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Approximate Emissivity Calculations for Polyatomic Molecules. I. CO_2*

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Approximate emissivity calculations for CO_2 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[1] and for (b) separated rotational lines.[2] 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.[1,2] For CO_2 it has been found that the total absorptivity at room temperature is substantially independent of pressure at pressures exceeding about 1 atmos,[3] 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.[3] 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[4] 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 important 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_2 in spite of the fact that several papers dealing with intensity measurements have been published recently.[5–7]

II. BASIC RELATIONS

Theoretical considerations of intensities for various transitions of the CO_2 molecule were summarized by Dennison a number of years ago.[8] We shall reproduce here the parts of the analysis which are useful for making approximate emissivity estimates on CO_2.

Frequencies (ν) and wave numbers (ω) corresponding to transitions between fixed energy levels are given by the Bohr frequency condition

$$\nu = c\omega = (\Delta W_V' + \Delta W_R')/h, \tag{1}$$

where $\Delta W_V'$ and $\Delta W_R'$ represent, respectively, the changes in vibrational and rotational energy corresponding to the frequency ν, h is Planck's constant, and c represents the velocity of light. According to the results of Dennison and Adel,[9,10] the rotational (W_R') and vibrational (W_V') energies for CO_2 are given, respectively, by the expressions

$$W_R' = hc(j^2+j-l^2)[0.3925-0.00058(n_1+\tfrac{1}{2}) +0.00045(n_2+1)-0.00307(n_3+\tfrac{1}{2})]+1.7hc(l^2-1) \tag{2}$$

and

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

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

[1] (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).

[2] (a) Penner, Ostrander, and Tsien, J. Appl. Phys. 23, 256 (1952); (b) S. S. Penner, J. Appl. Phys. 23, 825 (1952).

[3] Holm, Weber, and Penner, J. Appl. Phys. 23, 1283 (1952).

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

[5] A. M. Thorndike, J. Chem. Phys. 15, 868 (1947).

[6] D. F. Eggers, Jr. and B. L. Crawford, Jr., J. Chem. Phys. 19, 1554 (1951).

[7] Weber, Holm, and Penner, J. Chem. Phys. 20, 1820 (1952).

[8] D. M. Dennison, Revs. Modern Phys. 3, 280 (1931).

[9] D. M. Dennison, Revs. Modern Phys. 12, 175 (1940).

[10] 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_2 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_2O and CO_2 at 500°C," Contract Nonr 248-01, The Johns Hopkins University, March, 1952.

Here n_1, n_2, and n_3 are the vibrational quantum numbers associated with the fundamental vibration frequencies ν_1, ν_2, and ν_3, respectively. The quantum number l measures the angular rotation, in units of $h/2\pi$, which is associated with the degenerate (bending) ν_2 vibration. The rotational energy levels are identified by the rotational quantum number j.

The selection rules[9] for the transitions $n_1n_2{}^ln_3\rightarrow n_1'n_2'{}^{l'}n_3'$ may be summarized as follows. For the perpendicular bands, Δn_2 odd, Δn_3 even, $\Delta l=\pm 1$. For the parallel bands, Δn_2 even, Δn_3 odd, $\Delta l=0$. The rotational selection rules are $\Delta j=\pm 1, 0$.

The amplitude factors[8] for given rotational transitions are[11]

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

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

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

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

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

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

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

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

In Eqs. (4) to (4g) the convention has been adopted that the amplitude factor corresponding to the transition $j, l\rightarrow j', l'$ has been written as $\left(A_{j\ l}^{j'\ l'}\right)$.

The integrated absorption for a given transition from the lower-energy level $n_1n_2{}^ln_3$; j to the upper-energy level $n_1'n_2'{}^{l'}n_3'$; j' is designated as $S\equiv S(n_1n_2{}^ln_3;\ j\rightarrow n_1'n_2'{}^{l'}n_3';\ j')$ and is given[8] by the approximate relation

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

In Eq. (5), $\nu\equiv\nu(n_1n_2{}^ln_3;\ j\rightarrow n_1'n_2'{}^{l'}n_3';\ j')$ is the Bohr frequency corresponding to the indicated change in the quantum numbers;‡ 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 $l'\neq 0$; $\beta\equiv\beta(n_1n_2{}^ln_3\rightarrow n_1'n_2'{}^{l'}n_3')$ 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;‡ $Q_R'=\sum_j\sum_l g_{jl}\exp[-W_R'(j,l)/kT]$ = 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.[2]

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

$$\alpha(n_1n_2{}^ln_3\rightarrow n_1'n_2'{}^{l'}n_3')=\sum_j\sum_{j'}S(n_1n_2{}^ln_3;\ j\rightarrow n_1'n_2'{}^{l'}n_3';\ j').\tag{6}$$

