Relations Between Molecular Gas Absorptivities and Emissivities

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Abstract

Theoretical expressions have been derived for the re-
lations between gas absorptivities and emissivities for
the limit of zero optical depth and for the following
models of vibration-rotation bands: bands with constant
average absorption coefficients and well-defined widths;
just-overlapping spectral lines; non-overlapping disper-
sion lines with constant collision half-width and either
regular line spacing or with lines of equal intensity;
randomly distributed spectral lines with dispersion con-
tour; non-overlapping Doppler lines with either regular
line spacing or with lines of equal intensity; randomly
distributed Doppler lines for a special (unrealistic) as-
sumption relating to the temperature dependence of the
effective mean line spacing; non-overlapping spectral
lines with combined Doppler and collision broadening,
constant collision half-width and either regular line
spacing or with lines of equal intensity. The theoretical
formulae have been shown to provide a good correlation
for the available experimental data on CO_2, H_2O and CO.

I. Introduction

Theoretical expressions between gas absorptivities
and emissivities for various representations of molecular
vibration-rotation bands are of fundamental interest and
may also be useful for extending available gas emissivity
compilations to different conditions of temperature and
pressure because it is often easier to measure absorp-
tivities than emissivities. Representative results for
selected band models have been described in previous
publications [1-5]. In the present paper we present an
exhaustive review and extension of this earlier work in
which the most important restriction is the following: the
temperatures used for making absorptivity and emissivity
estimates must be sufficiently close to justify the as-

sumption that neither the spectral line shape nor the band
model are changed in character.

Theoretical relations for important band models are de-
rived in the following section of this paper. The correla-
tion of available experimental data for CO_2, H_2O and CO,
in terms of appropriate theoretical expressions, is de-
scribed in the third section.

II. Relations Between Absorptivities and Emissivities

The total absorptivity α_{ab} of a gaseous absorber at the
temperature T_g for blackbody radiation emitted at the
temperature T_s is defined by the relation

$$\alpha_{ab} = \frac{1}{\sigma T_s^4} \int_0^\infty R^0_{\omega, T_s} [1 - \exp - (P_{\omega, T_g} X)] d\omega \qquad (1)$$

where σ is the Stefan-Boltzmann constant, R^0_{ω, T_s} is the
spectral blackbody radiancy at T_s in the wave number
range between ω and $\omega + d\omega$, P_{ω, T_g} represents the
spectral absorption coefficient (in $cm^{-1} - atmos^{-1}$) of the
gas at T_g and ω, and X denotes the optical depth. Since
the vibration-rotation bands of molecular emitters lie in
well-defined spectral regions, we may replace equation
(1) by the approximate expression

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \int_{\Delta \omega_{i, T_g}} [1 - \exp(-P_{\omega, T_g} X)] d\omega \qquad (2)$$

where ω_i is the wave number at the center of the ith
vibration-rotation band which has an "effective" width
$\Delta \omega_{i, T_g}$ at the temperature T_g of the gaseous absorbers
and $R^0_{\omega_i, T_s}$ is the spectral blackbody radiancy evaluated
at ω_i and T_s.

A. Emission from a Blackbody and Absorption by Transparent Gases [2-5]. For optically thin layers of absorbing gases, (2) becomes

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} X \int_{\Delta\omega_{i, T_g}} P_{\omega, T_g} d\omega$$

or

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \alpha_{i, T_g} X \tag{3}$$

since

$$\alpha_{i, T} \equiv \int_{\Delta\omega_{i, T}} P_{\omega, T} d\omega \tag{4}$$

represents the integrated absorption (in $cm^{-2} - atmos^{-1}$) for the ith vibration-rotation band of the gas at T. But[1]

$$\frac{\alpha_{i, T}}{\alpha_{i, T_g}} = \frac{T_g}{T} \tag{5}$$

whence (3) becomes

$$\alpha_{ab} \simeq \frac{T_s}{T_g} \epsilon(T_s, X) \tag{6}$$

since the emissivity of transparent gases at the temperature T_s and optical depth X is defined by the expression

$$\epsilon(T_s, X) = \lim_{X \to 0} \frac{1}{\sigma T_s^4} \int_0^\infty R^0_{\omega, T_s} [1 - \exp(-P_{\omega, T_s} X)] d\omega \simeq$$

$$\lim_{X \to 0} \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \int_{\Delta\omega_{i, T_s}} [1 - \exp(-P_{\omega, T_s} X)] d\omega$$

or

$$\epsilon(T_s, X) \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \alpha_{i, T_s} X. \tag{7}$$

It is apparent that (6) is independent of any band model and of the spectral line shape and depends, in fact, only on the temperature dependence of the integrated intensity specified through (5). Accordingly, we expect that all of the theoretical formulae derived in subsequent

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[1]Equation (5) depends essentially only on the validity of the ideal gas law, i.e., on the assumption that the number of absorbers at constant pressure in a fixed geometric length is inversely proportional to the temperature if the Boltzmann population factor may be neglected.

sections for special band models and line shapes must reduce to (6) if they apply in the limit of zero optical depth. In this connection it is important to note that

$$\lim_{X \to 0} \epsilon(T, \beta X) = \beta \epsilon(T, X). \tag{8}$$

B. Emission from a Blackbody and Absorption by Vibration-Rotation Bands Characterized by Constant Average Absorption Coefficients [1-5]. When the ith vibration-rotation band is characterized by the constant absorption coefficient P_i over the effective width $\Delta\omega_{i, T_g}$, then (2) is replaced by the expression

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \Delta\omega_{i, T_g} [1 - \exp(-\overline{P}_{i, T_g} X)]. \tag{9}$$

However, to the order of approximation that constant average absorption coefficients may be used, it is easily shown [5] that

$$\frac{\Delta\omega_{i, T}}{\Delta\omega_{i, T_g}} = \left(\frac{T}{T_g}\right)^{1/2} \tag{10}$$

whence

$$\frac{\overline{P}_{i, T}}{\overline{P}_{i, T_g}} = \frac{(\alpha_{i, T}/\Delta\omega_{i, T})}{(\alpha_{i, T_g}/\Delta\omega_{i, T_g})} = \left(\frac{T_g}{T}\right)^{3/2} \tag{11}$$

where use has been made of (5). From (9), (10) and (11) it now follows that

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{1/2} \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \Delta\omega_{i, T_s} \times$$

$$\left\{1 - \exp\left[-\overline{P}_{i, T_s} \left(\frac{T_s}{T_g}\right)^{3/2} X\right]\right\}$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{1/2} \epsilon\left[T_s, \left(\frac{T_s}{T_g}\right)^{3/2} X\right] \tag{12}$$

since

$$\epsilon\left[T_s, \left(\frac{T_s}{T_g}\right)^{3/2} X\right] \simeq$$

$$\frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \int_{\Delta\omega_{i, T_s}} \times$$

$$\left\{1 - \exp\left[-P_{\omega, T_s} \left(\frac{T_s}{T_g}\right)^{3/2} X\right]\right\} d\omega \simeq$$

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$$\frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s}\, \Delta\omega_{i,T_s} \times$$

$$\left\{1 - \exp\left[-P_{i,T_s}\left(\frac{T_s}{T_g}\right)^{3/2} X\right]\right\} \quad (13)$$

for the assumed band model.

