

## Approximate Emissivity Calculations for Polyatomic Molecules. I. CO<sub>2</sub>\*

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Approximate emissivity calculations for CO<sub>2</sub> have been carried out, as a function of optical density, at 300 and at 600°K. The calculations involve the assumption that the rotational lines overlap extensively. This condition appears to be satisfied at total pressures above about 1 atmos. Comparison of the values calculated from spectroscopic data with the emissivities tabulated by Hottel and his collaborators shows satisfactory agreement. The analysis presented in this manuscript emphasizes the fact that it is possible to obtain reasonable estimates for the engineering emissivity without performing extensive analytical work, provided the physical principles are understood and the needed spectroscopic data are available.

### I. INTRODUCTION

IN a series of recently published papers we have attempted to estimate the engineering emissivities of diatomic molecules by utilizing basic spectroscopic constants. Tractable methods of calculation have been developed for (a) complete overlapping between rotational lines<sup>1</sup> and for (b) separated rotational lines.<sup>2</sup> Although accurate theoretical calculations of gas emissivities from spectroscopic data for polyatomic molecules involve formidable computational difficulties, it is to be expected that approximate calculations can be carried out with relatively little effort by utilizing approximations similar to those introduced for the study of diatomic molecules.<sup>1,2</sup> For CO<sub>2</sub> it has been found that the total absorptivity at room temperature is substantially independent of pressure at pressures exceeding about 1 atmos,<sup>3</sup> thus indicating extensive overlapping between rotational lines. Accordingly, it is not unreasonable to base the present preliminary calculations on the assumption that extensive overlapping between rotational lines does occur. The results would be expected to apply, for example, at room temperature for total pressures in excess of 1 atmos and at 3000°K at pressures in excess of 11 atmos.<sup>3</sup> Since it appears quite likely that the actual range of validity of the results covers a larger range of total pressures, we shall not hesitate to show that calculated emissivities agree reasonably well with empirical data obtained<sup>4</sup> at 1 atmos at a temperature of 600°K as well as at 300°K. Perhaps the most important conclusion which can be derived from the present analysis is the statement that the analytical labor involved in making approximate emissivity calculations for a polyatomic molecule with overlapping rotational lines is trivial provided the im-

portant physical principles are understood and the needed spectroscopic data are available. It is only fair to note, however, that all of the needed integrated intensity measurements have not yet been performed for CO<sub>2</sub> in spite of the fact that several papers dealing with intensity measurements have been published recently.<sup>5-7</sup>

### II. BASIC RELATIONS

Theoretical considerations of intensities for various transitions of the CO<sub>2</sub> molecule were summarized by Dennison a number of years ago.<sup>8</sup> We shall reproduce here the parts of the analysis which are useful for making approximate emissivity estimates on CO<sub>2</sub>.

Frequencies ( $\nu$ ) and wave numbers ( $\omega$ ) corresponding to transitions between fixed energy levels are given by the Bohr frequency condition

$$\nu = c\omega = (\Delta W_{V'} + \Delta W_{R'})/h, \quad (1)$$

where  $\Delta W_{V'}$  and  $\Delta W_{R'}$  represent, respectively, the changes in vibrational and rotational energy corresponding to the frequency  $\nu$ ,  $h$  is Planck's constant, and  $c$  represents the velocity of light. According to the results of Dennison and Adel,<sup>9,10</sup> the rotational ( $W_{R'}$ ) and vibrational ( $W_{V'}$ ) energies for CO<sub>2</sub> are given, respectively, by the expressions

$$W_{R'} = hc(j^2 + j - l^2)[0.3925 - 0.00058(n_1 + \frac{1}{2}) + 0.00045(n_2 + 1) - 0.00307(n_3 + \frac{1}{2})] + 1.7hc(l^2 - 1) \quad (2)$$

and

$$W_{V'} = hc[1351.2(n_1 + \frac{1}{2}) + 672.2(n_2 + 1) + 2396.4(n_3 + \frac{1}{2}) - 0.3(n_1 + \frac{1}{2})^2 - 1.3(n_2 + 1)^2 - 12.5(n_3 + \frac{1}{2})^2 + 5.7(n_1 + \frac{1}{2})(n_2 + 1) - 21.9(n_1 + \frac{1}{2})(n_3 + \frac{1}{2}) - 11.0(n_2 + 1)(n_3 + \frac{1}{2})]. \quad (3)$$

\* A. M. Thorndike, *J. Chem. Phys.* **15**, 868 (1947).

† D. F. Eggers, Jr. and B. L. Crawford, Jr., *J. Chem. Phys.* **19**, 1554 (1951).

<sup>1</sup> Weber, Holm, and Penner, *J. Chem. Phys.* **20**, 1820 (1952).

<sup>2</sup> D. M. Dennison, *Revs. Modern Phys.* **3**, 280 (1931).

<sup>3</sup> D. M. Dennison, *Revs. Modern Phys.* **12**, 175 (1940).

<sup>4</sup> Slight corrections to the listed numerical values have been noted by W. S. Benedict and his collaborators. For the present purposes these corrections are negligibly small. Recent work on frequencies of lines belonging to CO<sub>2</sub> is described in the following papers: Benedict, Herman, and Silverman, *J. Chem. Phys.* **19**, 1325 (1951); Taylor, Benedict, and Strong, *Progress Report on "Infrared Spectra of H<sub>2</sub>O and CO<sub>2</sub> at 500°C."* Contract Nonr 248-01, The Johns Hopkins University, March, 1952.

