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SCIENTIFIC REPORT

ABSORPTION BY CO₂ BETWEEN 6600 AND 7125 cm⁻¹
(1.4 Micron Region)

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ABSTRACT

The absorption by CO_2 in the $6600 - 7125 \text{ cm}^{-1}$ region (near 1.4μ) has been studied with a spectrometer having a spectral resolution of about 1 cm^{-1} . Spectra were obtained for 38 samples of CO_2 and $\text{CO}_2 + \text{N}_2$ with pressures as high as 15 atmospheres and paths as long as 933 meters. The strengths of the important bands and the half-widths of several lines have been measured. Photographs of the spectra of all the samples as well as a table of transmittance versus wavenumber are included. Also presented is a table of the integrated absorptance

$\int_{\nu'}^{\nu} A(\nu) d\nu$ versus ν , with tabulations for 135 different values of ν for the largest samples.

FOREWORD

This is the second of a series of very detailed reports being published on an extensive investigation of the absorption of infrared radiation by CO₂. These reports contain photographs of spectra and extensive tables which should provide most of the information required to interpret spectra of unknown samples, such as planetary atmospheres, or to calculate the transmission through paths which cannot be simulated in the laboratory.

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SECTION 1

INTRODUCTION AND SUMMARY

Most of the absorption by CO_2 in the $6600 - 7125 \text{ cm}^{-1}$ region ($\sim 1.4\text{-}1.5 \mu$) is due to the 00^0_3 bands of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$. A few difference bands and a combination band also absorb a small amount. The absorption in this region is so weak that it plays only a minor role in the heat balance of the atmosphere. But, because of a few rather unique features of the bands, they could be very useful in the interpretation of spectra of the atmospheres of Mars and Venus. The bands of $^{13}\text{C}^{16}\text{O}_2$ are well separated from those of $^{12}\text{C}^{16}\text{O}_2$; thus, it seems likely that the relative abundances of ^{12}C and ^{13}C isotopes could be determined. The difference bands $01^{13}\text{-}01^{10}$ are also easily distinguished from the 00^0_3 bands; and because of the strong temperature dependence of the strength of the difference band, quite a lot could also be learned about the temperature of a planetary atmosphere.

On the high wavenumber side of the very sharp head of the 00^0_3 band, is a region which is free of absorption lines, but there is considerable absorption due to the wings of lines at lower wavenumbers. Investigation of this region has provided much new information about the shapes of the wings of collision-broadened CO_2 lines. The absorption in this region is very strongly dependent on pressure and on the species of gas present with the CO_2 . Quantitative absorption measurements could, therefore, be useful in analyzing planetary atmospheres.

Before spectra of planetary atmospheres can be interpreted properly, or before the absorption along any given path can be calculated, the strengths, widths and positions of most of the absorption lines must be known accurately. Courtoy¹ has measured the positions of most of the lines with very good precision; but only limited information about strengths and

widths can be obtained from his work. Howard, Burch and Williams² have made some quantitative measurements on the absorption in this region, but they covered a limited range of pressures and path lengths and the spectral resolution of their instrument was low.

Kuiper³ has also investigated the absorption by large samples, but his spectra were obtained with only moderate resolution and with sample pressures of several atmospheres.

Because of the limitations of the previous work, the present investigation was undertaken for the purpose of obtaining data on samples covering wide ranges of pressure and absorber thickness and with sufficient resolution that many of the individual lines could be resolved. A long absorption cell with possible paths as great as 933 meters has enabled us to study samples of very large absorber thickness with sufficiently low pressures that the structure in the spectra is not smoothed out. A shorter absorption cell has also made it possible to study samples at pressures as great as 15 atmospheres in order to measure band strengths accurately. The mean half-width of some of the isolated lines has been measured; the half-widths of many more lines can also be determined by a careful analysis of the data.

The data are presented in great detail for the benefit of workers who require it for their analysis. Spectra of 13 samples covering a wide range of pressures and path lengths have been reproduced and digitized. The reproduced spectra are shown in Section 4 and a table of transmittance $T(\nu)$ versus wavenumber ν is presented in Section 5. Section 6 contains a table of $\int_{\nu'} A(\nu) d\nu$, the cumulative integrated absorptance; ν' is the smallest wavenumber considered for a given sample. Tabulations are made for as many as 135 different values of ν for the largest samples.

SECTION 2

EXPERIMENTAL METHODS

2.1 GAS SAMPLING

Samples of CO_2 and $\text{CO}_2 + \text{N}_2$ were contained in two different absorption cells which have been described previously.⁴ The longer cell has a base length of approximately 30 meters and was used at as many as 32 passes, giving a total path length of 933 meters. It is approximately 0.9 meters in diameter and can be evacuated to less than 1 micron of Hg or pressurized to as much as 2.5 atmospheres. The shorter cell has a base length of approximately 1 meter and was used at as many as 32 passes. It also can be evacuated or pressurized to as much as 15 atmospheres.

The CO_2 was taken from the vapor in a dewar which contained both liquid and vapor maintained at a temperature less than about -20°C by a relief valve which never allowed the pressure to exceed 300 psig. We found that there was considerably less water in the sample if it were drawn from the vapor over the liquid rather than drawing it from the liquid and allowing it to evaporate into the cell. It appeared as though most of the water in the CO_2 container was trapped in the liquid CO_2 ; and if the liquid was drawn off the H_2O was allowed to enter the absorption cell. Of course the pressure, and thus the temperature, in the dewar dropped considerably and the filling rate decreased as the vapor was drawn off. When the pressure decreased to a point where the filling rate was very low, the valves were closed and the dewar was allowed to warm up before the valves were reopened. Since the large cell was filled to the higher pressures only a few times, we did not feel it was worthwhile to build a heater to submerge in the dewars to decrease the filling time. Approximately two days were required to fill the large cell to 2.5 atmospheres from two dewars of CO_2 .

The cell could have been filled in much less time by drawing off the liquid CO₂ rather than the vapor, but the slower technique was chosen because of the drier samples which could be obtained. The amount of H₂O in the N₂ was much less than that in the CO₂; therefore, it was not necessary to take extreme care to reduce the amount of H₂O put into the sample with the N₂ which was drawn off as a liquid into a heat exchanger where it evaporated and entered the cell.

Before introducing a sample into the cell, it was pumped for several hours in order to get rid of most of the H₂O which was adsorbed on the walls. This can be very important, depending on the previous sample in the cell. Even after using this much care, the absorption by traces of H₂O in the sample was bothersome in some regions of the spectrum, particularly between 7000 and 7100 cm⁻¹.

CO₂ + N₂ mixtures were mixed in the cell. CO₂ was introduced to the desired pressure; N₂ was then added and the mixing was accomplished by fans inside the absorption cells. No attempt was made to change the relative abundances of the different isotopes of C or O in the samples studied. It is probably safe to assume that the natural abundances of these isotopes were present (C¹², 98.9%; C¹³, 1.1%; O¹⁶, 99.76%; O¹⁷, 0.04%; O¹⁸, 0.20%). Some results discussed in Section 3 indicate that the abundance of C¹³ was in fact about 1.1%. No check was made on the isotopes of O.

Sample pressures less than approximately 0.06 atm were measured with a U-tube oil manometer and a U-tube Hg manometer was used for pressures in the range 0.06 < P < 2 atm. All pressures > 2 atm were measured with a bourdon-type gauge. For all except the lowest pressures used, the errors arising from the uncertainty in the pressure measurements are probably negligible.

Since CO₂ varies significantly from a perfect gas at some of the higher pressures used in this investigation, it was necessary to account for the Van der Waals' forces giving rise to the deviation from the perfect gas. In calculating the absorber thickness u, the following equation was used:

$$u = W p L \frac{273}{\theta} (\text{atm cm})_{\text{STP}}. \quad (2-1)$$

L is the geometrical path length in centimeters,

p is the partial pressure of CO₂ in atmospheres,

θ is the sample temperature in degrees Kelvin.

273/θ accounts for the difference in density

between room temperature and standard temperature, and

W is a correction term which accounts for the Van der Waals' forces and is given adequately for the pressures used in this investigation by

$$W = 1.00 + 0.0047 p. \quad (2-2)$$

Except for a few samples at 431°K, all measurements were made with the samples at room temperature, approximately 296°K.

In order to relate the pressure of a sample to the half-width of the absorption lines, it is necessary to account for the different broadening abilities of CO₂ and N₂ when dealing with mixtures of these two gases. Burch, Gryvnak and Williams⁵ have used an equivalent pressure P_e given by

$$P_e = 1.3 p + (P - p), \quad (2-3)$$

where P is the total pressure. It is noted that the equivalent pressure approaches the total pressure for a very dilute mixture of CO₂ in N₂, which is a good approximation to the earth's atmosphere.

Since the simple classical theory predicts that the half-width of a line is proportional to the density of molecules, Equation (2-3) should probably be modified to account for Van der Waals' forces which cause the density to increase faster than the pressure. The adjustment can be made in the following way:

$$P_e = 1.3 W p + (P - p). \quad (2-3')$$

The factor 1.3 is not valid in all portions of the spectrum. But in a detailed study of the shapes of collision-broadened lines which will be described in a separate report,⁶ we have found that 1.3 is satisfactory in regions where most of the absorption is due to lines whose centers are a few tenths of a cm⁻¹ away. Therefore, it can be used near the stronger lines of most of the bands. However, the self-broadening factor should be considerably greater in a region such as that between 7100 cm⁻¹ and the head of the 00⁰3 band at approximately 6990 cm⁻¹ where the absorption is due to the wings of lines whose centers are several cm⁻¹ away. The difference in the self-broadening factor arises from the fact that the shape of the extreme wings of a self-broadened line is quite different from that of a nitrogen-broadened line. Equation (2-3') probably gives a good equivalent pressure in the spectral region covered by this report, except from 6990 to 7100 cm⁻¹ and from 6797 to 6810 cm⁻¹. These regions will be discussed in the report on collision-broadened lines mentioned above.

2.2 RECORDING AND CALIBRATION OF SPECTRA

The spectrometer is "home made" and is contained in a tank which could be evacuated to essentially eliminate absorption due to atmospheric gases outside of the absorption cell. The spectrometer tank, as well as another tank containing the radiation source and chopper, were connected to the absorption cell by means of flexible bellows so that all of the optical path external to the absorption cell could be evacuated.

The spectrometer is of the Ebert type with the main mirror having a 75 cm focal length. It utilized a small grating having a ruled area 64 x 64 mm with 600 lines/mm and blazed at 1.6 microns. The grating was used in the first order and a Si filter eliminated overlapping orders of shorter wavelength. A PbS cell cooled with liquid nitrogen was used as the detector. It was not necessary to cool the detector below dry ice temperature for operation in this wavelength region, but the dewar was designed to hold the liquid nitrogen for use at longer wavelengths. Cooling by liquid nitrogen was, therefore, more convenient and was used since the signal-to-noise ratio was approximately the same at both temperatures.