Equation (12) is a relation between the absorptivity α_{ab} for molecular absorbers at the temperature T_g and optical depth X and the emissivity of the same gas at the temperature T_s and the optical depth $(T_s/T_g)^{3/2} X$. Within the limitations of the assumed band model, (12) and other similar expressions suggest the possible determination of (infrared) emissivities from lower temperature absorptivity measurements.

C. Emission from a Blackbody and Absorption by Vibration-Rotation Bands Composed of Just-Overlapping Spectral Lines.

For just-overlapping spectral lines it may be shown[2] that

$$\int_{\Delta\omega_{i,T_g}} [1 - \exp(-P_{\omega,T_g} X)]\,d\omega \simeq$$

$$\Delta\omega_{i,T_g}\left\{h\left(\frac{\alpha_{i,T_g}X}{\Delta\omega_{i,T_g}}\right)[1 - \exp(-\alpha_{i,T_g}X/\Delta\omega_{i,T_g})]\right\}^{1/2} \quad (14)$$

where

$$h(x) = \ln Cx - Ei(-x),$$

C is Euler's constant, and

$$-Ei(-x) = \int_x^\infty \frac{1}{t}\exp(-t)\,dt$$

is the exponential integral. Using (5) and (10), it is apparent that

$$\int_{\Delta\omega_{i,T_g}} [1 - \exp(-P_{\omega,T_g} X)]\,d\omega \simeq$$

$$\left(\frac{T_g}{T_s}\right)^{1/2}\Delta\omega_{i,T_s}\left\{h\left[\frac{\alpha_{i,T_s}X(T_s/T_g)^{3/2}}{\Delta\omega_{i,T_s}}\right] \times\right.$$

$$\left.\left[1 - \exp-\frac{\alpha_{i,T_s}X(T_s/T_g)^{3/2}}{\Delta\omega_{i,T_s}}\right]\right\}^{1/2} \simeq$$

$$\left(\frac{T_g}{T_s}\right)^{1/2}\int_{\Delta\omega_{i,T_s}}\left\{1 - \exp\left[-P_{\omega,T_s} X\left(\frac{T_s}{T_g}\right)^{3/2}\right]\right\}d\omega.$$

Hence equation (2) becomes

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{1/2}\frac{1}{\sigma T_s^4}\sum_i R^0_{\omega_i,T_s}\int_{\Delta\omega_i,T_s} \times$$

$$\left\{1 - \exp\left[-P_{\omega,T_s} X\left(\frac{T_s}{T_g}\right)^{3/2}\right]\right\}d\omega$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{1/2}\epsilon\left[T_s, \left(\frac{T_s}{T_g}\right)^{3/2} X\right] \quad (15)$$

Comparison of (12) and (15) shows that the constant absorption coefficient approximation and the just-overlapping line approximation lead to the same relation between absorptivity and emissivity. This result is not unexpected since the assumed physical models are similar and since it is known that these two representations lead to practically identical emissivity estimates for diatomic molecules [3, 5].

D. Emission from a Blackbody and Absorption by Vibration-Rotation Bands with Non-Overlapping Dispersion Lines [2, 5].

For non-overlapping spectral lines, (2) becomes

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4}\sum_i R^0_{\omega_i,T_s}\sum_{j=0}^{\infty}2\pi b_{i,j,T_g}\,f\left(\frac{S_{i,j,T_g}X}{2\pi b_{i,j,T_g}}\right) \quad (16)$$

where b_{i,j,T_g} is the dispersion half-width of the jth line in the ith band at T_g, S_{i,j,T_g} is the corresponding integrated line intensity, and

$$f(x) = x[\exp(-x)][(J_0(ix) - iJ_1(ix)]$$

with J_0 and J_1 representing Bessel functions of the first kind of order zero and one, respectively. The relation between absorptivity and emissivity may be determined for two cases depending on the form of $S_{i,j}$.

1. Bands with Regular Spacing and Constant Collision Half-Width. We may now use[3] the following approximation to S_{i,j,T_g} for each branch of a vibration-rotation band:

$$S_{i,j,T_g} = \alpha_{i,T_g}\sqrt{\frac{hcB_{e_i}}{kT_g}}\,g\left(\sqrt{\frac{hcB_{e_i}}{kT_g}}\,j\right) \quad (17)$$

where

$$g(x) = x\exp(-x^2) \quad (18)$$

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[2] Reference 5, equation (58-37); the validity of (15) is independent of the approximation contained in (14), as may be verified readily by using the exact integral representation for the just-overlapping line model.

[3] Reference 5, equation (58-35).

and B_{e_i} is the usual rotational spectroscopic constant for the ith band. Hence (16) becomes, for $b_{i,j,T_g} = b_{i,T_g}$,

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} 2 \sum_{j=0}^{\infty} 2\pi b_{i,T_g} \times$$

$$f \left[\frac{\alpha_{i,T_g} \sqrt{\frac{hcB_{e_i}}{kT_g}} g\left(\sqrt{\frac{hcB_{e_i}}{kT_g}} j\right) X}{2\pi b_{i,T_g}} \right] \simeq$$

$$\frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} 2 \int_0^{\infty} 2\pi b_{i,T_g} \sqrt{\frac{kT_g}{hcB_{e_i}}} \times$$

$$f \left[\frac{\alpha_{i,T_g} \sqrt{\frac{hcB_{e_i}}{kT_g}} g(u)}{2\pi b_{i,T_g}} X \right] du$$

where the factor 2 preceding the sum over j accounts for the two branches of the vibration-rotation band. Using (5) and the relation

$$\frac{b_{i,T}}{b_{i,T_g}} = \left(\frac{T_g}{T}\right)^{\frac{1}{2}} \tag{19}$$

the preceding relation reduces to

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \int_0^{\infty} 2\pi b_{i,T_s} \sqrt{\frac{kT_s}{hcB_{e_i}}} \times$$

$$f \left[\frac{\alpha_{i,T_s} \sqrt{\frac{hcB_{e_i}}{kT_s}} g(u)}{2\pi b_{i,T_s}} \frac{T_s}{T_g} X \right] du \simeq$$

$$\frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} 2 \sum_j 2\pi b_{i,T_s} \times$$

$$f \left[\frac{\alpha_{i,T_s} \sqrt{\frac{hcB_{e_i}}{kT_s}} g\left(\sqrt{\frac{hcB_{e_i}}{kT_s}} j\right)}{2\pi b_{i,T_s}} \frac{T_s}{T_g} X \right]$$

or

$$\alpha_{ab} \simeq \epsilon\left(T_s, \frac{T_s}{T_g} X\right) \tag{20}$$

2. Bands with Equally Intense Spectral Lines and Constant Collision Half-Width. If all of the spectral lines of the ith band have the same integrated intensity $\overline{S}_{i,T_g}$ and

the same half-width b_{i,T_g} and there are N_{i,T_g} lines contributing, then (16) becomes