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† Failure to receive Referee's report and loss of the original manuscript caused unusual delay in publication time.

<sup>1</sup> (a) S. S. Penner, *J. Appl. Phys.* **21**, 685 (1950); (b) *J. Appl. Mech.* **18**, 53 (1951); (c) S. S. Penner and D. Weber, *J. Appl. Phys.* **22**, 1164 (1951).

<sup>2</sup> (a) Penner, Ostrander, and Tsien, *J. Appl. Phys.* **23**, 256 (1952); (b) S. S. Penner, *J. Appl. Phys.* **23**, 825 (1952).

<sup>3</sup> Holm, Weber, and Penner, *J. Appl. Phys.* **23**, 1283 (1952).

<sup>4</sup> W. H. McAdams, *Heat Transmission* (McGraw-Hill Book Company, Inc., New York, 1942), Chapter III by H. C. Hottel.

Here  $n_1$ ,  $n_2$ , and  $n_3$  are the vibrational quantum numbers associated with the fundamental vibration frequencies  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , respectively. The quantum number  $l$  measures the angular rotation, in units of  $h/2\pi$ , which is associated with the degenerate (bending)  $\nu_2$  vibration. The rotational energy levels are identified by the rotational quantum number  $j$ .

The selection rules<sup>9</sup> for the transitions  $n_1 n_2 n_3 \rightarrow n_1' n_2' n_3'$  may be summarized as follows. For the perpendicular bands,  $\Delta n_2$  odd,  $\Delta n_3$  even,  $\Delta l = \pm 1$ . For the parallel bands,  $\Delta n_2$  even,  $\Delta n_3$  odd,  $\Delta l = 0$ . The rotational selection rules are  $\Delta j = \pm 1, 0$ .

The amplitude factors<sup>8</sup> for given rotational transitions are<sup>11</sup>

$$\left( A_{j l}^{j l} \right)^2 = \frac{l^2}{j(j+1)}, \quad (4)$$

$$\left( A_{j-1 l}^{j l} \right)^2 = \frac{j^2 - l^2}{j(2j+1)} = \frac{2j-1}{2j+1} \left( A_{j-1 l}^{j-1 l} \right)^2, \quad (4a)$$

$$\left( A_{j l \mp 1}^{j l} \right)^2 = \frac{(j \pm l)(j \mp l + 1)}{4j(j+1)}, \quad l \neq 0, \quad (4b)$$

$$\left( A_{j 1}^{j 0} \right)^2 = \frac{1}{2}, \quad (4c)$$

$$\left( A_{j-1 l \mp 1}^{j l} \right)^2 = \frac{(j \pm l)(j \pm l - 1)}{4j(2j+1)}, \quad l \neq 0, \quad (4d)$$

$$\left( A_{j-1 1}^{j 0} \right)^2 = \frac{j-1}{2(2j+1)}, \quad (4e)$$

$$\left( A_{j l \pm 1}^{j-1 l} \right)^2 = \frac{(j \pm l)(j \pm l + 1)}{4j(2j-1)}, \quad l \neq 0, \quad (4f)$$

$$\left( A_{j 1}^{j-1 0} \right)^2 = \frac{j+1}{2(2j-1)}. \quad (4g)$$

In Eqs. (4) to (4g) the convention has been adopted that the amplitude factor corresponding to the transi-

tion  $j, l \rightarrow j', l'$  has been written as  $\left( A_{j l}^{j' l'} \right)$ .

The integrated absorption for a given transition from the lower-energy level  $n_1 n_2 n_3$ ;  $j$  to the upper-energy level  $n_1' n_2' n_3'$ ;  $j'$  is designated as  $S \equiv S(n_1 n_2 n_3; j \rightarrow n_1' n_2' n_3'; j')$  and is given<sup>8</sup> by the approximate relation

$$S = (8\pi^3 \nu N_T / 3hc Q_V Q_R') \times \{ \exp[-W_V'(n_1, n_2, n_3) + W_R'(j, l)] / kT \} \times g_{j' l'} \left( A_{j l}^{j' l'} \right)^2 \beta^2 [1 - \exp(-h\nu/kT)]. \quad (5)$$

<sup>11</sup> The amplitude factors given in Eqs. (4) to (4g) are 4 times as large as those listed by Dennison (reference 8) because we are using a Fourier series in time of the form  $\cos(2\pi\nu t)$  rather than  $\exp(2\pi i \nu t)$ .

In Eq. (5),  $\nu \equiv \nu(n_1 n_2 n_3; j \rightarrow n_1' n_2' n_3'; j')$  is the Bohr frequency corresponding to the indicated change in the quantum numbers;  $\ddagger N_T$  = total number of molecules per unit volume per unit pressure;  $g_{j' l'}$  = statistical weight of the upper state with  $g_{j' l'} = 2j' + 1$  for  $l' = 0$  and  $g_{j' l'} = 2(2j' + 1)$  for  $l' \neq 0$ ;  $\beta \equiv \beta(n_1 n_2 n_3 \rightarrow n_1' n_2' n_3')$  is a factor which must be determined empirically and corresponds to the matrix element of the electric moment in the molecule associated with the indicated change in (vibrational) quantum numbers;  $\ddagger Q_R' = \sum_j \sum_l g_{j l} \exp[-W_R'(j, l)/kT]$  = complete rotational partition function;  $Q_V' = \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp[-W_V'(n_1, n_2, n_3)/kT]$  = complete vibrational partition function.

