

The Emission of Radiation from Diatomic Gases. IV. Emissivity Calculations for CO and HCl for Nonoverlapping Rotational Lines as a Function of Temperature and Optical Density*

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Simplified expressions have been developed for the engineering emissivity of uniformly distributed diatomic gases for nonoverlapping rotational lines with a resonance contour. Unfortunately the rotational half-widths for spectral lines arising from transitions between excited vibrational energy levels are generally not known. For this reason it was necessary to make the assumption that the rotational half-widths for transitions of the form $n \rightarrow n+v$, $v=1$ or 2 , are identical. The theoretical analysis is, however, sufficiently general to be useful without modification when accurate data concerning the dependence of line-width on vibrational excitation become available. Explicit expressions have been obtained for the contributions to the total emissivity associated with individual vibration-rotation bands.

Representative emissivity calculations have been carried out for CO and HCl. Comparison of the calculated emissivities of CO with experimental data shows only fair agreement, suggesting either that the assumed description of rotational half-widths is inadequate or else that the empirical emissivity data are not reliable at elevated temperatures.

I. INTRODUCTION

IN previous publications we have described methods for the theoretical calculation of engineering emissivities of diatomic gases from spectroscopic data. Useful approximate methods have been obtained for the limiting cases of (a) extensive overlapping between rotational lines^{1,2} and (b) for separated rotational lines without overlapping at room temperature, provided the rotational lines are described by a dispersion formula.³ Emissivity estimates at elevated total pressures can be carried out without difficulty by using the tabulated numerical data presented previously (I). It is the purpose of the present analysis to provide useful approximate relations for emissivity calculations on diatomic gases at all temperatures for the special case when no overlapping occurs between collision-broadened rotational lines.

In Sec. II we present the basic relations for the engineering emissivity expressed as a sum of terms representing the contributions from individual vibration-rotation bands. Approximate relations are obtained on the assumption that the spectral half-widths for all rotational lines corresponding to the vibrational transitions $n \rightarrow n'$ are identical.

The results of extensive emissivity calculations as a function of temperature and optical density are presented in Sec. III for CO and HCl under conditions which will necessarily overestimate the correct values of the emissivity provided suitable numerical values have been used for integrated absorption and for rota-

tional half-width.† For large values of the optical density, a treatment based on nonoverlapping rotational lines becomes a very poor approximation since, in particular, spectral emissivities greater than unity can be obtained. In order to avoid difficulties of this sort, it is convenient to utilize the known limiting emissivities (I).

In Sec. IV the calculated emissivities for CO are compared with empirical measurements. Possible causes for observed discrepancies are considered.

II. BASIC RELATIONS

The engineering emissivity E is defined by the relation

$$E = \int_0^\infty R_\omega d\omega / \int_0^\infty R_\omega^0 d\omega, \quad (1)$$

where R_ω is the radiant energy emitted per unit area per unit time by the emitter under study into a solid angle of 2π -steradians in the wave-number interval between ω and $\omega+d\omega$ and R_ω^0 denotes the corresponding quantity for a blackbody. For uniformly distributed gaseous emitters

$$R_\omega = R_\omega^0 [1 - \exp(-P_\omega X)], \quad (2)$$

where P_ω denotes the spectral absorption coefficient. From Eqs. (1) and (2) it follows that

$$E = \int_0^\infty R_\omega^0 [1 - \exp(-P_\omega X)] d\omega / \sigma T^4, \quad (3)$$

where T is the temperature of the radiator and σ denotes the Stefan-Boltzmann constant.

† The term rotational half-width is used in the present report to denote one-half of the wave-number range for which the spectral absorption coefficient exceeds one-half of the maximum value for a given rotational transition. Thus it corresponds to the quantity which is sometimes referred to as the semihalf-width.

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¹ S. S. Penner, *J. Appl. Phys.* **21**, 685 (1950); *J. Appl. Mech.* **18**, 53 (1951). Hereafter referred to as I.

² S. S. Penner and D. Weber, *J. Appl. Phys.* **22**, 1164 (1951). Hereafter referred to as II.

³ Penner, Ostrander, and Tsien, *J. Appl. Phys.* **23**, 256 (1952). Hereafter referred to as III.

For nonoverlapping rotational lines with a Lorentz distribution and of half-width $b_{j \rightarrow j' n \rightarrow n'}$ for the rotational transition $j \rightarrow j'$ and for the vibrational transition $n \rightarrow n'$, it is readily shown that⁴⁻⁶

$$E = (\sigma T^4)^{-1} \sum_{j=0}^{\infty} \sum_{n=0}^{\infty} \sum_{n' > n}^{\infty} R^0(\omega_{j \rightarrow j' n \rightarrow n'}) \times [2\pi(b_{j \rightarrow j' n \rightarrow n'})f(x_{j \rightarrow j' n \rightarrow n'})], \quad (4)$$

where

$$f(x_{j \rightarrow j' n \rightarrow n'}) = x_{j \rightarrow j' n \rightarrow n'} \exp(-x_{j \rightarrow j' n \rightarrow n'})$$

and

$$\times [J_0(ix_{j \rightarrow j' n \rightarrow n'}) - iJ_1(ix_{j \rightarrow j' n \rightarrow n'})] \quad (5)$$

$$x_{j \rightarrow j' n \rightarrow n'} = S_{j \rightarrow j' n \rightarrow n'} X / 2\pi b_{j \rightarrow j' n \rightarrow n'}$$

Here $S_{j \rightarrow j' n \rightarrow n'}$ is the integrated absorption (expressed in $\text{cm}^{-2} \text{atoms}^{-1}$) of the rotational line associated with the rotational transition $j \rightarrow j'$ and the vibrational transition $n \rightarrow n'$, X is the optical density of the uniformly distributed emitters (expressed in cm atoms), and J_0 and J_1 denote Bessel functions of order zero and one, respectively. For optical densities at which the approximation of nonoverlapping between rotational lines applies, the values of n' which need to be considered normally are $n+1$ (fundamental vibration-rotation band) and $n+2$ (first overtone). The selection rules restrict the allowed values of j' to $j \pm 1$ for molecules with P and R branches and to $j' = j$, $j \pm 1$ for diatomic molecules with Q -branch (e.g., NO).

The values of $S_{j \rightarrow j' n \rightarrow n'}$ are given, in good approximation, by the relations^{6,7}

$$S_{j \rightarrow j-1}^{0 \rightarrow 1} = \alpha_F (\omega_{j \rightarrow j-1}^{0 \rightarrow 1} / \omega^*) [(j+\lambda)(j-\lambda)/j] \times [\exp(-E(0, j)/kT) F_{j \rightarrow j-1} G_{j \rightarrow j-1}^{0 \rightarrow 1} Q^{-1}], \quad (6)$$

$$S_{j-1 \rightarrow j}^{0 \rightarrow 1} = \alpha_F (\omega_{j-1 \rightarrow j}^{0 \rightarrow 1} / \omega^*) [(j+\lambda)(j-\lambda)/j] \times [\exp(-E(0, j-1)/kT) F_{j-1 \rightarrow j} G_{j-1 \rightarrow j}^{0 \rightarrow 1} Q^{-1}], \quad (7)$$

$$S_{j \rightarrow j}^{0 \rightarrow 1} = \alpha_F (\omega_{j \rightarrow j}^{0 \rightarrow 1} / \omega^*) [\lambda^2(2j+1)/j(j+1)] \times [\exp(-E(0, j)/kT) G_{j \rightarrow j}^{0 \rightarrow 1} Q^{-1}], \quad (8)$$

$$S_{j \rightarrow j' n \rightarrow n+1} / S_{j \rightarrow j' n \rightarrow n}^{0 \rightarrow 1} = (n+1) (\omega_{j \rightarrow j' n \rightarrow n+1} / \omega_{j \rightarrow j' n \rightarrow n}^{0 \rightarrow 1}) \times \{\exp[-E(n, j) + E(0, j)]/kT\} \times (G_{j \rightarrow j' n \rightarrow n+1} / G_{j \rightarrow j' n \rightarrow n}^{0 \rightarrow 1}), \quad (9)$$

$$S_{j \rightarrow j}^{0 \rightarrow 2} / S_{j \rightarrow j}^{0 \rightarrow 1} = (\omega_{j \rightarrow j}^{0 \rightarrow 2} / 2\omega^*) (\omega^* / \omega_{j \rightarrow j}^{0 \rightarrow 1}) \times (G_{j \rightarrow j}^{0 \rightarrow 2} / G_{j \rightarrow j}^{0 \rightarrow 1}) (\alpha_0 / \alpha_F) \simeq (\alpha_0 / \alpha_F) \times [1 + \exp(-hc\omega^*/kT)], \quad (10)$$

$$S_{j \rightarrow j' n \rightarrow n+2} / S_{j \rightarrow j' n \rightarrow n}^{0 \rightarrow 2} = [(n+2)(n+1)/2] \times (\omega_{j \rightarrow j' n \rightarrow n+2} / \omega_{j \rightarrow j' n \rightarrow n}^{0 \rightarrow 2}) \times \{\exp[-E(n, j) + E(0, j)]/kT\} \times (G_{j \rightarrow j' n \rightarrow n+2} / G_{j \rightarrow j' n \rightarrow n}^{0 \rightarrow 2}), \quad (11)$$

$$\alpha_F = \sum_j \sum_n S_{j \rightarrow j' n \rightarrow n+1} \simeq (\omega^* / \omega_e) (N_T \pi \epsilon^2 / 3\mu c), \quad (12)$$

$$\alpha_0 = [1 - \exp(-hc\omega^*/kT)] \times [1 + \exp(-hc\omega^*/kT)]^{-1} \sum_j \sum_n S_{j \rightarrow j' n \rightarrow n+2} = (N_T h \epsilon^2 / 24\pi c^3 \omega_e \mu^2 r_e^2) (\omega^* / \omega_e) (\rho_e'' + a_1)^2. \ddagger \quad (13)$$

