NASA TECHNICAL NOTE

NASA TN D-4798
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NASA TN D-4798

THEORETICAL MOLECULAR LINE ABSORPTION OF CO IN LATE SPECTRAL TYPE ATMOSPHERES

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1968

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ABSTRACT

The line positions, line intensities, and collisional line half-widths have been calculated for the fundamental, first-overtone, and second-overtone vibration-rotation bands of $C^{12}O^{16}$ and $C^{13}O^{16}$. The $C^{12}O^{16}$ and $C^{13}O^{16}$ line intensities were computed for temperatures ranging from 175 to $3500°K$ and were weighted in accordance with a terrestrial C^{12}/C^{13} abundance ratio. All lines within 5 to 6 orders of magnitude of the maximum line intensity of a band have been considered (~4500 lines at $3500°K$). Tables of the above molecular absorption line parameters are being published (Kunde, 1967).

The CO mass absorption coefficient has been computed for several late spectral type stellar-atmosphere conditions. The straight mean absorption coefficient has been evaluated for these conditions in several ways: (1) exactly, by using line-by-line integration techniques; (2) approximately, by using the quasi-random molecular-absorption band model; and (3) approximately, by computing the expression $S_T^m/\Delta\nu$, where S_T^m is the total line intensity in spectral interval $\Delta\nu$. Results of this investigation indicate that the simpler $S_T^m/\Delta\nu$ approximation represents the CO mean absorption coefficient in the late type atmospheres generally to an accuracy better than 1 percent, if the spectral intervals are greater than 5 cm^{-1}. The quoted accuracy is based on the fundamental band for $T = 2500°K$, pressures up to two atmospheres, and turbulent velocities up to 10 km/sec. The mean absorption coefficient $S_T^m/\Delta\nu$ has been determined for CO for temperatures of 1000, 2500, and $3500°K$.

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INTRODUCTION

The physical state of early spectral type atmospheres is fairly well known from both an observational and a theoretical viewpoint. In general, the opacity sources for these atmospheres are considered known, and representative model atmospheres have been developed to the point where the effects of non-greyness and line absorption have been included in the models. The current central problem in early type model atmospheres is the inclusion of non-LTE effects (Mihalas, 1966).

In contrast to the early spectral type atmospheres, the physical state of late spectral type atmospheres is relatively unknown observationally and theoretically. Until recently, little work had been done on late type atmospheres mainly because the sources of opacity, especially the molecular-line opacity, and their abundances were not known. Recent observations have identified some dominant sources of molecular opacity, essentially CO and H_2O, so that it is now feasible to construct exploratory late type model atmospheres including the effects of molecular absorption. In the construction of late type models, the main problem is knowing how to include molecular opacity in the algorithms already developed for non-grey models with continuous opacity sources. Several approximate methods for attacking the line-opacity problem have been discussed in the recent literature. They are (1) WT_ν-HT statistical procedure of Strom and Kurucz (1966), (2) the "rectangular-box" procedure of Gingerich (1966), (3) the harmonic-mean procedure of Auman (1967), and (4) the smeared-line model of Tsuji (1966a, 1966b). Besides line opacity, the equation of state and convection also presents problems in constructing realistic late type model atmospheres (Vardya and Kandel, 1967: Gingerich, Latham, Linsky and Kumar, 1967).

The main object of this paper is to find the simplest technique for adequately representing the molecular absorption of CO at elevated temperatures. The investigation consists essentially of three parts:

(1) Using an anharmonic vibrating-rotator molecular model, the line positions and line intensities have been calculated for the fundamental, first-overtone and second-overtone vibration-rotation

bands of $C^{12}O^{16}$ and $C^{13}O^{16}$. The line intensities have been computed for temperatures from 175 to 3500°K; collisional-line half-widths have also been determined for each line.

(2) The CO straight mean mass absorption coefficient has been calculated for several late type stellar atmosphere conditions. The mean absorption coefficient has been evaluated by line-by-line integration techniques, an approximation $S_T^m/\Delta\nu$, and by the quasi-random band model. The line-by-line procedure forms the basis for accurate spectrum analysis and for determining the molecular-absorption parameters required by the various methods proposed for solving the line-opacity problem, and also checks the accuracy of these same methods.

(3) The straight mean mass absorption coefficient $S_T^m/\Delta\nu$ is determined for the vibration-rotation bands of CO at 1000, 2500, and 3500°K.

A secondary purpose of this paper is to develop the quasi-random band model absorption coefficient to represent molecular line absorption. This model removes some of the limitations of the methods mentioned previously for solving the line opacity problem. The results of this investigation show that CO absorption can be represented accurately by the simpler $S_T^m/\Delta\nu$ approximation. Thus the quasi-random model has no application in this investigation.

GENERAL SURVEY OF MOLECULAR ABSORPTION IN LATE SPECTRAL TYPE ATMOSPHERES

Dissociation Equilibria

It has been known for some time that molecules occur in the solar atmosphere and in the atmospheres of stars whose spectral type is later than the sun's. It is possible to predict the molecular abundances in these atmospheres as a function of temperature, gas pressure, electron pressure, and initial atomic abundances by assuming the various constituents to be in dissociation equilibria. Dissociation equilibria studies (Russell, 1934; de Jager and Neven, 1956; Tsuji, 1964; Dolan, 1965; and Vardya, 1966) explain fairly well the observed spectra of the late type stars and the branching of the spectral sequence into the K-M, the K-S, and the G-R-N sequences. These studies have indicated that the resultant equilibrium concentrations of certain atomic and molecular species are extremely sensitive to the initially assumed H:C:N:O ratio. In general, diatomic molecules are predominant in the temperature range 2500 to 5000°K and—with the exception of H_2, CO and N_2—polyatomic molecules are predominant for temperatures less than 2500°K. The molecules which were predicted to be most abundant and also have active vibration-rotation bands are listed in Table 1 in order of decreasing abundance for the temperature range of 1000 to 2500°K. At these low temperatures the outgoing atmospheric radiation is concentrated in the red and infrared. Thus the molecular vibration-rotation bands are an important source of opacity, as they absorb strongly in the spectral regions where the outgoing radiation is a maximum.

Infrared Observations

Historically, infrared observations of stellar objects have been limited by the small amount of infrared energy radiated and by absorption in the earth's atmosphere. Recent improvement in infrared-detector sensitivity has led to an increasing number of infrared photometric and spectrophotometric measurements through atmospheric "windows."

Several groups have been active in infrared photometry. Wildey and Murray (1964a, 1964b) made the first photometric stellar observations through the atmospheric "window" between 8 and 14μ of 25 stars of spectral type B8 to M7. Wildey (1966) extended this work to 42 additional stars. A program of multicolor observations including 11 broad spectral intervals—of which 8 occur in the infrared—is being carried out at the Lunar and Planetary Laboratory, University of Arizona (Johnson, 1962; Johnson and Mitchell, 1963; Low and Johnson, 1964; Johnson, Mendoza and Wisniewski, 1965; Johnson, 1966a). These observations have contributed to interpretation of the problem of interstellar extinction and have been used to revise bolometric corrections and effective temperatures for various spectral types (Johnson, 1966b). An infrared sky survey is being carried out by Neugebauer, Martz, and Leighton (1965) of the California Institute of Technology for the spectral regions 0.68-0.92μ and 2.01-2.41μ. Results of the infrared photometric observations have indicated a number of very cool stars, some with temperatures apparently ranging as low as 700 to 1000°K (Johnson, Low, and Steinmetz, 1965; Johnson, Mendoza and Wisniewski, 1965; Johnson, 1966a).

Ground-based infrared spectrophotometric observations by Boyce and Sinton (1963, 1964a, 1964b), Sinton (1966), and Kuiper (1963, 1964) have led to the identification of H_2O and CO in the atmospheres of M giants and supergiants. On the Stratoscope II balloon flight of November 1963, the spectra of six red giants were obtained in the 1-3μ range (Woolf, Schwarzschild, and Rose, 1964). The spectra indicated absorption bands of H_2O at 1.13, 1.4, 1.9, and 2.7μ and of CO at 2.35μ. For Mira, it was estimated that H_2O absorbs about one-quarter of the total emitted energy.

Spinrad and Newburn (1965) have obtained low-dispersion spectra of 36 late type stars. The (201) vibration-rotation band of H_2O at 9400 Å was used to identify H_2O in these spectra, absorption being strong only in the coolest types, M7 and M8. The total amount of H_2O for the atmosphere of Mira was estimated as approximately $1/3$ gm/cm^2 near minimum light. The total H_2O abundance for Mira was found to vary with phase—the H_2O content being reduced as maximum light is approached (Spinrad, Pyper, Newburn and Younkin, 1966). Sinton (1966), also, has observed a variation

Table 1

Molecules in Late Spectral Type Atmospheres
(Tsuji, 1964).

Type	Dwarf	Giant	Supergiant
M-type stars:	H_2O	H_2O	H_2O
	CO	CO	CO
	CH_4	CO_2	CO_2
	NH_3		
	CO_2		
	HCN		
Carbon stars:	CH_4	HCN	HCN
	HCN	CH_4	CO
	CO	CO	C_2H_2
	C_2H_2	C_2H_2	CH_4
	CH_3	C_2H_4	

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in band strengths with changing phase for the Mira type variables. For R Leo, the intensity of the H_2O bands were strongest at minimum light and varied with phase appreciably while the CO-band intensity was relatively constant. In χ Cyg the phase variations of the H_2O and CO bands were found to vary in opposite directions. For 10 cool stars, Spinrad (1966) has identified several quadrupole lines of the first-overtone band of H_2 in the 1-micron region. For Mira and α Ori, the data indicated a phase change in H_2 abundance. For Mira, the H_2 abundance varied from 6×10^{26} to 2×10^{26} molecules/cm^2 as the phase varied from minimum to maximum light. Spinrad and Vardya (1966) have compiled a table of approximate stellar abundances for H_2O, H_2, and CO for seven M stars. The range in abundances is as follows:

$$H_2O: \quad 2 \times 10^{22} - 1 \times 10^{21} \text{ molecules/cm}^2,$$

$$H_2: \quad 6 \times 10^{26} - 1 \times 10^{26} \text{ molecules/cm}^2,$$

$$CO: \quad 1 \times 10^{24} - 2 \times 10^{22} \text{ molecules/cm}^2.$$

The above abundances are quite uncertain because of difficulties in observation and data reduction.

Both the first ($\Delta v = 2$) and second ($\Delta v = 3$) overtone bands of CO appear in spectra of M, N, and S stars obtained by McCammon, Münch, and Neugebauer (1967) in the spectral regions $1.5\text{-}1.8\,\mu$ and $1.9\text{-}2.5\,\mu$. The H_2O absorption was found to be stronger in the M-type stars than in the N and S type.

