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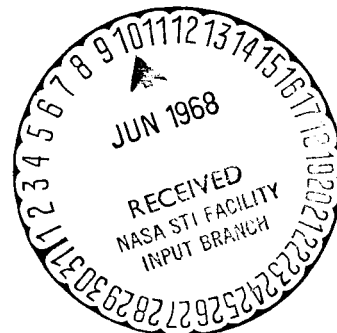
FINAL TECHNICAL REPORT
EXPERIMENTAL INVESTIGATION OF THE ABSORPTION
BY VARIOUS GASES OF PLANETARY INTEREST

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ABSTRACT

Spectral curves of transmission have been obtained in regions near 1.6 μ and 2.3 μ with approximately 0.3 cm^{-1} resolution for the following gases at 196°K: CH_4 , CH_3Cl , CH_3F , CH_2F_2 , CH_2ClF , CHF_3 , CHClF_2 , CHCl_2F , and C_2H_6 . Sample pressures varied between 2.0 and 2.5 torr with 32.9 meter path length. Path lengths up to more than 1 kilometer have also been used to study absorption by weak CO_2 bands from 4225 to 4540 and from 1140 to 1800 cm^{-1} . In the higher wavenumber interval most of the absorption is due to the 07^10 band of $\text{C}^{12}\text{O}^{16}\text{O}^{16}$, the 00^02 band of $\text{C}^{13}\text{O}^{16}\text{O}^{18}$, and the $16^00\leftarrow 01^10$ band of $\text{C}^{12}\text{O}_2^{16}$. The 10^00 and 02^00 bands of $\text{C}^{12}\text{O}_2^{16}$ and $\text{C}^{12}\text{O}^{16}\text{O}^{18}$ contribute most of the absorption in the 1140-1800 cm^{-1} interval. In this interval the absorption by the symmetric $\text{C}^{12}\text{O}_2^{16}$ molecule is pressure induced.

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SECTION 1

INTRODUCTION AND SUMMARY

The infrared absorption by a variety of gases of interest in the study of the atmospheres of Mars and other planets has been investigated. The first phase of this laboratory investigation has dealt with several gases which were suspected of occurring in small quantities in the Martian atmosphere and producing absorption near 1.6μ and 2.3μ . Absorption spectra of these gases, which were primarily methyl derivatives, were obtained in these two spectral regions with the samples maintained at 196°K (dry-ice temperature) to simulate the temperature of the Martian atmosphere. The spectral curves have been digitized and a Philco 2000 computer has been used to calculate extensive tables of transmittance and integrated absorbance for each sample. These tables as well as spectral curves which were plotted on convenient scales have been delivered to Dr. Lewis D. Kaplan and his associates at Jet Propulsion Laboratory in order that they could compare them with spectral curves of the Martian atmosphere obtained by Pierre and Janine Connes.¹ Section 2 summarizes the measurements made under this phase of the investigation.

The remainder of the investigation made use of Aeronutronic's unique capability of obtaining spectral curves with moderate-to-good resolution for samples with path lengths greater than a kilometer. Section 3 describes a set of measurements of the CO_2 absorption between 4225 and 4540 cm^{-1} . Most of the absorption in this region is due to three bands which are so weak that very long absorption paths are required in order to produce measurable absorption. This region is relatively free of absorption by gases in the earth's atmosphere, so that the bands can be observed in the spectra of planets containing large amounts of CO_2 . Our laboratory measurements can be compared with the planetary spectra to obtain information about the relative abundances of the various isotopes of C and O.

The results of a set of measurements of the absorption by very weak CO₂ bands between 1140 and 1800 cm⁻¹ are summarized in Section 4. Most of the absorption is due to the 10⁰0 and 02⁰0 bands of C¹²O₂¹⁶ and C¹²O₂¹⁶18. The transitions giving rise to these bands are forbidden² for the symmetric C¹²O₂¹⁶ molecule at low pressures; however, as the pressure is increased the interactions with neighboring molecules disturbs the symmetry so that the transitions can occur. The absorption coefficient for these pressure-induced bands is, therefore, proportional to pressure. Even at low pressures, the C¹²O₂¹⁶18 molecule is slightly asymmetric so that the transitions are allowed. However, because of the slight degree of asymmetry and the low abundance of O¹⁸, long paths are required to produce measurable absorption.