Here ω^* = wave number corresponding to the transition $j=0 \rightarrow j=0$, $n=0 \rightarrow n=1$; ω_e = wave number corresponding to an infinitesimal oscillation at the equilibrium internuclear distance; λ = quantum number measuring the electronic angular momentum about the internuclear axis; N_T = total number of molecules per unit volume; ϵ = rate of change of electric moment with internuclear distance; μ = reduced mass of the molecule; c = velocity of light; Q = complete partition function; $E(n, j)$ = energy of the n th vibrational and j th rotational level;

$$G_{j \rightarrow j' n \rightarrow n'} = 1 - \exp(-hc\omega_{j \rightarrow j' n \rightarrow n'} / kT);$$

$$F_{j \rightarrow j-1} = 1 + 8\gamma j [1 + (5\gamma j/4) - (3\gamma/4)];$$

$$F_{j-1 \rightarrow j} = 1 - 8\gamma j [1 - (5\gamma j/4) - (3\gamma/4)],$$

where $\gamma = h/8\pi^2 I c \omega_e$ with I representing the equilibrium moment of inertia; r_e = equilibrium internuclear distance; $\rho_e'' = p_e''/p_e'$, where p_e' and $p_e''/2$ represent, respectively, the coefficients multiplying $\xi = (r - r_e)/r_e$ and ξ^2 in the Taylor series expansion of the electric moment $p(\xi)$ about $\xi=0$; a_1 = mechanical anharmonicity constant, which is related to the usual spectroscopic constants through the equation $-\alpha_e = 3\gamma B_e(a_1 + 1)$. The quantities α_F and α_0 must be determined empirically.

Let

$$E_{F1} = (\sigma T^4)^{-1} \sum_{j=0}^{\infty} R^0(\omega_{j \rightarrow j}^{0 \rightarrow 1}) \times [2\pi(b_{j \rightarrow j}^{0 \rightarrow 1})f(x_{j \rightarrow j}^{0 \rightarrow 1})] \quad (14)$$

represent the contribution to the total emissivity made by rotational lines belonging to the $n=0 \rightarrow n=1$ vibrational transition. Equation (4) can evidently be written

‡ Equation (13) has been obtained from the analysis of Crawford and Dinsmore (reference 7). It is somewhat surprising that $\sum_j \sum_n S_{j \rightarrow j' n \rightarrow n+2}$ has temperature-dependent terms for a given number of molecules, even in first order.

⁴ R. Ladenburg and F. Reiche, *Ann. Physik* **42**, 181 (1913).

⁵ W. M. Elsasser, *Harvard Meteorological Studies No. 6* (Blue Hill Observatory, 1942).

⁶ S. S. Penner, *J. Chem. Phys.* **19**, 272, 1434 (1951).

⁷ B. L. Crawford, Jr., and H. L. Dinsmore, *J. Chem. Phys.* **18**, 983, 1682 (1950).

in the form

$$E = (\sigma T^4)^{-1} \sum_{j=0}^{\infty} R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) [2\pi(b_{j \rightarrow j', 0 \rightarrow 1})f(x_{j \rightarrow j', 0 \rightarrow 1})] \\ \times \sum_{n=0}^{\infty} \sum_{n' > n} [R^0(\omega_{j \rightarrow j', n \rightarrow n'})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 1})] \\ \times [2\pi(b_{j \rightarrow j', n \rightarrow n'})f(x_{j \rightarrow j', n \rightarrow n'})/2\pi(b_{j \rightarrow j', 0 \rightarrow 1}) \\ \times f(x_{j \rightarrow j', 0 \rightarrow 1})]. \quad (15)$$

Since E_{F1} can be calculated without difficulty (III), we shall express E in terms of E_{F1} by using Eq. (15) or a suitable modification of Eq. (15) successively for the vibrational transitions $0 \rightarrow 2$, $n \rightarrow n+1$, and $n \rightarrow n+2$. The calculations are simplified greatly by utilizing approximate expressions for the ratios appearing in the square brackets of Eq. (15).

The following relation follows obviously from the Planck blackbody distribution law:

$$R^0(\omega_{j \rightarrow j', n \rightarrow n'})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) = (\omega_{j \rightarrow j', n \rightarrow n'}/\omega_{j \rightarrow j', 0 \rightarrow 1})^3 \\ \times \{[\exp(u\omega_{j \rightarrow j', 0 \rightarrow 1}/\omega^*)] - 1\} \\ \times \{[\exp(u\omega_{j \rightarrow j', n \rightarrow n'}/\omega^*)] - 1\}^{-1}, \quad (16)$$

where $u = hc\omega^*/kT$. A general expression cannot readily be obtained for the ratio $[2\pi(b_{j \rightarrow j', n \rightarrow n'})f(x_{j \rightarrow j', n \rightarrow n'})/2\pi(b_{j \rightarrow j', 0 \rightarrow 1})f(x_{j \rightarrow j', 0 \rightarrow 1})]$. However, use of appropriate asymptotic forms leads to the relations

$$2\pi(b_{j \rightarrow j', n \rightarrow n'})f(x_{j \rightarrow j', n \rightarrow n'}) \simeq 2(S_{j \rightarrow j', n \rightarrow n'}b_{j \rightarrow j', n \rightarrow n'}X)^{\frac{1}{2}} \\ \text{for large values of } x_{j \rightarrow j', n \rightarrow n'}, \quad (17a)$$

$$2\pi(b_{j \rightarrow j', n \rightarrow n'})f(x_{j \rightarrow j', n \rightarrow n'}) \simeq S_{j \rightarrow j', n \rightarrow n'}X \\ \text{for small values of } x_{j \rightarrow j', n \rightarrow n'}. \quad (17b)$$

It is well known that Eq. (17a) forms a useful approximation for values of $x_{j \rightarrow j', n \rightarrow n'}$ as small as three.^{4,5} It is evident that the computation of emissivities as a function of temperature will generally require the use of Eq. (17a) for n less than some small integer, whereas for larger values of n the approximation given in Eq. (17b) will be more reasonable. For what particular values of n and n' a change is to be effected will evidently depend on the numerical values of the optical density, integrated absorption, and rotational half-width.

We proceed now to use Eqs. (15) to (17b) in conjunction with Eqs. (6) to (13) to obtain explicit relations for the contributions to the total emissivity made by various vibration-rotation bands. Unfortunately the values of $b_{j \rightarrow j', n \rightarrow n'}$ are usually not known whence we shall have to assume that $b_{j \rightarrow j', n \rightarrow n+1} = b_{j \rightarrow j', 0 \rightarrow 1} = b_F$ and $b_{j \rightarrow j', n \rightarrow n+2} = b_{j \rightarrow j', 0 \rightarrow 2} = b_0$.[§] Since the condition of non-

overlapping between rotational lines is not generally met for the Q branch and since, furthermore, NO is the only important diatomic molecule which exhibits a (weak) Q branch, further discussion will be restricted to the evaluation of E for diatomic molecules which have only P and R branches ($\lambda=0$).

A. Contributions to E made by the Vibrational Transition $n=0 \rightarrow n=2$ (E_{01})

Since $\omega_{j \rightarrow j', 0 \rightarrow 2} \simeq 2\omega_{j \rightarrow j', 0 \rightarrow 1} \simeq 2\omega^*$, Eq. (16) becomes

$$R^0(\omega_{j \rightarrow j', 0 \rightarrow 2})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq 8[\exp(u) + 1]^{-1}.$$

From Eqs. (10), (17a), and (17b) it is evident that

$$2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2})/2\pi b_F f(x_{j \rightarrow j', 0 \rightarrow 1}) \simeq (\alpha_0/\alpha_F)[1 + \exp(-u)]$$

for small values of $x_{j \rightarrow j', 0 \rightarrow 1}$, $x_{j \rightarrow j', 0 \rightarrow 2}$;

$$2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2})/2\pi b_F f(x_{j \rightarrow j', 0 \rightarrow 1}) \\ \simeq (\alpha_0/\alpha_F)^{\frac{1}{2}}(b_0/b_F)^{\frac{1}{2}}[1 + \exp(-u)]^{\frac{1}{2}}$$

for large values of $x_{j \rightarrow j', 0 \rightarrow 1}$, $x_{j \rightarrow j', 0 \rightarrow 2}$;

$$2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2})/2\pi b_F f(x_{j \rightarrow j', 0 \rightarrow 1}) \\ \simeq \frac{1}{2}(\alpha_0/\alpha_F)(1/b_F)(S_{j \rightarrow j', 0 \rightarrow 1}b_F X)^{\frac{1}{2}}[1 + \exp(-u)]$$

for large values of $x_{j \rightarrow j', 0 \rightarrow 1}$ and small values of $x_{j \rightarrow j', 0 \rightarrow 2}$.

We now obtain several special cases.

(a) If $x_{j \rightarrow j', 0 \rightarrow 1}$ and $x_{j \rightarrow j', 0 \rightarrow 2}$ are small, then

$$E_{01} \simeq 8[\exp(-u)](\alpha_0/\alpha_F)E_{F1}. \quad (18a)$$

Equation (18a) would be expected to apply only to very weak radiators, at low optical densities, and at the largest pressures which are consistent with the idea that no overlapping occurs between rotational lines.

(b) If $x_{j \rightarrow j', 0 \rightarrow 1}$ and $x_{j \rightarrow j', 0 \rightarrow 2}$ are large, then

$$E_{01} \simeq 8[\exp(-u)][1 + \exp(-u)]^{-\frac{1}{2}} \\ \times (\alpha_0/\alpha_F)^{\frac{1}{2}}(b_0/b_F)^{\frac{1}{2}}E_{F1}. \quad (18b)$$

Equation (18b) would be expected to apply to intense radiators at moderate or large values of the optical density, particularly at low pressures where b_0 and b_F are small.

