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SPECTRAL AND INTEGRATED INTENSITY OF CO FUNDAMENTAL BAND AT ELEVATED TEMPERATURES

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Abstract—The spectral absorption coefficient of CO fundamental band at temperatures from 300 to 1500°K is determined from the existing spectral absorption data in the strong-line approximation region and in the transition region. This has been achieved by use of the Godson approximation for the Elsasser function and the estimated mean values for the line half-width-spacing ratio at various temperatures. The resulting spectral absorption coefficients compare favorably with the available experimental data at room temperature and with the theoretical results at various temperatures. For the integrated intensity of the CO fundamental band extrapolated to STP the present investigation results in a value of 290 ± 16 atm^{-1} cm^{-2}, which again is in good agreement with the recent experimental data of Breeze and Ferriso.

NOMENCLATURE

A_ω,	spectral absorptivity;
A,	total band absorptance;
d,	line spacing;
D,	self-broadening constant;
J_n,	Bessel function of order n;
ℓ,	geometric path length;
$L(x)$,	Ladenberg and Reiche function defined by equation (5);
P_a,	partial pressure of absorbing gas;
P_e,	effective pressure of the gas;
P_ω,	spectral absorption coefficient;
S_ω,	line intensity;
T,	absolute temperature of the gas [°K];
u,	optical depth defined by equation (3);
x,	parameter defined by equation (6);
Y^0_ω,	line half-width–spacing ratio per unit atmosphere defined by equation (7);
Y_ω,	$= Y^0_\omega P_e$.

Greek symbols

α^0_ω,	line half-width per unit atmosphere;
α_ω,	$= \alpha^0_\omega P_e$;
α,	integrated intensity defined by equation (8);
ω,	wave number.

INTRODUCTION

In a previous publication [1], the authors have reported i.r. absorption data of CO fundamental and first-overtone bands at various thermodynamic and optical conditions. To ensure wide applications of these results, it is recognized that spectral absorptivity data must be reduced to basic spectroscopic parameters in order to predict spectral absorption at conditions different from those covered in the experiment [2, 3] and to calculate radiative heat transfer in real gases [4, 5]. In the i.r. region, these spectroscopic parameters are the line intensity-spacing ratio (S_ω/d) and the line half-width–spacing ratio (α_ω/d). The line intensity–spacing ratio is often referred to as the spectral absorption coefficient.

It is well established experimentally and theoretically [3, 6] that, for direct determination of the line intensity–spacing ratio, the optical conditions of the gas must be in the range of weak-line approximation. This could be achieved experimentally with very small path lengths for pure radiating gases or with medium

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path lengths but only with a mixture of the radiating gas and an inert gas at high pressures. Examples of such experiments have been performed recently by many investigators [7–9] mainly to determine the spectral and integrated intensity of CO_2 and H_2O at high temperatures. In case the gas path length is large or the total gas pressure is small, the spectral data are often in the region of strong-line approximation, and will yield only the product of the line intensity–spacing ratio and the line half-width–spacing ratio [3, 6].

For some gases such as CO and NO, which possess small (α_ω/d), the high pressure required to smear the rotational lines constitutes a formidable experimental problem in design of the i.r. apparatus, especially at elevated temperatures. As a result, much of the high-temperature experimental data on the i.r. absorption of these gases was obtained at relatively low pressures and consequently lies in the region of strong-line approximation, or in the transition region.

In the present paper, the line intensity–spacing ratio (or the spectral absorption coefficient) of the CO fundamental band is determined from the i.r. experimental data in the region of strong-line approximation and in the transition region by use of the Elsasser band model. The Elsasser band model is generally regarded as an appropriate model for representing spectral absorption of CO, due to the orderly distribution of the rotational lines of diatomic molecules [2, 3]. With the approximate Elsasser function, also indicated in the paper, the resulting spectral absorption coefficient would facilitate calculations of spectral absorptivity under various optical conditions at elevated temperatures.

