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SCIENTIFIC REPORT
STRENGTHS, WIDTHS, AND SHAPES OF THE LINES OF THE 3ν CO BAND

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ABSTRACT

Spectral curves of several CO samples have been used to investigate the 3ν band whose center is near 6350 cm^{-1}. The strength of the band for the common $C^{12}O^{16}$ isotope has been found to be 0.0130 ± 0.0005 atm^{-1} $cm^{-1}_{STP}cm^{-1}$. An empirical equation, $F_m = 1 + 0.011\ m$ has been derived to account for the influence of vibration-rotation on line strengths. The half-widths of the self-broadened lines at 1 atm pressure vary from approximately 0.090 cm^{-1} at $|m|=1$ to 0.062 cm^{-1} at $|m|=20$. The widths of self-broadened lines are 1.08 ± 0.005 times as great as N_2-broadened lines at the same pressure. The Lorentz line shape appears to be appropriate for the collision-broadened lines within a few cm^{-1} of their centers; but the extreme wings of the lines are sub-Lorentzian.

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INTRODUCTION

Carbon monoxide is a major constituent in many flames and rocket exhausts and consequently contributes to their infrared emission. The earth's atmosphere and the solar chromosphere also contain small amounts of CO which give rise to dozens of absorption lines in solar spectra. Therefore, a detailed knowledge of the infrared properties of this gas is important in many problems in the fields of astrophysics, meteorology, molecular spectroscopy, and chemistry. The infrared absorption bands of CO consist of regularly spaced lines whose strengths and widths vary slowly from one line to the next. These features have made it possible to obtain considerable information concerning band strengths, line widths, line shapes, the influence of vibration-rotation interaction on line strengths, the electric dipole-moment function, and the intermolecular force fields.

The fundamental and first overtone (ν and 2ν) bands of CO have been studied very thoroughly. However, data on the 3ν band are limited since it is very weak, and large samples are required to produce measureable absorption. The present investigation was undertaken to provide data on the strengths, widths, and shapes of the lines in the 3ν band. The new information provided by this work is of particular value in determining the effect of vibration-rotation interaction on line strengths, which, in turn, is useful in calculating the electric dipole-moment function.

LINE POSITIONS

The molecular constants tabulated by Benedict et al[1] were used to calculate the positions of lines P25 to R24 for the most common isotope, $C^{12}O^{16}$, and the results are listed in Table 1. The center of this band is at 6350.47 cm^{-1}, and the centers of the corresponding bands of the two next most common isotopes $C^{13}O^{16}$ and $C^{12}O^{18}$ occur at 6212.30 and 6200.75 cm^{-1}, respectively. There is essentially no overlapping of the $C^{12}O^{16}$ band by the other isotopic bands except in the P-branch beyond about P15. Because of centrifugal stretching, the lines in the R-branch get progressively closer together with increasing J until at R34 the lines fold back and form a band head at 6417.78 cm^{-1}. The quantities S_m and α_m^o listed in Table 1 are discussed below.

TABLE 1

LINE PARAMETERS
FOR THE 3ν BAND OF $C^{12}O^{16}$

Line	Line Center (cm^{-1})	S_m ($atm^{-1} cm^{-1}_{STP} cm^{-1}$)	α_m^o (cm^{-1})
P25	6223.17	0.49×10^{-5}	-
P24	29.50	0.76	-
P23	35.72	1.16	-
P22	41.84	1.74	-
P21	47.86	2.54	-
P20	6253.78	3.63	-
P19	59.60	5.10	0.0627
P18	65.31	7.00	0.0629
P17	70.92	9.40	0.0632
P16	76.43	12.3	0.0635
P15	6281.83	15.8	0.0639
P14	87.14	19.8	0.0644
P13	92.33	24.7	0.0648
P12	97.43	28.7	0.0653
P11	6302.42	33.5	0.0662
P10	6307.31	37.9	0.0672
P 9	12.10	41.7	0.0684
P 8	16.78	44.4	0.0698
P 7	21.35	45.7	0.0716
P 6	25.83	45.2	0.0737
P 5	6330.20	42.7	0.0762
P 4	34.46	37.9	0.0790
P 3	38.62	31.0	0.0823
P 2	42.67	22.2	0.0861
P 1	46.62	11.7	0.0900
R 0	6354.21	12.1	0.0900
R 1	57.84	24.1	0.0861
R 2	61.37	35.1	0.0823
R 3	64.80	44.9	0.0790
R 4	68.12	52.6	0.0762

TABLE 1 (Cont.)

LINE PARAMETERS
FOR THE 3ν BAND OF $C^{12}O^{16}$

Line	Line Center (cm^{-1})	S_m ($atm^{-1}cm^{-1}{}_{STP}cm^{-1}$)	α_m^o (cm^{-1})
R 5	6371.33	58.1×10^{-5}	0.0737
R 6	74.43	61.2	0.0716
R 7	77.43	62.1	0.0698
R 8	80.33	60.7	0.0684
R 9	83.11	57.8	0.0672
R10	6385.79	53.1	0.0662
R11	88.37	47.9	0.0653
R12	90.83	41.7	0.0648
R13	93.19	35.6	0.0644
R14	95.45	29.6	0.0639
R15	6397.59	24.3	0.0635
R16	99.63	19.1	0.0632
R17	6401.56	14.9	0.0629
R18	03.38	11.4	0.0627
R19	05.10	8.45	-
R20	6406.71	6.18	-
R21	08.20	4.41	-
R22	09.59	3.08	-
R23	10.88	2.12	-
R24	12.05	1.42	-

EXPERIMENTAL

Gas samples were obtained from a commercial cylinder of chemically-pure grade CO with the purity guaranteed to exceed 99.5%. No absorption by any impurity was observed in the region of interest. Pressures below 2 atm were measured with a U-tube Hg manometer, while higher pressures were measured with a Bourdon-type gauge. The samples were maintained at room temperature in a multiple-pass cell with a base length of approximately 1 meter. The cell is capable of pressures exceeding 200 psig, and the number of passes can be adjusted externally to more than 32 passes without disturbing the sample.

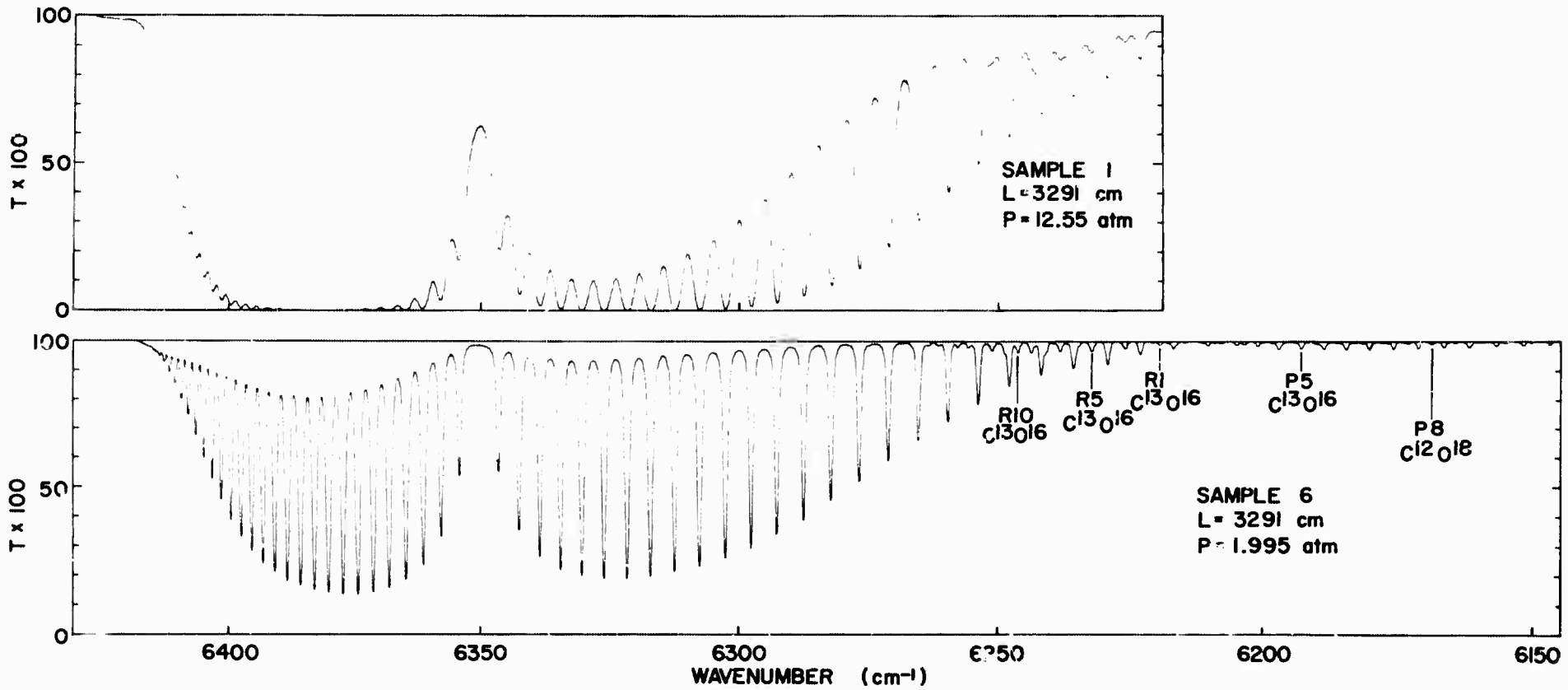
The absorber thickness u was calculated from the CO pressure p and the geometrical path length L by the use of the following equation:

$$u(\text{atm cm}_{STP}) = p(\text{atm})\, L(\text{cm})\, [1 + 0.0009p]\, 273/296. \qquad (1)$$

The factor 273/296 reduces the thickness to STP conditions, and the factor $[1 + 0.0009p]$, which accounts for a slight non-linearity in the relation between CO pressure and density, is insignificant except at the highest pressures used in this investigation. Since the quantity u has been reduced to STP conditions, it is equivalent to amagat-cm; in order to obtain u in units of gm/cm^2, the value given by Eq. (1) should be multiplied by 1.25×10^{-3} $(gm/cm^2)/atm\ cm$.

