

The modulus of elasticity changes by less than 2% over the entire temperature range investigated. The room temperature modulus using a simple beam is 11.75×10^6 psi. This value agrees very well with 11.6×10^6 psi given by Spinner¹⁰ using a dynamic (resonance) method.

6. CONCLUSION

Abrading decreases the strength of glass at these low temperatures in the same way as at higher temperatures. Lowering the test temperature increases the strength, up to a point, of both abraded and unabraded specimens. The breaking stress at 194°K and 296°K is dependent on the rate of loading but appears to be independent of the rate at 20°K and 76°K. Contact with liquid nitrogen and hydrogen does not appear to affect adversely the breaking stress.

The fatigue or endurance limit at 76°K appears to be greater than 9000 psi. However, since some of the specimens withstood loads of 10 000 psi for several

|| C. J. Parker (private communication).

¹⁰ Sam Spinner, *J. Am. Ceram. Soc.* **39**, 113 (1956).

hours and then fractured, the existence of some fatigue is indicated. There appears to be some agreement between these data and those of Vonnegut and Glathart. The agreement is good at 76°K and 296°K but deviates markedly at 194°K. This may result from the method used in plotting the data or from the fact that the specimens were tested in contact with acetone and dry ice in one case and air in the other.

The results of these tests show that the strength of glass is essentially the same at 20°K as it is at 76°K. In addition, at these low temperatures glass exhibits very little or no fatigue, and therefore much higher design stresses can be used for glass in cryogenic apparatus.

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Infrared Emissivities and Absorptivities of Gases*

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Approximate analytic expressions are obtained for the "effective band widths" and emissivities of diatomic molecules at elevated pressures.

The absorptivities of molecular vibration-rotation bands are evaluated for radiation emitted by similar molecular vibration-rotation bands and for radiation emitted by blackbodies. The results obtained for the absorptivity calculations compare favorably with available empirical correlations for H₂O.

The postulated model does not apply to CO₂ and, therefore, no satisfactory theoretical formula has been derived for the absorptivities of this molecule. The appendix (by A. Thomson) is devoted to a critical examination of the limits of validity of the effective band-width concept for different molecules.

I. INTRODUCTION

INFRARED emissivity calculations for diatomic gases were carried out some years ago for (a) elevated pressures where extensive overlapping occurs between the rotational lines of the vibration-rotation bands¹ and (b) low pressures and low optical densities where the rotational lines may be considered to be completely separated.²

In the following Sec. II we consider a formal addition to the ideas published in earlier papers and obtain approximate analytic expressions for the effective band

widths and emissivities of diatomic molecules in the special case where the occurrence of band heads may be ignored.

Section III is devoted to a quantitative discussion of the absorptivity of molecular vibration-rotation bands with overlapping rotational lines for radiation emitted either from molecular vibration-rotation bands or from a blackbody. Our theoretical results are compared with an empirical relation³ and are shown to be useful for correlating experimental data for water vapor for optical densities which are sufficiently high to justify the assumption that the rotational fine structure has been completely smeared out.

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¹ (a) S. S. Penner, *J. Appl. Phys.* **21**, 685 (1950); (b) S. S. Penner, *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 H. C. Hottel and R. B. Egbert, *Trans. Am. Inst. Chem. Eng.* **38**, 531 (1942); H. C. Hottel and H. G. Mangelsdorf, *Trans. Am. Inst. Chem. Eng.* **31**, 517 (1935). W. H. McAdams, *Heat Transfer mission* (McGraw-Hill Book Company, Inc., New York, 1954), third edition, Chap. III by H. C. Hottel.

II. APPROXIMATE ANALYTIC EXPRESSION FOR EFFECTIVE BAND WIDTHS AND EMISSIVITIES OF DIATOMIC MOLECULES⁴

The procedure for calculating effective band widths was described in an earlier publication.¹ We use the same physical ideas but obtain analytic expressions which are useful provided the formation of band heads can be ignored. In the event that band heads are important for the range of optical densities and temperatures considered, it is necessary to revert to the original numerical method of calculation.¹

For diatomic molecules without *Q* branch, the intensity distribution in a vibration-rotation band is dominated,² for large *j*, by the term

$$j \exp(-\epsilon(n, j)/kT),$$

where we refer to the transition $j \rightarrow j-1$.[†] Here *j* and *n* denote, respectively, the rotational and vibrational quantum numbers of the initial state, $\epsilon(n, j)$ is the corresponding energy, *k* equals the Boltzmann constant, and *T* is the absolute temperature. In the notation used by Mayer and Mayer,⁵ $\epsilon(n, j)/kT$ may be shown to be given by the expression

$$\epsilon(n, j)/kT = u_e(n + \frac{1}{2})[1 - x_e(n + \frac{1}{2})] + \gamma u_e j(j+1)[1 - (n + \frac{1}{2})\delta - 4\gamma^2 j(j+1)]. \quad (1)$$

The value of $j = j^*$ for which $j \exp[-\epsilon(n, j)/kT]$ attains a maximum is, approximately,

$$j^* \simeq (2\gamma u_e)^{-\frac{1}{2}}, \quad (2)$$

where $4\gamma^2 j(j+1)$, which accounts for band-head formation, and $(n + \frac{1}{2})\delta$ have been assumed to be negligibly small. More accurate results may be obtained by replacing γu_e everywhere by $\gamma u_e[1 - (n + \frac{1}{2})\delta]$. This correction causes a slow variation of band width with vibrational quantum number. The maximum value of $j \equiv j_{\max}$, which limits the effective band width, has been defined¹ by the relation

$$j_{\max} \exp[-\epsilon(n, j_{\max})/kT] = 10^{-3} j^* \exp[-\epsilon(n, j^*)/kT]. \quad (3)$$

Using Eqs. (1) and (2), it is readily shown that Eq. (3) may be rewritten as

$$\ln \left(\frac{j_{\max}}{j^*} \right)^2 - \left(\frac{j_{\max}}{j^*} \right)^2 + 14.8 = 0. \quad (4)$$

Equation (4) may be solved by an iteration procedure. The result is

$$j_{\max} \simeq (17.69)^{\frac{1}{2}} (j^*) = (8.84/\gamma u_e)^{\frac{1}{2}}. \quad (5)$$

⁴ Calculations similar to those described in this Sec. II were first proposed in 1951 by H. S. Tsien.

[†] Our calculations refer to the *R* branch; a similar analysis applies to the *P* branch.

⁵ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), Chap. 7.