The amplitude factors given in Eqs. (4) to (4g) are based on the assumption that vibration-rotation interactions have a negligibly small influence on amplitude factors. For this reason, the use of Eq. (5) involves somewhat cruder calculations than were employed in the calculations on diatomic molecules with nonoverlapping rotational lines.<sup>2</sup>

For the purposes of approximate radiant-heat transfer calculations, it is convenient to use the integrated absorption coefficient for a given band. Let

$$\alpha(n_1 n_2 n_3 \rightarrow n_1' n_2' n_3') = \sum_{j, j'} S(n_1 n_2 n_3; j \rightarrow n_1' n_2' n_3'; j'). \quad (6)$$

For the parallel bands  $\Delta l = 0$  and

$$\sum_{j'} g_{j' l} \left( A_{j l}^{j' l} \right)^2 = g_{j l}$$

according to the Burger and Dorgelo summation rules, which may be verified by use of Eqs. (4) to (4g) by utilizing the selection rules. Hence we obtain from Eqs. (5) and (6) the useful result

$$\alpha(n_1 n_2 n_3 \rightarrow n_1' n_2' n_3') = (8\pi^3 \beta^2 \nu N_T / 3hc Q_V) g_l \times \{ \exp[-W_V(n_1, n_2, n_3, l)/kT] \} [1 - \exp(-h\nu/kT)] \text{ with } g_l = 1 \text{ for } l = 0 \text{ and } g_l = 2 \text{ for } l \neq 0, \quad (7)$$

where we have set

$$W_V'(n_1, n_2, n_3) + W_R'(j, l) = W_V(n_1, n_2, n_3, l) + W_R(j),$$

$$Q_V = \sum_{n_1, n_2, n_3, l} \exp(-W_V/kT), Q_V' Q_R' = Q_V Q_R \text{ with } Q_R = \sum_j g_j \exp[-W(j)/kT],$$

and  $g_{j l} = g_j \times g_l$ . If the assumption is not made that  $\nu \equiv \nu \simeq \nu(n_1 n_2 n_3; 0 \rightarrow n_1' n_2' n_3'; 0)$  a slight correction is obtained to Eq. (7).<sup>12, 13</sup>

<sup>†</sup> Although we shall not indicate explicitly the changes in the (vibrational) quantum numbers involved, both  $\nu$  and  $\beta$  do, of course, vary from one vibration-rotation band to another.

<sup>12</sup> B. L. Crawford, Jr. and H. L. Dinsmore, J. Chem. Phys. 18, 983, 1682 (1950).

<sup>13</sup> Eggers and Crawford (reference 6) have shown how to relate for CO<sub>2</sub> the matrix coefficients to the coefficients of Taylor series expansions of the potential energy and dipole moment about their respective equilibrium values.