(c) If $x_{j \rightarrow j', 0 \rightarrow 1}$ is large and $x_{j \rightarrow j', 0 \rightarrow 2}$ is small, then

$$E_{01} \simeq 8(\alpha_0/\alpha_F)(1/b_F)[\exp(-u)]b_F X(\sigma T^4)^{-1} \\ \times \sum_{j=0}^{\infty} R^0(\omega_{j \rightarrow j', 0 \rightarrow 1})S_{j \rightarrow j', 0 \rightarrow 1}.$$

But $R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq R^0(\omega^*)$ and

$$\sum_{j=0}^{\infty} S_{j \rightarrow j', 0 \rightarrow 1} \equiv \alpha_{F1} \simeq \alpha_F [1 - \exp(-u)]^2.{}^7$$

Hence,

$$E_{01} \simeq 120u^5 \pi^{-4} (\alpha_0/\alpha_F) [(\alpha_F/u)X/\omega^*] \\ \times [\exp(-2u)][1 - \exp(-u)], \quad (18c)$$

§ For large values of u (i.e., low temperatures) it is evident that $R^0(\omega_{j \rightarrow j', 0 \rightarrow 2})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq 8 \exp(-u)$. For small values of u (i.e., high temperatures) it follows that $R^0(\omega_{j \rightarrow j', 0 \rightarrow 2})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq 4$.

§ This approximation is discussed more fully in paragraph IIG and in Appendix I.

where α_F/u is independent of temperature. Since α_0/α_F is generally very small compared to unity, Eq. (18c) will apply to many problems which are of practical interest.

B. Contributions to E made by the Vibrational Transitions $n \rightarrow n+1$ ($E_F = \sum_i E_{Fi}$).

Since $\omega_{j \rightarrow j', n \rightarrow n+1} \simeq \omega_{j \rightarrow j', 0 \rightarrow 1} \simeq \omega^*$, Eq. (16) becomes

$$R^0(\omega_{j \rightarrow j', n \rightarrow n+1})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq 1.$$

From Eqs. (9), (17a), and (17b) it can be seen that

$$2\pi b_F f(x_{j \rightarrow j', n \rightarrow n+1})/2\pi b_F f(x_{j \rightarrow j', 0 \rightarrow 1}) = (n+1) \exp(-nu)$$

for small values of $x_{j \rightarrow j', 0 \rightarrow 1}$, $x_{j \rightarrow j', n \rightarrow n+1}$;

$$2\pi b_F f(x_{j \rightarrow j', n \rightarrow n+1})/2\pi b_F f(x_{j \rightarrow j', 0 \rightarrow 1}) = (n+1)^{1/2} \exp(-nu/2)$$

for large values of $x_{j \rightarrow j', 0 \rightarrow 1}$, $x_{j \rightarrow j', n \rightarrow n+1}$;

$$2\pi b_F f(x_{j \rightarrow j', n \rightarrow n+1})/2\pi b_F f(x_{j \rightarrow j', 0 \rightarrow 1}) = \frac{1}{2}(n+1) \exp(-nu) (S_{j \rightarrow j', 0 \rightarrow 1} b_F X)^{1/2} (b_F)^{-1}$$

for large values of $x_{j \rightarrow j', 0 \rightarrow 1}$ and small values of $x_{j \rightarrow j', n \rightarrow n+1}$. It is again of interest to examine several special cases.

(a) If $x_{j \rightarrow j', 0 \rightarrow 1}$ and $x_{j \rightarrow j', n \rightarrow n+1}$ are small, then

$$E_F = E_{F1} [1 - \exp(-u)]^{-2}. \quad (19a)$$

Equation (19a) applies under the same conditions as Eq. (18a).

(b) If $x_{j \rightarrow j', 0 \rightarrow 1}$ and $x_{j \rightarrow j', n \rightarrow n+1}$ are large, then

$$E_F = \left\{ \sum_{n=0}^{\infty} (n+1)^{1/2} [\exp(-nu/2)] \right\} E_{F1}. \quad (19b)$$

It is evident that Eq. (19b) cannot apply in any real problem since $x_{j \rightarrow j', n \rightarrow n+1}$ must become small for sufficiently large values of n .

(c) If $x_{j \rightarrow j', 0 \rightarrow 1}$ is large and $x_{j \rightarrow j', n \rightarrow n+1}$ is large for $n < K$ but $x_{j \rightarrow j', n \rightarrow n+1}$ is small for $n \geq K$, then

$$E_F = E_{F1} \left\{ \sum_{n=0}^{K-1} (n+1)^{1/2} [\exp(-nu/2)] \right\} + \left\{ \sum_{n=K}^{\infty} (n+1) [\exp(-nu)] \right\} X (\sigma T^4)^{-1} \times \sum_{j=0}^{\infty} R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) S_{j \rightarrow j', 0 \rightarrow 1}.$$

But $R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq R^0(\omega^*)$, whence

$$E_F \simeq E_{F1} \left\{ \sum_{n=0}^{K-1} (n+1)^{1/2} [\exp(-nu/2)] \right\} + 15u^5 \pi^{-4} [(\alpha_F/u) X / \omega^*] \times \exp(-u) [1 - \exp(-u)] \times \left\{ \sum_{n=K}^{\infty} (n+1) [\exp(-nu)] \right\}, \quad (19c)$$

where the sum over n may be evaluated conveniently by noting that

$$\sum_{n=K}^{\infty} (n+1) [\exp(-nu)] = [1 - \exp(-u)]^{-2} - \sum_{n=0}^{K-1} (n+1) [\exp(-nu)].$$

Equation (19c) is a useful expression for E_F for most problems which arise in practice. Depending upon the numerical values of $S_{j \rightarrow j', 0 \rightarrow 1}$, X , b_F , and the temperature, the appropriate value for K will be an integer somewhere between 1 and 5.

C. Contributions to E made by the Vibrational Transitions $n \rightarrow n+2$ ($E_0 = \sum_i E_{0i}$).

For the evaluation of E_0 it is convenient to replace Eq. (15) by the relation

$$E_0 = (\sigma T^4)^{-1} \sum_{j=0}^{\infty} R^0(\omega_{j \rightarrow j', 0 \rightarrow 2}) [2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2})] \times \sum_{n=0}^{\infty} [R^0(\omega_{j \rightarrow j', n \rightarrow n+2})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 2})] \times [2\pi b_0 f(x_{j \rightarrow j', n \rightarrow n+2})/2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2})]. \quad (20)$$

By proceeding from Eq. (16) we obtain the result

$$R^0(\omega_{j \rightarrow j', n \rightarrow n+2})/R^0(\omega_{j \rightarrow j', 0 \rightarrow 2}) \simeq 1$$

since

$$\omega_{j \rightarrow j', n \rightarrow n+2} \simeq \omega_{j \rightarrow j', 0 \rightarrow 2}.$$

Equations (11), (17a), and (17b) lead to the relations

$$2\pi b_0 f(x_{j \rightarrow j', n \rightarrow n+2})/2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2}) = [(n+2)(n+1)/2] [\exp(-nu)]$$

for small values of $x_{j \rightarrow j', 0 \rightarrow 2}$ and $x_{j \rightarrow j', n \rightarrow n+2}$;

$$2\pi b_0 f(x_{j \rightarrow j', n \rightarrow n+2})/2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2}) = [(n+2)(n+1)/2]^{1/2} [\exp(-nu/2)]$$

for large values of $x_{j \rightarrow j', 0 \rightarrow 2}$ and $x_{j \rightarrow j', n \rightarrow n+2}$;

$$2\pi b_0 f(x_{j \rightarrow j', n \rightarrow n+2})/2\pi b_0 f(x_{j \rightarrow j', 0 \rightarrow 2}) = \frac{1}{2} [(n+2)(n+1)/2] \exp(-nu) (S_{j \rightarrow j', 0 \rightarrow 2} b_0 X)^{1/2} (b_0)^{-1}$$

for large values of $x_{j \rightarrow j', 0 \rightarrow 2}$ and small values of $x_{j \rightarrow j', n \rightarrow n+2}$.

Thus we obtain for E_0 the following approximate relations:

(a) For small values of $x_{j \rightarrow j', 0 \rightarrow 2}$ and $x_{j \rightarrow j', n \rightarrow n+2}$:

$$E_0 = \left\{ \sum_{n=0}^{\infty} [(n+2)(n+1)/2] [\exp(-nu)] \right\} E_{01} = [1 - \exp(-u)]^2 E_{01}. \quad (20a)$$

Equation (20a) constitutes a useful approximation for

moderate or small values of the optical density for most diatomic molecules.

(b) For large values of $x_{j \rightarrow j', 0 \rightarrow 2}$ and $x_{j \rightarrow j', n \rightarrow n+2}$

$$E_0 = \left\{ \sum_{n=0}^{\infty} [(n+2)(n+1)/2]^{\frac{1}{2}} [\exp(-nu/2)] \right\} E_{01}. \quad (20b)$$

Equation (20b) is of no practical interest since $x_{j \rightarrow j', n \rightarrow n+2}$ must become very small at all temperatures for sufficiently large values of n .

