MEASUREMENTS OF INTENSITIES AND NITROGEN-BROADENED LINEWIDTHS IN THE CO FUNDAMENTAL AT LOW TEMPERATURES*

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Abstract—Intensities and nitrogen-broadened half-widths of lines $R(0)$, $R(8)$ and $R(16)$ in the fundamental band of $^{12}C^{16}O$ have been measured at 83°K, 100°K, 150°K, 200°K and 298°K. The intensities of several other lines in the P- and R-branches of the band have also been measured at 298°K. The absolute intensity derived from the line intensity data using the Herman–Wallis formula is $S_v^o = 273 \pm 10 \, cm^{-2} \, atm^{-1}$ at S.T.P. A separate measurement employing the Wilson–Wells–Penner–Weber method has yielded $S_v^o = 277 \pm 4 \, cm^{-2} \, atm^{-1}$ at S.T.P. Both of these values are within 6 per cent of most of the previously published direct measurements of this parameter. The values for the line intensities reported earlier by other authors are lower by nearly 16 per cent.

INTRODUCTION

WHEN we began the present investigation, our primary objective has been to measure nitrogen-broadened half-widths in the CO fundamental and to deduce the temperature dependence of the line widths. We employed the Ladenburg–Reiche curve of growth which required intensity data on lines whose widths were to be measured. Our intensity measurements at 298°K, originally on $R(0)$, $R(8)$ and $R(16)$ and later extended to several lines in the P- and R-branches, had indicated discrepancies as high as 20 per cent between our data and those of BENEDICT et al.,[1] of HOOVER and WILLIAMS,[2] and of TUBBS and WILLIAMS.[3] Our values are larger. It also seemed from our measurements of N_2-broadened line widths of 298°K that if we had used the intensity data given in any of the above mentioned references, we would have obtained line widths that would have been larger by nearly 20 per cent than the values reported by BOUANICH and HAEUSLER,[4] BOUANICH and BRODBECK,[5] and by DRAEGERT and WILLIAMS.[6] It is important to emphasize the fact that the linewidth data given in Refs. (4)–(6) were obtained by using methods that did not at all require line intensity information. BOUANICH and HEUSLER[4] measured line widths directly in the fundamental and the second overtone, while BOUANICH and BRODBECK[5] measured line widths directly in the first overtone. DRAEGERT and WILLIAMS[6] measured the relative broadening abilities of CO and N_2, from which they deduced the nitrogen-broadened widths using the self-broadened line width data of HUNT et al.,[7] who also measured the half-widths directly in the first overtone. As will be discussed in the next section, the line widths determined for $R(0)$, $R(8)$ and $R(16)$ using our line intensity data are in good agreement with the values given in Refs. (4)–(6).

It has long been a puzzle as to why the values for the absolute intensity of the fundamental band of CO deduced[1-3,16] from line intensity measurements† should be lower by as much as 20 per cent than the direct measurements[8-15,17-20] of this parameter (Table 1). It became especially

†The measurements by LOCKE and HERZBERG[13] of the curves-of-growth of some resolved lines are an exception. The value for the absolute intensity they reported is 245 $cm^{-2} \, atm^{-1}$ at 300°K, which is 269 $cm^{-2} \, atm^{-1}$ at S.T.P. It is within 2 per cent of our value.

Table 1. Absolute intensity of the fundamental band of CO as reported by several investigators. The letters in the last column reflect the fact whether the measurements were performed on individual lines (L) or on the band as a whole (B). As much as possible, we have tried to obtain from each reference the precise temperature to which the reported value would correspond. The references with asterisk represent cases where we had to rely upon other references (shown in parentheses) where these values were quoted

Investigator(s)	S_v^0 $(cm^{-2} atm^{-1})_{S.T.P.}$	Reference	Type of measurement
Wetterblad (1924)	291	8*	B
Matheson (1932)	394	9*(1)	B
Havens (1938)	280	10*(12)	B
Dinsmore and Crawford (1949)	419 ± 82	11*(1)	B
Penner and Weber (1951)	258 ± 13	12	B
Locke and Herzberg (1953)	269	13	L
Coulon et al. (1954)	238	14*(1)	B
Vincent-Geisse (1954)	262	15	B
Shaw and France (1956)	238	16	L
Benedict et al. (1962)	236	1	L
Burch and Williams (1962)	262	17	B
Armstrong and Welsh (1965)	257 ± 4	18	B
Breeze and Ferriso (1965)	289 ± 30	19	B
Abu-Romia and Tien (1967)	290 ± 16	20	B
Hoover and Williams (1969)	213,225,236	2	L
Tubbs and Williams (1972)	210,233,242	3	L
Varanasi and Sarangi (1974)	273 ± 10	This work	B,L

intriguing when we recognized the fact[1,21] that vibration-rotation interaction had little effect on the relative line strengths in the CO fundamental.