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

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

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

$$\alpha(n_1n_2{}^ln_3\rightarrow n_1'n_2'{}^{l'}n_3')=(8\pi^3\beta^2\nu'N_T/3hcQ_V)g_l\times\{\exp-[W_V(n_1,n_2,n_3,l)/kT]\}[1-\exp(-h\nu/kT)]$$
$$\text{with } g_l=1 \text{ for } l=0 \text{ and } g_l=2 \text{ for } l\neq 0,\tag{7}$$

where we have set

$$W_{V'}(n_1n_2,n_3)+W_{R'}(j,l)=W_V(n_1,n_2,n_3,l)+W_R(j),$$

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

and $g_{jl}=g_j\times g_l$. If the assumption is not made that $\nu\equiv\nu'\simeq\nu(n_1n_2{}^ln_3;0\rightarrow n_1'n_2'{}^{l'}n_3';0)$ a slight correction is obtained to Eq. (7).[12,13]

[11] 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 $\exp(2\pi i\nu t)$.

‡ Although we shall not indicate explicitly the changes in the (vibrational) quantum numbers involved, both ν and β do, of course, vary from one vibration-rotation band to another.

[12] B. L. Crawford, Jr. and H. L. Dinsmore, J. Chem. Phys. 18, 983, 1682 (1950).

[13] Eggers and Crawford (reference 6) have shown how to relate for CO_2 the matrix coefficients to the coefficients of Taylor series expansions of the potential energy and dipole moment about their respective equilibrium values.

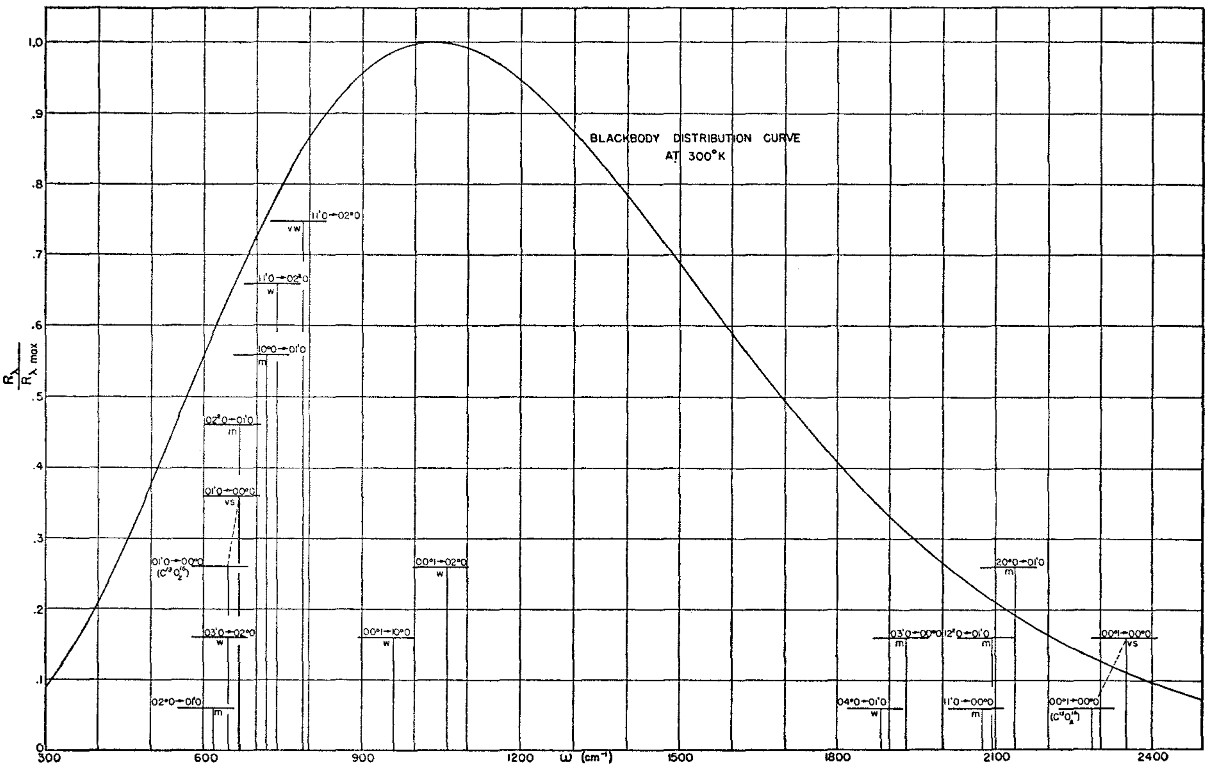

FIG. 1. Positions of centers of vibration-rotation bands, observed at room temperature, between 300 and 2400 cm^{-1}. The designations vs (very strong), s (strong), m (medium), w (weak), and vw (very weak) are those of Herzberg (reference 14). Also shown is the intensity ratio $R_\lambda/R_{\lambda\,\max}$ for a blackbody at 300°K.