SECTION 2

1.6 μ AND 2.3 μ SPECTRAL REGIONS

Spectral curves of 9 different gases were obtained in the intervals 3875-4740 cm^{-1} and 5700-6600 cm^{-1} with spectral resolutions of 0.25 and 0.3 cm^{-1} , respectively. The gases were suspected of being present in the atmospheres of other planets, particularly Mars. They were examined in our previous work² with resolution between 1 and 2 cm^{-1} , which was sufficient for comparison with the Mars data available then. However, better-resolved spectra were required to compare with improved Mars data obtained since the previous work by Drs. Pierre and Janine Connes.¹

The instrumentation and the methods of reducing the data have been described previously.² The samples were contained in a multiple-pass cell cooled with dry ice. A custom-made grating spectrometer was employed with a PbS detector cooled³ by liquid Freon 13 (CClF_3) to 192°K, the boiling point at one atmosphere. The signal-to-noise was better by at least a factor of 2 with the detector at this temperature rather than at liquid nitrogen temperature.

The spectral curves were digitized while they were being scanned, and a computer was used to calculate tables of transmittance and $\int A(\nu)d\nu$ vs ν . Curves of transmittance were plotted on convenient wavenumber scales, and copies of the tables and curves were sent to Dr. Lewis Kaplan of Jet Propulsion Laboratories for study.

The tables and curves are not included in this report since they were inordinately large due to the high resolution and the large spectral intervals covered. However, copies of the tables and figures are available from the authors. Table 2-1 contains a list of the gases studied, sample pressures, the integrated absorptances, and the limits over which the integrals were calculated. All the samples were at 196°K with a 32.9 meter path length.

TABLE 2-1
REGIONS STUDIED AND INTEGRATED ABSORPTANCE

Gas	Pressure (torr)	ν_a (cm^{-1})	ν_b (cm^{-1})	$\int_{\nu_a}^{\nu_b} A(\nu) d\nu$ (cm^{-1})
Methane (CH_4)	2.5	3871	4703	62.6
	2.2	5649	6210	14.5
Methyl Chloride (CH_3Cl)	2.3	3872	4635	146
	2.3	5640	6210	86.5
Methyl Fluoride (CH_3F)	2.2	3872	4621	150
	2.1	5640	6143	39.5
Methylene Fluoride (CH_2F_2)	2.5	3872	4615	170
	2.0	5640	6199	33.3
Fluorocarbon 31 (CH_2ClF)	2.1	3872	4618	114
	2.2	5640	6142	59.6
Fluoroform (CHF_3)	2.4	3988	4470	59.2
	2.4	5640	6031	9.4
Freon 22 (CHClF_2)	2.1	4058	4363	45.1
	2.2	5640	6000	23.1
Genetron 21 (CHCl_2F)	2.3	4158	4363	21.0
	2.1	5816	6001	30.0
Ethane (C_2H_6)	2.3	3872	4735	257
	2.3	5640	6070	91.5