(c) For large values of $x_{j \rightarrow j', 0 \rightarrow 2}$ and $x_{j \rightarrow j', n \rightarrow n+2}$ for $n < K$ and small values of $x_{j \rightarrow j', n \rightarrow n+2}$ for $n \geq K$,

$$E_0 = \left\{ \sum_{n=0}^{K-1} [(n+2)(n+1)/2]^{\frac{1}{2}} [\exp(-nu/2)] \right\} E_{01} \\ + 120(u/\pi)^4 (\alpha_0 X/\omega^*) \{ [\exp(2u)] - 1 \}^{-1} \\ \times \left\{ \sum_{n=K}^{\infty} [(n+2)(n+1)/2] [\exp(-nu)] \right\},$$

where⁷

$$\alpha_{01} = \sum_{j=0}^{\infty} S_{j \rightarrow j', 0 \rightarrow 2} \simeq \alpha_0 [1 - \exp(-u)] [1 - \exp(-2u)].$$

Hence,

$$E_0 = \left\{ \sum_{n=0}^{K-1} [(n+2)(n+1)/2]^{\frac{1}{2}} [\exp(-nu/2)] \right\} E_{01} \\ + 120u^5 \pi^{-4} (\alpha_0/\alpha_F) [(\alpha_F/u) X/\omega^*] \\ \times [\exp(-2u)] [1 - \exp(-u)] \\ \times \left\{ \sum_{n=K}^{\infty} [(n+2)(n+1)/2] [\exp(-nu)] \right\}. \quad (20c)$$

D. Contributions to E made by Vibrational Transitions $n \rightarrow n'$, $n' > n+2$.

The total contributions to radiant heat transfer from harmonics above the first overtone can be calculated by an obvious extension of the methods described above by using appropriate relations obtainable from the analysis of Crawford and Dinsmore.⁷

E. The Total Emissivity E

Suitable approximate expressions for the total engineering emissivity E can be obtained by combining the results given in the preceding paragraphs. A representative case, which may be considered to be a reasonable approximation for CO at small optical densities and for temperatures between 300°K and 1500°K, can be obtained as follows. The quantities $x_{j \rightarrow j', 0 \rightarrow 1}$ and $x_{j \rightarrow j', 0 \rightarrow 2}$ are considered to be large, whence it follows that E_{01} is given by Eq. (18b). Equation (19c) applies for E_F with $K=3$ and Eq. (20c) applies for E_0 with $K=1$.

Thus,

$$E = E_{F1} \left\{ \sum_{n=0}^2 (n+1)^{\frac{1}{2}} [\exp(-nu/2)] + 8 [\exp(-u)] \right. \\ \times [1 + \exp(-u)]^{-\frac{1}{2}} (\alpha_0/\alpha_F)^{\frac{1}{2}} (b_0/b_F)^{\frac{1}{2}} \left. \right\} \\ + 15u^5 \pi^{-4} [(\alpha_F/u) X/\omega^*] [\exp(-u)] \\ \times [1 - \exp(-u)] \{ [1 - \exp(-u)]^{-2} \\ - \sum_{n=0}^2 (n+1) [\exp(-nu)] \} + 8(\alpha_0/\alpha_F) \\ \times [\exp(-u)] \{ [1 - \exp(-u)]^{-3} - 1 \}. \quad (21)$$

Equation (21) has been written in such a way that E is given directly in terms of dimensionless parameters which depend only on the molecular constants and on E_{F1} .

An approximate expression for E_{F1} can be obtained very simply from Eq. (14) by utilizing the asymptotic form given in Eq. (17a) with the integrated absorption per rotational line given by Eqs. (6) and (7). Although the relation which is obtained by making such approximations as $R^0(\omega_{j \rightarrow j', 0 \rightarrow 1}) \simeq R^0(\omega^*)$ is entirely adequate for the present purposes, we shall not utilize the result obtained in this manner since a more accurate evaluation of E_{F1} from Eq. (14) has been carried out by Tsien (III). The resulting expression for E_{F1} is

$$E_{F1} = 30u^5 \pi^{-4} [\exp(-u)] [(\gamma b_F/\omega^*) (\alpha_F/u) (X/\omega^*)]^{\frac{1}{2}} \\ \times f(\gamma, \delta, x^*, u) \{ 1.225(2/\gamma u)^{\frac{1}{2}} \\ \times [1 + (3\gamma/2u)g(\gamma, \delta, u)] - 0.417 \}. \quad (22)$$

Here $f(\gamma, \delta, x^*, u)$ and $[1 + (3\gamma/2u)g(\gamma, \delta, u)]$ are functions which are defined elsewhere but are generally close to unity (Sec. III for details).

The expression given in Eq. (21) would be expected to overestimate[¶] the actual value of the engineering emissivity (a) because partial overlapping may occur between rotational lines and (b) because the asymptotic forms for $f(x)$ overestimate $f(x)$ for every value of x . Since the spectral emissivity of uniformly heated gases cannot exceed the spectral emissivity of a blackbody at the same temperature, Eq. (21) will evidently lead to invalid results for excessively large values of X . In this connection it will be useful to refer to the limiting emissivities computed in I.

We have developed two methods for the theoretical calculation of E , both of which overestimate the true value of E . For small and moderate values of X ,[†] Eq. (21) or a suitable modification of Eq. (21) represents a useful approximation provided the rotational spacing

[¶] Equation (21) will yield values for E which are too small at temperatures which are so high that Doppler-broadening becomes important. For spectral lines which are best described by combined Doppler- and collision-broadening the present treatment will require extensive revision. See Sec. IV in this connection.

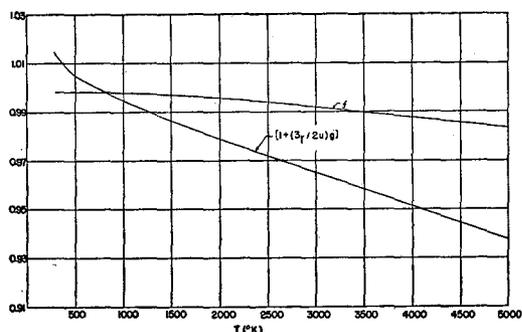


Fig. 1. The quantities f and $[1+(3\gamma/2u)g]$ as a function of temperature for CO.

is large compared to the collision half-width. For large values of X or at elevated pressures the use of average absorption coefficients is generally preferable (I). When very precise estimates are desired for the emissivity, it is possible to perform numerical calculations by evaluating the integral appearing in Eq. (3) directly. This procedure is indicated for partial overlapping between rotational lines and is facilitated by the use of computing machines.

F. Limits of Validity of the Theoretical Expression for E

The limits of validity of the relations derived in the preceding paragraphs for nonoverlapping rotational lines are defined by (a) the approximations involved in the use of asymptotic limiting forms and (b) the validity of the assumptions that

$$b_{j \rightarrow j', n \rightarrow n+1} = b_{j \rightarrow j', 0 \rightarrow 1} = b_F \quad \text{and} \quad b_{j \rightarrow j', n \rightarrow n+2} = b_{j \rightarrow j', 0 \rightarrow 2} = b_0.$$

The use of asymptotic limiting forms, in conjunction with the assumption that no overlapping occurs between rotational lines, will necessarily maximize the calculated values of E . This statement remains true independently of the choice of a particular one of the asymptotic forms given in Eqs. (17a) and (17b). Thus both x and $(2x/\pi)^{\frac{1}{2}}$ are larger than $f(x)$ for every value of x with $f(x) = x$ representing a better approximation for small values of x and $f(x) = (2x/\pi)^{\frac{1}{2}}$ being more adequate for large values of x . In general, the relation $f(x) = x$ is to be preferred for $x \leq (2/\pi)$ and the relation $f(x) = (2x/\pi)^{\frac{1}{2}}$ for $x \geq (2/\pi)$. Thus we arrive at the important conclusion that we have obtained reasonable upper limits for the emissivity as long as the line width and line shape are described correctly.

The effect on E of the assumed line shape and line width cannot be estimated in a satisfactory manner at the present time. Since we have neglected Doppler broadening entirely, the calculated values of E will be relatively too low as the temperature is raised. Representative calculations show, however, that at atmospheric pressure (and hence also at higher pressures) the Doppler half-width is generally small compared to the collision half-width at temperatures below about 2000°K

(Sec. IV). Therefore, it appears unlikely that the calculated values of E will be reduced significantly, in the temperature range for which experimental data are available, merely because of neglect of the contributions of Doppler broadening to the spectral line shape and half-width. On the other hand, it is entirely possible that relatively large errors are introduced by the approximations $b_{j \rightarrow j', n \rightarrow n+1} = b_F$ and $b_{j \rightarrow j', n \rightarrow n+2} = b_0$. Although semiquantitative considerations of the type given in Appendix I suggest that the effective collision diameter of diatomic molecules is not a sensitive function of vibrational quantum number, it is hardly justifiable to apply this conclusion to the optical collision diameter. Thus we are forced to note that the calculated values of E are unreliable at temperatures above about 500°K where radiant heat transfer from excited vibrational energy states begins to play an important role. The theoretical relations obtained in the present discussion can be modified, without difficulty, to allow for a more adequate description of line width if and when the needed experimental and/or theoretical data become available.

III. EMISSIVITY CALCULATIONS FOR NONOVERLAPPING ROTATIONAL LINES FOR CO AND HCl**

Equation (21) will now be used for representative emissivity calculations on CO and HCl. First we shall compute E_{F1} from Eq. (22). Next the contributions to radiant heat transfer arising from the transitions $n=1 \rightarrow n'=2$, $n=2 \rightarrow n'=3$, and $n=0 \rightarrow n'=2$ are evaluated. Finally the total emissivity E is determined according to Eq. (21).

A. Calculation of E_{F1}

The partial emissivity E_{F1} is determined by Eq. (22). Explicit expressions for f and $[1+(3\gamma/2u)g]$ have been given previously in III. Plots of these quantities are shown as a function of temperature for CO and HCl in Figs. 1 and 2, respectively. An adequate approximation

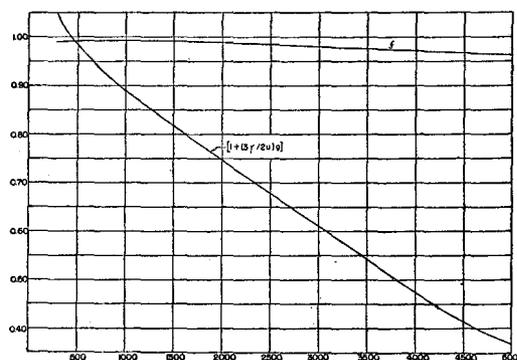


Fig. 2. The quantities f and $[1+(3\gamma/2u)g]$ as a function of temperature for HCl.

