Int. J. Heat Mass Transfer. Vol. 15, pp. 1477–1487. Pergamon Press 1972. Printed in Great Britain

THEORETICAL DETERMINATION OF THE ABSORPTION COEFFICIENT AND THE TOTAL BAND ABSORPTANCE INCLUDING A SPECIFIC APPLICATION TO CARBON MONOXIDE

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(*Received* 9 *July* 1971 *and in revised form* 3 *November* 1971)

Abstract—Analytical expressions are obtained for the absorption coefficient and total band absorptance for a vibrational-rotational band. Specific application is then made to carbon monoxide and good agreement with experimental results is obtained.

INTRODUCTION

THE ABSORPTION coefficient of a vibration–rotation band comprised of lines which have the dispersion form is given by

$$k_\nu = \sum_J \frac{S_J}{\pi} \frac{b_J}{(\nu - \nu_J)^2 + b_J^2} \tag{1}$$

where S_J, b_J and ν_J are the intensity, half-width and center of the Jth line in the band and the summation is carried out over all the lines in the band. In 1938, Elsasser [1] considered an idealized band consisting of an infinite sequence of lines, all having the same intensity S and half-width b, and located a distance d from each other with $\nu_J = Jd$. He summed the series in equation (1) for an infinite number of lines extending from $J = -\infty$ to $J = +\infty$ and obtained

$$k_\tau = \frac{S}{d} \frac{\sinh \beta}{\cosh \beta - \cos \tau} \tag{2}$$

where $\tau = 2\pi(\nu - \nu_0)/d$ and $\beta = 2\pi b/d$.

Now, the assumption of constant line intensities is only valid over a small spectral region so that the use of equation (2) is restricted. Furthermore, even over a narrow spectral region the contribution from lines of different intensities may be important. We shall therefore consider a more realistic variation of the line intensities.

Consider a vibration–rotation band to consist of two series of lines, called the R and P branches, with the spectral lines positioned according to [2]:

$$\begin{aligned} \nu_{J,R} &= \nu_0 + d(J+1); \quad J = 0, 1, 2, \ldots \\ \nu_{J,P} &= \nu_0 - dJ \quad\;\; ; \quad J = 1, 2, \ldots \end{aligned} \tag{3}$$

Here ν_0 is the frequency of the band center and J is the rotational quantum number associated with the lower rotational energy level in the transition which results in the spectral lines $\nu_{J,R}$ or $\nu_{J,P}$. Note that there is no spectral line at the band center. Thus, the idealized Elsasser model for a vibrational-rotational band consisting of R and P branches is given by

$$k_\tau = \frac{S}{d} \frac{\sinh \beta}{\cosh \beta - \cos \tau} - \frac{2\beta S}{d} \frac{1}{\beta^2 + \tau^2}. \tag{4}$$

The second term results from the fact that there is no line at the band center.

Note that the previous work of Elsasser assumed the lines to have the same intensity. In this paper we do not make this assumption. We shall therefore obtain the absorption coefficient, k_ν, when the line intensity S_J *varies* with the rotational quantum number J.

ANALYSIS

Edwards and Menard [3] proposed a simple, arbitrary model for the variation of the mean line intensity to spacing ratio, S/d; namely, an exponential function. Using this distribution we have

$$\begin{aligned} S_J &= S_0 \exp\left[-(\nu_{J,R} - \nu_0)/F_R\right], \quad \text{for the } R \text{ branch} \\ S_J &= S_0 \exp\left[-(\nu_0 - \nu_{J,P})/F_P\right], \quad \text{for the } P \text{ branch} \end{aligned} \tag{5}$$

where S_0, F_R and F_P are constants which are chosen so as to obtain the best approximations to the R branch and P branch intensity distributions. Substituting equation (5) into equation (1) gives

$$k_\tau = \frac{2\beta S_0}{d}\left\{\sum_{J=1}^{\infty} \frac{e^{-dJ/F_P}}{(\tau + 2\pi J)^2 + \beta^2} + \sum_{J=0}^{\infty} \frac{e^{-d(J+1)/F_R}}{(\tau - 2\pi[J+1])^2 + \beta^2}\right\}. \tag{6}$$

To evaluate the sums of these series consider the following function of the complex variable z:

$$f(z) = \frac{2\pi\beta S_0 \cot \pi z}{d}\left\{\frac{e^{-dz/F_P}}{(\tau + 2\pi z)^2 + \beta^2} + \frac{e^{-dz/F_R}}{(\tau - 2\pi z)^2 + \beta^2}\right\}. \tag{7}$$

This function is analytic in the domain, $R(z) \geqslant 0$ except at the simple poles located at $z = 0, +1, +2, \ldots$ and at $z = (|\tau| \pm \beta i)/2\pi$ [4].* Applying the residue theorem [4]

$$\frac{1}{2\pi i}\int_C f(z)\,dz = \text{sum of residues inside } C \tag{8}$$

where C is the contour (cf. Fig. 1) consisting of the lines $z = \pm iy$ (y varying from R to ε) and the semi-circles $z = \varepsilon e^{i\theta}$, $z = Re^{i\theta}$ (θ varying from $-\pi$ to π) and taking the limit of the integrals as R goes to infinity and ε goes to zero yields:

$$k_\tau = \frac{S_0}{d}\left\{\exp\left(\frac{-|\tau|d}{2\pi F}\right)\left[\frac{\cos(\beta d/2\pi F)\sinh\beta + \sin(\beta d/2\pi F)\sin|\tau|}{\cosh\beta - \cos\tau}\right] - \frac{2\beta}{\beta^2 + \tau^2} + I\right\} \tag{9a}$$

with $F = F_R$ for $\tau > 0$ and $F = F_P$ for $\tau < 0$ and

$$I = \frac{\beta}{\pi}\int_0^{\infty} \coth\left(\frac{y}{2}\right) \left\{\frac{(\tau^2 + \beta^2 - y^2)\left[\sin(yd/2\pi F_R) + \sin(yd/2\pi F_P)\right] - 2|\tau|y\left[\cos(yd/2\pi F_R) - \cos(yd/2\pi F_P)\right]}{(\tau^2 + \beta^2 - y^2)^2 + 4\tau^2 y^2}\right\} dy. \tag{9b}$$