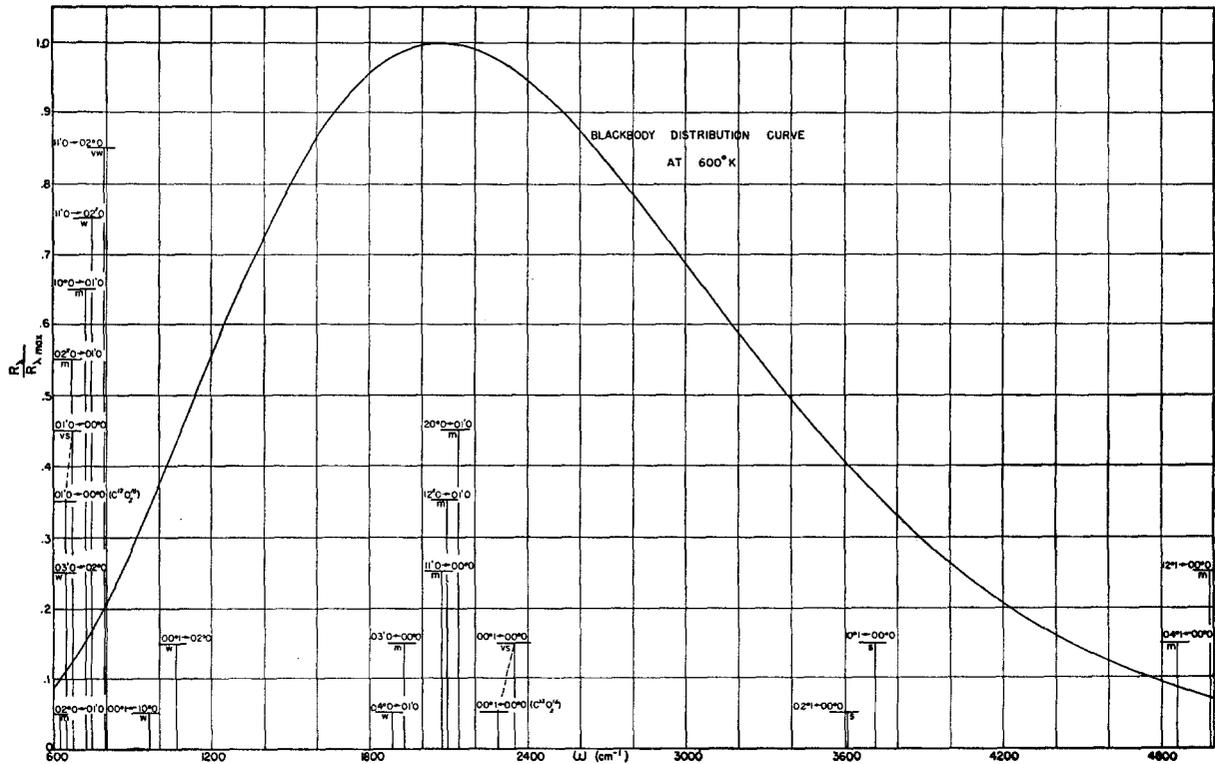


FIG. 2. Positions of centers of vibration-rotation bands, observed at room temperature, between 600 and 4800 cm<sup>-1</sup>. Also shown is the intensity ratio  $R_{\lambda}/R_{\lambda, \max}$  for a blackbody at 600°K.

rotation bands for CO<sub>2</sub> at 300°K has been drawn in Figs. 1 to 3. In these diagrams the abscissa is the wave number whereas the ordinate represents, in arbitrary units which vary from one band to another, the intensity. Integrated intensities at 300°K are given in Table I in so far as they are available.<sup>7</sup> For the strongest bands ( $\nu_2$  and  $\nu_3$  fundamentals) the contributions from the isotopic molecule C<sup>18</sup>O<sub>2</sub><sup>16</sup> are also shown. This chemical species constitutes about 1.1 percent of all of the CO<sub>2</sub> present and makes contributions to the total emissivity which are not negligibly small for moderate and large optical densities of emitter. Also shown in Figs. 1 to 3 are the spectral intensities of radiation emitted by a blackbody at 300, 600, and 1500°K, again utilizing arbitrary scales along the ordinates, which are, however, consistent for any one of the given temperatures.

Reference to Fig. 1 shows that the principal contribution to the total radiant heat transfer at room temperature must occur from the spectral region around the  $\nu_2$  fundamental. Thus it is readily shown<sup>1</sup> that the "limiting emissivity" for CO<sub>2</sub> at 300°K is in the neighborhood of 0.4 with more than 90 percent of the total contributions made by the wave-number region extending from 551 to 830 cm<sup>-1</sup>.

It is physically obvious that the engineering emissivity  $E$  at 300°K is determined by the 01<sup>0</sup>-00<sup>0</sup> transition in the limit of zero optical density of the

emitter. As was pointed out in an earlier publication,<sup>1</sup> the emissivity as a function of optical density (partial pressure  $p$  of emitter  $\times$  optical pathlength  $L$ ) for very small values of  $pL$  can be computed quite accurately either by utilizing a treatment applicable for nonoverlapping lines<sup>2</sup> or by using average absorption coefficients. The emissivity  $E_{667}$  of the band with center at 667 cm<sup>-1</sup>, as calculated from Eq. (30) of reference 2a,

TABLE I. Integrated intensities for vibration-rotation bands of CO<sub>2</sub> (reference 7).

Band center (cm <sup>-1</sup> )	Transition	$\alpha$ (cm <sup>-2</sup> -atmos <sup>-1</sup> )
5109	00 <sup>0</sup> →20 <sup>0</sup> 1	0.426
4984	00 <sup>0</sup> →12 <sup>0</sup> 1	1.01
4861	00 <sup>0</sup> →04 <sup>0</sup> 1	0.272
3716	00 <sup>0</sup> →10 <sup>0</sup> 1	42.3
3609	00 <sup>0</sup> →02 <sup>0</sup> 1	28.5
2349	00 <sup>0</sup> →00 <sup>0</sup> 1	2706
2137	01 <sup>0</sup> →20 <sup>0</sup> 0	0.147
2094	01 <sup>0</sup> →12 <sup>0</sup> 0	
2077	00 <sup>0</sup> →11 <sup>0</sup> 0	
1933	00 <sup>0</sup> →03 <sup>0</sup> 0	
1886	01 <sup>0</sup> →04 <sup>0</sup> 0	0.083
721	01 <sup>0</sup> →10 <sup>0</sup> 0	
668	01 <sup>0</sup> →02 <sup>0</sup> 0	171.5
667	00 <sup>0</sup> →01 <sup>0</sup> 0	
648	02 <sup>0</sup> →03 <sup>0</sup> 0	
618	01 <sup>0</sup> →02 <sup>0</sup> 0	
961	10 <sup>0</sup> →00 <sup>0</sup> 1	0.0219*
1064	02 <sup>0</sup> →00 <sup>0</sup> 1	0.0532*

\* Unpublished data obtained by D. Weber.



of empirical measurements<sup>4</sup> are also shown in Fig. 4. For  $pL \leq 0.06$  ft-atmos, the "empirical" data are really extrapolated results. Reference to Fig. 4 shows fair agreement between calculated and observed values of  $E$  for the reasonable values  $\alpha_{667} = 171$  and  $\alpha_{721} = 1$  cm<sup>-2</sup> atmos<sup>-1</sup>. At very small values of  $pL$  the calculated emissivities<sup>§</sup> are larger than the extrapolated empirical data but must be considered to be more reliable since they depend only on the numerical value of  $\alpha_{667}$ , which is known with fair accuracy.<sup>5-7</sup> Our ability to calculate  $E$  at very large values of  $pL$  is limited by the lack of adequate intensity data for the transitions 02<sup>0</sup>→01<sup>0</sup>, 11<sup>0</sup>→02<sup>0</sup>, and 11<sup>0</sup>→02<sup>0</sup>. However, it is clear that as  $pL$  is increased sufficiently above 3 ft-atmos,  $E$  must approach about 0.4 and will then increase only very slowly as exceedingly large values of  $pL$  are obtained.