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} N_{i,T_g} 2\pi b_{i,T_g} f\left(\frac{\overline{S}_{i,T_g} X}{2\pi b_{i,T_g}}\right). \tag{21}$$

By definition,

$$N_{i,T_g} = \frac{\Delta\omega_{i,T_g}}{d_{i,T_g}} \tag{22}$$

if d_{i,T_g} represents the average line spacing in the ith band at T_g. If we assume that

$$\frac{d_{i,T_g}}{d_{i,T_s}} = \left(\frac{T_s}{T_g}\right)^{\eta} \tag{23}$$

and use (10), then

$$\frac{N_{i,T_g}}{N_{i,T_s}} = \left(\frac{T_g}{T_s}\right)^{\eta+(\frac{1}{2})} \tag{24}$$

and

$$\frac{\overline{S}_{i,T_g}}{\overline{S}_{i,T_s}} = \frac{(\alpha_{i,T_g}/N_{i,T_g})}{(\alpha_{i,T_s}/N_{i,T_s})} = \left(\frac{T_s}{T_g}\right)^{\eta+(\frac{3}{2})} \tag{25}$$

From (21) to (25) it follows that

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4}\left(\frac{T_g}{T_s}\right)^{\eta} \sum_i R^0_{\omega_i, T_s} N_{i,T_s} 2\pi b_{i,T_s} \times$$

$$f\left[\frac{\overline{S}_{i,T_s}}{2\pi b_{i,T_s}}\left(\frac{T_s}{T_g}\right)^{\eta+1} X\right]$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{\eta} \epsilon\left[T_s, X\left(\frac{T_s}{T_g}\right)^{\eta+1}\right] \tag{26}$$

E. Emission from a Blackbody and Absorption by Randomly Distributed Spectral Lines with Dispersion Contour [4]. For the statistical model of a vibration-rotation band, it may be shown [2, 5–7] that

$$\int_{\Delta\omega_{i,T_g}} [1 - \exp(-P_\omega X)] d\omega \simeq$$

$$\Delta\omega_{i,T_g}\left[1 - \exp\left(-\frac{\overline{A}_{i,T_g}}{d_{i,T_g}}\right)\right] \tag{27}$$

where

$$\overline{A}_{i,T_g} = \int_0^\infty A_L \, \mathbb{P}(\overline{S}_i/S) \, d(\overline{S}_i/S) \qquad (28)$$

is the weighted mean value of the line absorption A_L with respect to the normalized intensity probability distribution function $\mathbb{P}(\overline{S}_i/S)$. For dispersion lines of half-width b, it is well-known [5] that

$$A_L \simeq SX \quad \text{for} \quad \frac{SX}{2\pi b} < \frac{2}{\pi} \qquad (29)$$

and

$$A_L \simeq 2\sqrt{SbX} \quad for \quad \frac{SX}{2\pi b} > \frac{2}{\pi}. \qquad (30)$$

Thus, for the range of values in which (29) applies for the contributing spectral lines, the relation between absorptivity and emissivity is determined by the optically thin gas approximation given in (6). On the other hand, for the square root region,

$$\overline{A}_i = 2\sqrt{b_i X} \int_0^\infty \mathbb{P}(\overline{S}_i/S)\sqrt{S} \, d(\overline{S}_i/S) =$$
$$\qquad (31)$$
$$\text{constant } \sqrt{\overline{S}_i b_i X}.$$

Hence, assuming that $\overline{S}_i = \alpha_i/(\Delta\omega_i/d_i)$ and using the previously specified temperature dependence for α_i [see (5)], $\Delta\omega_i$ [see (10)] and d_i [see (23)], we obtain

$$\frac{\overline{A}_{i,T_g}}{d_{i,T_g}} = \text{constant} \frac{\left[\overline{S}_{i,T_s} \, b_{i,T_s}\left(\dfrac{T_s}{T_g}\right)^{2-\eta} X\right]^{\frac{1}{2}}}{d_{i,T_s}}. \qquad (32)$$

Introduction of (27) and (32) into (2) leads to the result

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{\frac{1}{2}} \epsilon\left[T_s, X\left(\frac{T_s}{T_g}\right)^{2-\eta}\right]. \qquad (33)$$

It is important to observe that (33) does not reduce to (6) as X goes to zero. This result is not surprising in view of the fact that (33) has been derived specifically for the square root region, i.e., for values of X which are sufficiently large to justify use of the line absorption formula given in (30).

F. Emission from a Blackbody and Absorption by Non-Overlapping Spectral Lines with Doppler Contour. For

spectral lines with Doppler broadening, it is well known[4] that

$$\int_{\Delta\omega_{i,j}} [1 - \exp(-P_\omega X)] \, d\omega =$$
$$\qquad (34)$$
$$\omega_{i,j}\left(\frac{2\pi kT}{mc^2}\right)^{\frac{1}{2}} \sum_{n=1}^\infty - \frac{1}{n!\sqrt{n}} \, (-P'_{i,j} X)^n$$

where the integration interval over the jth line of the ith band $\Delta\omega_{i,j}$ has been extended from the band center ω_{ij} to $-\infty$ and $+\infty$, m represents the mass of the radiator, and

$$P'_{ij} = \frac{S_{i,j}}{\omega_{i,j}}\left(\frac{mc^2}{2\pi kT}\right)^{\frac{1}{2}} \qquad (35)$$

is the spectral absorption coefficient at the center of the jth line in the ith band. In view of (34) and (35), (2) becomes

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s}\left\{\sum_j \omega_i\left(\frac{2\pi kT}{mc^2}\right)^{\frac{1}{2}} \sum_{n=1}^\infty -\right.$$
$$\qquad (36)$$
$$\left. \frac{1}{n!\sqrt{n}}\left[-\frac{S_{i,j,T_g} X}{\omega_i}\left(\frac{mc^2}{2\pi kT}\right)^{\frac{1}{2}}\right]^n\right\}$$

where we have used the wave number at the band center $\omega_{i,j}$. We proceed to consider two special cases which are analogous to those treated for non-overlapping dispersion lines.

1. Diatomic Molecules with Regular Spacing. The rotational line intensities are again given by (17). Hence, proceeding as before,

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \, 2\omega_i\left(\frac{2\pi kT}{mc^2}\right)^{\frac{1}{2}} \times$$

$$\left\{\sum_{j=0}^\infty \sum_{n=1}^\infty - \frac{1}{n!\sqrt{n}}\left[-\frac{\alpha_{i,T_g} X}{\omega_i}\sqrt{\frac{hcB_{e_i}}{kT_g}} \, g(u)\left(\frac{mc^2}{2\pi kT}\right)^{\frac{1}{2}}\right]^n\right\}$$

where

$$u = \sqrt{\frac{hcB_{e_i}}{kT_g}} \, j;$$

thus

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \, 2\omega_i\left(\frac{2\pi kT_g}{mc^2}\right)^{\frac{1}{2}} \int_0^\infty \sqrt{\frac{kT_g}{hcB_{e_i}}} \times$$

[4]Reference 5, equation (16-8).

