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Transmissivity of Carbon Monoxide in the 2.3 μm Band Region

Final Report

2. 3 Microns

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ABSTRACT

Line strengths and self and nitrogen broadened half-widths have been determined from high resolution (0.12 cm^{-1}) spectroscopic measurements of selected lines in the 2.3μm band region of CO. The CO 0-2 total band strength is estimated to be 2.086 ± 0.146 cm^{-1} $(atm\text{-}cm)^{-1}$ STP which is higher than most previously reported values. The line half-widths are also generally higher than those in the literature.

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1. INTRODUCTION

This report presents the experimentally obtained results of a study made of the 0-2 absorption spectrum in the 2.3μm band region of carbon monoxide. The line parameters: line strength, and self and nitrogen broadened half widths are given for various principle lines in this spectral region. These results along with a calculated band strength value of $2.086 \pm 0.146\ \mathrm{cm}^{-1}\ (\mathrm{atm\ cm})^{-1}$ STP are comparatively higher than many of the previously reported results of experimental and theoretical studies of the first overtone band of CO. Our data analysis technique, which does include wing and base corrections applied to the measured equivalent widths, has produced results which are comparatively higher not only for this present study but also for an earlier study of the fundemental band of CO by Drayson et.al. (1973). In this report we discuss possible reasons for the differences between the results of our study and the results of other authors. Also, brief descriptions are given of the experimental and analytical methods used in this study.

2. EXPERIMENTAL

A complete description of the instrumentation and measurement procedure used in this study can be found in the report by Chaney (1972). A very brief description is as follows. A Jarrell Ash 1.83 meter Fastie Ebert vaccuum scanning spectrometer was used to make the actual spectroscopic measurements. The source of the infrared radiation was a General Electric 600 watt tungsten - iodide lamp cooled to $-78^{o}C$ with dry ice in ethyl alcohol. The gas sample cell was made from the entrance optics by means of having a sapphire window placed between the entrance optics flange and the spectrometer main frame. The cell dimensions were one meter from the input window to a diagonal mirror, one meter from the diagonal mirror to a spherical mirror, and one meter back from the spherical mirror to the entrance slit. Thus, the total optical path length was 3.0 meters. The detector output signal after passing through a pre-amplifier and phase lock amplifier was a d.c. signal which varied between 0 and ±5 volts. This signal was recorded on an analog chart recorder and was also digitized. The data was punched on IBM cards. The data scan rate was about 110 seconds per wavenumber. A signal to noise ratio of approximately 200:1 was obtained for most of the data.

Matheson Company carbon monoxide with a stated purity of 99.5% or higher was used in this study. Nitrogen gas from a large liquid nitrogen storage dewar was used in certian measurements to broaden the CO. The CO and N_2 mixtures were allowed to mix for periods on the order of eighteen hours before measurements were taken.

For all data scans the gas sample pressures were measured to within 0.01 mm of Hg and the room temperature was kept constant to within ±0.5°C. The gas sample cell temperature for all measurements was 25°C ± 2°C.

The 2.3μm band was studied with a Bausch and Lomb grating blazed at 4.0μm and filtered for the second order. The best measured resolution for this grating was 0.12 cm^{-1}. The band was isolated with a 2.07μm-2.708μm band pass optical coating laboratory interference filter. Eight regions of the band were investigated (Table 1). These regions were chosen because of the relative minimum of line overlap.

Table 1

Regions of the band studied

Region	Wavenumber [cm^{-1}]	C^{12} O^{16} Lines
1	4152-4156	P23
2	4193-4197	P15
3	4230-4232	P7
4	4233-4246	P4-P6
5	4255-4276	R3-P1
6	4283-4287	R6
7	4310-4315	R15-R16
8	4332-4336	R24-R25

3. ANALYSIS

The analysis method closely followed in this study was used by Drayson et.al. (1973) in the experimental study of the transmissivity of CO in the 4.6μm region. A complete description of the method can be found in that report.