** Numerical calculations were carried out by Mr. E. K. Björnerud and Mrs. B. MacDonald.

to E_{F1} for CO at all temperatures is evidently given by the relation (III)

$$E_{F1} \approx 0.6345u^5 [\exp(-u)] (\gamma u)^{-\frac{1}{2}} \times [(\gamma b/\omega^*) (X/\omega^*) (\alpha_F/u)]. \quad (22a)$$

The quantity E_{F1} has been computed as a function of temperature, according to Eq. (22) for CO and HCl. The numerical values were obtained by using the well-known result that the Lorentz half-width varies as $T^{-\frac{1}{2}}$ at constant pressure. For the conditions of interest in the present study it was assumed that

$$b \equiv b_c = b_F = b_0 = 0.076 (T/300)^{-\frac{1}{2}} \text{ cm}^{-1} \text{ for CO}^8$$

and

$$b \equiv b_c = b_F = b_0 = 0.10 (T/300)^{-\frac{1}{2}} \text{ cm}^{-1} \text{ for HCl},^9$$

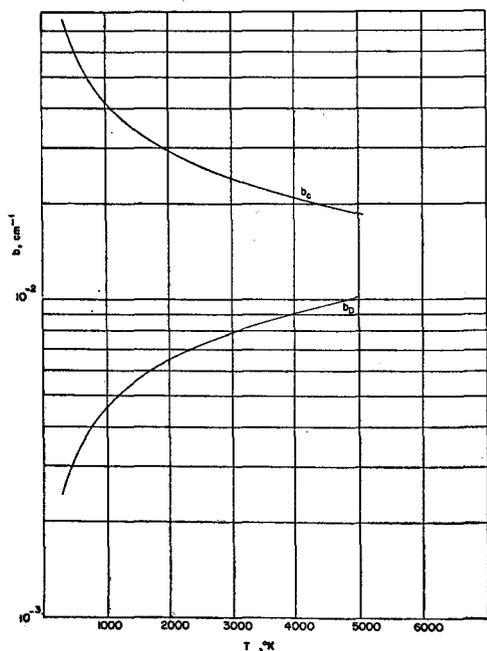


Fig. 3. Doppler half-width (b_D) and collision half-width (b_c) as a function of temperature for CO.

i.e., the spectral half-width b was set equal to the collision half-width b_c . It appears likely that Doppler-broadening will not make a significant contribution to E_{F1} at temperatures below about 2000°K. The Doppler half-widths (b_D) and collision half-widths (b_c) are plot-

⁸ S. S. Penner and D. Weber, *J. Chem. Phys.* **19**, 1351, 1361 (1951). *Note added in proof:* The value $b_0 = 0.076 \text{ cm}^{-1} \text{ atm}^{-1}$ at room temperature is based on an extrapolation using unpublished measurements of b_0 as a function of experimental slit width. W. S. Benedict and S. Silverman have studied the first overtone of CO with greatly improved resolution and have reported $b_0 = 0.095 \text{ cm}^{-1} \text{ atm}^{-1}$ for self-broadening (paper presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, June, 1952). The calculated emissivities are relatively insensitive to the numerical value used for b_0 . Thus, changing b_0 by a factor of two will generally change E by less than 10 percent.

⁹ S. S. Penner and D. Weber, paper presented at the *Symposium on Molecular Structure and Spectroscopy*, Ohio State University, Columbus, 1951.

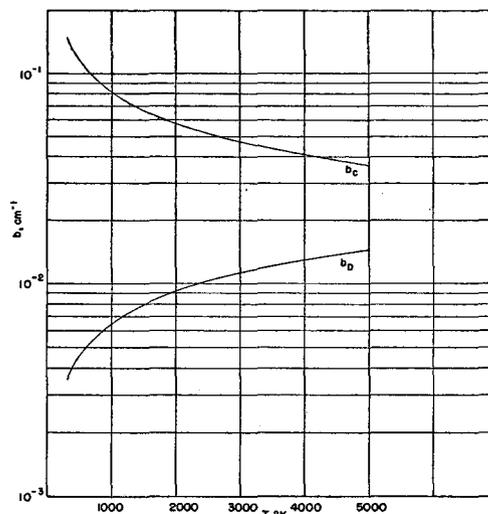


Fig. 4. Doppler half-width (b_D) and collision half-width (b_c) as a function of temperature for HCl.

ted as a function of temperature in Figs. 3 and 4 for CO and HCl, respectively.

The basic spectroscopic constants which were used for the numerical calculations are summarized in Table I. Numerical values for E_{F1} , as a function of temperature and optical density, have been calculated for CO and for HCl. The contributions to E made by the transitions $n=1 \rightarrow n'=2$ (E_{F2}), $n=2 \rightarrow n'=3$ (E_{F3}), $n=0 \rightarrow n'=2$ (E_{01}), and $n \rightarrow n+1$ for $n > 2$ ($E_F - E_{F1} - E_{F2} - E_{F3}$), $n \rightarrow n+2$ for $n > 0$ ($E_0 - E_{01}$) have also been determined.

The quantities E_{F1} , E_{F2} , E_{F3} , $E_F - \sum_{i=1}^3 E_{Fi}$, E_{01} , and $E_0 - E_{01}$ are plotted as a function of temperature for CO at optical densities of 0.30, 1.00, 2.00, and 10.00 cm atm in Figs. 5 to 8, respectively. The values of

TABLE I. Basic spectroscopic constants for CO^a and HCl.^b

Spectroscopic constant	CO	HCl
ω_e , cm ⁻¹	2169.81	2989.74
B_e , cm ⁻¹	1.93130	10.5909
α_e	0.017543	0.3019
D_e	5.95×10^{-6}	5.32×10^{-4}
$x_e \omega_e = x^* \omega^*$	13.284	52.05
$y_e \omega_e$	0.010	0.056
ω^* , cm ⁻¹	2143.14	2885.70
δ	9.0835×10^{-3}	2.85056×10^{-2}
x^*	6.1981×10^{-3}	1.8027×10^{-2}
$\gamma = B_e/\omega_e$	9.0111×10^{-4}	3.5424×10^{-3}
$uT = hc\omega^*/k$	3082.98	4150.99
α_0/u , cm ⁻² -atm ⁻¹	0.161 ^c	0.264 ⁹
α_F/u , cm ⁻² -atm ⁻¹	22.95 ^c	10.73 ⁹
$E(n, j) = \omega_e(n + \frac{1}{2}) - \omega_e x_e(n + \frac{1}{2})^2 + \omega_e y_e(n + \frac{1}{2})^3 + B_e j(j+1) - \alpha_e(n + \frac{1}{2})j(j+1) - D_e j^2(j+1)^2$		

^a Plyler, Benedict, and Silverman, *J. Chem. Phys.* **20**, 175 (1952).

^b G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 534.

^c S. S. Penner and D. Weber, *J. Chem. Phys.* **19**, 807, 817, 974 (1951).

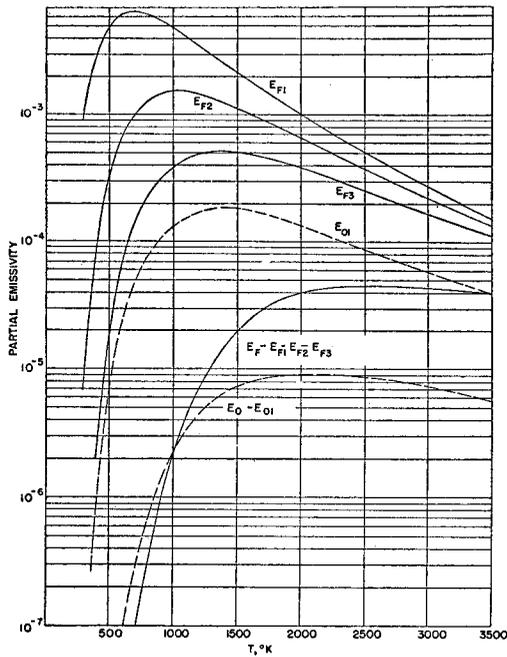


FIG. 5. Partial emissivities as a function of temperature for CO at $X=0.30$ cm atmos.

$E_{F1}, E_{F2}, E_{F3}, E_F - \sum_{i=1}^3 E_{Fi}, E_{O1}$, and $E_0 - E_{O1}$ are plotted as a function of temperature for HCl at optical densities of 1, 5, 20, 50, and 100 cm atmos in Figs. 9 to 13, respectively.

The total emissivities E are plotted as a function of temperature for CO at optical densities of 0.30, 1.00, 2.00, and 10.00 cm atmos in Figs. 14 to 17, respectively. Also shown in Figs. 14 to 17 are experimentally observed

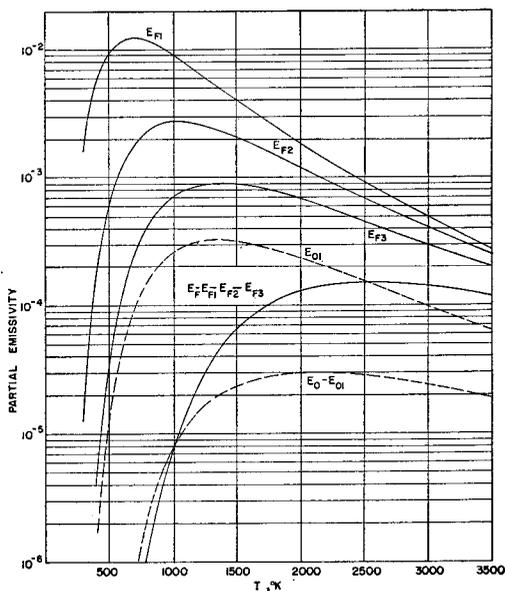


FIG. 6. Partial emissivities as a function of temperature for CO at $X=1.0$ cm atmos.