The discussion of emissivity calculations on CO<sub>2</sub> at 300°K as a function of  $pL$  is mostly of academic interest. However, it is instructive in so far as it exemplifies the inherent simplicity of the analysis if adequate spectroscopic data are available.

#### IV. APPROXIMATE EMISSIVITY CALCULATIONS AT 600°K

It is evident from Fig. 2 that the major contributions to radiant heat transfer at 600°K are made by vibration-rotation bands in the spectral region between 890 and 2400 cm<sup>-1</sup>. As  $pL$  goes to zero it is expected that the total emissivity  $E$  will become substantially equal to the emissivity of the intense  $\nu_3$  fundamental of C<sup>12</sup>O<sub>2</sub><sup>16</sup> with appropriate corrections for contributions from the isotopic species C<sup>13</sup>O<sub>2</sub><sup>16</sup>. Although we are unable to complete the emissivity calculations at 600°K, because the needed spectroscopic data are not available, the engineering emissivity is estimated correctly for small values of  $pL$ . This result emphasizes the fact that relatively accurate emissivity calculations for polyatomic molecules can be performed without difficulty as soon as the necessary intensity measurements are available.

For the weaker bands, i.e., for all bands but the  $\nu_3$  fundamental, we shall define the effective band width as the wave-number region for which  $S$  exceeds about 10<sup>-3</sup> of its maximum value. For the  $\nu_3$  fundamental we set the effective band width equal to the wave-number range for which  $(SpL/0.7) \geq 0.1$ .|| The long wave-

§ The dotted curve in Fig. 2 corresponds to  $\alpha_{667} = 29$  and  $\alpha_{721} = 1$  cm<sup>-2</sup> atmos<sup>-1</sup>. Although this curve represents a good fit of the empirical data, the result cannot be considered to be significant since  $\alpha_{667}$  is known to be much larger than 29 cm<sup>-2</sup> atmos<sup>-1</sup>.

|| Although the definitions of the effective band widths are somewhat arbitrary, it is easily shown that calculated values of  $E$  are quite insensitive to the chosen band widths. This result is caused by automatic choice of too small absorption coefficients for band widths which are too large, and conversely (compare reference 1a). Use of the quantity  $SpL/0.7 \geq 0.1$  assures inclusion within the band width of the  $\nu_3$  fundamental of all of the rotational lines with average emissivities in excess of 0.1. Substantially the same numerical values for the effective band widths of the  $\nu_3$  fundamental are obtained if the lines with  $SpL/0.7 \geq 10^{-1-n}$  are included, where  $n$  is a number which does not differ from unity by more than a factor of three or four.

number limit of the  $\nu_3$  fundamental is set equal to 2410 cm<sup>-1</sup>, i.e., 11 cm<sup>-1</sup> beyond the band head. This choice allows for the many tails of rotational lines which "spill" across the band-head limit. We proceed by calculating separately the partial emissivities for selected wave-number regions.

#### A. Contributions of the 00<sup>0</sup>1→10<sup>0</sup> and 00<sup>0</sup>1→02<sup>0</sup> Bands

The criterion  $(S/S_{\max}) \geq 10^{-3}$  for the weaker bands leads to band widths of the order of 140 cm<sup>-1</sup> at 600°K. The integrated intensity for a given vibration-rotation band at the arbitrary temperature  $T$ , divided by the measured value at 300°K, is obtained by the use of Eqs. (7), (8), or (9). From these relations we find for the integrated intensity  $\alpha$  of the band whose ground state is identified by the set of quantum numbers  $n_1 n_2' n_3$  the result

$$\begin{aligned} \alpha(T^\circ\text{K})/\alpha(300^\circ\text{K}) &= (300/T) \\ &\times \{Q_V(300^\circ\text{K}) \exp[W_V(00^0)/300k]\} \\ &\times \{Q_V(T^\circ\text{K}) \times \exp[W_V(00^0)/kT]\}^{-1} \\ &\times \{\exp[-W_V(n_1 n_2' n_3) - W_V(00^0)] \\ &\times [(kT)^{-1} - (300k)^{-1}]\} [1 - \exp(-h\nu/kT)] \\ &\times [1 - \exp(-h\nu/300k)], \quad (10) \end{aligned}$$

where

$$\begin{aligned} Q_V(T) \exp[W_V(00^0)/kT] &\simeq [1 - \exp(-1388hc/kT)]^{-1} \\ &\times [1 - \exp(-667hc/kT)]^{-2} \\ &\times [1 - \exp(-2349hc/kT)]^{-1}. \quad (11) \end{aligned}$$

The use of Eqs. (10) and (11) leads to the following results for the 00<sup>0</sup>1→10<sup>0</sup> and 00<sup>0</sup>1→02<sup>0</sup> bands, respectively:  $\alpha_{961}(600^\circ\text{K}) \simeq 9.29\alpha_{961}(300^\circ\text{K}) = 0.204$  cm<sup>-2</sup> atmos<sup>-1</sup>;  $\alpha_{1064}(600^\circ\text{K}) \simeq 7.22\alpha_{1064}(300^\circ\text{K}) = 0.385$  cm<sup>-2</sup> atmos<sup>-1</sup>. Hence the total contribution to the emissivity