Basically, the method of curve of growth was used to determine the values of the line strenths and line half widths of those spectral lines investigated. Measurements using the trapezoidal rule were made of the equivalent widths for each spectral line in which adequate data was available. For those lines in which weak isotopic line blending was observed, a correction equal to the product of the isotope line strength and absorber path length was subtracted from the total equivalent width. An iterative procedure was used to make the line parameter calculations. Initial values of the line parameters were taken from Kunde (1967). Additional corrections were made to the measured equivalent widths. Wing and base corrections from Korbe et.al. (1968) were applied. The wing and base corrected equivalent widths were corrected for doppler broadening. Correction expressions for a Voigt profile line were obtained from Yamada (1968).

The line strength and half width values calculated during an iteration were averaged and used as improved estimates for the following iteration. The iterative procedure continued until the difference between the newly calculated values and the previously calculated values differed by no more than 0.0002.

For the six spectral lines in which enough useable data was available to calculate all three line parameters the Herman Wallis (1955) formula was used to calculate the band strength of the first overtone of $C^{12}O^{16}$. An average of the six calculated band strengths was then used in the Herman Wallis formula to compute the line strengths of the other spectral lines in the study. These line strength values were then used to compute half-width values for those lines having enough self and/or N_2 broadened data.

4. RESULTS AND DISCUSSION

The line strengths and line half-widths of the R6, R3, R2, R1, R0 and P15 lines determined in this study are presented in Table 4. A band strength for the first overtone of $C^{12}O^{16}$ was calculated from the line strength of these six lines. These results are given in Table 2. For each spectral line the individual measurements are assumed to be normally distributed about the average line strength. One standard

Table 2

Band strength from individual measurements

Line	Number of Measurements	Line strength cm^{-1} $(atm.cm)^{-1}$ STP	Band Strength cm^{-1} $(atm.cm)^{-1}$ STP	Standard Deviation
R6	10	0.0876	1.9239	±3.6
R3	10	0.0678	2.0053	±4.9
R2	8	0.0562	2.1193	±4.4
R1	8	0.0358	1.9531	±3.2
R0	10	0.0207	2.2191	±6.2
P15	6	0.0292	2.1248	±2.0

deviation, stated in percentage of the average, is calculated from the individual measurements for each of the six lines.

The average band strength from these six measurements is 2.057 $cm^{-1}(atm.cm)^{-1}$STP. By assuming that the CO gas samples had an isotopic composition close to that of atmospheric CO, the average band strengths of the first overtones of $C^{13}O^{16}$, $C^{12}O^{18}$, and $C^{12}O^{17}$ were calculated to be 0.023, 0.004, and 0.0007 $cm^{-1}(atm.cm)^{-1}$STP, respectively. Thus, the total band strength of the first overtone of CO is estimated to be 2.086 ± 0.146 $cm^{-1}(atm.cm)^{-1}$STP. A discussion of the error estimate follows later in this section. This band strength is approximately 9% higher than the average of 1.88 $cm^{-1}(atm.cm)^{-1}$STP obtained from the previous studies of the 2.3 m band region listed in Table 3. The larger value of our band strength is due primarily to the wing and base corrections of the equivalent widths in our calculations. Our band strength value does compare most favorably with the value obtained by Schurin and Ellis (1966) who used the Wilson-Wells-Penner-Weber self broadening technique in their theoretical study.

The self-broadened line widths determined from this study are compared in Figure 1 with results from recent studies. Out values are approximately 10% greater than those obtained by Kostowski and Bass (1961) in their direct measurement study of the first overtone band of CO. There is fairly good agreement between our nitrogen broadened half-

Table 3

Band Intensities of the 2.3μm band of CO

year	Author	Band Intensity $cm^{-1}(atm.cm)^{-1}$ STP
1951	Penner and Weber	1.83
1954	Vincent and Geisse	1.83
1961	Kostkowski and Bass	1.95
1962	Oppenheim and Goldring	1.66
1965	Armstrong and Welsh	1.77±0.05
1966	Schurin and Ellis	2.15±0.1

width values and those values from recent studies. Although, again our half-width values are higher than those of other authors. The nitrogen broadened half-widths results are compared in Figure 2 with the results from recent investigations.