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$$\left\{ \sum_{n=1}^{\infty} - \frac{1}{n!\sqrt{n}} \left[\frac{-\alpha_{i,T_g}}{\omega_i} \sqrt{\frac{hcB_{e_i}}{kT_g}} \, g(u) \left(\frac{mc^2}{2\pi kT_g}\right)^{1/2} \right]^n \right\} du \simeq$$

$$\left(\frac{T_g}{T_s}\right) \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i,T_s} \, 2\omega_i \left(\frac{2\pi kT_s}{mc^2}\right)^{1/2} \int_0^\infty \sqrt{\frac{kT_s}{hcB_{e_i}}} \times$$

$$\left\{ \sum_{n=1}^{\infty} - \frac{1}{n!\sqrt{n}} \left[\frac{-\alpha_{i,T_s}}{\omega_i} \sqrt{\frac{hcB_{e_i}}{kT_s}} \times \right.\right.$$

$$\left.\left. \left(\frac{mc^2}{2\pi kT_s}\right)^{1/2} X \left(\frac{T_s}{T_g}\right)^2 g(u) \right] \right\} du$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right) \epsilon \left[T_s, \left(\frac{T_s}{T_g}\right)^2 X \right]. \qquad (37)$$

2. *Molecules with Equally Intense Spectral Lines.* For equally intense spectral lines, we may introduce (24) and (25) into equation (36). Hence

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i,T_s} N_{i,T_g} \omega_i \left(\frac{2\pi kT_g}{mc^2}\right)^{1/2} \sum_{n=1}^{\infty} -$$

$$\frac{1}{n!\sqrt{n}} \left[-\frac{\overline{S}_{i,T_g} X}{\omega_i} \left(\frac{mc^2}{2\pi kT_g}\right)^{1/2} \right]^n \simeq$$

$$\left(\frac{T_g}{T_s}\right)^{\eta+1} \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i,T_s} N_{i,T_s} \omega_i \left(\frac{2\pi kT_s}{mc^2}\right)^{1/2} \sum_{n=1}^{\infty} -$$

$$\frac{1}{n!\sqrt{n}} \left[-\frac{\overline{S}_{i,T_s}}{\omega_i} \left(\frac{mc^2}{2\pi kT_s}\right)^{1/2} X \left(\frac{T_s}{T_g}\right)^{\eta+2} \right]^n$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{\eta+1} \epsilon \left[T_s, X \left(\frac{T_s}{T_g}\right)^{\eta+2} \right]. \qquad (38)$$

G. Emission from a Blackbody and Absorption by Randomly Distributed Spectral Lines with Doppler Contour. Equations (27) and (28) apply for the specified model with the line absorption determined explicitly through (34) and (35). Hence

$$\overline{A}_i = \int_0^\infty A_L \, \wp(\overline{S}_i/S) \, d(\overline{S}_i/S)$$

$$= \omega_i \left(\frac{2\pi kT}{mc^2}\right)^{1/2} \int_0^\infty \wp(\overline{S}_i/S) \, d(\overline{S}_i/S) \sum_{n=1}^{\infty} -$$

$$\frac{1}{n!\sqrt{n}} \left[\frac{-SX}{\omega_i} \left(\frac{mc^2}{2\pi kT}\right)^{1/2} \right]^n \cdot$$

$$= \omega_i \left(\frac{2\pi kT}{mc^2}\right)^{1/2} \sum_{n=1}^{\infty} -$$

$$\frac{1}{n!\sqrt{n}} \left[-\frac{X}{\omega_i} \left(\frac{mc^2}{2\pi kT}\right)^{1/2} \right]^n \int_0^\infty S^n \, \wp(\overline{S}_i/S) \, d(\overline{S}_i/S)$$

$$= \omega_i \left(\frac{2\pi kT}{mc^2}\right)^{1/2} \sum_{n=1}^{\infty} - \frac{1}{n!\sqrt{n}} \left[-\frac{\overline{S}_i X}{\omega_i} \left(\frac{mc^2}{2\pi kT}\right)^{1/2} \right]^n c_n$$

where

$$c_n = \int_0^\infty \left(\frac{S}{\overline{S}_i}\right)^n \wp\left(\frac{\overline{S}_i}{S}\right) d\left(\frac{\overline{S}_i}{S}\right). \qquad (39)$$

If we assume again that

$$\frac{\overline{S}_{i,T_g}}{\overline{S}_{i,T_s}} = \frac{\alpha_{i,T_g}/(\Delta\omega_{i,T_g}/d_{i,T_g})}{\alpha_{i,T_s}/(\Delta\omega_{i,T_s}/d_{i,T_s})} = \left(\frac{T_s}{T_g}\right)^{\eta+(3/2)}$$

then

$$\overline{A}_{i,T_g} = \sqrt{\frac{T_g}{T_s}} \, \omega_i \left(\frac{2\pi kT_s}{mc^2}\right)^{1/2} \sum_{n=1}^{\infty} -$$

$$\frac{c_n}{n!\sqrt{n}} \left[-\frac{\overline{S}_{i,T_s}}{\omega_i} \left(\frac{mc^2}{2\pi kT_s}\right)^{1/2} X \left(\frac{T_s}{T_g}\right)^{\eta+2} \right]^n$$

and

$$\frac{\overline{A}_{i,T_g}}{d_{i,T_g}} = \left(\frac{T_g}{T_s}\right)^{(1/2)+\eta} \cdot \omega_i \left(\frac{2\pi kT_s}{mc^2}\right)^{1/2} \sum_{n=1}^{\infty} -$$

$$\frac{c_n}{n!\sqrt{n}} \left[-\frac{\overline{S}_{i,T_s}}{\omega_i} \left(\frac{mc^2}{2\pi kT_s}\right)^{1/2} X \left(\frac{T_s}{T_g}\right)^{\eta+2} \right]^n. \qquad (40)$$

In view of (27), the absorptivity is now given by the relation

$$\alpha_{ab} \simeq \sqrt{\frac{T_g}{T_s}} \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i,T_s} \Delta\omega_{i,T_s} \times$$

$$\left[1 - \exp -\left(\frac{\overline{A}_{i,T_g}}{d_{i,T_g}}\right) \right] \qquad (41)$$

where it is impossible to express $\overline{A}_{i,T_g}/d_{i,T_g}$ in terms of $\overline{A}_{i,T_s}/d_{i,T_s}$ with a suitably modified optical depth $X(T_s/T_g)^\epsilon$ except in the unlikely case that $\eta = -\frac{1}{2}$. In this special case,

$$\alpha_{ab} \simeq \sqrt{\frac{T_g}{T_s}} \, \epsilon \left[T_s, X \left(\frac{T_s}{T_g}\right)^{3/2} \right], \quad \eta = -\frac{1}{2}. \quad (42)$$

Thus, in general, it is not feasible to obtain an explicit relation between emissivity and absorptivity for randomly distributed spectral lines with Doppler contour.