Three different resolution schedules were used in recording the spectra: the approximate spectral slitwidths for each schedule at three different wavenumbers are given in Table 2-1.

TABLE 2-1

RESOLUTION SCHEDULES

ν (cm^{-1})	Spectral Slitwidth (cm^{-1})		
	Schedule A	Schedule B	Schedule C
6600	0.86	1.00	1.40
6800	0.92	1.07	1.50
7000	0.98	1.14	1.60

Resolution Schedule A or B was used in obtaining most of the spectra. However, C was used for spectra of a few samples at several passes of the absorption cell for which the signal was low because of reflection losses. By increasing the slitwidth a better signal-to-noise ratio was obtained. The schedule used for each spectrum is listed in Table 4-1.

CO₂ and H₂O lines whose positions are well known, or could be calculated, were used for the wavenumber calibration of the spectra. The calibration lines are separated by an average of about 10 cm⁻¹, which is sufficiently close that the spectrum could be assumed to be linear between them. All the lines used for calibration are listed in Table 4-2 and their positions are shown on the spectra in Section 4.

Background curves were obtained with the absorption cell evacuated for each number of passes for which sample spectra were obtained. The background curve was different for different numbers of passes since the reflectivity of the mirrors in the multiple-pass optics varies with wavenumber. The appropriate background curve, which represents 100 percent transmittance, was then fitted to each spectrum and traced on it. All the sample spectra extended beyond the region of absorption on both ends of the band so that dependable "tie-points" between a spectrum and its background could be established. The transmittance was determined from the ratio of the deflection of the sample spectrum to that of the background curve at the same wavenumber.

Each spectrum was examined and compared with others as a check for consistency. Small changes were made to account for H₂O absorption. The corrections could be made reasonably accurately by comparing the spectra with those of H₂O + N₂ samples at the proper pathlengths and pressures. The corrected spectra were then replotted and are shown in Section 4.

As each spectrum was being replotted, pairs of values related to transmittance and wavenumber were punched on IBM cards which served as input for a computer program used to calculate transmittance and integrated absorptance as a function of wavenumber. The results of these calculations are shown in Sections 5 and 6. The instrument and the technique used in the replotting and digitizing are described in Appendix C of Reference 4.

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SECTION 3

DISCUSSION OF ABSORPTION BANDS

3.1 IDENTIFICATION AND FEATURES OF THE ABSORPTION BANDS

All of the absorption bands of the various isotopes of CO_2 which might be expected to absorb appreciably in this region are listed in Table 3-1. ν_0 is the wavenumber of the center of the band for the species and transition indicated. The positions of several lines of the bands with reference "C" have been determined accurately by Courtoy.¹ The bands marked "K" were observed by Kuiper³ in the Venus spectrum and compared with laboratory data. Values of ν_0 for the bands marked SWP were determined from the energy levels given by Stull, Wyatt and Plass.⁷

Spectra of three quite different samples are shown in Figure 4-1 with the centers of the stronger bands indicated. The P-branch of the 02^23-02^20 , 10^03-10^00 , and 02^13-02^10 bands of $\text{C}^{12}\text{O}_2^{16}$ all overlap and are only partially resolved. The 01^13-01^10 and 00^03 bands of $\text{C}^{12}\text{O}_2^{16,18}$ also overlap the same region. (In the notation, the lower energy level is omitted when it is 00^00 .) The R-branches of all five of these bands are completely masked by the much stronger 00^03 and 01^13-01^10 bands of $\text{C}^{12}\text{O}_2^{16}$. Resolution considerably better than that used in this investigation would be required in order to positively identify very many of the lines of the five weak bands.

Although the 10^03-02^00 band of $\text{C}^{12}\text{O}_2^{16}$ should occur in a region which is free of lines of stronger CO_2 bands, we were not able to observe it. Most of the absorption near this band results from the wings of the lines of the 00^03 band. A few H_2O lines occur where one would expect to observe the R-branch; thus increasing the smallest detectable CO_2 absorption. An estimated maximum value for the strength was calculated and appears in Table 3-2.

TABLE 3-1

CO₂ BANDS BETWEEN 6600 AND 7100 cm⁻¹

ν_0 cm ⁻¹	Transition	Species	Reference*
6679.75	11 ¹ 2	C ¹² O ₂ ¹⁶	K, SWP
6745.05	01 ¹ 3-01 ¹ 0	C ¹³ O ₂ ¹⁶	K, C
6780.14	00 ⁰ 3	C ¹³ O ₂ ¹⁶	K, C
6884.6	01 ¹ 3-01 ¹ 0	C ¹² O ₂ ¹⁶ ¹⁸	SWP
6897.58	02 ² 3-02 ² 0	C ¹² O ₂ ¹⁶	SWP
6905.72	10 ⁰ 3-10 ⁰ 0	C ¹² O ₂ ¹⁶	SWP
6907.09	02 ⁰ 3-02 ⁰ 0	C ¹² O ₂ ¹⁶	SWP
6921.51	00 ⁰ 3	C ¹² O ₂ ¹⁶ ¹⁸	SWP
6935.05	01 ¹ 3-01 ¹ 0	C ¹² O ₂ ¹⁶	K, C
6972.49	00 ⁰ 3	C ¹² O ₂ ¹⁶	K, C
7008.49	10 ⁰ 3-02 ⁰ 0	C ¹² O ₂ ¹⁶	SWP

* K, Observed by Kuiper³C, Band centers and positions of several lines
measured by Courtoy¹SWP, Band centers calculated from energy levels
given by Stull, Wyatt and Plass⁷

Some interesting features of the transmission spectra in Figure 4-1 should be noted. The difference band $01^{13} \leftarrow 01^{10}$ associated with the 00^03 band of $C^{12}O_2^{16}$ is seen to be displaced to lower wavenumbers with its band head near 6950 cm^{-1} . The corresponding two bands for the C^{13} isotope appear between 6700 and 6800 cm^{-1} , the shift resulting from the heavier C isotope.

The 11^{12} band near 6680 cm^{-1} has a shape quite different from that of the other bands. Its P-branch is very weak while the Q- and R-branches are relatively strong.

The spectrum of sample 22 shows two very sharp changes in transmittance at approximately 6989 cm^{-1} and 6795 cm^{-1} . These arise from the fact that the lines get progressively closer as J-values increase in the R-branch. At about $J = 44$ they double back, causing several lines to occur very close together with none beyond a certain wavenumber referred to as the band head. The rather strong absorption between 6989 and 7100 cm^{-1} by samples 7 and 15 is due to the strong lines whose centers occur below the band head.

Comparison of the spectra of samples 7 and 15 shows that increasing the pressure shifts the wavenumber of minimum transmittance near 6795 cm^{-1} . At relatively low pressures, the minimum in transmittance occurs very close to the band head because there are many very closely spaced lines nearby. This is true although the lines which occur a few cm^{-1} lower ($J \approx 12-30$) are considerably stronger; but, of course, they are more widely separated. As the pressure is increased without changing the absorber thickness u , the absorption between the lines increases. (For purposes of discussion we can think of doing this by decreasing the path length.) The openings between the closely spaced lines soon become "filled-in" and the nearby absorption no longer increases with pressure. However, a much higher pressure is required to fill-in the wider openings between the stronger lines. Therefore, the absorption by them continues to increase with pressure and thus increase the absorption by them relative to the weaker lines near the band head, giving rise to a shift in the transmittance minimum.

Of course, such a shift could also be observed for the corresponding band of $C^{12}O_2^{16}$ provided the proper combination of sample parameters was chosen.

3.2 BAND STRENGTHS

The strength, or intensity, of an absorption band is given by

$$S_v = \int K(\nu) d\nu, \quad (3-1)$$

TABLE 3-2
BAND STRENGTHS

Band	Species	ν cm ⁻¹	Temperature °K	Portion	Strength atm ⁻¹ cm ⁻¹ STP cm ⁻¹
00 ⁰ ₃	C ¹² O ₂ ¹⁶	6972.49	296	R-Branch P-Branch Entire Band	0.0205 ± 0.001 0.0205 ± 0.002 0.0410 ± 0.003
01 ¹ ₃ -01 ¹ ₀	C ¹² O ₂ ¹⁶	6935.05	296	Entire Band ^a	0.0033
00 ⁰ ₃	C ¹² O ₂ ¹⁶	6972.49	431	R-Branch P-Branch Entire Band	0.020 ± 0.002 0.019 ± 0.003 0.039 ± 0.004
01 ¹ ₃ -01 ¹ ₀	C ¹² O ₂ ¹⁶	6935.05	431	Entire Band ^a	0.0083
00 ⁰ ₃	C ¹³ O ₂ ¹⁶	6780.14	296	R-Branch ^b P-Branch ^b Entire Band ^b	22.2 ± 1 × 10 ⁻⁵ 22.6 ± 2 × 10 ⁻⁵ 44.8 ± 2.5 × 10 ⁻⁵
01 ¹ ₃ -01 ¹ ₀	C ¹³ O ₂ ¹⁶	6745.05	296	Entire Band ^{a b}	3.7 × 10 ⁻⁵
11 ¹ ₂	C ¹² O ₂ ¹⁶	6679.75	296	R-Branch P + Q-Branch Entire Band	4.0 ± 0.3 × 10 ⁻⁵ 5.5 ± 0.4 × 10 ⁻⁵ 9.5 ± 0.6 × 10 ⁻⁵
10 ⁰ ₃ -02 ⁰ ₀	C ¹² O ₂ ¹⁶	7008.61	296	Entire Band	2 × 10 ⁻⁶

^aCalculated by assuming relative strengths of bands given by Equation (3-8).

^bBased on absorber thickness u for mixture with natural abundances of isotopes (C¹², 98.9%; C¹³, 1.1%; O¹⁶, 99.76%; O¹⁷, 0.04%; O¹⁸, 0.20%). To obtain strengths of C¹³O₂¹⁶ bands for pure C¹³O₂¹⁶, multiply tabulated strength by 91.

where the integration is performed over all ν for which there is appreciable absorption. $K(\nu)$ is the absorption coefficient which is related to $T'(\nu)$, the true transmittance that would be observed with infinite resolving power, by

$$T'(\nu) = \exp [-u K(\nu)] \quad , \text{ or } u K(\nu) = -\ln T'(\nu). \quad (3-2)$$

Of course, if more than one band contributes to the absorption at a given wavenumber, $K(\nu)$, used in (3-1) must include only the portion due to the band being considered.