A discussion of the errors and uncertainties involved with this study is useful when considering the validity of our results. Reichle (1969) has extensively discussed the inherent difficulties in making accurate determination of the line parameters in a study of this type. Possibly the greatest margin of error in this study lies in the difficulty in accurately locating the baselines of the absorption line. For those lines in which there were few or no closely neighboring isotopic lines we took an average of as many as 30 data points, (i.e. each data point corresponds to approximately 0.008 cm^{-1}) on either side of the spectral line.

TABLE 4

Measured Line Intensities and Half-Widths

Line	Isotope*	Line Center	S $\mathrm{cm^{-1}}$ $[\mathrm{atm^{-1}cm^{-1}}]$ STP	α_{CO} $\mathrm{atm^{-1}cm^{-1}}$	α_{N_2} $\mathrm{atm^{-1}cm^{-1}}$
R25	26	4335.02	.0014	-	-
R24	26	4333.04	.0022	-	-
R15	26	4311.95	.0364	-	-
R6	26	4285.00	.0873	.0804	.0674
R3	26	4274.74	.0678	.0849	.0775
R2	26	4271.17	.0562	.0940	.0878
R1	26	4267.54	.0358	.0860	.0806
R0	26	4263.83	.0207	.0857	.0822
P1	26	4256.21	.0188	.0805	-
P4	26	4244.26	.0610	.0877	-
P5	26	4240.13	.0687	-	-
P7	26	4231.68	.0747	-	.0667
P15	26	4195.11	.0292	.0742	.0567
R7	36	4193.86	.0011	-	-
P3	36	4155.60	.0006	-	-
P23	26	4154.19	.0024	.0552	-

---

*The notation used to identify the isotope is: 26=$C^{12}O^{16}$, 36 = $C^{13}O^{16}$.

Yet, for those lines having close neighboring isotope lines it was often necessary to take an average of as few as 10 data points for the base transmission line. In addition to the low amounts of noise present in the data we also had shifts in the background levels that were on the order of 1% per hour of data acquisition. This systematic slow change in background was apparently due to self-heating taking place in some part of the instrument. For certain data scans there was also some aperiodic variation in the background level over intervals of a few tenths of a wavenumber. These variations were normally quite small in amplitude, yet they were often easily recognizable in the computer drawn plots. The amplitudes of these variations normally were no larger than 1% of the amplitude of the spectral line. The cause of these variations is not fully understood. We feel that errors in measurements of the pressures, the total optical path length of the spectrometer, the temperatures, and our estimate of the isotopic composition of CO were fairly small, about on the order of less than 1%. We estimate the error due to wavenumber calibration and wavenumber shift caused by temperature changes to be less than 1%. Errors in the data transmission system are also very small having magnitudes less than 0.5%.

We, thus, estimate that the equivalent widths were measured to within 4% accuracy for most of the data. Due to the inherent difficulties in accurately measuring the relatively low equivalent widths of much of our data we estimate that our band strength is accurate to within ±7%. The error bars in Figures 1 and 2 are estimates of the dispersion of the experimentally obtained half-width values of this study about the plotted averages. Each error bar represents one standard deviation. It is important to note that these error bars do not totally represent the absolute error in the half-width measurements. Since there is some nonlinear dependence of the calculated half-widths upon the individual line strength estimates, the actual error estimates associated with these values may be somewhat greater in magnitude. Figure 3 shows a computer drawn plot of a scan of a portion of the 2.3μm absorption spectra of CO.