APPROXIMATE ELSASSER FUNCTION

In the Elsasser band model [3, 6], the spectral absorptivity as a function of pressure and path length is given in a complicated integral form and is often referred to as the Elsasser function. As there exists no general explicit expression, the function is tabulated in numerical form. It is well known, however, that explicit expressions for the spectral absorptivity can be obtained in the following two limiting cases: the weak-line approximation,

$$A_\omega = 1 - \exp(-P_\omega u) \tag{1}$$

and the strong-line approximation,

$$A_\omega = \operatorname{erf}[(\pi P_\omega Y_\omega^0) . (P_e u)]^{\frac{1}{2}} \tag{2}$$

$$u = P_a \ell,\ Y_\omega^0 = (Y_\omega/P_e) = (\alpha_\omega^0/d) \tag{3}$$

where P_ω is the spectral absorption coefficient (or the line intensity–spacing ratio), P_a the pressure of the absorbing gas, ℓ the geometric path length, α_ω^0 the line half-width per unit atmosphere, d the line spacing and P_e the effective pressure. For pure CO, $P_e = DP_a$ where the self-broadening constant $D = 1{\cdot}02$ for the fundamental band and is relatively independent of temperature [10].

While the above approximations have been frequently used in their respective regions, it is highly desirable to establish a continuous explicit expression for the Elsasser function. Not only will it be useful in correlating experimental data in the whole range, but it also gives a formula, which shows a general functional dependence of various parameters and can be manipulated mathematically, such as differentiation and integration. Indeed, such an approximation has been proposed by Godson [6] as:

$$A_\omega = \operatorname{erf}[\pi^{\frac{1}{2}} Y_\omega L(x)] \tag{4}$$

where $L(x)$ is the Ladenberg and Reiche function,

$$L(x) = x \exp(-x)[J_0(ix) - iJ_1(ix)] \tag{5}$$

with J_n being the Bessel function of order n and

$$x = (P_\omega u)/(2\pi Y_\omega). \tag{6}$$

Values of $L(x)$ defined by equation (5), are tabulated as functions of x in [3, 6]. A simple approximate expression for $L(x)$ has been suggested recently by Tien [11]. Comparison of the exact Elsasser function and the Godson approximation indicates that the agreement is extremely good when Y_ω is equal to or less than 0·1. For the CO fundamental band, it can be shown later that Y_ω is about 0·054 at room temperature (300°K) and 3 atm pressure. For the experimental data to be considered here, with temperatures greater than 300°K and pressures less than 3 atm [1], Y_ω is much smaller and consequently, the Godson approximation is even more applicable.

SPECTRAL ABSORPTION COEFFICIENT OF CO FUNDAMENTAL BAND

Calculation of the spectral absorption coefficient of CO fundamental band from spectral absorptivity data in the transition and the strong-line approximation regions can now be accomplished by use of equations (4) and (6) and the tabulated values of $L(x)$, provided that the dependence of Y_ω^0 on temperature and wavelength is known. At room temperature, the study by Oppenheim and Ben-Aryeh [2] shows that Y_ω^0 for CO fundamental band is almost independent of wavelength and may be assigned a mean value of 0·0175. At elevated temperatures covered in the present study, the rotational line spacing of diatomic molecules varies slightly with temperature and the variation will be neglected in this investigation. From simple arguments of kinetic theory, however, the line half-width is inversely proportional to the square root of temperature. Therefore, it follows,

$$Y_\omega^0 = 0{\cdot}0175\left(\frac{300}{T}\right)^{\frac{1}{2}} \tag{7}$$

which is in a slightly different form from that based on band correlation [1]. The quantity B_1^2 in equation (13) of [1] corresponds to $(4Y_\omega^0)$.

For each of the temperatures 300, 600, 900, 1200 and 1500°K, the spectral absorption coefficient P_ω was calculated, by use of equations (4, 6, 7) and the tabulated values of $L(x)$, from the experimental absorptivity data at various path lengths and pressures [1]. Values of P_ω as a function of wave number at the different temperatures are shown in Figs. 1–5. The symbols $_*$, □, △ and ○ used in these figures