The spectra were scanned with a spectral slitwidth of approximately 0.8 cm^{-1} by the use of a custom-made Ebert spectrometer utilizing a 64 mm x 64 mm grating with 600 lines per mm. The main mirror of the spectrometer has a focal length of 75 cm. A 750-watt projection bulb was used as a radiation source, and a liquid N_2 cooled PbS cell served as the detector. An Si filter eliminated overlapping orders of the shorter wavelength radiation. All of the optical components were contained in a vacuum tank joined to the absorption cell in order to eliminate absorption by atmospheric gases.

The parameters for 8 samples studied are listed in Table 2. Each spectrum was compared with spectra of other samples, including some which were not analyzed and are not included in Table 2 in order to correct for spurious deflections. The appropriate background curve, which was obtained with the absorption cell evacuated to correspond to 100% transmittance, was superimposed on each spectral curve. The spectral curves then were replotted with a constant 100% transmittance level by the use of a semi-automatic plotting and digitizing system. Two representative replotted spectral curves are shown in Fig. 1. As the spectra were



LEGENDS FOR FIGURES

Fig. 1 SPECTRAL CURVES OF TWO REPRESENTATIVE SAMPLES.

A few absorption lines in the corresponding bands of the $C^{13}O^{16}$ and $C^{12}O^{18}$ isotopes are indicated. Most of the absorption is due to the 3ν band of $C^{12}O^{16}$.

TABLE 2

SAMPLE PARAMETERS

Sam. No.	p (atm)	L (cm)	u (atm cm_{STP})
1	12.55	3291	38,800
2	12.55	826	9,720
3	12.55	416	4,900
4	6.10	1648	9,270
5	6.10	416	2,350
6	1.995	3291	6,080
7	1.000	3291	3,050
8	0.518	3291	1,570

being plotted, pairs of points related to wavenumber and transmittance were punched on IBM cards. The cards served as input for a Philco 2000 Computer which calculated the quantities desired for the data analysis. The experimental apparatus and techniques have been described in detail elsewhere.[2]

BAND STRENGTH

The true transmittance $T'(\nu)$ of a sample at wavenumber ν that would be observed with infinite resolution is related to u and the absorption coefficient $K(\nu)$ by the following equation:

$$T'(\nu) = \exp(-uK(\nu)), \qquad \text{or} \qquad -\ln T'(\nu) = uK(\nu). \tag{2}$$

If all of the absorption in a given spectral region is due to a single absorption band, the band strength S_ν is given by:

$$S_\nu = \int K(\nu)d\nu = -\frac{1}{u}\int \ln T'(\nu)d\nu. \tag{3}$$

This quantity is also frequently called band intensity or integrated absorption coefficient.

Because of the finite slitwidth of any spectrometer, it is usually not possible to measure the true transmittance $T'(\nu)$. However, if the absorption lines are sufficiently wide that variations in $K(\nu)$ are not too great within the spectral slitwidth of the spectrometer, $\int T(\nu)d\nu$ closely approximates $\int T'(\nu)d\nu$, where $T(\nu)$ is the observed transmittance, and the integration is performed over the entire band. Under this condition, the band strength S_ν can be determined from the measurable quantity $T(\nu)$ by use of the following equation:

$$S_\nu = -\frac{1}{u}\int \ln T(\nu)d\nu. \tag{4}$$

Systematic errors that arise in the determination of S_ν by the use of Eq. (4) because of the difference between $T'(\nu)$ and $T(\nu)$are usually such that the measured value is too small. However, the size of the errors can be estimated if approximate values for the line strengths, line widths, and slit width are known.

In order to estimate the errors introduced by substituting experimental values of $T(\nu)$ for $T'(\nu)$, we used the strengths and widths of several lines which are derived from our results discussed below and calculated the true transmittance we would expect for various samples. Examples for two samples are shown in Fig. 2, where the curves represent true transmittance. We then made use of a computer to calculate $T(\nu)_{calc}$, the transmittance curve we would expect to observe with our instrumental slit width; the results of this calculation are represented by the circles in Fig. 2. We will see below that the calculated values $T(\nu)_{calc}$ are in good agreement with the experimental results. The integrals $-\frac{1}{u}\int \ln T'(\nu)d\nu$ and $-\frac{1}{u}\int \ln T(\nu)_{calc}d\nu$ were calculated for both samples.

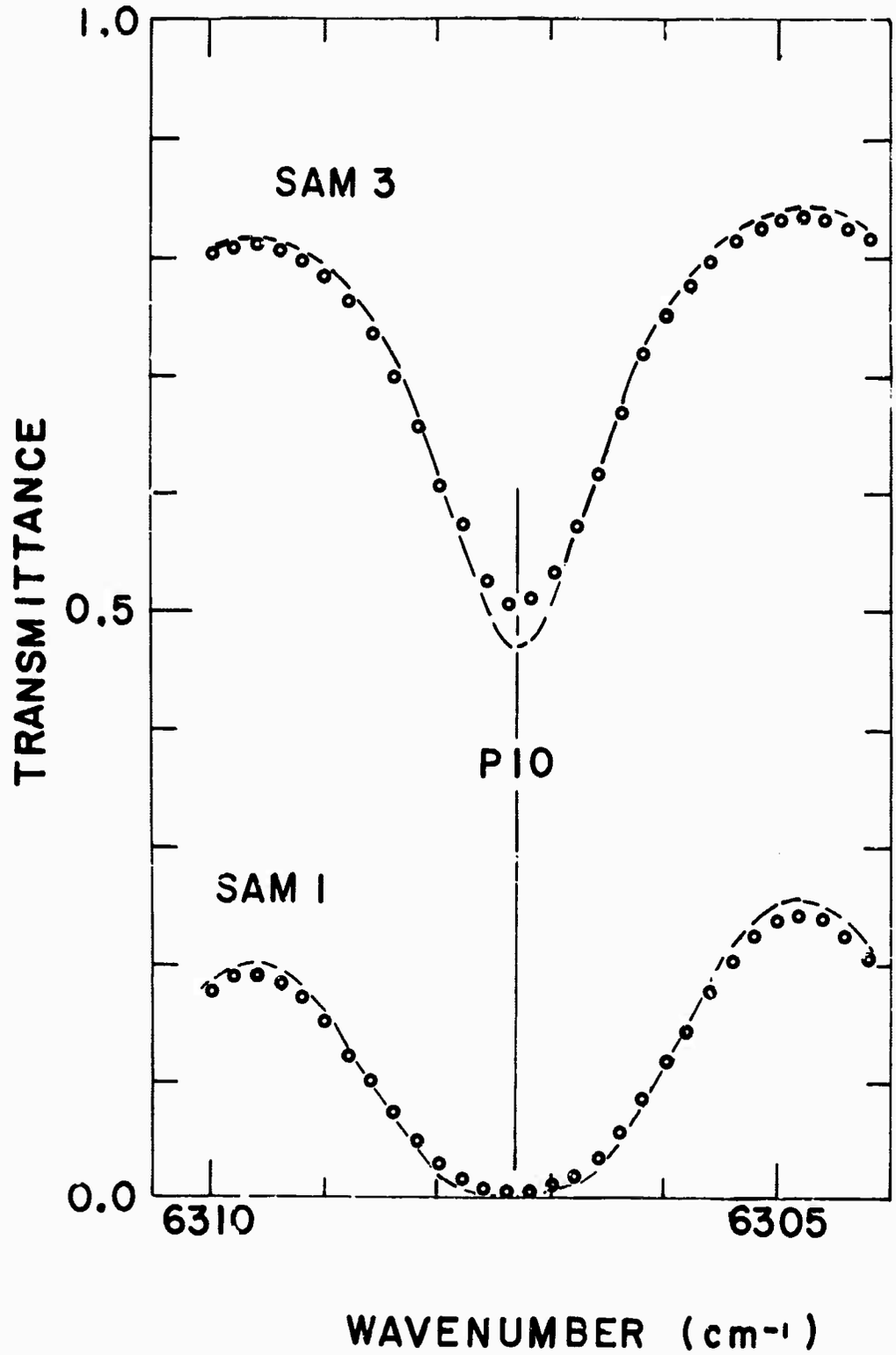


Fig. 2 CALCULATED CURVES OF TRANSMITTANCE WITH AND WITHOUT THE EFFECT OF FINITE SPECTRAL SLITWIDTH.

The curves represent the calculated true transmittance in the region near line P10 for Samples 1 and 3. The circles represent the values after accounting for the spectral slitwidth, approximately 0.8 cm^{-1}.

For Sample 3, the value based on $T(\nu)_{calc}$, is 0.990 times the value based on $T'(\nu)$. Thus, there is 1.0% error introduced by assuming $T'(\nu)$ can be substituted for $T(\nu)$. The calculated error is 7.5% for Sample 1 which is nearly opaque near the line center. If the true transmittance near the line centers is as much as 0.90, the spectral slitwidth may be several times greater than the line width without causing significant error in the band strength measurement. However, as demonstrated by the examples above, sizeable errors may be introduced as the transmittance near the line centers decreases. Of course, the errors are small when there is sufficient overlapping of the lines to eliminate the structure. A discussion of the systematic errors arising from finite slitwidth in the determination of band strengths and line strengths has been given by Penner[3] and by Kostkowski and Bass.[4]

Results for Samples 1-5 were used to determine S_ν, the strength of the entire band. In general, the larger samples were used in regions of weaker lines and smaller samples near the strong lines. The weight given to the value determined from any one sample for a given region of the band was based on estimated errors due to: misplacement of the background curve on the sample spectrum, recording errors, and improperly accounting for the difference between $T(\nu)$ and $T'(\nu)$. Errors in the values of u are probably less than 1 percent. On the basis of our results, we have concluded that the strength of the 3ν band of $C^{12}O^{16}$ is

$$S_\nu = 0.0130 \pm 0.0005 \text{ atm}^{-1}\text{cm}^{-1}{}_{STP}\text{cm}^{-1}. \qquad (5)$$

This value compares favorably with 0.0127 ± 0.0013 given by Schurin and Ellis,[5] but it is considerably larger than 0.0102 ± 0.001 which Plyler et al[6] found by comparing the maximum absorptance of several lines in the 3ν band with lines in the 2ν band whose strengths were known. (Plyler et al gave $0.0093 + 0.001$ $\text{atm}^{-1}\text{cm}^{-1}\text{cm}^{-1}$, but this value has not been reduced to standard temperature, 0°C.)