We note that when all the lines have the same intensity S_0, we have that $F_P = F_R = \infty$. For this condition the results for the absorption-coefficient from equations (9) correctly reduce to the Elsasser results for a vibrational–rotational band as given by equation (4).

We shall restrict our discussions to small values of the ratio b/F. We can then obtain useful, simple analytic results for the absorption coefficient and the total band absorptance for some limiting cases. We note that these restrictions need not be made since results may be

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* For completeness we note that simple poles also exist in the domain $R(z) < 0$.

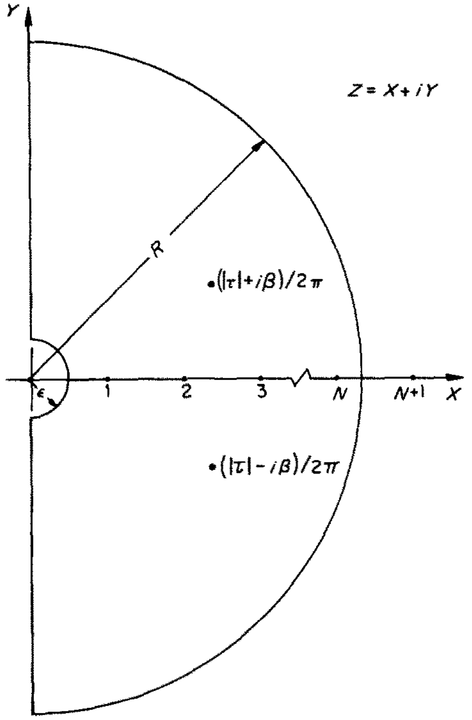

FIG. 1. Contour and singularities.

Table 1. Comparison of results for the absorption coefficient
$F_P = F_R = F$, $d/F = 0{\cdot}201$

τ \ $k_\tau / \frac{S_0}{d}$	$\beta = 0{\cdot}1$		$\beta = 1{\cdot}0$	
	Equation (10)	Numerical	Equation (10)	Numerical
1·57	0·014	0·013	0·057	0·130
3·14	0·025	0·022	0·18	0·204
4·71	0·077	0·072	0·49	0·526
6·28	16·3	16·36	1·6	1·699
7·85	0·074	0·075	0·49	0·560
9·42	0·035	0·033	0·27	0·306
11·00	0·068	0·065	0·45	0·493
12·60	13·0	13·39	1·3	1·425
15·70	0·029	0·029	0·23	0·265
17·28	0·057	0·054	0·38	0·414
18·85	11·0	10·95	1·1	1·194
20·42	0·051	0·053	0·34	0·399
25·13	8·9	8·956	0·89	0·964
31·42	7·3	7·325	0·73	0·791
39·27	0·028	0·029	0·19	0·224
50·27	4·0	4·008	0·40	0·435
59·69	0·0073	0·0076	0·059	0·071
69·12	2·2	2·193	0·22	0·240
80·11	0·0076	0·0077	0·051	0·060
89·54	0·0056	0·0061	0·038	0·050
100·53	0·80	0·803	0·080	0·089
150·80	0·16	0·161	0·016	0·018
201·06	0·032	0·032	0·0032	0·004
300·02	0·000	0·000	0·000	0·000

obtained by numerical integration. Discussion of the evaluation of the integral I, equation (9b), is given in Appendix A.

For small values of β, equation (9) yields

$$k_\tau = \frac{S_0}{d}\,\frac{\beta}{1 + (\beta^2/2) - \cos\tau}\exp\left(\frac{-|\tau|d}{2\pi F}\right) - \frac{2\beta(S_0/d)}{\tau^2 + \beta^2}. \qquad (10)$$

We have taken $d/2\pi F$ to be much smaller than unity. The presence of the terms of order β^2 in the denominators ensures a finite value for the absorption coefficient at the line centers; that is at $\tau = 2\pi(\nu - \nu_0)/d = 2\pi n$, or at $\nu = \nu_0 + nd$, for integer n. Comparison of equation (10) with the numerical results for the absorption coefficient is given in Table 1 for values of β equal to 0·1 and 1·0.

For moderately large values of β, the absorption coefficient decays exponentially from the band center according to*

$$\frac{k_\tau}{S_0/d} = \exp(-|\tau|d/2\pi F) = \exp(-|\nu - \nu_0|/F). \qquad (11)$$

It is clear that the overlapping smooths out the rapid spectral variation associated with the individual spectral lines. The numerical results for the absorption coefficient are given in Table 2 along with equation (11), for values of β equal to 3·0, 5·0, 7·0 and 10·0. An improved relation for the absorption coefficient can be obtained (cf. Appendix A) but in view of the approximate nature of the intensity distribution that was

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* We note that in the spectral region close to the band center, $|\nu - \nu_0| < d$, or $|\tau| < 2\pi$, we require that the absorption be small. Therefore equation (11) is not valid in this region. The referee has pointed out that an alternative approximation is also available [15].