The above infrared photometric and spectroscopic observations qualitatively verify the predictions of dissociation equilibria studies that H_2O, H_2, and CO are major molecular constituents in late type atmospheres. Considerable quantitative disagreement remains between abundances predicted by model-atmosphere theory and observational abundances (Spinrad and Newburn, 1965; Spinrad, 1966). Presumably these differences will disappear when more realistic model atmospheres are constructed which include the effects of molecular absorption and convection.

Model Atmospheres–Continuous Opacity Sources

The only set of late type models now in existence has been computed by Gingerich and Kumar (1963); Kumar (1964); and Gingerich, Latham, Linsky, and Kumar (1967). These radiative equilibrium models include only the effects of continuous sources of opacity: H, H$^-$, H$_2^-$, He$^-$, electron, and Rayleigh scattering from atomic and molecular hydrogen. Molecular absorption and convection have not been included in these models. They were constructed for a temperature range of 2500 to 4000°K and a surface-gravity range of log g = 2-5. They predict several interesting properties for late type atmospheres (Gingerich, Latham, Linsky, and Kumar, 1967):

(1) A large fraction of the hydrogen present is in molecular form. For example, in the outer layers of the 2500°K model, over 99 percent of the hydrogen is in molecular form.

(2) Very high pressures occur in the dwarf photospheres (~200 atm for log g = 5). Inclusion of molecular absorption is expected to lower these pressures by 1 to 2 orders of magnitude. Thus, even for these lowered pressures, the pressure-dependence of the molecular absorption may have to be included.

(3) Convective instability occurs at shallow optical depths, $\tau \sim 0.1$.

Properties (1) and (3) are not expected to change drastically with the construction of more realistic models.

Model Atmospheres—Molecular Absorption

Only a few investigations concerning molecular-absorption coefficients at elevated temperatures have yet been recorded. Yamashita (1962) has calculated the molecular absorption of (1) metallic atoms and the electronic bands of TiO; (2) rotational lines of CO, OH, and H_2O; and (3) vibration-rotation bands of H_2O and CO_2. The vibration-rotation bands of CO were not included. The absorption coefficient was averaged over very wide spectral intervals; for example, the vibration-rotation bands were averaged over the entire band.

To aid in the analysis of the Stratoscope II observations, Auman (1966, 1967) has theoretically calculated the molecular absorption of H_2O. The positions and strengths of the individual lines were calculated for the spectral region from $0.8-12.5\mu$ for temperatures of 1680, 2016, 2520, and 3360°K. The harmonic-mean opacity was calculated for spectral intervals of 100 cm^{-1}, assuming the lines to be Doppler-broadened, for rms turbulent velocities of 2, 4, and 8 km/sec. Water vapor was found to be the dominant source of opacity for $T < 2520°K$; the ratio of the opacity with H_2O to that without H_2O being as large as 2.4×10^3 at 2.60μ and 2520°K. The H_2O opacity has been included in a model atmosphere with $T = 2520°K$ and log $g = 3.0$. The inclusion of the H_2O opacity decreased the density at a given temperature in the convective region by a factor of 7 and lowered the boundary temperature by 9 percent.

In a recent investigation, Tsuji (1966a, 1966b) has determined the molecular absorption of the vibration-rotation and pure-rotation bands of H_2O, CO, and OH. These calculations were based on a smeared-line model (Golden, 1962; Patch, Shackleford, and Penner, 1963; and Golden, 1967) to approximate the molecular absorption. This model assumes that the rotational structure is smeared into a pseudo-continuum either by pressure-broadening or by a sufficient number of rotational lines to fill in all spectral gaps. Tsuji also assumes that the H_2O, CO, and OH molecules can be represented by a rigid rotator. On the above foundation Tsuji (1966c) has constructed several preliminary model atmospheres of solar composition.

MOLECULAR LINE ABSORPTION COEFFICIENT

A molecular absorption line can be described by four parameters: line position $\left(\nu_0\right)$, line intensity (S), relative line shape (b), and line half-width (α) —see Figure 1. The absorption coefficient is written in terms of these parameters as

$$k(\nu) \;=\; S\, b\left(\nu - \nu_0,\, \alpha\right) ,$$

(1)

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where the relative line shape $b(\nu - \nu_0, a)$ depends on the type of line-broadening mechanism considered. The line intensity is defined by the condition

$$S = \int_{-\infty}^{+\infty} k(\nu)\, d\nu . \qquad (2)$$

Line-by-Line Basis

The total line absorption coefficient at wave number ν is

$$k(\nu, P, T) = \sum_i S_i(T)\, b(\nu - \nu_{0_i}, a_i(P, T)) , \qquad (3)$$

Figure 1—Relative absorption coefficient in terms of molecular-absorption-line parameters.

where the summation includes all the individual absorption lines. As the monochromatic absorption coefficients are too numerous to handle routinely the absorption coefficient is averaged over a finite spectral interval

$$\bar{k}_{\Delta\nu}(P, T) = \frac{1}{\Delta\nu} \int_{\Delta\nu} k(\nu, P, T)\, d\nu . \qquad (4)$$

The method used to solve Equation 4 is patterned after the numerical technique developed by Drayson (1964, 1966). Basic to this procedure are a variable wave-number mesh, for evaluating the monochromatic absorption coefficient, and a division of the contribution of each line into a direct and a wing contribution. The basic spectral interval considered is $\Delta\nu = 0.1\ \text{cm}^{-1}$. This interval is divided into a variable number of subintervals depending on the positioning of the line centers within the interval. The above integral is evaluated numerically, using Legendre-Gauss quadrature (Stroud, 1966), as

$$\bar{k}_{\Delta\nu}(P, T) = \sum_j \frac{\nu_{Bj} - \nu_{Aj}}{2} \sum_{i=1}^{4} a_i\, k(\nu_{ij}, P, T) , \qquad (5)$$

where

$$\nu_{ij} = \frac{\nu_{Bj} - \nu_{Aj}}{2} x_i + \frac{\nu_{Bj} + \nu_{Aj}}{2} . \qquad (6)$$

The j-summation is for the subintervals in $\Delta\nu$; the i-summation represents four-point Legendre-Gauss quadrature for each subinterval, and ν_B and ν_A are the upper and lower wave-number
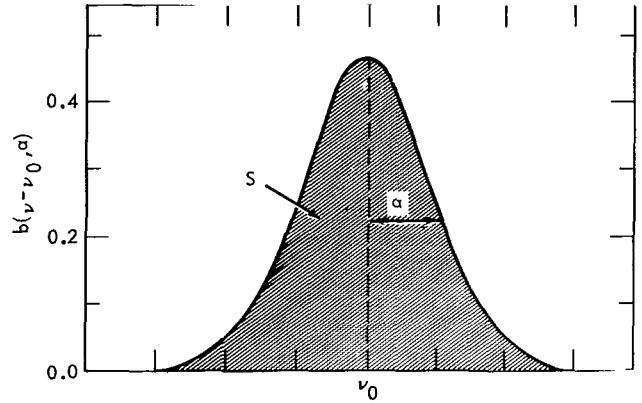
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boundaries of the subinterval. The function $k(\nu_{ij}, P, T)$ represents the monochromatic absorption coefficient at wave number ν_{ij} in $\Delta\nu$.

The wave-number mesh ν_{ij} for a 0.1-cm^{-1} interval is constructed in accordance with the following criterion. A single line is divided into subintervals with the subinterval boundaries placed at 0.0, 0.005, 0.01, 0.02, . . . , 0.09, 0.10 cm^{-1} from the line center. For lines whose centers are closer together than 0.1 cm^{-1}, the mesh is adjusted so that each line satisfies the above criterion until the midpoint between the two line centers is reached. If no lines occur in a 0.1-cm^{-1} interval, no subdivision occurs and only four mesh points are used. The maximum number of mesh points that can occur for an interval of 0.1 cm^{-1} is 80.

For each line, the monochromatic absorption coefficient for distances less than and greater than 4 cm^{-1} from the line center was considered as the direct and wing contribution, respectively. The direct contribution at ν_{ij} within an 0.1 cm^{-1} interval is

$$k_D\left(\nu_{ij}, P, T\right) = \sum_i S_i(T) b\left[\nu_{ij} - \nu_{0_i}, a_i(P, T)\right], \qquad (7)$$

$$\nu_A < \nu_{ij} < \nu_B, \qquad \nu_A - 4 < \nu_{0_i} < \nu_B + 4, \qquad \left|\nu_{ij} - \nu_{0_i}\right| < 4 \text{ cm}^{-1},$$

with the relative line shape given by the mixed Doppler-Lorentz line shape. The mixed-line shape was evaluated by means of a computer subroutine developed by Young (1965). The wing contribution is given by

$$k_w\left(\nu_{ij}, P, T\right) = \sum_i S_i(T) b\left[\nu_{ij} - \nu_{0_i}, a_i(P, T)\right], \qquad \nu_A - 4 \leq \nu_{0_i} \geq \nu_B + 4. \qquad (8)$$

For conditions representative of cool star atmospheres, the line shape is determined by collisional broadening for distances from the line center greater than 4 cm^{-1}. Substituting the line shape given by the Benedict modification of the Lorentz line shape (Equation 47) and the collisional half-width of Equation 52, in Equation 8 yields

$$k_w\left(\nu_{ij}, P, T\right) = \sum_i \frac{1}{\pi} \frac{S_i(T) a_{c_{0_i}} \cdot \frac{P}{P_0} \sqrt{\frac{T_0}{T}} \text{ C.F.}}{\left(\nu_{ij} - \nu_{0_i}\right)^2}, \qquad \left|\nu_{ij} - \nu_{0_i}\right| > 4 \text{ cm}^{-1}, \qquad (9)$$

where the half-width term in the denominator has been neglected. Rewriting Equation 9 gives

$$k_w\left(\nu_{ij}, P, T\right) = \frac{1}{\pi} \frac{P}{P_0} \sqrt{\frac{T_0}{T}} \text{ SM}(\nu_{ij}, T), \qquad (10)$$

where

$$SM(\nu, T) = \sum_i \frac{S_i(T) \alpha_{c_{0_i}} C.F.}{\left(\nu - \nu_{0_i}\right)^2} \quad , \qquad \left|\nu - \nu_{0_i}\right| > 4 \text{ cm}^{-1} . \tag{11}$$

Since the function $SM(\nu, t)$ does not vary rapidly with wave number, it is calculated at every 1 cm^{-1}; interpolation gives intermediate values. The total monochromatic absorption coefficient is obtained by adding the direct and wing contribution:

$$k\left(\nu_{ij}, P, T\right) = k_D\left(\nu_{ij}, P, T\right) + \frac{1}{\pi} \frac{P}{P_0} \sqrt{\frac{T_0}{T}} \, SM\left(\nu_{ij}, T\right) . \tag{12}$$

Combining Equations 3 and 4 gives, for the mean absorption coefficient,

$$\bar{k}_{\Delta\nu}(P, T) = \frac{1}{\Delta\nu} \sum_i S_i \int_{\Delta\nu} b\left(\nu - \nu_{0_i}, \alpha_i(P, T)\right) d\nu . \tag{13}$$

If the spectral interval $\Delta\nu$ is chosen large enough for the entire absorption line to lie within $\Delta\nu$, the mean absorption coefficient is

$$\bar{k}_{\Delta\nu}(P, T) = \sum_i \frac{S_i}{\Delta\nu} = \frac{S_T}{\Delta\nu} , \tag{14}$$

where the range of i is for all lines in $\Delta\nu$, and S_T is the total line intensity in $\Delta\nu$,

$$S_T = \sum_i S_i .$$

The mean absorption coefficient $S_T/\Delta\nu$ is only approximate for intervals where wing effects become significant—for example, in regions past band heads.