H. Emission from a Blackbody and Absorption by Non-Overlapping Spectral Lines with Combined Doppler and Collision Broadening and with Constant Collision Half-Width.

For combined Doppler and collision broadening the line absorption depends on $P'X$, on the Doppler half-width b_D, and on the line-shape parameter $a \simeq \dfrac{b_C}{b_D}\sqrt{\ln 2}$, viz.,

$$\frac{A_L \sqrt{\ln 2}}{2 b_D} = F(P'X; a) \quad (43)$$

where $b \equiv b_C$ is the collision half-width and the function F is the ordinate of the curves of growth [5]. Hence

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \sum_j \frac{2 b_{D,i,T_g}}{\sqrt{\ln 2}} \times$$
$$F\left[\frac{S_{i,j,T_g}}{\omega_i} \left(\frac{mc^2}{2\pi k T_g}\right)^{1/2} X; \quad a_{i,j,T_g} \right]. \quad (44)$$

1. Bands with Regular Spacing. For molecules with regular spacing, (17) applies and (44) becomes

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \sum_j \frac{2 b_{D,i,T_g}}{\omega_i} \times$$
$$F\left[\frac{\alpha_{i,T_g}}{\omega_i} \sqrt{\frac{hcB_{e_i}}{kT_g}} \, g(u) \left(\frac{mc^2}{2\pi k T_g}\right)^{1/2} X; \quad a_{i,T_g} \right]$$

where $g(x)$ is again defined by (18) and $u = \sqrt{hcB_{e_i}/kT_g}\,j$. Since [5]

$$\frac{b_{D,T_g}}{b_{D,T_s}} \simeq \left(\frac{T_g}{T_s}\right)^{1/2}$$

and

$$\frac{a_{i,T_g}}{a_{i,T_s}} = \left(\frac{T_s}{T_g}\right),$$

the preceding expression becomes

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right) \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} \int_0^\infty \frac{2 b_{D,i,T_s}}{\sqrt{\ln 2}} \times$$
$$F\left[\frac{\alpha_{i,T_s}}{\omega_i} \sqrt{\frac{hcB_{e_i}}{kT_s}} g(u) \left(\frac{mc^2}{2\pi k T_s}\right)^{1/2} X \left(\frac{T_s}{T_g}\right)^2; \right.$$
$$\left. a_{i,T_s} \left(\frac{T_s}{T_g}\right) \right] \sqrt{\frac{kT_s}{hcB_{e_i}}}\, du$$

or

$$\alpha_{ab} \simeq \frac{T_g}{T_s} \epsilon \left[T_s, X \left(\frac{T_s}{T_g}\right)^2; \quad a_{T_g} \right]. \quad (45)$$

According to (45), the absorptivity at T_g depends on the emissivity at T_s for an optical depth $X(T_s/T_g)^2$ with the line-shape parameter $a_{T_g} = a_{T_s}(T_s/T_g)$ evaluated at T_g.

2. Bands with Equally Intense Spectral Lines. For equally intense spectral lines with constant collision half-width, (44) becomes

$$\alpha_{ab} \simeq \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} N_{i,T_g} \frac{2 b_{D,i,T_g}}{\sqrt{\ln 2}} \times$$
$$F\left[\frac{S_{i,T_g} X}{\omega_i} \left(\frac{mc^2}{2\pi k T_g}\right)^{1/2}; \quad a_{i,T_g} \right].$$

Using the previously specified temperature dependence for the various terms occurring in the preceding relation, we find that

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{\eta+1} \frac{1}{\sigma T_s^4} \sum_i R^0_{\omega_i, T_s} N_{i,T_s} \frac{2 b_{D,i,T_s}}{\sqrt{\ln 2}} \times$$
$$F\left[\frac{S_{i,T_s}}{\omega_i} \left(\frac{mc^2}{2\pi k T_s}\right)^{1/2} X \left(\frac{T_s}{T_g}\right)^{\eta+2}; \quad a_{i,T_s} \left(\frac{T_s}{T_g}\right) \right]$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{\eta+1} \epsilon \left[T_s, X \left(\frac{T_s}{T_g}\right)^{\eta+2}; \quad a_{T_g} \right]. \quad (46)$$

I. Effect of Total Pressure on the Relation Between Absorptivities and Emissivities.

The preceding theoretical relations all involve the implicit assumption that the absorptivity and emissivity data refer to the same total pressure p. In practice it is, however, often advantageous to measure absorptivities and emissivities at dif-

ferent total pressures p_1 and p_2, respectively. In this case all of the theoretical relations involving collision broadening must be modified. Appropriate relations can be derived without difficulty if the effective collision half-width depends linearly on the pressure, i.e., the line broadening agent is assumed to be the same for the absorption and for the emission measurements. Thus

$$\frac{b_{i,T_g,p_1}}{b_{i,T_s,p_2}} = \frac{p_1}{p_2} \sqrt{\frac{T_s}{T_g}}. \qquad (47)$$

The use of (47) leads to the revised relations summarized below.

1. *Transparent Gases.* The derivation of (6) does not involve the spectral line shape and, therefore, (6) applies irrespective of the total pressures of the absorbing and emitting gases.

2. *Constant Average Absorption Coefficients and Just-Overlapping Lines.* As long as both p_1 and p_2 are sufficiently large to justify the use of one of the postulated models, (12) [and the same expression which has been repeated in (15)] applies.

3. *Non-Overlapping Dispersion Lines with Regular Spacing and Constant Collision Half-Width.* The use of (47) in place of (19) shows that the factor p_1/p_2 will occur outside the sum over bands and p_2/p_1 will occur as a multiplicative factor to X, i.e., (20) becomes

$$\alpha_{ab} \equiv \alpha_{ab}(T_s \rightarrow T_g, X, p_1) \simeq$$

$$\frac{p_1}{p_2} \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right) \left(\frac{p_2}{p_1} \right),\ p_2 \right]. \qquad (20a)$$

4. *Non-Overlapping Dispersion Lines of Equal Intensity with Constant Collision Half-Width.* Proceeding as before, it is apparent that (26) should be replaced by the expression

$$\alpha_{ab}(T_s \rightarrow T_g, X, p_1) \simeq$$

$$\left(\frac{p_1}{p_2} \right) \left(\frac{T_g}{T_s} \right)^{\eta} \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right)^{\eta+1} \left(\frac{p_2}{p_1} \right),\ p_2 \right]. \qquad (26a)$$

5. *Randomly Distributed Spectral Lines with Dispersion Contour.* Equation (33) is now replaced by the expression

$$\alpha_{ab}(T_s \rightarrow T_g, X, p_1) \simeq$$

$$\left(\frac{T_g}{T_s} \right)^{\frac{1}{2}} \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right)^{2-\eta} \left(\frac{p_1}{p_2} \right),\ p_2 \right] \qquad (33a)$$

since the collision half-width multiplies X in (31).