For the perpendicular bands $\Delta l \neq 0$ and

$$\sum_{j',l'} g_{j'l'}\left(A_j^{j'\ l'}{}_{l}\right)^2 = g_{jl},$$

$$\sum_{j'} g_{j'l'}\left(A_j^{j'\ l\pm1}{}_{l}\right)^2 = \tfrac{1}{2}g_{jl},\quad \sum_{j',l'} g_{j'l'}\left(A_j^{j'\ l'}{}_{0}\right)^2 = g_{jl}.$$

Hence

$$\alpha(n_1n_2{}^ln_3 \rightarrow n_1'n_2'{}^{l+1}n_3') = (4\pi^3\beta^2\nu' N_T/3hcQ_V)g_l \times\{\exp-[W_V(n_1,n_2,n_3,l)/kT]\}[1-\exp(-h\nu/kT)],$$
$$\text{where } g_l = 1 \text{ for } l=0 \text{ and } g_l = 2 \text{ for } l\neq 0, \quad (8)$$

and

$$\alpha(n_1n_2{}^ln_3 \rightarrow n_1'n_2'{}^{l-1}n_3') = (4\pi^3\beta^2\nu' N_T/3hcQ_V)g_l \times\{\exp-[W_V(n_1,n_2,n_3,l)/kT]\}[1-\exp(-h\nu/kT)]$$
$$\text{where } g_l = 1 \text{ for } l=0 \text{ and } g_l = 2 \text{ for } l\neq 0. \quad (9)$$

In using Eqs. (8) and (9) it should be noted particuarly that the quantities β^2 are generally different for the transitions involving $l\rightarrow l+1$ and $l\rightarrow l-1$. The ratios of the β^2 can be calculated theoretically to the harmonic oscillator approximation for harmonic bands (see Appendix I for details).

In the same manner as for emissivity calculations on diatomic molecules with overlapping rotational lines,[1] we shall find Eq. (5) useful for the determination of "effective band widths" whereas Eqs. (7) to (9) lead directly to "average absorption coefficients" for vibration-rotation bands. For the calculation of S it may be convenient to combine Eqs. (4) to (4g), (5), and (7) to (9). For example, for the positive branch of the ν_2 fundamental of CO_2, we obtain

$$S \simeq [\omega(01^10;j\rightarrow 00^00;j-1)/\omega(01^10;0\rightarrow 00^00;0)] \times (Q_R)^{-1}\times\alpha(01^10\rightarrow 00^00)\times(j+1) \times[\exp-(W_R/kT)], \quad (5a)$$

where ω denotes a wave number.

III. APPROXIMATE EMISSIVITY CALCULATIONS AT 300°K

The positions and approximate intensities of the stronger vibration-rotation bands of CO_2 at 300°K are well known.[5–10,14] A first approximation to the effective band width is obtained by utilizing relations such as Eq. (5a) and defining the effective band width as the wave-number range for which S exceeds 10^{-3} of its maximum value.[1] Utilizing this definition of band width, which we shall refine presently, a summary of vibration-

[14] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1951), Table 56 on p. 274. Herzberg's designations of band intensities as vs (very strong), s (strong), m (medium), w (weak), and vw (very weak) has been used in Figs. 1 to 3 to identify the approximate strengths of bands at room temperature.