Table 2. Comparison of results for the absorption coefficient $F_P = F_R = F, d/F = 0{\cdot}201$

κ_τ / $\frac{S_0}{d}$ / τ	Equation (11)	Numerical integration			
		$\beta = 3{\cdot}0$	$\beta = 5{\cdot}0$	$\beta = 7{\cdot}0$	$\beta = 10{\cdot}0$
6·28	0·82	0·716	0·569	0·517	0·476
7·85	0·78	0·644	0·576	0·528	0·482
9·42	0·74	0·564	0·567	0·532	0·485
11·00	0·70	0·610	0·570	0·531	0·485
12·60	0·67	0·672	0·570	0·526	0·481
15·70	0·60	0·503	0·523	0·502	0·467
17·28	0·58	0·530	0·512	0·489	0·457
18·85	0·55	0·574	0·503	0·476	0·446
20·42	0·52	0·498	0·478	0·460	0·434
25·13	0·45	0·481	0·430	0·413	0·395
31·42	0·37	0·400	0·362	0·353	0·343
39·27	0·28	0·288	0·287	0·286	0·284
50·27	0·20	0·227	0·212	0·212	0·214
59·69	0·15	0·141	0·157	0·163	0·167
69·12	0·11	0·128	0·123	0·126	0·131
80·11	0·077	0·083	0·088	0·092	0·098
89·54	0·057	0·064	0·067	0·071	0·077
100·53	0·040	0·050	0·050	0·053	0·058
150·80	0·008	0·012	0·013	0·015	0·018
201·06	0·002	0·003	0·004	0·005	0·007
300·02	0·000	0·001	0·001	0·002	0·002

used, equations (5), we have decided not to proceed further in this direction. We do note, however, that the procedure discussed above for the determination of the absorption coefficient may also be used for the more exact intensity distribution, equation (26). With this distribution it may be desirable to utilize more accurate relations for the absorption coefficient.

To determine the energy transport by radiation it is useful to have an expression for the total band absorptance, A, which is defined by

$$A = \int_{-\infty}^{\infty} [1 - e^{-k_\nu x}]\,d(\nu - \nu_0) \qquad (12)$$

where x is the pressure pathlength. We shall use the above relations for the absorption coefficient and obtain analytic results for A. It is, of course, possible to substitute the "general" expression for the absorption coefficient, equation (9) into equation (12) and integrate the resulting expression numerically to obtain the total band absorptance A.

We begin by substituting equation (11) into equation (12). Then, changing the independent variable from ν (or τ) to $(S_0x/d)\exp[(\nu - \nu_0)/F_P]$ and $(S_0x/d)\exp[-(\nu - \nu_0)/F_R]$ for the P and R branches, respectively, and carrying out the integration yields

$$A = F_P[\ln v_P + \gamma + E_1(v_P)] + F_R[\ln v_R + \gamma + E_1(v_R)] \qquad (13)$$

where $v_{P,R} = (S_0x/d)\exp(-d/F_{P,R})$, γ is Euler's constant (0·577...) and E_1 is the exponential integral [5]. Taking the series expansion for E_1 yields*

$$A = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{nn!}[F_P v_P^n + F_R v_R^n]. \qquad (14)$$

This relation is most useful for small values of the argument. For large values of the argument the asymptotic expansion for E_1 may be used and the corresponding result for the total band absorptance is then given by

$$A = F_P\left\{\ln v_P + \gamma + \frac{e^{-v_P}}{v_P}\left[1 - \frac{1}{v_P} + \frac{2}{v_P^2} - \ldots\right]\right\} + F_R\left\{\ln v_R + \gamma + \frac{e^{-v_R}}{v_R}\left[1 - \frac{1}{v_R} + \frac{2}{v_R^2} - \ldots\right]\right\}. \qquad (15)$$

The defining integral for the total band absorptance, equation (12) may also be written as follows:

$$\begin{aligned} A &= \sum_{n=-\infty}^{\infty} \int_{(n-\frac{1}{2})d}^{(n+\frac{1}{2})d} (1 - e^{-k_\nu x})\,d(\nu - \nu_0) \\ &= (d/2\pi) \sum_{n=-\infty}^{\infty} \int_{(2n-1)\pi}^{(2n+1)\pi} (1 - e^{-k_\tau x})\,d\tau \\ &= \sum_{n=-\infty}^{\infty} A_n. \end{aligned} \qquad (16)$$

This form is particularly suitable for the evaluation of the total band absorptance when β is small, that is, when the lines are effectively isolated. Now, using equation (10) for k_τ and

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* The leading term of the expansion can be directly obtained from $A = x\int_{-\infty}^{\infty} k_\nu\,d\nu$.

changing the variable of integration from τ to $\tau' = \tau - 2\pi n$, we obtain

$$A_n = \frac{d}{2\pi}\int_{-\pi}^{\pi}\left\{1 - \exp\left[-(S_0 x\beta/d) \times \left(\frac{\exp[-(|2\pi n + \tau'|)\,d/2\pi F]}{1 + \beta^2/2 - \cos\tau'} - \frac{2}{(\tau' + 2\pi n)^2 + \beta^2}\right)\right]\right\}\mathrm{d}\tau' \tag{17}$$

where F equals F_R for positive values of n and equals F_P for negative values of n.

