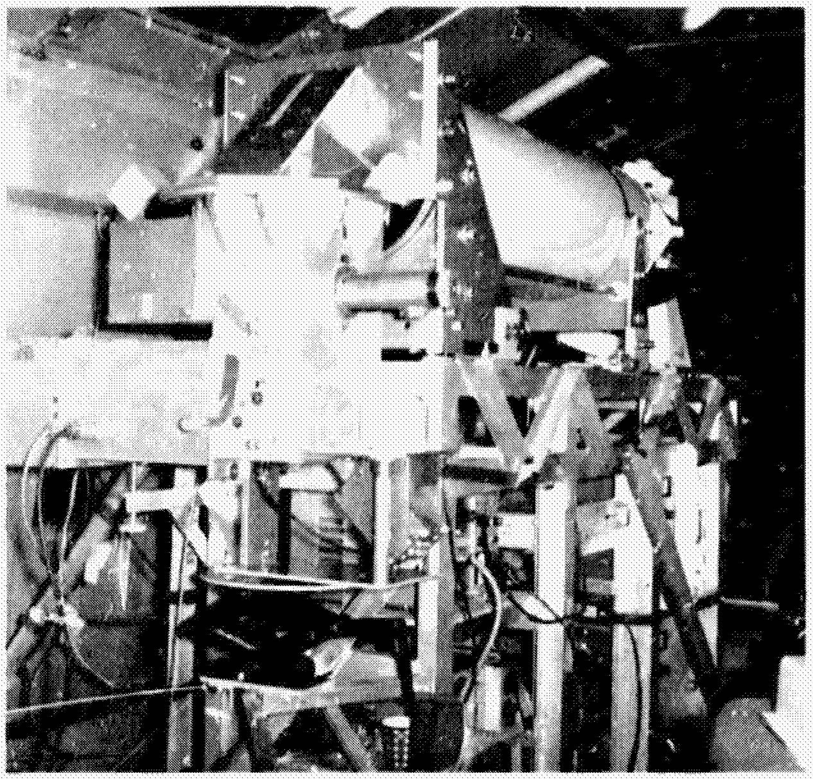


Fig. 7 Photograph of telescope and filter-wedge attachment to photometer. Cf. Fig. 6.

vibration that was transmitted to heliostat and telescope, the vibration damping, though not complete, was quite effective as judged at the guiding eyepiece. Also, the gyroscopes, when started in their proper orientations, performed nearly within their specifications (about 10 arc sec) even during periods of mild turbulence. The IR devices were attached to the telescope in flight and, during the takeoff and landing, were stowed in padded boxes securely anchored to the floor. The interferometer was attached to the telescope through special separators that further reduced vibrations; this proved essential.

As already indicated, the operational procedure developed by NASA-Ames consisted of observing a planet near meridian passage by flying the aircraft at the appropriate time on an east-west course whose latitude made the planet's altitude above the southern horizon 65° ± 5° or at most ±10°. Thus, for Mars (decl. −7°) the geographic latitude at observation was approximately 23° N, for Venus (decl. +26° to +21°), 46° to 41° N. In order to allow observations to continue for an hour or more, the east-west track was slightly curved, based on a schedule computed in advance at NASA-Ames. For example, parts of the Venus flight schedule of May 14 are reproduced in Table 2. The corresponding schedule for the moon, observed immediately afterwards for calibration, is shown in Table 3.

Table 4 lists the flights made during April–June 1967. The April 21–23 flights were out of Moffett Field, over the eastern Pacific off the coast of Mexico, with the actual trajectories shown in Figure 8. (The flight trajectories differ somewhat from those computed because the latter are derived on the assumption of no wind or some average value. At the 40,000-ft level, wind velocities often exceed 100 knots.) The May 14 Venus flight took place over southern Canada, as illustrated in Figure 9.

The April flights were mostly experimental and showed some instrumental weaknesses that were corrected for the May and June flights. Among these were improved telescope focusing, an arrangement that allowed continuous guiding on the Johnson photometer, and improved mounting of the interferometer to reduce vibrations. The choice of the optical window was also reconsidered. Three windows (each about 1 in thick) were available, composed of soda-lime, borosilicate crown, and fused quartz, respectively. It was initially assumed that *fused quartz* would be the most suitable, and it was used in the April flights. It was found, however, that the partial transmission of fused quartz from 3.0–3.6 microns was no compensation for the disadvantages resulting from absorptions at 1.4 and 2.2 microns. For this reason, the *borosilicate crown* window was used in the May and June flights. The transmission curves of the three windows, measured with the Perkin-Elmer spectrometer at NASA-Ames, are shown in Figure 10. Windows transparent for the region beyond 2.5 microns are urgently needed for future infrared spectroscopy. Possibilities under consideration include the use of Infrasil ($\lambda < 4\ \mu$), an Irtran 5 mosaic ($\lambda < 9\ \mu$), a polycrystalline silicon mosaic ($1.1 < \lambda < 1000\ \mu$), and an open window port connected with a vacuum-proof telescope.

A description of the Block *interferometer* has been published by its inventor, Lawrence Mertz (1965*a*, *b*), who graciously permitted the authors to use his personal instrument on the NASA 990 flights. A traveling mirror causes an interferogram with resolution of 20 cm^{-1} to be made every 0.8 sec. During 30 min, some 2000 interferograms are therefore produced. They are recorded on an Ampex Model 860 magnetic tape recorder. The reductions consist of, first, co-adding these records in one or two (or any other small number) of master interferograms; whereupon each of these is reduced to a spectrum by an IBM 1131 computer program cited by Mertz (1966). The very rapid scan of the interferometer appears to avoid the troubles that have in the past beset some of the slower interferometers.[1]

The present Mertz interferometer uses two standard uncooled PbS cells because of their rapid frequency response (>1000 cps). In the new Block interferometer now under construction (having 10 cm^{-1} resolution), cooled InAs detectors will be used instead, with a roughly 20-fold gain in sensitivity.

The *filter wedge* characteristics are shown in Figures 11–13. Figure 11 shows a combination of two semicircular filters cemented together into a single filter wheel about 10-cm diameter. One half transmits the region 1.3–2.5 μ, as indicated in Figure 11*a*; the other half from 2.1–4.2 μ. The bandwidths of the transmission peaks are listed in Table 5 and are seen to be close to 1 percent throughout the region covered. Figure 11*b* shows the peak transmission as a function of wavelength. It is noted that each filter

---

[1] Mertz (1965*a*) correctly stresses that the published critiques of earlier unsuccessful interferometers did not deal with unavoidable basic difficulties; and that, for instance, his technique of very rapid scans suffices to overcome disturbing scintillation effects (even without ratio recording). A similar comment was published by G. P. Kuiper in *Comm. LPL*, 1, 180, Jan. 1963.

TABLE 2

Computations of Venus Flight Trajectory, May 14, 1967

Ut	Lat.	Long	Object Elevation	Object Azimuth	Aircraft Heading	Aircraft Bank Ang.	Object Bearing to Flight Path
19^h 16^m 60^{s}0	46° 5.6	69° 55.9	69° 22.0	168° 19.5	263° 4.5	0° 2.0	265° 15.0
19 21 60.0	46 1.6	70 51.8	69 28.5	169 5.5	263 50.5	0 2.1	265 15.0
19 26 60.0	45 58.2	71 47.8	69 34.3	169 52.1	264 37.1	0 2.2	265 15.0
19 31 60.0	45 55.3	72 43.8	69 39.4	170 39.3	265 24.3	0 2.3	265 15.0
19 36 60.0	45 52.9	73 39.8	69 43.7	171 27.1	266 12.1	0 2.3	265 15.0
19 41 60.0	45 51.1	74 35.9	69 47.4	172 15.4	267 0.4	0 2.4	265 15.0
19 46 60.0	45 49.8	75 31.9	69 50.3	173 4.1	267 49.1	0 2.4	265 15.0
19 51 60.0	45 49.1	76 27.9	69 52.5	173 53.1	268 38.1	0 2.5	265 15.0
19 56 60.0	45 49.0	77 23.9	69 54.0	174 42.5	269 27.5	0 2.5	265 15.0
20 1 60.0	45 49.4	78 20.0	69 54.6	175 32.1	270 17.1	0 2.5	265 15.0
20 6 60.0	45 50.4	79 16.0	69 54.6	176 21.8	271 6.8	0 2.5	265 15.0
20 11 60.0	45 52.0	80 12.0	69 53.8	177 11.6	271 56.6	0 2.5	265 15.0
20 16 60.0	45 54.1	81 8.0	69 52.2	178 1.4	272 46.4	0 2.5	265 15.0
20 21 60.0	45 56.8	82 4.0	69 49.9	178 51.0	273 36.0	0 2.5	265 15.0
20 26 60.0	45 60.0	82 60.0	69 46.8	179 40.5	274 25.5	0 2.5	265 15.0
20 31 60.0	46 2.8	83 56.1	69 44.0	180 29.8	275 14.8	0 2.4	265 15.0
20 36 60.0	46 6.1	84 52.2	69 40.4	181 18.6	276 3.6	0 2.4	265 15.0
20 41 60.0	46 10.0	85 48.2	69 36.2	182 7.1	276 52.1	0 2.3	265 15.0
20 46 60.0	46 14.5	86 44.3	69 31.1	182 55.3	277 40.3	0 2.3	265 15.0
20 51 60.0	46 19.4	87 40.3	69 25.4	183 43.0	278 28.0	0 2.2	265 15.0
20 56 60.0	46 25.0	88 36.4	69 19.0	184 30.2	279 15.2	0 2.1	265 15.0

TABLE 3

Computations of Moon Flight Trajectory, May 14, 1967

Ut	Lat.	Long.	Object Elevation	Object Azimuth	Aircraft Heading	Aircraft Bank Ang.	Object Bearing to Flight Path
20^h 16^m 60^{s}0	46° 52.8	81° 36.5	63° 6.2	132° 9.5	226° 54.5	0° 0.	265° 15.0
20 21 60.0	46 26.4	82 18.4	63 39.2	132 20.9	227 5.9	0 0.	265 15.0
20 26 60.0	45 60.0	82 60.0	64 12.3	132 32.8	227 17.8	0 0.	265 15.0
20 31 60.0	45 33.4	83 41.0	64 46.1	132 45.5	227 30.5	0 0.	265 15.0
20 36 60.0	45 6.9	84 21.8	65 20.0	132 58.7	227 43.7	0 0.	265 15.0
20 41 60.0	44 40.5	85 2.4	65 54.1	133 12.7	227 57.7	0 0.	265 15.0
20 46 60.0	44 14.2	85 42.9	66 28.3	133 27.3	228 12.3	0 0.	265 15.0
20 51 60.0	43 48.1	86 23.2	67 2.7	133 42.5	228 27.5	0 0.	265 15.0
20 56 60.0	43 22.1	87 3.4	67 37.2	133 58.6	228 43.6	0 0.	265 15.0
21 1 60.0	42 56.2	87 43.5	68 11.7	134 15.5	229 0.5	0 0.	265 15.0
21 6 60.0	42 30.5	88 23.5	68 46.4	134 33.2	229 18.2	0 0.	265 15.0
21 11 60.0	42 4.9	89 3.4	69 21.1	134 51.9	229 36.9	0 0.	265 15.0
21 16 60.0	41 39.5	89 43.2	69 55.8	135 11.6	229 56.6	0 0.	265 15.0
21 21 60.0	41 14.2	90 22.9	70 30.6	135 32.5	230 17.5	0 0.	265 15.0
21 26 60.0	40 49.2	91 2.6	71 5.4	135 54.6	230 39.6	0 0.	265 15.0

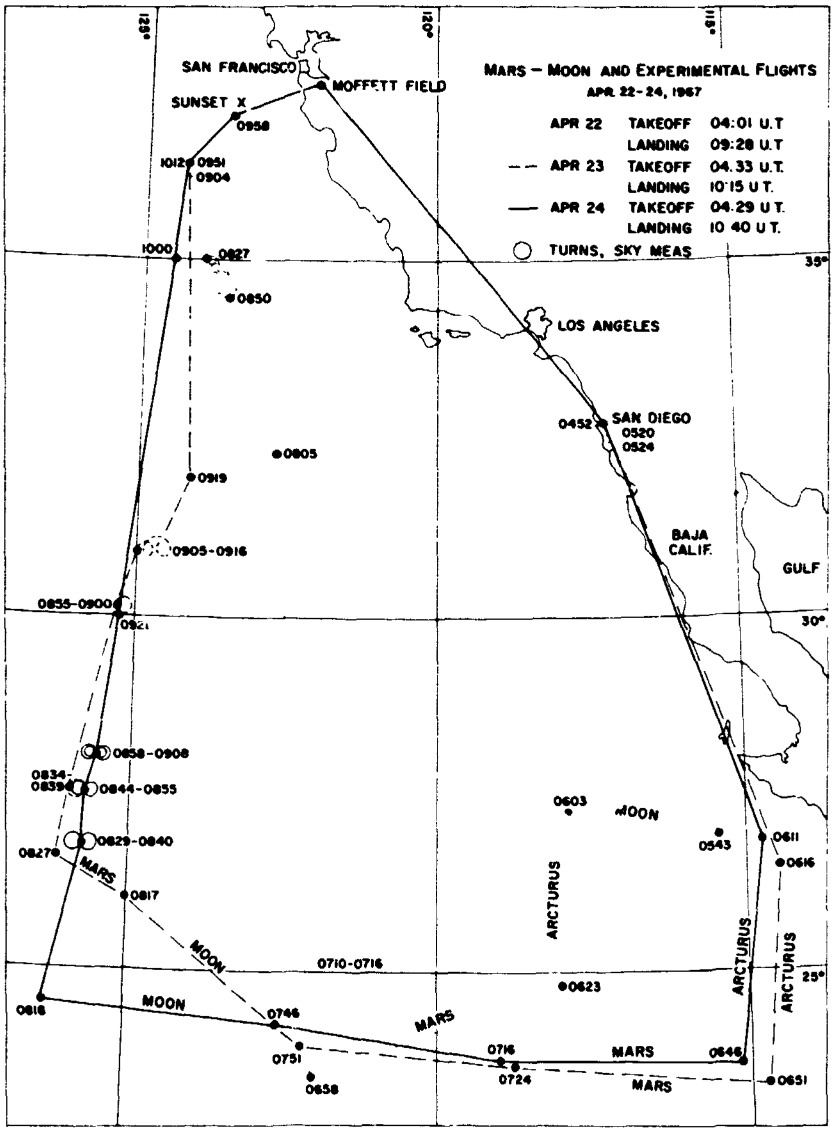


Fig. 8 Trajectories for three experimental flights, April 1967. The turns indicated were made for Dr. Low's IR program.

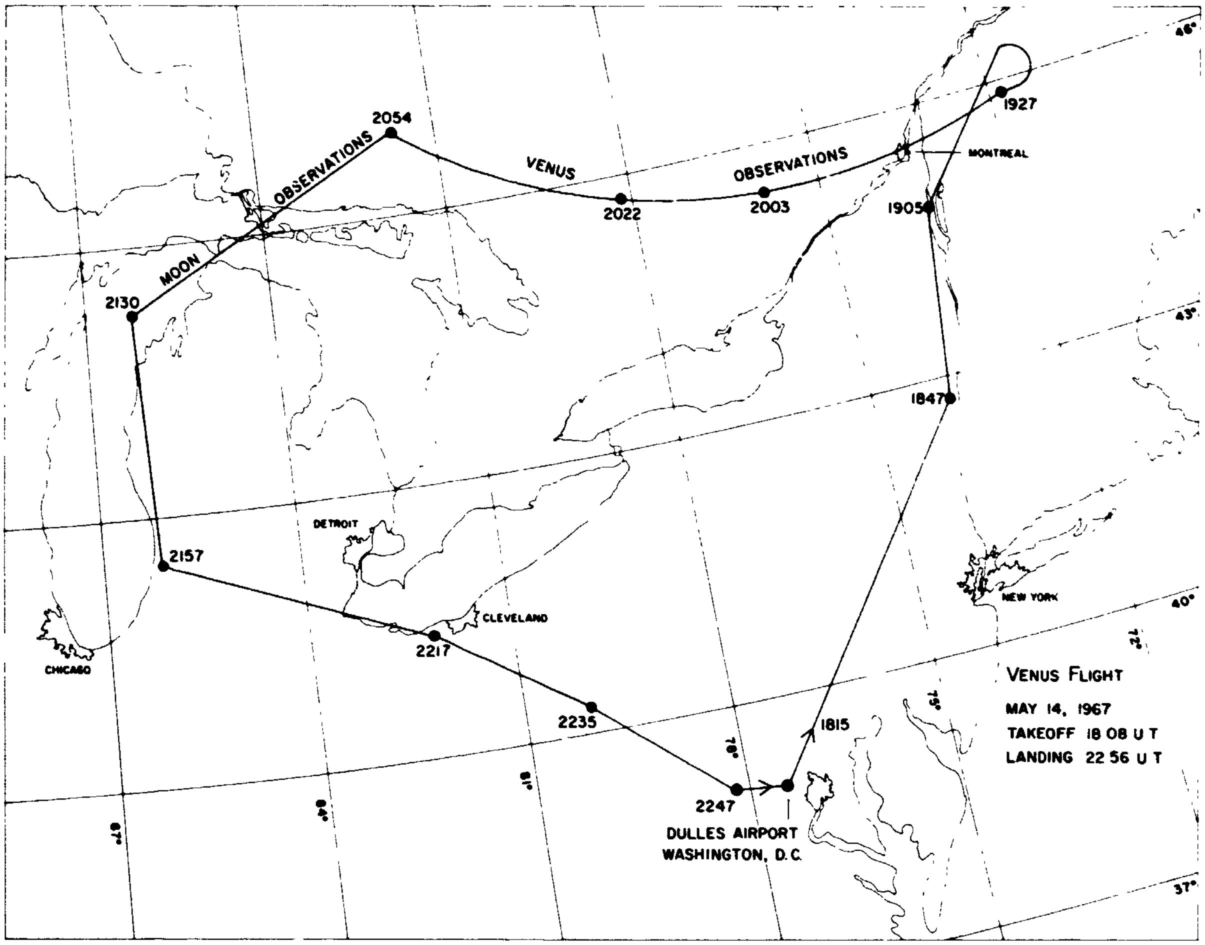
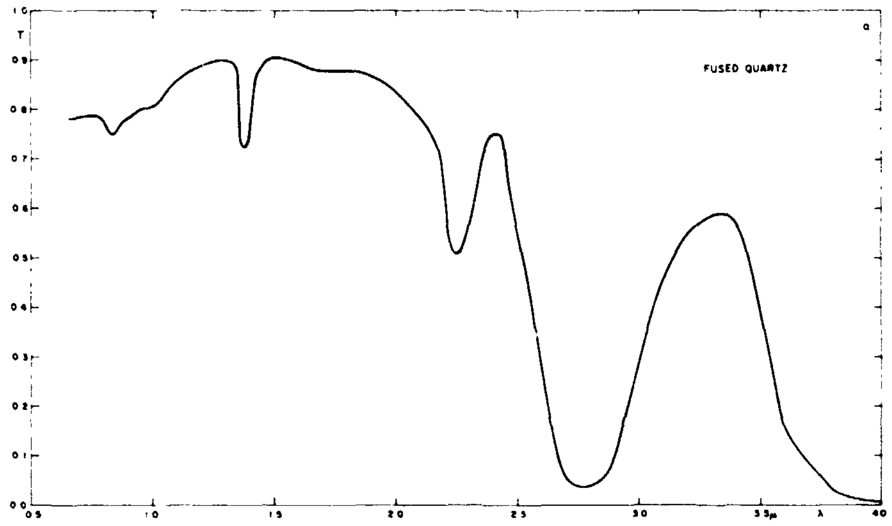