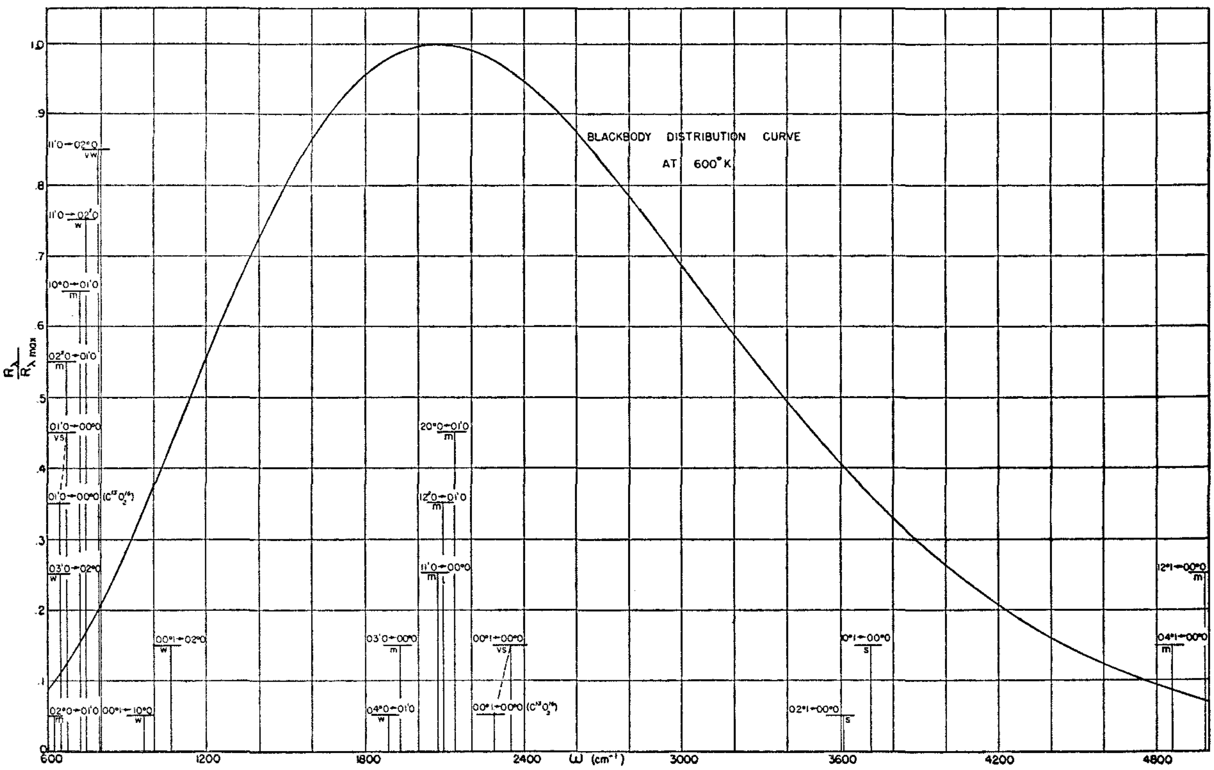

FIG. 2. Positions of centers of vibration-rotation bands, observed at room temperature, between 600 and 4800 cm^{-1}. Also shown is the intensity ratio $R_\lambda/R_{\lambda\,\max}$ for a blackbody at 600°K.

rotation bands for CO_2 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.[7] For the strongest bands (ν_2 and ν_3 fundamentals) the contributions from the isotopic molecule $C^{13}O_2^{16}$ are also shown. This chemical species constitutes about 1.1 percent of all of the CO_2 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 ν_2 fundamental. Thus it is readily shown[1] that the "limiting emissivity" for CO_2 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^{-1}.

It is physically obvious that the engineering emissivity E at 300°K is determined by the $01^{1}0 \rightarrow 00^{0}0$ transition in the limit of zero optical density of the emitter. As was pointed out in an earlier publication,[1] the emissivity as a function of optical density (partial pressure p of emitter×optical pathlength L) for very small values of pL can be computed quite accurately either by utilizing a treatment applicable for nonoverlapping lines[2] or by using average absorption coefficients. The emissivity E_{667} of the band with center at 667 cm^{-1}, as calculated from Eq. (30) of reference 2a,

TABLE I. Integrated intensities for vibration-rotation bands of CO_2 (reference 7).

Band center (cm^{-1})	Transition	α(cm^{-2}-atmos^{-1})
5109	$00^{0}0 \rightarrow 20^{0}1$	0.426
4984	$00^{0}0 \rightarrow 12^{0}1$	1.01
4861	$00^{0}0 \rightarrow 04^{0}1$	0.272
3716	$00^{0}0 \rightarrow 10^{0}1$	42.3
3609	$00^{0}0 \rightarrow 02^{0}1$	28.5
2349	$00^{0}0 \rightarrow 00^{0}1$	2706
2137	$01^{1}0 \rightarrow 20^{0}0$	
2094	$01^{1}0 \rightarrow 12^{2}0$	0.147
2077	$00^{0}0 \rightarrow 11^{1}0$	
1933	$00^{0}0 \rightarrow 03^{1}0$	0.083
1886	$01^{1}0 \rightarrow 04^{0}0$	
721	$01^{1}0 \rightarrow 10^{0}0$	
668	$01^{1}0 \rightarrow 02^{2}0$	
667	$00^{0}0 \rightarrow 01^{1}0$	171.5
648	$02^{0}0 \rightarrow 03^{1}0$	
618	$01^{1}0 \rightarrow 02^{0}0$	
961	$10^{0}0 \rightarrow 00^{0}1$	0.0219[a]
1064	$02^{0}0 \rightarrow 00^{0}1$	0.0532[a]

[a] Unpublished data obtained by D. Weber.