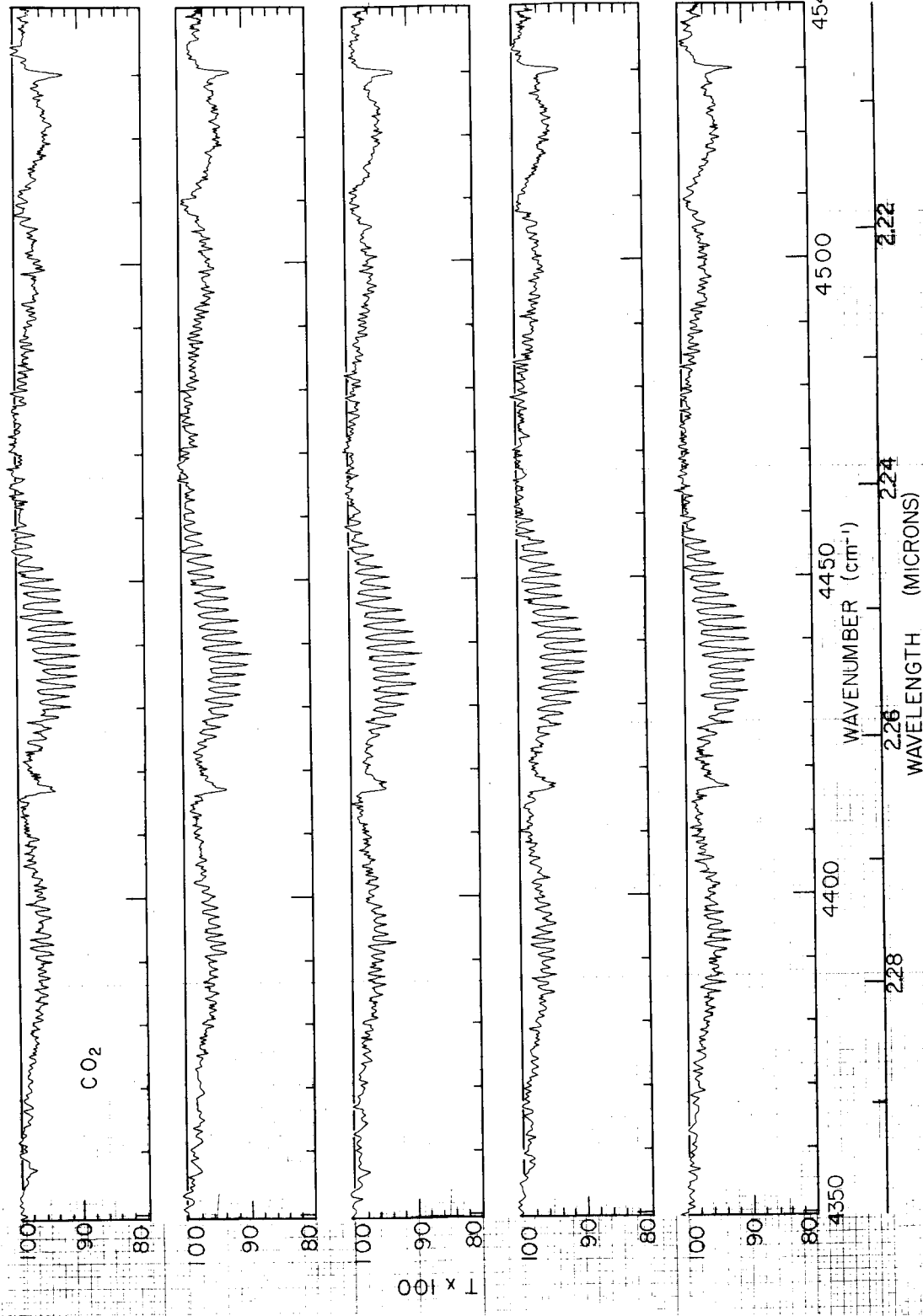
All samples are at 196°K with a path length of 32.9 meters.

SECTION 3

CO₂ ABSORPTION BETWEEN 4225 AND 4540 cm⁻¹

Pierre and Janine Connes¹ have observed some very weak CO₂ absorption bands between 4225 and 4540 cm⁻¹ in the spectrum of Venus. These were observable from ground level because of the small amount of telluric absorption and the vast quantity of CO₂ in the Venusian atmosphere. Since the CO₂ bands are very weak, the absorption is expected to be nearly proportional to CO₂ absorber thickness, u , even at the relatively low pressures in the upper atmosphere of Venus. Therefore, information derived from these bands, along with information on other bands whose absorption is nearly proportional to $(u p)^{1/2}$, should be valuable in determining the equivalent absorber thickness and pressure of the portion of the Venus atmosphere observed by infrared instruments.