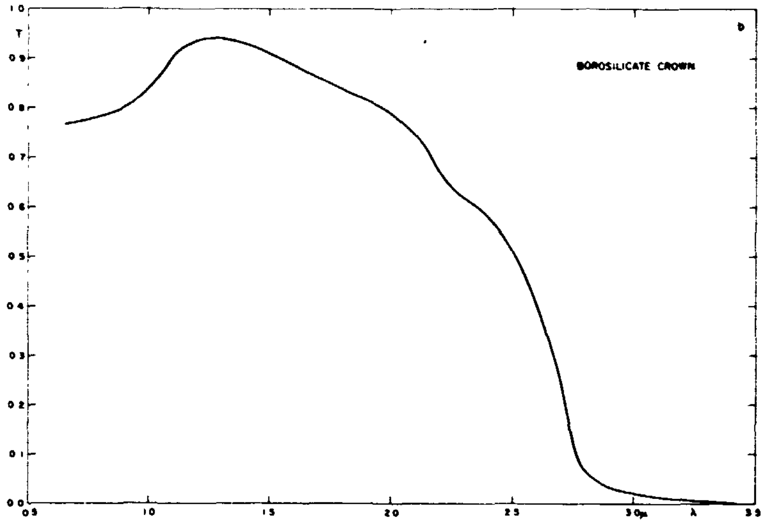
Fig. 9 Trajectory of Venus flight, May 14, 1967

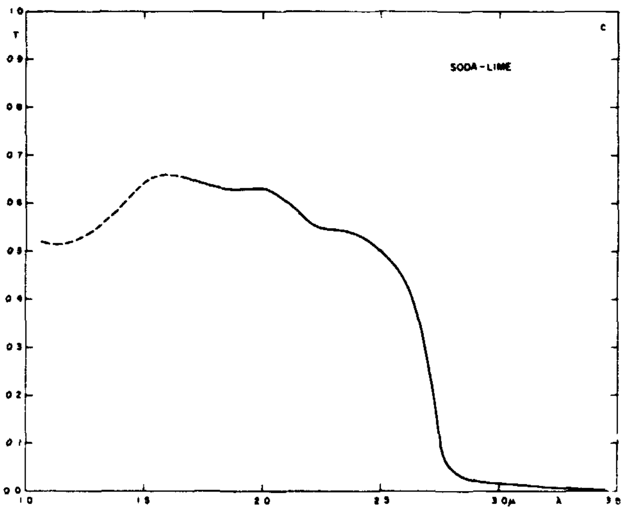
TABLE 4

NASA, AMES 990 JET, IR SPECTROSCOPY FLIGHTS APRIL-JUNE 1967

1967 DATE	TIME	OBJECT	R.A.	DEC.	LOCAL TRANSIT TIME
Fri, April 21	8 PM	Moon	11:59	+ 3:42	21:57
	9 PM	Mars	13:25	− 6:55	23:23
Sat, April 22	9 PM	Moon	12:53	− 3:20	22:46
	10-12 PM	Mars	13:24	− 6:56	23:17
Sun, April 23	9 PM	Moon	13:47	−10:14	23:37
	10-12 PM	Mars	13:22	− 6:50	23:12
Sun, May 14	2-3 PM	Venus	6:24	+25:47	14:56
	4 PM	Moon	7:53	+26:11	16:25
Sun, June 11	2 PM	Moon	8:34	+24:03	15:15
	3-4 PM	Venus	8:34	+21:06	15:15
Mon, June 12	6 PM	Moon	9:39	+19:20	16:14
	7-9 PM	Mars	13:02	− 6:52	19:37
Tue, June 13	6 PM	Moon	10:32	+14:07	17:03
	7-9 PM	Mars	13:03	− 7:00	19:34
Fri, June 23	11-2 PM	Sun	6:07	+23:2	12:02







Figs. 10a, b, and c Transmission curves of three available optical windows.

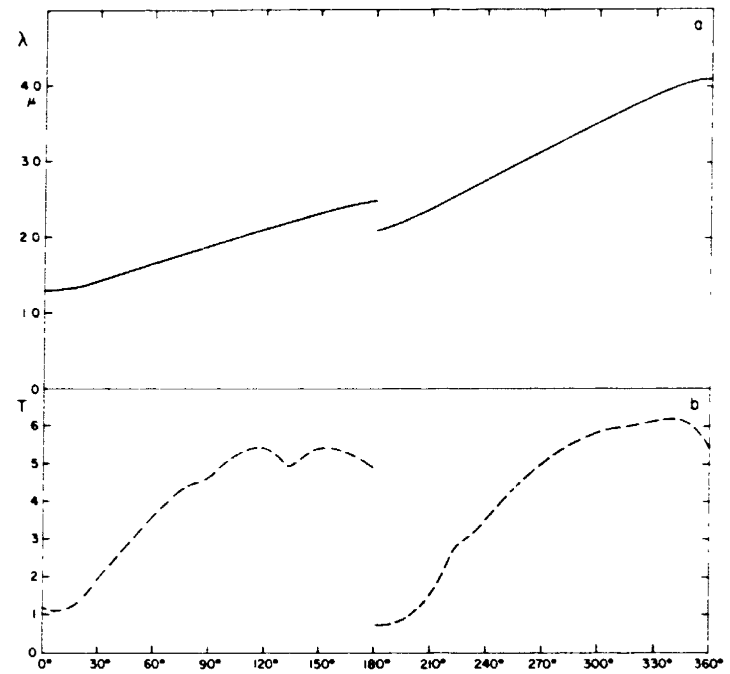


Fig. 11 Wavelength (*a*) and peak transmission (*b*) versus orientation of filter wheel having 1 percent bandwidth (Table 5).

is efficient only for approximately two thirds of its octave. Figure 12*a* shows similarly a complete interference wedge (two symmetrical halves) for the region 1.85–3.65 μ. Its peak transmission is very good, as is seen from Figure 12*b*. Figure 13 reproduces the shapes of the transmission peaks of the second filter. Its bandwidths in terms of filter position and wavelength are shown in Table 6. The filter wheels in the photometer turn at the rate of once per 10 sec.

Application of both the Mertz interferometer and the 1–4 μ filter wheel are presented in the following *Communications*.

A third attachment to be used in the program is a *grating spectrograph* with a short-focus camera, giving 40 A/mm in the photographic infrared. The grating has 600 lines/mm, is blazed for 1.6 μ first order or 8000 A second order. The collimator focal length is 37.5 in. = 95 cm; the camera focal length, 8 in. (20 cm).

TABLE 5

TRANSMISSION PROPERTIES OF FILTER WHEEL NO. 1

ANGLE	λ(μ)	BANDWIDTH %	HALF BRIGHTNESS (μ)	
0°	1.2707	0.822	1.2655	1.2759
30	1.4279	0.995	1.4208	1.4350
60	1.6406	0.945	1.6329	1.6484
90	1.8637	0.918	1.8552	1.8723
120	2.0869	0.995	2.0765	2.0973
150	2.3012	0.955	2.2903	2.3122
180	2.4777	0.891	2.4667	2.4887
180	2.09	0.91	2.0811	2.1001
210	2.33	1.15	2.3482	2.3213
240	2.69	1.01	2.6747	2.7018
270	3.07	0.984	3.0544	3.0854
300	3.34	0.994	3.4352	3.4707
330	3.82	0.97	3.7995	3.8352
360	4.10	1.01	4.0943	4.1353

TABLE 6

TRANSMISSION PROPERTIES OF FILTER WHEEL NO. 2

ANGLE	λ(μ)	BANDWIDTH %	HALF BRIGHTNESS (μ)	
0°	1.855	2.70	1.83	1.88
15	1.990	2.52	1.96	2.01
30	2.14	2.34	2.11	2.16
45	2.31	2.60	2.28	2.34
60	2.45	2.86	2.41	2.48
75	2.60	2.69	2.56	2.63
90	2.72	2.58	2.68	2.75
105	2.95	3.05	2.90	2.99
120	3.11	2.90	3.06	3.15
135	3.26	2.76	3.21	3.30
150	3.41	2.94	3.36	3.46
165	3.55	2.70	3.49	3.60
180	3.64	2.75	3.59	3.69

3. *Future Developments*

While for many years the potential of aircraft carrying IR recording equipment above the terrestrial water vapor had been recognized, the technical problems and the sensitivity limitations of the detectors are only now being overcome. Of particular importance is the development by Mertz of an IR spectral interferometer using rapid scans. Even so, much additional development is needed to make a program possible for an adequate number of important objects. Extension must be made in several directions: (1) greatly increased detector sensitivity in the 1–3 μ region (as indicated in Section 2), which would allow extension of the program to much fainter objects; (2) the development of a window port transmitting up to at least 8 microns and, ultimately, an open port with a heated heliostat and a vacuum-proof telescope; (3) increased spectral resolution for the brighter objects; (4) for calibration purposes (wavelength standards) in planetary and stellar IR spectroscopy, solar spectroscopy with higher resolution; (5) the development of a much larger telescope with an open window port. All these extensions are possible and together they will open up a new branch of astronomy.

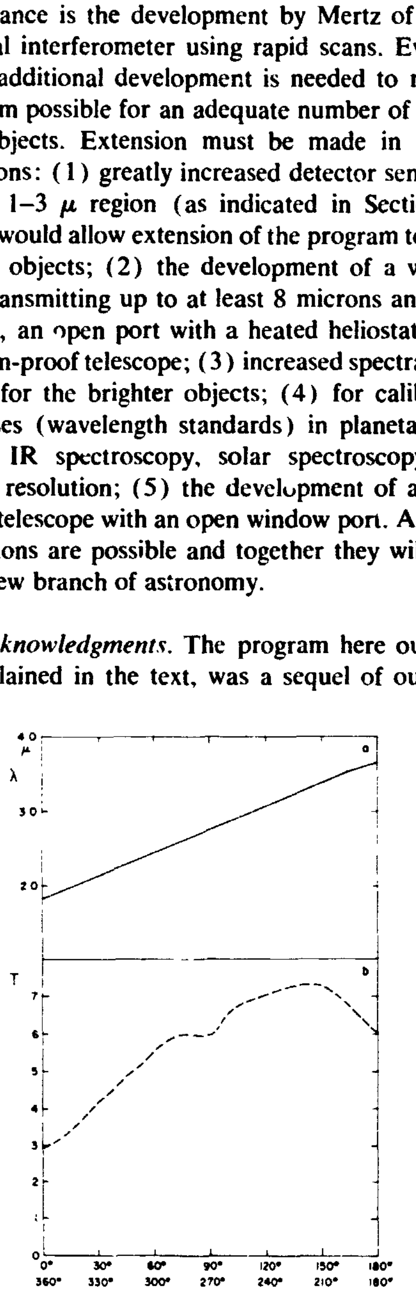


Fig. 12 Wavelength (*a*) and peak transmission (*b*) versus orientation of filter wheel having 3 percent bandwidth (Table 6).

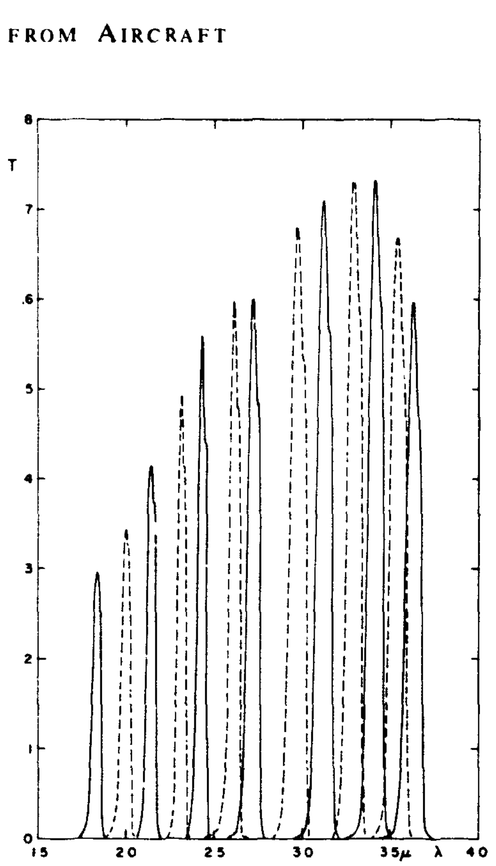


Fig. 13 Transmission peaks of filter wheel No. 2 for selected wavelengths.

Acknowledgments. The program here outlined, as explained in the text, was a sequel of our joint program with the Naval Ordnance Test Station. We are much indebted to Dr. P. St. Amand and the Commandant and staff of NOTS for their interest and generous assistance. The preliminary results published in these *Communications* were obtained with the NASA 990 Jet, made possible through mission-support by NASA Hq., and the facilities offered by the Airborne Sciences Group of the NASA-Ames Laboratories, headed by Dr. Michel Bader. Sincere thanks are due to Mr. R. Cameron and Mr. E. Peterson for assistance before and during the flights, and especially to the navigator, Mr. J. W. Kroupa, for translating our program wishes to acceptable flight schedules. The University Space Sciences Committee awarded the authors substantial grants that allowed us to get this program underway. Appreciation is expressed to Mr. Ferdinand de Wiess who designed and supervised the construction of the telescope support system and other components. We are much indebted to Mr. L. Mertz, Vice President of Block Associates, Cambridge, Massachusetts, for his interest in our program and for loaning us his interferometer. This instrument has proved a marvel

of simplicity and reliability under unusual field conditions and has so far been our principal spectral analyzer on the flights.

REFERENCES

Calfee, R. F., and Gates, D. M. 1966, "Calculated Slant-Path Absorption Distribution of Atmospheric Water Vapor," *Appl. Opt.*, **5** (2), 287–292.

Houghton, J. T. 1963, "Absorption in the Stratosphere by Some Water Vapour Lines in the ν_2 Band," *Quart. J. Roy. Meteorol. Soc.*, **89**, 332–338.

Houghton, J. T., Hughes, N. D. P., Moss, T. S., and Seeley, J. S. 1961, "An Atlas of the Infra-Red Solar Spectrum from 1 to 6.5 μ Observed from a High-Altitude Aircraft," *Phil. Trans. Roy. Soc. London*, **254** (1037), 47–123.

Houghton, J. T., Moss, T. S., Seeley, J. S., and Hawkins, T. D. F. 1957, "Some Observations of the Infrared Solar Spectrum from a High-Flying Aircraft," *Nature*, **180** (4596), 1187–1188.

Junge, C. E. 1963, *Air Chemistry and Radioactivity* (New York: Academic Press), p. 6.

Mertz, L. 1965*a*, "Astronomical Infrared Spectrometer," *A. J.*, **70**, 548–551.

————. 1965*b*, *Transformations in Optics* (New York: John Wiley & Sons).

————. 1966, "Infrared Spectrum of Saturn's Ring,"*A. J.*, **66**, 747.

Sissenwine, N., Grantham, D. D., and Salmela, H. A. 1966, "Mid-Latitude Stratospheric Humidity Regime to 30 Km," *Interim Notes on Atmospheric Properties No. 73* (Presented at AFCRL Scientific Balloon Symposium, Portsmouth, N. H., Sept. 14, 1966).

SUPPLEMENTARY REFERENCES

Beer, R. 1967, ' Fourier Spectrometry from Balloons," *Appl. Opt.*, **6** (2), 209–212.

Bottema, M. 1967, "Guiding of Balloon-Borne Telescopes by Off-Set Sun-Tracking," *Appl. Opt.*, **6** (2), 213–219.

Gassmann, G. J., and Pittenger, E. W. 1966, "Upper Atmospheric Research Using Aircraft," *Special Reports, No. 44*, Air Force Cambridge Research Laboratories, AFCRL-66–292, April 1966.

Gehrels, T. 1967, "Ultraviolet Polarimetry Using High-Altitude Balloons," *Appl. Opt.*, **6** (2), 231–233.

Kondratiev, K. Y., Nicolsky, G. A., Bandinov, I. Y., and Andreev, S. D. 1967, "Direct Solar Radiation up to 30 Km and Stratification of Attenuation Components in the Stratosphere," *Appl. Opt.*, **6** (2), 197–207.

Murcray, D. G., Murcray, F. H., and Williams, W. J. 1967, "A Balloon-Borne Grating Spectrometer," *Appl. Opt.*, **6** (2), 191–196.

Strong, J. 1967, "Balloon Telescope Optics," *Appl. Opt.*, **6** (2), 179–189.

No. 94 SOLAR COMPARISON SPECTRA, 1.0−2.5μ, FROM ALTITUDES 1.5−12.5 km

by G. P. KUIPER AND D. L. STEINMETZ

August 10, 1967

ABSTRACT

Infrared spectra of planets and stars taken from aircraft require solar calibrations showing the telluric spectrum in its dependence on the altitude of observation. In addition, since numerous solar lines are present as well, the blending of these with the telluric spectrum must be known in the analysis of the planetary spectra. The latter contain the same blends, in turn superposed on the absorption spectrum of the planetary atmosphere. This paper reproduces the solar spectra obtained on June 23, 1967, with the NASA 990 Jet and the Block interferometer, the same equipment used in the observation of Venus and Mars. The records were made from various altitudes; the increment is 5000 ft (1.5 km) up to 35,000 ft, with 1000 ft (0.3 km) increments near the ceiling altitude of 41,000 ft (12.5 km). Attention is called to the remarkable internal agreement of the records testifying to the excellent performance of the Block interferometer.

While the normal procedure of observing planetary spectra from the NASA CV 990 Jet has been to include lunar calibration spectra with the planetary spectral runs, it was, nevertheless, felt that direct solar observations from different altitudes would prove indispensable. The sunlight was observed through the borosilicate crown window, 12 × 14 in. in size, moved from its normal position in the 65° window port, to one of the ceiling ports of the aircraft. The sunlight fell on a screen freshly coated with magnesium oxide, and the interferometer was pointed directly at the MgO screen without intervening telescope. Because of the gradually decreasing reflectivity of MgO beyond 2.0 μ and because of the absence of the four reflecting surfaces used in the planetary observations (heliostat, two aluminized telescope mirrors and a 90° mirror near the focus), the distribution of the continuum in the solar spectra is not strictly comparable with that of the planetary and lunar observations published elsewhere in this series. The differences will not be large, however, and of no consequence for the purposes of this study, which is to provide high precision records of the solar and telluric absorption features with the precise resolution used in the planetary spectra. The times of observation are found in Table 1 together with the geographic longitude and latitude of the aircraft, the hour angle of the sun and its altitude above the horizon, the zenith distance, the air mass, and the outside temperature. The observations were conducted by Mr. Steinmetz alone; the analysis of the spectra shown in the figures was made by Dr. Kuiper. The records were made on magnetic tape, as usual; the interferograms were co-added by Mr. I. Coleman at Block Associates who also performed the computation of the spectra and the machine plotting of the results. We are deeply indebted to Mr. Coleman for his interest and competent handling of this phase of the operations.

The figures herewith reproduced show, without any retouching whatever, the original spectral traces. We have added single dashes denoting solar line

TABLE 1

NASA CV 990 SOLAR FLIGHT, JUNE 23, 1967

ALT (1000 FT)	UT	LONG.	LAT	$H_\odot$	ALT.$_\odot$	$Z_\odot$	SEC $Z_\odot$	OUTSIDE TEMP C	CABIN ALT (1000 FT)	FIG. NO.
5	18^h42^m	121.40	37.70	1^h26^m	66°44′	23°16′	1.089	—	—	1
10	18 51	120.65	38.00	1 14	68 49	21 11	1.072	+11	—	1
15	19 00	119.55	38.45	1 00	70 17	19 43	1.062	+03	—	—
25	19 09	118.30	38.90	0 46	71 31	18 29	1.054	−22	—	—
30	19 19	116.90	39.40	0 31	72 43	17 17	1.047	−32	5	3
35	19 35	116.45	40.05	—	73 10	16 50	1.045	−48	8	3
38	19 44	117.95	40.00	—	73 16	16 44	1.044	−54	8	3
39	19 50	118.80	40.00	—	73 22	16 38	1.044	−54	8	4
40	19 58	119.90	39.90	—	73 29	16 31	1.043	−54	9	4
41	20 04	120.75	39.85	—	73 34	16 26	1.043	−54	9	4
25	20 26	123.55	39.15	0 10	74 02	15 58	1.040	−25	6.8	2
20	20 35	122.95	38.25	0 21	75 00	15 00	1.035	−02	—	2
15	20 44	122.50	37.50	0 32	74 22	15 38	1.038	+01	1	2

absorptions, with the members of the Paschen and Bracket series identified. Nearly all of the remaining identifications may be taken from "An Atlas of the Infrared Solar Spectrum from 1 to 6.5 μ Observed from a High-Altitude Aircraft," by J. T. Houghton, N. D. P. Hughes T. S. Moss, and J. S. Seeley, 1961 (*Phil. Trans. Roy. Soc. London*, **254**, 47–123).