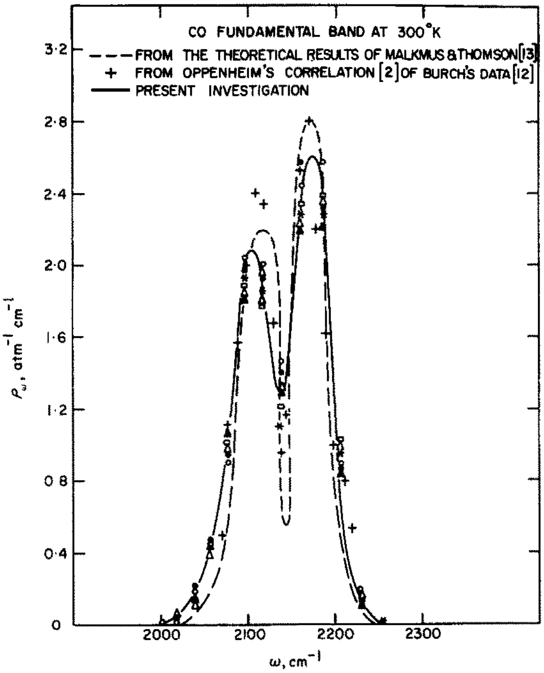

FIG. 1. Spectral absorption coefficient for fundamental band of CO at temperature 300°K.

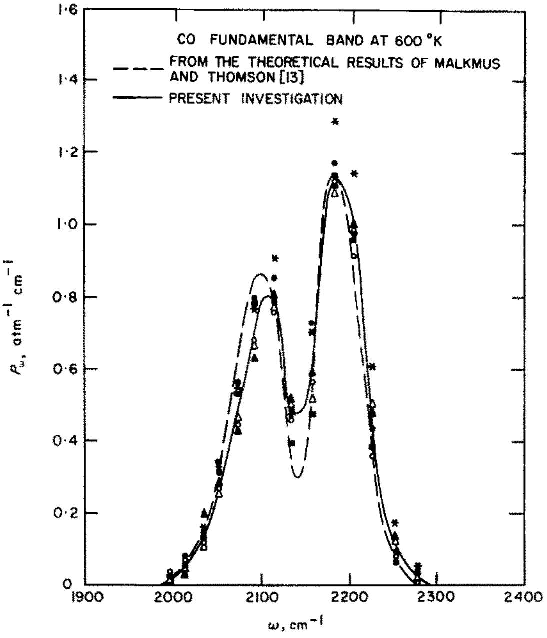

FIG. 2. Spectral absorption coefficient for fundamental band of CO at temperature 600°K.

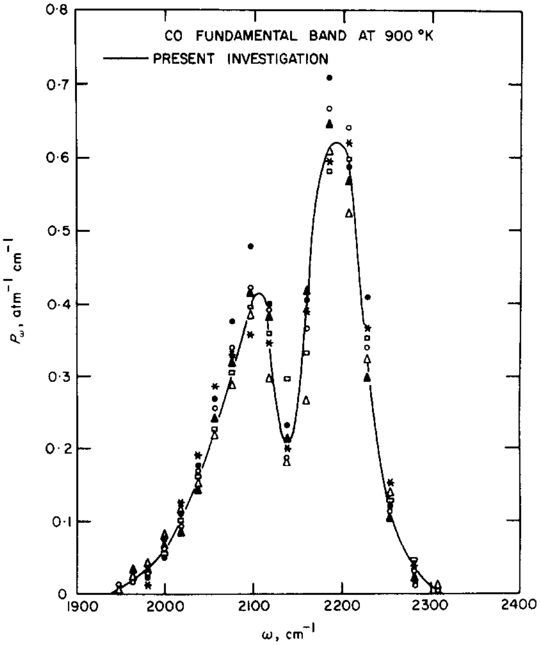

FIG. 3. Spectral absorption coefficient for fundamental band of CO at temperature 900°K.