TABLE I. Effective band widths of the fundamental vibration-rotation bands of CO and HCl computed from Eq. (7). The values given in parentheses were obtained by numerical calculations.¹

T (°K)	$\Delta\omega_F$ (CO) (cm ⁻¹)	$\Delta\omega_F$ (HCl) (cm ⁻¹)
300	239 (214)	560 (535)
500	308 (274)	724 (691)
1000	436 (379)	1022 (945)
1500	535 (465)	1250 (1178)
2000	617 (535)	1450 (1314)
3000	756 (630)	1772 (1665)

The effective band width of the fundamental vibration-rotation band is then given by the expression

$$\Delta\omega_F = \frac{1}{hc} \{ [\epsilon(1, j_{\max}) - \epsilon(0, j_{\max} - 1)] - [\epsilon(1, j_{\max} - 1) - \epsilon(0, j_{\max})] \} \quad (6)$$

with a similar relation holding for the harmonic and overtone bands. Using Eq. (1), it is found that, for large j_{\max} , Eq. (6) reduces to

$$\Delta\omega_F = 4\gamma u_e kT j_{\max} / hc = 11.9(\gamma u_e)^{\frac{1}{2}} kT / hc. \quad (7)$$

Reference to Eqs. (1) and (6) shows that, for small δ , the band widths of the harmonics and overtones equal $\Delta\omega_F$.

Representative values of $\Delta\omega_F$, computed from Eq. (7) for CO and HCl, are summarized in Table I. The values in parentheses are the results obtained previously¹ by numerical calculations with proper allowance for the occurrence of band heads. Reference to Table I shows that Eq. (7) represents the effective band widths of the fundamental vibration-rotation bands with adequate precision, at least up to temperatures of 3000°K.

The engineering emissivity *E* has been expressed¹ by the relation

$$E = [1 - \exp(-\alpha_F X / \Delta\omega_F)] \int_{\Delta\omega_F} R^0(\omega) d\omega / \sigma T^4 + [1 - \exp(-\alpha_0 X / \Delta\omega_0)] \int_{\Delta\omega_0} R^0(\omega) d\omega / \sigma T^4 + \dots, \quad (8)$$

where α_F and α_0 represent, respectively, the integrated absorption for the fundamental and first overtone (in cm⁻² atm⁻¹), $R^0(\omega)$ is the Planck radiation function (in erg cm⁻¹ sec⁻¹), σ is the Stefan-Boltzmann constant (in erg cm⁻² sec⁻¹ °K⁻⁴) and *X* is the optical density (in cm atm). With $\Delta\omega_F$ and $\Delta\omega_0$ given by Eq. (7), Eq. (8) may be used as an explicit representation of the engineering emissivity *E*.

III. ABSORPTIVITY OF MOLECULAR VIBRATION-ROTATION BANDS FOR RADIATION EMITTED BY MOLECULAR VIBRATION-ROTATION BANDS†

The following analysis utilizes the concept of an average absorption coefficient for an entire vibration-rotation band. For this reason, the results are applicable only at elevated pressures and moderate or large optical densities where extensive overlapping occurs between rotational lines.

Consider two isothermal parallel layers of the same gas at temperatures T_{G1} and T_{G2} with optical densities (in cm atmos) $X_1 = P_1 L_1$ and $X_2 = P_2 L_2$, respectively. Here P_1 and P_2 denote the partial pressures of absorber and emitter, respectively, whereas L_1 and L_2 represent the corresponding geometric path lengths throughout which the gas molecules are distributed.

$$\alpha(2 \rightarrow 1) = \frac{\int_0^\infty \{1 - \exp[-k(\omega, T_{G1})X_1]\} \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega}{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega} \quad (10)$$

We now assume¹ that the i th vibration-rotation band may be described by an average absorption coefficient $\bar{k}_i(T)$ over the effective band width $\Delta\omega_i(T)$ of the band whose center lies at $\bar{\omega}_i$. It has been shown previously¹ that, for the calculation of over-all emissivities [i.e., for evaluation of the denominator of Eq. (10)],

$$\bar{k}_i(T) = (1/\Delta\omega_i) \int k(\omega, T) d\omega \quad (11)$$

represents a good approximation for vibration-rotation bands at pressures which are sufficiently high to smear

$$\alpha(2 \rightarrow 1) = \sum_i \frac{\{1 - \exp[-\bar{k}_i(T_{G1})X_1]\} \{1 - \exp[-\bar{k}_i(T_{G2})X_2]\} R(\bar{\omega}_i, T_{G2}) \Delta\omega_i^*,}{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega} \quad (12)$$

where the approximation has been made of using the value of the Planck function at temperature T_{G2} evaluated at the band center for each vibration-rotation band. The quantity $\Delta\omega_i^*$ in Eq. (12) denotes the effective width of the narrower vibration-rotation band since no absorption occurs outside the limits of $\Delta\omega_i^*$.

† The analysis presented in this Sec. III applies to infinitely narrow beams of light passing in a direction normal to two parallel isothermal layers with optical depths X_1 and X_2 . Alternately, we may consider concentric hemispherical shells with radii X_2 and $X_1 + X_2$ and collimated beams of light directed from the center of curvature. If $X_1 + X_2$ is the radius of the outer gas layer, X_2 represents the radius of the inner gas layer, and we let X_2 approach zero and replace the gas layer by a blackbody, then we obtain the geometric configuration which is customarily employed for the determination of hemispherical absorptivities.

The total energy emitted by region 2 into an infinitesimal solid angle $\Delta\Omega$ which contains the normal to the interface, in unit time through unit area at the interface between regions 1 and 2, is

$$\Delta I_{2 \rightarrow 1} = \Delta\Omega \int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega, \quad (9)$$

where $k(\omega, T_{G2})$ is the absorption coefficient (in cm^{-1} atmos^{-1}) in region 2 at the wave number ω and temperature T_{G2} and $R(\omega, T_{G2})$ equals the Planck radiation function evaluated at the wave number ω and temperature T_{G2} . The fraction of the energy $\Delta I_{2 \rightarrow 1}$ which is absorbed in region 1, i.e., the absorptivity $\alpha(2 \rightarrow 1)$ of the gases in region 1 for radiation emitted from region 2, is

out the rotational fine structure in such a way that the spectral absorption coefficient $k(\omega, T)$ is no longer a rapidly varying function of ω . The integral in Eq. (11) extends over the i th vibration-rotation band. Exact evaluation of the numerator of Eq. (10), using reasonable representations of $k(\omega, T_{G1})$, shows again that, for moderate values of T_{G2}/T_{G1} , Eq. (11) is a good approximation.