Therefore, we extended the original premise of our work beyond the three lines $R(0)$, $R(8)$ and $R(16)$ and measured the intensities of several lines in the P- and R-branches at 298°K (Table 2), as well as the intensity of the whole band. The latter was measured using the method developed by the authors of Ref. (12).

EXPERIMENTAL DETAILS

The spectra were obtained using a commercially available Ebert-mounted grating monochromater, an i.r. glower, an InSb detector cooled to liquid nitrogen temperature, a mechanical chopper driven at 400 Hz, and a lock-in amplifier with its time constant set at 0·3 sec. Spectra were scanned at the rate of 0·36 cm⁻¹/min and the spectral transmission was recorded on a chart paper at a chart speed that corresponds to 0·2 cm⁻¹/inch. The signal to noise ratio, at 100 per cent transmission, was better than 200:1. The spectral resolution was (approximately) between 0·15 and 0·2 cm⁻¹ for most of the lines studied. It is more than adequate for measuring the curves-of-growth of CO lines.

The low-temperature absorption cell used in the present study has been described previously.[22,23] The length of this cell is 10·16 cm. We have also used cells of lengths equal to 0·56 cm and 1·08 cm and a one meter multiple reflection cell.

Special care was taken to avoid errors in determining the percentage concentration of CO in the mixtures of CO and N_2 we have used. Two mixtures with 0·11 and 1·04 per cent (by volume) of CO in N_2 were specially prepared for us by a commercial supplier. As the need arose, we also prepared several mixtures in lecture bottles in our laboratory. These samples contained 0·056, 0·259, 1·96, 3·92, 7·83 and 19·6 per cent (by volume) of CO in N_2. The total pressures were varied from 50 mm Hg to 3 atm. At lower temperatures, van der Waals correction was applied in determining the broadening pressure of N_2.

The measurements of the absolute intensity of the band using the Wilson–Wells–Penner–Weber method were performed using the 0·11 per cent mixture and a 5 cm long high pressure cell. Broadening pressures between 27 and 35 atm were used to obtain the data shown in Fig. 1. The spectral resolution was reduced to 0·3 cm⁻¹ so that the scanning rate could be fast enough to cover the entire band between 2025 and 2275 cm⁻¹ in a reasonable amount of time. Spectra were recorded at 18 cm⁻¹/min and 2 cm⁻¹/inch of chart paper with a signal-to-noise ratio of 300:1 and a time constant of 10 msec. The quantity $B \equiv \int_{2025\,cm^{-1}}^{2275\,cm^{-1}} \ln(1/\tau_\nu^a)\,d\nu$, where τ_ν^a is the apparent fractional transmission at the wave number ν was evaluated numerically.

Table 2. Calculated and observed line intensities at 298°K in the fundamental of $^{12}C^{16}O$. The errors in our experimental values reflect only the standard deviations over the number of measurements indicated in the parentheses after each value. The calculated intensities are based upon $S_v = 250 \text{ cm}^{-2} \text{ atm}^{-1}$ at 298°K, which corresponds to 273 cm^{-2} atm^{-1} at S.T.P.