We have investigated the absorption by very large samples between 4225 and 4540 cm⁻¹ in order to provide basic information about the strengths of CO₂ bands and to aid in the interpretation of spectra of planetary atmospheres containing large amounts of CO₂. A previous report⁴ covered the absorption above 4540 cm⁻¹, but the region immediately below was not included. Since the bands between 4250 and 4540 are very weak, we employed the longest absorption path practical (1187 m) for quantitative measurements with samples of pure CO₂ at 2.50 atm. Figure 3-1 shows 5 spectral curves obtained for the sample. The curves are relatively noisy since the transmittance scale has been expanded and the slitwidths were kept small (spectral resolution ≈ 0.25 cm⁻¹) to resolve much of the structure. Most of the real structure can be distinguished from the noise by comparing all five curves.



3-2

FIGURE 3-1

Since the absorptance was small, the major source of error was in placing the zero-absorptance curve on the sample curve. Small, long-term variations in the detector signal due to changes in the optical alignment, the source brightness, or amplifier gain necessitated extra care in order to reduce these errors. The following procedure was followed. Five separate curves of the sample described above were digitized and scanned over the 4250-4600 cm^{-1} region. Four zero-absorptance curves were also scanned over the same region with the absorption cell evacuated. After each curve was scanned, the deflection was checked at a few wavelengths and compared with the curve; if there was evidence of drift during the scan, the curve was discarded and another one was scanned. There were small differences in the deflections of the various zero-absorptance curves at the same wavelengths, but we found all four agreed quite well if they were normalized to the same value at some particular wavelength. From this we concluded that the fractional change in the signal was essentially the same at all wavelengths in the interval of interest. A "master" zero-absorptance curve was obtained by averaging the four separate ones after each had been normalized.

We found that when the master zero-absorptance curve was renormalized to fit a particular sample curve near 4225 cm^{-1} , the two curves were essentially coincident between 4225 and 4350 cm^{-1} . Therefore, we concluded that there was no appreciable absorption by bands whose centers occur near this region (4225-4350 cm^{-1}). Furthermore, if there is any continuum absorption, it is constant over the interval. The appropriate zero-absorptance curve was fitted to each sample curve, and the transmittance was determined from the ratio of the digitized deflection of the sample curve to the deflection of its zero-absorptance curve. A computer was used to perform the calculations, and an automatic plotter was employed to produce the five curves shown in Fig. 3-1.

Dr. William Benedict⁵ has compared the curves shown in Fig. 3-1 with Connes' Venus spectra which were obtained with considerably better resolution. The long paths and lower pressures in the Venus atmosphere, along with the better resolution, make it possible to observe more structure in Connes' data than in the laboratory data. However, the laboratory results are required to determine the band strengths and line strengths necessary to interpret Connes' data. Dr. Benedict has determined that the bands listed in Table 3-1 contribute to the absorption. Those marked with an asterisk (*) are the most prominent in Fig. 3-1. The Q branches of the 4529.87 cm^{-1} and the 4416.15 cm^{-1} bands are easily identifiable, as are several of the lines in the P and R branches of the lower wavenumber band. The transmittance maximum corresponding to the center of the 4508.75 cm^{-1} band is apparent, while the R branch of this band overlaps the P branch of the 4529.87 cm^{-1} band.