Introduction of average absorption coefficients for each vibration-rotation band in the numerator of Eq. (10) reduces the relation to

Thus

$$\Delta\omega_i^* = \Delta\omega_i(T_{G2}) \quad \text{for } T_{G2} \leq T_{G1}$$

and

$$\Delta\omega_i^* = \Delta\omega_i(T_{G1}) \quad \text{for } T_{G1} \leq T_{G2}.$$

From Eq. (11) and the relation $\int k(\omega, T) d\omega \sim T^{-1}$ it is apparent that

$$\frac{\bar{k}_i(T_{G1})}{\bar{k}_i(T_{G2})} = \frac{T_{G2} \Delta\omega_i(T_{G2})}{T_{G1} \Delta\omega_i(T_{G1})} \quad (13)$$

The first factor in Eq. (13) arises because the number density of absorbers is inversely proportional to the temperature.

The temperature dependence of $\Delta\omega_i$ may be determined from Eq. (7). Since γ is independent of temper-

ature and u_e is given by the relation

$$u_e = hc\omega_e/kT, \tag{14}$$

it follows that Eq. (7) becomes

$$\Delta\omega_i = 11.9(\gamma k\omega_e/hc)^{\frac{1}{2}} T^{\frac{1}{2}}, \tag{15}$$

whence

$$\frac{\bar{k}_i(T_{G1})}{\bar{k}_i(T_{G2})} = \left(\frac{T_{G2}}{T_{G1}}\right)^{\frac{1}{2}}. \tag{16}$$

In view of Eq. (15) we find that

$$\Delta\omega^*_i(T) = \Delta\omega_i(T_{G1}) = \left(\frac{T_{G1}}{T_{G2}}\right)^{\frac{1}{2}} \Delta\omega_i(T_{G2}) \tag{17}$$

for $T_{G2} \geq T_{G1}$

and

$$\Delta\omega^*_i(T) = \Delta\omega_i(T_{G2}) \tag{18}$$

for $T_{G1} \geq T_{G2}$.

Hence Eq. (12) becomes

$$\alpha(2 \rightarrow 1) = \sum_i \left(\frac{T_{G1}}{T_{G2}}\right)^{\frac{1}{2}} \frac{\{1 - \exp[-\bar{k}_i(T_{G2})X_1(T_{G2}/T_{G1})^{\frac{1}{2}}]\} \{1 - \exp[-\bar{k}_i(T_{G2})X_2]\} R(\bar{\omega}_i, T_{G2}) \Delta\omega_i(T_{G2})}{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega} \tag{19}$$

for $T_{G2} \geq T_{G1}$

and

$$\alpha(2 \rightarrow 1) = \sum_i \frac{\{1 - \exp[-\bar{k}_i(T_{G2})X_1(T_{G2}/T_{G1})^{\frac{1}{2}}]\} \{1 - \exp[-\bar{k}_i(T_{G2})X_2]\} R(\bar{\omega}_i, T_{G2}) \Delta\omega_i(T_{G2})}{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega} \tag{20}$$

for $T_{G1} \geq T_{G2}$.

It is now convenient to transform the summation over individual vibration-rotation bands back to an integration over wave numbers. Thus

$$\alpha(2 \rightarrow 1) = \left(\frac{T_{G1}}{T_{G2}}\right)^{\frac{1}{2}} \frac{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_1(T_{G2}/T_{G1})^{\frac{1}{2}}]\} \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega}{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega} \tag{21}$$

for $T_{G1} \leq T_{G2}$;

$$\alpha(2 \rightarrow 1) = \frac{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_1(T_{G2}/T_{G1})^{\frac{1}{2}}]\} \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega}{\int_0^\infty \{1 - \exp[-k(\omega, T_{G2})X_2]\} R(\omega, T_{G2}) d\omega} \tag{21}$$

for $T_{G1} \geq T_{G2}$.

In terms of tabulated isothermal hemispherical emissivities $E(T, X)$, Eq. (21) may be rewritten in the form

$$\alpha(2 \rightarrow 1) = \begin{cases} \left(\frac{T_{G1}}{T_{G2}}\right)^{\frac{1}{2}} \left\{ 1 - \frac{E[T_{G2}, X_2 + X_1(T_{G2}/T_{G1})^{\frac{1}{2}}] - E[T_{G2}, X_1(T_{G2}/T_{G1})^{\frac{1}{2}}]}{E(T_{G2}, X_2)} \right\} & \text{for } T_{G1} \leq T_{G2}, \\ \left\{ 1 - \frac{E[T_{G2}, X_2 + X_1(T_{G2}/T_{G1})^{\frac{1}{2}}] - E[T_{G2}, X_1(T_{G2}/T_{G1})^{\frac{1}{2}}]}{E(T_{G2}, X_2)} \right\} & \text{for } T_{G1} \geq T_{G2}. \end{cases} \tag{22}$$

Equation (22) represents the desired relation for the hemispherical absorptivity at a temperature T_{G1} of a gas characterized by vibration-rotation bands for radiation emitted by the same gas at a temperature T_{G2} .

A. Absorptivities of Water Vapor for Blackbody Radiation

Using measured values for the absorptivity of water vapor for blackbody radiation, Hottel³ obtained the

following empirical formula for the absorptivity

$$\alpha_H = \left(\frac{T_g}{T_s}\right)^{0.45} E[T_s, X(T_s/T_g)]. \tag{23}$$

Here α_H is the hemispherical absorptivity measured by Hottel for a layer of water vapor at temperature T_g and mean optical density X for radiation emitted by a blackbody at temperature T_s , and $E[T_s, X(T_s/T_g)]$ is the tabulated isothermal hemispherical emissivity cor-

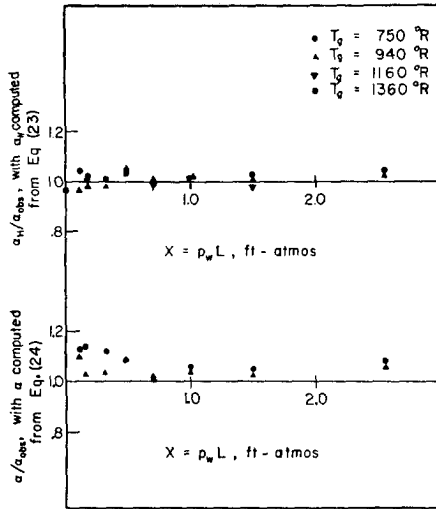


FIG. 1. The ratios α_H/α_{obs} and α/α_{obs} for blackbody radiation at a temperature $T_s=1160^\circ\text{R}$.

responding to the temperature T_s and an optical density $X(T_s/T_g)$. For blackbody radiation, Eq. (22) reduces to the expression (noting that $E(T, X_2)=1$ and that the first of the relations given in Eq. (22) applies now for $T_{G2} \leq T_{G1}$ as well as for $T_{G2} \geq T_{G1}$)

$$\alpha = \left(\frac{T_g}{T_s}\right)^{\frac{1}{2}} E[T_s, X(T_s/T_g)^{\frac{1}{2}}]. \quad (24)$$

Here T_{G2} has been replaced by T_s , T_{G1} by T_g and X_1 by X .