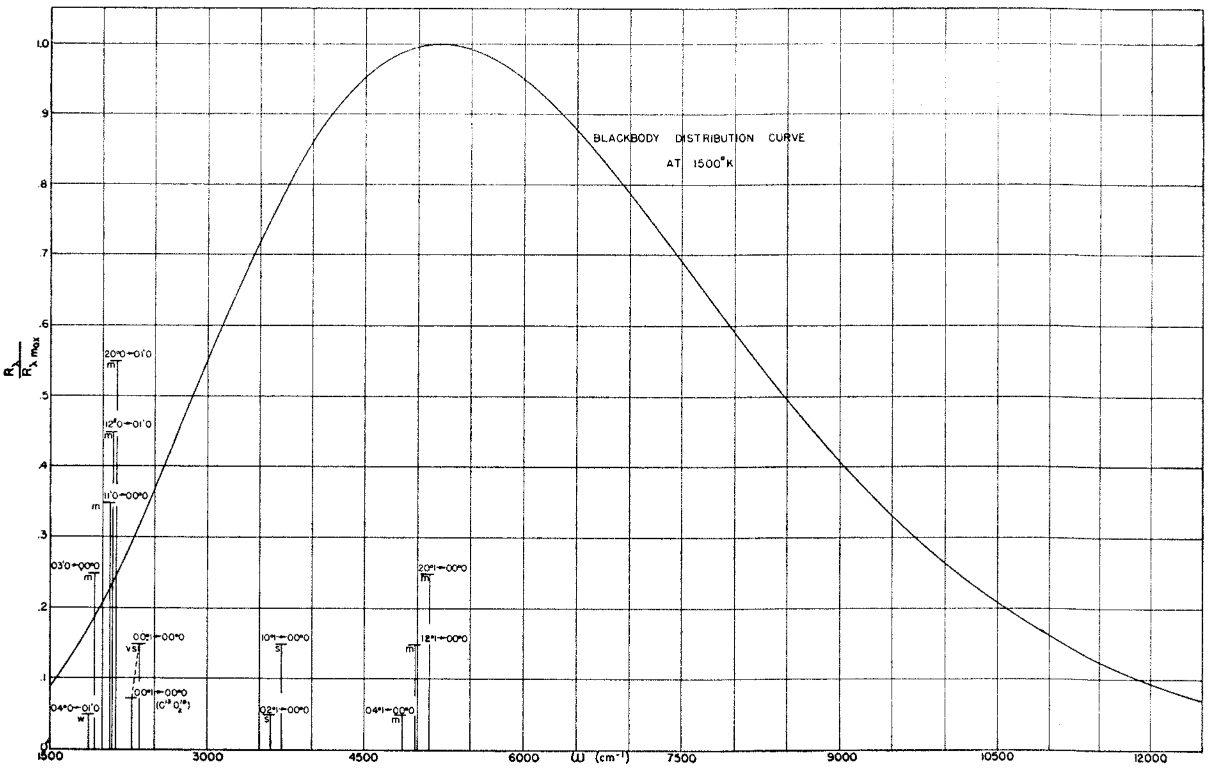

FIG. 3. Positions of centers of vibration-rotation bands observed at room temperature between 1500 and 12 000 cm^{-1}. Also shown is the intensity ratio $R_\lambda/R_{\lambda\ \max}$ for a blackbody at 1500°K.

is plotted as a function of pL in Fig. 4 and labeled "approximation for nonoverlapping lines." The corresponding quantity obtained by using the average absorption coefficient[7] $\bar{P}X=(171\ \text{cm}^{-2}\ \text{atmos}^{-1})/(106\ \text{cm}^{-1})$ over the effective band width extending from 600 to 706 cm^{-1} gives results which are practically identical with those obtained for nonoverlapping rotational lines as pL is reduced below about 0.02 ft-atmos. As pL is increased Eq. (30) of reference (2a) rapidly fails to apply and yields excessively large values not only for E_{667} but also for the total engineering emissivity E. Needless to say, for $pL\leq 0.02$ ft-atmos, the numerical value of E_{667} is to be identified with the value of E.