LINE STRENGTHS

According to the Herman-Wallis[7] formula, the strength S_m of a CO line is related to the band strength S_v by the following equation:

$$S_m = \frac{S_v \, |m| \left(\nu/\nu_c\right) F_m \exp - \left[\frac{B'' \, m(m-1) \, hc}{\kappa\theta}\right]}{Q} \tag{6}$$

The line index number $m = J'' + 1$ in the R-branch and $-J''$ in the P-branch. ν_c is the wavenumber of the center of the band, ν is the wavenumber of the line being calculated, κ is the Boltzmann's constant, and θ is the temperature in degrees Kelvin. B'', the rotational constant, is 1.9226 for the ground state of $C^{12}O^{16}$. The partition function Q, which is normalized so that S_v equals the sum of all the line strengths, is equal to 107.3 when $\theta = 296°$ K and $F_m = 1$.

The factor F_m accounts for vibration-rotation interaction and has been expressed by Herman and Wallis by an equation of the form:

$$F_m = 1 + a\,m + \epsilon(m, m^2) \tag{7}$$

These workers found that $a = 0.00528$ and that $\epsilon(m, m^2)$ represents only a small term for $|m|$ less than approximately 25 for the 2ν CO band. We have measured S_m, from which F_m was calculated, for more than 40 lines of the 3ν band and have used the results to check the form of Eq. (7) and to determine the value of the coefficient a.

S_m is related to $k_m(\nu)$, the portion of the absorption coefficient due to the single line of interest, by

$$S_m = \int k_m(\nu) d\nu, \tag{8}$$

where the integration is performed over all the region where there is significant absorption.

We will see in a following section that $k(\nu)$ within a few cm^{-1} of the center of a collision-broadened line can be approximated by the Lorentz equation:

$$k_m(\nu) = \frac{S_m}{\pi} \frac{\alpha_m}{(\nu - \nu_{mo})^2 + \alpha_m^2}. \tag{9}$$

The center of line m is at ν_{mo} and its half-width α_m is proportional to pressure. S_m is independent of pressure over the range of pressures employed in the present investigation.

The total absorption coefficient $K(\nu)$ is the sum of the absorption coefficients for all the lines contributing at that wavenumber. At sufficiently small absorber thicknesses and low pressures there is negligible overlapping of the lines, and $K(\nu)$ at any point represents the contribution of only one line. Under this condition the line strength is given by

$$S_m = -\frac{1}{u} \int_m \ln T'(\nu) d\nu, \tag{10}$$

where the integration is performed over the region including the absorption by the line of interest. The resolving power of our instrument was not sufficiently high that we could safely substitute $T(\nu)$ for $T'(\nu)$ to determine strengths from measurements on samples at low pressures for which there was negligible overlapping of the lines. Therefore, it was necessary to use samples at high pressures and account for overlapping. The corrections for small errors introduced by assuming $T'(\nu) = T(\nu)$ for the high pressure samples were calculated by the method described above in connection with the band strength.

Let us consider a band of many equally intense, equally spaced lines which have equal widths and are sufficiently broadened that $T'(\nu) \cong T(\nu)$. The strength of one of the lines near the center of this band could be determined by substituting $T(\nu)$ for $T'(\nu)$ in Eq. (10) and integrating between the two points midway between the line of interest and its adjacent lines. Although a good portion of the contribution of the line might fall outside of the interval being integrated, this loss would be cancelled by the contribution within the interval by lines whose centers occur outside. Of course, this is true only under the condition that the band extends sufficiently far on both sides of the line being considered that all of its contribution occurs within the band. It would, of course, not be true for a line near the end of the band if part of its contribution fell outside the interval of integration, and the absorption by nearby lines did not make up for the loss. Although the CO band is not entirely like this model, the lines from approximately $|m| = 5$ to $|m| = 12$ in both the P- and R-branches are not greatly different from those described. Therefore, the strengths of these lines can be determined with little error by substituting $T(\nu)$ for some of the high pressure samples for $T'(\nu)$ in Eq. (10). However, the strengths of adjacent lines are quite different for $|m|$ less than 5 or greater than 12; therefore, errors might arise in the measured strengths of overlapping lines since the contribution of a line outside its interval would be different from the contribution inside the interval by other lines.

In order to account for overlapping in the calculation of the strength S_m of the line with index number m, we made use of the following equation:

$$S_m = -\frac{1}{u}\int_{\text{interval } m} \ln T(\nu)d\nu - \left[\sum_{i \neq m}\int_{\text{interval } m} k_i(\nu)d\nu\right] + \int_{\text{outside interval } m} k_m(\nu)d\nu. \qquad (11)$$

The first term on the right hand side of the equation was measured from the spectral curve of one of the high pressure samples by integrating over the interval m which extends from the point midway between lines m and m-1 to the point midway between m+1 and m. The second term is the contribution within interval m by lines other than m; the third term is the contribution of line m outside its interval. The second and third terms had to be estimated; therefore, the strengths calculated by this method were considered reliable only when the second and third terms of the equation were less than about 6 or 8 percent of S_m. In order to estimate terms 2 and 3, we first assumed the strengths were given by the first term of Eq. (11) and used data for low pressure samples to estimate values of α by the method described in the following section. These approximate values of S and α were then substituted into Eq. (9) to obtain expressions for k. These expressions were then substituted into Eq. (11) to calculate the corrected strengths.

The positions of the isotopic lines of $C^{13}O^{16}$ and $C^{12}O^{18}$ and $C^{12}O^{17}$ were calculated from the constants given by Benedict et al.[1] Since these bands are displaced to lower wavenumbers from the main band, only their R-branches contribute significantly in the region of interest. The strengths of the isotopic lines were assumed to be related to the strengths of the corresponding lines of the $C^{12}O^{16}$ band by the ratio of their abundances. The contributions of the isotopic lines were then calculated and subtracted from the measured quantities. We believe that the corrections for isotopic lines were adequate to provide reliable measurements for lines out to P21. For larger $|m|$ in the P-branch, the ratio of the contribution of the rarer isotopes to the more common isotope increases. Furthermore, the accuracy of the determination of the line strength, even without the contribution of the isotopic lines, is less for lines of large $|m|$ because the absorptance is small and errors due to misplacement of the background curve become important.

In order to determine the nature of the function F_m, we used Eq. (6) to calculate line strengths with F_m set equal to unity for all m and $S_v = 0.0130\ \text{atm}^{-1}\text{cm}^{-1}_{STP}\text{cm}^{-1}$. These calculated values were then divided into the corresponding observed values and the ratio was plotted against m in Fig. 3. Values for the four lines nearest the band center in each branch were not included because of the uncertainty due to overlapping. According to the Herman-Wallis formula (Eq. (7)), we expect F_m, which is