| Line	S_J (cal) (cm^{-2} atm^{-1})	S_J (obs) (cm^{-2} atm^{-1})				
		(This Work)		(Ref. 1)	(Ref. 2)	(Ref. 3)
P(28)	0·0334	0·037 ± 0·0021	(13)	0·0293		
P(27)	0·0541	0·056 ± 0·0014	(8)	0·0486		
P(12)	6·38	6·44 ± 0·29	(4)	5·514		
P(11)	7·31	7·23 ± 0·26	(9)	6·251		
P(7)	9·49	9·49 ± 0·26	(4)	7·924		
P(5)	8·66	8·44 ± 0·09	(3)	7·536		
P(4)	7·61	7·84 ± 0·08	(13)	6·737		
P(3)	6·16	5·90 ± 0·24	(11)	5·376		
P(1)	2·26	2·36 ± 0·14	(5)	1·933		
R(0)	2·31	2·33 ± 0·07	(5)	2·006	1·73	1·85
R(2)	6·59	6·22 ± 0·15	(6)	5·452	4·73	5·43
R(3)	8·32	7·97 ± 0·23	(8)	6·603	5·82	6·85
R(8)	10·8	10·7 ± 0·38	(19)	9·167	7·01	8·44
R(12)	7·22	7·08 ± 0·06	(8)	6·554	5·64	6·00
R(16)	3·25	3·34 ± 0·06	(9)	2·844	2·73	2·83
R(22)	0·509	0·54 ± 0·03	(11)	0·475		0·485
R(23)	0·347	0·365 ± 0·012	(10)	0·325		0·321
R(25)	0·153	0·178 ± 0·0033	(10)	0·155		
R(27)	0·0619	0·0716 ± 0·002	(7)	0·0594		
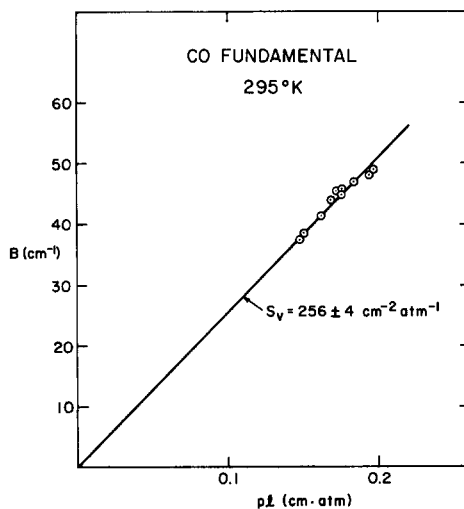
Fig. 1. Determination of the absolute intensity of the CO fundamental using the WILSON–WELLS–PENNER–WEBER method.[12] $l = 5$ cm, $p_{CO}/p_T = 0·011, 26·7 \le p_T \le 34·7$ atm and $T = 295$°K.

RESULTS AND DISCUSSION

The procedure we have employed for measuring the line strengths and widths involves the well-known Ladenburg–Reiche curve-of-growth, which is explained in considerable detail by BENEDICT et al.[24] It may not always be possible, in a practical sense, to rigorously satisfy the linearity condition while using the curve-of-growth for determining intensities. To correct for the

non-linearity, some preliminary estimates of both the intensity and the half-width of a line have to be used in an iterative procedure. We used the intensity data of BENEDICT et al.[1] and the half-width data of BOUANICH and BRODBECK,[5] for $R(0)$, $R(8)$ and $R(16)$, as our first 'guesses'. As our measured intensities at 298°K for these three lines were larger by nearly 20 per cent than the values given by BENEDICT et al.,[1] in all of our subsequent experiments, we used for 'first guesses' of the intensities of the other lines at 298°K, and of $R(0)$, $R(8)$ and $R(16)$ at lower temperatures, values derived using our measured intensities for $R(0)$, $R(8)$ and $R(16)$ at 298°K and the HERMAN–WALLIS formula.[21] The half-width data of Ref. (5) were used for all of the measurements at 298°K. At lower temperatures, the 'initial guesses' of the line widths (in intensity measurements only), were made by using the theoretical dependence of line width upon temperature. For CO–N₂ collisions, quadrupole–quadrupole interaction being the dominant one, an approximation given by BIRNBAUM,[25] based upon ANDERSON–TSAO–CURNUTTE theory,[26,27] is

$$\frac{\gamma^\circ(T)}{\gamma^\circ(298°K)} = \left(\frac{298}{T}\right)^{0.75} \tag{1}$$

Actually, a least-squares fit of our line width data (see below) has indeed resulted in equation (1) which may be a mere coincidence rather than an experimental verification of the approximate theoretical relation. It should be noted, however, that in the present determination of line intensities, errors of up to 20 per cent in the line widths could be tolerated as the value of the Ladenburg–Reiche parameter $u < 0.25$ for all of the lines studied. Here $u \equiv Spl/2\pi\gamma$, where S ($\text{cm}^{-2}\,\text{atm}^{-1}$) is the line intensity, p (atm) is the partial pressure of CO, l (cm) is the cell length and γ (cm^{-1}) is the half-width.

