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

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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  $1.0-2.5 \mu$  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,

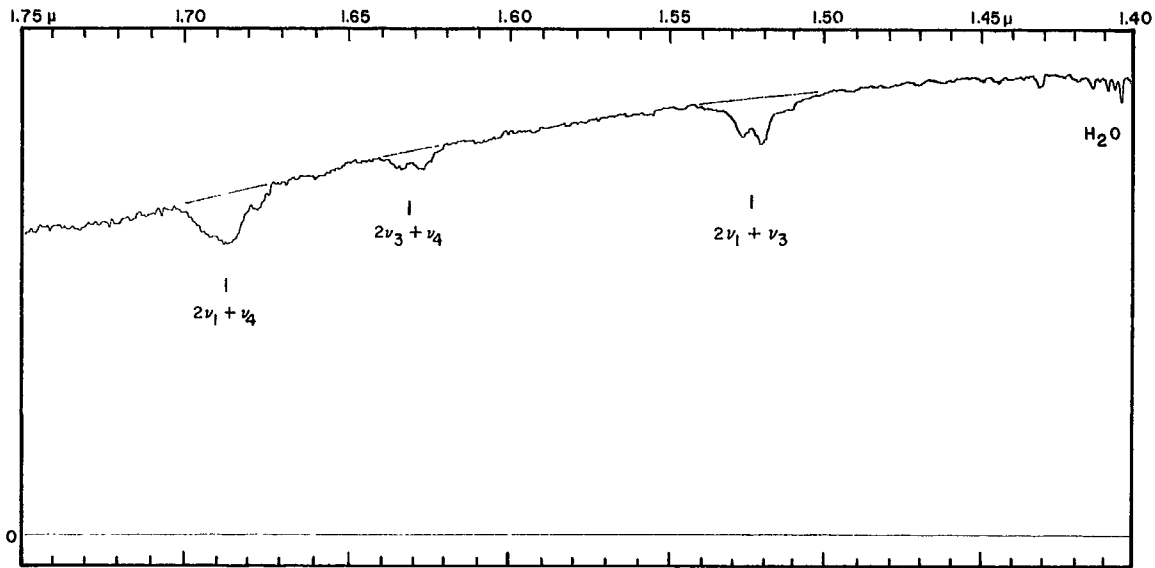


Fig. 1 Absorption spectrum of 39 cm of  $C_3O_2$  at  $p = 600$  mm,  $1.40 - 1.75 \mu$ , with classifications derived by U. Fink in Part III. Straight lines suggest undisturbed continuum level.

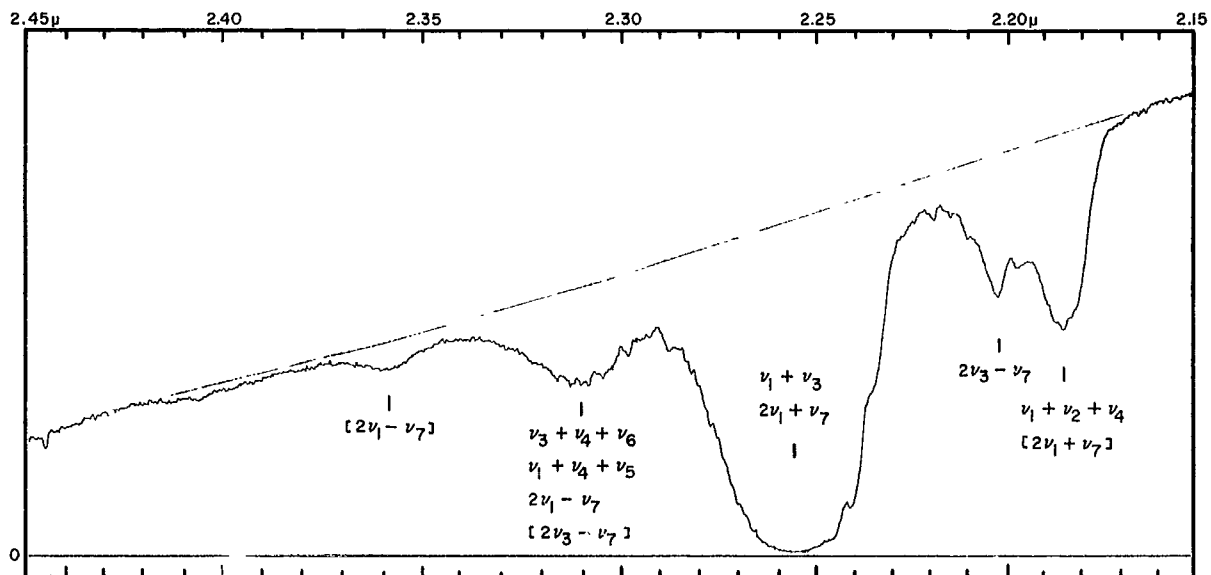


Fig. 2 Absorption spectrum of 39 cm of  $C_3O_2$  at  $p = 600$  mm,  $2.15 - 2.45 \mu$ , with classifications derived by U. Fink in Part III. Straight lines suggest undisturbed continuum level.