At elevated temperatures the number of molecular absorption lines that must be considered— for a polyatomic molecule in particular—is so great that even present-day computing facilities are not adequate for routine line-by-line computation. Auman (1967), for example, considered approximately 2.3 million H_2O lines in his investigation. Thus it is desirable to resort to a different approach; this is discussed in the next section.

Band Models

Various band models have been proposed to represent molecular band absorption for a finite spectral interval. Two models, in general, have received the most attention. The Elsasser model assumes that the spectral lines are of equal intensity and uniformly spaced; while the random or statistical model assumes that the line intensities can be represented by a probability distribution with the line positions occurring at random. A third model, the "quasi-random" model, has recently been developed to correct certain defects of the Elsasser and the random models. For the purposes of this investigation, only the random and quasi-random model are of interest.

Random Model

The mathematical formulation of the random or statistical model is developed in Appendix A. Assuming the line positions occurring in spectral interval $\Delta\nu$ to be distributed at random, Equation A5 gives the average absorption coefficient $\bar{k}(\nu)$ at ν due to n lines in $\Delta\nu$ as

$$\bar{k}(\nu) = \frac{\int_0^\infty \int_0^\infty \int_{\Delta\nu} n\, S_i\, b\left(\nu - \nu_{0_i}, \alpha_i\right) P'\left(\alpha_i\right) P\left(S_i\right) d\nu_{0_i}\, dS_i\, d\alpha_i}{\int_0^\infty \int_0^\infty \int_{\Delta\nu} P\left(S_i\right) P'\left(\alpha_i\right) d\nu_{0_i}\, dS_i\, d\alpha_i} . \tag{15}$$

Quasi-Random Band Model

To correct certain limitations of the Elsasser and statistical band models, the quasi-random band model has been developed (Wyatt, Stull, and Plass, 1962). The quasi-random model differs from other band models in several ways:

(1) Method of spectral division: To determine the average absorption coefficient for the interval Δ, Δ is subdivided into smaller intervals ϵ. The vibration-rotation lines occurring in ϵ are assumed to have a random distribution of line positions. The average absorption coefficients for the ϵ's within Δ are then arithmetically averaged to give the average absorption coefficient for Δ. In principle, the exact line positions are obtained by allowing ϵ to approach zero.

(2) Line-intensity distribution: The lines in a subinterval ϵ are divided into subgroups, each subgroup covering one intensity decade. The intensity distribution is then simulated by the number of lines and the average intensity $\bar{S}$ for each decade. For four intensity decades, Equation 15 yields the average coefficient due to one subinterval as

$$\bar{k}(\nu) = \sum_{l=1}^{4} \frac{1}{\epsilon} \int_\epsilon n_l\, \bar{S}_l\, b\left(\nu - \nu_{0_i}, \bar{\alpha}_l\right) d\nu_{0_i} , \tag{16}$$

where the total number of lines in ϵ is

$$n = \sum_{l=1}^{4} n_l .$$

(3) Wing effects: The contribution to the absorption coefficient of a given subinterval from the wings of lines in adjacent subintervals is properly taken into account.

For the quasi-random model, the total average absorption coefficient at ν in subinterval ϵ_k is

$$\bar{k}_k (\nu) = \sum_{j=1}^{\infty} \bar{k}_j (\nu) , \qquad (17)$$

where $\bar{k}_j (\nu)$ is the contribution to $\bar{k}_k (\nu)$ from the n_j lines in interval ϵ_j. The direct contribution $\bar{k}_k (\nu)$ is caused by the lines in interval ϵ_k when $j = k$. The wing contribution is due to all remaining intervals for which $j \neq k$. Combining Equations 16 and 17 gives

$$\bar{k}_k (\nu) = \sum_{j=1}^{\infty} \left(\sum_{l=1}^{4} \frac{n_l \bar{S}_l}{\epsilon} \int_{\epsilon} b\left(\nu - \nu_{0_i}, \bar{\alpha}_l\right) d\nu_{0_i} \right)_j . \qquad (18)$$

If the ϵ interval is chosen large enough for the lines to lie entirely within ϵ, Equation 18 reduces to $S_T/\Delta\nu$, which is the same as the expression given by Equation 14. From Equation 18, the average absorption coefficient for each subinterval ϵ can be evaluated. The quasi-random average absorption coefficient for interval Δ is determined by arithmetically averaging the $\bar{k}_k (\nu)$'s of the subintervals contained in Δ. The line shape is treated in the manner described in the next section. The integral in Equation 18 is evaluated numerically. .

To evaluate Equation 18 requires the specification of the following parameters:

(1) ϵ, Δ, subinterval and interval size (in this investigation $\epsilon = 5$ cm^{-1}, while Δ has been varied from 5 to 100 cm^{-1}).

(2) n_l, $\bar{S}_l$, $\bar{\alpha}_l$—the number of lines, the average line intensity, and the average collisional-line half-width for each intensity decade and for each subinterval.

(3) Line shape, $b\left(\nu - \nu_{0_i}, \bar{\alpha}_l\right)$.

A program was developed for the IBM 360, to determine values of n_l, $\bar{S}_l$, and $\bar{\alpha}_{c_l}$ for each subinterval, from input tables of the individual line parameters ν_0, S, and α_{c_0}.

MOLECULAR LINE PARAMETERS FOR CO

Line Position

The term value of a vibrating anharmonic rotator (Herzberg, 1950) is

$$T' \left(cm^{-1} \right) = \omega_e \ (v + 1/2) - \omega_e x_e \ (v + 1/2)^2 + \omega_e y_e \ (v + 1/2)^3$$

$$+ \omega_e z_e \ (v + 1/2)^4 + B_v \ J(J + 1) - D_v J^2 \ (J + 1)^2 , \tag{19}$$

where

$$B_v = B_e - \alpha_e \ (v + 1/2) + \gamma(v + 1/2)^2 , \tag{20}$$

$$D_v = D_e + \beta(v + 1/2) . \tag{21}$$

It is convenient to define a rotational quantum index m by $m = J + 1$ for the R branch and $m = -J$ for the P branch. The term values given by Equation 19, plus the vibration and rotation selection rules, yield the predicted line positions. The constants needed to solve Equation 19 are well known for CO. The values listed by Benedict, Herman, Moore, and Silverman (1962) were used in this investigation, with the exception of ω_e for $C^{13}O^{16}$ which is incorrect in their paper. The correct value is 2121.462 (Mills and Thompson, 1953). These constants yield line positions that agree with experimental line positions within 0.05 cm^{-1} and 0.5 cm^{-1} for the fundamental and first-overtone bands, respectively.

Line Intensity

An optical depth can be defined by

$$d\tau = -k^m \ (\nu) \ \rho_g \ ds , \tag{22}$$

where $k^m (\nu)$ is the mass absorption coefficient, ρ_g is the density of the absorbing gas, and s is the geometrical path length. To conform to the system of units used in laboratory measurements, it is necessary to transform the mass absorption coefficient $k^m (\nu)$ into an absorption coefficient per unit length per unit pressure $k^{lp} (\nu)$. The transformation is made by defining

$$k^{lp} (\nu) = k^m (\nu) \rho_g / p , \tag{23}$$

and

$$du(cm \ atm) = -p \ ds , \tag{24}$$

where p is the partial pressure of the absorber in atmospheres and u is the optical path length in cm atm. The absorption coefficient $k^{1p}(\nu)$ has units of cm^{-1} atm^{-1}. Equation 22 may now be written

$$d\tau = k^{1p}(\nu) du .$$

(25)

The absorption coefficient transformation also requires redefining line intensity. The normalization condition for the line strength requires that

$$\int_{-\infty}^{+\infty} k^m(\nu) d\nu = S^m \left(cm \cdot gm^{-1} \right) ,$$

(26)

and

$$\int_{-\infty}^{+\infty} k^{1p}(\nu) d\nu = S^{1p} \left(cm^{-2} atm^{-1} \right) ,$$

(27)

where the transformed line intensity S^{1p} is related to S^m by

$$S^{1p} = S^m \rho_g/p = \frac{S^m M \left(1.01325 \times 10^6 \right)}{R_m T} ,$$

(28)

where $R_m = 8.314 \times 10^7$, and M is the molecular weight. The factor 1.01325×10^6 is due to the change in pressure units.

The line intensity, S^{1p}, for a transition from quantum state 1 to quantum state u is given by Penner (1959, Equations 7-124)

$$S^{1p} = \frac{8\pi^3 \nu_{1u}}{3 hc g_1} \left(N_1/p \right) \left| R_{1u} \right|^2 \left[1 - \exp -\left(\frac{hc \nu_{1u}}{kT} \right) \right] ,$$

(29)

where ν_{1u} is the transitional wave number, g_1 is a statistical weight, N_1 is the number of molecules per unit volume in the lower quantum state, and R_{1u} is the electric-dipole-moment matrix element. Equation 29 is based on a distribution of quantum states in thermodynamic equilibrium. The dipole-moment matrix elements are related to the Einstein coefficient for induced absorption (Penner, 1959) by

$$B_{1u} = \frac{2\pi}{3\hbar^2} \left| R_{1u} \right|^2 .$$

(30)

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Penner defines the dipole-moment matrix element for a transition from a lower state of vibrational and rotational quantum numbers v and J to a upper state of v' and J' as

$$|R_{1u}|^2 = S_J \left| R_{v,J}^{v',J'} \right|^2 ,$$

(31)

$$R_{v,J}^{v',J'} = \int_0^\infty \psi_{v',J'}(r) M(r) \psi_{v,J}(r) \, dr ,$$

(32)

$$S_J = J , \qquad P \text{ branch} ,$$

(33)

$$S_J = J + 1 , \qquad R \text{ branch} ,$$

(34)

where r is the internuclear distance, $M(r)$ is the dipole moment, and $\psi(r)$ represents the solution to the radial Schrödinger equation. Using the Maxwell-Boltzmann distribution and Equation 31 transforms Equation 29 to

$$S^{1p}(T) = \frac{8\pi^3 \nu_{1u}}{3 hc} \cdot \frac{N_0(T)}{p} \frac{e^{-E_1/kT}}{Q} S_J \left| R_{v,J}^{v',J'} \right|^2 \left[1 - \exp\left(-\frac{hc\,\nu_{1u}}{kT} \right) \right] ,$$