In Figs. 1 to 3 we have plotted the ratios of the calculated§ to the observed³ absorptivities, using both

Eqs. (23) and (24), for various values of the gas temperature T_g and blackbody temperature T_s . Reference to Figs. 1 to 3 shows that Eqs. (23) and (24) represent the experimental data about equally well. In this connection it is of interest to note that the measured absorptivities were obtained at a total pressure of one atmosphere for partial pressures of water vapor varying from zero to one atmosphere. Since Eq. (24) was derived for overlapping rotational lines, it is not expected to apply at very low pressures and optical densities. It is apparent from Figs. 1 to 3 that significant deviations from Eq. (24) occur only at the lowest optical densities, a conclusion which is evidently in accord with expectations.

B. Absorptivities of Carbon Dioxide Vapor for Blackbody Radiation

Using measured values of the absorptivity of carbon dioxide vapor for blackbody radiation, Hottel and Mangelsdorf³ obtained the following empirical formula for the absorptivity

$$\alpha_H = \left(\frac{T_g}{T_s}\right)^{0.66} E[T_s, X(T_s/T_g)]. \quad (25)$$

For the absorption of blackbody radiation by carbon dioxide, Eq. (24) does not yield a satisfactory correlation of observed results. The reason for this discrepancy becomes apparent if it is noted that the effective bandwidth estimates obtained in Sec. II are invalid for carbon dioxide because of the presence of the exceedingly strong ν_3 fundamental. In this case the tails of intense rotational lines located near the band center

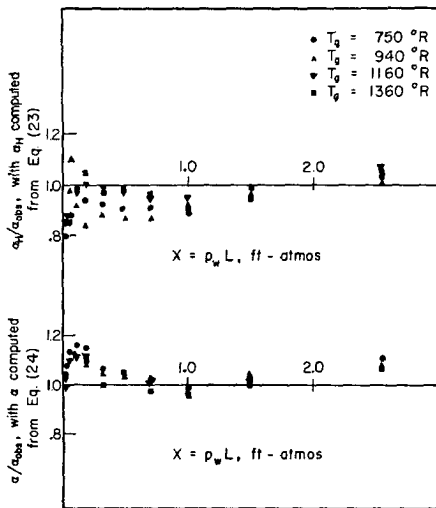


FIG. 2. The ratios α_H/α_{obs} and α/α_{obs} for blackbody radiation at a temperature $T_s=1760^\circ\text{R}$.

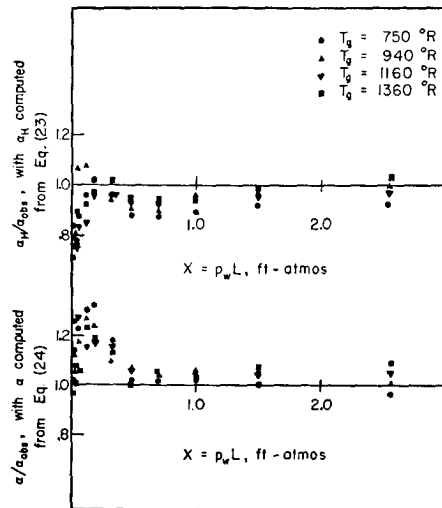


FIG. 3. The ratios α_H/α_{obs} and α/α_{obs} for blackbody radiation at a temperature $T_s=2500^\circ\text{R}$.

§ For calculation of the absorptivities α_H and α , values of $E(T, X)$ tabulated by Hottel³ were used. The hemispherical emissivity $E(T, X)$ has been plotted as a function of the temperature T and the optical density $X = P_w L$ for a total pressure P_T

of one atmosphere in the limiting case in which the water vapor partial pressure P_w becomes negligibly small. For values of P_w and P_T different from 0 and 1, respectively, an empirical correction factor C_w must be used; this depends on $P_T + P_w$ and on $P_w L$.³

make appreciable contributions at wavelengths outside of the "effective band width." Limiting conditions for failure of the theoretical band limit estimates are easily derived from this physical picture and are considered in greater detail in the Appendix.

IV. GENERAL CONCLUSIONS

In the present paper we have used the concept of effective widths for vibration-rotation bands with average absorption coefficients to obtain an analytical expression for the radiative emissivities of diatomic molecules. The simple formulas agree with earlier numerical calculations which have been shown previously to be in accord with available empirical data.

Using the same physical model, we have derived also analytical expressions for the isothermal molecular absorptivities referring to radiation emitted from a blackbody. In accord with expectations, our formula for H₂O provides a good correlation for absorptivities determined experimentally by H. C. Hottel. On the other hand, the theoretical absorptivity results do not agree with the measured values for CO₂ because the effective band width is not well defined for this molecule. This failure of the model, which we have used in the past with some measure of success in order to account for the fundamental parameters required in radiant heat transfer calculations, has prompted us to carry out a careful scrutiny of its limits of applicability. These studies are described in detail in the Appendix.

APPENDIX: LIMITS OF VALIDITY OF THE EFFECTIVE BAND-WIDTH APPROXIMATION¹¹

The effective band-width approximation described in Sec. III fails to apply both at very low and at very high pressures and optical densities. At low pressures and optical densities, the rotational fine structure is insufficiently smeared out and the notion of an average absorption coefficient for the entire vibration-rotation band is no longer useful. On the other hand, at high pressures and optical densities, the intense rotational lines near the band center make appreciable contributions at wavelengths outside the "effective band width." In the following discussion we shall restrict our attention to the large optical density limit of the approximate calculations.