The strengths of the bands of interest in this report are essentially independent of pressure over the range of pressures used. However, as the pressure is increased, the widths of the lines increase until at 15 atmospheres they are greater than the spectral slitwidth used by us ($\sim 1 \text{ cm}^{-1}$). When this is the case, the observed transmittance $T(\nu) \approx T'(\nu)$, the true transmittance. Then, by combining (3-1) and (3-2), we obtain

$$S_\nu = -\frac{1}{u} \int \ln T(\nu) d\nu. \quad (3-3)$$

Measurements from a few different samples of CO_2 with N_2 added to a total pressure of approximately 15 atmospheres were used in Equation (3-3) to determine the strengths of the more important bands. Where possible, the samples used in any spectral region were chosen so that the absorptance was between 0.1 and 0.7. Under this restriction $A(\nu)$ was large enough to be measured reliably but not too large for $-\ln T(\nu)$ to be determined accurately. As $A(\nu) \rightarrow 1$, $T(\nu) \rightarrow 0$ and $-\ln T(\nu)$ gets very large; thus a small error in $T(\nu)$ could produce a large error in $\int \ln T(\nu) d\nu$.

It is also possible, under certain conditions, to determine band strengths from transmission spectra when the lines are much narrower than the spectral slitwidth. If $uK(\nu) \ll 1$ for all ν , $T'(\nu)$ can be expressed by the first two terms of a series formed by expanding (3-2) to get $T'(\nu) = 1 - uK(\nu)$. The true absorptance $A'(\nu) \equiv 1 - T'(\nu)$ is given by

$$A'(\nu) = u K(\nu). \quad (3-4)$$

It has been shown² that, under the usual spectroscopic conditions,

$$\int A(\nu) d\nu = \int A'(\nu) d\nu, \quad (3-5)$$

where $A(\nu)$ and $A'(\nu)$ are the observed and true absorptances, respectively. In order for Equation (3-5) to be valid, the integration must be carried out over the region containing essentially all the absorption.

Thus, we see that if $u K(\nu) \ll 1$, the band strength can be obtained from a measurable quantity $A(\nu)$ by

$$S_v = \int K(\nu) d\nu = \frac{1}{u} \int A(\nu) d\nu. \quad (3-6)$$

The absorptance is said to be in the linear region when the conditions exist for the validity of Equation (3-6).

The major disadvantage with working in the linear region is that the absorptance is small and large errors can arise from noise in the spectrum and from slight misplacement of the background curve. The advantages are that the measurements can be made with low resolution and that the pressures need not be as high as when using larger values of $A(\nu)$ [smaller $T(\nu)$] in Equation (3-4).

Plass⁸ has calculated the maximum values of $A(\nu)$ which can be used in Equation (3-6) for various band models having different line strength distributions and different ratios of line width to line spacing. He has also calculated the percentage error introduced under conditions for which the linear relationship is not quite valid. Therefore, if we have some knowledge of the widths and spacing of the lines, we can use Plass' results to determine a correction factor for a band strength calculated by the use of (3-6). This technique is frequently quite helpful when dealing with CO_2 which has reasonably regular line spacing.

For $\Sigma \leftarrow \Sigma$ fundamental or overtone bands such as $\text{CO}_2^0 3$, the strength S_m of a given line within a band is related to the strength S_v of the entire band by

$$S_m = S_v |m| \exp \left[- \frac{B'' m(m-1)}{k\theta} \right] / Q_r. \quad (3-7)$$

$m = J + 1$ for the R-branch and $-J$ for the P-branch. B'' is the rotational constant of the lower state; k is Boltzmann's constant, and θ is the temperature. Q_r is the rotational partition function. Equation (3-7) is not valid for a $\Pi \leftarrow \Sigma$ band such as $11^1 2$.

The results of the band strength measurements are summarized in Table 3-2. Since u is expressed in $\text{atm cm}_{\text{STP}}$ according to Equation (2-1), values of band strengths are in $\text{atm}^{-1} \text{cm}_{\text{STP}}^{-1}$. The STP refers to the absorber thickness but not to the temperature at which the measurements are made.

The P-branches of the $00^0 3$ bands of both $\text{C}^{13}\text{O}_2^{16}$ and $\text{C}^{12}\text{O}_2^{16}$ are overlapped by the P- and R-branches of the difference bands. Therefore, any measurement in the region of overlapping necessarily includes the contributions of all these bands. In order to calculate the different contributions, it was assumed that the relative strengths of the bands are given by⁹

$$\frac{S_v(01^{13}-01^{10})}{S_v(00^{03})} = 2 \exp(-hc 667.4/k\theta). \quad (3-8)$$

θ is the absolute temperature; 667.4 cm^{-1} is the difference between the energy levels 01^{10} and 00^{00} ; and h , c , and k represent the usual physical constants. The factor 2 arises from the double degeneracy of the 01^{10} state. By substituting the proper values into Equation (3-8), we obtain 0.078 for 296°K , and 0.215 for 431°K , the two temperatures at which measurements were made.

The strengths of the R-branches of the 00^{03} bands were measured directly since they are relatively free of lines from other bands. The P-branches of the 00^{03} bands were determined by subtracting the calculated strengths of the $01^{13}-01^{10}$ band from the combined strengths. It is noted that the strengths of the P- and R-branches are very nearly equal. A summation of the strengths of all the lines given by Equation (3-7) indicates that the R-branch should contribute approximately 52% and the P-branch 48%. The deviation of our measurements from this ratio is less than the uncertainty.

A comparison of the changes in transmittance at the band heads near 6990 and 6950 cm^{-1} indicates that Equation (3-8) is at least valid to within 15 or 20%. At 296°K the change in the envelope near 6950 cm^{-1} for a sample having absorber thickness u_1 and equivalent pressure P_e is approximately the same as that near 6990 cm^{-1} for a sample with the same P_e and $u_2 = 0.078 u_1$. There are no two samples which differ in u by exactly a factor of 0.078, the theoretical ratio of the strengths of the bands. But, it is possible to estimate the change in transmittance for a given u from smooth curves through points representing different samples.

The strength of the $01^{13}-01^{10}$ band of $\text{C}^{12}\text{O}_2^{16}$ is seen to increase with temperature between 296°K and 431°K with part of the increase coming at the expense of the 00^{03} band. The combined strengths of these two bands are 0.0443 ± 0.002 at 296°K and 0.0473 ± 0.004 at 431°K . Because of the uncertainty in the measurements, it is not possible to determine if the increase is significant. At 431°K , the estimated error is larger than at room temperature because of reduced stability in the optics and possible error in temperature measurement which results in a corresponding error in the value of u used in the calculation.

The strength of the 00^{03} band of $\text{C}^{12}\text{O}_2^{16}$ is approximately 91.5 times that of the $\text{C}^{13}\text{O}_2^{16}$ band, where the value of u used in the calculation was that of both $\text{C}^{13}\text{O}_2^{16}$ and $\text{C}^{12}\text{O}_2^{16}$ in a sample for which the abundance of the isotopes was not intentionally altered. If we assumed that the strength of the band was not altered by changing the C isotope, the relative strengths should be in proportion to their abundances, 98.9/1.1 = 90. Since this ratio is in good agreement with the observed ratio of 91.5, it is probably safe to assume that the isotopes in our samples were present in their natural abundances.

The R-branch of the 11^{12} band is reasonably well isolated from the P- and Q-branches and its strength could be determined separately. But, because of the overlapping of the P- and Q-branches, it would be difficult to measure the individual contributions. The 10^03-02^00 band could not be detected; therefore, it was only possible to set an upper limit on its strength. It is almost certainly not more than 2×10^{-5} , and is probably quite a bit less.

3.3 HALF-WIDTHS OF ABSORPTION LINES

The shape of a collision-broadened CO_2 absorption line within a few cm^{-1} of its center can usually be represented by the Lorentz line-shape equation¹⁰

$$k(\nu) = \frac{S_m}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2} \quad (3-9)$$

$k(\nu)$ is the absorption coefficient of the single line; S_m is its strength, ν_0 is the line center, and α is the half-width which is proportional to pressure.

Under the condition that $S_m u / 2\pi\alpha \gg 1$, an absorption line is opaque within a few half-widths of its center. The line is then commonly referred to as a strong line.

Ladenberg and Reiche¹¹ have shown that the integrated absorptance of a strong line with Lorentz shape is given by

$$\int A(\nu) d\nu = 2 \sqrt{S_m u \alpha} \quad \text{or} \quad \alpha = \frac{[\int A(\nu) d\nu]^2}{4 S_m u} \quad (3-10)$$

where the integration is carried out over all wavenumbers where there is appreciable absorption. If the conditions for a strong line of known strength are satisfied, α can be determined by Equation (3-10) from a spectrum in which the line is resolved. If the conditions are not satisfied, $\int A(\nu) d\nu$ will show a less-than-square root dependence on pressure.

Lines P2 to P20 (J2 - J20 in the P-branch) of the 00^03 band of $\text{C}^{12}\text{O}_2^{16}$ occur in a region which is free of lines of other bands. It can be seen from the spectra of a few samples at pressures less than 1 atm, that there is but little overlapping of these lines. The finite slitwidth of the spectrometer causes the spectra to appear as if there is more overlapping than there really is. If we assume that overlapping is negligible, the integrated absorptance $\int A(\nu) d\nu$ over the region containing these lines can be treated as the sum of the integrated absorptances

of all the lines. Then by using values of S_m calculated by use of Equation (3-7), we can determine α by Equation (3-10) from some of our data on samples at relatively long paths and low pressures for which the strong line condition is satisfied.

It is also possible to determine the mean half-width of several adjacent lines from $\int A(\nu) d\nu$ over the interval in which the lines occur. Values of $\int A(\nu) d\nu$ for samples 18, 19, 32 and 34 over the region containing lines P6 to P20 ($m = -6$ to -20) were used to calculate $\bar{\alpha}^0$, a mean half-width of self-broadened CO_2 at a pressure of 1 atm. (The superscript is used with α , p and $k(\nu)$ to denote a pressure of 1 atm.) The calculations were made by the use of the following equation which can be derived on the basis of the preceding discussion.

$$\bar{\alpha}^0 = \frac{p^0}{4 u p} \left[\frac{\int A(\nu) d\nu}{\sum_{m=-6}^{-20}} (S_m)^{1/2} \right]^2. \quad (3-11)$$

Plass'⁸ calculated results on the validity of strong-line and non-overlapping approximations were then used to calculate a correction factor for the value determined by Equation (3-11) from each sample. The correction factors depend on the parameters $Su/2\pi\alpha$ and $2\pi\alpha/d$, where d is the line spacing.

After applying the correction factors, which did not exceed a few percent for any of the four samples used, we arrived at $\bar{\alpha}^0 = 0.100$ for the P6 to P20 lines. The four values obtained from the different samples deviated from the mean by less than $\pm 3\%$, but the uncertainty is probably greater than this. At best, the accuracy of the half-widths cannot be better than the values of strengths used in the calculations.

On the basis of Equation (2-3), we can conclude that the mean half-width of these lines broadened to 1 atm with N_2 would be $0.100/1.3 = 0.077 \text{ cm}^{-1}$.