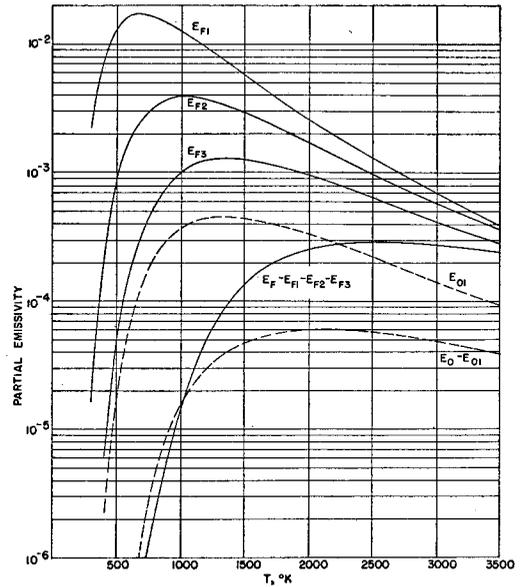


FIG. 7. Partial emissivities as a function of temperature for CO at $X=2.0$ cm atmos.

emissivities reported by Ullrich,¹⁰ limiting emissivities E_L computed by the method described in I and the quantity $E_{F1}(T/300)$. The total emissivities E are plotted as a function of temperature for HCl at optical densities of 1, 5, 20, 50, and 100 cm-atmos in Figs. 18 to 22, respectively, together with the corresponding values of the limiting emissivity E_L .

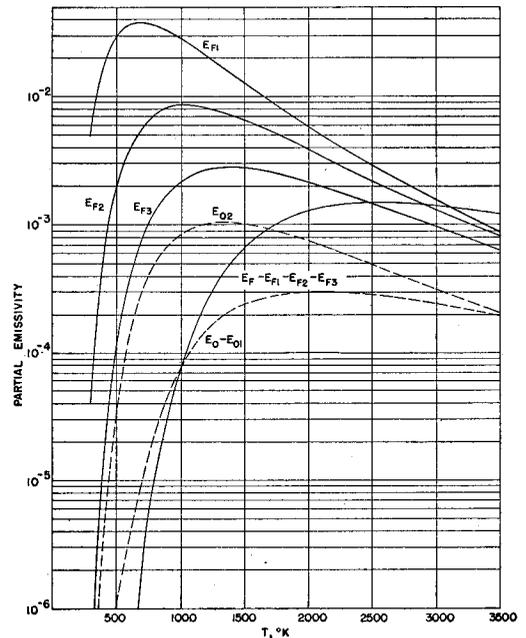


FIG. 8. Partial emissivities as a function of temperature for CO at $X=10$ cm atmos.

¹⁰ W. Ullrich, Doctor of Science thesis, M.I.T., Cambridge, 1935.

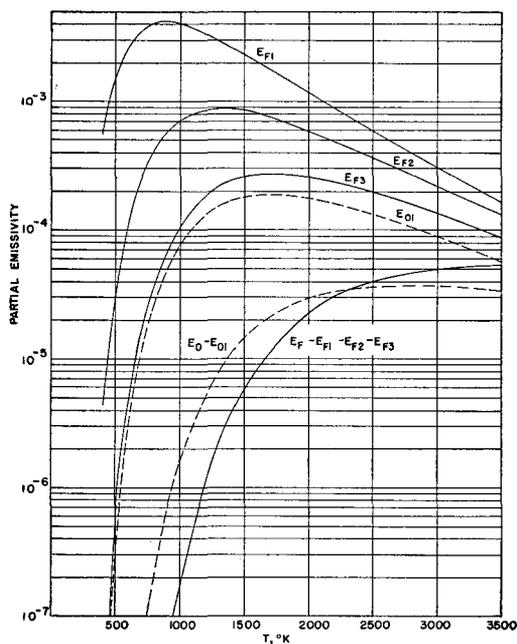


FIG. 9. Partial emissivities as a function of temperature for HCl at $X = 1.0$ cm atmos.

IV. DISCUSSION OF RESULTS

The principal source of error in the present calculations is probably the result of inadequate description of line widths and line shape. In this connection it is of interest to note that the more adequate theories of line broadening developed by Weisskopf,¹¹ Lindholm,¹² Van

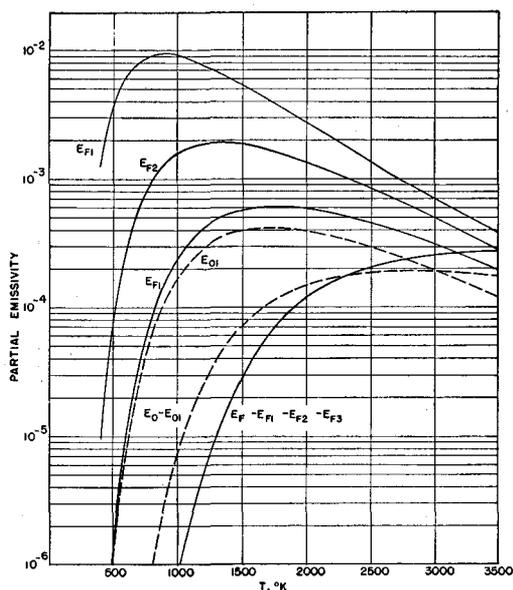


FIG. 10. Partial emissivities as a function of temperature for HCl at $X = 5$ cm atmos.

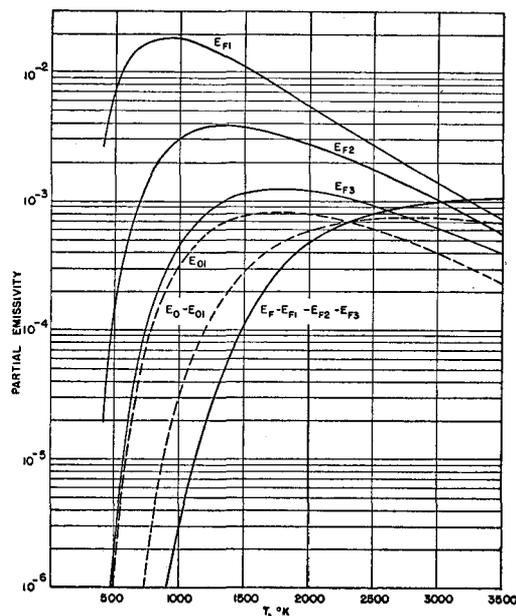


FIG. 11. Partial emissivities as a function of temperature for HCl at $X = 20$ cm atmos.

Vleck and Weisskopf,¹³ Van Vleck and Margenau,¹⁴ Margenau,¹⁵ and others¹⁶ all lead to a decrease of collision half-width with temperature, which does not differ greatly from the assumed proportionality with $T^{-\frac{1}{2}}$.

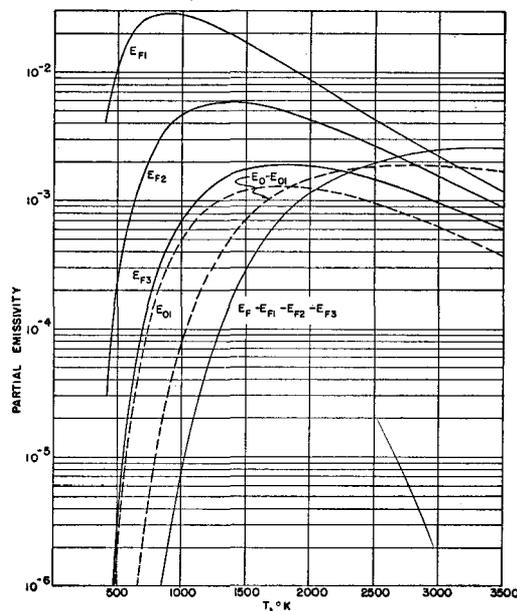


FIG. 12. Partial emissivities as a function of temperature for HCl at $X = 50$ cm atmos.

¹³ J. H. Van Vleck and V. F. Weisskopf, *Revs. Modern Phys.* **17**, 227 (1945).

¹⁴ J. H. Van Vleck and H. Margenau, *Phys. Rev.* **76**, 1211 (1949). Van Vleck and Margenau have demonstrated the equivalence of line shapes in absorption and emission, a result which has been tacitly assumed throughout the present analysis.

¹⁵ H. Margenau, *Phys. Rev.* **82**, 156 (1951).

¹⁶ P. W. Anderson, *Phys. Rev.* **76**, 647 (1949).

¹¹ V. F. Weisskopf, *Physik. Z.* **34**, 1 (1933).

¹² E. Lindholm, dissertation, Uppsala, 1942.

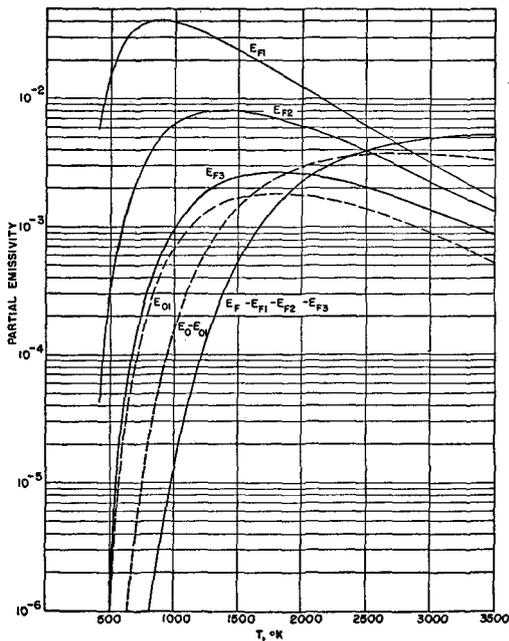


FIG. 13. Partial emissivities as a function of temperature for HCl at $X=100$ cm atmos.