It can be shown that A_n is small for $n = 0$ as well as for moderate and large values of $|n|$. Thus, the primary contribution to the total band absorptance, A, comes from only a few terms, namely, A_1, A_{-1}, A_2, A_{-2}, etc. In these integrals, the second term in the exponential (cf. equation (17)) is smaller than the first term and may be neglected in performing the integrations. Furthermore, the primary contribution is from the region very close to the line centers where $\tau' = 0$ so that $\exp[-(|n + \tau'/2\pi|)\,d/F] \approx \exp[-|n|\,d/F]$. Thus, for A_1, A_{-1}, A_2, A_{-2}, etc. we have that

$$A_n \approx \frac{d}{\pi}\int_{0}^{\pi}\left\{1 - \exp\left[\frac{-y_n\beta}{1 + \beta^2/2 - \cos\tau'}\right]\right\}\mathrm{d}\tau' \tag{18}$$

where $y_n = (S_0 x/d)\exp(-|n|\,d/F)$. Note that $y_1 = v$. Defining now a new integration variable, ϕ, according to

$$\cos\phi = \frac{1 - (1 + \beta^2/2)\cos\tau'}{1 + \beta^2/2 - \cos\tau'}$$

we obtain

$$\frac{\mathrm{d}A_n}{\mathrm{d}(y_n/\beta)} = \beta d\exp[-(1 + \beta^2/2)\,y_n/\beta]\,I_0(y_n/\beta) \tag{19}$$

where I_0 is the modified Bessel function of order zero.

There are several limiting cases for which A_n may be readily integrated. First, for $y_n\beta/2 \ll 1$ we obtain

$$A_n = y_n d\,\mathrm{e}^{-y_n/\beta}\,[I_0(y_n/\beta) + I_1(y_n/\beta)]. \tag{20}$$

Substituting equation (20) into equation (16) and making use of the Euler–MacLaurin formula we obtain

$$\frac{A}{\beta} = (F_P v_P/\beta)\,\mathrm{e}^{-v_P/\beta}\,[I_0(v_P/\beta)(2 + \beta/v_P) + 2I_1(v_P/\beta)] - F_P + (F_R v_R/\beta)\,\mathrm{e}^{-v_R/\beta} \times [I_0(v_R/\beta)(2 + \beta/v_R) + 2I_1(v_R/\beta)] - F_R. \tag{21}$$

It is interesting to note that equation (21) may also be obtained directly from equation (1) by considering the spectral lines to be isolated from one another. Thus, the total band absorptance as given by equation (21) may be interpreted as resulting from the summation of the absorptions from isolated lines. For v_P and $v_R \ll \beta$, equation (21) yields the following linear dependence on u, with $u = S_0 x/d$:*

$$A = (F_P\,\mathrm{e}^{-d/F_P} + F_R\,\mathrm{e}^{-d/F_R})\,u. \tag{22}$$

Note that $v_{P,R} = u\,\mathrm{e}^{-d/F_{P,R}}$.

Another limiting case we consider is $y_n/\beta \gg 1$ or, equivalently, $|n| \ll (F/d)\ln(u/\beta) \equiv N$. For this condition, we obtain from equation (19)

$$A_n = d\,\mathrm{erf}[(y_n\beta/2)^{\frac{1}{2}}]. \tag{23}$$

We may now obtain the total band absorptance, A, by summing equation (23). Using the Euler–MacLaurin formula we obtain

$$A/2 = F_P\int_0^{[\beta u\exp(-d/F_P)/2]^{\frac{1}{2}}}\mathrm{erf}(z)\frac{\mathrm{d}z}{z} + F_R\int_0^{[\beta u\exp(-d/F_R)/2]^{\frac{1}{2}}}\mathrm{erf}(z)\frac{\mathrm{d}z}{z}. \tag{24}$$

For the limiting case given by $y_n/\beta \gg 1$ as well

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* This result can be directly obtained from $A = x\int_{-\infty}^{\infty} k_\nu\,\mathrm{d}\nu$

as $y_n\beta/2 \ll 1$, so that $\beta \ll y_n \ll 2/\beta$, we obtain

$$A = d(2\beta u/\pi)^{\frac{1}{2}}\left[\frac{1}{e^{d/2F_P} - 1} + \frac{1}{e^{d/2F_R} - 1}\right]. \qquad (25)$$

A convenient summary of various limiting expressions is presented in Appendix B.

RESULTS

In the preceding analysis we have obtained theoretical relations for the total band absorptance. Numerical results may be readily obtained and these are presented in Fig. 2 for a broad range of values of the optical depth, u, and the pressure broadening parameter, β. We have taken $F_P = F_R = F$.

