

**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

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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 desiccator over P_2O_5 for 24 hrs. The intermediate, diacetyl tartaric anhydride $(CH_3COO)_2C_4H_2O_3$, was pyrolyzed at $680^\circ C$ 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 $-78^\circ C$. The C_3O_2 was distilled at room temperature (B. P.

$7^\circ C$) 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 $0^\circ C$. 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,

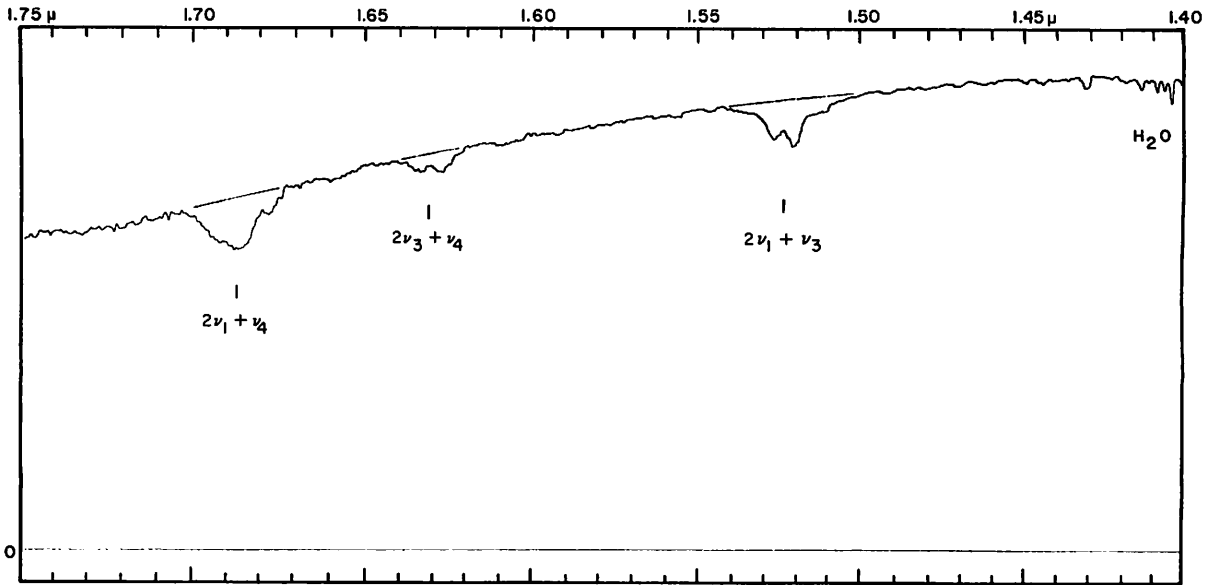


Fig. 1 Absorption spectrum of 39 cm of C_3O_2 at $p = 600$ mm, $1.40 - 1.75 \mu$, with classifications derived by U. Fink in Part III. Straight lines suggest undisturbed continuum level.

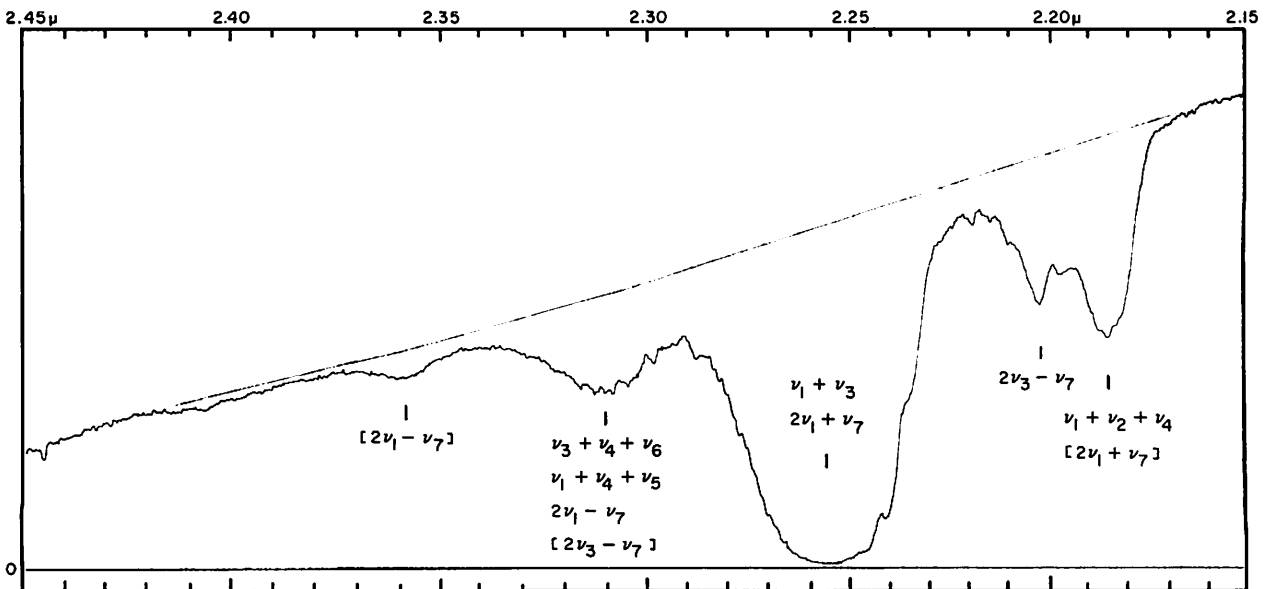


Fig. 2 Absorption spectrum of 39 cm of C_3O_2 at $p = 600$ mm, $2.15 - 2.45 \mu$, with classifications derived by U. Fink in Part III. Straight lines suggest undisturbed continuum level.