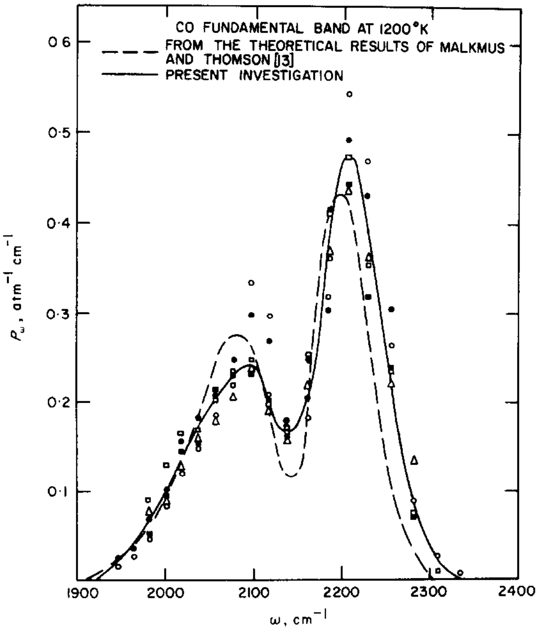

FIG. 4. Spectral absorption coefficient for fundamental band of CO at temperature 1200°K.

refer to values of the spectral absorption coefficient obtained from the spectral absorptivity data at 1, 5, 10 and 20 cm, respectively.† It is clearly shown that all spectral data points at different optical and thermodynamic conditions can be well correlated with a single line as indicated. At room temperature, a comparison has been made in Fig. 1 with the existing results of Oppenheim and Ben-Aryeh [2], which were obtained from the experimental data of Burch and Williams [12] by way of equation (1). Good agreement is indicated.

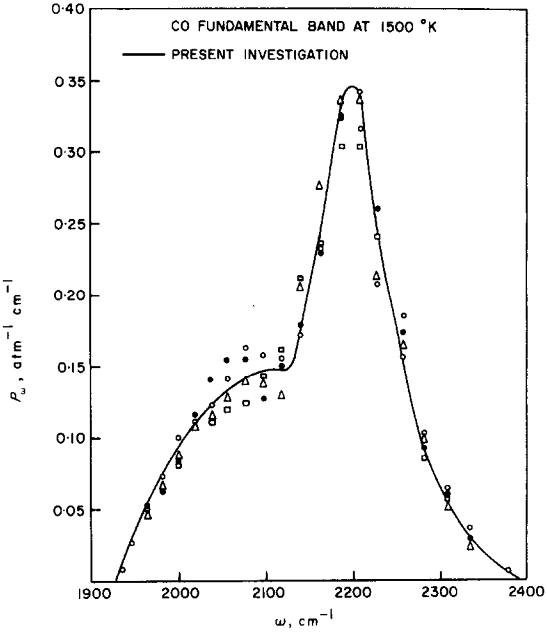

FIG. 5. Spectral absorption coefficient for fundamental band of CO at temperature 1500°K.

To compare with the theoretical prediction of the spectral absorption coefficient for CO fundamental band, the theoretical results of Malkmus and Thomson [13] for the spectral emissivity in the weak-line approximation has been converted into the spectral absorption coefficient by use of equation (1) and are shown in

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† The black symbols indicate that the spectral absorption coefficient was calculated from absorptivity data having the same path length as the corresponding white symbols but at a different pressure.

Figs. 1, 2 and 4. Again, the agreement is quite good, and part of the deviation may have resulted from the effect of the spectral slit width used in the experimental study [1]. The monochromator employed in that study was operating in a range of spectral slit widths between 7 and 12 cm^{-1}, while the theoretical results of Malkmus and Thomson are based on the average over a single line spacing, which is about 3·8 cm^{-1} for CO fundamental band.

It should be emphasized here that, combined with equations (4) and (7), the spectral absorption coefficient as presented in Figs. 1–5 for various temperatures renders a convenient analytical description of the spectral absorptivity or emissivity for the whole range of optical conditions.

INTEGRATED INTENSITY OF CO FUNDAMENTAL BAND

For practical calculations, it is often convenient to use the total band absorptance, which becomes in the optical thin limit in the weak-line-approximation region ($P_\omega u \ll 1$),

$$A = \int A_\omega \,\mathrm{d}\omega = \int [1 - \exp(-P_\omega u)]\,\mathrm{d}\omega = u \int P_\omega \,\mathrm{d}\omega = \alpha u \qquad (8)$$

where α is called the integrated intensity and is often investigated by molecular spectroscopists. By measuring the area under the spectral absorption curve, the integrated intensity for CO fundamental band at various temperatures has been determined and their values are shown in Table 1. To compare with existing experimental data, a mean value for the integrated intensities given in Table 1 and extrapolated to the density of STP is obtained. The value of 290 ± 16 cm^{-2} atm^{-1} is almost in perfect agreement with that recently reported by Breeze and Ferriso based on their high-temperature data [14], and is about 10 per cent higher than that of Penner and Weber from their room-temperature data [3]. With such agreement, no attempt has been processed to modify the simple expression for Y_ω^0 to yield closer results to those of Penner [3].