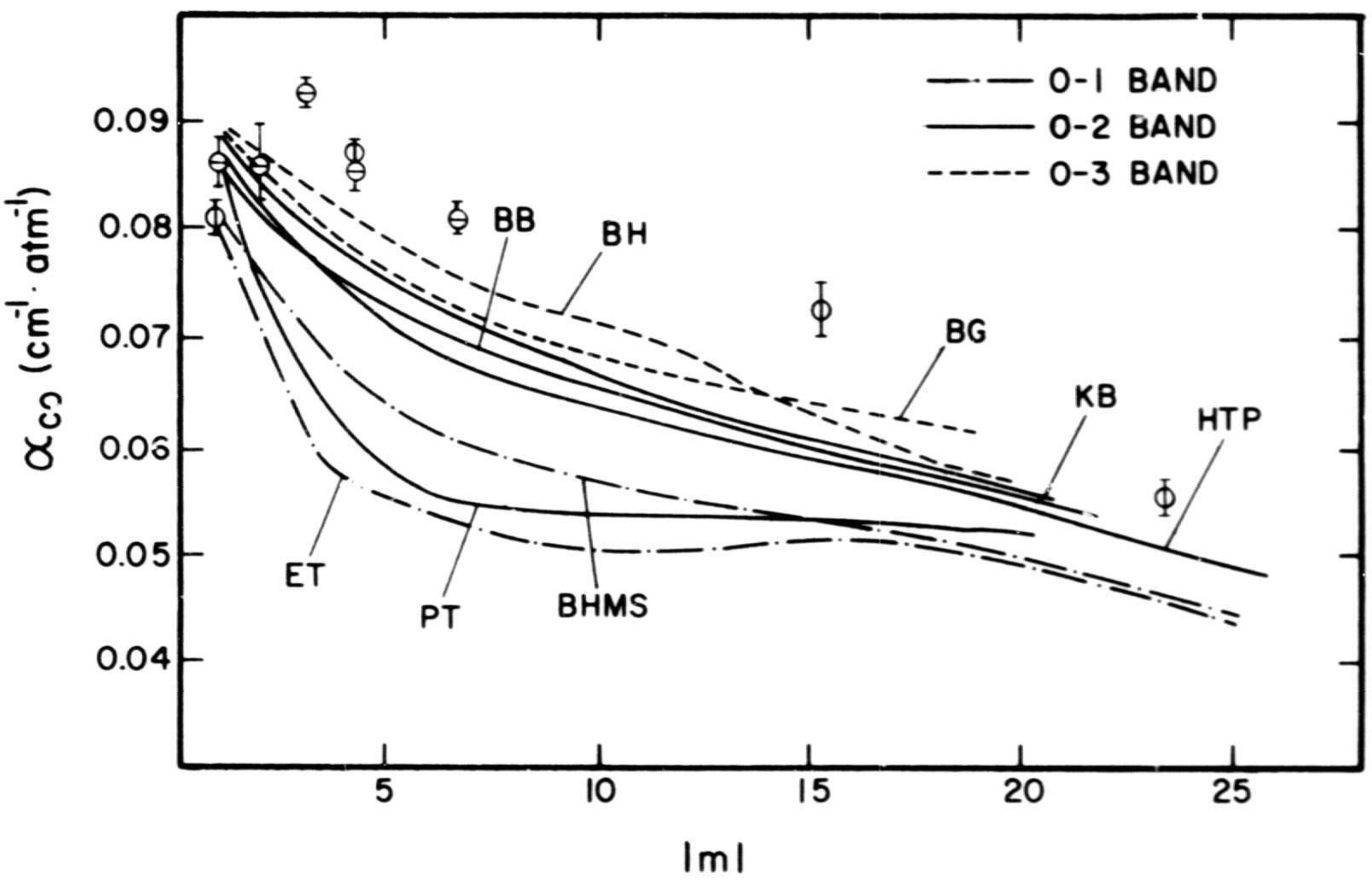


Figure 1: Self-Broadened half-widths of CO lines versus |m| results of this work (Φ-P branch and ⊖ -R branch) are shown along with results in the 0-1 band of Eaton and Thompson (1959)-ET; Benedict et.al. (1962)-BHMS; 0-2 band of Kostkowski and Bass (1961)-KB; Plyler and Thibault (1963)-PT; Hunt et.al. (1968)-HTP; Bouanich and Brodback (1974)-BB; 0-3 band of Burch and Gryvnak (1967)-BG; Bouanich and Haeusler (1972)-BH.