(35)

where N_0 is the total number of molecules per unit volume and Q is the partition function. The above expression is normalized for standard temperature ($T_0 = 273.18\,°K$) and pressure ($p_0 = 1$ atm) by

$$S_{STP}^{1p}(T) = \frac{N_0(T_0)}{p_0} \frac{p}{N_0(T)} S^{1p}(T) = \frac{T \, S^{1p}(T)}{T_0} .$$

(36)

From Equations 35 and 36,

$$S_{STP}^{1p}(T) = \frac{8\pi^3 \nu_{1u}}{3 hc} \frac{N_0(T_0)}{p_0} \frac{e^{-E_1/kT}}{Q} S_J \left| R_{v,J}^{v',J} \right| \left[1 - \exp\left(-\frac{hc\,\nu_{1u}}{kT} \right) \right] .$$

(37)

Assuming the ideal gas law,

$$S_{STP}^{1p}(T) = \frac{8\pi^3 \nu_{1u}}{3 hc} \, 1/kT_0 \, \frac{e^{-E_1/kT}}{Q} S_J \left| R_{v,J}^{v',J'} \right| \left[1 - \exp\left(-\frac{hc\,\nu_{1u}}{kT} \right) \right] .$$

(38)

This transformation allows the line intensity to be computed as a molecular parameter independent of the actual number of molecules present. In this normalized system of units, the optical path

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is

$$du_{STP} \text{ (cm atm) } = (T_0/T)du , \qquad\qquad (39)$$

and the optical depth is

$$d\tau = k_{STP}^{1p} \, du_{STP} . \qquad\qquad (40)$$

The corresponding transformation to mass absorption units for the line intensity is

$$S^m(T) = \frac{R_m T_0}{M(1 \times 10^6)} S_{STP}^{1p}(T) . \qquad\qquad (41)$$

The dipole moment is expressed as a power-series expansion about the equilibrium internuclear separation, r_e:

$$M(r) = \sum_i M_i \left(r - r_e\right)^i . \qquad\qquad (42)$$

The expansion coefficients M_i are determined from laboratory measurements of infrared band intensities. By this method, Young and Eachus (1966) have determined the dipole moment of CO to be

$$M(r) = \pm .112 + 3.11 \left(r - r_e\right) - .15 \left(r - r_e\right)^2 - 2.36 \left(r - r_e\right)^3 . \qquad\qquad (43)$$

The dipole moment matrix elements of Young and Eachus, calculated by numerical evaluation of the integral of Equation 32, were used in this investigation. The accuracy of the matrix elements determined in this manner depends mainly on the accuracies of the infrared band intensities and the Taylor expansion of the dipole moment.

The partition function is given by Herzberg (1950):

$$Q = \sum_{v=0}^{\infty} \sum_{J=0}^{\infty} (2J + 1) \, e^{-hcT'_{v,j}/kT} , \qquad\qquad (44)$$

and is presented in Figure 2 for $C^{12}O^{16}$ and $C^{13}O^{16}$.

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Line Shape

A monochromatic absorption line may be broadened by one or more of many different types of line-broadening mechanisms, both physical and geometrical. The mechanisms of importance for this investigation are

(1) Collisional or pressure broadening caused by collisions with neighboring atoms or molecules,

(2) Doppler broadening caused by random molecular thermal motions,

(3) Turbulent broadening.

For a collision-broadened Lorentz line,

$$b\left(\nu - \nu_0, \, \alpha_c\right) = \frac{\alpha_c}{\pi} \frac{1}{\left(\nu - \nu_0\right)^2 + \alpha_c^2}, \qquad (45)$$

where α_c is the collisional half-width. The relative Doppler line shape is

$$b\left(\nu - \nu_0, \, \alpha_D\right) = \frac{\sqrt{\ln 2}}{\alpha_D \sqrt{\pi}} \exp\left(- \frac{\left(\nu - \nu_0\right)^2 \ln 2}{\alpha_D^2}\right), \quad (46)$$

Figure 2—Partition function of $C^{12}O^{16}$ and $C^{13}O^{16}$ as function of temperature.

where α_D is the Doppler half-width at half-maximum. As the Lorentz line shape is theoretically valid only near the line center (1-3 cm^{-1}) (Bohm, 1960; Goody, 1964), various experimental studies have been made to determine the line shape of the collision-broadened wing. The experimental studies for various molecules such as HCL, CO, and CO_2 have indicated that the line wings are not Lorentzian. Experiments on absorption by the fundamental and first overtone of CO (Benedict, Herman, Moore and Silverman, 1962) have shown that the Lorentz line shape should be modified by an exponential multiplying factor, dependent on $|\nu - \nu_0|$ for $|\nu - \nu_0| > d$ cm^{-1}. The modified line shape is

$$b\left(\nu - \nu_0, \, \alpha_c\right) = b_{Lorentz}^{\left(\nu - \nu_0, \, \alpha_c\right)} \text{ C.F. }, \qquad |\nu - \nu_0| > d \text{ cm}^{-1}, \qquad (47)$$

where the correction factor (C.F.) is

$$\text{C.F.} = e^{-a\left(\left|\nu - \nu_0\right| - d\right)b'}. \qquad (48)$$

The line shape of Equation 47 is called the "Benedict modification" of the Lorentz line shape. The constants were found to be d = 4 cm^{-1}, b' = 1, and a = 0.015 for CO-CO collisions. In this study

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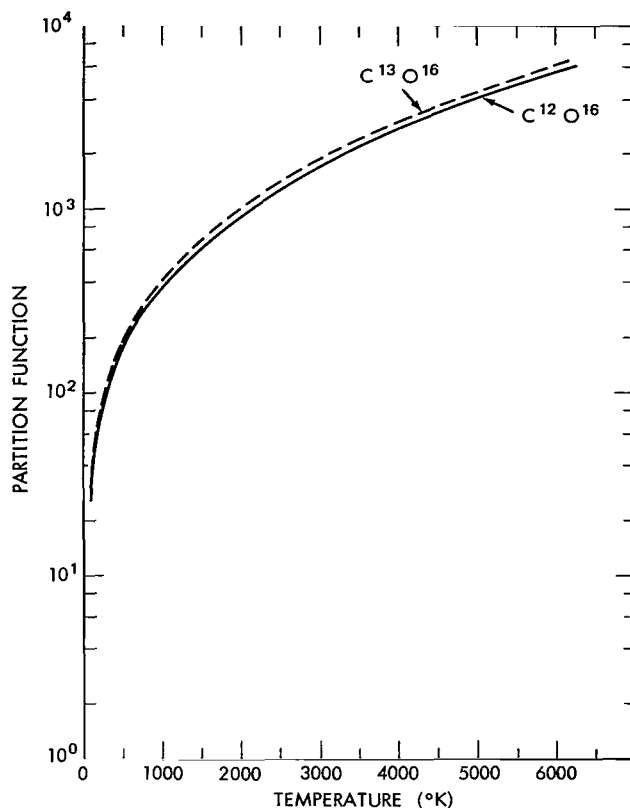it is assumed that the CO line shape caused by broadening by foreign gases is the same as for self-broadening.

The line half-width caused by thermal and turbulent broadening was assumed to be

$$a_t = \nu/c \sqrt{\frac{2\,kT}{M}\ln 2 + \xi_t^2}\ , \tag{49}$$

where ξ_t is the rms turbulent velocity.

Collisional-Line Half-Width

Kinetic theory relates the line half-width to the effective collision cross-section σ (Smith, Lackner, and Volkov, 1955) as

$$a_c = \frac{N'(T)\,\overline{V}(T)\,\sigma(T)}{2\pi c}\ , \tag{50}$$

where $N'(T)$ is the number of particles per unit volume and $\overline{V}(T)$ is the mean relative velocity of the colliding particles. Theories for determining the effective collision cross section have developed along several lines. For optical transitions, collisions may be described adiabatically; in the infrared and microwave region, diabatic collisions (in which the collision can induce a transition in the radiating molecule) must be considered. The diabatic theory of Anderson (1949) allows the effective collision cross section to be defined in terms of the intermolecular forces. This theory is most easily applied when one type of intermolecular force dominates. The largest collision cross sections are associated with long-range forces (dipole-dipole). In general, experimental cross sections are larger than would be estimated from kinetic theory (Townes and Schawlow, 1955).

Collisional line widths have been measured for self-broadened and foreign-broadened CO (Eaton and Thompson, 1959a, 1959b; Crane-Robinson and Thompson, 1962a, 1962b; Benedict, Herman, Moore and Silverman, 1962). Figures 1 and 2 of a paper by Shaw and Houghton (1964) plot the experimental-line collisional half-widths of the fundamental band of $C^{12}O^{16}$ for CO-CO and CO-N_2 collisions as a function of rotational quantum number. Figure 3 of the present paper (Kunde)
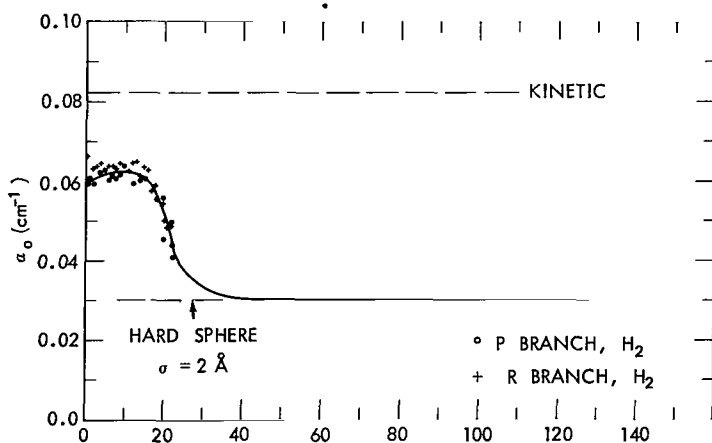

Figure 3—Collisional half-width of CO as function of rotational quantum index at pressure of one atmosphere and room temperature. The experimental values are for CO-H_2 collisions (Crane-Robinson and Thompson, 1962b). The solid curve was adopted for this investigation.

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plots the experimental half-widths for the CO fundamental for CO-H$_2$ collisions for T = 300°K and P = 1 atm. The experimental data are available only for low values of the rotational quantum number. For application to cool star atmospheres, the half-widths must be known for higher values of the rotational quantum number; also, the half-width dependence on temperature must be known.