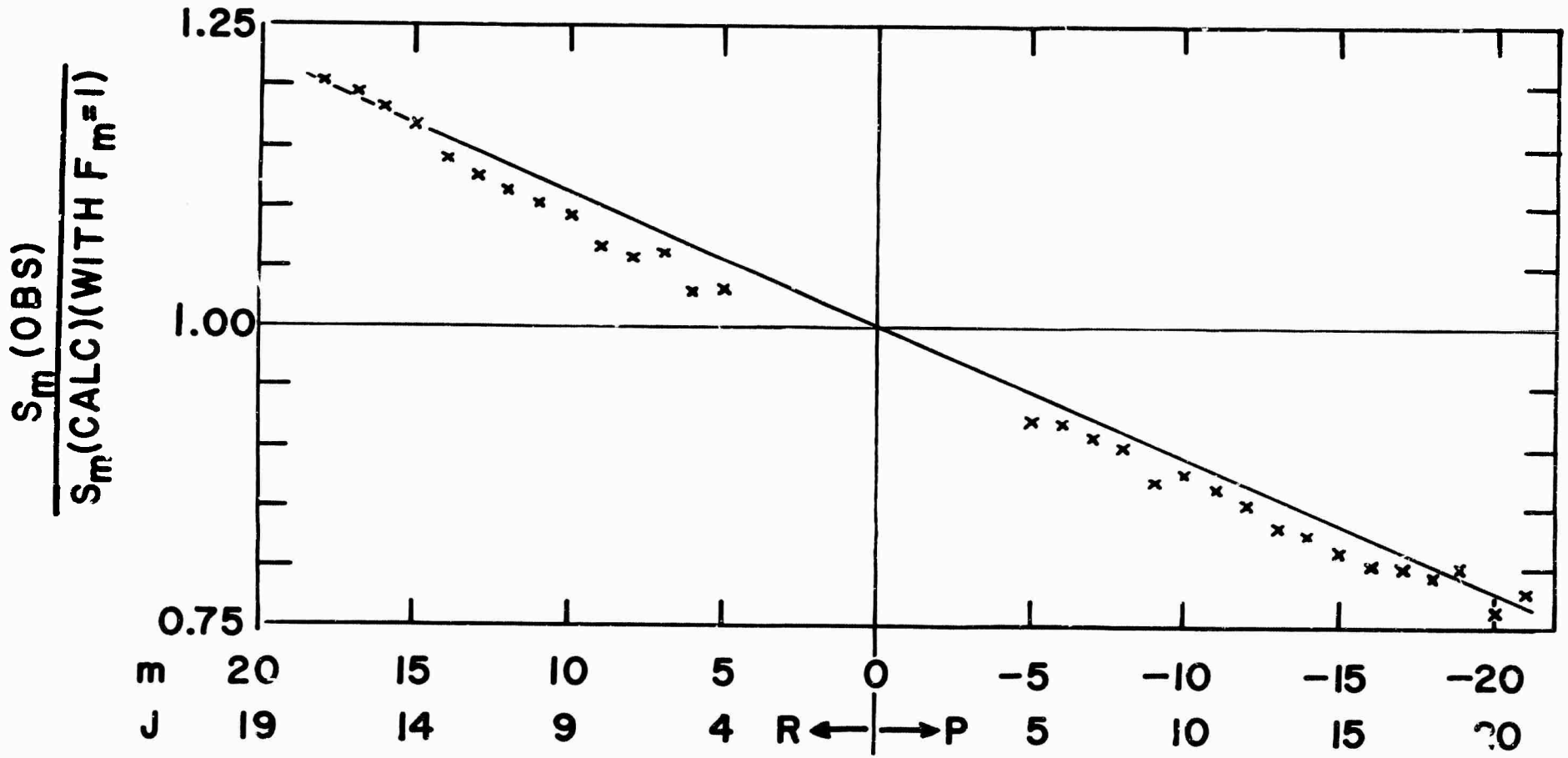


Fig. 3 PLOT OF S_m (Observed)/S_m(Calculated with F_m = 1) VERSUS m. The calculated values were obtained by substituting into Eq. (6), $F_m = 1$, and $S_v = 0.0130\ atm^{-1}cm^{-1}{}_{STP}cm^{-1}$. If we assume $F_m = 1 + a\ m$, the coefficient a can be found from the slope of the straight line. The abscissa is drawn with m increasing toward the left to correspond to the spectral curves in Fig. 1.

proportional to the ratio plotted in Fig. 3, to be of the form $1 + am + \ldots$ Since F_m is expected to be unity for $m = 0$, a "best-fit" straight line was drawn with the constraint that it pass through the point where the ratio is 1 at $m = 0$. We note that this straight line falls above most of the data points, particularly those for $|m|$ between 5 and 12 which are considered to be most accurate. Part of this discrepancy arises from the need for a different constant Q in Eq. (6) when F_m is not unity. From the slope of the straight line, we can deduce that $a \cong 0.011$.

By summing the calculated strengths of all the lines with $F_m = 1 + 0.011\ m$ in Eq. (6), we have found that Q should be 108.4, which is approximately 1% greater than 107.3, which was used to calculate the quantity plotted in Fig. 3. If 108.4 had been used, each of the values plotted would have been increased by approximately 1%; this would significantly reduce the average distance between the points and the solid line. According to the theory developed by Herman and Wallis, F_m might be expected to have a quadratic term, but the coefficient for such a term cannot be derived from our results since there is some scatter in all the data, and the reliable measurements are limited to $|m| \leq 22$.

Figure 4 shows a plot of the S_m versus m. The points correspond to the measured values while the curve is drawn through points based on Eqs. (6) and (7) with S_v given by Eq. (5), $a = 0.011$, and $Q = 108.4$, the appropriate value for $a = 0.011$. The agreement between the experimental and calculated values is seen to be quite good. Values of S_m on which the curve is based are listed in Table 1.

Since a positive value of a in Eq. (7) causes an increase in the strengths of the lines of the R-branch and a decrease in those of the P-branch, we can determine a without finding the strengths of the individual lines if we ignore the higher order term in F_m. This is done by comparing the ratio of the total strength of the R-branch, S_R, to the total strength of the P-branch, S_P. It is of interest to use this technique to determine the coefficient a and to compare it with the value obtained above, where the strengths of the individual lines were considered. We have substituted several different values of a into Eq. (7) to find values of F_m, which were then used in Eq. (6) to determine the sums of the strengths of all of the lines in the R-branch and P-branch. The ratio S_R/S_P was then calculated and plotted against a in Fig. 5 to provide the basis for the solid curve. The strengths of the R- and P-branches were determined from the spectral curves for Samples 2, 3, and 5. The average of the ratios S_R/S_P measured for the three samples was 1.47. We see from the curve in Fig. 5 that this ratio corresponds to $a = 0.0112$, which is in excellent agreement with the values determined by considering the strengths of more than 40 separate lines.

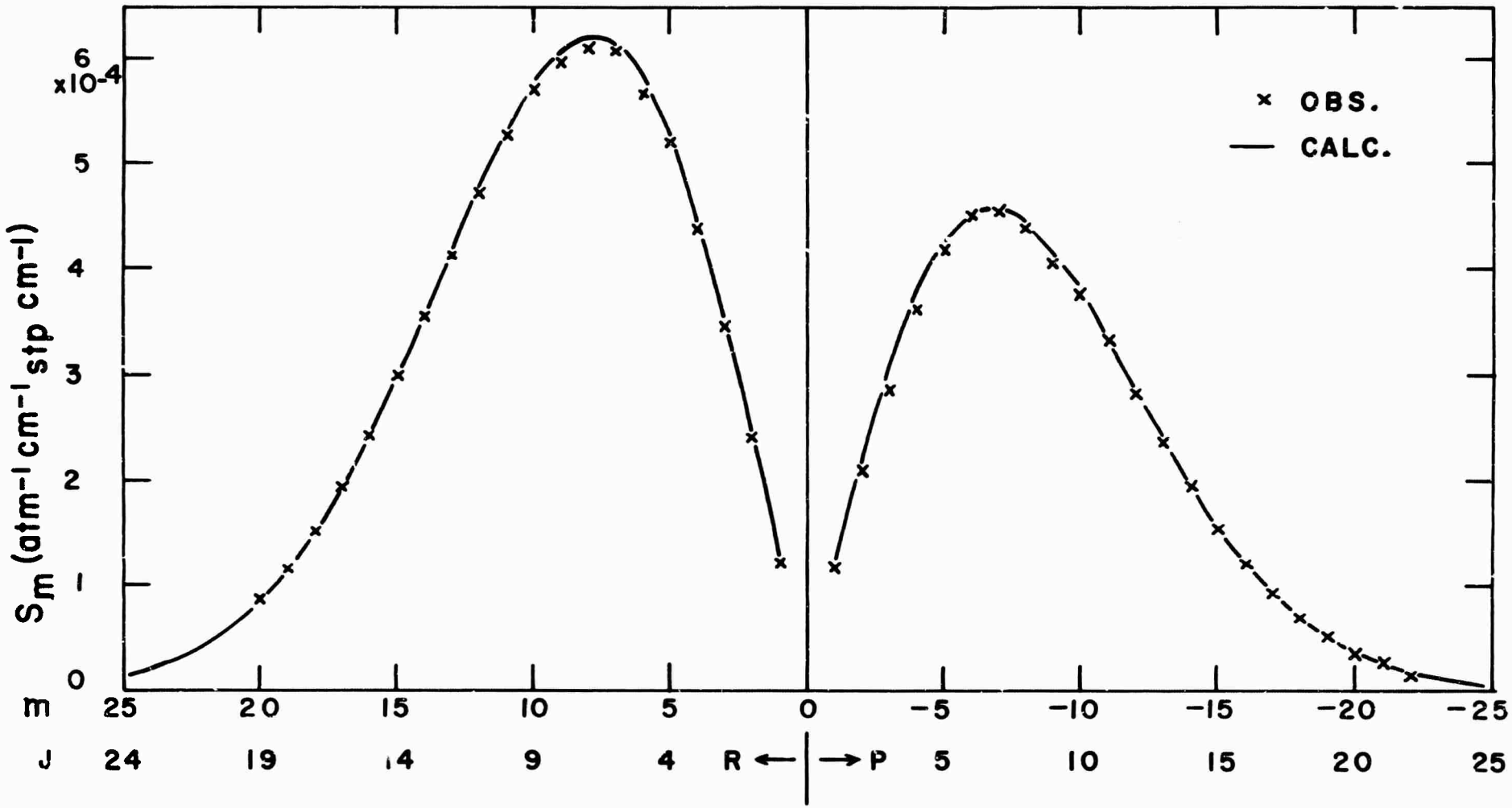


Fig. 4 PLOT OF CALCULATED AND OBSERVED S_m VERSUS m.

The curve is drawn through points which represent the calculated values of S_m. The x's correspond to observed values.