The series of solar spectra demonstrates very graphically the tremendous importance of spectral observation in the infrared from altitudes above 40,000 ft (12 km). The spectra taken at 5000 and 10,000 ft (1.5 and 3.0 km) may be regarded as typical for what can be done from a mountain observatory under average and excellent conditions, respectively. The spectrum taken at 15,000 ft represents what has been achieved at the mountain observatories in the southwestern United States during the coldest parts of winter, after an invasion of an Arctic air mass. Even this condition is very far from achieving the almost complete absence of water-vapor absorptions around 40,000 ft (12 km). At the same time, of course, the CO_2 absorptions are greatly reduced. The spectra also demonstrate, as had been anticipated from the moisture profile in the atmosphere discussed elsewhere in this series, that no appreciable further gains can be expected by going still higher. This conclusion is not expected to hold for the heaviest absorptions of water vapor at still longer wavelengths nor for the strongest absorptions of CO_2, CH_4, and N_2O at longer wavelengths. This may be seen from the atlas by Houghton, *et al.* referred to above.

A quantitative review of the telluric H_2O absorptions shown by the records will be published elsewhere.

Acknowledgments. The work here reported was made possible by the facilities of the NASA CV 990 Jet and its expert staff. The spectral observations themselves were made with the Block interferometer graciously made available by its owner, Mr. Lawrence Mertz. As mentioned in the text, the reductions were carried out with the facilities at Block Associates by Mr. Isaiah Coleman, to whom we are deeply indebted. The high-altitude program was supported by a grant by the Space Sciences Committee of the University of Arizona.

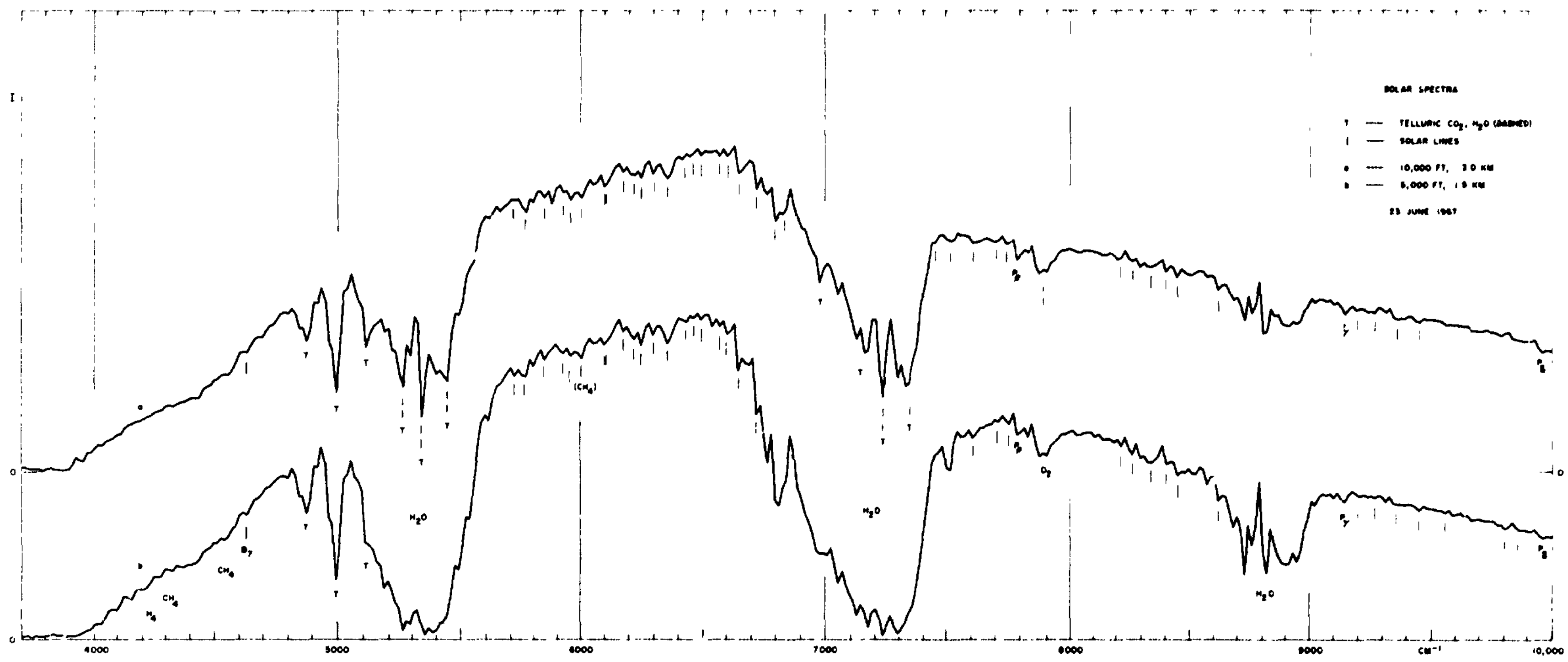


Fig. 1 Solar spectra observed from 1.5 and 3.0 km (5,000 and 10,000 ft).

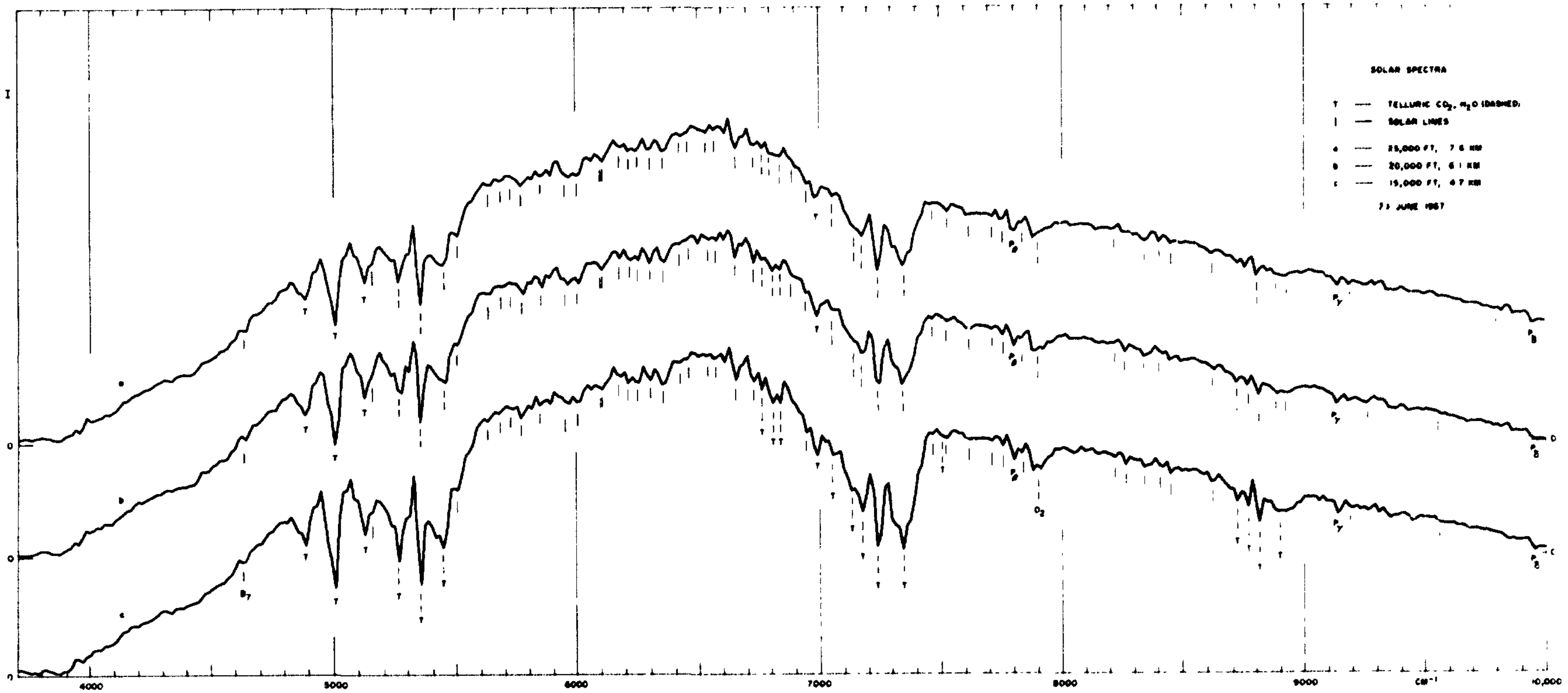


Fig. 2 **Solar spectra observed from 4.7, 6.1, and 7.6 km (15,000, 20,000, and 25,000 ft).**

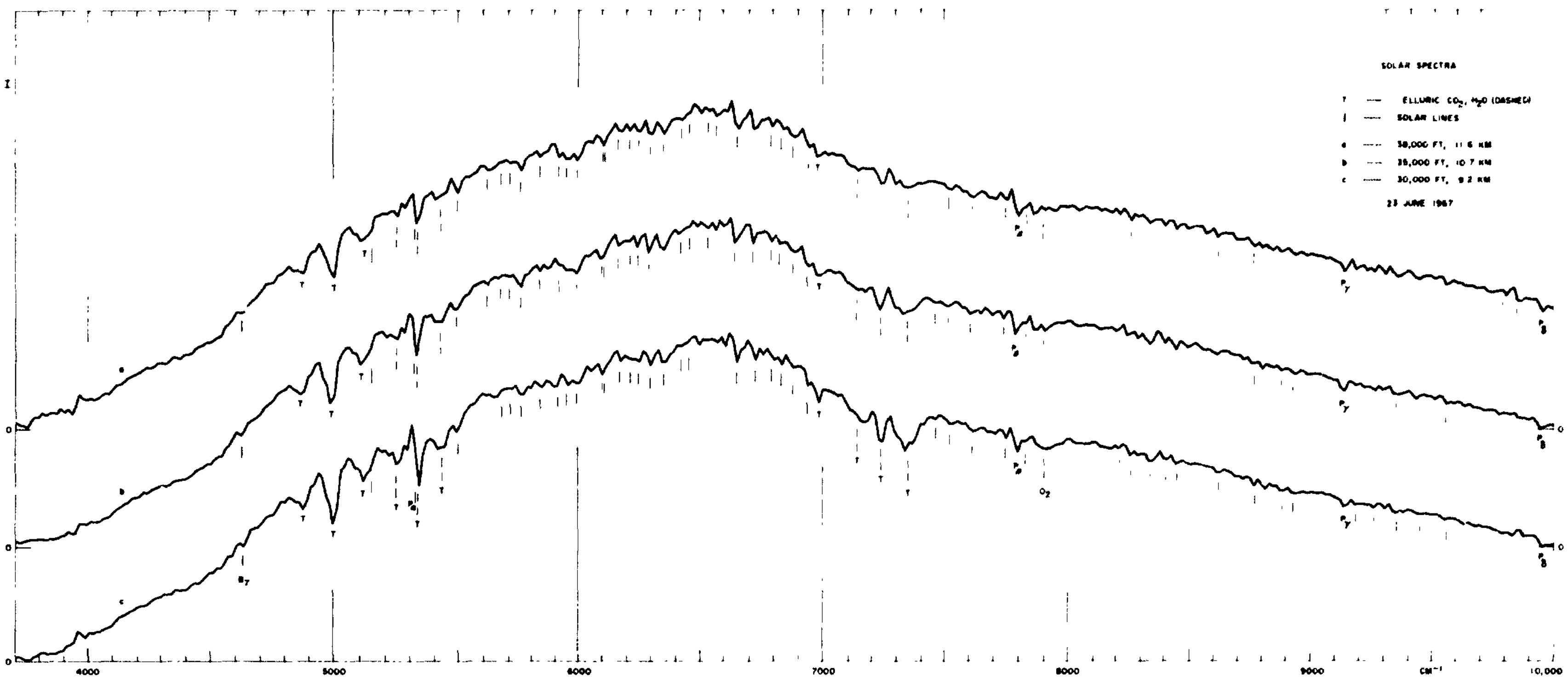


Fig. 3 Solar spectra observed from 9.2, 10.7, and 11.6 km (30,000, 35,000, and 38,000 ft).

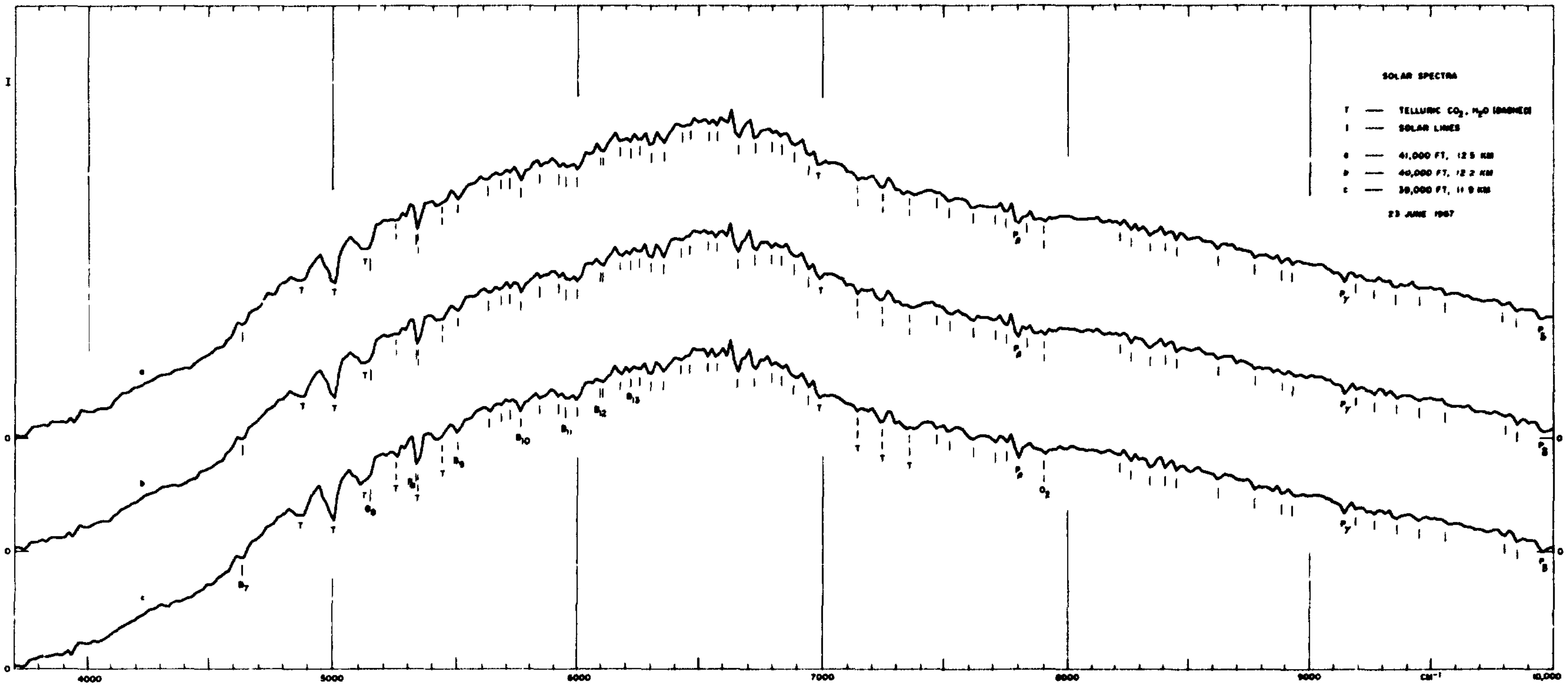


Fig. 4 Solar spectra observed from 11.9, 12.2, and 12.5 km (39,000, 40,000, and 41,000 ft).

N69-12640

No. 95 HIGH ALTITUDE SPECTRA FROM NASA CV 990 JET I: VENUS, 1–2.5 MICRONS, RESOLUTION 20 CM^{-1}

by G. P. Kuiper and F. F. Forbes

November 15, 1967

ABSTRACT

Results from two high-altitude flights in the Spring of 1967 show the Venus atmosphere to be essentially devoid of water vapor and ice crystals. One or two new absorption bands are found, further study of which is deferred until the acquisition of spectra with higher resolution scheduled for late November 1967. The importance is stressed of powerful IR spectral studies from the lower stratosphere.

1. *Introduction*

Infrared spectral observation of planets and stars from the lower stratosphere presents novel opportunities that have been outlined in *Comm. LPL* No. 93. The present paper deals with the first results of this program. It is based on data obtained during two flights with the NASA CV 990 Jet, on May 14, and June 11, 1967. The principal result is that in the observable part of the Venus atmosphere ($T \leq 320°$ K) water vapor is essentially absent. It followed that the comparatively large amounts of water vapor derived spectroscopically from balloons and at ground-based observatories were spurious; and that atmospheric models of the planet, based on these earlier observations and invoking a large greenhouse effect by water vapor and water clouds, could not be valid. A news release covering these results was issued by the University of Arizona on May 27, 1967, and was printed in the *New York Times* on May 28, 1967. A more precise statement was submitted to *Science News* and published in the July 22 issue (Eberhart 1967). The upper limit of the mixing ratio H_2O/CO_2 there given was 4.10^{-7}.

On both flights the combination of heliostat and 12-in. telescope was used, as described in *Comm. LPL* No. 93. It was equipped with the Block 20 cm^{-1} interferometer kindly lent to us by Mr. L. Mertz, vice president of Block Associates. The 65° window used in both flights was Borosilicate Crown (transmission curve, *ibid.*, p. 167, Fig. 10*b*).

2. *Flight Schedules and Elevation Angles of Sources*

The pre-computed schedule for the May 14, 1967, flight (without knowledge of wind conditions) and the actual trajectory are found in *Comm. LPL* No. 93, p. 164, Tables 2 and 3; and p. 166, Figure 9. The pre-computed schedule for the June 11 flight is reproduced in abbreviated form in Table 1 and plotted together with the actual trajectory in Figure 1.

In both flights the moon served for calibration of telluric absorptions. On the May 14 flight, the Venus observations extended from 19^h27^m–20^h54^m UT, the moon observations from 21^h00^m–21^h25^m UT. The astronomical coordinates were as follows:

Venus,	May 14, 20^h00^m UT:	$6^h23^m + 25°47'$
Moon,	May 14, 21^h10^m UT:	$7^h48^m + 26°21'$.

Since the moon observations were made about 1 hr after the average of the Venus observations, and since the actual aircraft latitude at the center of the Venus observations was about 45°30′ and for the

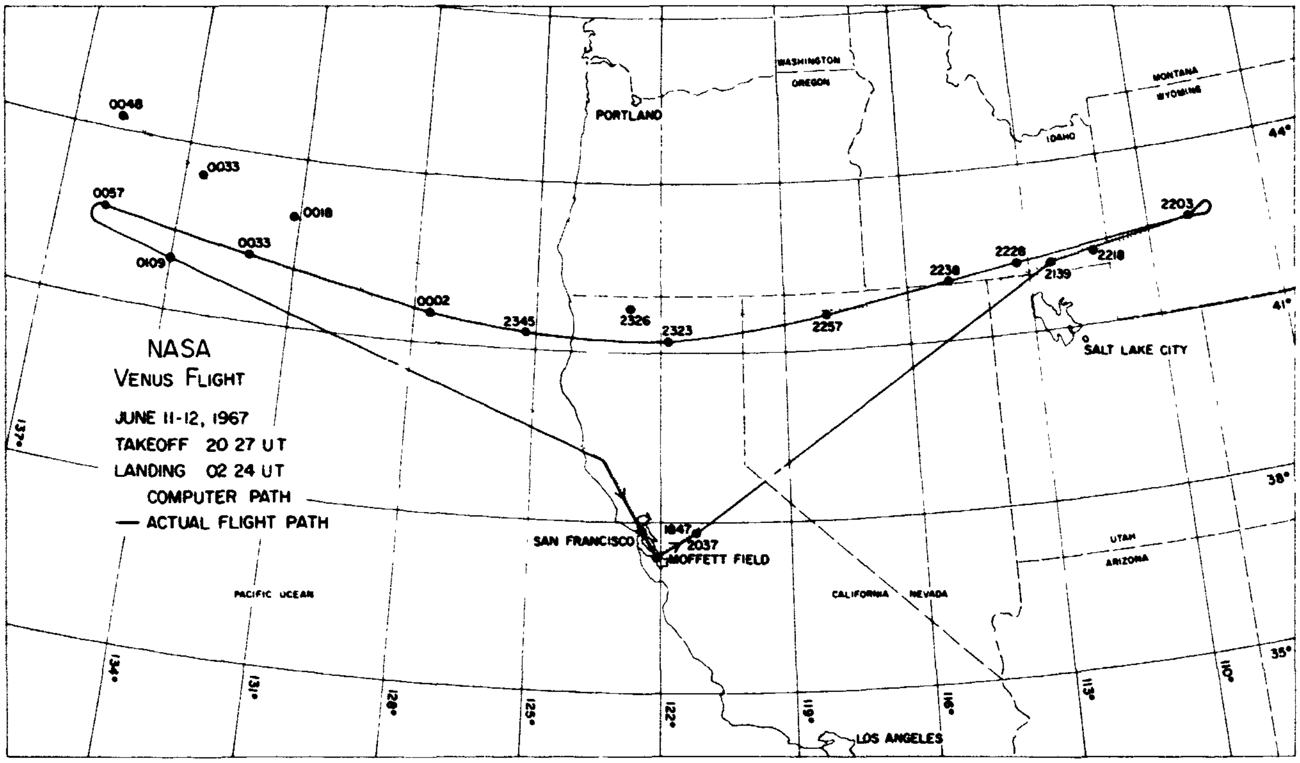


Fig. 1 Flight schedules, precomputed and actual, of the June 11, 1967, Venus Flight.