We now wish to make a direct comparison with experimental data and shall demonstrate how this may be achieved from the fundamental spectroscopic results. The mean line intensity S_J is given by ([6], p. 276)

$$S_J = \alpha\sqrt{\left(\frac{hcB_e}{kT}\right)}\,[\eta \exp(-\eta^2)] \qquad (26)$$

with

$$\eta = \sqrt{\left(\frac{hcB_e}{kT}\right)}\,J. \qquad (27)$$

We consider the fundamental vibration–rotation band of carbon monoxide which has the band center at 2143 cm^{-1} (4·7 microns), the line spacing, $d = 2Be = 3{\cdot}863\ \mathrm{cm}^{-1}$ ([7], pp. 213 and 358) and the integrated band intensity, $\alpha = \int S_J\,\mathrm{d}J$ ([6], p. 153, equations 7–117). The intensity variation used in this study is of the form (cf. equations (5)]

$$S_J = \alpha\sqrt{\left(\frac{hcB_e}{kT}\right)}\,D_1 \exp(-D_2\eta). \qquad (28)$$

If necessary, distinction could easily be made between the P and R branches. We require the integrated band intensity resulting from equations (26) and (28) to be the same. This gives $D_2 = 2D_1$. We therefore obtain [cf. equations (5)]

$$F(\mathrm{cm}^{-1}) = \frac{1}{D_1}\left(\frac{kTB_e}{hc}\right)^{\frac{1}{2}} = \frac{19{\cdot}2}{D_1}\left[\frac{T(^\circ\mathrm{K})}{273}\right]^{\frac{1}{2}} \qquad (29)$$

$$S_0\,(\mathrm{atm}^{-1}\,\mathrm{cm}^{-2}) = D_1\alpha\left(\frac{hcB_e}{kT}\right)^{\frac{1}{2}} = 0{\cdot}1\,D_1\alpha(T)\left[\frac{273}{T(^\circ\mathrm{K})}\right]^{\frac{1}{2}}. \qquad (30)$$

Note that the product $FS_0 = \alpha B_e = \alpha d/2$.

We will now make a direct comparison with

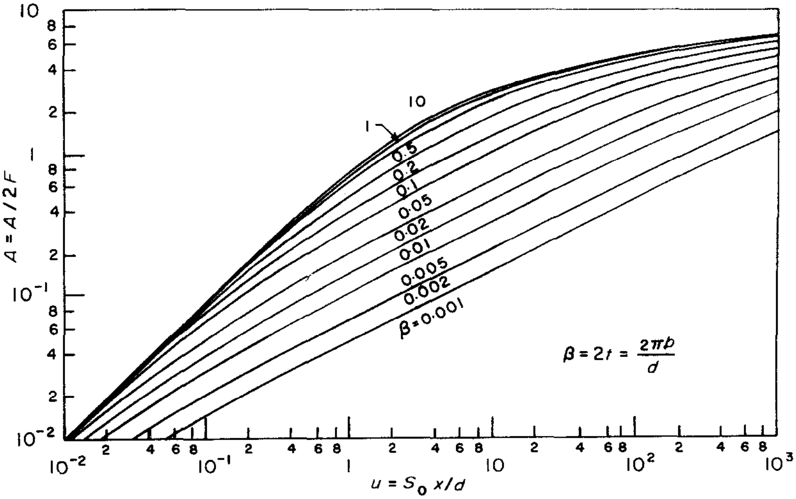

FIG. 2. Total band absorptance from present results.

the experimental data of Burch and Williams [8] for the fundamental vibration rotation band of carbon monoxide. They specify a value of 260 (atm cm)$^{-1}$ cm^{-1} for the integrated band intensity, α, at 273°K. The line half width must also be known and this is given by $b(\mathrm{cm}^{-}1) = 0{\cdot}076\ [T(°\mathrm{K})/300]^{-\frac{1}{2}} P_e$ ([6], p. 305). For pure carbon monoxide $P_e = 1{\cdot}02\,P$ where P is the gas pressure in atmospheres. The line spacing, d, has been given above so we may directly calculate the broadening parameter and obtain $\beta = 2\pi b/d = 0{\cdot}126\ [T(°K)/300]^{-\frac{1}{2}} P_e$. There remains the specification of the constant D_1. We arbitrarily take D_1 equal to unity.

The total band absorptance A may now be directly calculated and the results are presented in Table 3 and Fig. 3 for a temperature of 300°K. The experimental data of Burch and Williams [8] are also given in Table 3 and Fig. 3 and the agreement is seen to be very good over the broad range of pressures and path lengths that they studied.

We note that Edwards and Menard [3] obtained a correlation for the total band absorptance based on various limiting relations. Tien and Lowder [9] then obtained a single expression for the correlation which is given by:

$$\bar{A} = \frac{A}{C_3} = \ln\left\{U f(t)\left[\frac{U+2}{U+2f(t)}\right] + 1\right\} \tag{31}$$

where

$$U = \alpha x/C_3, \quad t = \pi b/d = (C_2^2/4\alpha C_3)\,P_e = B^2 P_e \tag{32a}$$

$$f(t) = 2{\cdot}94\,[1 - \exp(-2{\cdot}60\,t)] \tag{32b}$$

with C_2 and C_3 being determined from the experimental data. Note that $t \equiv \beta/2$. The results from equation (31) for carbon monoxide are also presented in Table 3. The agreement between the correlation [3, 9] and the experimental data of Burch and Williams [8] is good but, in general, not as successful as the present theoretical results over the entire range of pressures and path lengths.