We determine the line intensity S_J from the measured apparent equivalent width W_J^a (cm^{-1}) by means of the relation

$$S_J = \frac{W_J^a}{pl}\,\frac{1}{[L(u)/u - \epsilon]}, \tag{2a}$$

where

$$\epsilon = (2\gamma/\pi)(1/\nu_m - 2/\delta_J). \tag{2b}$$

Here $L(u)$ is the Ladenburg–Reiche function, $2\nu_m$ is the frequency interval over which the actual area measurement was carried out and δ_J is the local line spacing. The approximate expression given in equation (2b) for ϵ, the so-called 'wing correction', involves the following assumptions: (a) The line retains its Lorentz shape between ν_m and $\delta_J/2$. (b) $k_\nu^a pl \ll 1$ for $\nu_m \leq \nu - \nu_0 < \delta/2$, (in our measurements, $k_{\nu_m}^a pl \leq 0.01$); k_ν^a is the apparent absorption coefficient. (c) The line contour does not have significant curvature over a spectral slit-width so that slit-function correction to ϵ may be ignored. (d) The so-called wing of a line loses its meaning once it enters the 'domain' of the neighboring line, which we assume begins at $\pm\delta_J/2$ from the center of that line. Therefore, we have accounted for the so-called 'wing correction' by extending the wing of a line only as far as $\delta_j/2$. The measured W^a may already reflect the influence of the neighboring lines and, thus, a partial compensation for the loss of absorption by the measured line beyond $\delta_J/2$, if any. A typical example of this type of analysis is shown in Table 3 for the line $R(2)$. It is not clear from a careful reading of Ref. (1) whether the wing correction has been considered. Neither of the corrections we mention here appear to have been considered in Refs. (2) and (3). The values in

Table 3. Determination of the intensity S_J (cm^{-2} atm^{-1}) from measured apparent equivalent widths W_J^a (cm^{-1}) of line $R(2)$ using equation (2). $l = 1.08$ cm, $p/p_{T_1} = 0.01014$, $u = 0.163$, $L(u)/u = 0.925$ and $\delta_J = 1.87$ cm^{-1}.

$$T = 298°K$$

p_T (atm)	ν_m (cm^{-1})	W_J^a	W_J^a/pl	S_J (cm^{-2} atm^{-1})		
				Equation (2) with ϵO	Equation (2) with $\epsilon(\delta_J)$	Equation (2) with $\epsilon(\infty)$
1·0	0·6	0·0585	5·21	5·63	5·98	6·15
1·5	0·7	0·0914	5·42	5·86	6·30	6·57
2·0	0·8	0·1149	5·11	5·53	5·97	6·32
2·5	1·0	0·1501	5·35	5·78	6·16	6·61
3·0	1·0	0·1749	5·19	5·61	6·06	6·60

the last column of Table 3 represent upper bounds for the intensities that one would get if the wings of the line were extended out to $\pm\infty$. The departure from the small u ('linear') asymptote of the curve-of-growth is seen to be about 8 per cent. The wing contribution amounts to about 6 per cent at 1 atm and to about 8 per cent at 3 atm.

The largest uncertainty in curve-of-growth measurements is in the determination of the base line (100 per cent transmission curve). We believe this source of error to be practically non-existent in our experiments. Transmission through the empty cell was measured several times during the many hours of measurement on each spectral line with the signal-to-noise ratio exceeding 200:1. We could not find any detectable (>0.5 per cent) drift in the base line. Furthermore, we found that, for $p_T \le 1$ atm, transmission through the empty cell and the cell filled with the absorbing gas to be practically the same at ν_m.

Using the HERMAN–WALLIS formula,[21] we can derive an estimate for the absolute intensity of the band. Our measured line intensity data shown in Tables 2 and 3 and in Figs. 2 and 3 yielded $S_v^o = 273 \pm 10$ cm^{-2} atm^{-1} at S.T.P. This value is in excellent agreement with the value $S_v^o = 277 \pm 4$ cm^{-2} atm^{-1} at S.T.P. we have measured, using the WILSON–WELLS–PENNER–WEBER
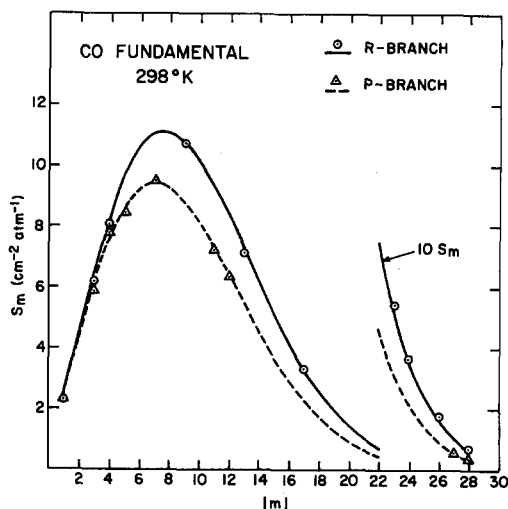