TABLE 1

UT	Latitude	Longitude	Object Elevation	Object Azimuth	Aircraft Heading	Aircraft Bank Angle	Object Bearing To Flight Path
22ʰ40ᵐ00ˢ	41°47.′9	115° 6.′9	69° 4.′7	169°49.′0	264°34.′0	0°4.′1	265°15.′0
22 48 00	41 43.5	116 26.0	69 13.7	171 33.5	266 18.5	0 4.3	265 15.0
22 56 00	41 40.9	117 45.1	69 20.1	173 19.7	268 4.7	0 4.3	265 15.0
23 4 00	41 40.2	119 4.3	69 23.7	175 7.2	269 52.2	0 4.4	265 15.0
23 12 00	41 41.4	120 23.5	69 24.5	176 55.4	271 40.4	0 4.4	265 15.0
23 20 00	41 44.4	121 42.6	69 22.5	178 43.9	273 28.9	0 4.4	265 15.0
23 28 00	41 49.2	123 1.7	69 17.6	180 32.3	275 17.3	0 4.4	265 15.0
23 36 00	41 56.0	124 20.6	69 9.9	182 19.8	277 4.8	0 4.3	265 15.0
23 44 00	42 4.2	125 39.4	68 59.9	184 6.0	278 51.0	0 4.2	265 15.0
23 52 00	42 13.8	126 58.1	68 47.4	185 50.4	280 35.4	0 4.1	265 15.0
24 0 00	42 25.2	128 16.6	68 32.3	187 32.9	282 17.9	0 4.0	265 15.0
24 8 00	42 38.3	129 34.9	68 14.7	189 13.0	283 58.0	0 3.8	265 15.0
24 16 00	42 53.1	130 52.9	67 54.6	190 50.4	285 35.4	0 3.7	265 15.0
24 24 00	43 9.5	132 10.6	67 32.1	192 24.9	287 9.9	0 3.5	265 15.0
24 32 00	43 27.4	133 28.1	67 7.4	193 56.3	288 41.3	0 3.3	265 15.0
24 40 00	43 46.8	134 45.3	66 40.7	195 24.5	290 9.5	0 3.0	265 15.0
24 48 00	44 7.6	136 2.2	66 11.9	196 49.4	291 34.4	0 2.8	265 15.0
24 56 00	44 29.7	137 18.9	65 41.3	198 10.8	292 55.8	0 2.6	265 15.0
25 4 00	44 53.1	138 35.3	65 9.0	199 28.9	294 13.9	0 2.3	265 15.0

moon observations, about 46°0′ (*ibid.*, Fig. 9), the altitudes at observation were close to 70.0° for both objects.

On the June 11 flight the coordinates were:

Venus, June 11, 23^h00^m UT: $8^h33^m + 21°07'$
Moon, June 11, 22^h25^m UT: $8^h35^m + 23°59'$.

Since the sources were only some 3° apart and the diameter of the finder field was 5°, it was possible without course changes of the aircraft to make alternate runs on them and on the sky near each merely by resetting the heliostat. The interferometer runs are listed in Table 2. Supplementary data for the June 11 flight are found in Appendix A.

3. *Ground-Based Venus Spectrum and Checks on Interferometer*

Prior to the May and June 1967 Venus flights, the interferometer had been tested in a series of observations with the 61-in. NASA telescope of the Catalina Observatory on March 30–31, 1967. The planets Venus and Mars were observed as were the stars Betelgeuse and R S Cancri. The Venus spectrum is reproduced in Figure 2. It is the straight average of two spectra, each of which was based on about 190 interferograms (3.8 min. each run). The solar spectrum is indicated by dots where it differs from Venus; it was taken from *Comm. LPL* No. 94, Figure 1, with minor adjustments of the intensity scale, smooth with wavelength, to fit the Venus continuum. The position of Venus at the time of observation was $2^h41^m + 16° 13'$; it was 5^h05^m past the meridian at the mean epoch 2^h40^m UT, or nearly 20° above the horizon. The large air mass, 2.90, accounts for the heavy telluric absorptions, which roughly match those of the 5000-ft level at unit air mass (*Comm.* No. 94). The identifications have been taken from *Comm. LPL* No. 15.

The spectrum in Figure 2 is comparable to the Venus spectrum recorded with a single-channel spectrometer on the 36-in. telescope of the Kitt Peak National Observatory in 1962 (Kuiper, *Comm. LPL* No. 15, Figs. 1, 2, and 4), both as to resolution (300 at 1.6 μ versus 600 for the one channel) and in signal to noise. The total recording time for the one-channel spectrometer (which used a cooled PbS cell) was about 160 min. Figure 2 was recorded with the 61-in. telescope, the interferometer, and uncooled PbS cells, in 7.6 min. This scanning time would have been reduced to 2 min. however, with the silicon lenses since installed by Mr. Mertz which reduced the image sizes to the detector dimensions, ¼ mm square. The 2-min. figure makes the efficiency of the interferometer just about equal to that theoretically expected (the predicted time is $\frac{1}{4} \times 1/300 \times V_1^2/V_2^2 \times S^2/A^2 \times 160$ min, in which the factor 4 stems from the resolution ratio of 2; 300 is the interferometer resolution at 1.6 μ; V_1/V_2 is the ratio of the planet intensities on the two dates, 1.2; *S* is the sensitivity ratio of cooled versus uncooled PbS cells, about 10; and *A* the ratio of the collecting areas of the telescopes, 3). The Mertz design has therefore fully succeeded.

The principal results of Figure 2 are the better definition of the CO_2 absorption from 4400–4600 cm^{-1}, left uncertain in *Comm. LPL* No. 15 because of an unexplained instrumental absorption near 2.2 μ (later found to be due to fuzed quartz); and the Venus absorption near 5850 cm^{-1} (1.709 μ), suspected in 1962, but left open because of inadequate precision.

4. *Results of the Two NASA CV 990 Flights*

Figure 3 shows the average of two traces of the planet Venus taken on the first flight (May 14, 1967) between $20^h 10^m$–40^m UT, each representing 13 min. of observing. The elevation was 37,000 ft (11.3 km). Because sunlight fell on the 65° window through which the Venus observations were made, some scattered radiation entered the interferometer beam. The amount was evaluated through separate observing runs made on the sky close to the planet. The approximate level of the continuous solar spectrum so derived is indicated by the dashed curve in Figure 3. The intensity of the scattered sunlight is 25–30 percent of the total. An independent determination of this ratio is possible from the depth of the strongest CO_2 bands in the planet. Comparison of Figures 3 and 2 suggest how this determination may be made.

In order that the remaining telluric absorptions might be allowed for, a lunar spectrum was obtained under essentially identical conditions, immediately upon completion of the Venus observations. The spectrum is reproduced in Figure 4. It is found to be in general agreement with the solar spectra observed at the 35,000 and 38,000 ft altitudes, reproduced in *Comm. LPL* No. 94. The identifications shown in Figure 4 are taken from the solar spectra. A minor disturbance is noted at 5810 cm^{-1}, which is the third harmonic of 60-cycle hum introduced in the co-adding process. The dotted curve near that frequency indicates the estimated undisturbed profile.

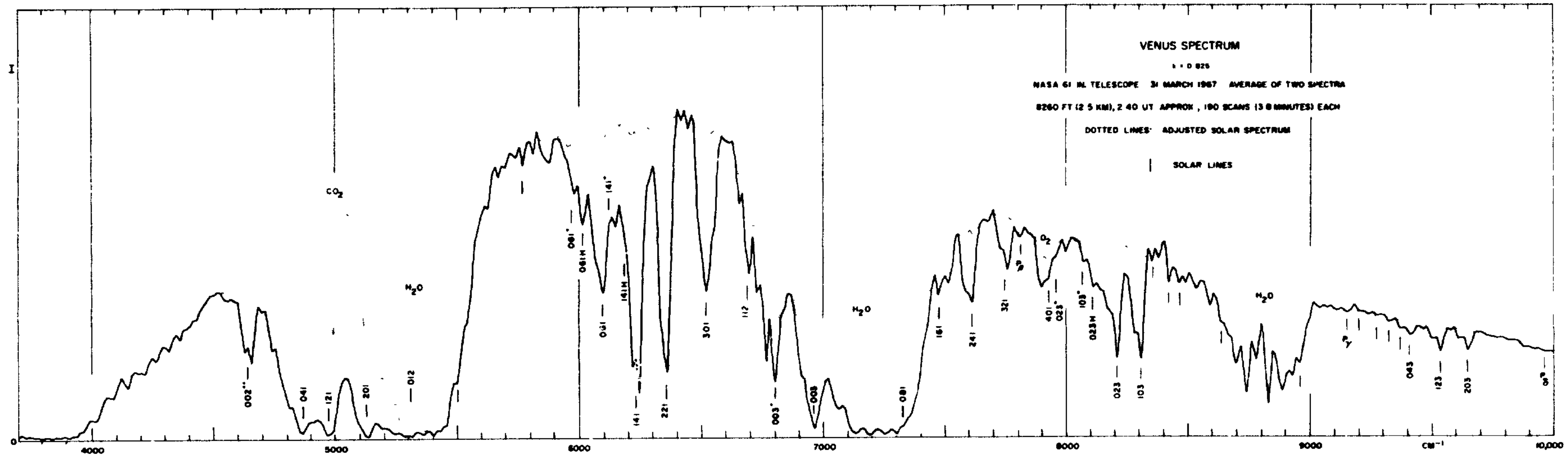


Fig. 2 Spectrum of Venus obtained with Mertz Interferometer, 61-in. telescope, March 31, 1967. Venus absorptions contained between dotted line (adjusted solar spectrum) and full-drawn line (Venus spectrum). Band classifications are of CO_2 molecues; H = hot band; * C^{13} isotopic band, ** oxygen O^{18} isotopic band.

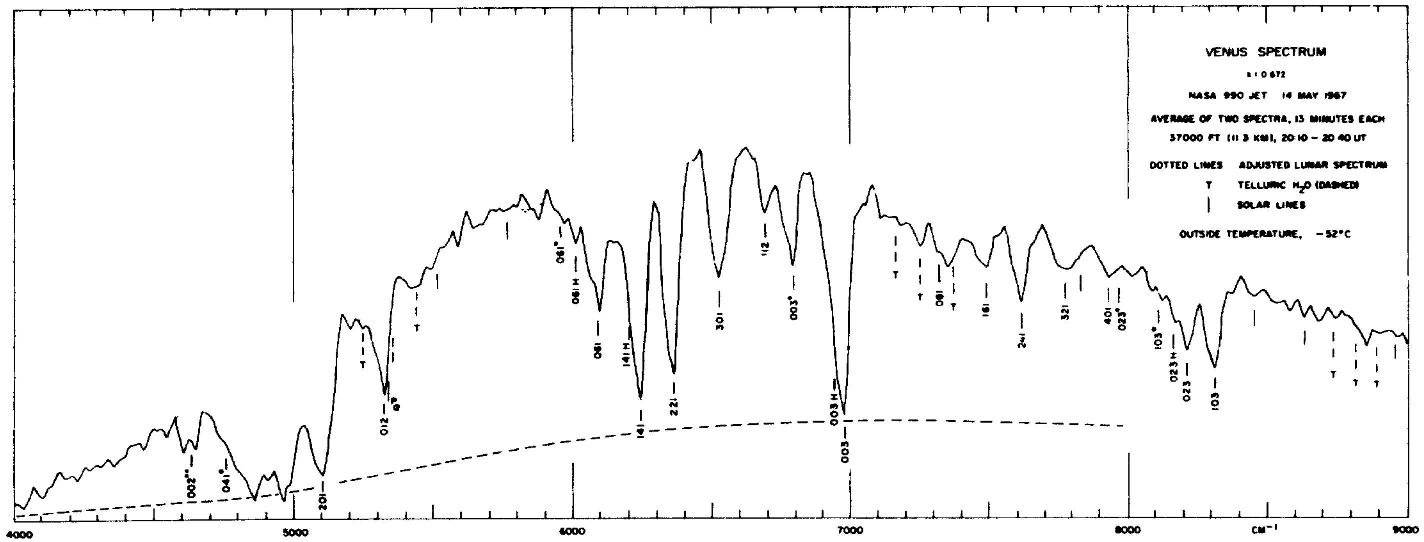


Fig. 3 Venus spectrum, the first obtained at high altitude, May 14, 1967. Venus absorptions are contained between dotted line (adjusted lunar spectrum) and full-drawn line (Venus spectrum). Dashed line near bottom indicates average intensity of scattered sunlight contribution from aircraft window.

The identifications of the CO_2 bands in Figure 3 were taken from *Comm. LPL* No. 15. Of special interest is, of course, the strength of the water-vapor absorptions in the Venus spectrum and any dips in the continuous spectrum attributable to absorptions by ice crystals in the Venus atmosphere. These matters are reviewed in the next section with the aid of laboratory calibrations of water vapor made in *Comm. LPL* No. 96.

As is apparent from Table 2, the circumstances of the June 11 Venus flight were photometrically excellent since the proximity of the moon allowed alternating observations, Moon-Venus-Moon-Venus, in each case supplemented by sky records. Figure 5 shows the first lunar calibration spectrum of this flight. Comparison of it with the high-altitude solar spectra reproduced in *Comm. LPL* No. 94 shows excellent agreement for the 38,000-40,000 ft level.

Figure 6 presents the average of two Venus spectra based on 29 min. and 30 min. observing runs (cf. Table 2). Throughout, the basic spectra were plotted mechanically, directly from the computer output. The averaging of the two spectral traces (each about 1 m long) was done by Mrs. A. Agnieray, by averaging the ordinates for nearly a thousand wavelength points after making minor adjustments of the abscissae so that the sharp spectral features would come into complete coincidence for blocks of 500 to 1000 cm^{-1}. These small adjustments were needed because of a minor scale difference between the spectral plots. It is felt that this averaging has been done with complete objectivity.

The identifications in Figure 6 are based on *Comm. LPL* No. 15 supplemented by solar lines of Figure 5, present also in Figure 6.

The remaining Venus and moon spectra, obtained during the last two runs (cf. Table 2), are reproduced in Figures 7 and 8. Figure 7 is again an average, derived by Mrs. A. Agnieray from two mechanically-plotted spectral traces based on 10- and 13-min runs, respectively. The noise level in Figure 7 is somewhat greater than in Figure 6, partly because of the shorter observing run and also apparently because of increased engine vibrations at the ceiling altitude of the aircraft. Thus, the lunar spectrum of Figure 8 is also noisier than Figure 5 although the observing run was slightly longer.

Referring to the general program described in *Comm. LPL* No. 93, it was initially considered quite uncertain whether the interferometer could be used at all, since obviously even minute displacements of the moving mirror due to vibration would lead to spurious results. Even with the telescope and heliostat-stand shock-mounted to the aircraft, the initial interferometer results were indeed found "vibration-limited." This was overcome by shock mounting the interferometer on the telescope as well. It was, of course, attempted to obtain Venus records with lunar comparisons at ceiling altitude. This, however, resulted in increased engine vibrations (and one of the cabin compressors to blow out just upon termination of the last Venus run). In addition to an increase in noise level, the lunar spectrum showed minor spurious peaks at $n \times 1935$ cm^{-1}, the 60-cycle hum. The peaks at n equals 2, 3, 4, and 5 are within the range of Figure 8 and since their cause was known, they have been deleted (leaving small gaps). Ultimately a more definitive reduction of the Venus spectra here reproduced may become feasible.

TABLE 2

INTERFEROMETER RUNS ON THE JUNE 11 VENUS FLIGHT

OBJECT	JUNE 11/12 UT	NO. OF SCANS	ALTITUDE (FT)	FIG. NO.
Moon	22^h20^m–29^h	471	38,900	5
Sky n. M	22 30 –35	251	38,900	—
Venus	22 41 –10	1418	38,900	6
Sky n. V	23 11 –16	267	38,900	—
Venus	23 30 –00	1493	41,050	6
Venus	24 03 –13	491	41,400	7
Sky n. V	24 13 –20	312	41,400	—
Moon	24 21 –31	500	41,400	8
Venus	24 37 –50	600	41,400	7
Sky n. V	24 50 –55	230	41,400	—

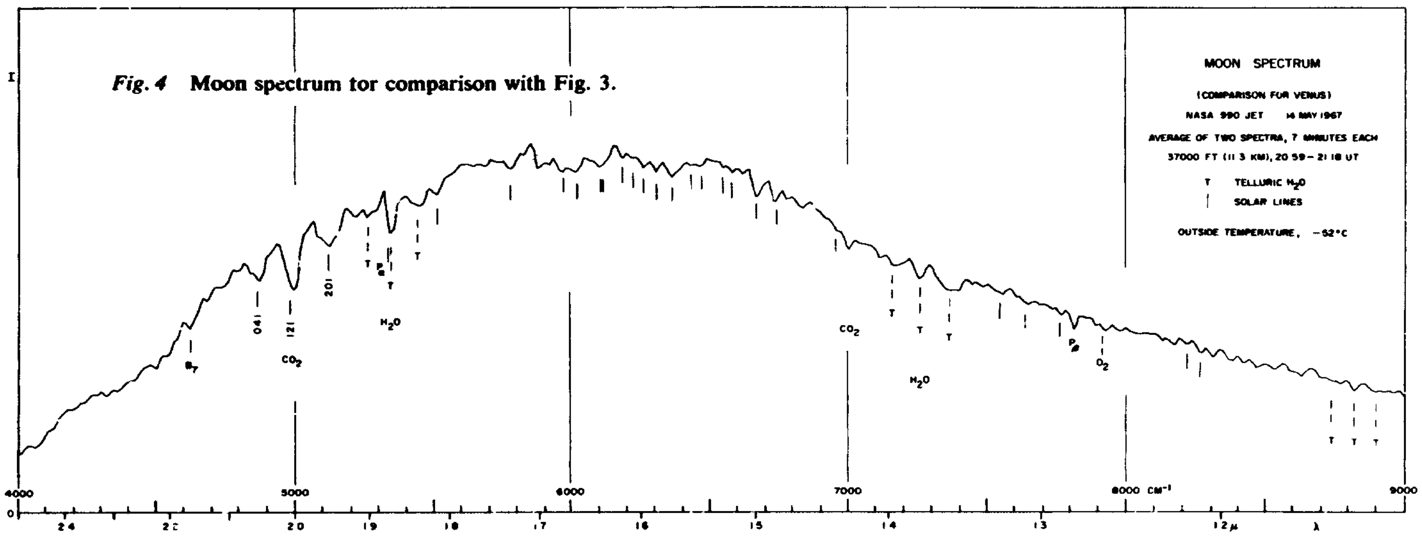


Fig. 4 Moon spectrum tor comparison with Fig. 3.