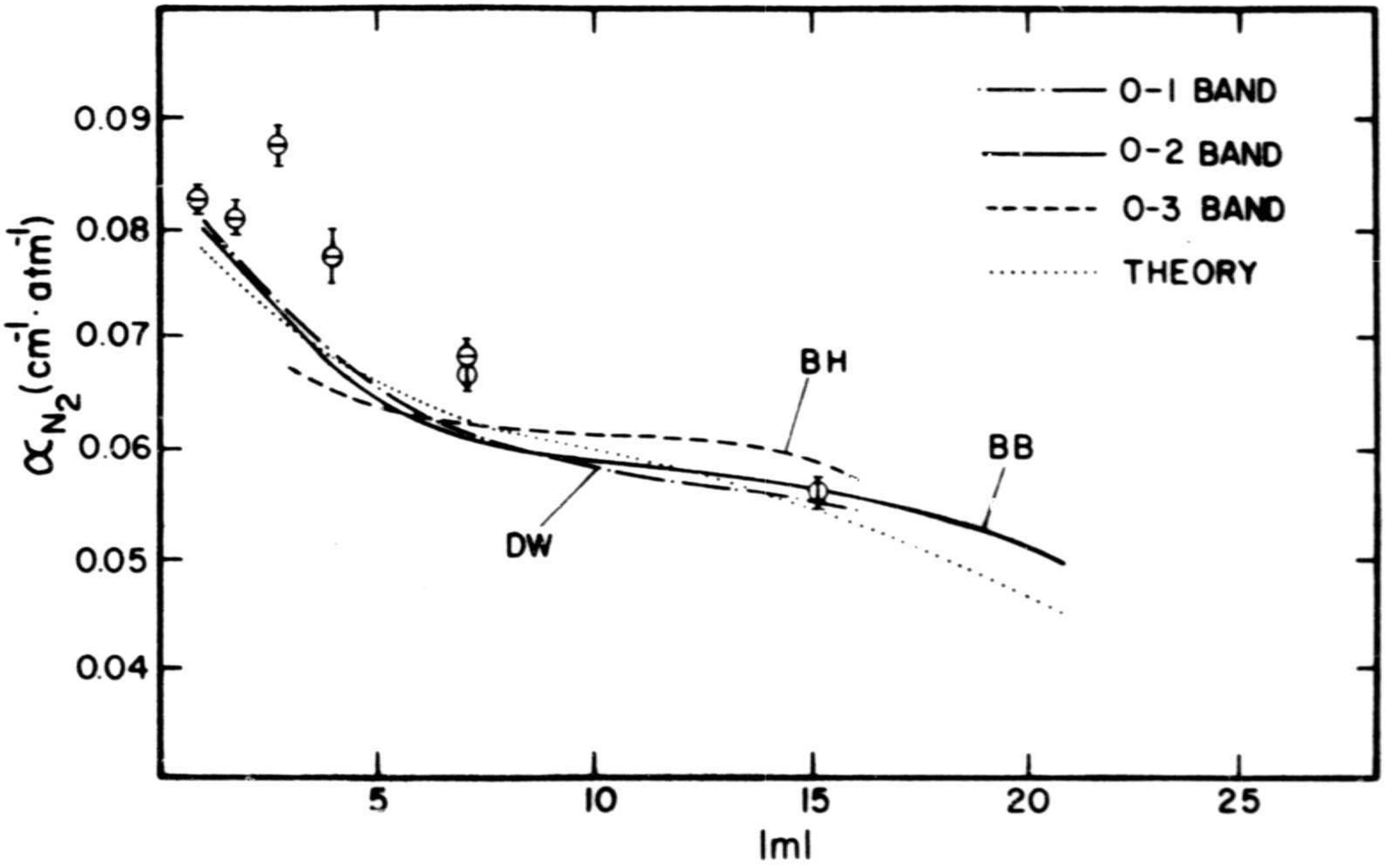


Figure 2: Nitrogen Broadened half-widths of CO lines versus |m| results of this work (Φ - P branch and Θ - R branch) are shown with the theoretical (.....) and experimental (0-3 band) results