Fig. 2. Comparison of observed line intensities S_m (cm^{-2} atm^{-1}) in the P-branch (triangles) and in the R-branch (circles) of the CO fundamental with the HERMAN–WALLIS formula[21], using $S_v = 250$ cm^{-2} atm^{-1}, at 298°K.
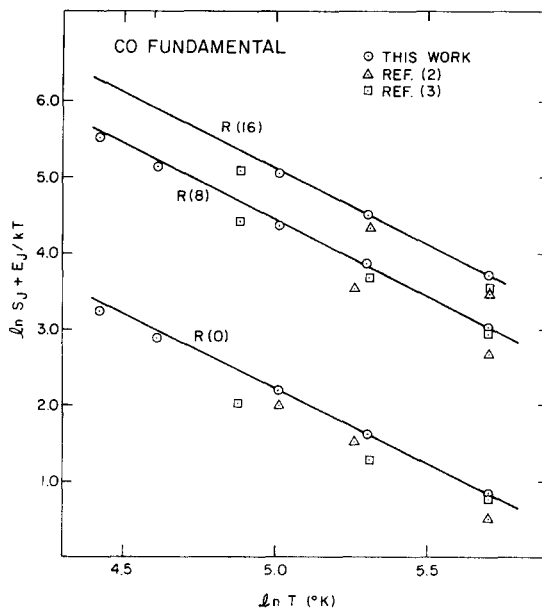
Fig. 3. Intensities of $R(0)$, $R(8)$ and $R(16)$ in the CO fundamental at 83°K, 100°K, 150°K, 200°K and 298°K. The straight lines represent the HERMAN–WALLIS formula[21] with $S_v(T) = 273\,(273/T)\,\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$.

Table 4. Intensities of lines $R(0)$, $R(8)$ and $R(16)$ in the fundamental band of $^{12}\mathrm{C}^{16}\mathrm{O}$ at 83°K, 100°K, 150°K, 200°K and 298°K. The quoted errors reflect only the standard deviations over the number of measurements indicated in the parentheses after each value

| Line | $S_J(\mathrm{cm}^{-2}\,\mathrm{atm}^{-1})$ | | | | |
	83°K	100°K	150°K	200°K	298°K
$R(0)$	$25\cdot3 \pm 0\cdot82$ (6)	$17\cdot9 \pm 0\cdot36$ (11)	$9\cdot01 \pm 0\cdot54$ (6)	$5\cdot17 \pm 0\cdot18$ (17)	$2\cdot33 \pm 0\cdot70$ (5)
$R(8)$	$22\cdot8 \pm 0\cdot62$ (7)	$23\cdot4 \pm 1\cdot2$ (11)	$20\cdot5 \pm 1\cdot3$ (11)	$18\cdot6 \pm 1\cdot3$ (11)	$10\cdot7 \pm 0\cdot38$ (19)
$R(16)$			$1\cdot03 \pm 0\cdot04$ (8)	$2\cdot15 \pm 0\cdot09$ (7)	$3\cdot34 \pm 0\cdot06$ (9)

method[12] (Fig. 1). The line intensities calculated at 298°K according to the HERMAN–WALLIS formula[21] and using $S_v = 250\,\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$, which corresponds to $273\,\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$ at S.T.P., are compared with the observed line intensities in Table 2 and Fig. 2. The intensities at lower temperatures of $R(0)$, $R(8)$ and $R(16)$ were also calculated using the Herman–Wallis formula and the relation $S_v(T) = (273/T)S_v^{\circ}$, with $S_v^{\circ} = 273\,\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$. The results of this calculation are compared with our experimental data in Fig. 3.

Thus, it appears that $S_v^{\circ} = 273 \pm 10\,\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$ is most consistent with all of our intensity measurements. A further proof, though less direct, that our line intensity measurements are accurate is provided by a comparison of the nitrogen-broadened line widths that we obtain at 298°K for $R(0)$, $R(8)$ and $R(16)$, using our line intensity values, with directly measured line widths reported in Refs. (4–6). For $R(0)$, we obtained $\gamma^{\circ}_{\mathrm{CO-N_2}} = 0\cdot0841 \pm 0\cdot0015\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$, which compares favorably with $0\cdot08\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ (Ref. 4), $0\cdot0817\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ (Ref. 5), and $0\cdot0812\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ (Ref. 6). For $R(8)$ our value is $0\cdot0655 \pm 0\cdot003\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ which is in good agreement with $0\cdot06\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ (Ref. 4), $0\cdot063\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ (Ref. 5) and $0\cdot0594\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ (Ref. 6).