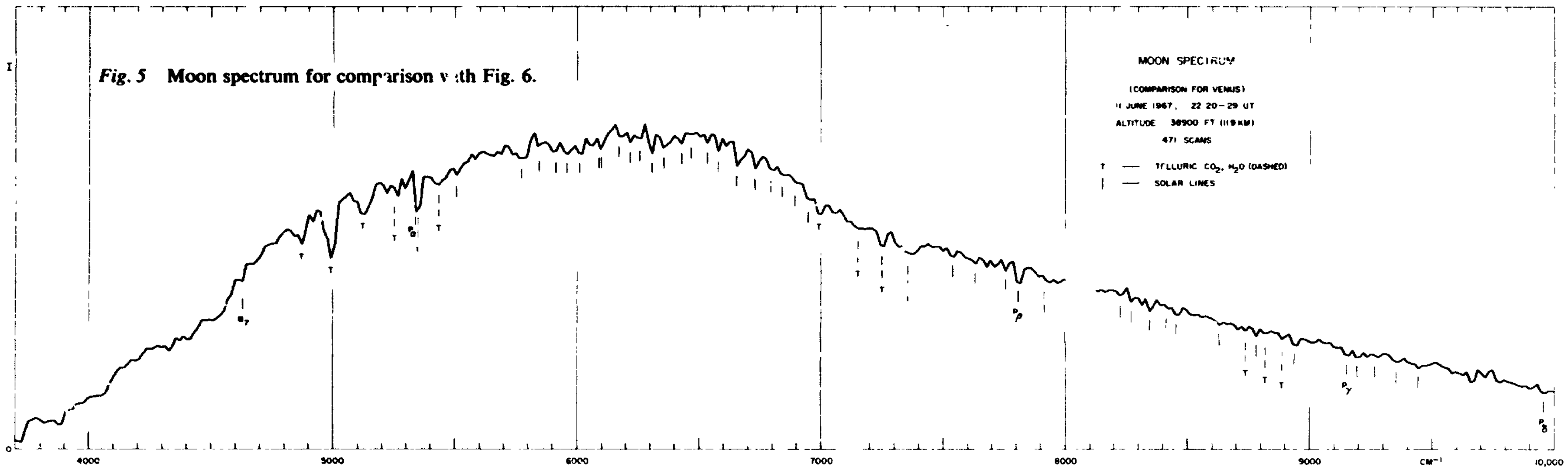


Fig. 5 Moon spectrum for comp'arison v ;th Fig. 6.

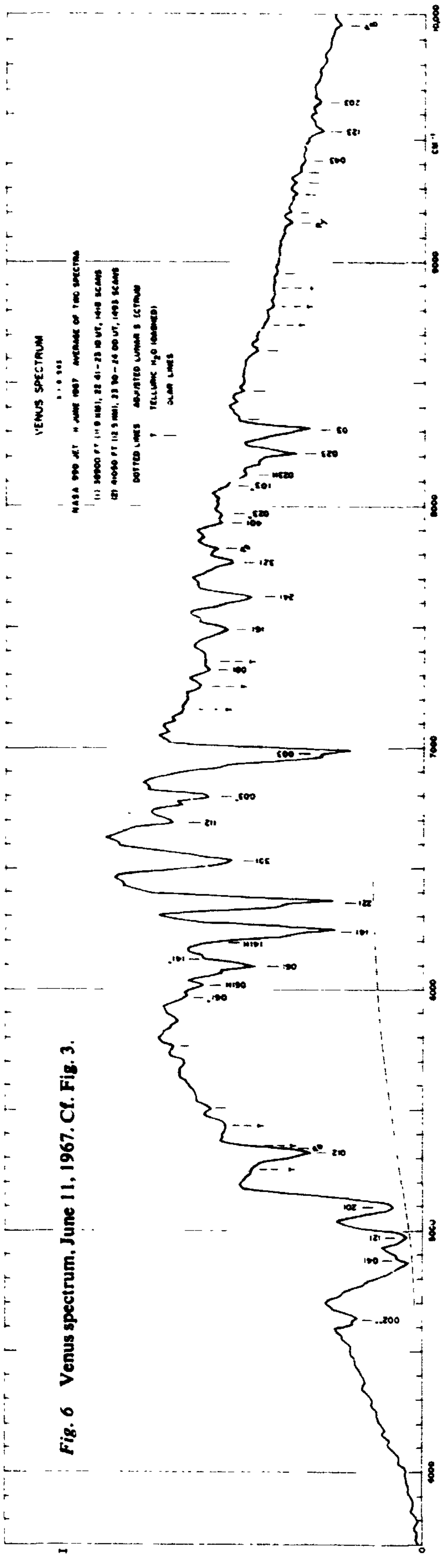


Fig. 6 **Venus spectrum, June 11, 1967. Cf. Fig. 3.**

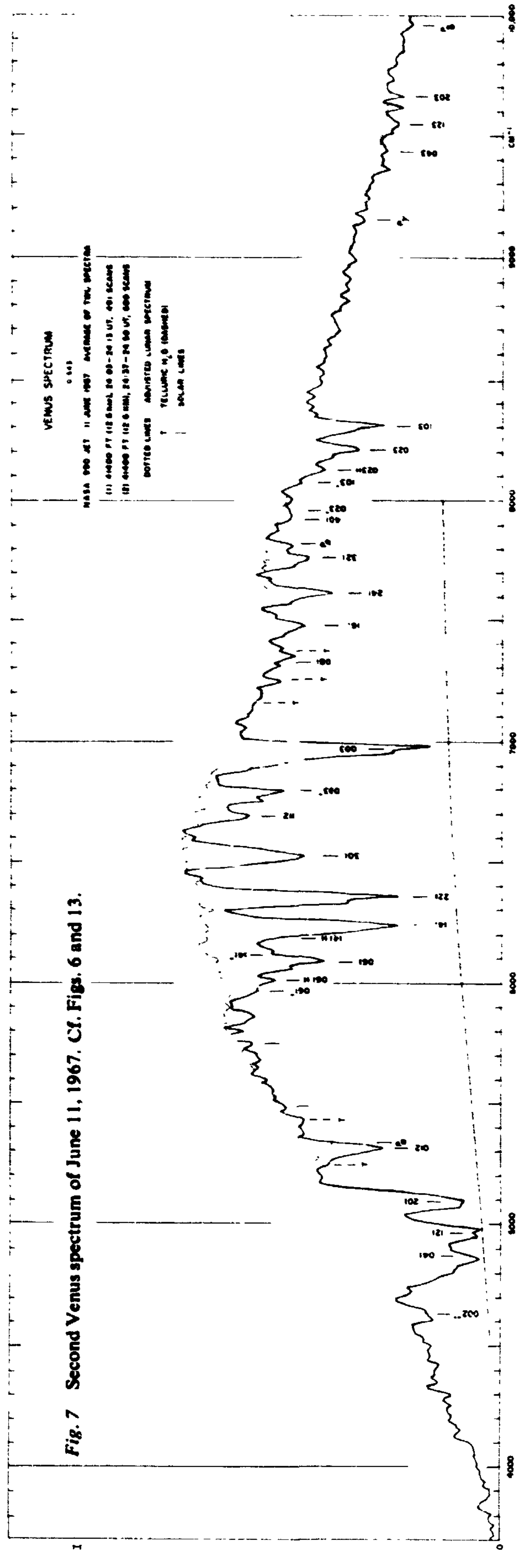


Fig. 7 **Second Venus spectrum of June 11, 1967. Cf. Figs. 6 and 13.**

5. *Water-Vapor Content of Venus Atmosphere*

Two moderately strong water-vapor bands, at 1.4 and 1.9 μ are present in the spectral range covered as well as the weaker band at 1.13 μ.

Each of the three pairs of Venus and Moon spectra contain water-vapor bands of very nearly equal strength, showing that the Venus contribution is zero or very small. Nonetheless, it is necessary to calibrate the intensities in terms of precipitable water in order that the difference and its precision may be made quantitative. The curves of growth needed for this calibration are found in *Comm. LPL* No. 96, Figure 3. Two pressures were used, ambient laboratory air ($p = 70$ cm) and $p = 15$ cm, corresponding to the atmospheric 200 mb level from which the Venus and moon observations were made (since the water vapor is concentrated toward the lower levels even at that altitude, $p = 200$ mb rather than the average of 100 mb was regarded appropriate).

As explained in *Comm. LPL* No. 96, the 200 mb calibrations suffered from a minor complication due to a short (37 cm) air path in ambient laboratory air. The Venus and moon records likewise had a short air path at higher pressure. The cabin altitude for most of the observations was around 9700 ft (cf. Appendix A), corresponding to a pressure of 706 mb; and the air path 4 m (mirror-heliostat-Cassegrain telescope-interferometer). Thus, as found from the measured water-vapor pressures, listed in Appendix A, the cabin contribution to the optical path was 1.5–2 microns of water. The total amount may actually have been less since the measures were made with a sling psychrometer in the open cabin area near the telescope, not within the plastic sheet loosely enclosing the optical train, shielding it from the proximity of the three observers, and allowing fresh compressed outside air to enter directly. Since the outside frost point must have been around −70°C, the actual water-vapor content within the enclosure may have been only a few tenths of the amount measured in the cabin at large. In any case, during the Venus and moon observations the cabin contributions will have been almost identical. During the second Venus flight the manpower aboard the aircraft was limited to the flight personnel and the three observers, so the spectral records were made under optimal conditions.

Table 3 lists for each of the records, Figures 3–8, the average UT of observation, the aircraft position (taken from *Comm. LPL* No. 93, Fig. 8 and Fig. 1), the local time (computed from the UT and the aircraft longitude), the hour angle of the source at the mid-time of observation, the declination of the source, its computed zenith angle, and the corresponding air mass (secant Z). Since about 30 percent of the continuum in Figure 3 is due to sunlight on the aircraft window, the effective air mass determining the strength of the telluric absorptions is $0.3 \times 1.55 + 0.7 \times 1.064 = 1.21$. The lunar spectrum, Figure 4, which was not appreciably diluted by sunlight, corresponds to the air mass 1.085.

For each of the records, Figures 3–8, the percent absorptions in the 1.4 and 1.9 μ water vapor bands were measured. The results are contained in Table 4. The branch designations are the same as used in *Comm. LPL* No. 96. It was found that in spite of the efforts to retain feature 1.9a, this could not be done since the Venus absorption was uncertain due to the blending with one of the CO_2 bands. A similar but less serious complication exists for

TABLE 3

FLIGHT DATA AND AIR MASSES FOR SPECTRA

FIG. NO.	OBJECT	MEAN UT	AIRCRAFT POSITION	LOCAL T	HOUR ANGLE	DECLINATION	ZENITH ANGLE	AIR MASS
3	Venus	20^h25^m	78°30′W,45°50′N	15^h11^m	0^h15^m W	+25°47′	20°0′	1.064
	Sun	— —	— — —	— —	3 15 W	18 36	49.50	1.550
4	Moon	21 08	83 20 W,46 22 N	15 35	0 56 W	26 21	22.1	1.085
5	Moon	22 25	112 45 W,42 19 N	14 54	0 20.5 E	24 00	19.0	1.058
6	Venus	23 20	121 22 W,41 14 N	15 15	0 00	21 06	20.08	1.065
	Sun	— —	— — —	— —	3 15.5 W	23 06	44.29	1.402
7	Venus	24 26	131 26 W,42 06 N	15 40	0 25 W	21 06	21.8	1.077
	Sun	— —	— — —	— —	3 40.5 W	23 06	49.12	1.531
8	Moon	24 26	131 26 W,42 06 N	15 40	0 31 W	23 42	19.9	1.064

TABLE 4

MEASURED PERCENT ABSORPTIONS OF H_2O BANDS

ABS.	FIG. 3 (V)	FIG. 4 (M)	FIG. 5 (M)	FIG. 6 (V)	FIG. 7 (V)	FIG. 8 (M)	$\frac{5+8}{2}$
1.9c	8.8	7.9	7.3	7.2	9.4	8.1	7.7
1.4a	5.0	6.1	6.9	5.3	5.2	6.2	6.5^5
1.4b	9.4	6.9^5	9.8	8.9	11.0	7.9	8.6^5
1.4c	8.2:	7.3	8.4	6.8	6.1	5.4^5	6.9

feature 1.4c which was retained in the table with half weight. Feature 1.4b (the central Q branch) was given half weight also because of its narrow profile.

The absorption depths of Table 4, converted into microns of water vapor, give for the difference Venus-Moon, based on Figure 3 and 4, the amount $20\ \mu - 17\ \mu = 3\ \mu$. If the lunar comparison is scaled up to the larger effective telluric air mass of Venus (cf. above) the amount would be $(1.21/1.085) \times 17\ \mu = 19\ \mu$, leaving $1\ \mu$ for the two-way transmission in the Venus atmosphere.

The $17\ \mu$ of vapor in the lunar spectrum is interpreted as follows. As stated earlier in Section 5, an amount not over $1.5–2\ \mu$ was contained in the cabin air path, which will correspond to roughly double this amount when reduced to $p = 200$ mb. This leaves $13–15\ \mu$ for the outside atmosphere, or $12–14\ \mu$ at unit air mass. According to *Comm. LPL* No. 93, Table 1, the amount expected above the 37,000 ft = 11.3 km level is $8\ \mu$ from 11.3–19.5 km and a somewhat uncertain amount of $2–6\ \mu$ above, making a total of $10–14\ \mu$. The amount measured on the May 14 flight is therefore consistent with the table.

Another verification of our calibrations comes from the observations in the $6.3\ \mu$ band of H_2O made by Dr. Peter M. Kuhn of ESSA, Boulder, Colorado, on the same flights of the total overlying water-vapor content made from an instrument attached to the wall of the aircraft (no cabin contribution). These accord well with the amounts derived here. The telluric amounts vary from approximately $15\ \mu$ for a flight at 37,000 ft to about $10\ \mu$ for a flight at 40,000 ft.

Since Figure 6 is the average of two records obtained at slightly different altitudes, it should be compared to the average of the lunar spectra, Figures 5 and 8, making a strictly comparable pair. This comparison is the strongest of the three and should receive double weight. The reduced measures of Table 4 give $-2\ \mu$ for the difference Venus−Moon. It is estimtaed that the contamination of the Venus spectrum by sunlight on the aircraft window requires the Venus figure to be corrected by $-1\ \mu$, to $-3\ \mu$.

The third comparison is between Figures 7 and 8, given weight 1 because of the shorter run and increased noise level. The measures yield Venus − Moon $= +4\ \mu$, which again requires small negative correction for blending to about $+3\ \mu$.

The weighted average of the three determinations is $-0.5 \pm 1.3\ \mu$ (mean error). With allowance for possible small systematic effects, we adopt:

water-vapor content, two-way transmission, $0 \pm 2\ \mu$.

In order that the mixing ratio H_2O/CO_2 may be derived, the depth of penetration into the Venus atmosphere must be estimated. This penetration is probably larger than corresponds to visual observation. The hot bands of CO_2 in the $\lambda = 1–2\ \mu$ region seem slightly stronger than those obtained in laboratory spectra taken at 295° K, as may be seen from a comparison of the 023H band with 241 which is nearly of equal intensity (*Comm. LPL* No. 15, Figs. 8, 9, 17a, 18a, and 23), and indicate that in $\lambda = 1–2\ \mu$ the penetration occurs to about 300°K. For the $0.8\ \mu$ region Spinrad (1967) has just published a temperature for the $5\nu_3$ hot bands and found surprisingly, 400°–450° K. Since it has been assumed that the fractional water-vapor content in the Venus atmosphere increases with depth, the CO_2 hot bands are especially relevant for the interpretation of H_2O absorptions. For a two-way transmission to the level defined by the hot bands of CO_2, the estimated CO_2 content is 4–8 km-atm. The *upper limit* of the mixing ratio, H_2O/CO_2, is therefore $(2.5–5)\ 10^{-7}$. This figure is the same as the upper limit, 4.10^{-7}, published in *Science News*, July 22, 1967, on the basis of a provisional analysis.

Our result on the near absence of water vapor (amount < 2 microns in 2-way transmission) is in marked contrast with the observation of Dollfus

(1963), who found 280 microns for the 2-way transmissions from the 1.4 μ band of H_2O; of Bottema, Plummer, and Strong (1964), who found 110–470 microns from the 1.13 μ band; of Belton and Hunten (1966), who found 317 microns from the .82 μ band; and Spinrad (1966), who found 250 microns also from the .82 μ band. The Dollfus result might be due to residual Venus CO_2 absorption entering his 1.4 μ filter. T. Owen (1967) has suspected that the results based on the .82 μ band are due to a solar line in the wing of the observed telluric water-vapor line, λ 8189 A, because other telluric lines of equal strength lack the corresponding Venus companion.

After the results of the May 14 flight were announced, we have become aware of several new ground-based observations of Venus made during 1967 which have also given zero results, with uncertainties of 20–40 microns, as is inevitable from spectral observations made from existing observatory sites.

6. *Ice Crystals in the Venus Clouds*

A strict absence of water vapor from the Venus atmosphere would, of course, preclude the presence of H_2O ice crystals in the upper layers. Since the presence of ice crystals has been claimed on empirical grounds, we examine both theoretical expectation, using the upper limit for the water-vapor content found in Section 5, and the direct empirical evidence.

The fractional H_2O vapor content was found $< 4.10^{-7}$. If at the radiometric level of 220° K the atmospheric pressure is about 0.3 bar (cf. *Comm. LPL* No. 101), the H_2O vapor pressure there would be $< 10^{-7}$ bar or $< 10^{-2.4}$ of the saturation pressure at that temperature. No saturation could occur even if the adiabatic gradient extended upward to 200° K, at which level the pressure would be 0.63 that of the 220° K level and the H_2O vapor pressure $< 10^{-1.4}$ of the local saturation pressure. It is therefore not possible for water condensations (liquid or ice) to occur anywhere in the Venus atmosphere (unless there were a zone with $T << 200°$ K).

Direct evidence on the occurence of H_2O ice crystal absorption was considered by Kuiper (1962) who concluded that his evidence in the 2 μ region was negative; and by Bottema, Plummer, Strong, and Zander (1965) and by Strong (1965), who concluded that their evidence was positive. The 1965 results were extensively used by Sagan and Pollack (1965) in their discussion of "Properties

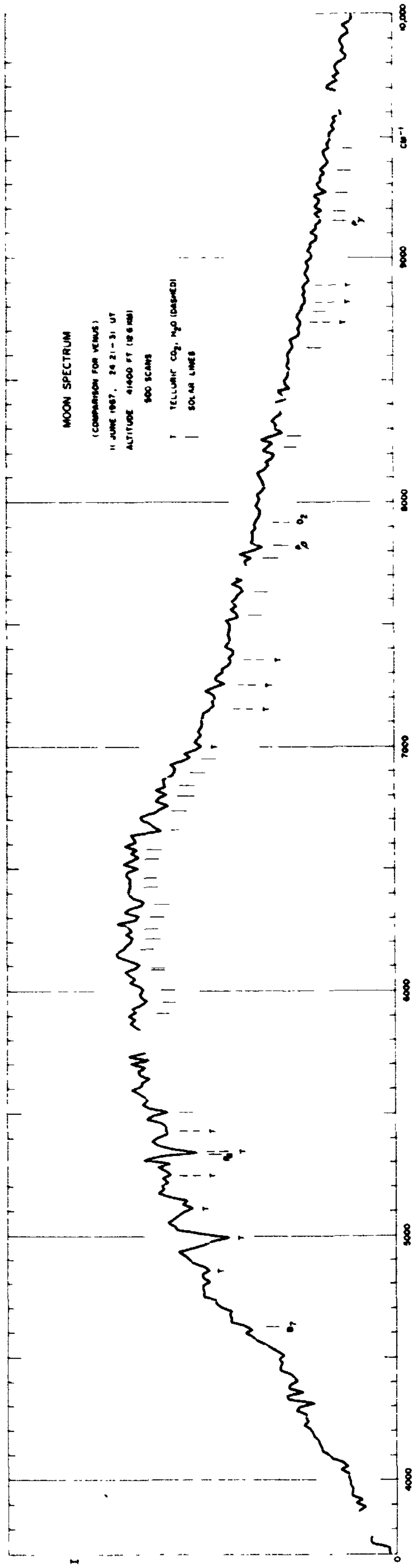


Fig. 8 Moon spectrum, comparison for Fig. 7.

of the Clouds of Venus." The conclusions by Bottema *et al.* (adopted by Sagan and Pollack) were based on a balloon flight made on October 28, 1964, during which a low-resolution (0.1 μ) spectrum of Venus was obtained between 1.7 and 3.4 μ. This spectrum is reproduced here in Figure 9 and may be compared with Figures 3, 6, and 7. As seen from Figure 9, Bottema *et al.* attribute about 0.8 of the dip at 2 μ to ice absorption in the Venus cloud. Our Figures 3, 6, and 7 show that instead the Venus CO_2 absorptions are wholly responsible. The small island of the continuum at 1.93 μ (5180 cm^{-1}) left between the (012) band and the triad at 2 μ, which occurs close to the deepest point of the ice absorption (Kuiper 1962, Fig. 7*b;* and Bottema *et al.* 1965) is precisely in line with the continuum on either side (cf. Figs. 3, 6, 7). The identification of the H_2O ice absorption on Venus is therefore incorrect.