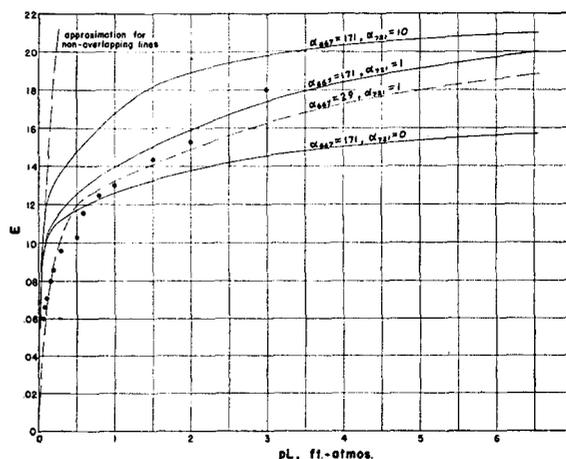


FIG. 4. Engineering emissivity  $E$  as a function of  $pL$  for CO<sub>2</sub> at 300°K. Integrated intensities  $\alpha$  are expressed in cm<sup>-2</sup> atmos<sup>-1</sup>. The results based on empirical measurements (see reference 4) are shown as circles.

TABLE II. Absolute intensities at 300 and at 600°K for several vibration-rotation bands in the 5-micron region, based on intensity calculations using harmonic oscillator approximations (see Appendix I). The value  $0.147 \text{ cm}^{-2} \text{ atm}^{-1}$  for the sum of the bands centered at 2137, 2094, and 2077  $\text{cm}^{-1}$  served as standard to fix the absolute intensity scale.

Transition	$\alpha$ at 300°K ( $\text{cm}^{-2}\text{-atmos}^{-1}$ )	$\alpha$ at 600°K ( $\text{cm}^{-2}\text{-atmos}^{-1}$ )
00 <sup>0</sup> →11 <sup>0</sup>	0.12	0.040
01 <sup>0</sup> →12 <sup>0</sup>	0.020	0.032
01 <sup>0</sup> →20 <sup>0</sup>	0.0045	0.0075
01 <sup>0</sup> →12 <sup>0</sup>	0.00048	0.00079
02 <sup>0</sup> →13 <sup>0</sup>	0.0012	0.0099
03 <sup>0</sup> →14 <sup>0</sup>	0.000038	0.0020
02 <sup>0</sup> →21 <sup>0</sup>	0.00019	0.0015
10 <sup>0</sup> →21 <sup>0</sup>	0.00029	0.0026
11 <sup>0</sup> →30 <sup>0</sup>	0.0000053	0.00026

obtained from the two bands under discussion is

$$E_{961} + E_{1064} = 0.052[1 - \exp(-1.40 \times 10^{-3} pL)] + 0.017[1 - \exp(-4.15 \times 10^{-3} pL)] + 0.054[1 - \exp(-2.75 \times 10^{-3} pL)], \quad (12)$$

where  $pL$  is expressed in  $\text{cm-atmos}$ .

### B. Contributions Made by the Bands between 1800 and 2210 $\text{cm}^{-1}$

It is known from the recent work of Taylor, Benedict, and Strong<sup>15</sup> that an appreciable number of vibration-rotation bands, in addition to the bands shown in Fig. 1 in this region, are observable at 500°C.¶ Since all of these bands involve transitions to excited energy levels, their integrated intensities would be expected to increase as the temperature is raised. Rough absolute intensity estimates for several bands in the 5-micron region are given in Table II at 300 and 600°K. The relative intensity estimates were obtained by using the greatly oversimplified harmonic oscillator approximation described in Appendix I. Thus the contribu-

TABLE III. Emissivities  $E_{2349}$  for  $\text{C}^{12}\text{O}_2^{16}$  and  $\text{C}^{18}\text{O}_2^{16}$  at 600°K as a function of optical density.<sup>a</sup>

$pL$ , $\text{cm-atmos}$	$pL$ , $\text{ft-atmos}$	$E_{2349}(\text{C}^{12}\text{O}_2^{16})$	$E_{2349}(\text{C}^{18}\text{O}_2^{16})$	$E_{2349}(\text{total})$
0.1	0.0033	0.018	0.0005	0.019
0.5	0.0164	0.033	0.0016	0.035
1.0	0.033	0.037	0.0025	0.040
5.0	0.164	0.050	0.0070	0.057
15	0.492	0.051	0.011	0.062
50	1.64	0.052	0.011	0.063
100	3.28	0.053	0.012	0.065
200	6.56	0.055	0.012	0.067

<sup>a</sup> The tabulated values of  $E_{2349}(\text{C}^{18}\text{O}_2^{16})$  correspond to the values which must be added to  $E_{2349}(\text{C}^{12}\text{O}_2^{16})$  in order to obtain  $E_{2349}(\text{total})$ . They do not include emissivities in the (black) region of the  $\nu_3$  fundamental of  $\text{C}^{12}\text{O}_2^{16}$  which is overlapped by the  $\nu_3$  fundamental of  $\text{C}^{18}\text{O}_2^{16}$ .