Similarly, for $R(16)$ we obtain $0.0553 \pm 0.0035 \text{ cm}^{-1} \text{ atm}^{-1}$ which agrees well with $0.0555 \text{ cm}^{-1} \text{ atm}^{-1}$ (Ref. 4), $0.0538 \text{ cm}^{-1} \text{ atm}^{-1}$ (Ref. 5) and $0.0538 \text{ cm}^{-1} \text{ atm}^{-1}$ (Ref. 6). We have used the theoretical line intensities shown in Fig. 3 in determining the line widths merely to avoid experimental scatter as much as possible in Fig. 4, which we used to deduce the temperature dependence of $\gamma^{\circ}_{CO-N_2}$.

The line widths were obtained using the relation $\gamma = Spl/2\pi u$, where u is determined from $L(u)/u = (W^a/SPl) + \epsilon$. A least-squares fit of a straight line to the data on $R(8)$, as plotted in Fig. 4, has yielded a slope of 0.746, i.e. the relation $\gamma^{\circ} \sim T^{-0.746}$. The root-mean-square of the deviations in $-ln\,\gamma^{\circ}$ about the fitted straight line is 0.007. Straight lines drawn parallel to this line seem to fit the data for $R(0)$ and $R(16)$ also quite well. Between 83°K and 100°K, for both $R(0)$ and $R(8)$ (we were not able to measure $R(16)$ with our 10·16 cm absorption cell at these temperatures), we found the dependence of γ° upon T to be rather weak; the line widths are nearly equal at these two temperatures. A similar trend was found[28] for C_2H_2–C_2H_2 and C_2H_2–H_2 line widths at 171°K and 200°K. However, for the temperature range of practical interest (200–300°K), it appears reasonable to use our empirically found relation $T^{-0.746}$. It is interesting to compare this result with the approximate relation given by BIRNBAUM,[25] which follows from the theoretical formulation due to ANDERSON,[26] TSAO and CURNUTTE[27] only when there is either a single interaction or a dominant interaction that affects the line width. If the interruption function[25–27] for this particular interaction can be written as $S_2(b) \sim b^{-n}$, where b is an impact parameter, then it can be shown[25] that $\gamma^{\circ} \sim T^{-(n+4)/2n}$. In CO–N$_2$ collisions, the dominant interaction is the quadrupole–quadrupole interaction, for which $n = 8$.[25,27] Thus, it would appear that $\gamma^{\circ} \sim T^{-0.75}$. It must be emphasized, however, that the remarkable coincidence between this relation and our empirical result should not be interpretted as a verification of the theoretical relation in view of the many assumptions involved in deriving the above relation, in particular, and in the line-broadening theory, in general.
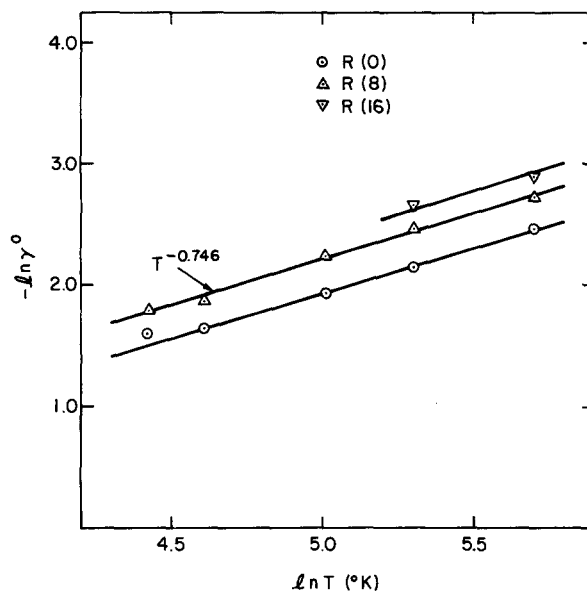

Fig. 4. Nitrogen-broadened line widths of $R(0)$, $R(8)$ and $R(16)$ in the CO fundamental at 83°K, 100°K, 150°K, 200°K and 298°K. The straight line $ln\,\gamma = -0.746\,ln\,T + 0.007$ is shown as the least-squares fit to the data on $R(8)$.