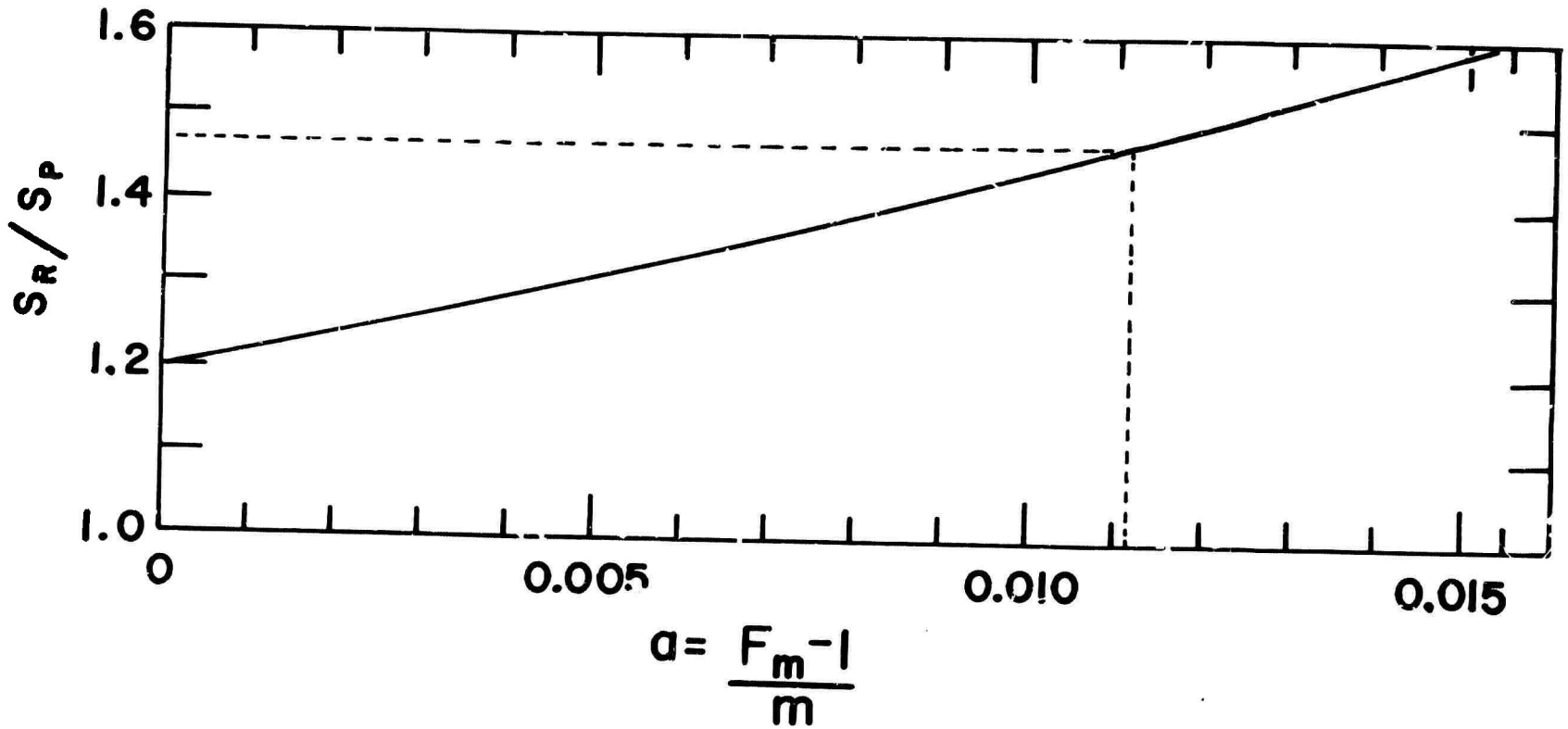


Fig. 5 PLOT OF THE RATIO OF THE CALCULATED STRENGTHS OF THE R- AND P-BRANCHES VERSUS THE COEFFICIENT a.

The calculations are based on the assumption that $F_m = 1 + a\,m$. The experimental results indicated $S_R/S_P = 1.47$, which corresponds to $a = 0.0112$.

The method which uses S_R/S_P to measure the coefficient a has the advantage that it is not necessary to determine strengths of individual lines. Consequently, it is not necessary to be concerned with effects of overlapping lines; furthermore, it is possible to measure the strengths of entire branches from spectral curves obtained with lower resolution than is required to measure individual line strength. However, it should be noted that the ratio method is based on $F_m = 1 + am$ with no higher order terms. In order to determine if higher order terms are significant and, if so, to determine their coefficients, it is necessary to measure the strengths of the individual lines.

Young and Eachus[8] have used results of previous measurements on the band strengths and rotational line strengths to calculate the dipole moment function M(r) for CO. The F-factor which they derive for the 3ν band from theoretical considerations is shown by the broken curve in Fig. 6; the solid curve ($F = 1 + 0.011\ m$) represents our experimental results. The agreement is seen to be good over the range of m covered in the experimental work. Coefficients of the higher order terms required to produce the curve of Young and Eachus cannot be derived from our results. Samples with longer paths or at higher temperatures are required to measure line strengths from which the high order terms can be checked. Although our results provide little check for the validity of Young and Eachus' calculations for large $|m|$, they tend to confirm these workers' choice of dipole moment function which was based on limited data, particularly with regard to line strengths in the 3ν band.

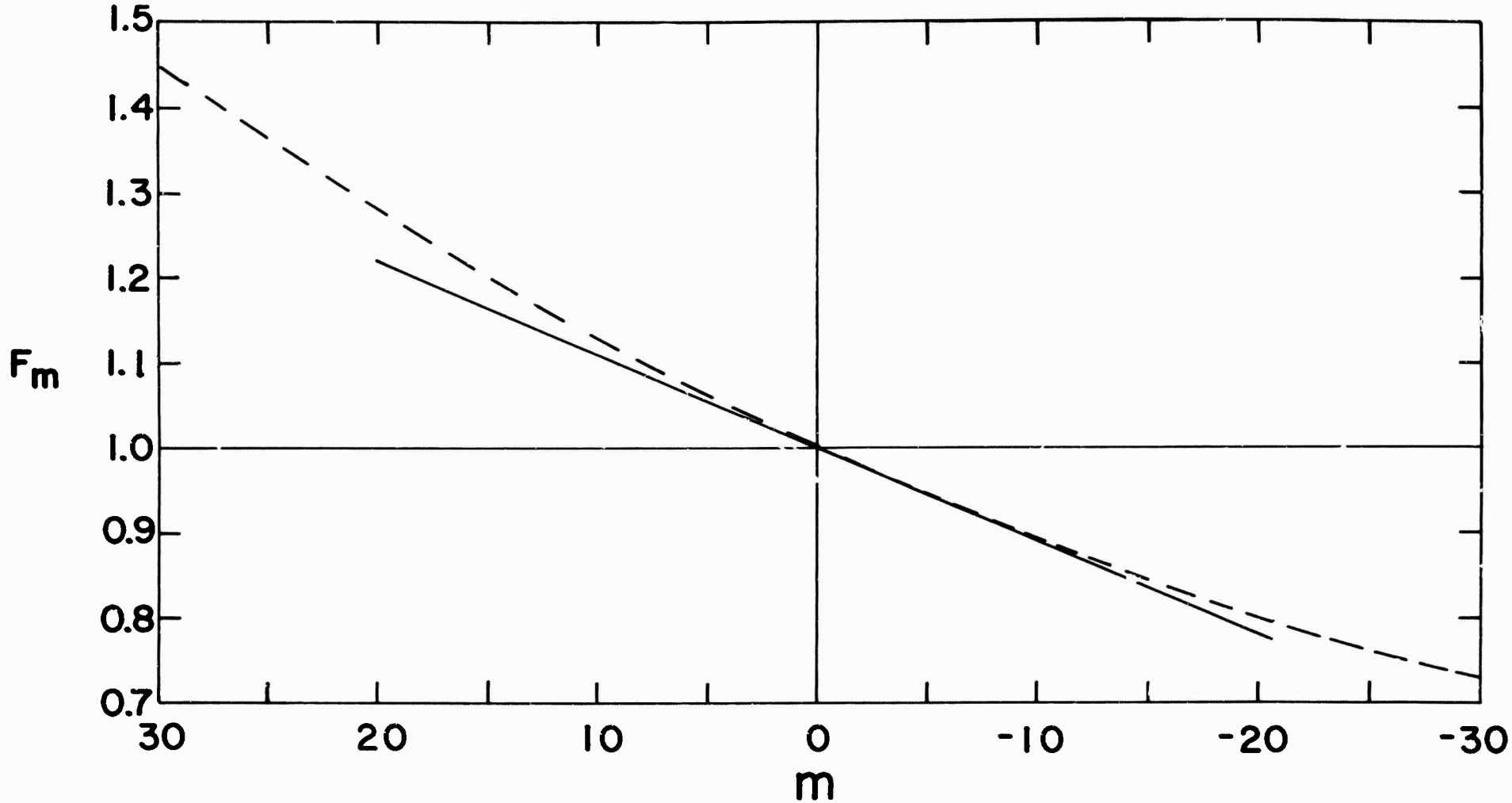


Fig. 6 F_m PLOTTED VERSUS m.

The solid line represents the results of the present investigation, $F_m = 1 + 0.011\ m$. The broken curve is based on theoretical work by Young and Eachus.[8]

LINE WIDTHS

It is well known that the shapes of collision-broadened absorption lines usually can be approximated, at least within a few cm^{-1} of the line centers, by the Lorentz equation (Eq. (9)). Ladenberg and Reiche[9] have shown that the equivalent width $\int_m A(\nu)d\nu$ of an isolated absorption line having the Lorentz shape is given by:

$$\int_m A(\nu)d\nu = 2\pi\alpha_m L(x_m), \text{ where} \tag{12}$$

$$L(x) = x e^{-x}\left[J_o(ix) - iJ_1(ix)\right]. \tag{13}$$

$J_o(ix)$ and $J_1(ix)$ are the Bessel functions of order 0 and 1, respectively, and

$$x_m = \frac{S_m u}{2\pi\alpha_m}. \tag{14}$$

The line half-width is related to pressure p by

$$\alpha_m = \alpha_m^o p/p^o, \tag{15}$$

with p^o equal to standard pressure, one atmosphere.

Values of L(x) have been tabulated by Kaplan and Eggers[10]; a copy of the table is also included as an appendix in Reference 11. If $x_m \gg 1$, Eq. (12) reduces to the simple form of:

$$\int_m A(\nu)d\nu = 2(S_m u \alpha_m)^{1/2}. \tag{16}$$

Under this condition, we see that it is possible to determine α_m from measurements of $\int_m A(\nu)d\nu$ if S_m and u are known. As x_m decreases, the dependence of $\int_m A(\nu)d\nu$ on α_m becomes less. At $x_m = 1$, $\int_m A(\nu)d\nu$ varies approximately as $\alpha_m^{1/3}$ for a constant value of S_m and u; for $x_m \ll 1$, $\int_m A(\nu)d\nu$ is independent of α_m.