The P2 and P4 lines were omitted from the calculation since their strengths are so much less than the others that they could not be considered strong lines for the samples used. The lines beyond P20 were not used since they are overlapped by the $01^{13}-01^{10}$ band, and the R-branch was omitted because of considerable overlapping and less regular spacing. The data could be used to determine half-widths of lines in these regions, but more sophisticated techniques would be required.

In making the calculations, the integrated absorptance was taken over the interval between 6952.2 and 6968.4 cm^{-1} . The first point is midway between P20 and P22 and the latter is midway between P4 and P6. For the samples used, this integral is very nearly the contribution of the

lines whose centers occur within the interval. The contribution of the wings of lines outside the interval is small and is partially cancelled by the contribution of the wings of the lines within the interval which is lost.

The integrated absorptances over small intervals bounded by points midway between adjacent lines were used in Equation (3-10) to calculate the half-widths of each of the lines individually. Because of the narrowness of the intervals measured, one would expect some "scatter" in the values calculated for the different lines. For example, the values of $\bar{\alpha}^0$ determined from sample 19 varied between 0.098 and 0.111, and no significant change with J-value could be observed.

Benedict¹⁰ has found that the half-widths of CO₂ lines in the 15 μ region measured by Madden¹² can be fitted by the following empirical equation.

$$\bar{\alpha}_m^0 = 0.050 + 0.12 \exp \left[-0.16 |m| \right] + 0.0042 |m| \exp \left[-\frac{B'' m(m-1)}{k\theta} \right]. \quad (3-12)$$

This equation gives 0.119 cm⁻¹ for P6 and 0.093 cm⁻¹ for P20 with the values for the intermediate lines falling between these extremes. A mean value of 0.103 was obtained by inserting half-widths from Equation (3-12) into the following equation

$$\bar{\alpha}^0 = \left[\frac{\sum S_m^{1/2} \alpha_m^{1/2}}{\sum S_m^{1/2}} \right]^2 \quad (3-13)$$

The summation was made over $m = -6$ to $m = -20$ (P6 to P20).

The mean value of 0.103 based on Equations (3-12) and (3-13) is in good agreement with our 0.100; the uncertainty in line strengths alone could easily account for this discrepancy. Spectra obtained with better resolution would be required in order to determine if there is any significant variation in α^0 with J-value.

3.4 ABSORPTION BETWEEN 6990 and 7100 cm⁻¹

It is well known that the absorption coefficient $k(\nu)$ of a single collision-broadened absorption line is proportional to pressure at any point more than a few half-widths from the line center. (For a discussion of collision-broadened lines see references 6, 8 or 13.) Therefore, we would expect the absorption coefficient between about

6990 and 7100 cm^{-1} to be proportional to pressure, since the absorption is due to the sum of wing contributions of several lines. We have demonstrated that this proportional relationship is true, as will be seen below.

For a sample of pure CO_2 , where there is self-broadening only, the absorption coefficient is given by

$$K_s(\nu) = K_s^0(\nu) p/p^0, \quad (3-14)$$

where the subscript s refers to self-broadening and the superscript o indicates a pressure of 1 atm.

Since there are no absorption lines of significance in this region, the transmittance would not change appreciably over one spectral slitwidth; therefore, we can assume that $T(\nu)$ the transmittance observed with a finite slit is very close to the true transmittance $T'(\nu)$. We can therefore, determine $K(\nu)$ from Equation (3-2).

By combining Equations (3-2) and (3-14), we get, for a pure CO_2 sample,

$$K_s^0(\nu) = -\frac{p^0}{u p} \ln T(\nu). \quad (3-15)$$

In the case of a mixture of CO_2 plus a non-absorbing foreign gas with partial pressure p_f , the absorption coefficient is given by the sum of the contributions of the foreign gas and the CO_2 ,

$$K(\nu) = K_s(\nu) + K_f(\nu). \quad (3-16)$$

Since K_f is proportional to p_f , Equation (3-15) can be rewritten as

$$-\frac{1}{u} \ln T(\nu) = K_s^0(\nu) p/p^0 + K_f^0(\nu) p_f/p^0. \quad (3-17)$$

From curves of transmittance of pure CO_2 samples covering wide ranges of pressure and path length, we have determined $K_s^0(\nu)$ for the region from about 6991 to 7100 cm^{-1} . Because of the finite slitwidth of the spectrometer (about 1 cm^{-1}) and possible errors as large as $\pm 0.5 \text{ cm}^{-1}$ in calibration, we were not able to get accurate values between 6991 cm^{-1} and the band head at 6988.5 cm^{-1} . In this narrow interval $K_s^0(\nu)$ changes so rapidly that it cannot be considered constant over a slit width, and small errors in calibration also result in large errors in the calculated values of $K_s^0(\nu)$.

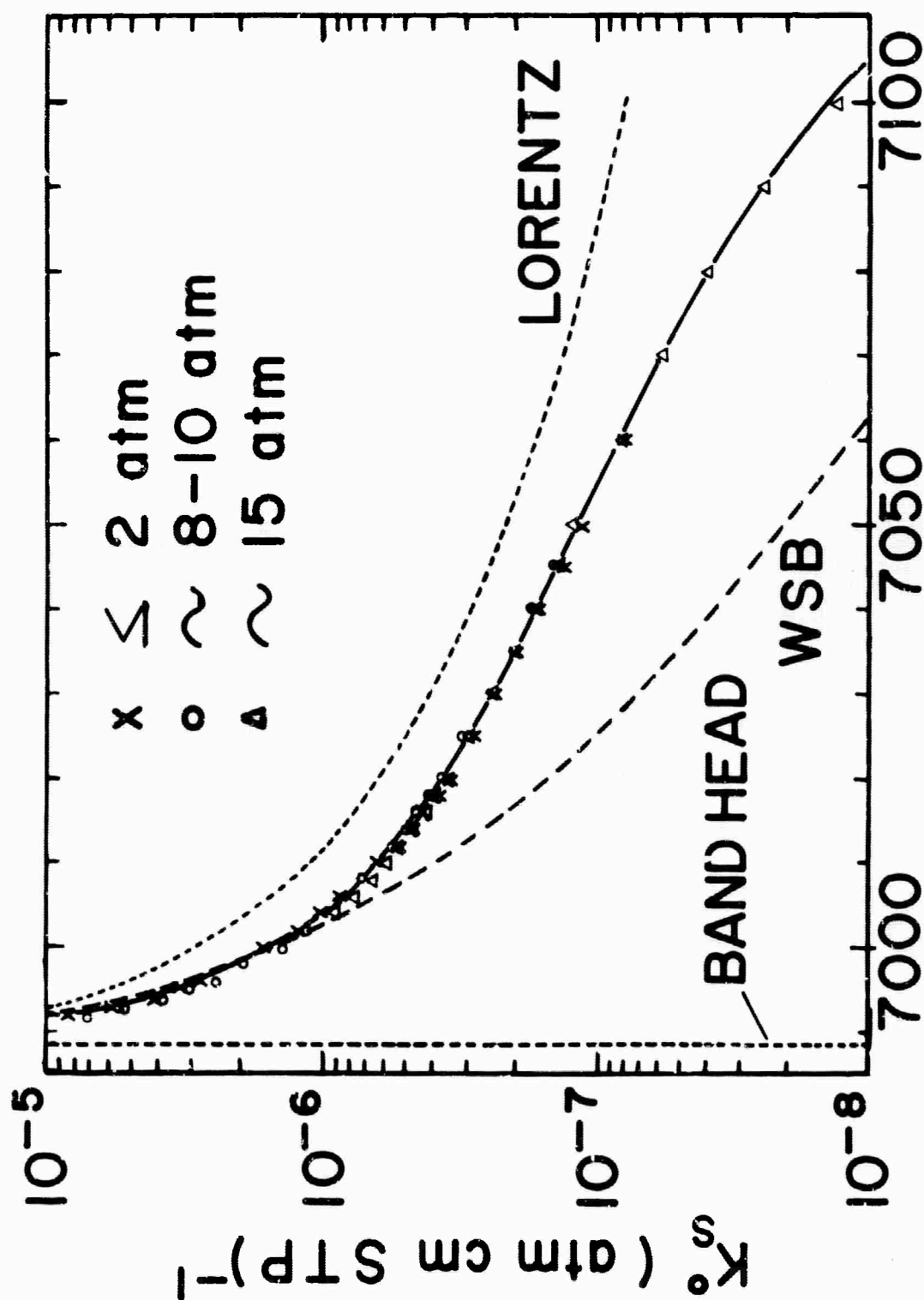


FIGURE 3-1 K_s^0 FOR CO_2 SELF-BROADENING VERSUS ν BETWEEN 6990 AND 7100 cm^{-1} .

The various geometrical figures on the solid curve correspond to samples having different total pressures. K_s^0 , the absorption coefficient for self-broadening at pressure p atmospheres, can be found by multiplying K_s^0 from the figure by p . The curve marked "Lorentz" would be obtained if the lines had a Lorentz shape. The curve marked WSB would be obtained if the lines had the shape found by Winters, Silverman and Benedict¹⁰ for the lines in the 4.3μ band.

Figure 3-1 shows a plot of $K_S^0(\nu)$ versus ν for the region above the band head. The various geometrical figures correspond to samples having different total pressures. Since they all fall on the same curve, we can conclude that the absorption coefficient is, as we assumed, proportional to pressure.

Also shown in Figure 3-1 are two curves of calculated absorption coefficient. The one marked "Lorentz" was obtained by assuming all the absorption lines had the Lorentz shape while the curve marked "WSB" was obtained by using the line shape found by Winters, Silverman, and Benedict¹⁰ for the lines of the 4.3 μ band. In order to perform the calculations we used line strengths given by Equation (3-7) from the value of band strength given in Table 3-2. Half-widths given by Equation (3-12) were used.

It is apparent that the lines of the 00^0_3 band are sub-Lorentzian in the wings: that is, they absorb less than a Lorentz shaped line with the same half-width. However, they absorb considerably more than do those in the 4.3 μ band.

After having found $K_S^0(\nu)$ we were able to determine $K^0(\nu)$ by Equation (3-17) for He and N₂ from samples of CO₂ mixed with each of these gases. The results are shown in Figure 3-2 where a portion of the curve for pure CO₂ is included for comparison. Since it is not possible to obtain as large a value of u in a mixture as in a pure gas, and since the broadening abilities of N₂ and He are much less than that of CO₂, we were only able to measure $K^0(\nu)$ for N₂ and He over the region shown.

It is apparent that quite a lot could be learned about the shapes of the wings of collision-broadened CO₂ lines from the measurements beyond the band head. We have carried out quite an extensive set of measurements such as those described above for several different broadening gases in three different spectral regions; near 2400 cm⁻¹, near 3800 cm⁻¹ and the one shown here. From these measurements we have gained considerable new information about line shapes. The results of this investigation will appear in a separate report⁶ within the next few weeks.