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 I  
FUNDAMENTAL FREQUENCIES USED

ASSIGNMENT	DESIGNATION	BAND CENTER, CM <sup>-1</sup>	WAVELENGTH (μ)
$\nu_1$	$\sigma_g^+$	2200	4.55
$\nu_2$	$\sigma_g^+$	830	12.05
$\nu_3$	$\sigma_u^+$	2270	4.41
$\nu_4$	$\sigma_u^+$	1570	6.37
$\nu_5$	$\pi_g$	580	17.24
$\nu_6$	$\pi_u$	550	18.18
$\nu_7$	$\pi_u$	63[190]	159[52.6]

It is apparent that the most sensitive test for the pressure of C<sub>3</sub>O<sub>2</sub> on Venus within the spectral region considered is by means of the  $\nu_1 + \nu_3$  band at 2.26 μ (4440 cm<sup>-1</sup>). Fortunately, this region is free from strong CO<sub>2</sub> absorptions.

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much indebted to Dr. Schaefer and Miss Linda Honig for their assistance with the production of the C<sub>3</sub>O<sub>2</sub> sample.

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- For the Production of C<sub>3</sub>O<sub>2</sub>, 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<sub>3</sub>O<sub>2</sub> 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<sub>3</sub>O<sub>2</sub>, 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 as reflected from a MgO screen. As with the ultraviolet test for SO<sub>2</sub> (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<sub>3</sub>O<sub>2</sub>. 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 100 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

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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  $6.37 \mu$  ( $1570 \text{ cm}^{-1}$ ) 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  $15 \mu$ . Its purpose is: (a) to find the strongest absorption bands in the region 2-15  $\mu$  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  $15\mu$ - $16.7 \mu$  (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  $-79^\circ \text{C}$ ; 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  $\nu_3$  band of  $CO_2$  at  $4.26 \mu$  ( $2349 \text{ cm}^{-1}$ ) 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  $2500 \text{ cm}^{-1}$  and  $\pm 10 \text{ cm}^{-1}$  at  $1000 \text{ cm}^{-1}$ .

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  $4.35 \mu$  ( $2300 \text{ cm}^{-1}$ ) 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  $\nu_4$  at  $6.37 \mu$  ( $1570 \text{ cm}^{-1}$ ). 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  $3.23 \mu$  ( $3100 \text{ cm}^{-1}$ ) 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.