Figure 3 also presents the line half-widths corresponding to a kinetic cross section, to London dispersion forces, and to a hard-sphere collision. The observed cross section is evidently smaller than the kinetic cross section. It has been suggested that this is because of short-range interactions that depend on a high power of 1/r (Anderson, 1949). Long-range interactions are not expected to be important in CO-H$_2$ collisions, as H$_2$ has no dipole moment and CO has only a very weak dipole moment. For CO-H$_2$ collisions, the short-range interactions that may possibly be important are

(1) dipole-quadrupole $\left(\propto r^{-4} \right)$,

(2) quadrupole-quadrupole $\left(\propto r^{-5} \right)$,

(3) dipole-induced dipole $\left(\propto r^{-6} \right)$,

(4) London dispersion $\left(\propto r^{-6} \right)$,

(5) quadrupole-induced dipole $\left(\propto r^{-7} \right)$,

(6) exchange forces due to direct interaction of the electronic-charge distributions of the colliding molecules.

Crane-Robinson and Thompson (1962b) have evaluated types (3) and (4) and find London dispersion forces the most significant. In Figure 3, the half-widths due to London dispersion forces do not have the observed dependence on rotational quantum number. The half-widths given by the solid line were used where the half-width for high J values was somewhat arbitrarily assumed to correspond to a hard-sphere collision diameter of $\sigma = 2$ Å. This same curve is assumed to apply to all vibrational levels. Penner (1952) has shown that the cross section is not a sensitive function of vibrational level.

The temperature dependence of the line half-width for interactions of the type $1/r^n$ is

$$\alpha \propto 1 \Big/ \sqrt[n]{T} \,, \tag{51}$$

if n is large (Townes and Schawlow, 1955). From Equations 50 and 51, the collisional-line half-width for CO-H$_2$ collisions at pressure P and temperature T can now be written as

$$\alpha_c (P, T, m) = \alpha_{c_0} \left(P_0, T_0, m \right) P/P_0 \sqrt{T_0/T} \,, \tag{52}$$

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where $\alpha_{C_0}\left(P_0, T_0, m\right)$ is given by the solid curve of Figure 3. In any event, the accuracy of the collisional half-width is not a critical factor in the stellar-atmosphere situations considered in this investigation; the Doppler and turbulence broadening are the dominant line-broadening mechanisms.

Using the formulation and basic molecular data discussed above, a computer program was developed for an IBM 360 to generate line position, line intensity, and collisional half-width at a given temperature for each line of the fundamental and first- and second-overtone bands considered. The $C^{12}O^{16}$ and $C^{13}O^{16}$ line intensities were weighted according to a terrestrial $C^{12}O^{16}/C^{13}O^{16}$ abundance ratio of 89.2 (Benedict, Herman, Moore and Silverman, 1962). Tables of line positions, line intensities, and collisional half-widths are given for a temperature range from 175 to 3500°K for the fundamental and first- and second-overtone bands (Kunde, 1967). Figures 4, 5, and 6 present the line intensities, S^m, at 2500°K for the fundamental and first- and second-overtone bands, respectively. For a given band at a given temperature, the calculations include all lines within approximately 5 to 6 orders of magnitude of the maximum line intensity. At 2500°K, 3030 lines were considered for the fundamental band. Young (1966) has presented the line intensities, S_{STP}^{1p}, for the fundamental and first- and second-overtone bands at $T = 3000°K$.
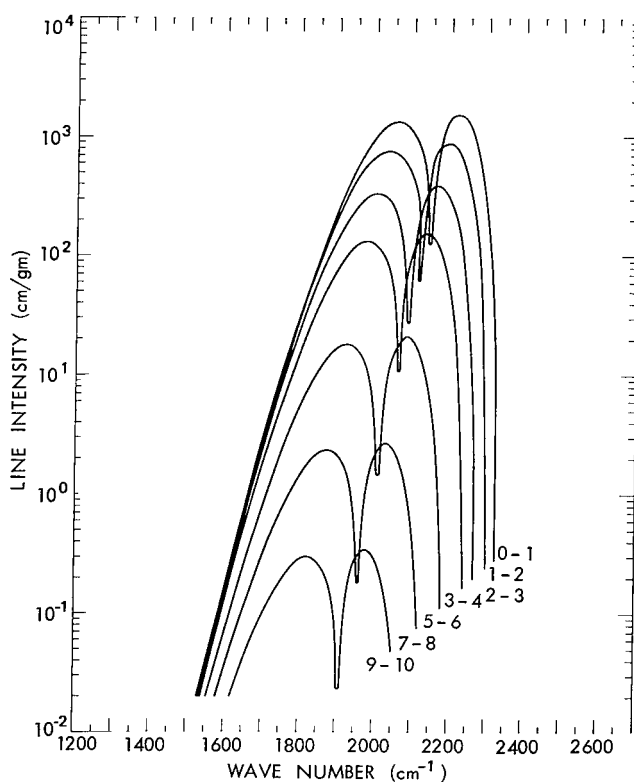

Figure 4—Line intensities corresponding to a mass absorption coefficient for various vibrational levels of the $C^{12}O^{16}$ fundamental band at 2500°K.
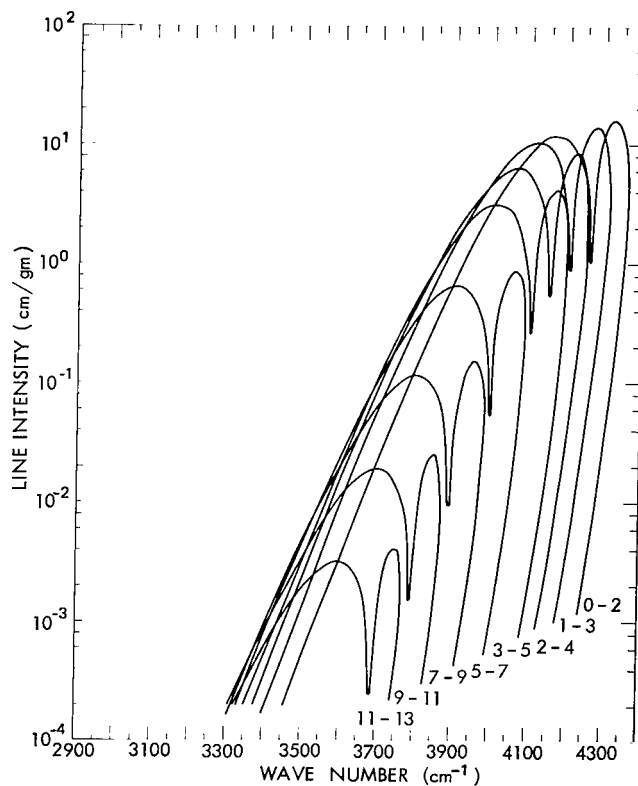
Figure 5—Line intensities corresponding to a mass absorption coefficient for various vibrational levels of the $C^{12}O^{16}$ first-overtone band at 2500°K.

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COMPARISON OF THEORETICAL AND EXPERIMENTAL ABSORPTION DATA FOR CO

To check the accuracy of the CO molecular parameters computed in the previous section, the absorption by CO has been computed theoretically by direct integration. The theoretical absorption was then compared to existing laboratory absorption data at planetary temperatures (Burch, Gryvnak, Singleton, France, and Williams, 1962) and at elevated temperatures (Abu-Roma and Tien, 1966). Figures 7 and 8 present comparisons at 300°K for the fundamental and first-overtone bands, respectively. The figures also indicate the experimental pressures, optical path lengths, total band absorptions (W), and the theoretical total band absorptions. The theoretical computations are based on the Benedict modification of the Lorentz line shape. The theoretical and experimental absorption curves are indicated by the dashed and solid curves, respectively. The theoretical transmittances are averaged over $25-cm^{-1}$ intervals, while the experimental

Figure 6—Line intensities corresponding to a mass absorption coefficient for various vibrational levels of the $C^{12}O^{16}$ second-overtone band at 2500°K.

transmittances correspond to a resolution of approximately 25 cm^{-1} and 15 to 20 cm^{-1} for the fundamental and first-overtone bands, respectively. The theoretical absorption curves agree with the experimental absorption curves almost within the experimental error, although there are indications that the theoretical curves systematically underestimate absorption in the center of the P and R branches. The total band absorptions agree within 10 percent.

Abu-Romia and Tien (1966) have measured the spectral absorption and the total band absorption of the fundamental and first-overtone bands of CO at temperatures up to 1500°K. Table 2 compares the theoretical and experimental total band absorptions for the fundamental band at 1500°K. There is general agreement to within 15 percent except for the first case which can probably be attributed to experimental inaccuracy. Comparison of the spectral absorption curves indicates that the theoretical absorption is generally greater than the experimental absorption by about 10 to 20 percent for the spectral range 1950 to 2225 cm^{-1}. Considerable disagreement exists for wave numbers less than 1950 cm^{-1} and greater than 2225 cm^{-1}. Possibly, CO_2 absorption affects the experimental values on the high wave-number side of the band.