Comparison of the spectra of samples 7 and 15 in Figure 4-1 shows that increasing the pressure has the effect of shifting the 00^0_3 band of C¹²O₂¹⁶. In the region above the band head the absorption is a function of the product pu as can be seen by Equation (3-15). Therefore, sample 7 absorbs more than sample 15, although the latter has the larger value of u . But, between 6800 and 6900 cm⁻¹, the absorption is due primarily to lines whose centers are nearby, rather than by the extreme wings of lines. This results in a strong dependence on u and a weak dependence on p , particularly for pressures high enough that the widths of the lines are not small relative to their spacings. Therefore, sample 15 absorbs more in this region than does sample 7. Thus, the apparent shift is due to a difference in the effect of pressure in the different regions of the band, and not to a shift in line centers.

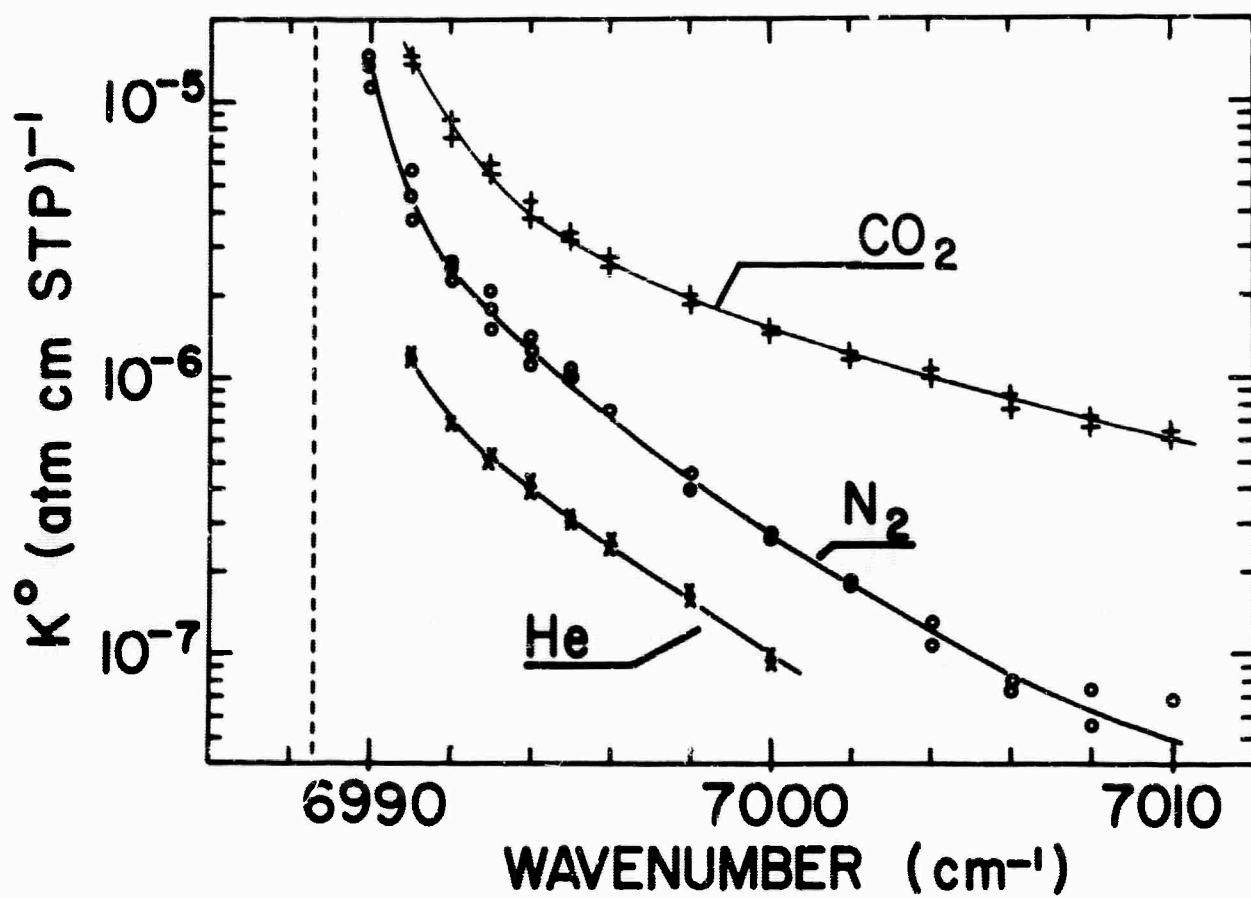


FIGURE 3-2 K° VERSUS ν BETWEEN 6990 AND 7010 cm^{-1} FOR BROADENING BY CO_2 , N_2 AND He .

SECTION 4

SAMPLE PARAMETERS AND TRANSMISSION SPECTRA

4.1 SAMPLE PARAMETERS

The parameters for the 38 samples used in this investigation are summarized in Table 4-1. The following pressures are expressed in both atmospheres and torr (mm Hg):

- p partial pressure of CO₂
- P total pressure due to CO₂ and N₂
- P_e the equivalent pressure which accounts for the difference between self-broadening and foreign broadening by nitrogen. It is given by
$$P_e = 1.3 W p + (P - p)$$
 where W is a Van der Waals correction given by Equation (2-2).

Also included in the table are the values of path length and absorber thickness given by Equation (2-1). The resolution schedule corresponds to the spectral slitwidth of the spectrometer used to record the spectrum. Each schedule is related to slitwidth according to Table 2-1. Replotted spectra are shown in the pages indicated in the last two columns. All samples were at 296°K, with the exception of 37 and 38 which were at 431°K.

TABLE 4-1

SAMPLE PARAMETERS

Sam. No.	p	P	P _e	p	P	P _e
	torr	torr	torr	atm	atm	atm
1	1900	1900	2500	2.50	2.50	3.29
2	1920	1920	2520	2.53	2.53	3.32
3	1920	1920	2520	2.53	2.53	3.32
4	1900	1900	2500	2.50	2.50	3.29
5	760	760	992	1.00	1.00	1.31
6	760	760	992	1.00	1.00	1.31
7	11,100	11,100	15,500	14.6	14.6	20.3
8	11,100	11,100	15,500	14.6	14.6	20.3
9	7600	7600	10,300	10.0	10.0	13.6
10	7600	7600	10,300	10.0	10.0	13.6
11	7600	7600	10,300	10.0	10.0	13.6
12	7600	7600	10,300	10.0	10.0	13.6
13	6080	6080	8200	8.00	8.00	10.8
14	3020	11,100	12,100	4.00	14.6	15.9
15	1522	1522	1995	2.00	2.00	2.62
16	6080	11,100	13,200	8.00	14.6	17.4
17	175	707	760	0.230	0.930	1.00
18	175	175	228	0.230	0.230	0.300
19	88	88	114	0.116	0.116	0.150
20	29.4	29.4	38.2	0.0387	0.0387	0.050
21	58.5	212	230	0.0770	0.279	0.303
22	58.5	58.5	76.1	0.0770	0.0770	0.100
23	1520	1520	1990	2.00	2.00	2.62
24	1520	1520	1990	2.00	2.00	2.62
25	17.8	223	228	0.0234	0.293	0.300
26	17.8	72	77.2	0.0234	0.0947	0.102
27	17.8	17.8	23.1	0.0234	0.0234	0.0304
28	8.95	8.95	11.6	0.0118	0.0118	0.0153
29	760	11,100	2025	1.00	14.6	2.67
30	506	9800	9955	0.666	12.9	13.1
31	165	9800	9850	0.217	12.9	13.0
32	506	506	660	0.666	0.666	0.868
33	165	710	760	0.217	0.934	1.00
34	165	165	215	0.217	0.217	0.283
35	5.8	21	22.7	0.0076	0.0276	0.0299
36	5.8	5.8	7.54	0.0076	0.0076	0.0099
*37	6080	6080	8200	8.00	8.00	10.8
*38	1535	1535	2010	2.02	2.02	2.65

*Samples 37 and 38 were at a temperature of 431°K; all others at 296°K.

TABLE 4-1
(continued)

Sam. No.	L Path meters	u aim cm STP	Res. Sch.	Pages on which spectra appear	
				6000- 6800 -1 cm	6800- 7100 -1 cm
1	933	217,000	B	4-7	4-12
2	469	110,000	B	4-7	
3	237	55,700	B	4-8	4-12
4	121	28,000	B	4-8	4-11
5	933	86,200	B	4-7	
6	237	21,900	B	4-7	4-12
7	32.9	47,300	B	4-5	4-6
8	8.26	11,900	A		4-11
9	32.9	31,700	B	4-8	4-12
10	16.5	15,900	B	4-8	4-11
11	8.26	7,930	B		4-10
12	4.16	3,990	B		4-12
13	32.9	25,100	A		4-12
14	32.9	12,200	A		4-10
15	469	87,100	A	4-6	4-6
16	32.9	25,100	A	4-7	
17	469	9,940	B	4-8	4-9
18	469	9,940	B	4-8	4-11
19	933	9,940	B		4-12
20	933	3,320	C		4-12
21	469	3,320	B		4-10
22	469	3,320	B	4-6	4-6
23	32.9	6,100	A		4-10
24	8.26	1,530	A		4-11
25	469	1,010	B		4-12
26	469	1,010	B		4-10
27	469	1,010	B		4-9
28	933	1,010	C		4-10
29	4.16	384	A		4-11
30	16.5	1,010	B		4-11
31	16.5	330	B		4-11
32	16.5	1,010	B		4-10
33	16.5	330	B		4-11
34	16.5	330	B		4-12
35	469	329	B		4-10
36	469	329	B		4-12
*37	4.16	2,170	A		4-12
*38	8.26	1,050	A		4-9

4.2 CALIBRATION AND TRANSMISSION SPECTRA

Reproductions of the replotted spectra are shown on pages 4-6 to 4-12. Except for Figure 4-1, which includes the entire spectral region covered in this report, the spectra are divided into two intervals and shown separately. The 6600 to 6800 cm^{-1} interval is shown on pages 4-7 and 4-8, and the 6800 to 7100 cm^{-1} interval on pages 4-9 to 4-12. The numbers enclosed in rectangles correspond to the sample numbers given in Table 4-1.

In most cases two or three spectra are included in a single panel of each figure in order to conserve space. The selection of the spectra for any given panel was based on how well they would fit together; no attempt was made to put them in any particular order.

In reducing the data, calibration points were taken at intervals which were short compared to the period of a small periodic error in the screw used to rotate the grating of the spectrometer. Therefore, it can be assumed that the spectra are linear between calibration points. Any error in the determination of the position of a line which might result from this assumption would probably be less than $\pm 0.2 \text{ cm}^{-1}$. The positions of known H_2O and CO_2 calibration lines used for calibration are given in Table 4-2. The H_2O lines appeared in the original spectra of some of the large CO_2 samples because of the H_2O which was present as an impurity. The CO_2 lines used for calibration are designated in the upper panels of the spectra on pages 4-7 and 4-9. The numbers on the spectra correspond to the calibration line number.