of Bouanich and Haeusler (1972) - BH; and results of Draegert and Williams (1968) (0-1 band)-DW; and Bouanich and Brodbeck (1974) (0-2 band) -BB.

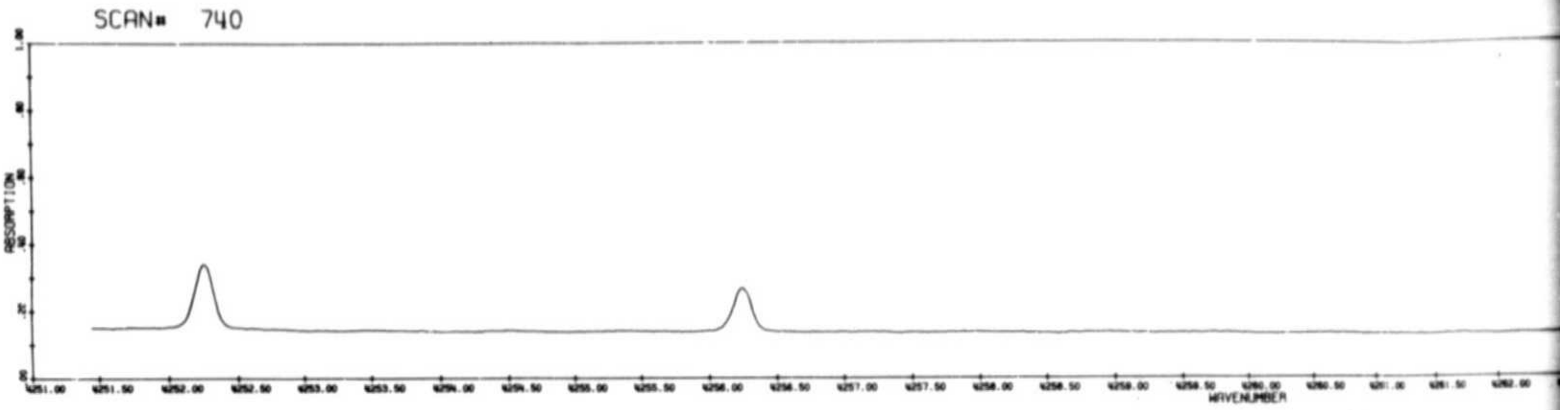
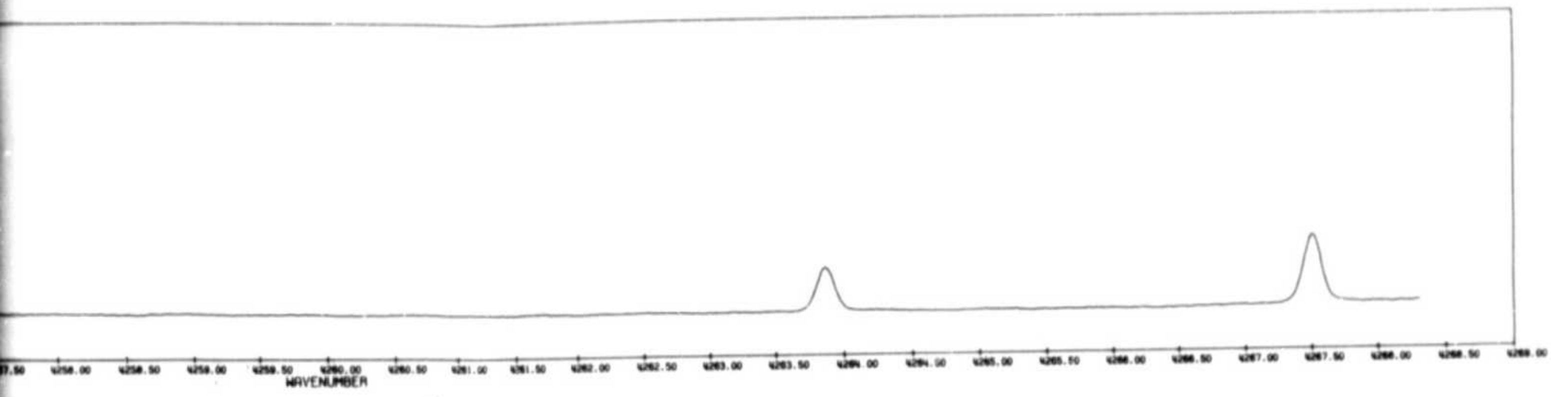