Figure 9 shows the band intensities as a function of temperature. The solid line results from a summation of the line intensities of the individual vibration-rotation lines computed in this investigation. The dashed curve represents the theoretical temperature dependence computed for a
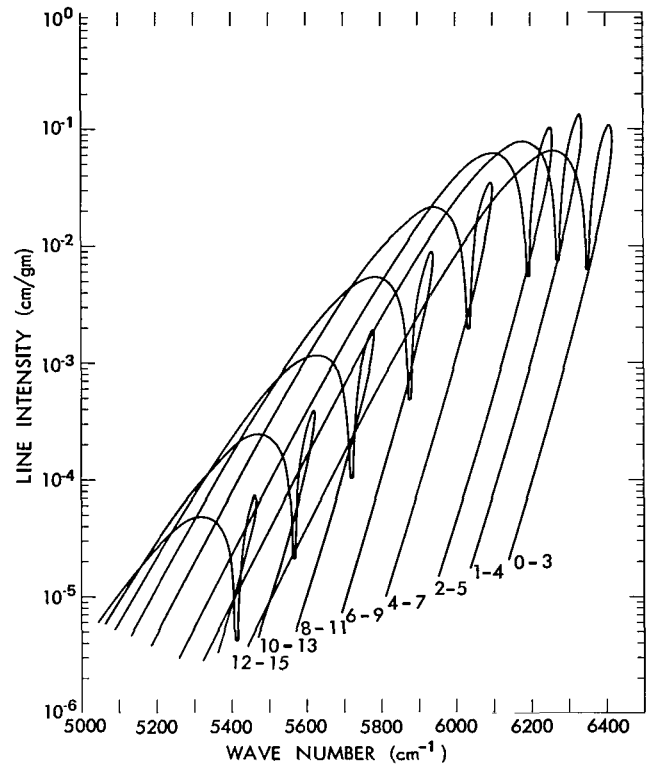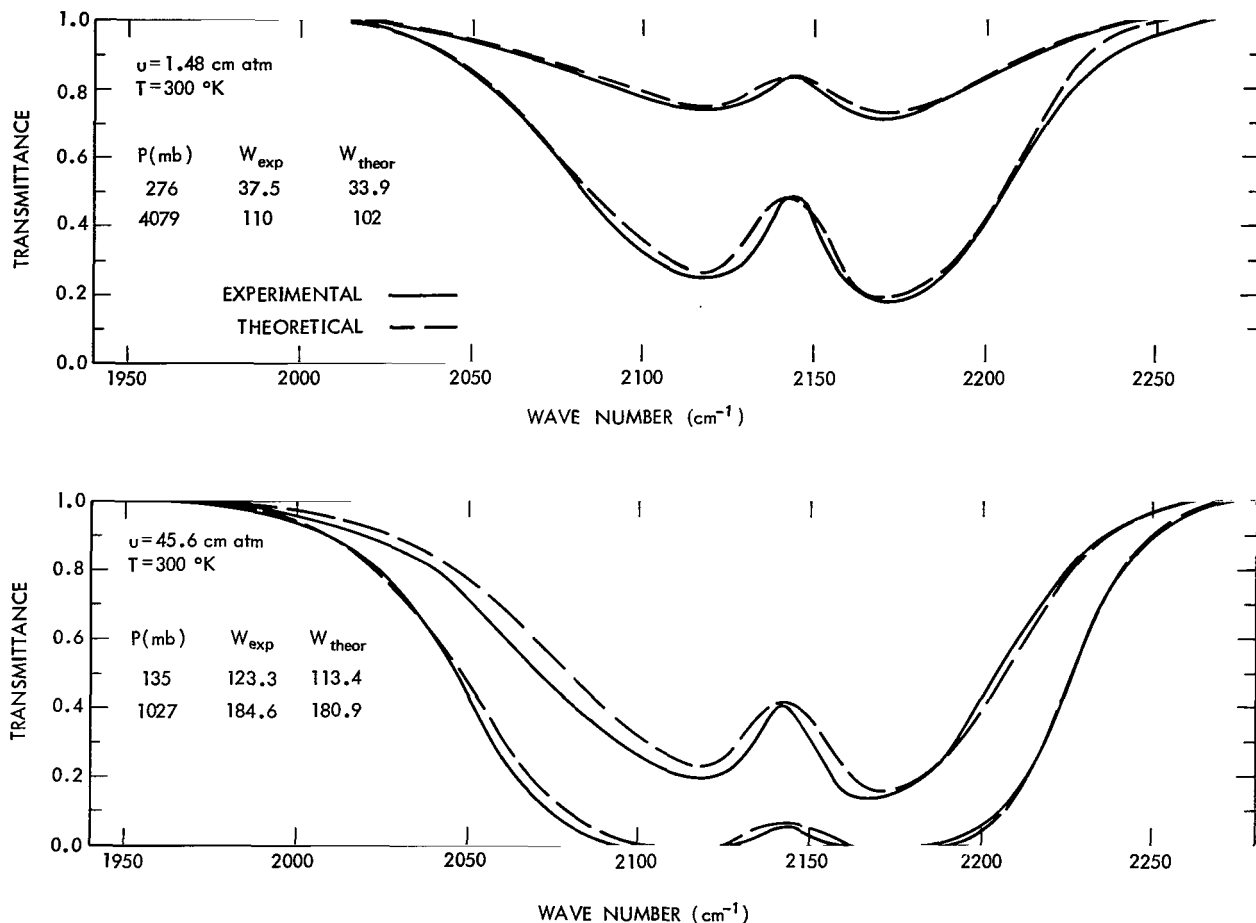
Figure 7—Comparison of theoretical absorption curves and total band absorption with experimental data (Burch, Gryvnak, Singleton, France, and Williams, 1962) for the fundamental band.

harmonic-oscillator/rigid-rotator model by Breeze, Ferriso, Ludwig, and Malkmus (1965). The solid and dashed curves are normalized at 273°K. Deviations of the solid and dashed curves at the higher temperatures probably result from anharmonicity and vibration-rotation interaction. Breeze and Ferriso (1965) have shown that the relative experimental temperature dependence of the fundamental and first-overtone CO bands also agrees with the relative theoretical temperature dependence for the range 2500 to 5000°K. Thus, indirectly, the computed band intensities of this investigation have the correct relative temperature dependence.

Comparison of the theoretical and experimental absorption data for CO indicates that the CO molecular parameters computed in this investigation predict CO absorption within 10 to 20 percent at the elevated temperatures. Improvement of molecular-parameter accuracy depends on more complete knowledge of the dipole moment for high values of internuclear separation and of the collisional line shape for foreign-broadened gases. In addition, more accurate experimental absorption data are needed at the elevated temperatures.
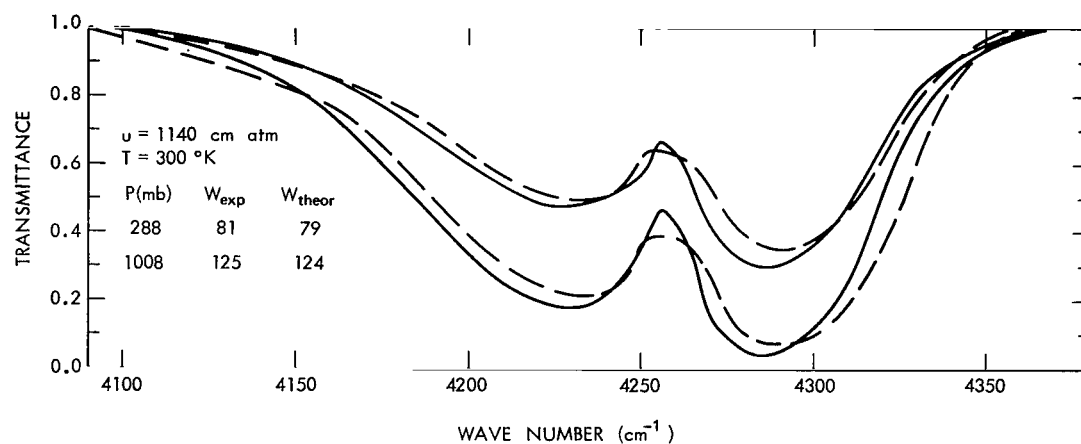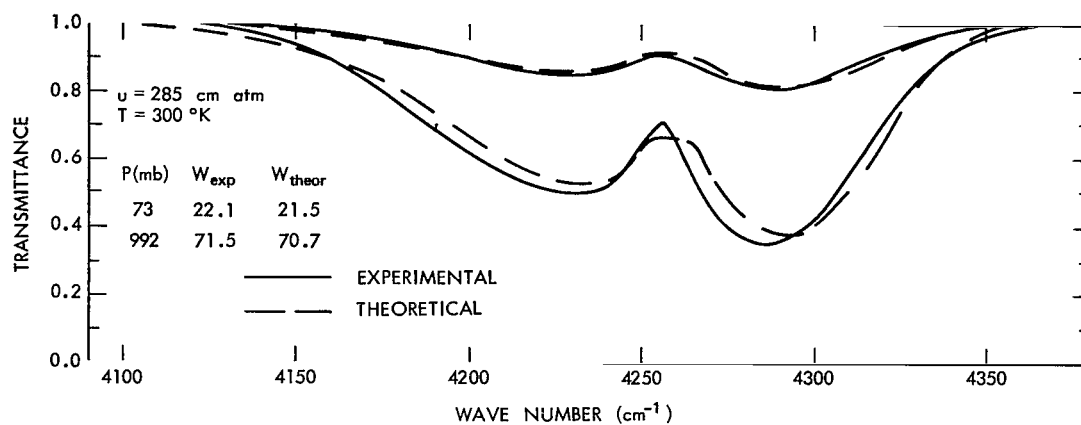
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Figure 8—Comparison of theoretical absorption curves and total band absorption with experimental data (Burch, Gryvnak, Singleton, France, and Williams, 1962) for the first-overtone band.

Table 2

Comparison of Theoretical and Experimental (Abu-Romia and Tien, 1966)
Total Band Absorption for CO Fundamental Band at 1500°K.

u_{1500} (cm atm)	u_{273} (cm atm)	P (atm)	W_{exp} (cm^{-1})	$W_{theo.}$ (cm^{-1})
5	0.9	1.0	40.0	62.0
10	1.8	2.0	117.0	115.0
15	2.7	3.0	190.0	163.0
20.0	3.6	1.0	121.0	125.3
40.0	7.3	2.0	236.0	216.7
60.0	10.9	3.0	306.0	280.0

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COMPARISON OF EXACT, APPROXIMATE $S_T^m/\Delta \nu$, AND QUASI-RANDOM BAND MODEL MEAN ABSORPTION COEFFICIENTS

Exact Mean Absorption Coefficient

The straight mean absorption coefficient was evaluated by direct integration for spectral intervals of 0.1, 1.0, and 5 cm^{-1}, as shown in Figures 10, 11, and 12 respectively. Three cases have been chosen to represent late-type atmospheres:

(1) T = 2500°K, P = 0.0 atm, ξ_t = 0.0 km/ sec, Doppler

(2) T = 2500°K, P = 2.0 atm, ξ_t = 0.0 km/ sec, Collisional-Doppler

(3) T = 2500°K, P = 0.0 atm, ξ_t = 10 km/ sec, Doppler-Turbulent

For case 2, the Benedict modification of the Lorentz line shape was used. Test computations with the Lorentz line shape agreed to within 1 percent of the Benedict modification in the band center where the wing contribution is very small. In regions where the wing contribution is an appreciable fraction of the total absorption coefficient, such as the region short of 1700 cm^{-1} and the region past the 0 → 1 band head, the Lorentz contribution may be 10 to 100 times larger than the Benedict modification.

Figure 9—Comparison of band intensities as function of temperature. The solid lines were obtained by summation of the individual vibration–rotation line intensities computed in this investigation. The dashed lines represent the theoretical temperature dependence computed for a harmonic–oscillator/rigid–rotation model (Breeze, Ferriso, Ludwig, and Malkmus, 1965).

The present computation scheme establishes approximately 175,000 wave-number mesh points within the fundamental CO band for evaluation of monochromatic-absorption coefficient. The running time for one case is approximately 90 to 120 minutes on an IBM 360. The present direct-integration program can be optimized considerably for computations at conditions typical of late-type atmospheres; say, by approximating the mixed-line shape (rather than using a general subroutine) and reducing the number of subintervals for a given line. These modifications would probably more than halve the computing time.