TABLE 4-2
CALIBRATION TABLE

Line No.	ν cm^{-1}	Line No.	ν cm^{-1}
1	7117.5 H*	16	6834.1 H
2	7071.0 H	17	6804.3 H
3	7045.5 H	18	6771.6
4	7021.8 H	19	6773.4
5	6978.7	20	6765.5
6	6965.7	21	6756.5
7	6959.9	22	6749.0
8	6953.4	23	6740.9
9	6946.2	24	6732.1
10	6938.4	25	6722.7
11	6929.9	26	6709.2
12	6923.9	27	6688.7 R12*
13	6917.6	28	6682.0 R2
14	6907.5	29	6669.5 P12
15	6871.2 H	30	6659.6 P22
		31	6648.2 P32

*The wavenumbers designated with an H are those of H₂O lines given by Mohler.¹⁴ Wavenumbers of lines 27-31 were calculated by us from information given by Courtoy¹ on rotational constants. The numbers adjacent to the wavenumbers of these lines refers to the line in 11¹₂ band of C¹²O₂¹⁶. For example, R12 corresponds to the line in the R-branch which arises from a transition from the J = 12 state. All other lines are from Courtoy.

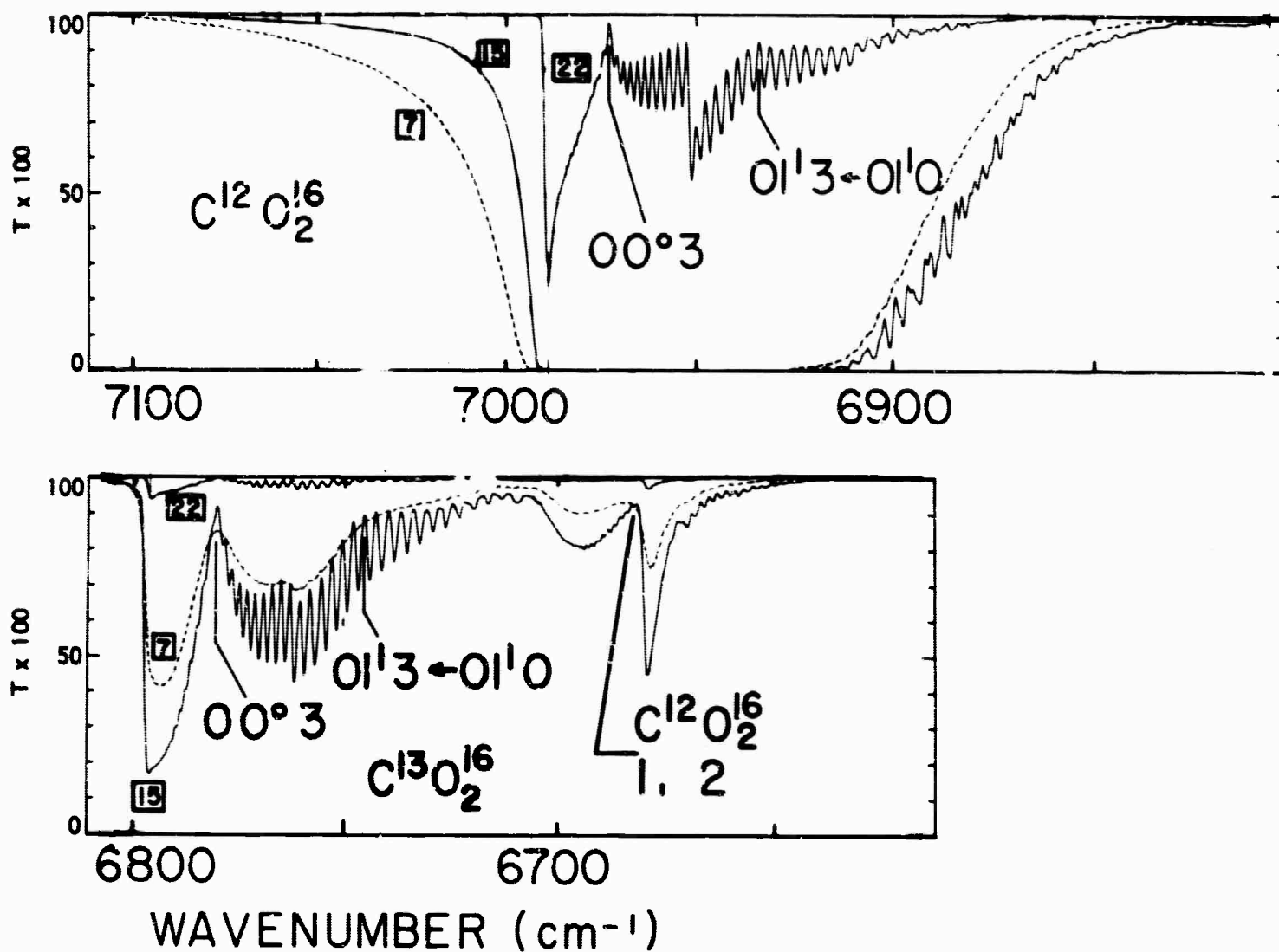
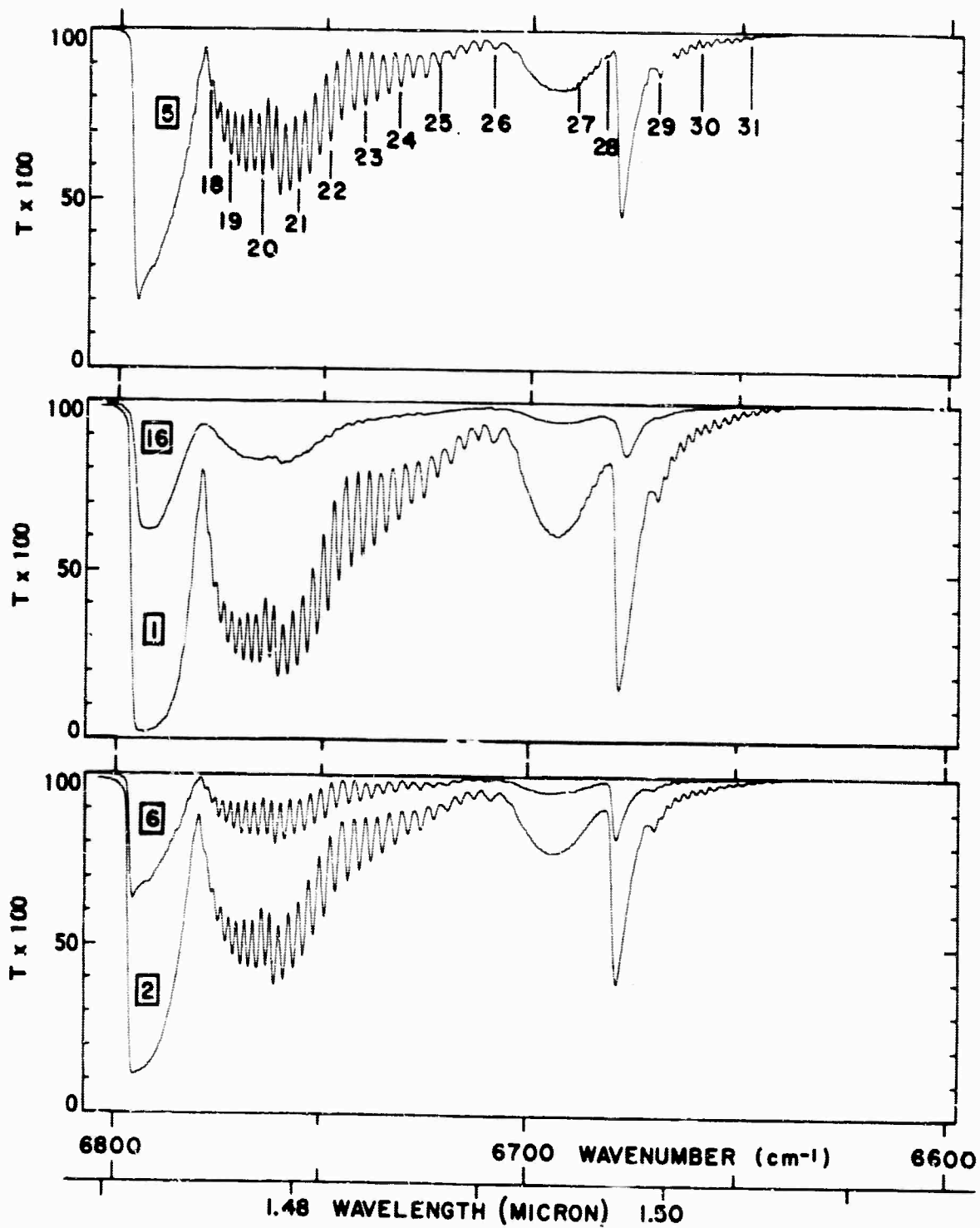
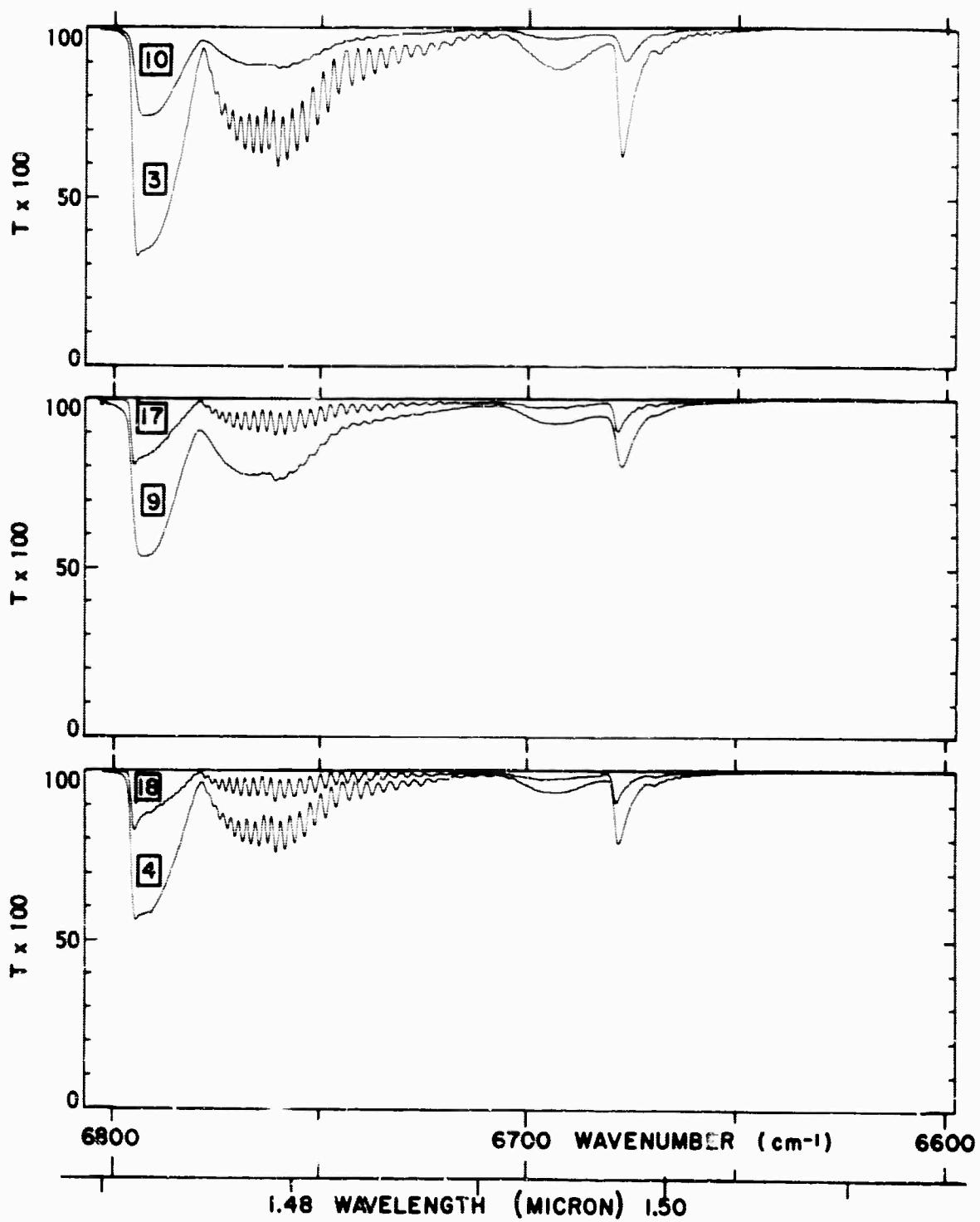
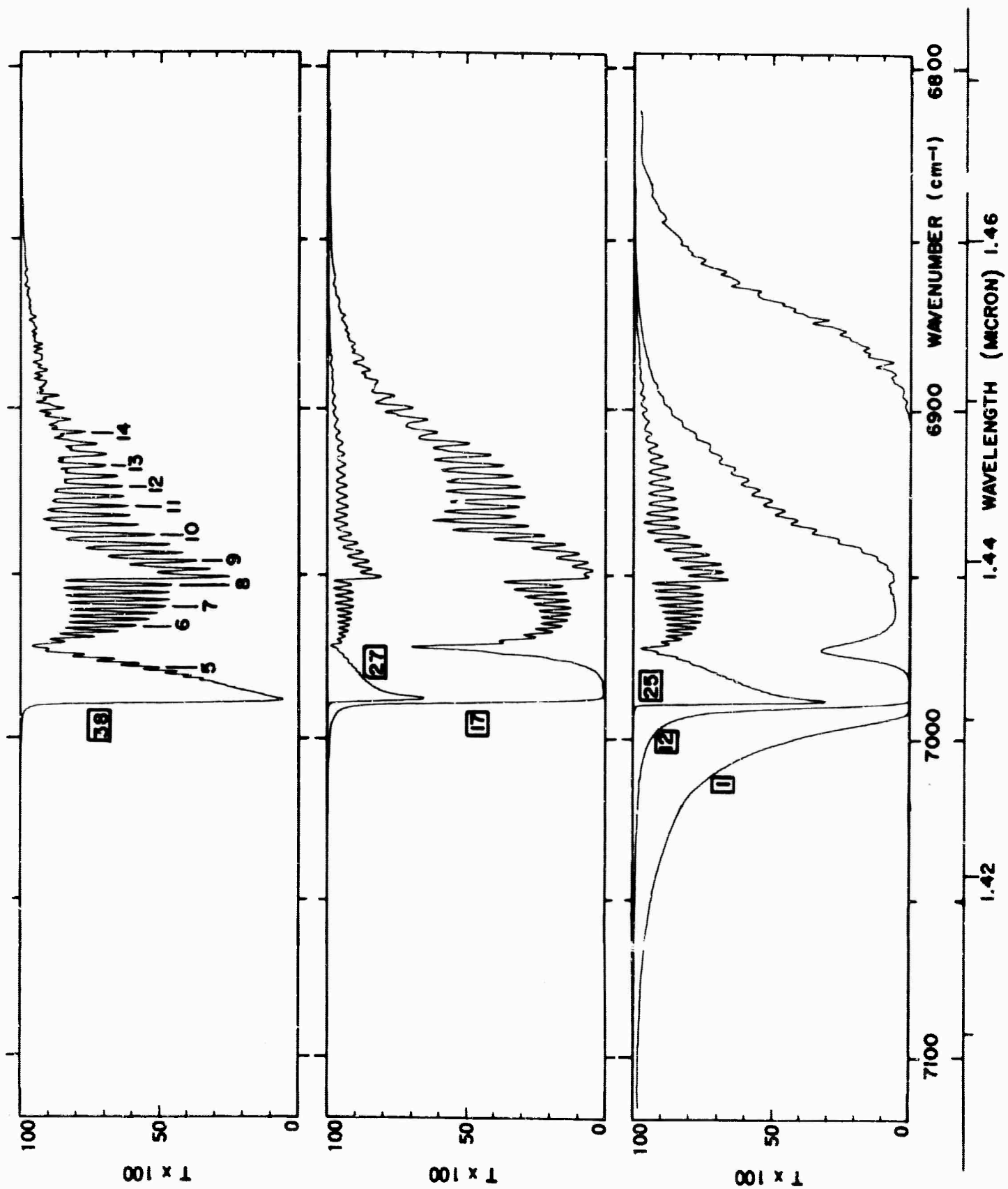