It is noted in passing that the total water-vapor content in a column above an ice-cloud layer on Venus was computed by Menzel and Whipple (1955) to be 130 microns (one-way transmission), or 300–400 μ in two-way transmission. This amount is 200 times the upper limit found in this paper for the much *deeper* atmosphere observed at $\lambda = 1\text{–}2\ \mu$.

7. *Concluding Remarks*

The observed limits on water vapor and ice absorptions show that the Venus clouds are not water, solid or liquid. The only reservation is obviously the formal possibility that somewhere high on the planet a layer exists of such low temperature ($< 180°$ K) that condensation of H_2O can occur in spite of the very low upper limit of the mixing ratio, H_2O/CO_2, derived in this paper. Even then it would still be necessary to require that the absorption near $\lambda = 2\ \mu$ be negligible; i.e., that the particles be very small ($< 0.2\ \mu$). Whether such a possibility actually exists will be examined in a later paper which will also review the atmospheric composition on the basis of present results augmented by data from two flights made after the completion of this paper with a new interferometer whose resolution is 8 cm^{-1}.

The present study shows the advantages of a major reduction in the strength of the telluric spectrum, even at the very modest resolution used. Major gains may be expected from a large increase in spectral resolution and an extension to longer wavelengths; present technology and the airborne facilities allow both. Ultimately, a larger beam than the present 12 in. will be needed to capture the full potential of the NASA CV 990 platform.

Acknowledgments. The Venus observations here reported were made during two flights with the NASA CV 990 Jet as part of the spring 1967 program outlined in *Comm. LPL* No. 93. We are indebted to NASA Hq. and NASA-Ames for support in making the CV 990 facility available and to the NASA-Ames staff for their advice and expert assist-

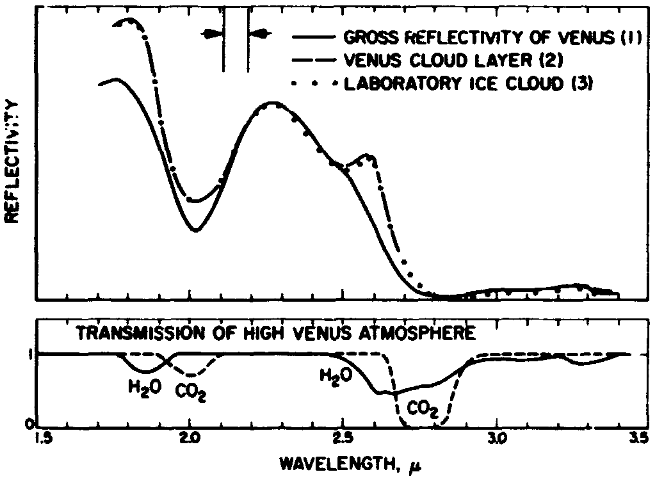


Fig. 9 High-altitude balloon spectrum of Venus and its interpretation according to Strong (1965). The observed spectrum is the full-drawn line. (Reproduced by permission of California Institute of Technology.)

ance throughout the program. We are personally indebted to Mr. Lawrence Mertz for the loan of his interferometer, to Mr. I. Coleman of Block Associates for making the reductions of the interferograms; and to the University of Arizona Space Sciences Committee for a grant in aid. We wish to thank Mr. D. Steinmetz for his collaboration during the flights, Mrs. A. Agnieray for her assistance in preparing the figures, and Dr. T. Owen for helpful discussions of the text. The planetary program at this Laboratory is supported by the National Aeronautics and Space Administration Grant NsG 161-61.

REFERENCES

Belton, M. J. S., and Hunten, D. M. 1966, *Ap. J.*, **146**, 307–308.

Bottema, M., Plummer, W., and Strong, J. 1964, *Ann. d'ap.*, **28**, 225–228.

Bottema, M., Plummer, W., Strong, J., and Zander, R. 1965, *J. Geophys. Res.*, **70**, 4401–4402.

Dollfus, A. 1963, *C. R. Acad. Sci., Paris*, **256**, 3250–3253.

Eberhart, J. 1967, "Earth's Secretive Sister," *Sci. News*, **92**, No. 4, July 22, pp. 86–87.

Kuiper, G. P. 1962, *Comm· LPL*, No. 15, Figs. *7a* and *7b* and accompanying discussion.

Menzel, D. H., and Whipple, F. L. 1955, *Pub. Astr. Soc. Pac.*, **67**, 161–168.

Owen, T. 1967, Private communication and *Ap. J.* (in press).

Sagan, C., and Pollack, J. B. 1965, *Proceedings CalTech-JPL Lunar and Planetary Conference*, Sept. 13–18, 1965, pp. 155–163.

Spinrad, H., and Shawl, S. 1966, *Ap. J.*, **146**, 328–329.

Strong, J. 1965, "Balloon Telescope Studies of Venus," *Proceedings CalTech-JPL Lunar and Planetary Conference*, Sept. 13–18, 1965, pp. 147–149.

APPENDIX A

LOG OF JUNE 11 VENUS FLIGHT
(For geographic positions, cf. Fig. 1)

UT	ALT. 1000 FT	ATM T °C	CABIN WET BULB	CABIN DRY BULB	CABIN ALT.	CABIN $P(H_2O)$ MM	REMARKS
20:45	24.2	−20	—	—	—	—	
21:30	32.9	−46	—	—	—	—	
21:38	32.9	−46	7.0	23.1	8400	1.47	
21:45	34.1	−48	—	—	8400	—	
21:50	35.7	−52	—	—	8400	—	
21:53	37.1	−54	—	—	8350	—	
21:56	38.7	−54	—	—	8350	—	
21:57	39.0	−52	3.3	17.0	8350	0.68	
22:00	39.0	−52	—	—	8350	—	
22:05	39.0	−54	—	—	8350	—	Excellent; solid clouds below 30,000 ft.
22:10	39.0	−52	—	—	8350	—	
22:18	39.0	−52	—	—	8350	—	Start moon run.
22:27	39.0	−51	4.7	19.7	8350	0.79	
22:29.5	39.0	−51	—	—	8350	—	End moon run; start sky.
22:35	39.0	−51	—	—	8350	—	End sky.
22:41	39.0	−51	4.7	19.7	8350	0.79	Start Venus run.
23:02	39.0	−52	4.3	19.6	8350	0.40	Clear!
23:11	39.0	—	—	—	8350	—	End Venus, start sky.
23:16	39.0	—	—	—	8350	—	End sky.
23:17	39.0	−53	4.7	20.4	8350	0.52	Started to climb. Some black tape on windows to suppress small reflections.
23:19	39.7	−52	—	—	9750	—	
23:20	40.1	−52	—	—	9750	—	Start Venus run.
23:26	40.7	−52	—	—	9750	—	Clear! 50% cover below 20,000 ft.
23:32	41.1	−52	4.4	20.7	9750	—	
23:37	41.1	−53	—	—	9750	—	Crossing Pacific Coast.
23:49	41.1	−52	4.3	20.4	9650	0.38	Solid layer of low fog over ocean.
24:00	41.1	−52	—	—	9650	—	End Venus run, reverse tape.
0:03–10	41.1	−53	—	—	9650	—	Venus
0.12	41.1	−52	4.4	20.4	9650	0.47	Sky spectr
0.19	41.1	−55	—	—	9650	—	To Moon ,some turbulence
0:24	41.1	−56	4.3	20.3	9650	0.42	Moon, sea fog below.
0.31	41.1	−57	—	—	9650	—	To Sky.
0.36	41.1	—	—	—	9650	—	End sky, to Venus (last run).
0:40	41.1	−58	4.1	20.3	9650	0.37	
0:45	41.1	−59	—	—	9700	—	
0:50	41.1	−60	4.2	20.3	9750	0.44	End Venus; to sky.
0:54	41.1	−60	3.9	19.7	9650	0.42	End sky; end observations.
0:55	41.1	−60	—	—	9650	—	

Very clear throughout. On the return flight the tropopause was at 40,200 ft, 1:02 UT at −60°C.

The water-vapor reductions are based on *Smithsonian Physical Tables*, 9th Ed., 1954, Tables 634 and 635, Part 3. For the extremely low humidities involved these may not be quite accurate. They lead to a dew point of about −27°C, higher than expected for compressed outside air having a frost point of about −70°C. The amounts in microns per meter are numerically almost the same as the vapor pressure in mm, since $(p/760) \times (18/29) \times 0.001255 \times 10^6 \simeq p$.

No. 96 CALIBRATION OF WEAK 1.4 AND 1.9 μ H_2O ABSORPTIONS

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

November 11, 1967

ABSTRACT

This paper summarizes laboratory measurements of the intensity of the 1.4 and 1.9 μ water-vapor bands in support of airborne observations of the planets Venus and Mars.

The Venus observations and moon comparisons described in *Comm. LPL* No. 95 require an approximate calibration of the 1.4 and 1.9 μ bands of water vapor so that the observed absorptions may be converted to abundance. The calibrations must match the astronomical spectra in resolution in order that the measured absorptions refer to the same features. Only a few laboratory spectra were obtained with the interferometer used in the observations of Venus and the moon before it was returned to Cambridge, Mass. These are reproduced in Figure 1. As noted in the legend, the spectra were obtained at the ambient pressure of 70 cm Hg so that the absorption depths may be enhanced by pressure broadening relative to the 200 mb atmospheric records. Record *c* is unduly noisy; records *a* and *b* are a good match for the astronomical records.

All other calibrations were made subsequent to the return of the interferometer, using the A-spectrometer of LPL with a very wide slit so as to simulate the band resolution used in the interferometer. Two sets of records were obtained, one at the ambient laboratory pressure (70.5 cm) and one at the reduced pressure of about 15 cm, corresponding to the 200 mb atmospheric level from which the planetary observations were made. Since the water vapor has a much smaller scale height than the atmosphere at large, even at that level (*Comm. LPL* No. 93, Table 1), the pressure of 200 mb or 15 cm is considered more representative than the average of 100 mb.

Figure 2 reproduces the records obtained in laboratory air at p = 70 cm with the water-vapor content determined with a wet- and dry-bulb thermometer and a variable air path. Each band is characterized by its three branches, the depths of which can be measured without much ambiguity and should not be dependent on the precise value of the spectral resolution. The results of these depth measures are shown graphically in Figure 3. The central (*b*) branch of the 1.9 μ band has been omitted since it cannot be used on Venus, owing to the strong CO_2 band 012 and the solar Paschen α line, which together obliterate the H_2O absorption.

The curves of growth in Figure 3 have a nearly parabolic shape for amounts in excess of 8–10 μ of water vapor, i.e., the band intensity increases approximately as the square root of the abundance. The 72 μ points of Figure 2, though outside the diagram, were measured and used in drawing the dashed curves of Figure 3. Even for smaller amounts some curvature is present. Since pressure broadening extends the linear part of the curve of growth, it follows that pressure effects are present even for these smaller amounts of water vapor, which is not surprising in view of the width and spacing of the

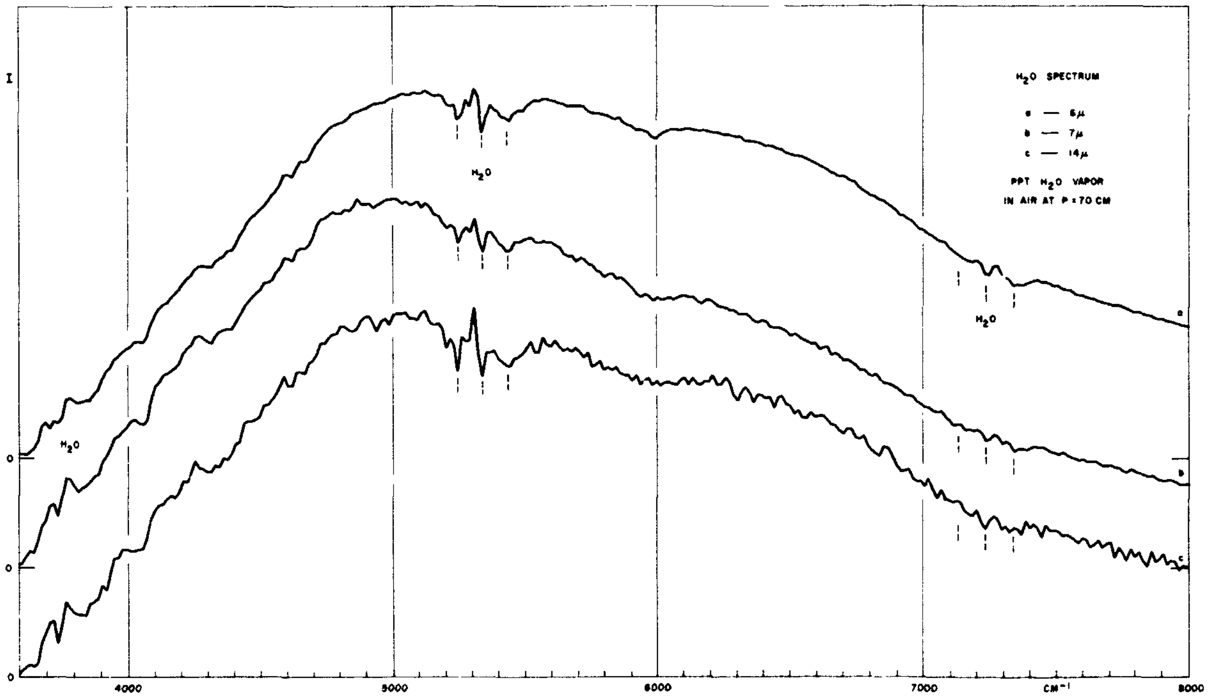


Fig. 1 Sample laboratory spectra of 1.4 and 1.9 μ bands of H_2O with Mertz interferometer.

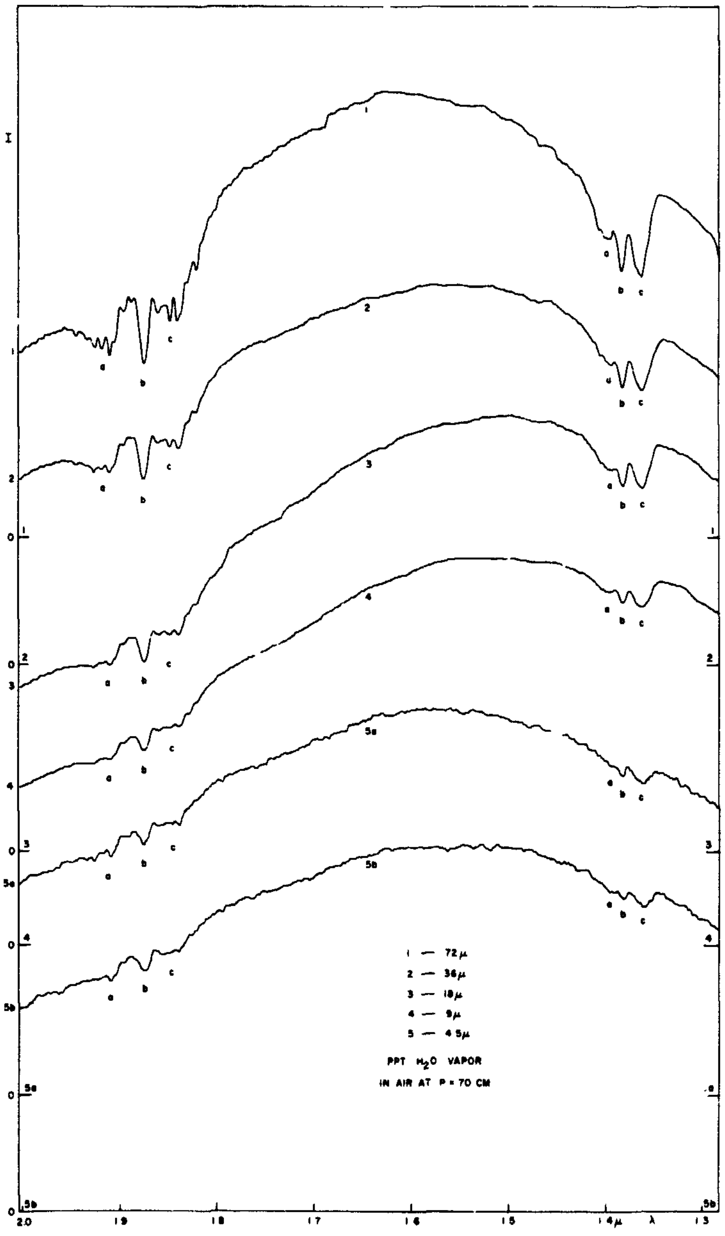


Fig. 2 Laboratory calibration spectra of 1.4 and 1.9 μ water-vapor bands made at atmospheric pressure using A-spectrometer with adjusted resolution.

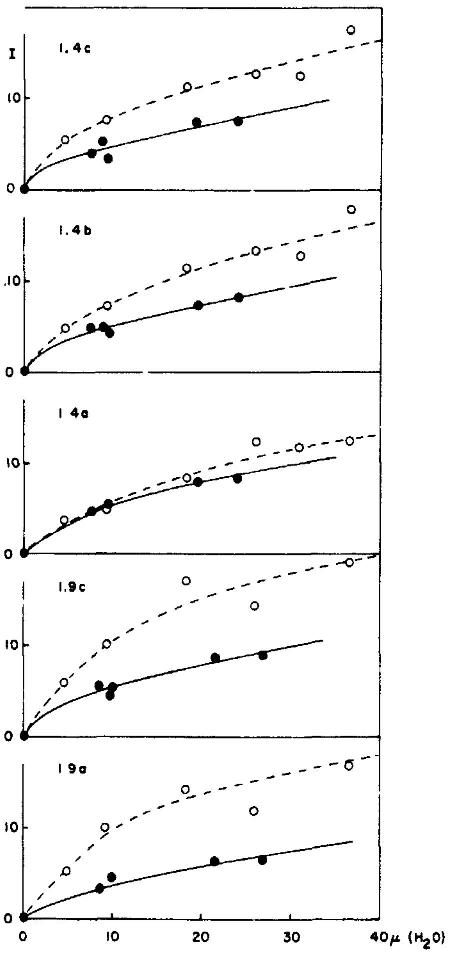


Fig. 3 Curves of growth of five absorption features of water vapor identified in Fig. 2 using two pressures: (1) *lower*, measures made at 200 mb (solid dots and full-drawn line); (2) *upper*, measures at ambient laboratory pressure, p = 70 cm, based in part on Fig. 2.

unresolved rotational lines responsible for the bands (in other words, the individual rotational lines are no longer weak even for a shallow band).

The calibrations at p = 15 cm Hg were made with a single-pass tube, 6.76 m long, equipped with pump and manometer; the water-vapor content of the ambient laboratory air was progressively increased by boiling water and measured at the time the air was admitted to the tube.

Normally three records were obtained for each of the following amounts of water vapor per meter in the ambient laboratory air: 3.7 μ, 4.3 μ, 4.3 μ (on a second day), 9.7 μ, and 12.5 μ. The tube pressures were not quite the same for the 1.4 and 1.9 μ bands. The percentage absorptions were derived and plotted in Figure 3. The comparatively small additional abundance due to the 37 cm laboratory air path was multiplied by an extra factor 1.5 to allow approximately for its higher pressure.

It is seen that pressure affects different branches differently, with the intensity ratio at a given abscissa reaching $\sqrt{p_1/p_2} = 2.2$ in some cases. The pressure effect is small in the *a* branch of the 1.4 μ band.

Calibrations with different resolution will be published as needed in future programs.

Acknowledgments. Dr. A. B. Binder assisted in the early phases of the laboratory work. The planetary spectroscopic program is supported by the National Aeronautics and Space Administration Grant NsG 161-61.