Figure 10 plots the mean absorption coefficient, for $\Delta \nu$ = 0.1 cm^{-1}, at every 0.1 cm^{-1} for the region near the center of the R branch. At this resolution, the increasing wing contribution is evident (as turbulent or collisional broadening is considered), with the absorption coefficient varying by orders of magnitude between the various cases. Figure 11 plots the mean absorption coefficient,
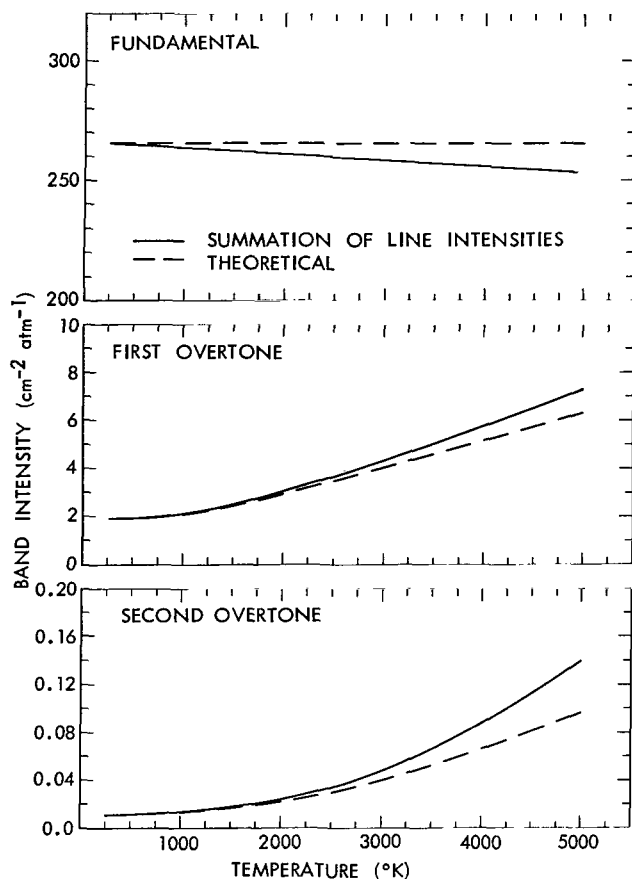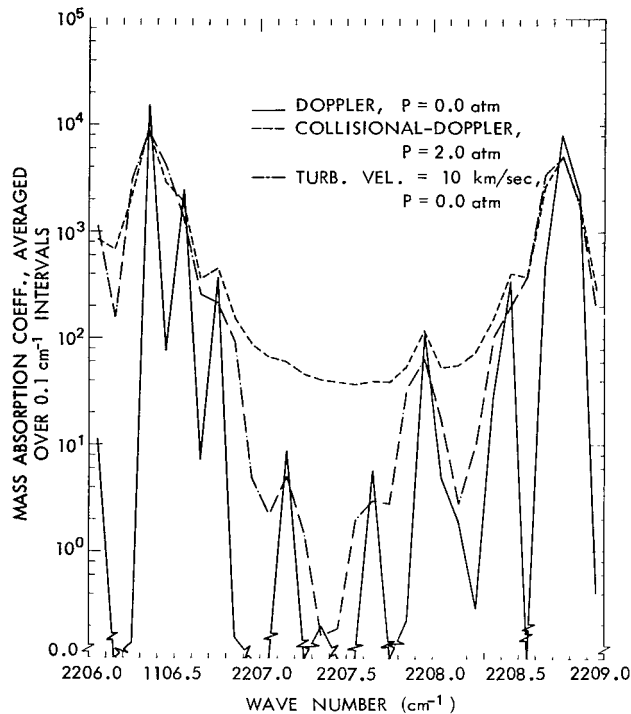
Figure 10—Straight mean mass absorption coefficient for 0.1-cm^{-1} intervals for a portion of the CO fundamental band at 2500°K. The mean absorption coefficient was obtained by direct integration.

Figure 11—Straight mean mass absorption coefficient for 1.0-cm^{-1} intervals for a portion of the CO fundamental band at 2500°K. The mean absorption coefficient was obtained by direct integration.

for $\Delta\nu = 1.0$ cm^{-1}, at every 0.5 cm^{-1}. Only the cases for pure Doppler and pure collisional broadening are indicated. Absorption-coefficient variations due to turbulent broadening are of the same order as the variations due to pure collisional broadening. Figure 12 plots the mean absorption coefficient, for $\Delta\nu = 5$ cm^{-1}, at every 5 cm^{-1}; note that the absorption coefficient is on a linear scale. Only case 1 (pure Doppler broadening) is shown, as the absorption coefficient for the other two cases agrees with this to within 5 percent. It is evident that as the spectral interval width is increased (Figures 10 to 12) the mean absorption coefficient approaches the limiting condition of $S_T^m/\Delta\nu$. Thus pressure effects connected with the collisional line shape may be neglected for
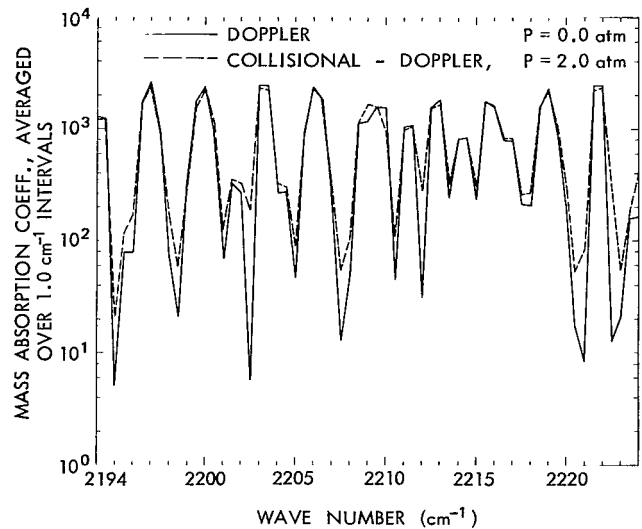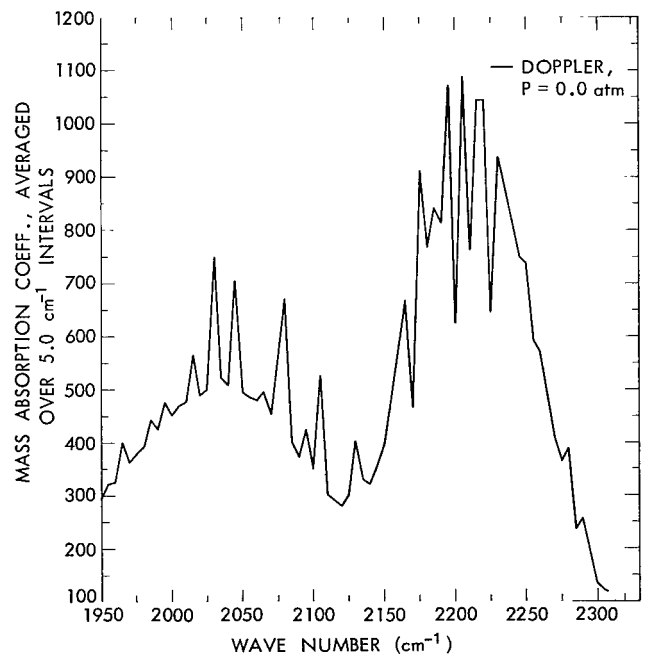

Figure 12—Straight mean mass absorption coefficient for 5-cm^{-1} intervals for a portion of the CO fundamental band at 2500°K. The mean absorption coefficient was obtained by direct integration.

CO even for pressures of several atmospheres. The negligible pressure effect can be attributed mainly to the small CO-H$_2$ collision cross section. For larger collision cross section, pressure effects would presumably have more effect on the mean absorption coefficient at resolutions comparable to $\Delta\nu = 5$ cm^{-1}. Turbulent velocity effects, also, are negligible for $\Delta\nu > 5$ cm^{-1}.

Quasi-Random Band Model Mean Absorption Coefficient

The smallest subinterval spectral width chosen for the quasi-random model was $\epsilon = 5$ cm^{-1}. Comparison of the quasi-random mean absorption coefficient with the mean obtained from direct integration for the CO fundamental indicates that agreement is generally within 5 percent, with occasional disagreement up to 10 percent for each of the three cases. At $\Delta\nu = 10$ cm^{-1}, the agreement is generally within 1 percent, with occasional disagreement up to 5 to 10 percent. The computing time for one case, using the quasi-random model, is 1 to 2 minutes on the IBM 360. As illustrated in the previous section for typical late type stellar atmosphere conditions, wing effects are negligible even for $\Delta\nu = 5$ cm^{-1}. Under these conditions the simpler $S_T^m/\Delta\nu$ approximation can be used and thus the quasi-random model will be discussed no further in this investigation.

Approximate $S_T^m/\Delta\nu$ Mean Absorption Coefficient

The approximate mean absorption coefficient $S_T^m/\Delta\nu$ has been determined for the fundamental band of CO at temperatures of 1000, 2500, and 3500°K and is shown in Figure 13 for $\Delta\nu = 100$ cm^{-1}. The dashed portions of the curves indicate the region beyond the $0 \rightarrow 1$ band head, where $S_T^m/\Delta\nu$ is only approximate. Comparison of $S_T^m/\Delta\nu$ with the mean absorption coefficient determined by direct integration indicates agreement with each of the three cases within 1 percent, except for the region short of 1600 cm^{-1} where differences of 5 to 10 percent occur. Because line wing effects are negligible, the dashed portions of the curves in Figure 13 do accurately represent the mean absorption coefficient. Figures 14 and 15 show values of $S_T^m/\Delta\nu$ for 100 cm^{-1} for the first- and second-overtone bands at 1000, 2500, and 3500°K. Even at this low resolution, band heads are apparent in both overtones.
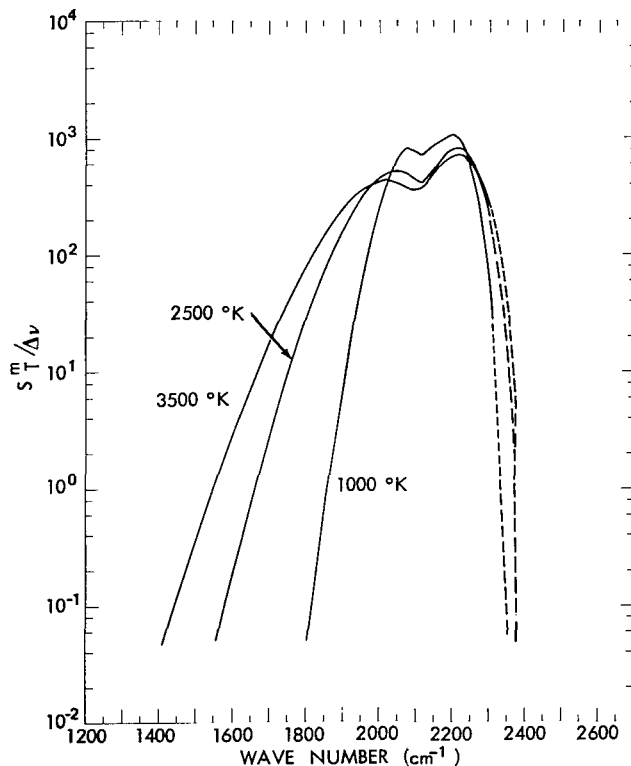