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	σ_g^+	2200	4.55
ν_2	σ_g^+	830	12.05
ν_3	σ_u^+	2270	4.41
ν_4	σ_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 2.26μ (4440 cm^{-1}). Fortunately, this region is free from strong CO_2 absorptions.

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much indebted to Dr. Schaefer and Miss Linda Honig for their assistance with the production of the C_3O_2 sample.

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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 0.5 m-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.

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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 6.37μ (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 15μ . 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 - 16.7μ (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 4.26μ (2349 cm^{-1}) was used for this purpose. Slight shifts in the scale on the recording paper were noted that correspond to $\pm 35 \text{ cm}^{-1}$ at 2500 cm^{-1} and $\pm 10 \text{ cm}^{-1}$ 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 4.35μ (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 6.37μ (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 3.23μ (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.

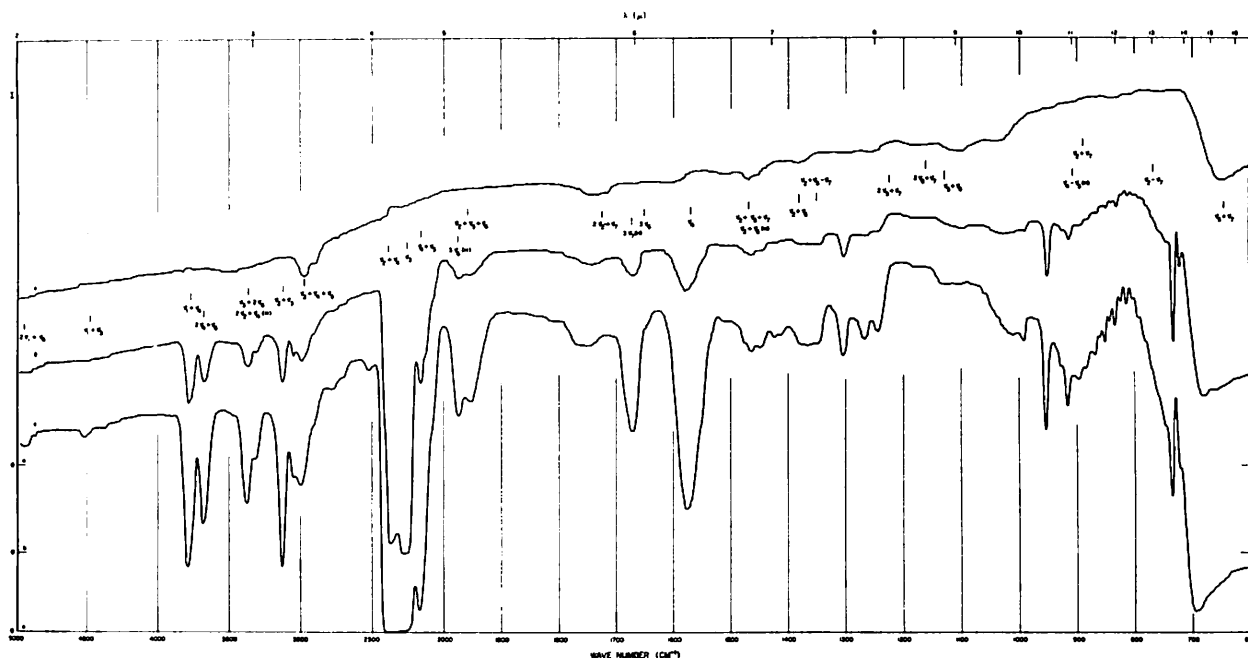


Fig. 1 The infrared spectrum of C_3O_2 , 2.0-15.0 μ recorded with a Beckman IR-4 spectrometer, (a) blank with only windows of NaCl in gas cell, (b) 0.72 mm-atm C_3O_2 at pressure 5.5 mm Hg, (c) 93 mm-atm C_3O_2 at pressure 705 mm Hg. Frequency scale as calibrated by manufacturer.

PART III: CLASSIFICATION OF C_3O_2 VIBRATIONAL BANDS

by UWE FINK

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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 .

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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).

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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	$\nu_3 + \nu_4 + \nu_6$	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 .

TABLE OF CONTENTS

No. 93	Program of Astronomical Spectroscopy from Aircraft by G. P. Kuiper, F. F. Forbes, and H. L. Johnson	155
No. 94	Solar Comparison Spectra, 1.0–2.5 μ by G. P. Kuiper and D. L. Steinmetz	171
No. 95	High Altitude Spectra. I: Venus, 1–2.5 Microns by G. P. Kuiper and F. F. Forbes	177
No. 96	Calibration of Weak 1.4 and 1.9 μ H ₂ O Absorptions in High Altitude Planetary Spectra by G. P. Kuiper and D. P. Cruikshank	191
No. 97	An Upper Limit for the Abundance of SO ₂ in the Venus Atmosphere by D. P. Cruikshank and G. P. Kuiper	195
No. 98	Upper Limits for the Abundance of COS and H ₂ S in the Venus Atmosphere by D. P. Cruikshank	199
No. 99	The Infrared Spectrum of Carbon Suboxide	201
	Part I: Region 1–2.5 Microns by G. P. Kuiper, G. T. Sill (O. Carm.) and D. P. Cruikshank	201
	Part II: Region 2–15 Microns by D. P. Cruikshank and G. T. Sill	203
	Addendum: Ultraviolet Test for C ₃ O ₂ in the Venus Atmosphere by D. P. Cruikshank and G. T. Sill	204
	Part III: Classification of C ₃ O ₂ Vibrational Bands by Uwe Fink	206