Many detailed theoretical and experimental studies of spectral line shapes have appeared in the recent literature.⁶ It is known that, even for impact broadening, the spectral absorption coefficients $P_{j \rightarrow j+1}(\omega)$ and

$P_{j \rightarrow j-1}(\omega)$ of the j th rotational lines in the P and R branches, respectively, are complicated functions of the wave number ω .⁶ However, for the present purposes it is sufficient to obtain an approximate estimate of the spectral absorption coefficient near the band limit by using the Lorentz distribution

$$P_{j \rightarrow j \pm 1}(\omega) = \frac{(S_{j \rightarrow j \pm 1})(b/\pi)}{(\omega - \omega^0_{j \rightarrow j \pm 1})^2 + b^2}, \tag{A1}$$

where $S_{j \rightarrow j+1}$ and $S_{j \rightarrow j-1}$ are the integrated intensities for the lines centered at $\omega^0_{j \rightarrow j+1}$ and $\omega^0_{j \rightarrow j-1}$, in the P and R branches, respectively, and b equals the collision (semi-) half-width, which is assumed to be uniform for the entire vibration-rotation band.

If the anharmonicity terms in the energy expression are neglected, then the spectral absorption coefficient at a wave number ω for the rotational transition $j \rightarrow j - 1$ is, for large values of j ,

$$P_{j \rightarrow j-1}(\omega) \simeq \frac{\alpha \gamma u_e j [\exp(-\gamma u_e j^2)](b/\pi)}{(\omega - \omega^0_{j \rightarrow j-1})^2 + b^2}, \tag{A2}$$

where the line strength $S_{j \rightarrow j-1}$ has been approximated by

$$S_{j \rightarrow j-1} \simeq \alpha \gamma u_e j \exp(-\gamma u_e j^2) \tag{A3}$$

with α representing the integrated intensity for the entire vibration-rotation band. Similarly

$$P_{j \rightarrow j+1} = \frac{\alpha \gamma u_e j [\exp(-\gamma u_e j^2)](b/\pi)}{(\omega - \omega^0_{j \rightarrow j+1})^2 + b^2} \tag{A2a}$$

represents the spectral absorption coefficient for the transition $j \rightarrow j + 1$ whose line strength is also

$$S_{j \rightarrow j+1} \simeq \alpha \gamma u_e j \exp(-\gamma u_e j^2). \tag{A3a}$$

Evidently

$$\sum_{j=0}^{\infty} (S_{j \rightarrow j-1} + S_{j \rightarrow j+1}) = \alpha.$$

Let the wave number at the center of the vibration-rotation band, corresponding to the (forbidden) transition $j=0 \rightarrow j=0$, be identified by ω_0 . If the centers of the rotational lines are uniformly spaced with a wave-number difference q then

$$(\omega - \omega^0_{j \rightarrow j-1})^2 = (\omega - \omega_0 - qj)^2$$

and

$$(\omega - \omega^0_{j \rightarrow j+1})^2 = (\omega - \omega_0 + qj)^2.$$

The total spectral absorption coefficient at the wave number ω is

$$P(\omega) = \sum_{j=0}^{\infty} (P_{j \rightarrow j-1}(\omega) + P_{j \rightarrow j+1}(\omega)) \tag{A4}$$

or, explicitly,

¹¹ By A. Thomson.

⁶ See, for example, H. A. Lorentz, Proc. Akad. Sci. Amsterdam 8, 59 (1906); W. Lenz, Z. Physik 80, 423 (1933); V. F. Weisskopf, Physik. Z. 34, 1 (1933); E. Lindholm, Arkiv. Mat. Astron. Fysik. 32, 17 (1945); J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. 17, 227 (1945); J. H. Van Vleck and H. Margenau, Phys. Rev. 76, 1211 (1949); P. W. Anderson, Phys. Rev. 76, 647 (1949); H. Margenau, Phys. Rev. 82, 156 (1951); S. Bloom and H. Margenau, Phys. Rev. 90, 791 (1953); R. E. Mayerott and H. Margenau, Phys. Rev. 99, 1851 (1955).

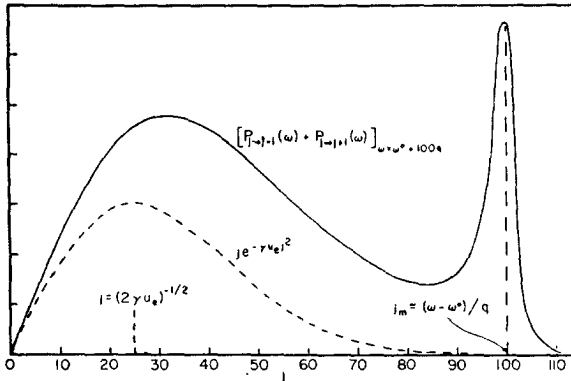


FIG. 4. The quantity $P_{j \rightarrow j-1}(\omega) + P_{j \rightarrow j+1}(\omega)$ evaluated at $\omega = \omega_0 + 100q$ as a function of j for $b/q = 2.5$ and $(2\gamma u_e)^{-1/2} = 25$. The dashed curve represents $j \exp(-\gamma u_e j^2)$.

$$P(\omega) = \alpha \gamma u_e \left(\frac{b}{\pi}\right) \sum_{j=0}^{\infty} j \left[\exp(-\gamma u_e j^2) \right] \times \left[\frac{1}{(\omega - \omega_0 - qj)^2 + b^2} + \frac{1}{(\omega - \omega_0 + qj)^2 + b^2} \right]. \quad (\text{A5})$$

The quantity $(P_{j \rightarrow j-1}(\omega) + P_{j \rightarrow j+1}(\omega))$ has been evaluated numerically and is plotted in Fig. 4 as a function of j for $\omega = \omega_0 + 100q$, $b/q = 2.5$, and $(2\gamma u_e)^{-1/2} = 25$. These values apply approximately for the ν_3 fundamental of CO_2 at a temperature of 820°K and a pressure of 31 atmos.

For an approximate analytic evaluation of $P(\omega)$ it is convenient to separate the sum appearing in Eq. (A5) into three distinct parts which we denote by $P'(\omega)$, $P''(\omega)$, and $P'''(\omega)$, such that

$$P(\omega) = P'(\omega) + P''(\omega) + P'''(\omega).$$

Here $P'(\omega)$ represents the contribution to the sum in Eq. (A5) for which $0 \leq j \leq j_m - Q - 1$, $P''(\omega)$ is the part for which $j_m - Q \leq j \leq j_m + Q$, $P'''(\omega)$ equals the part for $j_m + Q + 1 \leq j < \infty$, Q is an integer (which will be specified presently) much larger than b/q , and j_m is the largest integer less than $(\omega - \omega_0)/q$. It is apparent that we have chosen ω to lie in the P branch since $\omega > \omega_0$.

In the following Secs. A, B, and C, $P'(\omega)$, $P''(\omega)$, and $P'''(\omega)$ will be evaluated, respectively, at a wave number ω well removed from the band center, i.e., at $\omega - \omega_0$ appreciably larger than $2q/(2\gamma u_e)^{1/2}$.