Figure 13—Straight mean mass absorption coefficient for 100-cm^{-1} intervals for the CO fundamental band at 1000, 2500, and 3500°K. The mean absorption coefficient is based on the $S_T^m/\Delta\nu$ approximation. The dashed portions of the curves indicate the region beyond $0 \rightarrow 1$ band head, where $S_T^m/\Delta\nu$ is only approximate.
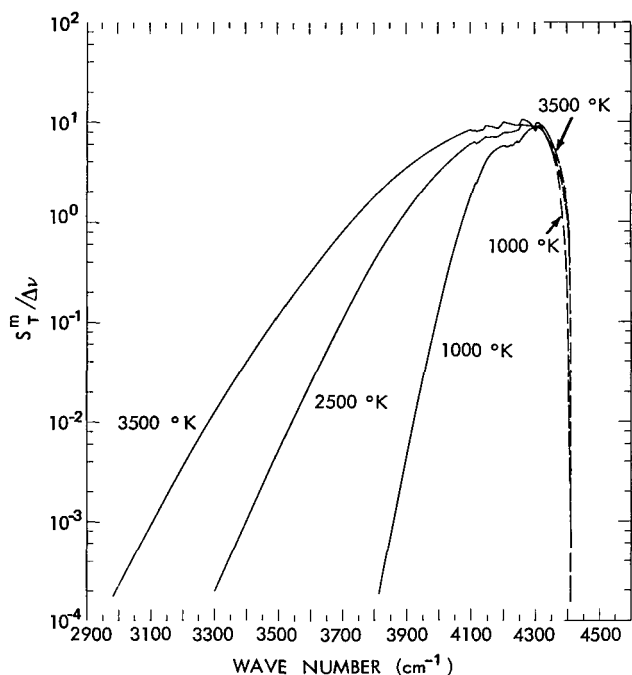
Figure 14—Straight mean mass absorption coefficient for 100-cm^{-1} intervals for the CO first-overtone band at 1000, 2500, and 3500°K. The mean absorption coefficient is based on the $S_T^m/\Delta\nu$ approximation. The dashed portions of the curves indicate the region beyond $0 \to 1$ band head, where $S_T^m/\Delta\nu$ is only approximate.
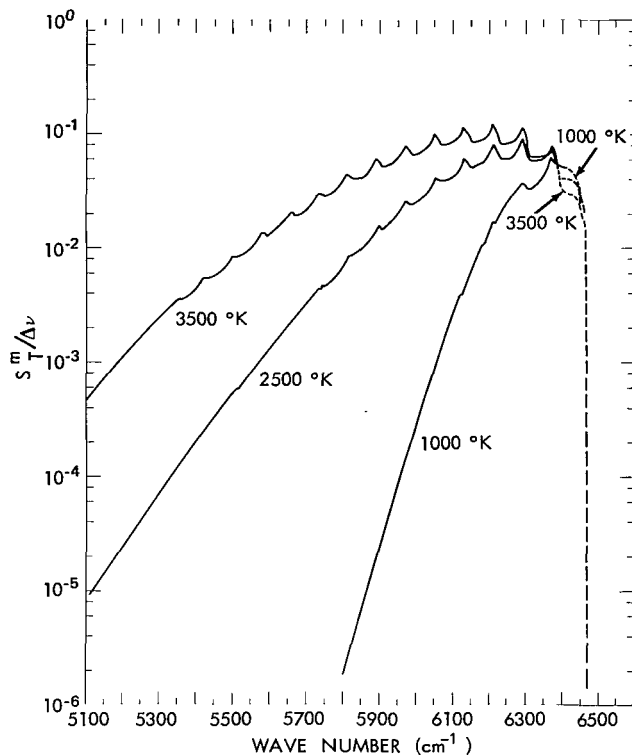

Figure 15—Straight mean mass absorption coefficient for 100-cm^{-1} intervals for the CO second-overtone band at 1000, 2500, and 3500°K. The mean absorption coefficient is based on the $S_T^m/\Delta\nu$ approximation. The dashed portions of the curves indicate the region beyond $0 \to 1$ band head, where $S_T^m/\Delta\nu$ is only approximate.

CONCLUSIONS

The main results and conclusions of this investigation are:

(1) From an anharmonic vibrating-rotator molecular model, the molecular absorption line parameters have been derived for $C^{12}O^{16}$ and $C^{13}O^{16}$. The line positions, line intensities, and collisional-line half-widths have been computed for temperatures from 175 to 3500°K.

(2) The CO straight mean mass absorption coefficient has been evaluated, by direct integration techniques, by the approximation $S_T^m/\Delta\nu$, and by the quasi-random band model. The direct integration technique allows a check on the accuracy of the $S_T^m/\Delta\nu$ approximation and of the quasi-random band model.

(3) The quasi-random model is more accurate than the $S_T^m/\Delta\nu$ approximation when the effects of line wings must be considered. For late type atmospheres, wing effects were not important for pressures up to two atmospheres or turbulent velocities up to 10 km/sec. The $S_T^m/\Delta\nu$ approximation represents CO absorption very accurately in late type atmospheres for spectral intervals larger than 5 cm^{-1}.

(4) The parameter $S_T^m / \Delta \nu$ has been determined for the CO vibration-rotation bands for temperatures of 1000, 2500, and 3500°K at spectral intervals of 100 cm^{-1}.

Further investigations will extend similar calculations to other molecular absorption bands. Above 3000°K, electronic spectra should be important; in the range of 1000°K for M-type stars, polyatomic molecules such as CH_4, NH_3, and HCN should be considered. For carbon-rich stars, the molecular absorption of CH_4 and HCN is important.

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. A. Bell for his advice and guidance throughout the course of this investigation. The author is also indebted to L. A. Young, who provided the CO dipole moment matrix elements, and to Mr. Frank Bartko and Dr. Barney Conrath for helpful discussions on the contents of this paper.

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(See also References for Appendix A)

Appendix A

Statistical Band Model

The statistical model (Goody, 1952; Plass, 1958) considers a spectral interval of width $\Delta\nu$ containing n total lines with each individual line having intensity S_i, half-width α_i and center wave number ν_i occurring within $\Delta\nu$. Let $N(\nu_1 \cdots \nu_n)\, d\nu_1 \cdots d\nu_n$ represent the probability that the ith line occurs between ν_i and $\nu_i + d\nu_i$, $P(S_i)\, dS_i$ the probability that the ith line has an intensity between S_i and $S_i + dS_i$, and $P'(\alpha_i \cdots \alpha_n)$ the probability that the ith line has a half-width between α_i and $\alpha_i + d\alpha_i$. Assuming that $\nu_1 \cdots \nu_n$, $\alpha_1 \cdots \alpha_n$, $S_i \cdots S_n$ are mutually independent, the probability of finding the set of n lines with $\nu_1 \cdots \nu_n$, $\alpha_1 \cdots \alpha_n$, $S_1 \cdots S_n$ is

$$N(\nu_1 \cdots \nu_n)\, P(S_1 \cdots S_n)\, P'(\alpha_1 \cdots \alpha_n)\, d\nu_1 \cdots d\nu_n\, dS_1 \cdots dS_n\, d\alpha_1 \cdots d\alpha_n \,. \tag{A1}$$

The average absorption coefficient $\bar{k}(\nu)$ at ν is found by averaging $k(\nu)$ over the probability distribution of the set of n lines

$$\bar{k}(\nu) = \frac{\displaystyle\int_0^\infty \cdots \int_0^\infty \int_0^\infty \cdots \int_0^\infty \int_{\Delta\nu} \cdots \int_{\Delta\nu} k(\nu) N(\nu_1 \cdots \nu_n) P(S_1 \cdots S_n) P'(\alpha_1 \cdots \alpha_n)\, d\nu_1 \cdots d\nu_n dS_1 \cdots dS_n d\alpha_1 \cdots d\alpha_n}{\displaystyle\int_0^\infty \cdots \int_0^\infty \int_0^\infty \cdots \int_0^\infty \int_{\Delta\nu} \cdots \int_{\Delta\nu} N(\nu_1 \cdots \nu_n) P(S_1 \cdots S_n) P'(\alpha_1 \cdots \alpha_n)\, d\nu_1 \cdots d\nu_n dS_1 \cdots dS_n d\alpha_1 \cdots d\alpha_n} \tag{A2}$$

The absorption coefficient $k(\nu)$ is given by

$$k(\nu) = \sum_{i=1}^{n} S_i\, b(\nu - \nu_i, \alpha_i) \,, \tag{A3}$$

where S_i is the line intensity subject to the normalization condition

$$\int_{-\infty}^{+\infty} k_i(\nu)\, d\nu = S_i \,, \tag{A4}$$

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and $b\left(\nu - \nu_i, a_i\right)$ is the relative line shape. Assuming that the line positions are distributed at random in $\Delta\nu$ $\left(N\left(\nu_i\right) = \text{constant}\right)$, $\bar{k}(\nu)$ can be written:

$$\bar{k}(\nu) = \frac{\displaystyle\int_0^\infty \int_0^\infty \int_{\Delta\nu} n\, S_i\, b\left(\nu - \nu_i, a_i\right)\, P'\left(a_i\right)\, P\left(S_i\right)\, d\nu_i\, dS_i\, da_i}{\displaystyle\int_0^\infty \int_0^\infty \int_{\Delta\nu} P'\left(a_i\right)\, P\left(S_i\right)\, d\nu_i\, dS_i\, da_i}\ . \tag{A5}$$

For example, consider the case where all the spectral lines are of equal intensity S and equal half-width a. Then

$$\bar{k}(\nu) = \frac{n \displaystyle\int_{\Delta\nu} S\, b\left(\nu - \nu_i, a\right)\, d\nu_i}{\Delta\nu} = n\, \bar{k}'\,(\nu)\ , \tag{A6}$$

where

$$\bar{k}'\,(\nu) = \frac{S \displaystyle\int_{\Delta\nu} b\left(\nu - \nu_i, a\right)\, d\nu_i}{\Delta\nu}\ . \tag{A7}$$

The parameter $\bar{k}'\,(\nu)$ represents the average absorption coefficient at ν—averaged with respect to center wave number—for a line of intensity S and half-width a whose center wave number ν_i occurs at random in $\Delta\nu$. A second example is given by

$$P(S) = S_0^{-1} \exp\left(-\frac{S}{S_0}\right), \tag{A8}$$

$$P'(a) = \text{constant}, \tag{A9}$$

for which

$$\bar{k}(\nu) = \frac{n\, S_0 \displaystyle\int_{\Delta\nu} b\left(\nu - \nu_i, a\right)\, d\nu_i}{\Delta\nu}\ . \tag{A10}$$

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