Table 5. Nitrogen-broadened half-widths, $\gamma^\circ_{CO-N_2}$ (cm^{-1} atm^{-1}), of $R(0)$, $R(8)$, and $R(16)$ in the fundamental band of $^{12}C^{16}O$ at several low temperatures. Indicated errors are standard deviations over the number of measurements given in parentheses following each value

Line	$\gamma^\circ_{CO-N_2}$ (cm^{-1} atm^{-1})				
	83°K	100°K	150°K	200°K	298°K
$R(0)$	0·201 ± 0·004 (13)	0·193 ± 0·01 (12)	0·143 ± 0·004 (7)	0·116 ± 0·005 (6)	0·0841 ± 0·0015 (6)
$R(8)$	0·164 ± 0·008 (13)	0·153 ± 0·008 (5)	0·106 ± 0·006 (5)	0·0843 ± 0·0004 (5)	0·0655 ± 0·003 (8)
$R(16)$				0·0694 ± 0·0007 (7)	0·0553 ± 0·0035 (11)

Table 6. Measured data, at 295°K, on spectral absorption coefficient k_ν (cm^{-1} atm^{-1}), line spacing δ_J (cm^{-1}), and line intensity S_J (cm^{-2} atm^{-1}) in the CO fundamental

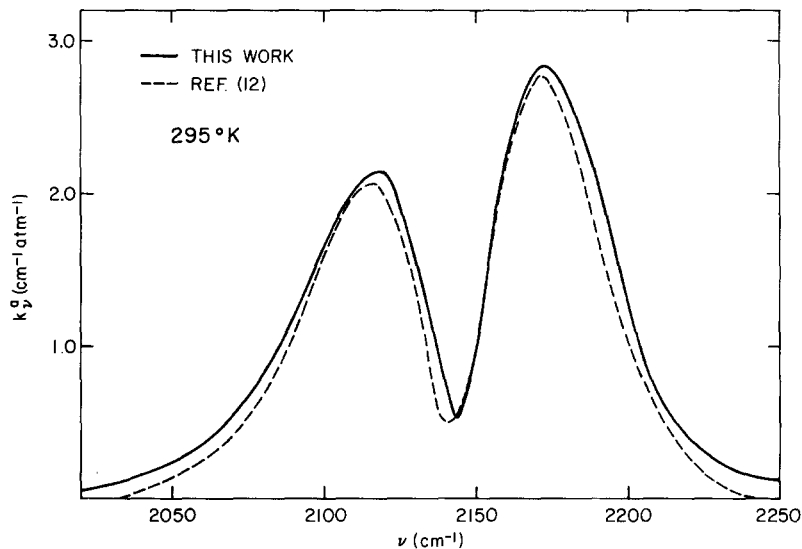| Line	δ_J Ref. (1)	k_ν (Fig. 6)	$S_J \sim k_\nu \cdot \delta_J$	S_J (Table 2)
$P(12)$	4·25	1·42	6·04	6·44
$P(11)$	4·23	1·66	7·02	7·23
$P(7)$	4·09	2·16	8·83	9·49
$P(5)$	4·02	2·00	8·04	8·44
$P(4)$	3·98	1·80	7·16	7·84
$P(3)$	3·95	1·42	5·61	5·90
$R(0)$	3·88	0·58	2·25	2·33
$R(2)$	3·71	1·60	5·93	6·22
$R(3)$	3·70	2·04	7·55	7·97
$R(8)$	3·53	2·78	9·81	10·7
$R(12)$	3·38	2·06	6·96	7·08
$R(16)$	3·23	1·06	3·42	3·34

Fig. 5. Spectral absorption coefficients in the CO fundamental obtained using high broadening pressures to smear out the rotational structure. Solid curve represents our data ($T = 295°K$ and $P_{N_2} = 500$ psi) and the dotted line is taken from PENNER and WEBER[12] ($T = 297°K$ and $P_{H_2} = 700$ psi).

CONCLUDING REMARKS

The value $S_v^o = 273 \pm 10 \, \text{cm}^{-2} \, \text{atm}^{-1}$ derived in this paper from line intensity and band intensity measurements is in excellent agreement with the infrared dispersion measurement by HAVENS,[10] with the value deduced by LOCKE and HERZBERG[13] from the curves-of-growth of some resolved lines, and is within 6 per cent of most of the other direct measurements[8,12,14,15,17-20] of this quantity presented in Table 1. Infrared dispersion measurements have led to accurate band intensities more consistently than any of the other experimental methods (see JAFFE's review[8]). We find it most reassuring that our estimate for S_v^o is within 2 per cent of the value obtained by HAVENS.[10] It is also worth noting that WEISBACK and CHACKERIAN[29] have recently found that $S_v^o = 270 \, \text{cm}^{-2} \, \text{atm}^{-1}$ yielded the best agreement between measured and calculated dipole moment matrix elements. Thus, we are able to conclude that the previous line intensity measurements[1-3,16] are in error.