6. *Non-Overlapping Spectral Lines with Doppler Contour.* As long as the postulated model remains applica-

ble, the total pressure cannot affect the results since it has no influence on the Doppler half-width. Thus (37), (38) and (42) hold independently of the values of p_1 and p_2.

7. *Non-Overlapping Spectral Lines with Combined Doppler and Collision Broadening, Constant Collision Half-Width, and Regular Line Spacing.* Examination of the relations preceding (45) shows that

$$\alpha_{ab}(T_s \rightarrow T_g, X, p_1) \simeq$$

$$\left(\frac{T_g}{T_s} \right) \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right)^2 ;\ a_{T_g,p_1};\ p_2 \right], \qquad (45a)$$

i.e., the line-shape parameter must be evaluated at T_g and p_1. Here

$$a_{T_g,p_1} = a_{T_s,p_2} \left(\frac{T_s}{T_g} \right) \left(\frac{p_1}{p_2} \right).$$

8. *Non-Overlapping Spectral Lines with Combined Doppler and Collision Broadening, Constant Collision Half-Width, and Lines of Equal Intensity.* It is easily seen that

$$\alpha_{ab}(T_s \rightarrow T_g, X, p_1) \simeq$$

$$\left(\frac{T_g}{T_s} \right)^{\eta+1} \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right)^{\eta+2} ;\ a_{T_g,p_1};\ p_2 \right]. \qquad (46a)$$

III. Discussion of Results and Correlation of Experimental Data

In accord with the general result obtained in (6), it is apparent that the absorptivity at T_g and the emissivity at T_s for $p_1 = p_2 = p$ must be related, in general, in such a way that

$$\alpha_{ab} = \left(\frac{T_g}{T_s} \right)^{\beta-1} \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right)^{\beta} ;\ a_{T_g} \right] \qquad (48)$$

provided it has not been explicitly postulated that X cannot be arbitrarily small [compare equation (33)]. The absolute values of β depend on the assumed band model and are summarized in Table I for the cases considered in section II. It should be noted that ϵ depends on the line-shape parameter a only in the special case of combined Doppler and collision broadening. The following interesting summary statements may be made:

(1) For otherwise comparable assumptions, $\beta = 1$ or $1 + \eta$ for dispersion lines and $\beta = 2$ or $2 + \eta$ for lines

TABLE I. SUMMARY OF THEORETICAL RELATIONS BETWEEN ABSORPTIVITIES AT T_g AND EMISSIVITIES AT T_s FOR $p_1 = p_2 = p$.

MODEL:	PHYSICAL CONDITIONS FOR WHICH THE MODEL APPLIES:	β IN EQUATION (48)	REMARKS
constant average absorption coefficients for vibration-rotation bands. just-overlapping spectral lines.	at elevated pressures where the rotational fine structure is smeared out.	$\frac{3}{2}$	
non-overlapping dispersion lines with regular spacing and constant collision half-width.	molecules without Q-branch at moderate temperatures for sufficiently low pressures.	1	
non-overlapping dispersion lines of equal intensity and constant half-width.	molecules without Q-branch at elevated temperatures for sufficiently low pressures.	$1 + \eta$	At moderate temperatures, $\eta = 0$, and this case reduces to the preceding limiting conditions.
non-overlapping Doppler lines with regular line spacing.	moderate temperatures and sufficiently low pressures to make $b_C \ll b_D$.	2	
non-overlapping Doppler lines of equal intensity.	elevated temperatures and sufficiently low pressures to make $b_C \ll b_D$.	$2 + \eta$	At moderate temperatures, $\eta = 0$, and this case reduces to the preceding limiting conditions.
non-overlapping spectral lines with regular spacing, constant collision half-width, and combined Doppler and collision broadening.	moderate temperatures and pressures which are sufficiently small to justify the neglect of overlapping between spectral lines.	2	
combined Doppler and collision broadening for non-overlapping lines of equal intensity with constant half-width.	elevated temperatures and moderate pressures for molecules with large rotational spacing.	$2 + \eta$	At moderate temperatures, $\eta = 0$, and this case reduces to the preceding limiting condition.
randomly distributed dispersion lines of equal intensity for sufficiently large optical depths to make the dominant line absorption vary as the square root of the optical depth.	complicated molecules (e.g., H_2O) at moderate or large pressures for temperatures sufficiently low to make $b_C \gg b_D$.	$\alpha_{ab} = \sqrt{\dfrac{T_g}{T_s}} \, \epsilon \left[T_s, X \left(\dfrac{T_s}{T_g} \right)^{2-\eta} \right]$ and Eq. (48) does not apply.	
randomly distributed Doppler lines.	...	$\beta = \frac{3}{2}$ for $\eta = -\frac{1}{2}$	This case is of no physical interest.

with Doppler broadening or combined Doppler and collision broadening.[5]

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[5] The value of β for combined Doppler and collision broadening is not directly comparable to β for the other cases because the absorptivity is related to an emissivity at the temperature T_s but with a line-shape parameter a evaluated at T_g. This is not a physically realizable case, and is therefore not directly useful. If we were able to refer the absorptivity to an emissivity at T_s with the line-shape parameter evaluated at T_s then β would depend on the optical depth and the line-shape parameter, and would equal 2 or 2 + η only in the limiting case of collision broadened lines.

(2) For overlapping lines $\beta = \frac{3}{2}$.
We now proceed to consider briefly the correlation of available experimental data by means of our theoretical formulae.

A. Carbon Dioxide. Hottel and Mangelsdorf [8] have obtained the empirical relation

$$(a_{ab}, CO_2)_{H-M} \simeq \left(\frac{T_g}{T_s} \right)^{\frac{1}{3}} \epsilon \left[T_s, X \left(\frac{T_s}{T_g} \right) \right]. \quad (49)$$

It is apparent that (49) cannot apply in the limit of zero optical depth since it does not reduce to (6). Hence it is reasonable to assume that the important contributions to α_{ab} and ϵ are made by non-overlapping dispersion lines which are sufficiently strong so that the emissivity varies as the square root of the optical depth. On this assumption, we may use the relation obtained for randomly distributed dispersion lines in (33) for the derivation of an effective value of η for CO_2, viz.,

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{1/2} \epsilon\left[T_s, \ \sqrt{X\left(\frac{T_s}{T_g}\right)\left(\frac{T_s}{T_g}\right)^{1-\eta}}\right]$$

or

$$\alpha_{ab} \simeq \left(\frac{T_g}{T_s}\right)^{\eta/2} \epsilon\left[T_s, \ \sqrt{X\left(\frac{T_s}{T_g}\right)}\right].$$