A. Evaluation of $P'(\omega)$

$P'(\omega)$ is given by the expression

$$P'(\omega) = \alpha \gamma u_e \left(\frac{b}{\pi}\right) \sum_{j=0}^{j_m - Q - 1} \left[\exp(-\gamma u_e j^2) \right] \times \left[\frac{1}{(\omega - \omega_0 - qj)^2 + b^2} + \frac{1}{(\omega - \omega_0 + qj)^2 + b^2} \right]. \quad (\text{A6})$$

For $Q^2 \gg b^2/q^2$ the term b^2/q^2 is always negligibly small compared with $((\omega - \omega_0)/q - j)^2$ or $((\omega - \omega_0)/q + j)^2$ and Eq. (A6) may be approximated by

$$P'(\omega) \approx \frac{\alpha \gamma u_e b}{q^2 \pi} \int_0^{j_m - Q - 1/2} j \left[\exp(-\gamma u_e j^2) \right] \times \left\{ \frac{1}{\left(\frac{\omega - \omega_0}{q} - j\right)^2} + \frac{1}{\left(\frac{\omega - \omega_0}{q} + j\right)^2} \right\} dj. \quad (\text{A7})$$

Since $(\omega - \omega_0)/q > j_m - Q - \frac{1}{2}$, the integral in Eq. (A7) may be evaluated by expanding the term in parentheses in a Taylor series about $j = 0$. The result is

$$P'(\omega) = \frac{\alpha b}{\pi(\omega - \omega_0)^2} \sum_{\nu=0}^{\infty} (2\nu + 1) \frac{\nu!}{y^\nu} \left[1 - e^{-X_m} \sum_{p=0}^{\nu} \frac{X_m^p}{p!} \right] \equiv \frac{\alpha b}{\pi(\omega - \omega_0)^2} \eta \quad (\text{A8})$$

where we have introduced the notation

$$y = \gamma u_e (\omega - \omega_0)^2 / q^2 \quad (\text{A9})$$

and

$$X_m = \gamma u_e (j_m - Q - \frac{1}{2})^2. \quad (\text{A10})$$

For representative values of y and X_m it turns out that a considerable number of terms is required for the evaluation of $P'(\omega)$ according to Eq. (A8). For this reason it may be preferable to determine $P'(\omega)$ from Eq. (A7) by a graphical integration.

B. Evaluation of $P''(\omega)$

The method for evaluating $P''(\omega)$ depends on whether or not the rotational fine structure is smeared out. As will appear in the analysis, for values of $b/q \leq 0.5$ the treatment with allowance for fine structure is appropriate. For larger values of b/q the analysis given in Sec. B(2) applies.

1. Appreciable Rotational Fine Structure ($b/q \leq 0.5$)

From Eq. (A5) and the definition of $P''(\omega)$ it is apparent that

$$P''(\omega) = P''_1(\omega) + P''_2(\omega) = \alpha \gamma u_e \left(\frac{b}{\pi}\right) \left\{ \sum_{j=j_m-Q}^{j_m+Q} \frac{j \exp(-\gamma u_e j^2)}{(\omega - \omega_0 - qj)^2 + b^2} + \sum_{j=j_m-Q}^{j_m+Q} \frac{j \exp(-\gamma u_e j^2)}{(\omega - \omega_0 + qj)^2 + b^2} \right\}. \quad (\text{A11})$$

The value of Q is always chosen sufficiently small to permit the approximation

$$P''_2(\omega) = \alpha\gamma u_e \left(\frac{b}{\pi}\right) \frac{1}{(\omega - \omega_0 + qj_m)^2} \times \int_{j_m - Q}^{j_m + Q} j [\exp(-\gamma u_e j^2)] dj = \frac{\alpha b \exp[-\gamma u_e(j_m^2 + Q^2)]}{\pi (\omega - \omega_0 + qj_m)^2} \sinh(2\gamma u_e j_m Q). \quad (A12)$$

For $Q \ll j_m$, $P''_2(\omega)$ is found to be very small, i.e., the contribution of R-branch lines at a particular wave number of the P branch is negligibly small.

For sufficiently small values of Q , $P''_1(\omega)$ may be approximated by

$$P''_1(\omega) = \frac{\alpha\gamma u_e b}{\pi q^2} j_m [\exp(-\gamma u_e j_m^2)] \times \sum_{j=j_m-Q}^{j_m+Q} \left[\frac{1}{\left(\frac{\omega - \omega_0}{q} - j\right)^2 + \left(\frac{b}{q}\right)^2} \right], \quad (A13)$$

where $j \exp(-\gamma u_e j^2)$ has been replaced by $j_m \exp(-\gamma u_e j_m^2)$, an approximation which should be fairly good in the present case since the principal contribution to $P''_1(\omega)$, which is associated with the line identified by the quantum number j_m , has thereby been evaluated correctly. Owing to the existence of appreciable rotational fine structure, it is not permissible to replace the sum in Eq. (A13) by an integral. However, since $Q^2 \gg b^2/q^2$, the sum appearing in Eq. (A13) may be expressed by the following relation:

$$\sum_{j_m-Q}^{j_m+Q} \left[\frac{1}{\left(\frac{\omega - \omega_0}{q} - j\right)^2 + \frac{b^2}{q^2}} \right] \approx \sum_{-\infty}^{\infty} \left[\frac{1}{\left(\frac{\omega - \omega_0}{q} - j\right)^2 + \frac{b^2}{q^2}} \right] - \int_{(j_m+Q+\frac{1}{2})}^{\infty} \frac{dj}{\left(\frac{\omega - \omega_0}{q} - j\right)^2} - \int_{-\infty}^{j_m-Q-\frac{1}{2}} \frac{dj}{\left(\frac{\omega - \omega_0}{q} - j\right)^2} = \sum_{-\infty}^{\infty} \left[\frac{1}{\left(\frac{\omega - \omega_0}{q} - j\right)^2 + \frac{b^2}{q^2}} \right] - \frac{2}{(Q + \frac{1}{2})}, \quad (A14)$$

where $[j_m - (\omega - \omega_0/q)]^2$ has been neglected compared to $(Q + \frac{1}{2})^2$. Using an identity valid for B not an integer, viz.,⁷

$$\frac{\pi \sin \pi Z}{z \sin \pi B \sin \pi(z - B)} = \sum_{-\infty}^{\infty} \frac{1}{(B + j)(z - B - j)}, \quad (A15)$$

with $z = 2ib/q$ and $B = (\omega - \omega_0 + ib)/q$ [where $i = (-1)^{\frac{1}{2}}$], Eq. (A13) becomes