Table 3. *Total band absorptance of the carbon monoxide fundamental: experiment* (*Burch and Williams* [8]). *Present theoretical results, correlation* (*Tien and Lowder* [9], *Edwards and Menard* [3]). *Temperature* 300°*K*, P_e (*atm*) = 1·02 P (*atm*)

Effective pressure P_e (atm)	Pressure path length PX (atm cm)	Experimental data [8] A (cm^{-1})	Present theoretical results A (cm^{-1})	Correlation equation (31) [3, 9]
0·0263	10^{-3}	0·17	0·17	0·22
	10^{-2}	0·77	0·76	1·24
	10^{-1}	2·9	2·7	3·0
	1	10	8·8	9·4
	10	33	28·4	44·5
0·0526	10^{-3}	0·20	0·19	0·23
	10^{-2}	0·98	1·01	1·58
	10^{-1}	3·8	3·7	4·7
	1	14	12·5	15
	10	42	40·1	60
0·1315	10^{-3}	0·23	0·21	0·23
	10^{-2}	1·4	1·4	1·9
	10^{-1}	5·4	5·6	7·9
	1	20	19·8	25·9
	10	64	60·3	83·1
0·329	10^{-3}	0·23	0·23	0·24
	10^{-2}	1·8	1·78	2·12
	10^{-1}	8·6	8·4	11·9
	1	31	30·8	40·7
	10	89	83·8	108
	10^{-2}	180	170	192
1	10^{-3}	0·23	0·23	0·24
	10^{-2}	2·1	2·1	2·26
	10^{-1}	14	12·8	16·2
	1	53	54·3	61·1
	10	130	124	138
	10^{2}	190	219	224
3·95	10^{-3}	0·23	0·23	0·24
	10^{-2}	2·5	2·3	2·3
	10^{-1}	20	18·5	19·5
	1	87	92·3	83·6
	10	170	180	170

Experimental data for carbon monoxide at room temperature and at elevated temperatures has been obtained by Tien and Giedt [10] and Abu-Romia and Tien [11]. A comparison of the present theoretical results with these experimental data is given in Table 5 along with the correlation noted above [3, 9]. At 1800°K, for the large pressure path lengths, the correlation is in better agreement with the experimental

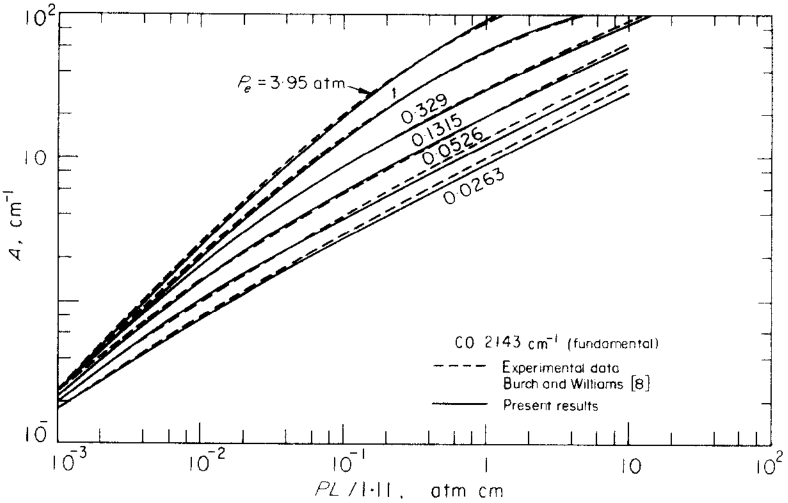

FIG. 3. Comparison of present results with experimental data of Burch and Williams.

data.* Also refer to Edwards [12]. We also note that experimental results at temperatures up to 2700°K have been recently published by Giedt and Travis [14].

For completeness, both the correlation and the present results for the total band absorptance are shown in Fig. 4. The results are presented on a generalized dimensionless basis, so that there is no restriction to a particular gas. It can be shown that $C_3 = 2F$, $U = u$. Significance differences do result, especially at the lower pressures, where the present theoretical results mental data (cf. Table 3).

Table 4. Values of the integral,

$$G(x) = \int_0^x [erf(z)/z]\, dz$$

x	$G(x)$
0·000707	0·0008
0·002236	0·0026
0·007071	0·0080
0·022361	0·0253
0·070711	0·0798
0·223610	0·2510
0·707110	0·7573
2·236100	1·7866
7·071100	2·9378
22·361000	4·0891
70·711000	5·2404

Values of the Integral, $G(x) = \int_0^x [\mathrm{erf}(z)/z]\, dz$.

In closing we note that it is also possible to use the more accurate mean line intensity of equation (26) and obtain results for the absorption coefficient and the total band absorptance. One proceeds in a manner similar to that prescribed in the present study although the resulting relations are correspondingly more complex.

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* It is probably possible to improve the agreement between the present results and the experimental data. For example, the broadening parameter at $P_e = 1$ atm, $t = \beta/2 = \pi b/d$, as deduced from the data is given by 0·0838 $(300/T(°\mathrm{K}))^{0.42}$ [11] in contrast to the value which results from the basic spectroscopic constants, viz. 0·063 $(300/T(°\mathrm{K}))^{0.50}$. However, at elevated temperatures additional bands should also be included so as to properly account for the contribution resulting from transitions among higher vibrational levels.

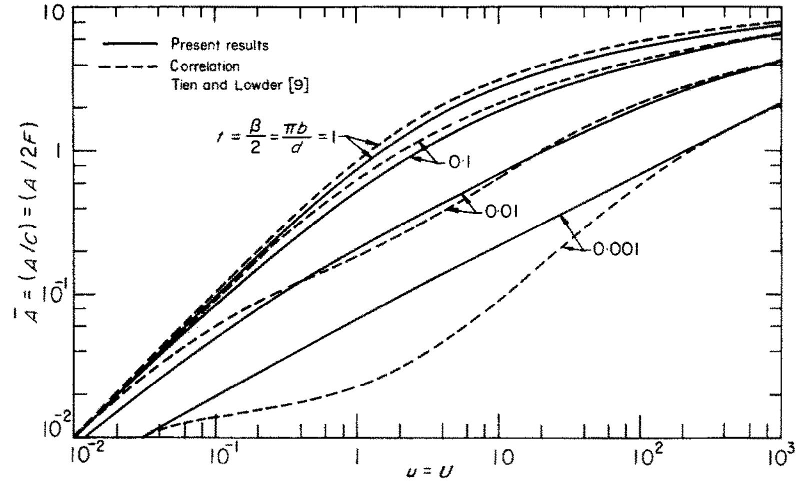

FIG. 4. Comparison of present results with correlation of Tien and Lowder.