Table 1. Integrated intensity of CO fundamental band at elevated temperatures

Temperature (°K)	300	600	900	1200	1500
Integrated intensity, ($\text{cm}^{-2}\text{atm}^{-1}$)	264	134	86	72	58

CONCLUDING REMARKS

It should be mentioned in conclusion that possible investigation of the spectral absorption coefficient for the CO first-overtone band could have been accomplished in the same way as for the fundamental band. It is recognized, however, that the existing absorption profiles of CO first-overtone band [1] have been distorted and neither the band center nor the *P* and *R* branches of the band could be identified with a reasonable degree of accuracy. This is mainly due to the large spectral slit widths used in the experimental study and the insufficient amplification of the recorded spectral data. Accordingly, it is decided to exclude any data on the spectral absorption coefficient of CO first-overtone. Theoretical calculations of the spectral absorption coefficient of CO first-overtone band in the weak-line-approximation region has been reported by Young [15].

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Résumé—Le coefficient d'absorption spectrale de la bande fondamentale de CO au x températures allant de 300° à 1500°K est déterminé à partir des données existantes d'absorption spectrale dans la région d'approximation par une ligne intense et dans la région de transistion. Ceci a été accompli en utilisant l'approximation de Godsen pour la fonction d'Elsasser et les valeurs moyennes estimées pour le rapport de la demi-largeur des lignes à leur especement à différentes températures. Les coefficients d'absorption spectrale qui en résultent concordent avec les données expérimentales disponibles à température ambiante et avec les résultats théoriques à différentes températures. L'étude actuelle conduit à une valeur de 290 ± 16 atm^{-1} cm^{-2} pour l'intensité globale de la bande fondamentale de CO extrapolée à STP, valeur qui est également en bon accord avec les données expérimentales récentes de Breeze et Ferriso.

Zusammenfassung—Der spektrale Absorptionskoeffizient der CO Fundamentalbande wurde bei Temperaturen von 300° bis 1500°K aus den vorhandenen Spektralabsorptionsdaten im Näherungsbereich der starken Linien und im Übergangsbereich bestimmt. Dies wurde erreicht mit Hilfe der Godson-Näherung für die Elsässer-Funktion und der geschätzten Mittelwerte für Verhältnisse halber Linienbreiten-Abstände bei verschiedenen Temperaturen. Die sich ergebenden spektralen Absorptionskoeffizienten sind gut mit verfügbaren Versuchsdaten bei Zimmertemperatur und mit theoretischen Werten bei verschiedenen anderen Temperaturen vergleichbar. Für die Gesamtintensität der CO Fundamentalbande ergibt sich nach der gegenwärtigen Untersuchung bei Extrapolation auf STP der Wert 290 ± 16 atm^{-1} cm^{-2}, der wieder gut mit kürzlich erhaltenen Versuchswerten von Breese und Ferriso übereinstimmt.

Аннотация—На основе имеющихся данных в области приближений сильной линии и переходной области определяется коэффициент спектрального поглощения основной полосы CO при температурах от 300° до 1500°K. С этой целью применяется аппроксимация Годзона для функции Эльзассера и расчетных средних значений отношения полуширины линии к расстоянию между ними при различных температурах. Полученные спектральные коэффициенты поглощения хорошо согласуется с известными экспериментальными данными при комнатной температуре и с теоретическими результатами при различных температурах. В данном исследовании для интегральной интенсивности основной полосы CO, экстраполированной на нормальную температуру и давление, получены значения 290 ± 16 $атм^{-1}$ $см^{-2}$, которые также хорошо согласуются с последними экспериментальными данными Бриза и Ферризо.