On the other hand, (49) becomes

$$(\alpha_{ab,CO_2})_{H-M} \simeq \left(\frac{T_g}{T_s}\right)^{2/3} \epsilon\left[T_s, \ \sqrt{X\left(\frac{T_s}{T_g}\right)}\right]$$
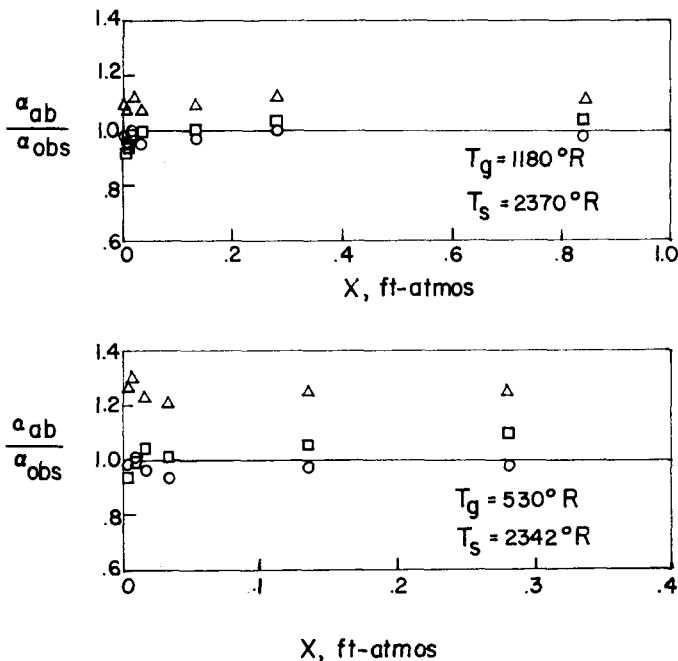
and

$$(\eta)_{CO_2} \simeq 4/3.$$

FIGURE 1. THE RATIOS OF CALCULATED TO OBSERVED ABSORPTIVITIES FOR CO_2 AS A FUNCTION OF OPTICAL DEPTH [CALCULATED USING EQUATION (49): O; CALCULATED USING EQUATION (33) WITH $\eta = 4/3$: □; CALCULATED USING (33) WITH $\eta = 1$: △].

The fact that (33) with $\eta = 4/3$ provides a good correlation of the available experimental results is illustrated in Fig. 1. It is interesting to observe that the choice $\eta = 1$, which is the appropriate value for water in the statistical model, leads to notably poorer correlation of data than $\eta = 4/3$.

Although η is independent of X, equation (33) with $\eta = 4/3$ should not be used either for very large or for very small values of X since it was derived by using the line absorption relation appropriate for the square root region [compare equation (31)].

B. Water [4]. A comparison of observed and calculated results is shown in Fig. 2 for water vapor. Reference to Fig. 2, and to data for larger values of X which are not
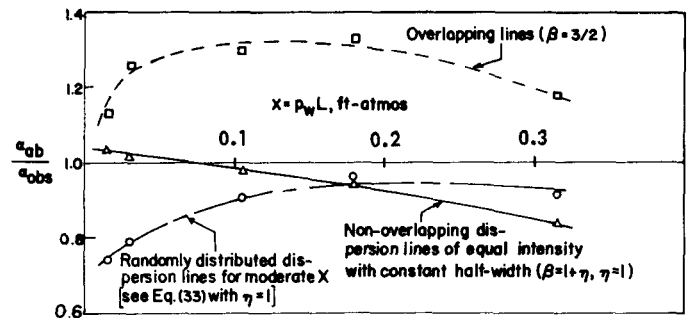
FIGURE 2. THE RATIOS OF CALCULATED ABSORPTIVITIES α_{ab} TO OBSERVED ABSORPTIVITIES α_{obs} AS A FUNCTION OF OPTICAL DEPTH FOR WATER VAPOR USING DIFFERENT BAND MODELS ($T_s = 2500$ R, $T_g = 750$ R, TOTAL PRESSURE $p = 1$ ATMOS; FROM OLFE AND PENNER [3]).

plotted, shows that equation (33) gives a fair representation for X greater than about 0.1 or 0.2 ft-atmos; $\beta = 3/2$ holds for very small values of X and also for X greater than about 0.5 ft-atmos; $\beta = \eta + 1 = 2$ applies for X less than about 0.2 ft-atmos.[6] Equation (33) is seen to apply when the absorption is dominated by dispersion lines in the square root region irrespective of the extent of overlapping between lines.

C. Carbon Monoxide. Careful absorptivity measurements for carbon monoxide have been performed recently in our laboratory by U. P. Oppenheim [10]. The experimental results obtained at very low pressures where $\beta = 1$, and at elevated pressures where $\beta = 3/2$, are shown in Figs. 3 and 4, respectively. Reference to the data plotted in Figs. 3 and 4 shows very satisfactory agreement with theoretical predictions. It is interesting to observe (see Fig. 4) that the overlapping line models fail to apply at elevated temperatures for constant pressure and optical depth. This conclusion is in accord with predictions since both the collision half-width and the number of absorbers in the light path decrease for the specified conditions, i.e., the requirements for use of an overlapping line model must break down at suffi-

[6]The estimate $\eta = 1$ for water vapor has been derived from correlation of measured emissivity data by means of the statistical model [2, 5].
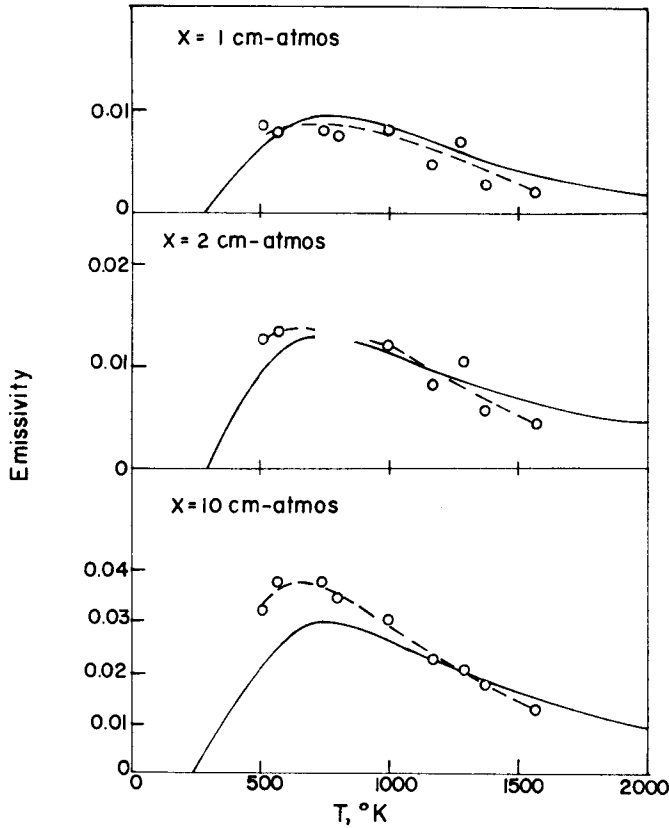
FIGURE 3. THE TOTAL EMISSIVITY OF CO AS A FUNCTION OF TEMPERATURE FOR VARIOUS OPTICAL DEPTHS AND A TOTAL PRESSURE OF 1 ATMOS. THE SOLID CURVE IS THE EMISSIVITY CALCULATED FROM BASIC PRINCIPLES USING A NON-OVER-LAPPING LINE THEORY [5], WHILE THE CIRCLES INDICATE POINTS CALCULATED USING EQUATION (20) AND ABSORPTION MEASUREMENTS (FROM U. P. OPPENHEIM [10]).