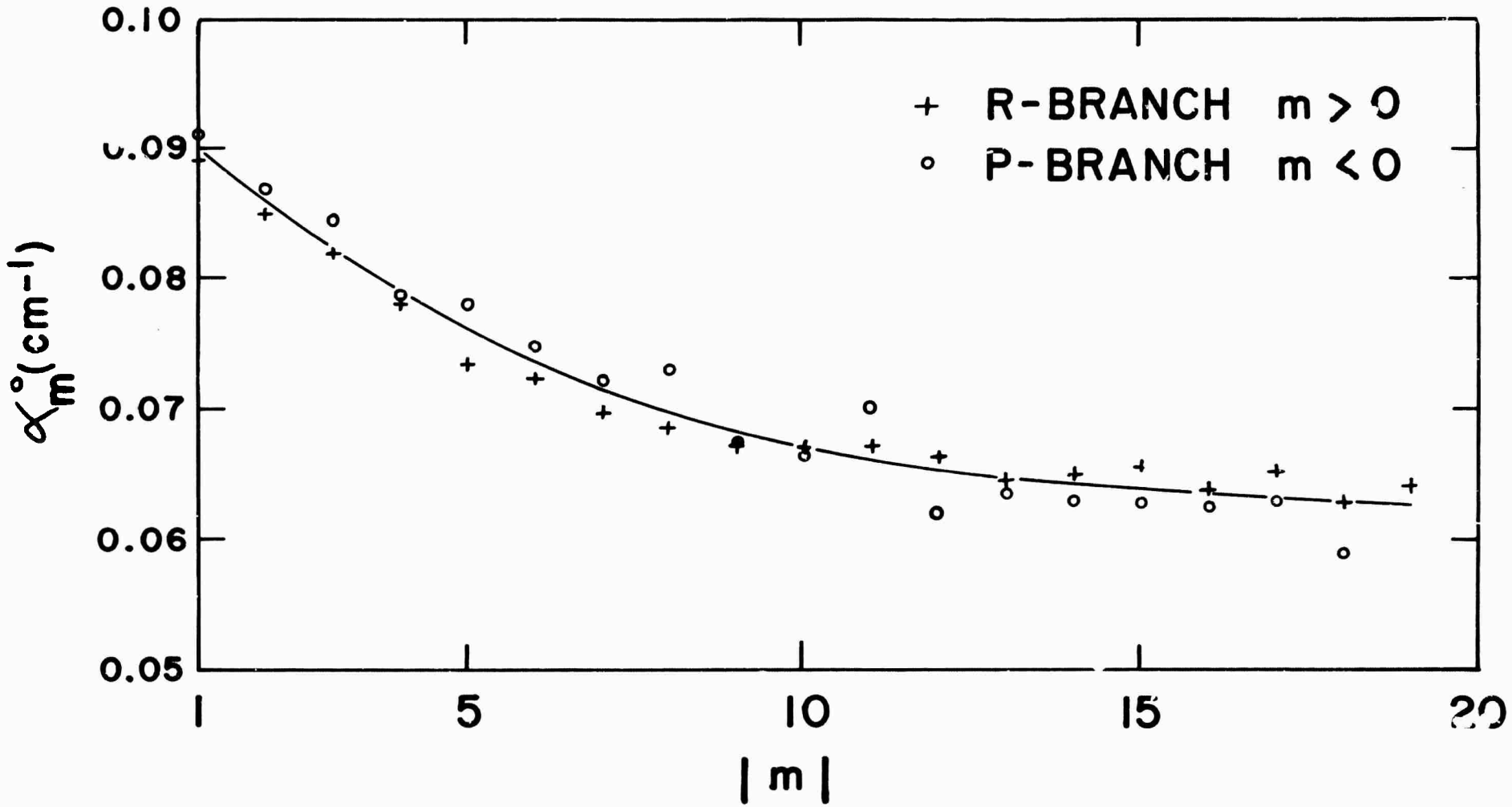
Values of $\int_m A(\nu)d\nu$ were determined for several lines from the spectral curves of Samples 6, 7, and 8. Since these samples were at pressures of 2 atm or less, there was little overlapping of many of the lines, and the measured absorption was due almost entirely to the line whose center occurred within each interval. The intervals were bounded by the points

midway between line centers. Some correction had to be made for the contribution of the less abundant isotopes when measuring lines P15 to P18 of the $C^{12}O^{16}$ band; no half-width measurements were made on lines beyond P18 since corrections for the isotopic lines were too large to be made accurately.

The calculations of α_m were made by a reiterative process. A value of α_m was assumed for a given line and for a given sample and substituted into Eq. (14) with the appropriate values of S_m and u to calculate x. Then the tabulated values of L(x)[10] were used to calculate $\int_m A(\nu)d\nu$. By comparing this calculated value with the observed value, we were able to estimate a more accurate value of α_m which was then substituted into Eq. (14). The calculation was repeated as many times as necessary for the observed and calculated values of $\int_m A(\nu)d\nu$ to agree.

The value of α_m which produced the proper $\int_m A(\nu)d\nu$ was then used in Eq. (15) to calculate α_m^o, the line half-width at one atmosphere pressure. Values of α_m^o determined from Samples 6, 7, and 8 were averaged with more weight given to the sample having the best conditions for the measurement of a particular line. The averaged values are plotted against $|m|$ in Fig. 7 where different symbols represent the P- and R-branches. The difference between the observed values for the same value of $|m|$ in the two branches is probably less than our experimental uncertainty. Therefore, it seems probable that no information is lost by assuming that the half-widths are functions of $|m|$ only. Because of the consistency of the data, we believe that the uncertainty in the values of α_m^o represented by the smooth curve is less than 6 or 8% for $3 \leq |m| \leq 15$. The uncertainty may be somewhat greater for the weaker lines since small errors in $\int_m A(\nu)d\nu$ cause large errors in the calculated widths when x is not large. Values of α_m^o represented by the smooth curve are listed in Table 1.

Figure 8 shows a comparison of five different investigations in which values for the α_m^o have been determined for the fundamental or one of the first two overtone bands of CO. Table 3 summarizes the bands studied, the spectral slitwidth, and the methods used by each of the five sets of workers. Shaw and Houghton[12], whose work is described below, are also included in the table. Benedict et al[1] did not find any significant difference between the widths of the lines of the fundamental and first overtone bands, and Plyler and Thibault[13] observed no difference between the widths of lines of the same value of m for the first and second overtone bands. Thus, it seems likely that the variation in half-widths of the lines in the different bands is small. We note that all the results show the same trend, with α_m^o decreasing for increasing $|m|$. However, the variation between some of the results is greater than the experimental uncertainties given by the authors. The results of this work are in very good agreement with those of Kostkowski and Bass[14], except for $|m|$ greater than approximately 15. Part of the discrepancy for large $|m|$ may have been caused by one of the sets of workers not making proper allowance



LEGENDS FOR FIGURES (Cont.)

Fig. 7 OBSERVED HALF-WIDTHS OF SELF-BROADENED CO LINES AT 1 atm PLOTTED VERSUS |m|.

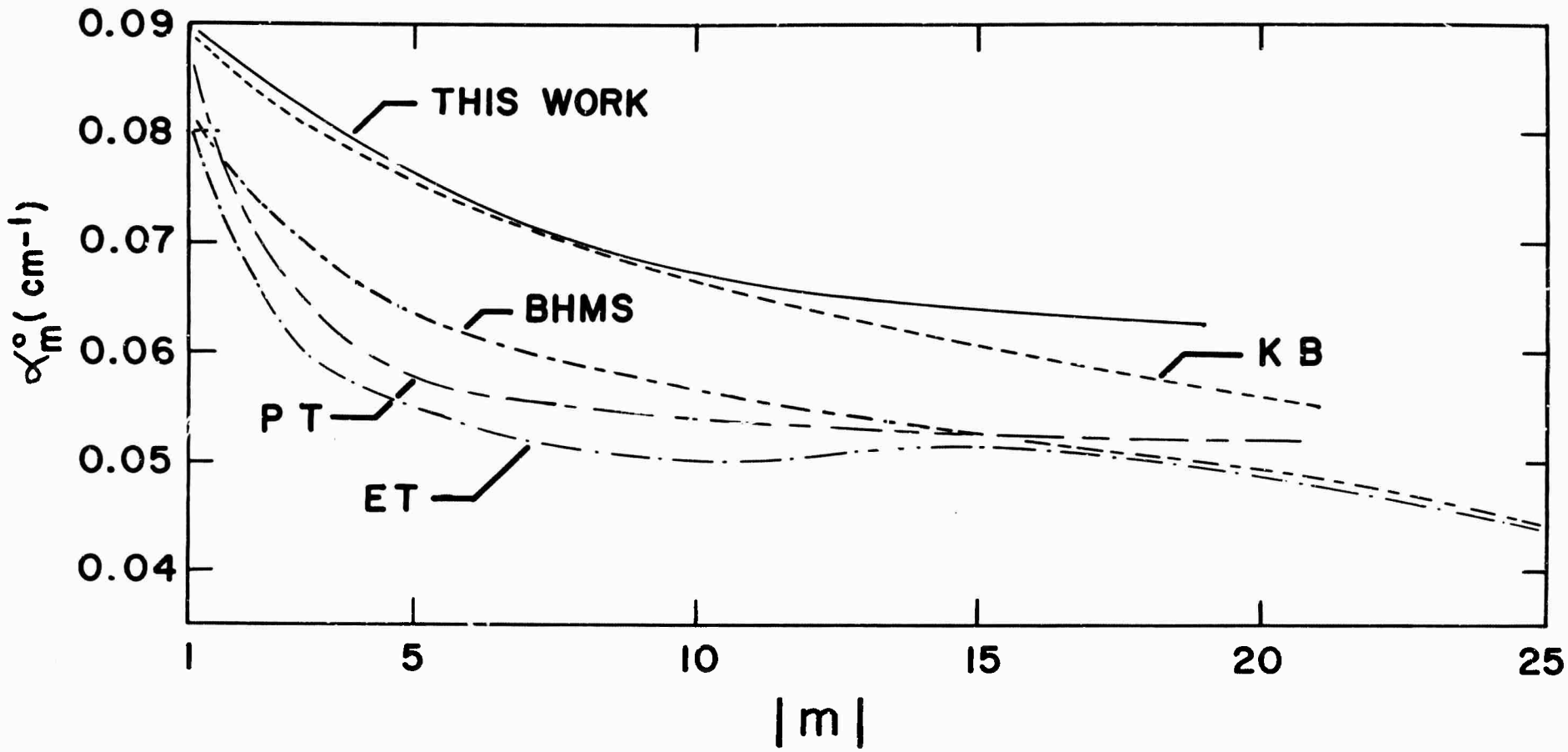


Fig. 8 COMPARISON OF HALF-WIDTHS OF CO LINES MEASURED BY VARIOUS WORKERS.