As the optical density is increased to moderate values of pL, it becomes necessary first to include the $01^10\rightarrow 00^00$ transition for $C^{13}O_2^{16}$, which is assumed to represent 1.1 percent of the total CO_2, and for which the integrated intensity is roughly the same as for the $C^{12}O_2^{16}$ species. In treatments using average absorption coefficients it is, of course, necessary to add absorption coefficients rather than emissivities in regions in which partial overlapping between effective band widths occurs. Finally, the contributions made by the $10^00\rightarrow 01^10$ and $02^00\rightarrow 01^10$ bands must be included; both of these are designated by Herzberg[14] as being of "medium" intensity whereas the $03^10\rightarrow 02^00$ and $11^10\rightarrow 02^20$ bands are labeled "weak" and the $11^10\rightarrow 02^00$ band is said to be "very weak."

Strictly speaking, room-temperature emissivity calculations for CO_2 cannot be carried further because the integrated intensities for the weaker bands are not available. However, it is easily shown that results in fairly good agreement with Hottel's data[4] are obtained if reasonable estimates are made for the strongest of the bands which has not yet been included in determining E.

It is known from rough unpublished measurements[7] that the integrated intensity α_{721} for the $10^00\rightarrow 01^10$ band is of the order of 1 cm^{-2} atmos^{-1}. Emissivity calculations treating α_{721} as a variable parameter between 0 and 10 cm^{-2} atmos^{-1} are shown in Fig. 4. The curves labeled $\alpha_{721}=0$, $\alpha_{721}=1$, and $\alpha_{721}=10$ with $\alpha_{667}=171$ correspond to the calculated values of E for the various assumed values of pL. In making these calculations the concept of the effective band width was refined in so far as the effective band width for the ν_2 fundamental was set equal to the wave-number range for which $SpL/0.7\geq 0.1$. This definition of band width for strong bands has the important advantage of making the band width a weak function of pL, in agreement with empirical measurements.[1b] The contributions to E made by the $00^01\rightarrow 10^00$ and $00^01\rightarrow 02^00$ bands are very small but have also been included. To these bands Weber assigns the following values at 300°K: $\alpha_{961}=0.0219$ cm^{-2} atmos^{-1}, $\alpha_{1064}=0.0532$ cm^{-2} atmos^{-1}.

In addition to the calculated emissivities, the results of empirical measurements[4] 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^{-2} atmos^{-1}. At very small values of pL the calculated emissivities§ are larger than the extrapolated empirical data but must be considered to be more reliable since they depend only on the numerical value of α_{667}, which is known with fair accuracy.[5–7] Our ability to calculate E at very large values of pL is limited by the lack of adequate intensity data for the transitions $02^00 \rightarrow 01^10$, $11^10 \rightarrow 02^20$, and $11^10 \rightarrow 02^00$. 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_2 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^{-1}. As pL goes to zero it is expected that the total emissivity E will become substantially equal to the emissivity of the intense ν_3 fundamental of $C^{12}O_2^{16}$ with appropriate corrections for contributions from the isotopic species $C^{13}O_2^{16}$. 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 ν_3 fundamental, we shall define the effective band width as the wave-number region for which S exceeds about 10^{-3} of its maximum value. For the ν_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-number limit of the ν_3 fundamental is set equal to 2410 cm^{-1}, i.e., 11 cm^{-1} 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 $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$ Bands

The criterion $(S/S_{\max}) \geq 10^{-3}$ for the weaker bands leads to band widths of the order of 140 cm^{-1} 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 α of the band whose ground state is identified by the set of quantum numbers $n_1 n_2{}^l n_3$ the result

$$\begin{aligned}\alpha(T°\mathrm{K})/\alpha(300°\mathrm{K}) = {} & (300/T) \\ & \times\{Q_V(300°\mathrm{K})\exp[W_V(00^00)/300k]\} \\ & \times\{Q_V(T°\mathrm{K})\times\exp[W_V(00^00)/kT]\}^{-1} \\ & \times\{\exp-[W_V(n_1n_2{}^ln_3)-W_V(00^00)] \\ & \times[(kT)^{-1}-(300k)^{-1}]\}[1-\exp(-h\nu/kT)] \\ & \times[1-\exp(-h\nu/300k)], \quad (10)\end{aligned}$$

where

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

The use of Eqs. (10) and (11) leads to the following results for the $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$ bands, respectively: $\alpha_{961}(600°\mathrm{K}) \simeq 9.29\alpha_{961}(300°\mathrm{K}) = 0.204$ cm^{-2} atmos^{-1}; $\alpha_{1064}(600°\mathrm{K}) \simeq 7.22\alpha_{1064}(300°\mathrm{K}) = 0.385$ cm^{-2} atmos^{-1}. Hence the total contribution to the emissivity