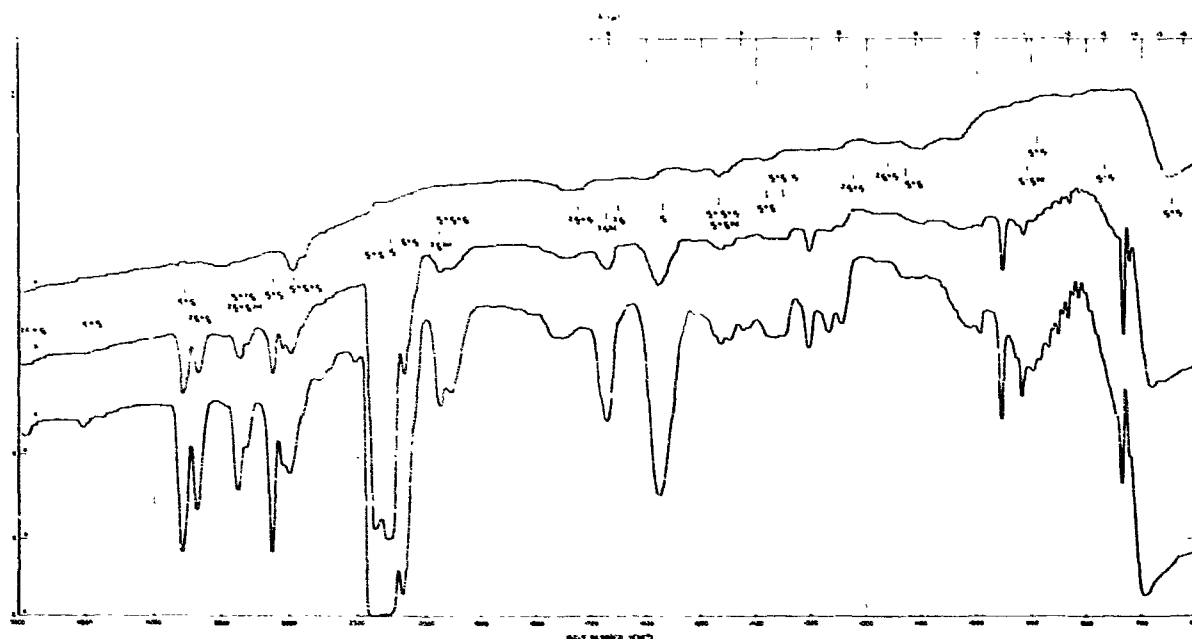


Fig. 1 The infrared spectrum of  $C_3O_2$ , 2.0-15.0  $\mu$  recorded with a Beckman IR-4 spectrometer. (a) blank with only windows of NaCl in gas cell, (b) 0.72 mm-atm  $C_3O_2$  at pressure 5.5 mm Hg, (c) 93 mm-atm  $C_3O_2$  at pressure 705 mm Hg. Frequency scale as calibrated by manufacturer.

### 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  $\Sigma_u^+$  and  $\Pi_u$  are infrared-active (Herzberg 1962, p. 253 ff).

The frequency of the bending mode  $\nu_7$  is still in some doubt. Older papers (Long et al. 1954, Aleksandrov et al. 1964) use the frequency of  $192\text{ cm}^{-1}$  for  $\nu_7$  reported by O'Loane (1953). More recent measurements (Miller and Fateley 1964), however, indicate that the above identification is erroneous. A lower value of  $63\text{ cm}^{-1}$  (Miller et al. 1955) or  $72\text{ cm}^{-1}$  (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) ( $61.6\text{ cm}^{-1}$ ) and measurements of the fine structure of the band at  $3200\text{ cm}^{-1}$  by Lafferty et al. (1964) ( $25\text{--}70\text{ cm}^{-1}$ ).

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  $63\text{ cm}^{-1}$  for  $\nu_7$  was preferred but calculations were made also with the older value of  $190\text{ cm}^{-1}$ . The latter numbers are put in brackets in the Tables. Since  $\nu_7$  has such a low frequency, the state,  $\nu_1 \nu_2 \nu_3 \nu_4 \nu_5 \nu_6$  with  $V = 0$  and  $\nu_7$  with  $V = 1$ , can have a population comparable to the ground state. Difference bands with  $\nu_7$  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  $\mu$  region and the ones listed in Tables 2 and 3. Of the possible binary combinations, only  $\nu_1 + \nu_2$  is within this wavelength region. It is clear that it must be identified with the strong band at 4430  $\text{cm}^{-1}$ . 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, $\text{cm}^{-1}$	WAVELENGTH ( $\mu$ )
1 + 3	$\Sigma_u^+$	4470	2.24
1 + 4	$\Sigma_u^+$	3770	2.65
2 + 3	$\Sigma_u^+$	3100	3.23
3 + 5	$\Pi_u$	2850	3.51
1 + 6	$\Pi_u$	2750	3.64
2 + 4	$\Sigma_u^+$	2400	4.17
1 + 7	$\Pi_u$	2263[2390]	4.42[4.18]
4 + 5	$\Pi_u$	2150	4.65
1 - 7*	$\Pi_u$	2137[2010]	4.68[4.98]
2 + 6	$\Pi_u$	1380	7.25
5 + 6	$\Sigma_u^+$	1130	8.85
2 + 7	$\Pi_u$	893[1020]	11.20[9.80]
2 - 7*	$\Pi_u$	767[640]	13.04[15.6]
5 + 7	$\Sigma_u^+$	643[770]	15.55[13.0]
5 - 7*	$\Sigma_u^+$	513[390]	19.5[25.6]

\*Difference bands with  $\nu_2$  were included because of its low frequency and the consequent population of that state. Numbers in brackets are calculated with the value of 190  $\text{cm}^{-1}$  for  $\nu_2$ .