In order to estimate the effect of Doppler broadening on the emissivity, representative numerical calculations of intensities for combined collision- and Doppler-broadening have been carried out. These calculations show that the effect of Doppler broadening on the calculated emissivities of CO must be negligibly small at temperatures below about 3000°K.

For HCl it is well known that the Lorentz collision

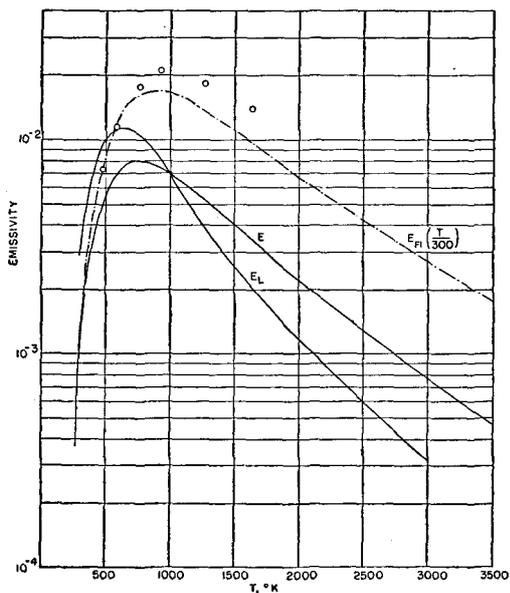


FIG. 14. Calculated and observed emissivities as a function of temperature for CO at $X=0.30$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L ; empirical relation: $E_{F1}(T/300)$; data obtained from empirical measurements: o).

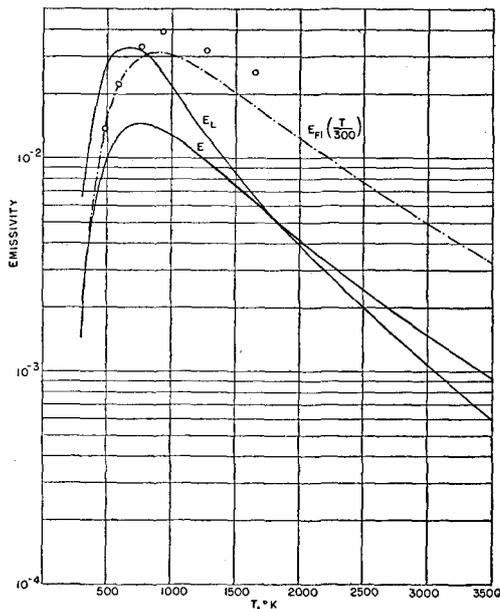


FIG. 15. Calculated and observed emissivities as a function of temperature for CO at $X=1.0$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L ; empirical relation: $E_{F1}(T/300)$; data obtained from empirical measurements: o).

formula does not represent experimentally determined transmission measurements adequately.^{9,12} For this reason the emissivities calculated for nonoverlapping rotational lines should not be considered as being reliable to within much more than a factor of about two.

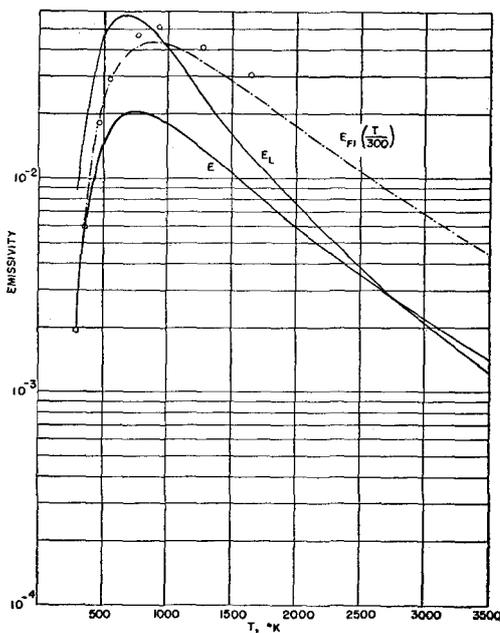


FIG. 16. Calculated and observed emissivities as a function of temperature for CO at $X=2.0$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L ; empirical relation: $E_{F1}(T/300)$; data obtained from empirical measurements: o).

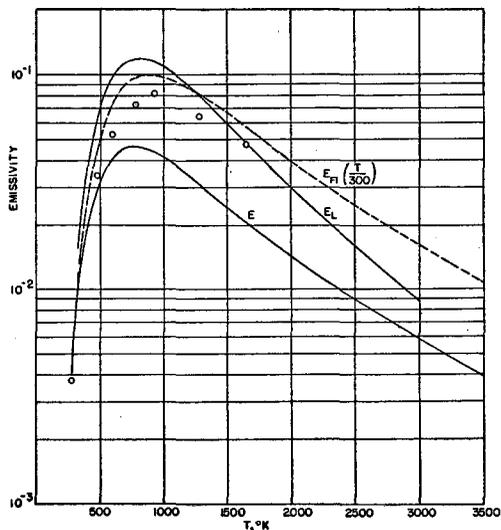


FIG. 17. Calculated and observed emissivities as a function of temperature for CO at $X=10.0$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L ; empirical relation: $E_{F1}(T/300)$; data obtained from empirical measurements: o).

To summarize, the calculated emissivities represent upper limits except in so far as the half-widths of excited vibrational energy states may have been underestimated. The optical densities for which numerical calculations have been performed were chosen in such a way that the asymptotic expressions used and the neglect of overlapping between rotational lines constitute very reasonable approximations. In fact, unless the collision half-width varies with temperature and vibrational quantum number in an unpredictable manner, it would be expected that the calculated emissivities are in error by less than about 20 percent.

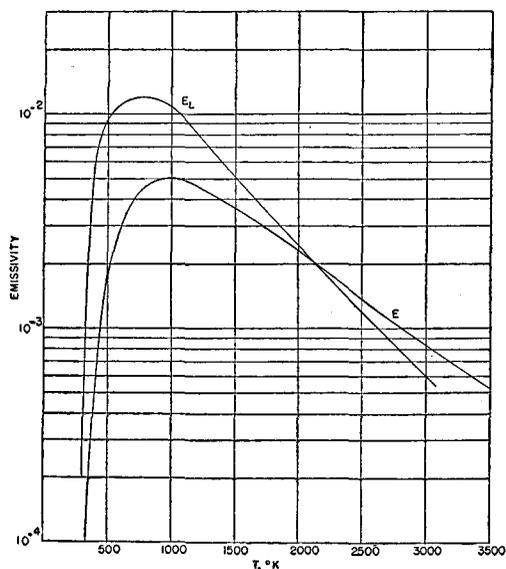


FIG. 18. Total emissivities as a function of temperature for HCl at $X=1$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L).

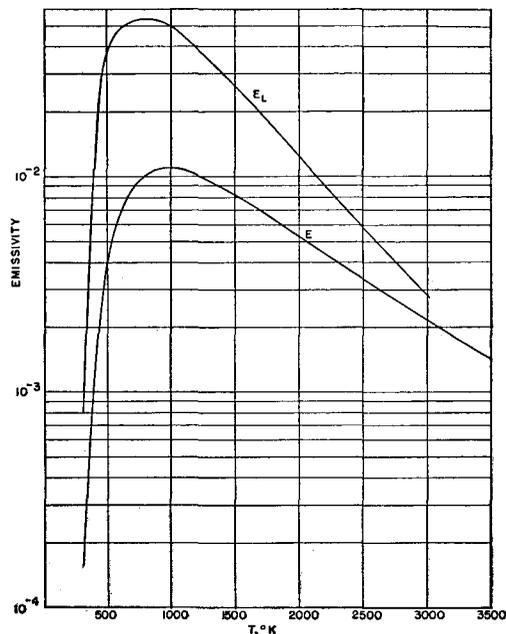


FIG. 19. Total emissivities as a function of temperature for HCl at $X=5$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L).

Reference to Figs. 14 to 17 permits a direct comparison between emissivity values calculated from spectroscopic data and empirically observed emissivities for CO. It is apparent that the experimentally determined emissivities are represented quite well by the function $E_{F1}(T/300)$ for which no theoretical justification can be given. According to Ullrich,¹⁰ the empirically determined values of the emissivities have a probable error of not over 20 percent for temperatures between about 500 and 1300°K if $0.5 \leq X \leq 5$ cm atmos. However, the

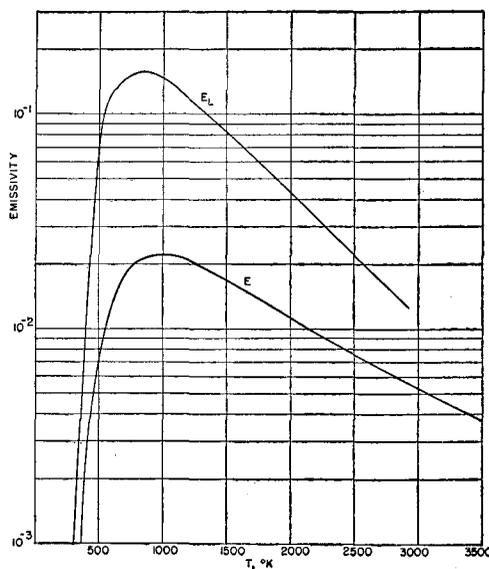


FIG. 20. Total emissivities as a function of temperature for HCl at $X=20$ cm atmos (emissivities based on treatment for nonoverlapping rotational lines: E ; limiting emissivities: E_L).