No. 97 SULPHUR COMPOUNDS IN THE ATMOSPHERE OF VENUS I: AN UPPER LIMIT FOR THE ABUNDANCE OF SO_2

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

October 20, 1967

ABSTRACT

From the SO_2 electronic bands near 3000 A an upper limit of 0.05 mm-atm has been derived for the SO_2 content of the Venus atmosphere.

This paper deals with the possible presence of SO_2 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 A (Herzberg 1966), which in many respects resemble the O_3 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 A first order and was used in the second order, giving a dispersion of 8.1 A/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 A, 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 SO_2 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 SO_2 absorption cell had 2.5 mm path-length, made from two disks of Optosil I (Englehardt 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 SO_2 gas.

The development of the SO_2 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

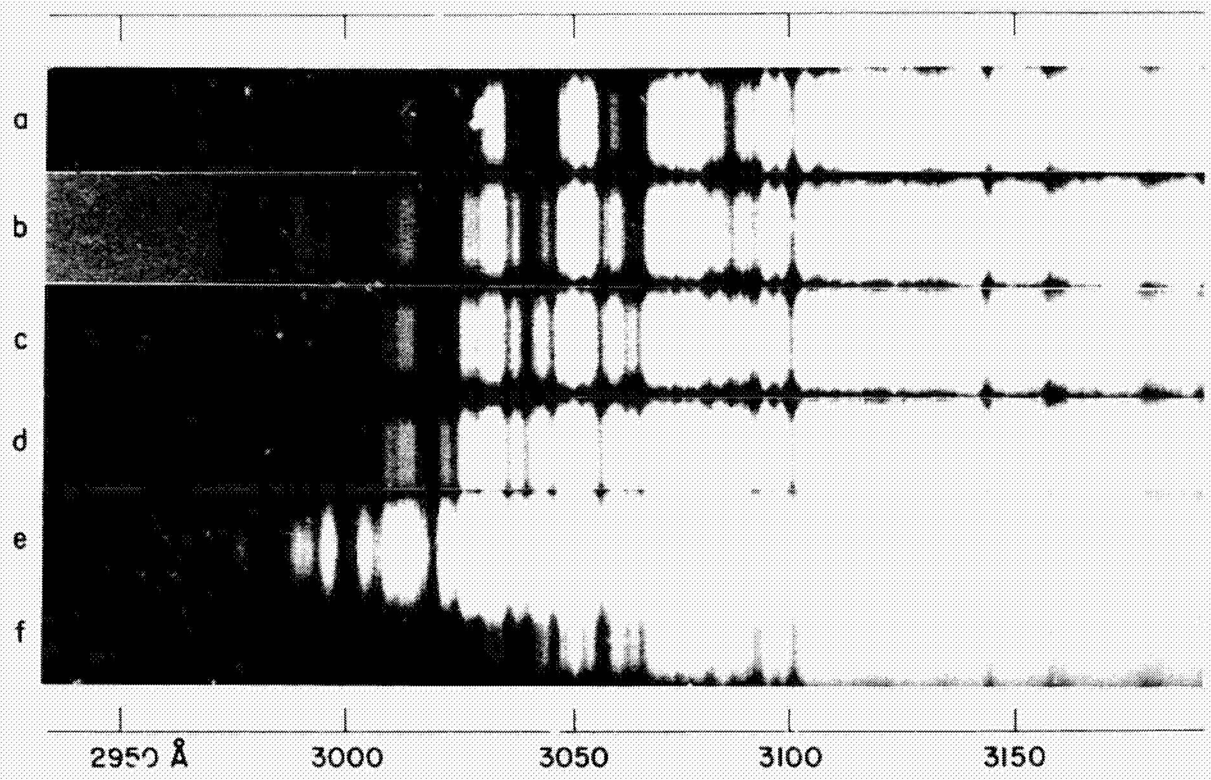


Fig. 1 Comparison of Venus spectrum (e) with sun observed through different amounts of SO_2: (a) 2.3 mm-atm; (b) 1.0 mm-atm; (c) 0.5 mm-atm; and (d) 0.1 mm-atm. (f) is the sky adjacent to Venus.

so that the total pressure in the cell was always 1 atm. The bands centered at about 3004 and 3020 A 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 A 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 3.37×10^{-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 1 μ region. Particle scattering rather than Rayleigh scattering will therefore limit the penetration even at 3000 A. 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 A 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.

No. 98 SULPHUR COMPOUNDS IN THE ATMOSPHERE OF VENUS II: UPPER LIMITS FOR THE ABUNDANCE OF COS AND H_2S

Carbonyl sulfide + hydrogen sulfide

by D. P. Cruikshank

October 20, 1967

ABSTRACT

Laboratory spectra of small amounts of carbonyl sulfide and hydrogen sulfide are discussed relative to their abundance in the Venus atmosphere. The upper limits to the mixing ratios relative to a two-way transmission in the Venus atmosphere, 4 km-atm. of CO_2 are: COS $< 10^{-6}$, and $H_2S < 2 \times 10^{-4}$.

1. Introduction

This paper presents results of attempts to estimate the upper limits of the abundances of carbonyl sulfide (COS) and hydrogen sulfide (H_2S) in the Venus atmosphere using new spectroscopic data. Such limits are especially relevant to the Venus problem because of the computer models of chemical and thermodynamic equilibria in planetary atmospheres (Lewis 1968, and Lippincott *et al.* 1967) that are now available. The sulfur gases also relate directly to the current level of volcanic activity on Venus.

2. Carbonyl Sulfide

Tracings of the near-infrared spectrum of COS were published by Kuiper and Cruikshank (1964). The strongest band in the region 0.9–2.6 μ is centered at 2.44 μ. New tracings of this and adjacent bands with resolution ($\lambda/\Delta\lambda$) 7000 are shown in Figure 1 for different amounts of the gas from 4.7 mm-atm to 50 mm-atm, all at 705 mm Hg pressure and room temperature. No COS is detected in the Venus atmosphere where the laboratory spectra are compared with the Venus tracings of Kuiper (1962), Moroz (1964), and [illegible] r and Forbes (1967). The latter are much [illegible] because the heavy telluric water-vap[illegible] ly reduced. An upper limit of [illegible] way transmission in the Venus atmosphere may be established on the basis of this comparison. For 4 km-atm CO_2 in the Venus atmosphere two-way transmission, this corresponds to an upper limit to the mixing ratio of 10^{-6}.

3. Hydrogen Sulfide

The test for H_2S is less sensitive than for COS because of contamination of the Venus spectrum by many bands of CO_2. The ultraviolet electronic bands occur as a broad continuum from 1900–2700 Å (Herzberg 1966, p. 489) and are therefore unsuitable for our purpose. A strong vibrational band at 1.58 μ lies on a branch of the 301 band of $C^{13}O_2$ (1.5714 μ) which is very strong in the Venus spectrum. The 101 band of H_2S at 1.94 μ is similarly blended with CO_2 in the atmospheres of the earth and Venus, and with telluric H_2O. A rough upper limit of 1 m-atm for H_2S can be established, however, using Kuiper's spectra and those of Moroz (1964) with the H_2S spectra of Cruikshank (1967). Relative to 4 km-atm CO_2 in the Venus atmosphere, this corresponds to an upper limit in the mixing ratio of 2×10^{-4}.

Acknowledgment. The planetary program at this Laboratory is supported by National Aeronautics and Space Administration Grant NsG 161-61.

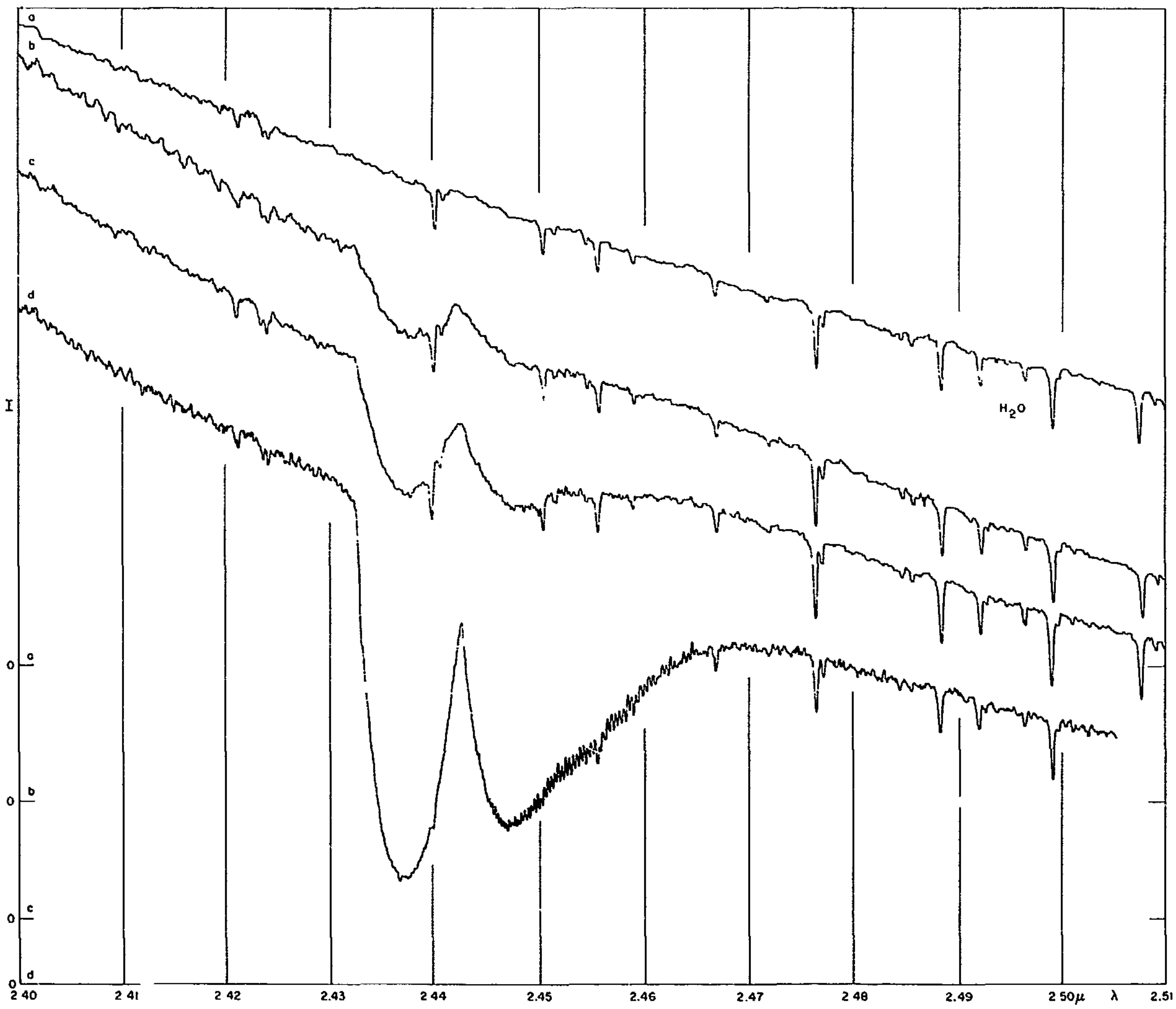


Fig. 1 A portion of the infrared spectrum of COS showing the development of the band with various amounts of gas. (a) Blank run with no COS but 4.36 m laboratory air in optical path, including spectrometer, (b) same air path with 4.7 mm COS at p = 1 atm, (c) air path with 7.1 mm COS at p = 1 atm, (d) air path with 50 mm COS at p = 1 atm. B-spectrometer slit 0.05 mm, detector width 0.05 mm.

REFERENCES

Cruikshank, D. P. 1967, "Laboratory Spectra for Testing the Presence of Minor Constituents in Planetary Atmospheres, II: C_2H_2, C_2H_4, C_2H_6, CH_3SH, CH_3NH_2, H_2S," *Comm. LPL*, 6, 1–30.

Herzberg, G. 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, 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, 117–189.

Kuiper, G. P., and Cruikshank, D. P. 1964, "Laboratory Spectra for Testing the Presence of Minor Constituents in Planetary Atmospheres, I: CH_4, NH_3, N_2O, CO, COS, Region 1–2.5 μ," *Comm. LPL*, 2, 141–165.

Lewis, J. S. 1968, "An Estimate of the Surface Conditions of Venus," *Icarus*, (in press).

Lippincott, E. R., Eck, R. V., Dayhoff, M. O., and Sagan, C. 1967, "Thermodynamic Equilibria in Planetary Atmospheres," *Ap. J.*, 147, 753–763.

Moroz, V. I. 1964, "New Observations of the Infrared Spectrum of Venus ($\lambda = 1.2$–3.8 μ)," *Astronomicheskii Zhurnal*, 41, 711–719, (*Sov. Astr.-AJ*, 8, 566–572, 1965).

No. 99 THE INFRARED SPECTRUM OF CARBON SUBOXIDE
PART I: REGION 1–2.5 MICRONS

by G. P. Kuiper, G. T. Sill (O. Carm.) and D. P. Cruikshank

November 22, 1967

ABSTRACT

Laboratory tests of the spectrum of C_3O_2 in the region of 1-2.5 microns are presented in order to establish the most favorable tests for the presence of this gas on Venus and Mars. The results are shown in Figures 1 and 2.

One of the more interesting gases of which traces may be present in the Venus atmosphere is carbon suboxide, C_3O_2. It will be produced photochemically in a mixture of carbon dioxide and carbon monoxide under the influence of several types of radiation (far ultraviolet, X-ray, electrons and protons) so that traces must be produced in the upper atmosphere of Venus. Since its near-infrared spectrum apparently has not been observed before, absorption spectra of the gas have been obtained in the lead-sulfide region. The gas was produced by one of us (G. S.) with the assistance of Dr. John Schaefer and Linda Honig of the University of Arizona Department of Chemistry.

Diacetyl tartaric anhydride was produced by the acetylation of tartaric acid with acetic anhydride. The product was crystallized from solution, washed with benzene and dried in a vacuum dessicator over P_2O_5 for 24 hrs. The intermediate, diacetyl tartaric anhydride $(CH_3\ COO)_2\ C_4H_2O_3$, was pyrolyzed at 680° C in a vycor pyrolysis tube to produce the carbon suboxide and large amounts of byproduct, acetic acid and carbon monoxide. The acetic acid was first removed with a water condenser and the carbon suboxide collected in a dry-ice acetone trap at $-78°$ C. The C_3O_2 was distilled at room temperature (B. P. 7° C) and the distillate collected again in a dry-ice acetone trap.

Two sets of records were obtained, one of which is reproduced in Figures 1 and 2. Both used a 39 cm cell placed between the filament source and a positive lens which made an image of the source on the spectrometer slit in order that the collimator beam would be filled. For the first records, a small amount of C_3O_2 gas was admitted to the tube but its pressure was not readily determined. In the second set, the gas pressure was approximately 600 mm, in equilibrium with the C_3O_2 liquid boiling in a water-and-ice bath at 0° C. During the spectral runs some polymerization of the gas occurred on the walls of the cylindrical Pyrex tube, but it is not believed that the gas pressure was diminished drastically. No observable bands occurred in the interval 1.0–2.5 μ outside the intervals reproduced in Figures 1 and 2. The continuum in the figures was not normalized from the original recordings, but the approximate position of the undisturbed level is indicated by the smooth lines added to the tracings.

The classification of the higher overtones of C_3O_2 is not readily made on the basis of the available literature (Herzberg 1945; Lafferty, Maki, and Plyer 1963; Aleksandrov, Tyulin, and Tatevskii 1963,

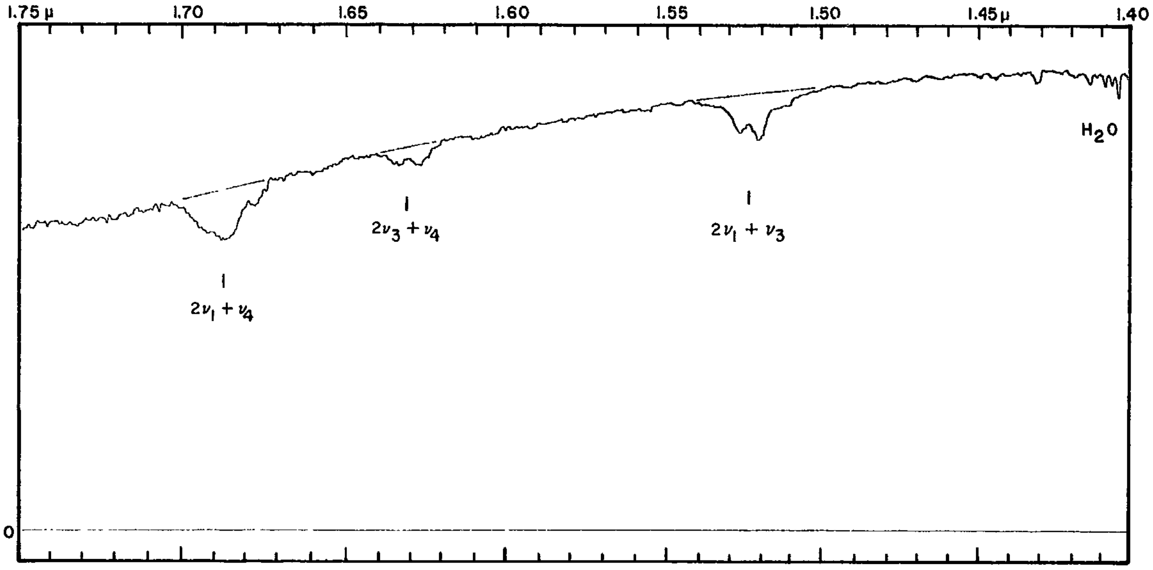


Fig. 1 Absorption spectrum of 39 cm of C_3O_2 at $p = 600$ mm, 1.40 — 1.75 μ, with classifications derived by U. Fink in Part III. Straight lines suggest undisturbed continuum level.

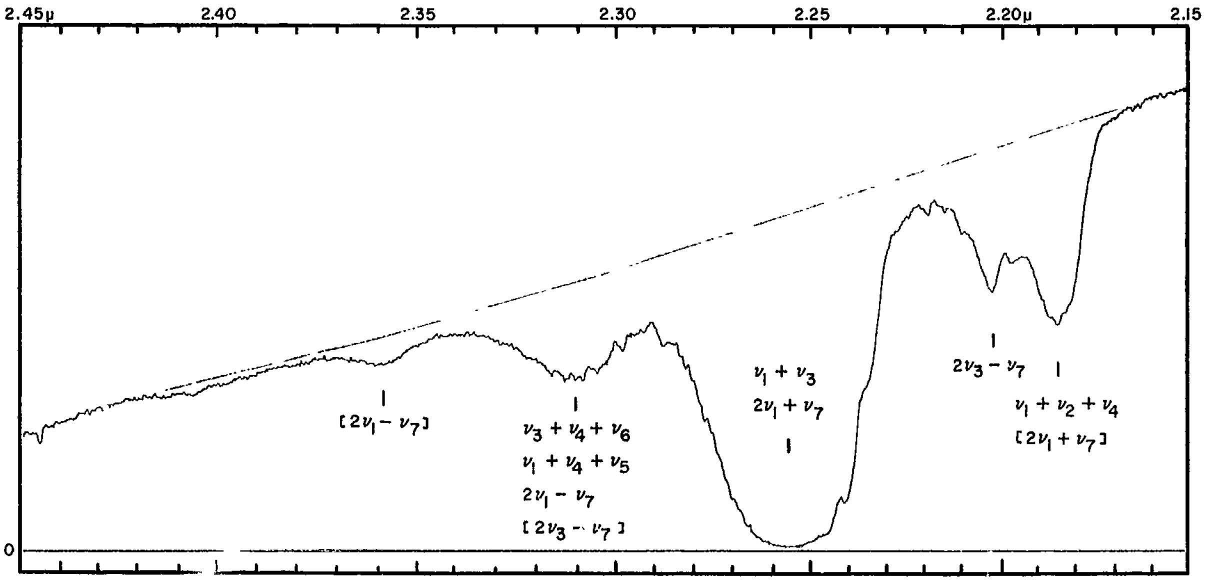


Fig. 2 Absorption spectrum of 39 cm of C_3O_2 at $p = 600$ mm, 2.15 — 2.45 μ, with classifications derived by U. Fink in Part III. Straight lines suggest undisturbed continuum level.