⁷ E. T. Copson, *Theory of Functions of a Complex Variable* (Oxford University Press, Oxford, 1944), p. 157, Example 40.

$$P''_1(\omega) = \frac{\alpha\gamma u_e j_m \exp(-\gamma u_e j_m^2)}{q} \times \left[\frac{\tanh(2\pi b/q)}{\cos 2\pi \left(\frac{\omega - \omega_0}{q}\right)} - \frac{2b/\pi q}{(Q + \frac{1}{2})} \right] \left[\frac{1}{1 - \frac{\cosh(2\pi b/q)}{\cosh(2\pi b/q)}} \right]. \quad (A16)$$

2. Rotational Fine Structure Smeared Out ($b/q \geq 0.5$)

For $b/q \geq 0.5$ the quantity $P''_2(\omega)$ is still given in good approximation by Eq. (A12); it is again negligibly small. The second contribution to $P''(\omega)$ may now be written as

$$P''_1(\omega) \approx \frac{\alpha\gamma u_e b}{\pi} \int_{j_m - Q - \frac{1}{2}}^{j_m + Q + \frac{1}{2}} \frac{j \exp(-\gamma u_e j^2)}{(\omega - \omega_0 - qj)^2 + b^2} dj, \quad (A17)$$

because, for the larger values of b/q , the rotational fine structure is smeared out and, therefore, the sum may be approximated by an integral. A first estimate for $P''_1(\omega)$ is then obtained by replacing the numerator in the integral by the constant value $j_m \exp(-\gamma u_e j_m^2)$. Thus

$$P''_1(\omega) \approx \frac{\alpha\gamma u_e}{\pi q} j_m [\exp(-\gamma u_e j_m^2)] \times \left\{ \tan^{-1} \left[\frac{(j_m + Q + \frac{1}{2})q - (\omega - \omega_0)}{b} \right] - \tan^{-1} \left[\frac{(j_m - Q - \frac{1}{2})q - (\omega - \omega_0)}{b} \right] \right\}; \quad (A18)$$

in particular, at the center of the j_m th line where $\omega - \omega_0 = j_m q$,

$$P''_1(\omega = \omega_0 + j_m q) \approx \frac{2\alpha\gamma u_e}{\pi q} j_m [\exp(-\gamma u_e j_m^2)] \times \tan^{-1}[(Q + \frac{1}{2})q/b]. \quad (A19)$$

since $\tan^{-1}[(Q + \frac{1}{2})q/b] = -\tan^{-1}[-(Q + \frac{1}{2})q/b]$.

A more satisfactory evaluation for the integral of Eq. (A17) may be obtained by expanding the term $j \exp(-\gamma u_e j^2)$ in a Taylor series around $j = j_m$. We find

$$j \exp(-\gamma u_e j^2) = \exp(-\gamma u_e j_m^2) \left\{ j_m - (2\gamma u_e j_m^2 - 1)(j - j_m) + [2\gamma u_e j_m(2\gamma u_e j_m^2 - 3)] \frac{(j - j_m)^2}{2} + [-3(2\gamma u_e) + 6(2\gamma u_e)^2 j_m^2 - (2\gamma u_e)^3 j_m^4] \frac{(j - j_m)^3}{6} + [15(2\gamma u_e)^2 j_m - 10(2\gamma u_e)^3 j_m^3 + (2\gamma u_e)^4 j_m^5] \frac{(j - j_m)^4}{24} - \dots \right\}. \quad (A20)$$

Since $P''_1(\omega)$ varies smoothly with ω for sufficiently large values of b/q , it is sufficient to evaluate $P''_1(\omega)$ at $\omega = \omega_0 + j_m q$ and to connect the resulting discrete points in order to obtain the curve of $P''_1(\omega)$ as a function of ω . Neglecting the quartic and higher powers of $j - j_m$ in Eq. (A20), it is now found from Eqs. (A17) and (A20) that

$$P''_1(\omega = \omega_0 + j_m q) = \frac{\alpha \gamma u_e j_m \exp(-\gamma u_e j_m^2)}{q} \times \left\{ \frac{2}{\pi} \tan^{-1}[(Q + \frac{1}{2})q/b] + \frac{2\gamma u_e b^2}{\pi q^2} (2\gamma u_e j_m^2 - 3) \right. \\ \left. \times \{ (Q + \frac{1}{2})q/b - \tan^{-1}[(Q + \frac{1}{2})q/b] \} \right\}. \quad (A21)$$

C. Evaluation of $P'''(\omega)$

For the sake of simplicity we restrict the following evaluation to $\omega = \omega_0 + j_m/q$. Since $Q^2 \gg b^2/q^2$ we find from

$$P'''(\omega_0 + j_m/q) = \frac{\alpha \gamma u_e b}{\pi q^2} \sum_{j=j_m+Q+1}^{\infty} j [\exp(-\gamma u_e j^2)] \times \left[\frac{1}{(j - j_m)^2 + (b/q)^2} + \frac{1}{(j + j_m)^2 + (b/q)^2} \right]$$

the following relation for (overlapping) rotational lines:

$$P'''(\omega_0 + j_m/q) \approx \frac{\alpha \gamma u_e b}{\pi q^2} \int_{j_m+Q+\frac{1}{2}}^{\infty} j [\exp(-\gamma u_e j^2)] \times \left[\frac{1}{(j - j_m)^2} + \frac{1}{(j + j_m)^2} \right] dj. \quad (A22)$$

The integral in Eq. (A22) can be evaluated conveniently by expanding the terms $j \exp(-\gamma u_e j^2)$ and $(j - j_m)^{-2}$ in power series around the lower limit of integration $j = j_m + Q + \frac{1}{2}$. In this manner it is easily shown that

$$P'''(\omega_0 + j_m/q) < \frac{\alpha \gamma u_e b}{\pi q^2} [\exp(-\gamma u_e (j_m + Q + \frac{1}{2})^2)] \times (j_m + Q + \frac{1}{2}) \left[\frac{1}{(Q + \frac{1}{2})} + \frac{1}{(2j_m + Q + \frac{1}{2})} \right].$$

However, according to Eq. (A8),

$$P'(\omega_0 + j_m/q) = \frac{\alpha b}{\pi q^2 j_m^2} \eta, \quad (A23)$$

where $\eta = 1.7$ for the following typical values: $j_m/j^* = 4$, $j_m = 100$, $y = 8$, $Q = 5$, $\gamma u_e = 1/2(j^*)^2 = 1/1250$, $x_m \approx 7$.