TABLE 3-1
 CO_2 BANDS BETWEEN 4400 AND 4540 cm^{-1}

ν_0 cm^{-1}	Energy Levels	Isotope
*4416.15	07 ¹ 0	12, 16, 16
4485.60	01 ¹ 2-01 ¹ 0	13, 16, 18
*4508.75	00 ⁰ 2	13, 16, 18
4524.9	00 ⁰ 2	13, 16, 17
4527.28	15 ¹ 0	13, 16, 16
*4529.87	16 ⁰ 0-01 ¹ 0	12, 16, 16

The wavenumbers of the band centers are based on values obtained from Connes'¹ spectra of Venus by Dr. William Benedict⁵. The most prominent bands are marked with an asterisk (*). The numbers in the right-hand column refer to the isotopes of C, O, and O, respectively. Identification of the energy levels are from Stull, Wyatt, and Plass.⁶

SECTION 4

CO₂ ABSORPTION BETWEEN 1140 AND 1800 cm⁻¹

Most of the CO₂ absorption between 1140 and 1800 cm⁻¹ is due to the 10⁰0 and 02⁰0 bands.² The positions of the centers of these bands have been calculated for the four most common isotopes from the energy levels tabulated by Stull, Wyatt, and Plass⁶ and are listed in Table 4-1. These bands are forbidden for the symmetric C¹²O₂¹⁶ and C¹³O₂¹⁶ molecules at low pressures. However, as the pressure is increased² the interaction of the molecules with their neighbors disturbs the symmetry,² and the transitions occur. The absorption coefficient $k(\nu)$ (in atm⁻¹ cm⁻¹) due to one of these pressure-induced bands is, therefore, proportional to pressure, and $-\ln T(\nu)$ is proportional to p^2L . $T(\nu)$ is the transmittance, p is the pressure, and L is the path length. Because of the asymmetry of the C¹²O₂¹⁶O¹⁸ and C¹²O₂¹⁶O¹⁷ molecules, they can absorb at low pressures, and the dependence of their absorption on pressure and absorber thickness is similar to most CO₂ bands. Any absorption by C¹³O₂¹⁶ would be pressure induced and the ratio of its strength to that of the corresponding C¹²O₂¹⁶ band is probably approximately 1.1:99, the same as the ratio of the abundances of C¹³ and C¹². One would expect the strengths of the C¹²O₂¹⁶O¹⁸ bands to be approximately 10 times that of the C¹²O₂¹⁶O¹⁷ bands since the asymmetry of the former molecule is twice as much as the latter, and the abundance of O¹⁸ is five times as great as that of O¹⁷. The strength of each difference band with O¹⁸ as the lower state is expected to be approximately 4% as great as the associated fundamental or overtone band which arises from the same change in quantum numbers. This relationship is based on the assumption that the strengths are proportional to the populations of the lower energy levels involved in the transition. At room temperature the population of the O¹⁸ level is approximately 4% of the O¹⁶ level.