ACKNOWLEDGEMENTS

The authors acknowledge with appreciation the support of this research by the National Science Foundation and the assistance of J. C. Lin.

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APPENDIX A

Evaluation of the Integral Defined in Equation (9*b*)

The integral in equation (9b) under the condition $F_P = F_R = F$ is given by

$$I = \frac{2\beta}{\pi} \int_0^\infty \coth (y/2) \frac{(\tau^2 + \beta^2 - y^2) \sin (yd/2\pi F)}{(\tau^2 + \beta^2 - y^2)^2 + 4\tau^2 y^2} \, dy. \tag{A.1}$$

We choose y_0 such that $\coth (y) \simeq 1$ for $y \geqslant y_0$ and obtain

$$I = \frac{1}{\pi} \int_0^{y_0} \coth (y/2) \, G \, dy + \frac{1}{\pi} \int_{y_0}^\infty G \, dy \tag{A.2}$$

Table 5. Total band absorptance: experiment (Tien and Giedt [10], *Abu Romia and Tien* [11], *Burch and Williams* [8]. *present theoretical results, correlation (Tien and Lowder* [9], *Edwards and Menard* [3]). *Carbon monoxide fundamental*

Temperature (°K)	Effective pressure P_e (atm)	Pressure path-length PX (atm cm)	Experimental data (Tien and Giedt [10], Abu-Romia and Tien [11]) (cm^{-1})	Experimental data (Burch and Williams [8]) (cm^{-1})	Present results	Correlation equation (31) [3, 9]
300	0·51	0·5	22·0	27	27·5	31·7
	1·02	1·0	48·5	53	53·9	61·6
	2·04	2	90·0	95	93·2	100·5
	3·06	3	127·2	125	122	126·3
	0·255	1·25	30·2	31	31·2	34·3
	0·51	2·5	58·2	60	60·0	69·5
	1·02	5	112·0	110	99·6	113·5
	2·04	10	159·2	150	152	160·5
	3·06	15	193·5	180	187	187·3
	0·255	2·5	45·0	44	43·3	44·9
	0·51	5	89·0	80	78·6	91·4
	1·02	10	148·0	130	126	138·9
	2·04	20	184·0	170	188	186·2
	3·06	30	205·0		219	209·7
	0·255	5	66·0	60	60·0	69·5
	0·51	10	122·0	105	99·6	115·6
	1·02	20	169·0	155	152	164·2
	2·04	40	210·0		212	212·0
	3·06	60	226·0		250	239·0
1800	1·02	10	129		141	147
	1·53	15	172		193	193
	2·04	20	195		237	230
	2·55	25	247		274	258
	3·06	30	278		308	282
	1·02	20	159		184	200
	1·83	30	221		247	254
	2·04	40	268		297	291
	2·55	50	317		337	323
	3·06	60	347		372	343

where

$$G = \left[\frac{\beta - y}{\tau^2 + (\beta - y)^2} + \frac{\beta + y}{\tau^2 + (\beta + y)^2}\right] \sin(yd/2\pi F). \tag{A.3}$$

Equation (A.2) may also be written in the form

$$I = B_1 + B_2 + B_3 \tag{A.4}$$

with

$$B_1 = \frac{1}{\pi}\int_0^{y_0} \coth(y/2)\, G\, \mathrm{d}y \tag{A5}$$

$$B_2 = -\frac{1}{\pi}\int_0^{y_0} G\, \mathrm{d}y$$

$$B_3 = \frac{1}{\pi}\int_0^{\infty} G\, \mathrm{d}y. \tag{A.7}$$

After some manipulation the integral, B_3, defined in equation (A.7) may be written as follows:

$$B_3 = \underbrace{\frac{2}{\pi}\int_0^{\beta} \frac{\beta - y}{\tau^2 + (\beta - y)^2} \sin(yd/2\pi F)\, \mathrm{d}y}_{B_{3,a}} + \frac{1}{\pi} \sin(\mathrm{d}\beta/2\pi F)$$
$$[\mathrm{e}^{-\mathrm{d}\tau/2\pi F}\, Ei^{(\mathrm{d}\tau/2\pi F)} + \mathrm{e}^{\mathrm{d}\tau/2\pi F}\, Ei(-\mathrm{d}\tau/2\pi F)] \tag{A.8}$$

where Ei is the exponential integral function (13). In obtaining equation (A.8) we have made use of equations 3.723–5 of [13]. Combining the integrals, $B_{3,a}$ and B_2, making the approximation $\sin(yd/2\pi F) \simeq yd/2\pi F$, and evaluating the resulting integral yields

$$(B_2 + B_{3,a})(-\pi 2\pi F/d) = 2\beta - \tau \tan^{-1}\left(\frac{\beta - y_0}{\tau}\right) - \tau \tan^{-1}\left(\frac{\beta + y_0}{\tau}\right) + \beta \log \tau^2 - \frac{\beta}{2} \log [\tau^2 + (\beta - y_0)^2] [\tau^2 + (\beta + y_0)^2]. \quad \text{(A.9)}$$