For the given numerical values we find from Eqs. (A22) and (A23) that

$$\frac{P'''(\omega_0 + j_m/q)}{P'(\omega_0 + j_m/q)} < \frac{1}{2\eta} \left(\frac{j_m}{j^*} \right)^2 \left\{ \exp \left[-\frac{1}{2} \left(\frac{j_m + Q + \frac{1}{2}}{j^*} \right)^2 \right] \right\} \times (j_m + Q + \frac{1}{2}) \left[\frac{1}{(Q + \frac{1}{2})} + \frac{1}{(2j_m + Q + \frac{1}{2})} \right] = 0.012.$$

Thus it has been demonstrated that the contribution of $P'''(\omega)$ to $P(\omega)$ is negligibly small.

D. Total Spectral Absorption Coefficient

The total absorption coefficient has been shown to be approximately

$$P(\omega) = P'(\omega) + P''_1(\omega). \quad (A24)$$

According to Eq. (A8),

$$P'(\omega) = \frac{\alpha b}{\pi(\omega - \omega_0)^2} \eta, \quad (A8)$$

where the given expression for $P'(\omega)$ applies for all values of b/q provided Q is chosen in accord with the condition $Q^2 \gg b^2/q^2$. The quantity $P''_1(\omega)$ is determined by Eq. (A16) for $b/q \leq 0.5$; it is given by Eq. (A21) for $b/q \geq 0.5$. We note that for $b/q \gg 1$ the first two terms in Eq. (A16) become identical with the value of $(2/\pi) \tan^{-1}[(q/b)(Q + \frac{1}{2})]$. Therefore the sum of the two terms appearing in the braces of Eq. (A16), when added to the second term of Eq. (A21), is a valid representation for $b/q \gg 1$. On the other hand, for small values of b/q the two terms in the braces of Eq. (A16) reduce to roughly $\pi(b/q)$ whereas the correction term to the arctangent in Eq. (A21) is about two orders of magnitude smaller for $Q = 5$, $j_m = 100$, $j^* = (2\gamma u_e)^{-\frac{1}{2}} = 25$. Hence, for all values of b/q , we have the following approximate representation for $P''_1(\omega)$:

$$P''_1(\omega) = \frac{\alpha \gamma u_e j_m \exp(-\gamma u_e j_m^2)}{q} \times \left\{ \left\{ 1 - \frac{\cos[2\pi(\omega - \omega_0)/q]}{\cosh(2\pi b/q)} \right\}^{-1} \times \tanh \left(\frac{2\pi b}{q} \right) - \frac{(2b/\pi q)}{(Q + \frac{1}{2})} + \frac{2\gamma u_e b^2}{\pi q^2} (2\gamma u_e j_m^2 - 3) \right. \\ \left. \times \left\{ \frac{q}{b} (Q + \frac{1}{2}) - \tan^{-1} \left[\frac{q}{b} (Q + \frac{1}{2}) \right] \right\} \right\}. \quad (A25)$$

TABLE II. Relevant spectroscopic constants for CO, HCl, CO₂, and H₂O.

Molecule	α_P (cm ⁻² atm ⁻¹)	q (cm ⁻¹)	b_P^a (cm ⁻¹)
CO(fundamental)	237 (300/T) ^a	3.86	0.1 <i>b</i> (T/300) ^{-1/2}
HCl(fundamental)	160 (300/T) ^b	21.2	0.1 <i>b</i> (T/300) ^{-1/2}
CO ₂ (ν_3 fundamental)	2700 (300/T) ^c	0.791	0.1 <i>b</i> (T/300) ^{-1/2}
H ₂ O(hypothetical band)	<1000 (300/T) ^d	~10	0.1 <i>b</i> (T/300) ^{-1/2}

^a S. S. Penner and D. Weber, J. Chem. Phys. **19**, 807 (1951).

^b S. S. Penner and D. Weber, J. Chem. Phys. **21**, 649 (1953).

^c Weber, Holm, and Penner, J. Chem. Phys. **20**, 1820 (1952).

^d Assumed value.

^e Representative experimental data suggest that $b_P \approx 0.10$ cm⁻¹ at 1 atm and 300°K. See, for example, D. Weber and S. S. Penner, J. Chem. Phys. **21**, 1503 (1953).

E. Large Optical Density Limit for the Validity of the "Effective Band-Width Approximation"

The limiting value of the optical density X_u , for which our effective band-width estimate applies, may be defined by

$$X_u = 0.2/P'(\omega_0 + \Delta\omega/2) \tag{A26}$$

since $P'(\omega_0 + \Delta\omega/2)$ is a slowly varying function of $\Delta\omega$. Evidently $P'(\omega_0 + \Delta\omega/2)$ is the contribution to $P(\omega)$ of the tails of the intense rotational lines at the limit of the effective band width. For $\eta = 1.7$, Eq. (A26) becomes

$$X_u \approx 0.1\pi(\Delta\omega)^2/4\alpha b. \tag{A27}$$

Relevant spectroscopic data for CO, HCl, CO₂, and H₂O are given in Table II for the most intense vibration-rotation bands. In Table III the values of X_u are listed for various temperatures and pressures.

TABLE III. Optical density limits X_u for CO, HCl, CO₂, and H₂O.

Molecule	T (°K)	$\Delta\omega$ (cm ⁻¹)	for $b/q = 0.1$ X_u (cm atm)	X_u at $p = 1$ atm (cm atm)
CO(fundamental)	300	239	74	370
	1000	436	820	7700
	3000	756	7400	114 000
HCl(fundamental)	300	560	35 000	700 000
	1000	1022	>35 000	>700 000
	3000	1722	>35 000	>700 000
CO ₂ (ν_3 fundamental)	300	108	2.6	2.1
	1000	197	30	45
	3000	342	260	660
H ₂ O(hypothetical band for $\alpha_P < 1000$ cm ⁻² atm ⁻¹ at 300°K)	300	400	>1200	>12 000
	1000	720	>14 000	>12 000
	3000	1250	>120 000	>12 000

F. Low Optical Density Limit for the Validity of the Effective Band-Width Approximation

The practical optical density limit[¶] for the validity of the effective band-width approximation cannot be determined, in general, without a careful study of the relative importance of different vibration-rotation bands. In general, a more profitable line of approach than a detailed study of line structure in the wings of vibration-rotation bands involves a direct comparison of engineering emissivities evaluated according to various limiting procedures.^{1,2}

[¶] This phrase is to be interpreted in the sense that the engineering emissivity calculations are good to perhaps 20%.