Table 1). The assignments made in Figures 1 and 2 are based on the above references and a study by Dr. Uwe Fink found in Part III.

TABLE 1

FUNDAMENTAL FREQUENCIES USED

ASSIGNMENT	DESIGNATION	BAND CENTER, CM $^{-1}$	WAVELENGTH (μ)
ν_1	$\sigma^+{}_g$	2200	4.55
ν_2	$\sigma^+{}_g$	830	12.05
ν_3	$\sigma^+{}_u$	2270	4.41
ν_4	$\sigma^+{}_u$	1570	6.37
ν_5	π_g	580	17.24
ν_6	π_u	550	18.18
ν_7	π_u	63[190]	159[52.6]

It is apparent that the most sensitive test for the pressure of C_3O_2 on Venus within the spectral region considered is by means of the $\nu_1 + \nu_3$ band at 2.26 μ (4440 cm^{-1}). Fortunately, this region is free from strong CO_2 absorptions.

Acknowledgments. The planetary program is supported by the National Aeronautics and Space Administration through Grant NsG 161-61. We are much indebted to Dr. Schaefer and Miss Linda Honig for their assistance with the production of the C_3O_2 sample.

REFERENCES

Aleksandrov, A., Tyulin, V., and Tatevskii, V. 1963, "Vibrational Spectra of Carbon Suboxide (C_3O_2) in Different States of Aggregation," *Optics and Spectroscopy,* **17** (1), 19–22.

Herzberg, G. 1945, *Molecular Spectra and Molecular Structure,* Vol. II in *Infrared and Raman Spectra of Polyatomic Molecules* (New York: D. Van Nostrand Co.).

Lafferty, W., Maki, A., and Plyler, E. 1963, "High-Resolution Infrared Determination of the Structure of Carbon Suboxide," *J. Chem. Phys.,* **40,** (1), 224–229.

For the Production of C_3O_2, cf. N. Rabjohn, ed. 1963, *Organic Synthesis* (New York: John Wiley and Sons), Vol. IV p. 242; and C. D. Hurd and F. D. Pilgrim, 1933, *Journ. Amer. Chem. Soc.,* **55,** 757.

ADDENDUM

ULTRAVIOLET TEST FOR C_3O_2 IN THE VENUS ATMOSPHERE

by D. P. CRUIKSHANK AND G. T. SILL (O. CARM)

In order to test the ultraviolet spectrum of Venus for traces of C_3O_2, spectra of the sun in the region 3100--3600 Å were obtained through an absorption cell containing 35.1 cm-atm (at pressure 62.2 cm Hg) of the gas. Sunlight was reflected from a MgO screen. As with the ultraviolet test for SO_2 (Cruikshank and Kuiper, 1967), a wide slit of 250 μ was used to soften the profiles of the numerous Fraunhofer lines in this spectral region. Eastman 103a-0 plates were used, and the dispersion was 8 Å/mm.

There were no detectable bands in our spectra of this small amount of C_3O_2. This is consistent with the results of Thompson and Healey (1936) who found that the bands in this spectral region begin to show with about 0 [illegible] cm-atm of the gas. It follows that *the infrared fundamental and overtone absorptions provide the most sensitive tests* for the possible presence of carbon suboxide on Venus in the wavelength regions accessible in ground-based or high-altitude airborne observations.

We are grateful to Mr. Allen Thomson who assisted in obtaining the observations.

REFERENCES

Cruikshank, D. P. and Kuiper, G. P. 1967. "Upper Limits for the Abundance of SO_2 on Venus." *Comm. LPL* No. 97, 195–197.

Thompson, H. W., and Healey, N. 1936, "The Spectrum and Photochemistry of Carbon Suboxide," *Proc. Royal Soc. London,* **157,** 331–347.

PART II: REGION 2-15 MICRONS

by D. P. CRUIKSHANK AND G. T. SILL (O. CARM.)

ABSTRACT

Two tracings of the infrared spectrum of C_3O_2 are presented for establishing suitable tests for the presence of C_3O_2 in planetary atmospheres. It is estimated that a strong blended band at 6.37 μ (1570 cm^{-1}) could be detected on Mars or Venus if present in amounts greater than 0.05 mm-atm.

This paper extends the spectral observations of C_3O_2 to 15 μ. Its purpose is: (a) to find the strongest absorption bands in the region 2-15 μ accessible from high-altitude aircraft using modern detectors, and (b) to determine the minimum amount of gas detectable in the spectrum of a planet.

Carbon suboxide was prepared by pyrolysis of diacetyltartaric anhydride as described in Part I. The gas was placed in a cell of 10-cm length having NaCl windows, with total thickness 4 mm, and the spectrum was traced with a Beckman IR-4 spectrometer having an NaCl prism.

Figure 1 shows three spectra: two different amounts of C_3O_2 and a blank run with the gas cell evacuated. Some small residual absorptions are seen in the spectrum of the gas cell alone; these are attributed to impurities in the NaCl windows, including absorbed water. The Beckman IR-4 spectrometer is a double-beam instrument and thus compensates for the strong absorptions of CO_2 and H_2O in the air path in the optical path. From 15μ-16.7 μ (near the long wavelength limit of the instrument) the compensation is not complete; and this region, which does not contain C_3O_2 bands significant here, is not included in Figure 1.

In Figure 1, spectrum (b) was obtained with a partial pressure of 5.5 mm Hg of C_3O_2 in the 10-cm gas cell, or 0.72 mm-atm. The gas cell was connected with the reservoir of liquid C_3O_2 at −79° C; 5.5 mm Hg is the vapor pressure at this temperature *(Handbook of Chemistry and Physics)*. Spectrum (c) was obtained with the cell having been filled by flushing it with vapor of the boiling liquid C_3O_2 at room temperature.

The wavelength calibration of the spectrometer was checked by operating it in a single-beam mode so that the absorptions of the air path in the optical train would be recorded. The ν_3 band of CO_2 at 4.26 μ (2349 cm^{-1}) was used for this purpose. Slight shifts in the scale on the recording paper were noted that correspond to ± 35 cm^{-1} at 2500 cm^{-1} and ± 10 cm^{-1} at 1000 cm^{-1}.

The positions of the fundamental infrared active bands with their permitted binary and ternary combinations are indicated in the lower scale of Figure 1. These data were taken from the computations of Dr. Fink (Part III).

The pyrolysis of diacetyltartaric anhydride yields acetic acid, carbon dioxide, and carbon monoxide as byproducts. To test for these contaminants in the spectrum of C_3O_2, we made individual spectral tracings with various quantities of each compound using the same spectrometer. In Figure 1 we have indicated the positions of the absorption bands due in part to possible contaminants. The coincidence of bands of CO_2, CO, and CH_3COOH with those of C_3O_2 may be partially caused by the C-O bonds common to all of these compounds. In no case is the contamination of the C_3O_2 bands in Figure 1 expected to be more than 3-5 percent.

The most suitable band system for tests in planetary atmospheres would be that centered near 4.35 μ (2300 cm^{-1}) were it not for the very strong CO_2 band at the same wavelength, making it unsuitable for tests in the atmospheres of Venus and Mars. The most suitable band for tests in planetary atmospheres appears to be ν_4 at 6.37 μ (1570 cm^{-1}). We estimate on the basis of curve (b) that 0.1 mm-atm of C_3O_2 would still be detectable in the infrared spectrum of a planet. This band thus provides an exceedingly sharp test for the presence of carbon suboxide in planetary atmospheres provided the observations are made at high altitude.

The band at 3.23 μ (3100 cm^{-1}) designated $\nu_2 + \nu_3$ may also provide a sensitive test in a more accessible spectral region, but higher resolution is required because of the sharpness of the band.

Acknowledgments. — We are grateful to the Department of Chemistry of the University of Arizona for the use of the spectrometer. The program of infrared spectroscopy at the Lunar and Planetary Laboratory is supported by NASA Grant NsG 161-61.

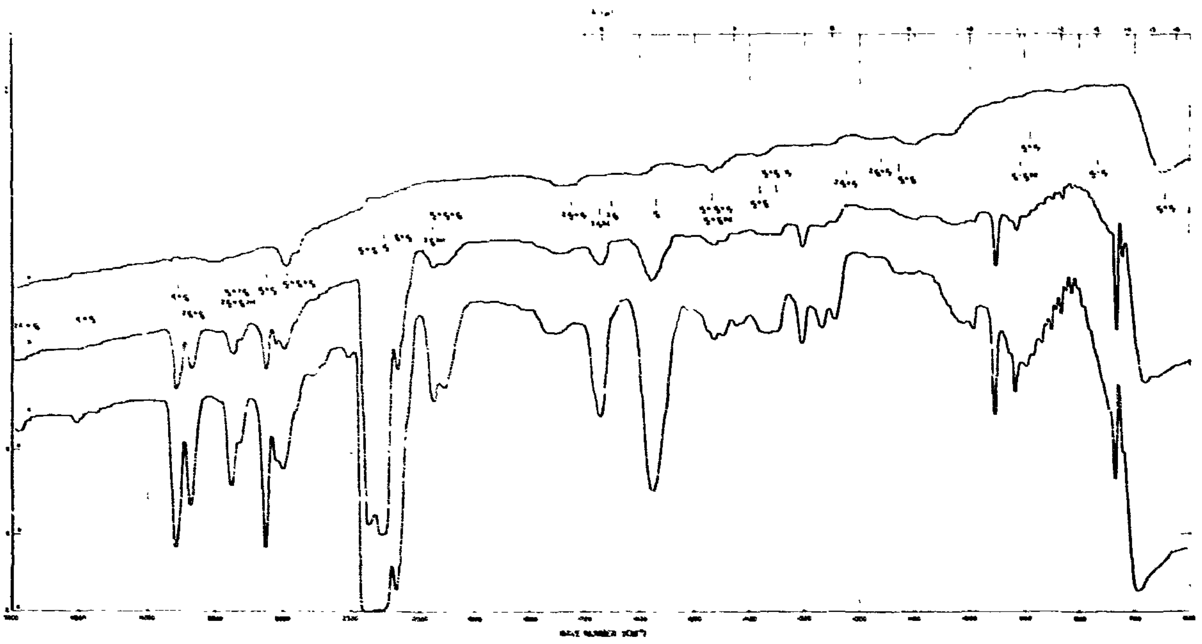


Fig. 1 The infrared spectrum of C_3O_2, 2.0-15.0 μ recorded with a Beckman IR-4 spectrometer. (a) blank with only windows of NaCl in gas cell, (b) 0.72 mm-atm C_3O_2 at pressure 5.5 mm Hg, (c) 93 mm-atm C_3O_2 at pressure 705 mm Hg. Frequency scale as calibrated by manufacturer.

PART III: CLASSIFICATION OF C_3O_2 VIBRATIONAL BANDS

by UWE FINK

Department of Physics, University of Arizona

It is now well established (see the references) that C_3O_2 is a linear molecule belonging to the point group $D_{\infty h}$. The seven fundamental frequencies are listed in Table 1 together with their symmetry species. Bands belonging to the symmetry species Σ^+_u and Π_u are infrared-active (Herzberg 1962, p. 253 ff).

The frequency of the bending mode ν_7 is still in some doubt. Older papers (Long et al. 1954, Aleksandrov et al. 1964) use the frequency of 192 cm^{-1} for ν_7 reported by O'Loane (1953). More recent measurements (Miller and Fateley 1964), however, indicate that the above identification is erroneous. A lower value of 63 cm^{-1} (Miller et al. 1965) or 72 cm^{-1} (Smith and Leroi 1966) has been reported for the gas and liquid phases, respectively. These measurements are substantiated by thermodynamic calculations by McDougall et al. (1965) (61.6 cm^{-1}) and measurements of the fine structure of the band at 3200 cm^{-1} by Lafferty et al. (1964) (25–70 cm^{-1}).

In order to assign possible transitions to the observed bands, all binary and ternary infrared-active bands were calculated from the fundamentals listed in Table 1. They are given with increasing wavelengths in Table 2. The more recent value of 63 cm^{-1} for ν_7 was preferred but calculations were made also with the older value of 190 cm^{-1}. The latter numbers are put in brackets in the Tables. Since ν_7 has such a low frequency, the state, $\nu_1\ \nu_2\ \nu_3\ \nu_4\ \nu_5\ \nu_6$ with $V = 0$ and ν_7 with $V = 1$, can have a population comparable to the ground state. Difference bands with ν_7 can then be quite strong and are therefore included in the Tables.

In Table 4 is presented a comparison between the bands observed in the laboratory in the 1–2.5 μ region and the ones listed in Tables 2 and 3. Of the possible binary combinations, only $\nu_1 + \nu_3$ is within this wavelength region. It is clear that it must be identified with the strong band at 4430 cm^{-1}. The weaker bands are probably due to ternary combinations. From the table it can be seen that a plausible identification can be made for every observed feature. Errors in the fundamental frequencies as well as neglect of the anharmonicity constants and of Fermi resonance can easily account for the differences between the observed and calculated frequencies. Their effects must be examined more thoroughly if a more precise identification of the spectrum is desired.

TABLE 2

ALL POSSIBLE INFRARED-ACTIVE BINARY COMBINATIONS

ASSIGNMENT	DESIGNATION	BAND CENTER, CM⁻1	WAVELENGTH (μ)
1 + 3	Σ^+_u	4470	2.24
1 + 4	Σ^+_u	3770	2.65
2 + 3	Σ^+_u	3100	3.23
3 + 5	Π_u	2850	3.51
1 + 6	Π_u	2750	3.64
2 + 4	Σ^+_u	2400	4.17
1 + 7	Π_u	2263[2390]	4.42[4.18]
4 + 5	Π_u	2150	4.65
1 − 7*	Π_u	2137[2010]	4.68[4.98]
2 + 6	Π_u	1380	7.25
5 + 6	Σ^+_u	1130	8.85
2 + 7	Π_u	893[1020]	11.20[9.80]
2 − 7*	Π_u	767[640]	13.04[15.6]
5 + 7	Σ^+_u	643[770]	15.55[13.0]
5 − 7*	Σ^+_u	513[390]	19.5[25.6]

*Difference bands with ν_7 were included because of its low frequency and the consequent population of that state. Numbers in brackets are calculated with the value of 190 cm^{-1} for ν_7.

TABLE 3

ALL POSSIBLE INFRARED-ACTIVE TERNARY COMBINATIONS

ASSIGNMENT	DESIGNATION	BAND CENTER, CM⁻1	WAVELENGTH (μ)
3 + 3 + 3	Σ^+_u	6810	1.47
1 + 1 + 3	Σ^+_u	6670	1.50
3 + 3 + 4	Σ^+_u	6110	1.64
1 + 1 + 4	Σ^+_u	5970	1.68
3 + 4 + 4	Σ^+_u	5410	1.85
1 + 2 + 3	Σ^+_u	5300	1.89
3 + 3 + 6	Π_u	5090	1.96
1 + 3 + 5	Π_u	5050	1.98
1 + 1 + 6	Π_u	4950	2.02
4 + 4 + 4	Σ^+_u	4710	2.12
3 + 3 + 7	Π_u	4603[4730]	2.17[2.11]
1 + 2 + 4	Σ^+_u	4600	2.17
3 + 3 − 7*	Π_u	4477[4350]	2.23[2.30]
1 + 1 + 7	Π_u	4463[4590]	2.24[2.18]
3 + 4 + 6	Π_u	4390	2.28
1 + 4 + 5	Π_u	4350	2.30
1 + 1 − 7*	Π_u	4337[4210]	2.31[2.38]
2 + 2 + 3	Σ^+_u	3930	2.54
3 + 4 + 7	Π_u	3903[4030]	2.56[2.48]
3 + 4 − 7*	Π_u	3777[3650]	2.65[2.74]
4 + 4 + 6	Π_u	3690	2.71
2 + 3 + 5	Π_u	3680	2.72
1 + 2 + 6	Π_u	3580	2.79
3 + 5 + 5	Σ^+_u	3430	2.92
3 + 6 + 6	Σ^+_u	3370	2.97
1 + 5 + 6	Π_u	3330	3.00
2 + 2 + 4	Σ^+_u	3230	3.10
4 + 4 + 7	Π_u	3203[3330]	3.12[3.00]
1 + 2 + 7	Π_u	3093[3220]	3.23[3.11]
2 + 4 + 5	Π_u	2980	3.36
1 + 2 − 7*	Π_u	2967[2840]	3.37[3.52]
3 + 6 + 7	Σ^+_u	2883[3010]	3.47[3.32]
1 + 5 + 7	Π_u	2843[2970]	3.52[3.37]
3 + 6 − 7*	Σ^+_u	2757[2630]	3.63[3.80]
4 + 5 + 5	Σ^+_u	2730	3.66
1 + 5 − 7*	Π_u	2717[2590]	3.68[3.86]
4 + 6 + 6	Σ^+_u	2670	3.75
3 + 7 + 7	Σ^+_u	2396[2650]	4.17[3.77]
3 + 7 − 7*	Π_u	2270	4.41
2 + 2 + 6	Π_u	2210	4.52
4 + 6 + 7	Σ^+_u	2183[2310]	4.58[4.33]
2 + 5 + 6	Σ^+_u	1960	5.10
2 + 2 + 7	Π_u	1723[1850]	5.80[5.41]
5 + 5 + 6	Π_u	1710	5.85
4 + 7 + 7	Σ^+_u	1696[1950]	5.90[5.13]
6 + 6 + 6	Π_u	1650	6.06
2 + 2 − 7*	Π_u	1597[1470]	6.26[6.80]
2 + 5 + 7	Σ^+_u	1473[1600]	6.79[6.25]
2 + 5 − 7*	Σ^+_u	1347[1220]	7.42[8.20]
5 + 5 + 7	Π_u	1223[1350]	8.18[7.41]
6 + 6 + 7	Π_u	1163[1290]	8.60[7.75]
7 + 7 + 7	Π_u	189[570]	52.9[17.5]

*Difference bands with ν_7 (see Table 2).

REFERENCES

Aleksandrov, A. P., Tyulin, V. I., and Tatevskii, V. M. 1964, *Optics and Spectroscopy,* **17**, 19.

Herzberg, G. 1962, *Infrared and Raman Spectra of Polyatomic Molecules* (New York: D. van Nostrand Co., Inc.).

Lafferty, W. J., Maki, A. G., and Plyler, E. K. 1964, *J. Chem. Phys.,* **40**, 224.

Long, D. A., Murfin, F. S., and Williams, R. L. 1954, *Proc. Roy. Soc. London,* **A223**, 251.

McDougall, L. A., and Kilpatrick, J. E. 1965, *J. Chem. Phys.,* **42**, 2311.

Miller, F. A., and Fateley, W. G. 1964, *Spectrochim. Acta* **20**, 253.

Miller, F. A., Lemmon, D. H., and Witkowski, R. E. 1965, *Spectrochim. Acta* **21**, 1709.

O'Loane, J. K. 1953, *J. Chem. Phys.* **21**, 672.

Smith, W. H., and Leroi, G. E. 1966, *J. Chem. Phys.* **45**, 1767.

TABLE 4

BANDS OBSERVED IN THE LABORATORY AND POSSIBLE IDENTIFICATIONS

OBSERVED BANDS		IDENTIFICATIONS		
λ	ν	ν	ASSIGN.	DESIGNATION
1.52	6560	6670	$2\nu_1 + \nu_3$	Σ^+_u
1.63	6130	6110	$2\nu_3 + \nu_4$	Σ^+_u
1.69	5930	5970	$2\nu_1 + \nu_4$	Σ^+_u
2.18	4580	4600	$\nu_1 + \nu_2 + \nu_4$	Σ^+_u
		[4590]	$2\nu_1 + \nu_7$	Π_u
2.20	4540	4480	$2\nu_3 - \nu_7$	Π_u
2.26	4430*	4470	$\nu_1 + \nu_3$	Σ^+_u
		4460	$2\nu_1 + \nu_7$	Π_u
2.31	4330	4390	$\nu_2 + \nu_4 + \nu_6$	Π_u
		4350	$\nu_1 + \nu_4 + \nu_5$	Π_u
		[4350]	$2\nu_3 - \nu_7$	Π_u
		4340	$2\nu_1 - \nu_7$	Π_u
2.36	4240	[4210]	$2\nu_1 - \nu_7$	Π_u

*Strong band. Numbers in brackets are calculated with the value of 190 cm^{-1} for ν_7.