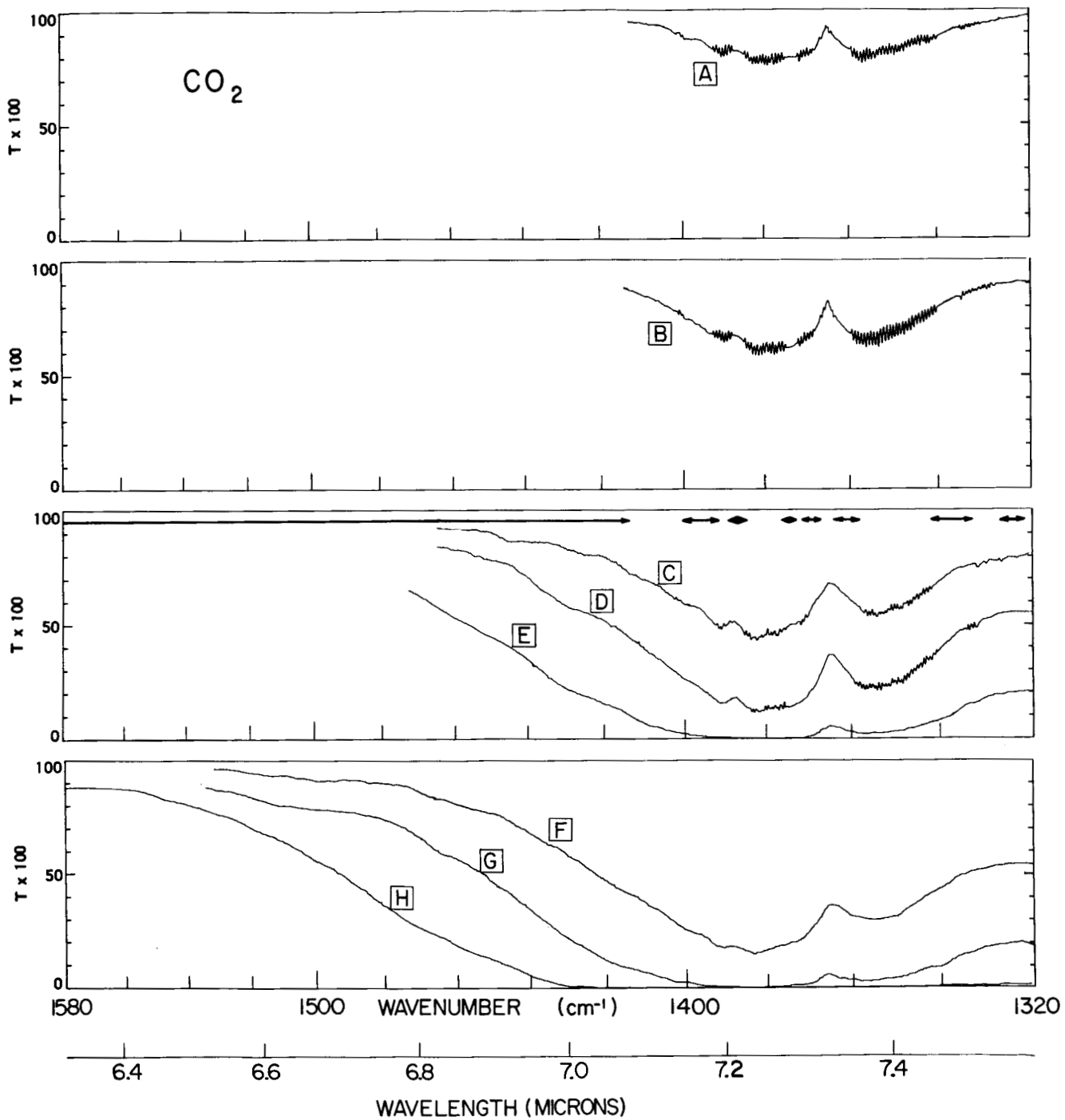


FIGURE 4-1

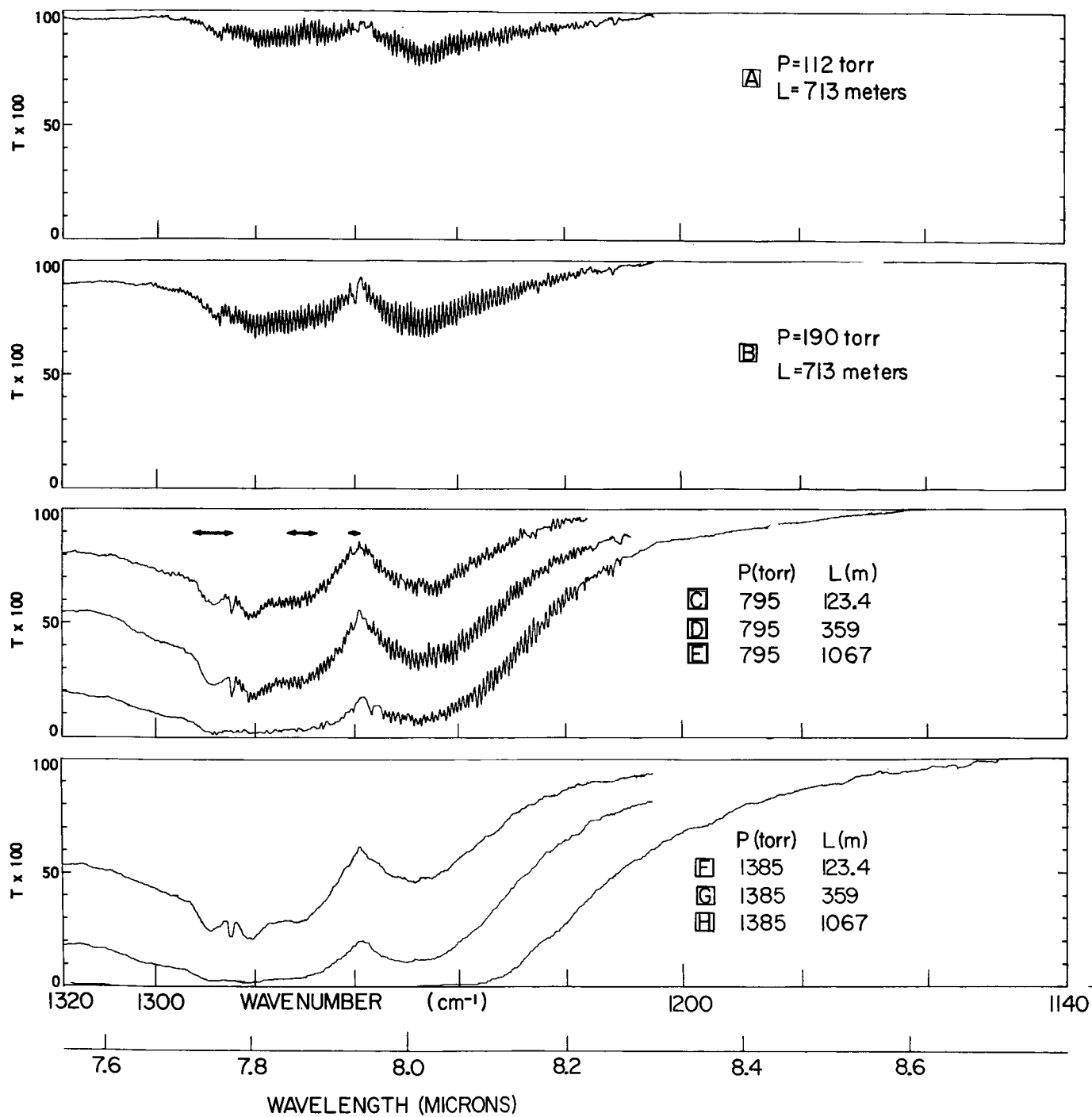


FIGURE 4-2

TABLE 4-1
BAND CENTERS

Isotope	$10^{\circ}0$	$02^{\circ}0$	$11^{1}0-01^{1}0$	$03^{1}0-01^{1}0$
12, 16, 16	1388.20	1285.43	1409.45	1265.11
13, 16, 16	1370.11	1265.84	1388.65	1248.03
12, 16, 18	1365.89	1259.49	1386.93	1239.29
12, 16, 17	1376.03	1272.35	1397.28	1251.98

The numbers in the first column correspond to the isotopes of C, O, and O, respectively. Band centers are in cm^{-1} and are based on energy levels tabulated by Stull, Wyatt, and Plass.

On the basis of the above discussion, we expect most of the pressure-induced absorption to be due to the $10^{\circ}0$ and $02^{\circ}0$ bands of $C^{12}O^{16}O^{16}$ and the major portion of the intrinsic absorption to arise from the same transitions of the $C^{12}O^{16}O^{18}$ band. This is indeed the case, as can be seen in Figs. 4-1 and 4-2 which contain spectral curves for a variety of samples covering a wide range of pressures and path lengths. The curves were replotted from the original spectral curves by the method described previously.^{3,4} The spectral slitwidth for curves A to E varies from approximately 0.45 cm^{-1} at 1200 cm^{-1} to 0.70 cm^{-1} at 1500 cm^{-1} . Curves F, G, and H were scanned with the spectral slitwidth approximately 30 per cent greater.