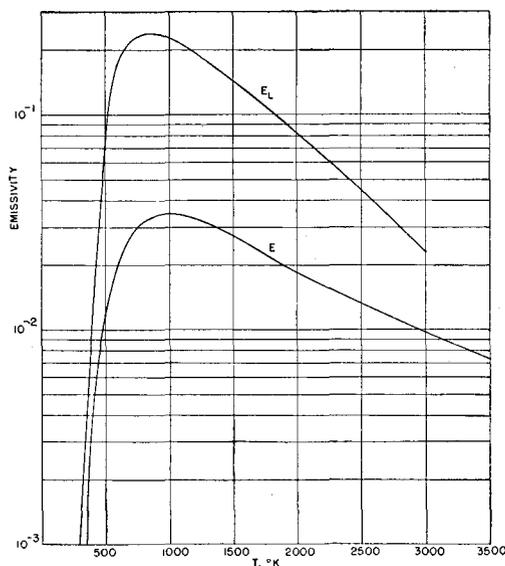


FIG. 21. Total emissivities as a function of temperature for HCl at $X=50$ cm atmos (emissivities based on treatment for non-overlapping rotational lines: E ; limiting emissivities: E_L).

discrepancies between calculated and observed emissivities are outside of the probable limits of error of either investigation, except for the reservations noted previously with regard to dependence of line width on vibrational excitation. The result that the calculated emissivities deviate more from the empirical measurements the higher the temperature is consistent with the idea that the optical collision diameter increases rapidly with vibrational excitation. In this connection it may be of interest to note also that Ullrich had increasing difficulties with his experimental studies at elevated temperatures because of diffusion of air into the high temperature chamber containing the carbon monoxide.¹⁰ It is evident that the apparent emissivities will be much too large if only a trace of CO_2 is formed in the reaction vessel because of the very large value for the integrated absorption of vibration-rotation bands belonging to CO_2 . Thus it is not entirely certain that all of the observed discrepancies are the result of faulty description of line widths.

In conclusion we note again the very successful semi-quantitative representation which is obtained for the emissivity, even at relatively low pressures, by using the very simple method described in I. Relevant limiting emissivities are identified by the symbol E_L and are also shown in Figs. 14 to 17. The result that E_L does not differ greatly from the calculated values of E for the smallest optical densities follows from the fact that the approximate treatment given in I holds accurately for very small values of the optical density as well as at elevated total pressures. In view of the previously discussed uncertainties concerning line widths, it is recommended that emissivity estimates for practical purposes be performed by the simple method given in I,

at least until it is possible to utilize a sound description of line shape and half width.

Reference to the calculated emissivity values for HCl shows again that E_L and E differ relatively less for the smallest and largest values of the optical density. In this case the treatment based on the assumption that no overlapping occurs between rotational lines would be expected to yield more reasonable estimates for the emissivity than the treatment described in I. The preceding statement follows from the fact that the spacing between the rotational lines of HCl is very large compared to the half-width unless the total pressures are exceedingly large (*viz.*, in excess of 1000 psia).

APPENDIX I. EFFECT OF VIBRATIONAL EXCITATION ON THE COLLISION DIAMETER

The collision (Lorentz) half-width b is customarily used to estimate an "optical collision diameter" ρ . It is well known that

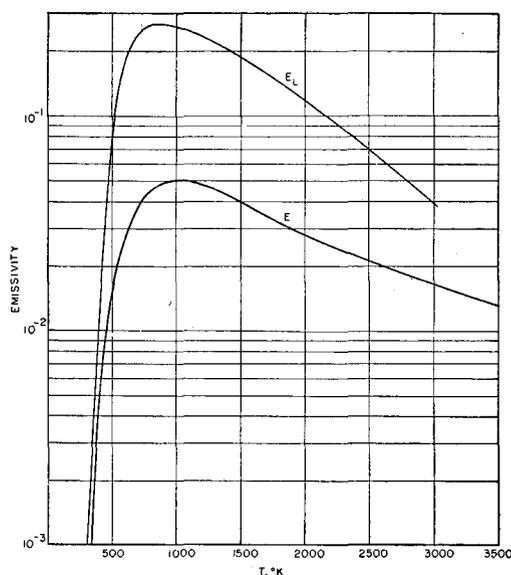


FIG. 22. Total emissivities as a function of temperature for HCl at $X=100$ cm atmos (emissivities based on treatment for non-overlapping rotational lines: E ; limiting emissivities: E_L).

the square of the optical collision diameter (ρ^2) is proportional to the Lorentz half-width (b) and is related qualitatively to the square of the collision diameter of transport theory (σ_{AB}^2) for the ground vibrational energy level.⁸ Unfortunately it is hardly safe to extrapolate the tenuous relation observed for molecules in their ground vibrational level to molecules in excited vibrational levels. For this reason we consider the following arguments to be really useful only for estimating the dependence of σ_{AB} on vibrational quantum number. The results concerning the probable variation of σ_{AB} with vibrational quantum number are of interest in connection with a determination of the limits of validity of calculated transport coefficients as the temperature is raised.¹⁷ It should be noted, however, that application of the present considerations to the theoretical calculation of transport properties cannot be made

¹⁷ S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1939); C. F. Curtiss and J. O. Hirschfelder, *J. Chem. Phys.* **17**, 550 (1949); Hirschfelder, Bird, and Spotz, *J. Chem. Phys.* **16**, 968 (1948).

without an analysis of the dependence of intermolecular force fields on vibrational excitation.

In order to obtain a semiquantitative estimate for the effect of vibrational excitation on σ_{AB} , we assume the simple physical model shown in Fig. 23. Although σ_{AB} is not accurately equal to $\bar{r} + 2r_0 + r_A + r_B$ because of distortion of the electronic charge distribution of atoms in molecules and because molecules are not spherically symmetrical, the model is probably good enough for the problem under discussion. We proceed by showing first that $2r_0$ is small and varies very slowly with vibrational excitation. Next it is shown that \bar{r} also varies very slowly with vibrational quantum number.

According to the Born-Oppenheimer approximation,¹⁸ the complete wave equation for diatomic molecules may be separated into two equations which describe the electronic and nuclear motion

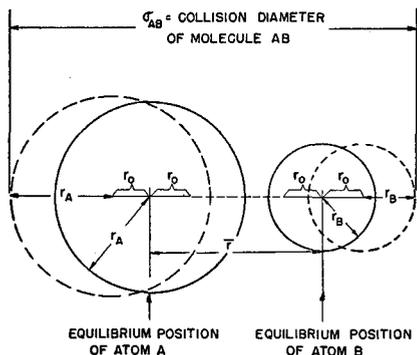


FIG. 23. Schematic representation of diatomic molecule (\bar{r} = equilibrium internuclear distance, obtained from spectroscopic measurements, etc.; $2r_0$ = amplitude of oscillation of nuclei about their respective equilibrium positions, estimated by using the harmonic oscillator approximation; $2r_A$ and $2r_B$ represent, approximately, the equivalent collision diameters of atoms A and B).

independently. The radial part of the nuclear wave equation is found to be identical with the wave equation for the one-dimensional harmonic oscillator if we assume a Hooke's law internuclear potential function.^{††} In accord with the usual probability inter-

¹⁸ See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York), Chapter X.

^{††} The refinements resulting from the use of a Morse potential are hardly warranted for the present discussion.

TABLE II. Numerical values for σ_{AB} in the ground vibrational state, $2r_0$, α_e/B_e , and $2r_0/\sigma_{AB}$ for representative diatomic molecules.

Molecule	σ_{AB} (from viscosity data, in A units) ^a	$2r_0 = 2(h/\pi^2 u c \omega_e)^{\frac{1}{2}}$ (in A units)	α_e/B_e	$2r_0/\sigma_{AB}$
H ₂	2.968	0.4942	4.922×10^{-2}	0.1665
N ₂	3.681	0.1806	9.303×10^{-3}	0.0491
NO	3.470	0.1948	1.044×10^{-2}	0.0561
N ₂	3.433	0.2066	1.092×10^{-2}	0.0602
CO	3.590	0.1905	9.084×10^{-3}	0.0531
Cl ₂	4.115	0.2336	6.973×10^{-3}	0.0568
Br ₂	3.859	0.2043	3.399×10^{-3}	0.0529
I ₂	4.982	0.1989	3.133×10^{-3}	0.0399
HCl	3.305	0.4290	2.851×10^{-2}	0.1298

^a From the values given by J. O. Hirschfelder et al., reference 17.

pretation of the square of the wave function, we may equate $r_0 = r_0(n)$ for the n th vibrational energy level to the distance from the equilibrium position at which the square of the radial wave function, $|\psi_n(r)|^2$, has fallen substantially to zero.

Reference to the plots of $\psi_n(r)$ or $|\psi_n(r)|^2$ vs r given by Pauling and Wilson¹⁹ for $n=0, 1, 2, 3, 4, 5, 6$, and 10 shows that $r_0(n)/r_0(0) \sim 2$ for $0 < n \leq 10$ with $r_0(0) \simeq (h/\pi^2 u c \omega_e)^{\frac{1}{2}}$. Representative values of $2r_0(0)$ for diatomic molecules are summarized in Table II.

The dependence of \bar{r} on vibrational excitation is obtained conveniently from the well-known relation²⁰

$$B_v \simeq B_e - \alpha_e(n + \frac{1}{2}), \quad (\text{A-1})$$

where $B_v = h/8\pi^2 u c \bar{r}^2$ and $B_e = h/8\pi^2 u c r_e^2$. Since $\alpha_e/B_e \ll 1$, we obtain from Eq. (A-1) the result

$$\bar{r}/r_e = [1 - (\alpha_e/B_e)(n + \frac{1}{2})]^{-\frac{1}{2}} \simeq 1 + \frac{1}{2}(\alpha_e/B_e)(n + \frac{1}{2}). \quad (\text{A-2})$$

From the numerical values given for α_e/B_e in Table A-1 it is evident that \bar{r}/r_e is only very slightly greater than unity for the values of n which are encountered in practical applications. Furthermore, reference to Table A-I shows that $2r_0(0)/\sigma_{AB}$ is small, whence it follows that the collision diameter of diatomic molecules is not a sensitive function of vibrational excitation.

¹⁹ Reference 18, pp. 74-76.

²⁰ See, for example, G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 106.