<sup>15</sup> Taylor, Benedict, and Strong, Progress Report on "Infrared Spectra of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at 500°C," Contract Nonr 248-01, The Johns Hopkins University, Baltimore, March, 1952.

¶ Data of the type presented in reference 15 are valuable aids in performing emissivity calculations. For example, the spectroscopic emission records indicate, at least qualitatively, the vibration-rotation bands which must be included, at temperatures up to 773°K.

tions of both mechanical and of electrical anharmonicities to the intensity have been neglected.

As is evident from the experimental data shown in reference 15, a large number of vibration-rotation bands remain for which even rough intensity data are not available. For this reason no result can be given for the contributions made to the engineering emissivity by the vibration-rotation bands between 1800 and 2100  $\text{cm}^{-1}$ .

### C. Contributions from the $\nu_3$ Fundamental

From the measured integrated intensity<sup>7</sup> for the  $\nu_3$  fundamental at 300°K and by use of Eqs. (10) and (11) we find  $\alpha_{2349} = 1060 \text{ cm}^{-2} \text{ atm}^{-1}$  at 600°K. Of the total integrated intensity per  $(\text{cm}^{-1}) \times (\text{cm}^{-1} \text{ atm}^{-1})$  of

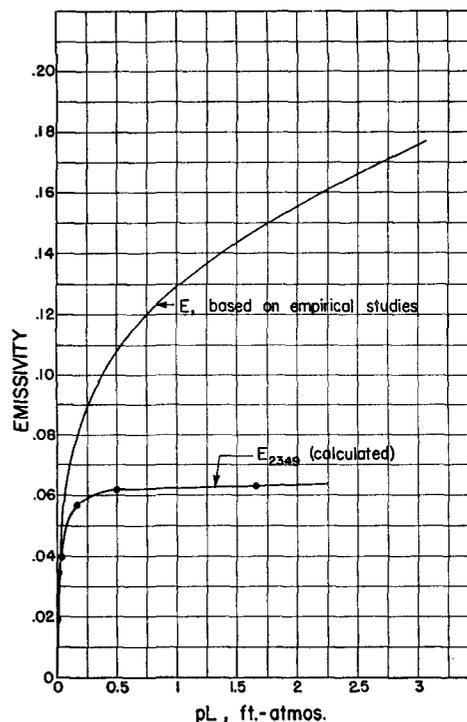


FIG. 5. Engineering emissivity  $E$  as a function of  $pL$  for  $\text{CO}_2$  at 600°K, based on the empirical correlations of H. C. Hottel and R. B. Egbert. Also shown are the calculated contributions to the total emissivity made by the  $\nu_3$  fundamental.

$\text{CO}_2$ ) we associate 98.9 percent with  $\text{C}^{12}\text{O}_2^{16}$  and 1.1 percent with  $\text{C}^{18}\text{O}_2^{16}$ . For the intense  $\nu_3$  fundamental the effective band width corresponds to the wave-number range  $\Delta\omega_{2349}$  for which  $(SpL/0.7) \geq 0.1$  with the band width of the isotopic species determined similarly. In general, the  $\text{C}^{12}\text{O}_2^{16}$  band is black before the isotopic band makes appreciable contributions. The emissivities at 600°K,  $E_{2349}$ , calculated by the use of average absorption coefficients  $\bar{P} = \alpha/\Delta\omega$ , are summarized in Table III as a function of  $pL$ . Comparison of  $E_{2349}(\text{total})$  with the empirical data<sup>4</sup> plotted in Fig. 5 shows that for  $pL \leq 0.033 \text{ ft-atmos}$ ,  $E_{2349}(\text{total})$  is practically identical with the engineering emissivity  $E$ . The result is in accord with expectations and shows

clearly that useful emissivity data can be obtained with practically no analytical work once the physical principles are understood clearly.

**D. Contribution of the 02<sup>0</sup>1→00<sup>0</sup>0 and 10<sup>0</sup>1→00<sup>0</sup>0 Bands**

From the measured integrated intensities<sup>7</sup> we find  $\alpha_{3609} = 9.70 \text{ cm}^{-2} \text{ atm}^{-1}$  for the 02<sup>0</sup>1→00<sup>0</sup>0 band and  $\alpha_{3716} = 14.4 \text{ cm}^{-2} \text{ atm}^{-1}$  for the 10<sup>0</sup>1→00<sup>0</sup>0 band at 600°K. The effective band widths extend from 3539 cm<sup>-1</sup> to 3679 cm<sup>-1</sup> and from 3646 cm<sup>-1</sup> to 3716 cm<sup>-1</sup>, respectively. Using average absorption coefficients the following results are obtained:

$$E_{3609} + E_{3716} \approx 0.0047[1 - \exp(-6.92 \times 10^{-2} pL)] + 0.0017[1 - \exp(-1.72 \times 10^{-1} pL)] + 0.0017[1 - \exp(-1.03 \times 10^{-1} pL)]. \quad (13)$$

**E. The Total (Engineering) Emissivity**

The total (engineering) emissivity is obtained by adding the partial emissivities from selected spectral regions. Since estimates of partial emissivities were not included for all of the important vibration-rotation bands, no general expression for the engineering emissivity can be given although useful results have been obtained for small values of the optical density (compare Sec. IVC and Fig. 5).