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TABLE 3

## ALL POSSIBLE INFRARED-ACTIVE TERNARY COMBINATIONS

ASSIGNMENT	DESIGNATION	BAND CENTER, $\text{cm}^{-1}$	WAVELENGTH ( $\mu$ )
3 + 3 + 3	$\Sigma_u^+$	6810	1.47
1 + 1 + 3	$\Sigma_u^+$	6670	1.50
3 + 3 + 4	$\Sigma_u^+$	6110	1.64
1 + 1 + 4	$\Sigma_u^+$	5970	1.68
3 + 4 + 4	$\Sigma_u^+$	5410	1.85
1 + 2 + 3	$\Sigma_u^+$	5300	1.89
3 + 3 + 6	$\Pi_u$	5090	1.96
1 + 3 + 5	$\Pi_u$	5050	1.98
1 + 1 + 6	$\Pi_u$	4950	2.02
4 + 4 + 4	$\Sigma_u^+$	4710	2.12
3 + 3 + 7	$\Pi_u$	4603[4730]	2.17[2.11]
1 + 2 + 4	$\Sigma_u^+$	4600	2.17
3 + 3 - 7*	$\Pi_u$	4477[4350]	2.23[2.30]
1 + 1 + 7	$\Pi_u$	4463[4590]	2.24[2.18]
3 + 4 + 6	$\Pi_u$	4390	2.28
1 + 4 + 5	$\Pi_u$	4350	2.30
1 + 1 - 7*	$\Pi_u$	4337[4210]	2.31[2.38]
2 + 2 + 3	$\Sigma_u^+$	3930	2.54
3 + 4 + 7	$\Pi_u$	3903[4030]	2.56[2.48]
3 + 4 - 7*	$\Pi_u$	3777[3650]	2.65[2.74]
4 + 4 + 6	$\Pi_u$	3690	2.71
2 + 3 + 5	$\Pi_u$	3680	2.72
1 + 2 + 6	$\Pi_u$	3580	2.79
3 + 5 + 5	$\Sigma_u^+$	3430	2.92
3 + 6 + 6	$\Sigma_u^+$	3370	2.97
1 + 5 + 6	$\Pi_u$	3330	3.00
2 + 2 + 4	$\Sigma_u^+$	3230	3.10
4 + 4 + 7	$\Pi_u$	3203[3330]	3.12[3.00]
1 + 2 + 7	$\Pi_u$	3093[3220]	3.23[3.11]
2 + 4 + 5	$\Pi_u$	2980	3.36
1 + 2 - 7*	$\Pi_u$	2967[2840]	3.37[3.52]
3 + 6 + 7	$\Sigma_u^+$	2883[3010]	3.47[3.32]
1 + 5 + 7	$\Pi_u$	2843[2970]	3.52[3.37]
3 + 6 - 7*	$\Sigma_u^+$	2757[2630]	3.63[3.80]
4 + 5 + 5	$\Sigma_u^+$	2730	3.66
1 + 5 - 7*	$\Pi_u$	2717[2590]	3.68[3.85]
4 + 6 + 6	$\Sigma_u^+$	2670	3.75
3 + 7 + 7	$\Sigma_u^+$	2396[2650]	4.17[3.77]
3 + 7 - 7*	$\Pi_u$	2270	4.41
2 + 2 + 6	$\Pi_u$	2210	4.52
4 + 6 + 7	$\Sigma_u^+$	2183[2310]	4.58[4.33]
2 + 5 + 6	$\Sigma_u^+$	1960	5.10
2 + 2 + 7	$\Pi_u$	1723[1850]	5.80[5.41]
5 + 5 + 6	$\Pi_u$	1710	5.85
4 + 7 + 7	$\Sigma_u^+$	1696[1950]	5.90[5.13]
6 + 6 + 6	$\Pi_u$	1650	6.06
2 + 2 - 7*	$\Pi_u$	1597[1470]	6.26[6.80]
2 + 5 + 7	$\Sigma_u^+$	1473[1600]	6.79[6.25]
2 + 5 - 7*	$\Sigma_u^+$	1347[1220]	7.42[8.20]
5 + 5 + 7	$\Pi_u$	1223[1350]	8.18[7.41]
6 + 6 + 7	$\Pi_u$	1163[1290]	8.60[7.75]
7 + 7 + 7	$\Pi_u$	189[570]	52.9[17.5]

\*Difference bands with  $\nu_2$  (see Table 2).

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TABLE 4  
BANDS OBSERVED IN THE LABORATORY AND  
POSSIBLE IDENTIFICATIONS

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

\*Strong band. Numbers in brackets are calculated with the value of  $190 \text{ cm}^{-1}$  for  $\nu_5$ .