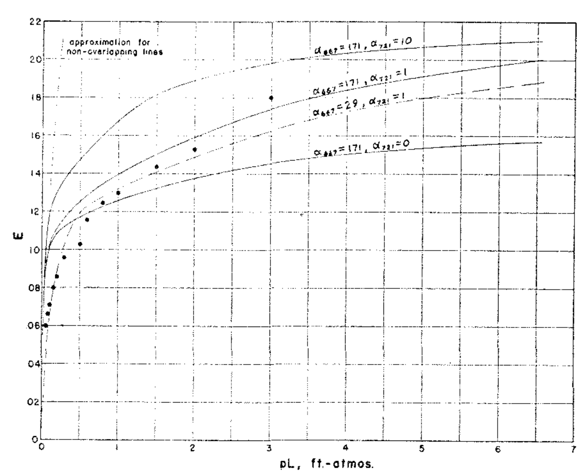

FIG. 4. Engineering emissivity E as a function of pL for CO_2 at 300°K. Integrated intensities α are expressed in cm^{-2} atmos^{-1}. The results based on empirical measurements (see reference 4) are shown as circles.

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

‖ 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 ν_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 ν_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.

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 cm^{-2} $atmos^{-1}$ for the sum of the bands centered at 2137, 2094, and 2077 cm^{-1} served as standard to fix the absolute intensity scale.

Transition	α at 300°K (cm^{-2}-$atmos^{-1}$)	α at 600°K (cm^{-2}-$atmos^{-1}$)
$00^00 \rightarrow 11^10$	0.12	0.040
$01^10 \rightarrow 12^20$	0.020	0.032
$01^10 \rightarrow 20^00$	0.0045	0.0075
$01^10 \rightarrow 12^00$	0.00048	0.00079
$02^20 \rightarrow 13^30$	0.0012	0.0099
$03^30 \rightarrow 14^40$	0.000038	0.0020
$02^20 \rightarrow 21^10$	0.00019	0.0015
$10^00 \rightarrow 21^10$	0.00029	0.0026
$11^10 \rightarrow 30^00$	0.0000053	0.00026

obtained from the two bands under discussion is

$$E_{961}+E_{1064}=0.052[1-\exp(-1.40\times10^{-3}pL)]+0.017[1-\exp(-4.15\times10^{-3}pL)]+0.054[1-\exp(-2.75\times10^{-3}pL)], \quad (12)$$

where pL is expressed in cm-atmos.

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

It is known from the recent work of Taylor, Benedict, and Strong[15] 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 contributions 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 cm^{-1}.

C. Contributions from the ν_3 Fundamental

From the measured integrated intensity[7] for the ν_3 fundamental at 300°K and by use of Eqs. (10) and (11) we find $\alpha_{2349}=1060$ cm^{-2} $atmos^{-1}$ at 600°K. Of the total integrated intensity per (cm^{-1})$\times$(cm^{-1} $atmos^{-1}$ of CO_2) we associate 98.9 percent with $C^{12}O_2^{16}$ and 1.1 percent with $C^{13}O_2^{16}$. For the intense ν_3 fundamental the effective band width corresponds to the wave-number range $\Delta\omega_{2349}$ for which $(SpL/0.7)\geq0.1$ with the band width of the isotopic species determined similarly. In general, the $C^{12}O_2^{16}$ 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}(total) with the empirical data[4] plotted in Fig. 5 shows that for $pL\leq0.033$ ft-atmos, E_{2349}(total) is practically identical with the engineering emissivity E. The result is in accord with expectations and shows

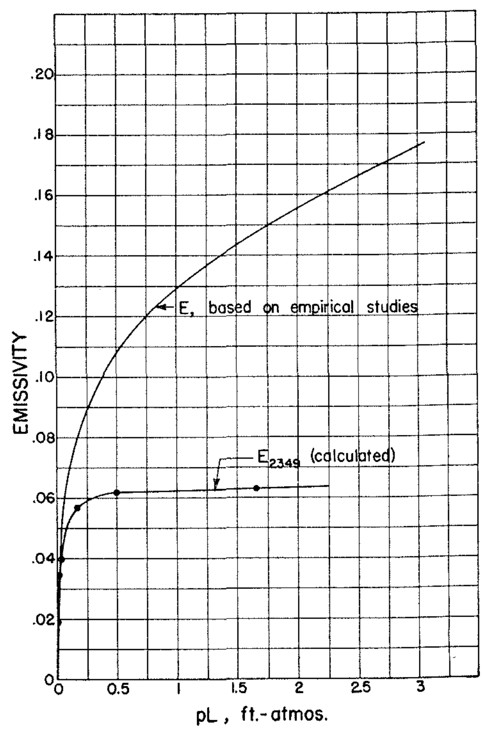

FIG. 5. Engineering emissivity E as a function of pL for CO_2 at 600°K, based on the empirical correlations of H. C. Hottel and R. B. Egbert. Also shown are the calculated contributions to the total emissivity made by the ν_3 fundamental.