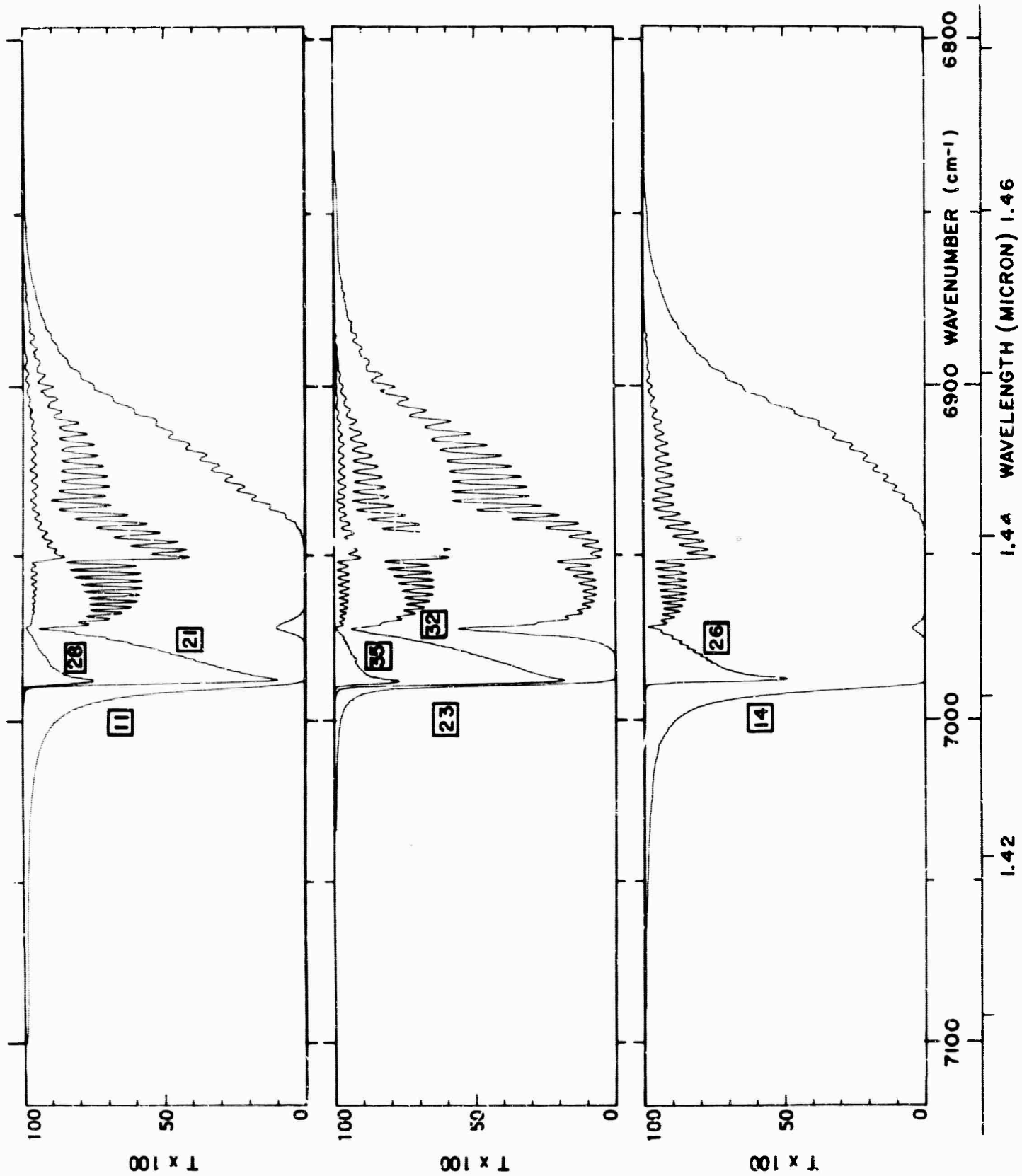
FIGURE 4-1 REPRESENTATIVE SPECTRA OF THE 6600 - 7100 cm^{-1} REGION.