**APPENDIX I. RELATIVE INTENSITY CALCULATIONS FOR CO<sub>2</sub> USING HARMONIC OSCILLATOR APPROXIMATIONS\*\***

It is well known that harmonic bands with nonzero matrix components are predicted even to the harmonic oscillator approximation. Calculations of this sort are useful for rough relative intensity estimates although mechanical as well as electrical anharmonicity corrections are neglected. Representative relative intensity estimates have been given, for example, by Benedict<sup>15</sup> and by Kaplan.<sup>16</sup> For the present applications it will be convenient to present a general equation for relative intensities of harmonic bands involving changes in the vibrational quantum number  $\nu_2$ .

The desired result is obtained readily by using the normalized wave functions for the isotropic plane oscillator and an integral involving associated Laguerre

\*\* The author is indebted to Dr. W. S. Benedict and to Dr. L. D. Kaplan for helpful correspondence concerning intensity estimates for harmonic bands of CO<sub>2</sub>.

<sup>16</sup> L. D. Kaplan, J. Chem. Phys. 18, 186 (1950).

TABLE (A-I). Relative intensities for harmonic bands in the 5 $\mu$  region based on harmonic oscillator wave functions.

Transition	$g_l R(n_1 n_2^l 0 \rightarrow n_1' n_2^{l'} 0)$	$\delta(n_1 n_2^l 0 \rightarrow n_1' n_2^{l'} 0)$ at 300°K	$\delta(n_1 n_2^l 0 \rightarrow n_1' n_2^{l'} 0)$ at 600°K
00 <sup>0</sup> →11 <sup>0</sup>	1	1	1
01 <sup>0</sup> →12 <sup>0</sup>	4	0.164	0.810
01 <sup>0</sup> →20 <sup>0</sup>	0.9 <sup>a</sup>	0.0376	0.187
01 <sup>0</sup> →12 <sup>0</sup>	0.1 <sup>a</sup>	0.00395	0.0196
02 <sup>0</sup> →13 <sup>0</sup>	6	0.0101	0.248
03 <sup>0</sup> →14 <sup>0</sup>	8	0.000315	0.0507
02 <sup>0</sup> →21 <sup>0</sup>	0.9 <sup>a</sup>	0.00155	0.0382
10 <sup>0</sup> →21 <sup>0</sup>	1.8 <sup>a</sup>	0.00238	0.0656
11 <sup>0</sup> →30 <sup>0</sup>	0.9 <sup>a</sup>	0.0000438	0.00638

<sup>a</sup> Adjusted according to Benedict to concentrate most of the intensity of resonating bands in the highest frequency member (reference 15).

polynomials first obtained by Schrödinger.<sup>17</sup> In this manner it is easily shown that

$$\begin{aligned} & [\beta(n_1 n_2^l n_3 \rightarrow n_1 n_2^{l'} n_3)]^2 / [\beta(n_1 0^0 n_3 \rightarrow n_1 1^1 n_3)]^2 \\ & = R(n_2^l \rightarrow n_2^{l'}) = [k! k'! / (k+l)!] \\ & \times (p!)^2 \left\{ \sum_{\tau=0}^{\leq k, k'} \binom{p-l}{k-\tau} \binom{p-l'}{k'-\tau} \binom{-p-1}{\tau} \right\}^2, \quad (A1) \end{aligned}$$

where  $k = (1/2)(n_2 - l)$ ,  $k' = (1/2)(n_2' - l')$ ,  $p = (1/2)(l + l' + 1)$ , and  $\binom{n}{k}$  denotes a binomial coefficient.

By combining Eqs. (7) to (9) with Eq. (A1) the following useful result is obtained:

$$\begin{aligned} & \alpha(n_1 n_2^l n_3 \rightarrow n_1 n_2^{l'} n_3) / \alpha(n_1 0^0 n_3 \rightarrow n_1 1^1 n_3) = \delta(n_2^l \rightarrow n_2^{l'}) \\ & = g_l R(n_2^l \rightarrow n_2^{l'}) [v(n_1 n_2^l n_3 \rightarrow n_1 n_2^{l'} n_3) / \\ & v(n_1 0^0 n_3 \rightarrow n_1 1^1 n_3)] \{ \exp[-W_V(n_1, n_2, n_3, l) \\ & - W_V(n_1, 0, n_3, 0)] / kT \} \{ 1 - \exp[-h\nu(n_2^l \rightarrow \\ & n_2^{l'}) / kT] \} \times \{ 1 - \exp[-h\nu(0^0 \rightarrow 1^1) / kT] \}^{-1}. \quad (A2) \end{aligned}$$

Numerical values of  $R(n_2^l \rightarrow n_2^{l'})$  calculated from Eq. (A1) are identical with Benedict's estimates,<sup>15</sup> which utilized data given by Shaffer.<sup>18</sup>

Following Benedict we shall assume that resonance between  $2\nu_2$  and  $\nu_1$  is exact, an approximation which will not change the order of magnitude of the calculated results although it is not in accord with observed infrared and Raman intensities. By utilizing Eqs. (A1) and (A2) relative intensities have been computed for a number of bands in the 5 $\mu$  region at 300 and at 600°K. The results are summarized in Table (A-I).

<sup>17</sup> E. Schrödinger, Ann. Physik 80, 483 (1926).

<sup>18</sup> W. H. Shaffer, Revs. Modern Phys. 16, 245 (1944).