ciently high temperatures. The relative positions for broadening with He or A are in accord with the known pressure dependence and absolute values of the collision half-width for these broadening agents [11]. Finally, the observed lower temperature deviations from an over-lapping line model at smaller optical depths serve to emphasize the fact that both the product of integrated intensity with optical depth and the effective half-width are important in determining the range of validity of an overlapping line model.

D. Relations Useful in the Interpretation of Experimental Data. In the interpretation of experimental results it may be useful to utilize a number of obvious relations for the rates of change of absorptivities with optical depth and temperature.

For transparent gases, (6) applies and the emissivity is a linear function of optical depth, i.e.,

$$\alpha_{ab}(T_s \to T_g, X, p_1) \equiv \alpha_{ab} \simeq \frac{T_s}{T_g} \epsilon(T_s, X) \equiv$$

$$\frac{T_s}{T_g} X \epsilon_{T_s} \qquad (50)$$

and

$$\left[\frac{\partial \ln \alpha_{ab}(T_s \to T_g, X, p_1)}{\partial \ln X}\right]_{\text{l.r.}} = 1 \qquad (51)$$

where the subscript l.r. identifies results appropriate for the "linear region." On the other hand, in the "square-root region," (identified by the subscript s.r.r.)[7], equation (48) becomes

$$\alpha_{ab}(T_s \to T_g, X, p_1) \equiv \alpha_{ab} \simeq$$

$$\left(\frac{T_s}{T_g}\right)^{1-(\beta/2)} \sqrt{X} \epsilon_{T_s; a_{T_g}; p_1} \qquad (52)$$

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[7]The phrases "linear region" and "square-root region" should be interpreted to mean that the important contributions to the emissivity are made by spectral lines in such a way that the emissivity varies effectively linearly or as the square root of the optical depth, respectively.
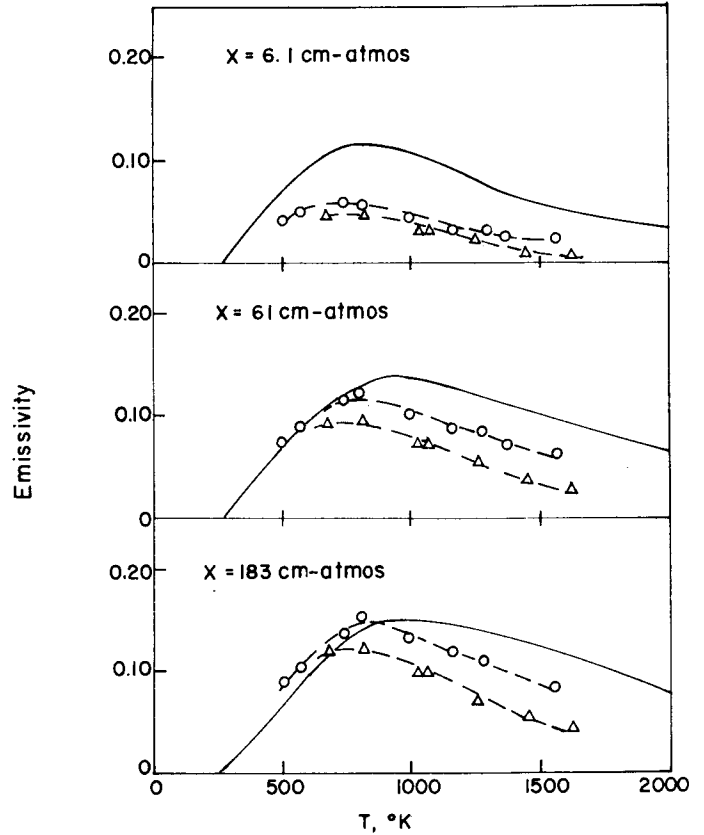

FIGURE 4. THE TOTAL EMISSIVITY OF CO AS A FUNCTION OF TEMPERATURE FOR VARIOUS OPTICAL DEPTHS. THE SOLID CURVE IS THE EMISSIVITY CALCULATED FROM BASIC PRIN-CIPLES USING AN OVERLAPPING LINE THEORY [5] [CALCU-LATED FROM EQUATION (12) AND USING ABSORPTION MEAS-UREMENTS OF CO-A MIXTURES AT A TOTAL PRESSURE OF 35 ATMOS: O; CALCULATED FROM (12) AND USING ABSORPTION MEASUREMENTS OF CO-He MIXTURES AT A TOTAL PRESSURE OF 18 ATMOS: Δ (FROM U. P. OPPENHEIM [10]).

12

and

$$\left[\frac{\partial \ln \alpha_{ab}(T_s \rightarrow T_g, X, p_1)}{\partial \ln X}\right]_{s.r.r.} = \frac{1}{2}. \qquad (53)$$

Equation (53) holds also for the statistical model [compare equation (33)] if ϵ can be shown to vary as the square root of the optical depth.

It is apparent from (50) that

$$\frac{\partial \ln \epsilon_{T_s}}{\partial \ln T_s} = \left[\frac{\partial \ln \alpha_{ab}(T_s \rightarrow T_g, X, p_1)}{\partial \ln T_s}\right]_{l.r.} - 1 \qquad (54)$$

whereas it follows from (52) for pure dispersion lines that

$$1 - \frac{\beta}{2} = \left\{\left[\frac{\partial \ln \alpha_{ab}(T_s \rightarrow T_g, X, p_1)}{\partial \ln T_s}\right]_{s.r.r.} - \frac{\partial \ln \epsilon_{T_s}}{\partial \ln T_s}\right\}$$

and

$$1 - \frac{\beta}{2} = 1 + \left\{\left[\frac{\partial \ln \alpha_{ab}(T_s \rightarrow T_g, X, p_1)}{\partial \ln T_s}\right]_{s.r.r.} - \left[\frac{\partial \ln \alpha_{ab}(T_s \rightarrow T_g, X, p_1)}{\partial \ln T_g}\right]_{l.r.}\right\}. \qquad (55)$$

Equation (55) suggests the possibility of a direct experimental determination of β for spectral lines in the square-root region.

The preceding considerations may be extended without difficulty for the derivation of results appropriate for other selected experimental conditions.

Acknowledgment

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