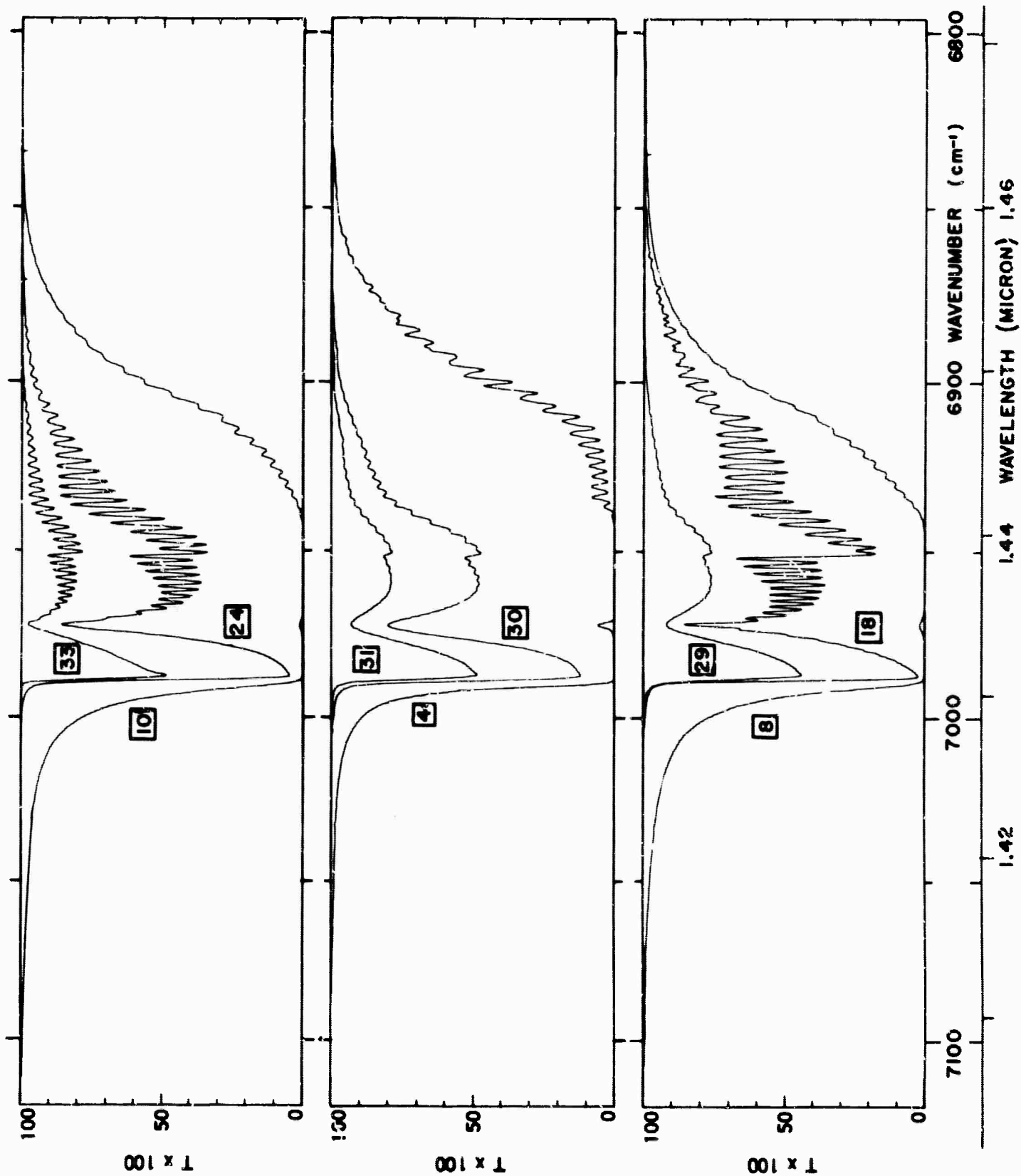
The positions of the centers of the stronger bands are indicated. Other bands in this region are listed in Table 3-1. The numbers enclosed in rectangles are sample numbers. The parameters for all the samples are listed in Table 4-1.

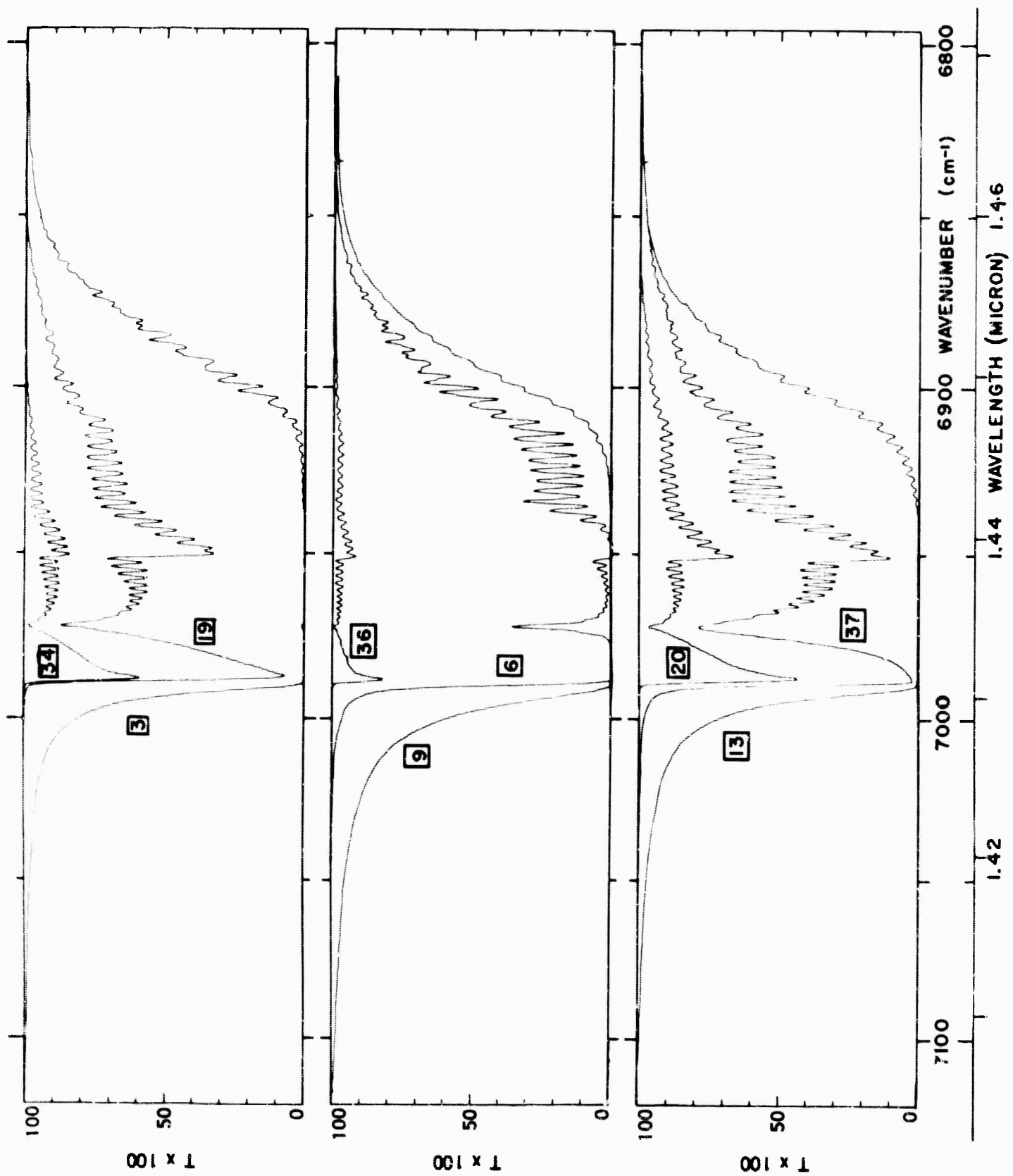












SECTION 5

TABLE OF TRANSMITTANCES

Tables 5-1 and 5-2 consist of values of transmittance, in percent, recorded at intervals of 0.2 cm^{-1} in the region from 6630 to 6806 cm^{-1} and from 6813 to 7125 cm^{-1} , respectively. The 0.2 cm^{-1} interval is sufficiently small that the original spectra could be approximated very closely by plotting the tabulated values and joining the points with straight lines. The first column gives the wavenumber in cm^{-1} , and the second column gives the corresponding wavelength in microns. The tables were made by stripping and photographing portions of the computer output which was obtained from the spectra by the technique described in Section 2.

The CO_2 partial pressure p , the total pressure P due to $\text{CO}_2 + \text{N}_2$, and the absorber thickness u for each sample are shown at the top of the column corresponding to that sample. These parameters are repeated on alternate pages for convenience. Each sample is designated by the same number as in Table 4-1 and in the spectra in Section 4. All samples were at 296°K , with the exception of 37 and 38 which were at 431°K .

Values of transmittance are not tabulated over regions of small absorptance ($T \approx 1$) for some of the samples. The absorptance between 6806 and 6813 cm^{-1} is completely negligible except for a few of the largest samples. For these samples it is safe to assume that the absorptance varies linearly between the values tabulated at 6806 and 6813 cm^{-1} . All values for a given wavenumber appear on a single page.

Table 5-1 (continued)

Year	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000
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Table 5-2

[illegible]

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Table 5-2 (continued)

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	2438	2439	2440	2441	2442
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Table 5-2 (continued)

Year	1900	1901	1902	1903	1904	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
1900	1900	1901	1902	1903	1904	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100

Table 5-2 (continued)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

[illegible]

Table 5-2 (continued)

Time	Lat	Long	Alt	Speed	Heading	Roll	Pitch	Yaw	Acc	Mag	Temp	Hum	Pres	Wind	Wave	Cloud	Vis	Weather
00:00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
00:01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01
00:02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02
00:03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03	10.03
00:04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04
00:05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05
00:06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06	10.06
00:07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07
00:08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08	10.08
00:09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09	10.09
00:10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10
00:11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11
00:12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12	10.12
00:13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13
00:14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14	10.14
00:15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15	10.15
00:16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16
00:17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17	10.17
00:18	10.18	10.18	10.18	10.														

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SECTION 6

TABLES OF INTEGRATED ABSORPTANCE

Values of the integrated absorptance are presented in Tables 6-1 and 6-2 for the regions below and above 6806 cm^{-1} , respectively. The tables do not cover the entire interval for all the samples. In general, the tables include only the region over which the absorptance is great enough to be measured with reasonable accuracy. The calculations were usually made for groups of from 3 to 5 samples at a time with the limits of integration the same for all the samples in a given group. The lower limit of integration ν' , which is shown at the top of each column, was chosen at a point below which there was little absorption.

The integrated absorptance between any two wavenumbers listed can be found by subtracting the values tabulated at the two points. All of the significant figures are carried in the table in order to avoid losing information when dealing with narrow intervals. The table was formed by stripping and photographing part of the computer output with the proper headings pieced in above each section.

Over a portion of Table 6-2 there are too many values listed at a given wavenumber to include them all on one page. Therefore, they were arranged to appear on successive pages which can be seen simultaneously.

In regions where the structure in the spectra is regular, the integrated absorptance was calculated at wavenumbers midway between the line centers. Therefore, in the case of no overlapping, the difference between

two successive tabulated values is the equivalent width of the absorption line in the interval. In some other regions where the structure was not particularly regular, the integrated absorptance was calculated at wavenumbers corresponding to absorptance minima. In still other regions where there was but little structure or where the absorptance minima would shift as the pressure or absorber thickness was changed, the values were calculated at integral wavenumbers or possibly at integral half-wavenumbers, depending on the amount of information one might expect to obtain from closer readings.

The important parameters for each sample are shown at the top of the column corresponding to that sample. All samples were at 296°K, with the exception of 37 and 38 which were at 431°K.

Table 6-1

6-3

Table 6-2 $[\int_{\nu'}^{\nu} A(\nu) d\nu]$ [illegible]

Table 6-2 $[\int_{\nu'} A(\nu) d\nu]$ [illegible]

SECTION 7

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