TABLE III. Emissivities E_{2349} for $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$ at 600°K as a function of optical density.[a]

pL, cm-atmos	pL, ft-atmos	$E_{2349}(C^{12}O_2^{16})$	$E_{2349}(C^{13}O_2^{16})$	E_{2349}(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

[a] The tabulated values of $E_{2349}(C^{13}O_2^{16})$ correspond to the values which must be added to $E_{2349}(C^{12}O_2^{16})$ in order to obtain E_{2349}(total). They do not include emissivities in the (black) region of the ν_3 fundamental of $C^{12}O_2^{16}$ which is overlapped by the ν_3 fundamental of $C^{13}O_2^{16}$.

[15] Taylor, Benedict, and Strong, Progress Report on "Infrared Spectra of H_2O and 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.

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

D. Contribution of the $02^01\to00^00$ and $10^01\to00^00$ Bands

From the measured integrated intensities[7] we find $\alpha_{3609}=9.70$ cm^{-2} atmos^{-1} for the $02^01\to00^00$ band and $\alpha_{3716}=14.4$ cm^{-2} atmos^{-1} for the $10^01\to00^00$ band at 600°K. The effective band widths extend from 3539 cm^{-1} to 3679 cm^{-1} and from 3646 cm^{-1} to 3716 cm^{-1}, respectively. Using average absorption coefficients the following results are obtained:

$$E_{3609}+E_{3716}\simeq0.0047[1-\exp(-6.92\times10^{-2}pL)]+0.0017[1-\exp(-1.72\times10^{-1}pL)]+0.0017[1-\exp(-1.03\times10^{-1}pL)]. \quad (13)$$

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_2 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[15] and by Kaplan.[16] 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 ν_2.

The desired result is obtained readily by using the normalized wave functions for the isotropic plane oscillator and an integral involving associated Laguerre polynomials first obtained by Schrödinger.[17] In this manner it is easily shown that

$$[\beta(n_1n_2^ln_3\to n_1n_2'^{l'}n_3)]^2/[\beta(n_10^0n_3\to n_11^1n_3)]^2=R(n_2^l\to n_2'^{l'})=[k!k'!/(k+l)!]\times(p!)^2\left\{\sum_{\tau=0}^{\leq k,k'}\binom{p-l}{k-\tau}\binom{p-l'}{k'-\tau}\binom{-p-1}{\tau}\right\}^2, \quad (A1)$$

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:

$$\alpha(n_1n_2^ln_3\to n_1n_2'^{l'}n_3)/\alpha(n_10^0n_3\to n_11^1n_3)=\delta(n_2^l\to n_2'^{l'})=g_lR(n_2^l\to n_2'^{l'})[\nu(n_1n_2^ln_3\to n_1n_2'^{l'}n_3)/\nu(n_10^0n_3\to n_11^1n_3)]\{\exp-[W_V(n_1,n_2,n_3,l)-W_V(n_1,0,n_3,0)]/kT\}\{1-\exp[-h\nu(n_2^l\to n_2'^{l'})/kT]\}\times\{1-\exp[-h\nu(0^0\to1^1)/kT]\}^{-1}. \quad (A2)$$

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

Following Benedict we shall assume that resonance between $2\nu_2$ and ν_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 5μ region at 300 and at 600°K. The results are summarized in Table (A-I).

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

Transition	$g_lR(n_1n_2^l0\to n_1'n_2'^{l'}0)$	$\delta(n_1n_2^l0\to n_1'n_2'^{l'}0)$ at 300°K	$\delta(n_1n_2^l0\to n_1'n_2'^{l'}0)$ at 600°K
$00^00\to11^10$	1	1	1
$01^10\to12^20$	4	0.164	0.810
$01^10\to20^00$	0.9[a]	0.0376	0.187
$01^10\to12^00$	0.1[a]	0.00395	0.0196
$02^20\to13^30$	6	0.0101	0.248
$03^30\to14^40$	8	0.000315	0.0507
$02^20\to21^10$	0.9[a]	0.00155	0.0382
$10^00\to21^10$	1.8[a]	0.00238	0.0656
$11^10\to30^00$	0.9[a]	0.0000438	0.00638

[a] Adjusted according to Benedict to concentrate most of the intensity of resonating bands in the highest frequency member (reference 15).

** 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_2.

[16] L. D. Kaplan, J. Chem. Phys. 18, 186 (1950).

[17] E. Schrödinger, Ann. Physik 80, 483 (1926).

[18] W. H. Shaffer, Revs. Modern Phys. 16, 245 (1944).