The curves represent results of: KB, Kostkowski and Bass[14]; BHMS, Benedict, Herman, Moore, and Silverman[1]; PT, Plyler and Thibault[13]; and ET, Eaton and Thompson[15].

TABLE 3

METHODS OF DETERMINING α_m^o

Investigator	CO Band	Slitwidth cm^{-1}	Method
This work	3ν	0.8	From $\int A(\nu)d\nu$
Kostkowski & Bass[14]	2ν	0.25	From ratio of absorption coefficients at center of line and midway between lines
Benedict et al[1]	ν and 2ν	0.2	From $\int A(\nu)d\nu$
Plyler and Thibault[13]	2ν and 3ν	0.08	From width of line on spectral curve with small correction for slitwidth
Eaton & Thompson[15]	ν	0.5	From combination of $\int A(\nu)d\nu$ and attenuation at line center
Shaw and Houghton[12]	ν	25	Comparing calculated $\int A(\nu)d\nu$ for entire band with low resolution spectral curves

for overlapping lines. In the R-branch, the lines are close together and, because of the rapid decrease in S_m with increasing m, there is significant contribution by the much stronger lines nearby. In the P-branch the lines of the $C^{13}O^{16}$ isotope must be taken into account.

There is fair agreement among the lower three curves, but they are consistently below those representing this work and that of Kostkowski and Bass. The large discrepancies cannot be a result of different methods of measurement. We used essentially the same method as Benedict et al, but our method was completely different from that used by Kostkowski and Bass, whose results agree best with ours. Eaton and Thompson[15] also determined the width of one of the lines by essentially the same method as ours; then they used another method, which involved the observed transmittances at the centers of the lines, to obtain the ratios of the widths of the other lines to the width of the one which had been measured. Plyler and Thibault determined the widths directly from spectral curves obtained with good resolution by applying a small correction term to account for the finite slitwidth. The method in which

$\int_m A(\nu)d\nu$ is used to determine α_m is based on the Lorentz line shape over the interval where there is significant absorption. Although collision-broadened lines of some gases appear to be sub-Lorentzian in the wings, there are considerable data which tend to confirm the Lorentz line shape for collision-broadened lines within a few cm^{-1} of the line centers.[1] Some results of the present investigation which are discussed below tend to confirm the Lorentz line shape near the line centers. Nearly all the absorption by the samples we used to measure α_m^o occurred within 2 cm^{-1} of the centers of the lines. Thus, our values are essentially independent of the shapes of the lines beyond this distance.

Shaw and Houghton[12] used a widely accepted value, 239 $atm^{-1}cm^{-1}{}_{STP}cm^{-1}$, for the strength of the fundamental band to calculate the strengths of the individual lines. They assumed that the absorption lines had a Lorentz shape with widths approximately equal to those represented by the BHMS curve in Fig. 8. Then they used several different values of absorber thickness and pressure corresponding to samples which had been investigated experimentally by Burch and Williams[16] to calculate the transmittance and $\int A(\nu)d\nu$ for the entire band. Serious discrepancies were found between their calculated values of $\int A(\nu)d\nu$ and those observed experimentally. However, they found that the discrepancies decreased if, in their calculations, they used values of α_m^o which were approximately 1.25 times as great as those given by the BHMS curve. We see from Fig. 8 that the values of α_m^o which provided the best fit for Shaw and Houghton (1.25 times the BHMS values) are approximately equal to those derived from the present investigation.

In view of the good agreement between calculated transmittances based on our line strengths and widths and experimental results discussed below, we believe that the uncertainty in the values of α_m^o representing this work in Figs. 7 and 8 is less than $\pm$ 8% for $|m| < 15$. The uncertainty is probably somewhat greater for larger $|m|$. The results of Shaw and Houghton and of Kostkowski and Bass tend to confirm our results, although the values indicated in Fig. 8 for three other sets of workers are considerably lower. The discrepancies, although sizeable, are not extremely great and are difficult to explain since the ultimate accuracy of various methods used should be about the same, and there is no correlation between methods and results.

N_2 BROADENING OF ABSORPTION LINES

Equivalent pressure P_e, given by the following equation, is a convenient parameter when dealing with CO absorption by mixtures of CO in N_2 or in air, which is approximately 80% N_2.

$$P_e = Bp + p_{N_2} = (B - 1)\, p + P, \tag{17}$$

where p, p_{N_2}, and P are the CO partial pressure, N_2 partial pressure, and total pressure, respectively. B is the ratio of the self-broadening ability to the broadening ability of N_2. We note that P_e approximates P for dilute mixtures of CO in N_2 ($p \ll p_{N_2}$).

We have used a technique described previously[17] to measure B for the 3ν band of CO. As an example, a spectral curve was obtained for a sample consisting of 760 torr of pure CO with a path length of 1648 cm. The path length was then adjusted to 3291 cm and 381 torr of CO was introduced to the cell to produce the same absorber thickness as in the previous sample. The sample pressure was then increased by adding N_2; spectral curves were scanned with the sample at various pressures. At a total pressure of 795 torr the absorption essentially was the same as that produced by the 760 torr sample of pure CO. Since the absorber thickness and absorption were the same for both samples, the equivalent pressures were necessarily the same. By substituting the pressures into Eq. (17), we obtain a value of B = 1.09 for this measurement.

This experiment was repeated at several different combinations of pressures and path lengths. Longer paths and relatively high pressures provided information in the regions of minimum absorption between the lines; shorter paths and lower pressures were more useful near the line centers. The results indicated that

$$B = 1.08 \pm 0.05$$

gives the best fit to the data in the regions between the lines as well as near the line centers. Since the same value of B fits both regions, we conclude that self-broadened CO lines have approximately the same shape as N_2-broadened lines, at least within 2 or 3 cm^{-1} of their centers.

The value of B derived from this investigation for the 3ν band is approximately the same as those found by Burch and Williams[16] for the fundamental and first overtone bands: 1.02 ± 0.06 and 1.08 ± 0.06, respectively. It appears from these results that the ratio of self- to N_2-broadening is not appreciably different, if at all, for the different bands.

CALCULATED TRANSMITTANCE AND LINE SHAPE

In order to check the consistency of our results, we used the values of S_m and α_m^o derived from our measurements and listed in Table 1 to calculate the transmittance of Samples 1 and 3 at several different wavenumbers. We then calculated the distortion of the true transmittance curve by the finite spectral slit width of the spectrometer used in the measurements. The values of $T(\nu)_{calc}$ calculated in this manner are compared with the experimental curves in Fig. 9. We recall from Fig. 2 that the lines were sufficiently broad for Samples 1 and 3 that there was little distortion of the spectral curves due to the finite slitwidth; therefore, the values of $T(\nu)_{calc}$ are not strongly dependent on the slit function used in the calculation.

The circles in Fig. 9 correspond to calculations based on the Lorentz line shape and the plus signs correspond to a modified Lorentz shape suggested for the fundamental band by Benedict et al[1] and given by

$$k(\nu) = k(\nu)(\text{Lorentz})\,\chi,$$

$$\text{where } \chi = 1 \qquad \text{for } |\nu - \nu_o| \leq 4\ \text{cm}^{-1}, \text{ and} \tag{18}$$

$$\chi = \exp -\left[0.015(|\nu - \nu_o| - 4)\right] \qquad \text{for } |\nu - \nu_o| > 4\ \text{cm}^{-1}.$$

$k(\nu)(\text{Lorentz})$ is given by Eq. (9).

In the regions shown in Fig. 9, most of the absorption is due to lines whose centers occur within a few cm^{-1}. Therefore, the absorption is only slightly dependent on the shape of the lines where $|\nu - \nu_o| > 4\ cm^{-1}$, as evidenced by the similarity between the values based on different line shapes. Only a few points based on the modified line shape are shown in Fig. 9 since most of them are essentially coincident with the corresponding points based on the Lorentz shape. The very good agreement between the observed and calculated curves tends to confirm the consistency of our results. The line strengths are based on Samples 1 and 3, which are used in the comparison, as well as other high pressure samples. The line widths were derived from spectral curves of samples at lower pressures. The absorption coefficient at the absorption minima (transmittance maxima) between the lines is nearly proportional to S_m and to α_m. However, near