The $C^{12}O^{16}O^{18}$ bands have been observed with poorer resolution from samples enriched in O^{18} by Eggers and Arends.⁷ Their positions of the band centers agree with ours to less than the experimental uncertainties. The pressure-induced $C^{12}O^{16}$ bands have been observed by Welsh, Crawford, and Locke.⁸ At the pressures used in the present work, the pressure-induced component of the $C^{12}O^{16}O^{18}$ absorption is apparently considerably less than the intrinsic component resulting from the asymmetry.

The major errors in the spectral curves result from errors in placing the zero-absorbance curves on the sample curves and from absorption by H_2O which appeared as an impurity in the CO_2 in spite of efforts to keep it dry. Since many strong H_2O lines exist between 1300 and 1800 cm^{-1} , only a trace of H_2O was required to produce considerable absorption. Most of the H_2O absorption was accounted for before the curves were replotted by comparing the original curves with spectral curves of H_2O with N_2 as a broadening gas. Above approximately 1440 cm^{-1} , the corrections were made at points between the stronger H_2O lines, and a smooth curve was drawn through the corrected values at these points. Values of transmittance given by Curve H for the largest sample studied are probably accurate to less than 0.05 between 1440 and 1580 cm^{-1} . No structure, except for that due to H_2O , was observed in any of the curves between approximately 1430 and 1800 cm^{-1} . The curves have not been included between 1580 and 1800 cm^{-1} since the CO_2 absorption was so small and the H_2O absorption so great that reliable curves could not be obtained. The absorbance by the CO_2 in the largest sample (H) was probably less than 0.02 at 1800 cm^{-1} . The H_2O absorption also caused irregularities in the structure of the $C^{12}O^{16}O^{18}$ bands. In some places where the H_2O absorption was slight, the curve was corrected and was drawn as we believed it would be without the H_2O . In a few other places, where the H_2O absorption covered an area which included as many as 5 or 6 CO_2 lines, no attempt was made to reconstruct the CO_2 structure. Instead, a smooth line was drawn to represent the average CO_2 absorbance. These places are apparent in Curves A, B, C, and D of Fig. 4-1. Intervals containing significant absorption by H_2O are indicated by arrows in the third panel of Figs. 4-1 and 4-2. Other irregularities in the curves due

to H₂O absorption which has not been accounted for still exist. One example is near 1260 cm⁻¹, the center of the 02⁰⁰ band of C¹²O¹⁶O¹⁸. Considerable noise also still remains in some of the curves.

In order to improve the accuracy with which the zero-absorptance curves could be placed on the curves, we performed the following experiment to determine the transmittance of the largest sample near the ends of the curves (1140 and 1585 cm⁻¹). We carefully adjusted the optics for maximum detector signal with the multiple-pass optics adjusted to 36 passes (L = 1067 m) and 1380 torr of pure CO₂ in the cell. The detector signal was measured at these two wavenumbers and the pressure was reduced to 760 torr where another set of measurements were made. The cell was then evacuated and the procedure was repeated. The transmittance of the large sample (P = 1380 torr, L = 1067 m) was found to be 0.995 (+ 0.005-0.02) at 1140 cm⁻¹ and 0.77 ± 0.02 at 1585 cm⁻¹. Approximately half the absorption at 1585 cm⁻¹ was due to H₂O and the contribution by CO₂ was approximately proportional to the square of the pressure, as would be expected for pressure-induced absorption.

The zero-absorptance curve for this sample was adjusted to give the proper transmittance at these points. The curves were also adjusted for the smaller samples so that $-\ln T(1585 \text{ cm}^{-1})$, after accounting for H₂O absorption, was proportional to p²L. For the smaller samples, $-\ln T(1140 \text{ cm}^{-1})$ was essentially zero. Below 1140 cm⁻¹ there was negligible absorption by even the largest sample until we reached about 1115 cm⁻¹, where there was approximately 1 percent absorptance due to the wings of the lines of the 00¹-02⁰⁰ band.

SECTION 5

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