The remaining integral, B_1, may be readily evaluated for the conditions $\sin(yd/2\pi F) \approx yd/2\pi F$ and $\tau^2 + \beta^2 \gg y_0^2$*, by using equation (2.479–8) of [13]. The result is

$$B_1 = \frac{1}{\pi} \frac{d}{2\pi F} \left(\frac{11{\cdot}1}{\tau^2 + \beta^2}\right) 2\beta \quad \text{(A.10)}$$

where we have used $y_0 = 4$. We finally obtain for equation (A.4) the result that

$$I = \frac{1}{\pi} \frac{d}{2\pi F} \left\{\frac{22{\cdot}2\,\beta}{\tau^2 + \beta^2} - 2\beta + \tau \left[\tan^{-1}\left(\frac{\beta - 4}{\tau}\right) + \tan^{-1}\left(\frac{\beta + 4}{\tau}\right)\right] + \frac{\beta}{2} \log ([\tau^2 + (\beta - 4)^2][\tau^2 + (\beta + 4)^2]/\tau^4)\right\} + \frac{1}{\pi} \sin(d\beta/2\pi F) [\mathrm{e}^{-d\tau/2\pi F} Ei(d\tau/2\pi F) - \mathrm{e}^{d\tau/2\pi F} E_1(d\tau/2\pi F)] \quad \text{(A.11)}$$

subject to the restrictions noted above. The absorption coefficient, k_τ, has been evaluated from equations (9a) and (A.11) and the results are tabulated in Tables 1 and 2 under the columns designated numerical.

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* This restriction can be omitted, for example, by expanding $\coth(y/2)$ and directly evaluating the resulting integral. This has been carried out to obtain the numerical values presented in Table 1 for the smaller values of τ.

APPENDIX B

Simplified Limiting Expressions for the Total Band Absorptance

We consider the condition $\exp(-d/2F) \approx 1$ for $F = F_P$ and $F = F_R$. The result for the total band absorptance for large values of β is then given by

$$\frac{A}{F_P + F_R} = \ln u + \gamma + E_1(u) \quad \text{(B.1)}$$

For small values of β the following results are obtained:

$$\frac{A}{F_P + F_R} = \beta \left\{\frac{u}{\beta} \mathrm{e}^{-u/\beta} \left[I_0\left(\frac{u}{\beta}\right)\left(2 + \frac{\beta}{u}\right) + 2I_1\left(\frac{u}{\beta}\right)\right] - 1\right\} \quad \text{for } u \ll 2/\beta; \quad \text{(B.2)}$$

$$\frac{A}{F_P + F_R} = 2 \int_0^{(u\beta/2)^{\frac{1}{2}}} \operatorname{erf}(z) \frac{\mathrm{d}z}{z} = \frac{4}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n (u\beta/2)^{(2n+1)/2}}{n!\,(2n + 1)^2} \quad \text{for } u \gg \beta; \quad \text{(B.3)}$$

$$\frac{A}{F_P + F_R} = 2\left(\frac{2\beta u}{\pi}\right)^{\frac{1}{2}} \quad \text{for } \beta \ll u \ll \frac{2}{\beta} \quad \text{(B.4)}$$

and

$$\frac{A}{F_P + F_R} = \ln(u\beta/2) + 2(0{\cdot}98) \quad \text{for } \frac{2}{u} \ll \beta \ll u. \quad \text{(B.5)}$$

The integral in equation (B.3), $\int_0^x [\operatorname{erf}(z)/z]\,\mathrm{d}z$ is tabulated in Table 4.

DÉTERMINATION THÉORIQUE DU COEFFICIENT D'ABSORPTION ET ABSORPTION TOTALE AVEC APPLICATION SPÉCIFIQUE À L'OXYDE DE CARBONE

Résumé—Des expressions analytiques sont obtenues pour le coefficient d'absorption et l'absorption totale pour une bande vibration-rotation. Une application spécifique est faite au cas de l'oxyde de carbone et un bon accord avec les résultats expérimentaux est obtenu.

THEORETISCHE BESTIMMUNG DES ABSORPTIONSKOEFFIZIENTEN UND DER GESAMTBANDABSORPTION MIT SPEZIELLER ANWENDUNG AUF KOHLENMONOXID

Zusammenfassung—Für ein Vibrations-Rotationsband sind analytische Beziehungen für den Absorptionskoeffizienten und die Gesamtbandabsorption angegeben. Eine spezielle Anwendung wurde für Kohlenmonoxid vorgenommen; gute Übereinstimmung mit Versuchsergebnissen wurde erzielt.

ТЕОРЕТИЧЕСКИЙ РАСЧЕТ КОЭФФИЦИЕНТА ПОГЛОЩЕНИЯ И СУММАРНОЙ СПЕКТРАЛЬНОЙ ПОГЛОЩАТЕЛЬНОЙ СПОСОБНОСТИ ПРИМЕНИТЕЛЬНО К ОКИСИ УГЛЕРОДА

Аннотация—Получены аналитические выражения для коэффициента поглощения и суммарной спектральной поглощательной способности вибрационно-вращательной полосы. Затем приводится частный случай применения к окиси углерода, и получено хорошее соответствие с экспериментальными результатами.