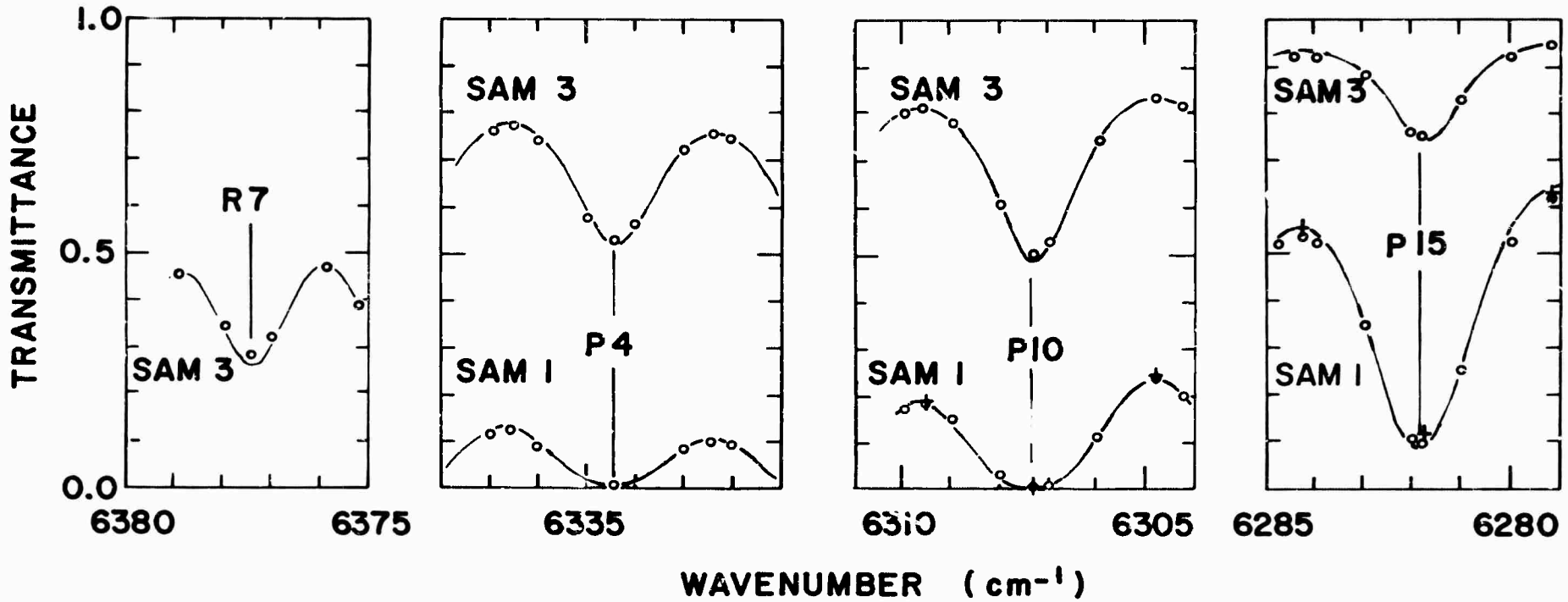


Fig. 9 OBSERVED AND CALCULATED TRANSMITTANCE IN VARIOUS REGIONS WHERE MOST OF THE ABSORPTION IS DUE TO NEARBY LINES.

The curves represent experimental measurements. The O's and +'s correspond to calculations based on the Lorentz and a modified Lorentz line shape (Eq. 18), respectively. The calculations made use of experimentally determined values of S_m and α_m^o and accounted for the instrumental slitwidth.

the line centers, the absorption coefficient is proportional to S_m, but weakly dependent on α_m. In fact, when α_m is approximately equal to the spectral slit width or greater, the absorptance observed near the line center decreases with increasing α_m (if u is constant). Therefore, we conclude that the good agreement between observed and calculated transmittances cannot result from the use of line strengths which were consistently too high or too low and from widths which were wrong in such a way as to compensate for the errors in strengths. We also conclude from Fig. 9 that the Lorentz line shape approximates the true shape of the lines within a few cm^{-1} of their centers.

Fig. 10 shows a similar comparison between $T(\nu)_{calc}$ and observed $T(\nu)$ in two regions where a significant part of the absorption is due to the extreme wings of lines whose centers are several cm^{-1} away. Near the band center there is a wider gap between adjacent lines than at any other place, except in the very weak part of the P-branch. The first 1 or 2 lines in the P- and R-branches are much weaker than the others nearby ($|m| \cong 4$ to 12); therefore, the stronger lines contribute significantly to the absorption near the band centers. No lines occur beyond the band head at 6417.78 cm^{-1} ($m = 35$), and the ones just below the band head are very weak. Therefore, a large part of the absorption near the band head is also expected to be due to the extreme wings of distant lines. We see that the observed absorptance is considerably less than that calculated by using either the Lorentz or the modified Lorentz line shape. This result indicates that the extreme wings of the lines are sub-Lorentzian; i.e., they absorb less than a Lorentz line having the same width. The modified shape predicts approximately the correct absorptance near the band center; but, like the Lorentz shape, it predicts too much absorption near the band head. Although there is always some difficulty in determining the proper position of the 100 percent transmittance curve near the edge of a band where the absorptance decreases gradually, we believe that the curve of observed transmittance near the band head is probably accurate to $\pm$ 0.01.

Because of the limited amount of data in regions where much of the absorption is due to distant lines, we were not able to derive a line shape which would predict accurately the absorptance at every place within the band. It was also not possible to determine if the lines are symmetrical about their centers. However, except near the band center or band head, the Lorentz shape or the modified shape (Eq. 18) appear to be adequate for the range of pressures used in the present investigation.

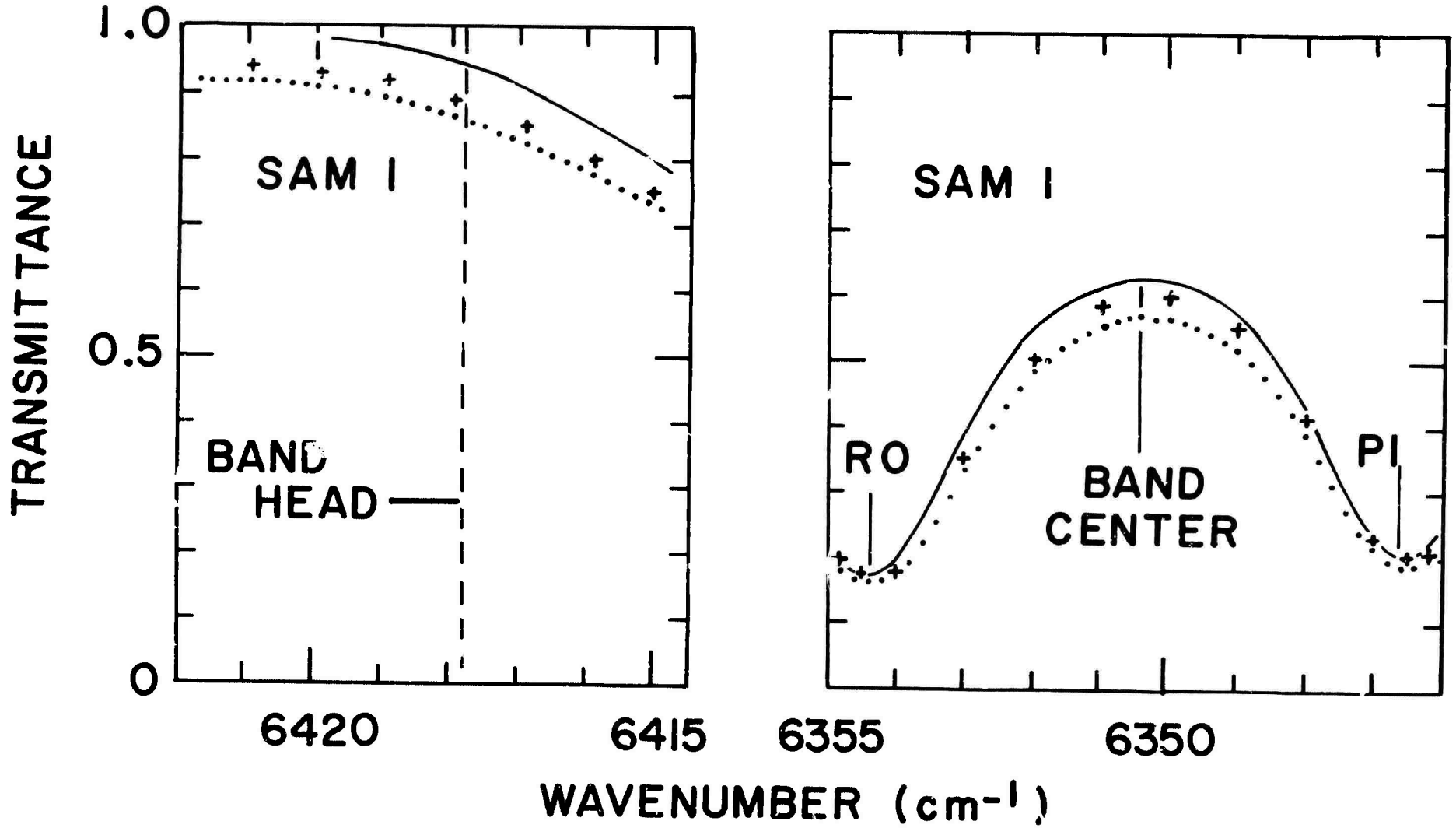


Fig. 10 OBSERVED AND CALCULATED TRANSMITTANCE IN VARIOUS REGIONS WHERE SOME OF THE ABSORPTION IS DUE TO DISTANT LINES.

The solid curves represent experimental measurements. The dotted curve and +'s correspond to calculations based on the Lorentz and a modified Lorentz line shape (Eq. 18), respectively. The calculations made use of experimentally determined values of S_m and α_m^o and accounted for the instrumental slitwidth.

SUMMARY

From the spectral curves of several samples of CO, we have determined: the strength of the 3ν CO band, the strengths and widths of more than 40 individual lines, the coefficient of the linear term in the Herman-Wallis factor which accounts for the effect of vibration-rotation interaction on line strengths, and the ratio of the broadening abilities of CO to N_2. The results exhibit good internal consistency and demonstrate that the Lorentz line shape is adequate for collision-broadened lines, except near the band center and band head. The absorption at these places indicates that the extreme wings of the lines are sub-Lorentzian.

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13. ABSTRACT

Spectral curves of several CO samples have been used to investigate the 3ν band whose center is near 6350 cm^{-1}. The strength of the band for the common $C^{12}O^{16}$ isotope has been found to be 0.0130 ± 0.0005 atm^{-1} cm^{-1} $_{STP}$ cm^{-1}. An empirical equation, $F_m = 1 + 0.011\ m$ has been derived to account for the influence of vibration-rotation on line strengths. The half-widths of the self-broadened lines at 1 atm pressure vary from approximately 0.090 cm^{-1} at $|m|=1$ to 0.062 cm^{-1} at $|m| = 20$. The widths of self-broadened lines are 1.08 ± 0.005 times as great as N_2-broadened lines at the same pressure. The Lorentz line shape appears to be appropriate for the collision-broadened lines within a few cm^{-1} of their centers; but the extreme wings of the lines are sub-Lorentzian.

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