Finally, it is interesting to compare the line intensity data in the present paper with values obtained by the method proposed by VARANASI and BANGARU.[30] The latter employs the just-overlapping line approximation,[12] $k_v \simeq S_J/\delta_J$, which is valid at broadening pressures high enough to smear out the rotational fine structure completely (Fig. 5). Using the tabulated[1] line positions in the CO fundamental, and the absorption coefficient data such as those shown in Fig. 5, we have derived the line intensities shown in Table 6. The intensities obtained using the curve-of-growth procedure and the just-overlapping line approximation differ from each other by 9 per cent or less.

Note added in Proof—We have recently[31] employed the Herman–Wallis formula, together with $S_v^o = 273 \, \text{cm}^{-2} \, \text{atm}^{-1}$ at S.T.P., successfully for calculating line intensity data [see Table 2 of Ref. (31)] required in line width measurements. In this connection, it should be noted that the intensities given in the second column of Table 2 of Ref. (31) correspond to 150°K instead of 100°K.

REFERENCES

1. W. S. BENEDICT, R. HERMAN, G. E. MOORE and S. SILVERMAN, *Astrophys. J.* **135**, 277 (1962).
2. G. M. HOOVER and D. WILLIAMS, *J. opt. Soc. Am.* **59**, 28 (1969).
3. L. TUBBS and D. WILLIAMS, *J. opt. Soc. Am.* **62**, 423 (1972).
4. J. P. BOUANICH and C. HAEUSLER, *JQSRT* **12**, 695 (1972).
5. J. P. BOUANICH and C. BRODBECK, *JQSRT* **13**, 1 (1973).
6. D. A. DRAEGERT and D. WILLIAMS, *J. opt. Soc. Am.* **58**, 1399 (1968).
7. R. H. HUNT, R. A. TOTH and E. K. PLYLER, *J. chem. Phys.* **49**, 3909 (1968).
8. T. WETTERBLAD (1924), Ph.D. Dissertation, as quoted by J. H. JAFFE (1961) *Advances in Spectroscopy—II*, p. 263. Interscience, New York.
9. L. MATHESON, *Phys. Rev.* **40**, 813 (1932).
10. R. J. HAVENS, Ph.D. Dissertation, University of Wisconsin, Madison (1938).
11. H. L. DINSMORE and B. L. CRAWFORD, Jr., Rept. NR-019-101, University of Minnesota (1949).
12. S. S. PENNER and D. WEBER, *J. chem. Phys.* **19**, 807 (1951). See also S. S. PENNER, *Quantitative Molecular Spectroscopy and Gas Emissivities*, Addison-Wesley, Reading, Massachusetts (1959).
13. J. L. LOCKE and L. HERZBERG, *Can. J. Phys.* **31**, 504 (1953).
14. R. COULON, L. GALATRY, B. OKSENGORN and B. VODAR, *J. Phys. Radium* **15**, 641 (1954).
15. J. VINCENT-GEISSE, *J. Phys. Radium* **15**, 539 (1954).
16. J. H. SHAW and W. L. FRANCE, Rept. No. 4, Contract AF 19(604)–1003, The Ohio State University (1956).
17. D. E. BURCH and D. WILLIAMS, *Appl. Opt.* **1**, 587 (1962).
18. R. L. ARMSTRONG and H. L. WELSH, *Can. J. Phys.* **43**, 547 (1965).
19. J. C. BREEZE and C. C. FERRISO, *J. chem. Phys.* **43**, 3253 (1965).
20. M. M. ABU-ROMIA and C. L. TIEN, *Int. J. Heat Mass Transfer* **10**, 1779 (1967).
21. R. HERMAN and R. F. WALLIS, *J. chem. Phys.* **23**, 637 (1955).
22. P. VARANASI, S. SARANGI and L. PUGH, *Ap. J.* **179**, 977 (1973).
23. S. SARANGI and P. VARANASI, *JQSRT* **14**, 365 (1974).
24. W. S. BENEDICT, R. HERMAN, G. E. MOORE and S. SILVERMAN, *Can. J. Phys.* **34**, 830 (1956).
25. G. BIRNBAUM, *Adv. Chem. Phys.* **12**, 487 (1967).
26. P. W. ANDERSON, *Phys. Rev.* **76**, 647 (1949).

27. C. J. TSAO and B. CURNUTTE, *JQSRT* **2**, 41 (1962).
28. P. VARANASI and B. R. P. BANGARU, *JQSRT* **15**, 267 (1975).
29. M. L. WEISBACH and C. CHACKERIAN, Jr., *J. chem. Phys.* **59**, 4274 (1973).
30. P. VARANASI and B. R. P. BANGARU, *JQSRT* **14**, 1253 (1974).
31. P. VARANASI, *JQSRT* **15**, 191 (1975).