Figure 3: Example of partial spectrum of the 2.3μm
CO across the center of the band.
Cell length = 300 cm, partial pressure c
torr, partial pressure of N_2 = 75.0 torr
25.0°C.



le of partial spectrum of the 2.3μm band of
ross the center of the band.
length = 300 cm, partial pressure of CO = 5.0
partial pressure of N_2 = 75.0 torr, temperature
C.

FOLDOUT FRAME

2

APPENDIX: DATA SUMMARY

Scan No.	Wave Number cm^{-1}	Lines $CO^{12}O^{16}$	Pressure mm Hg	
			CO	N_2
615-616	4255-4276	R0, P1	2.5,5	
618-623	4255-4276	R2, P1	5,20,40,80, 160,320	
624	4255-4276	R0	5	5
627	4255-4276	R0	5	75
630	4255-4276	R0, P1	5	
636	4255-4276	R2,R1,P1	2.5	
644	4255-4276	P1	5	
659	4283-4287	R6	5	35
660	4255-4276	R3, R1	5	35
662	4230-4232	P7	5	35
667	4283-4287	R6	5	155
668	4255-4276	R3, R1	5	155
670	4230-4232	P7	5	35
671	4193-4197	P15	5	155
675	4283-4287	R6	5	690.7
676	4255-4276	R3,R2,R1	5	690.7
678	4230-4232	P7	5	690.7
679	4193-4197	P15	5	636.5
683	4283-4287	R6	12.5	
684	4255-4276	R3,R2,R1	12.5	

APPENDIX: DATA SUMMARY (concluded)

Scan No.	Wave Number cm^{-1}	Lines CO^{12} O^{16}	Pressure mm Hg	
			CO	N$_2$
685	4233-4256	P4	12.5	
688	4152-4156	P23	12.7	
691	4283-4287	R6	25	
692	4255-4276	R3,R1,P1	25	
695	4293-4197	P15	25	
699	4283-4287	R6	75	
700	4255-4276	R3,R2,R1	75	
701	4233-4256	P4	75	
703	4193-4197	P15	75	
704	4152-4156	P23	75	
707	4283-4287	R6	150	
708	4255-4276	R3, R2	150	
711	4193-4197	P15	150	
731	4283-4287	R6	5	15
732	4255-4276	R3, R2	5	15
739	4283-4287	R6	5	75
740	4255-4276	R3, R2	5	75
742	4230-4232	P7	5	75
747	4283-4287	R6	5	315
748	4255-4276	R3,R2,R1	5	315
751	4193-4197	P15	5	315

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