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SPECTROSCOPIC BAND MODELS FOR DIAGNOSTICS

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The University of Tennessee Space Institute

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NOTICES

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FOREWORD

The work reported herein was sponsored by Headquarters, Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 65701F, Project 4344, Task 37.

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This technical report has been reviewed and is approved.

Vincent A. Rocco Captain, USAF Research and Development Division Directorate of Technology	Harry L. Maynard Colonel, USAF Director of Technology

ABSTRACT

A major phase of this report involved a compilation of information and critical evaluation of that information as it pertains to the diagnostic problem. The information is gathered together in a bibliography of books, reports, and published articles and is discussed in Section II. The investigation of the feasibility of applying the theory of band models to the diagnostic problem of determining temperatures and concentrations has led to the development of a mathematical inversion technique based on low-resolution emission-absorption spectroscopy. Band model theory and much of its literature is summarized in this report. The inversion of the Curtis-Godson approximation of a statistical band model with Lorentz lines of constant width is presented in detail. Experiments were performed to verify the technique but are inconclusive at this time.

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SECTION I
INTRODUCTION

Intensive efforts have been expended in developing non-interference diagnostic methods based on spectroscopy for determining direct in situ quantitative values of the chemical and thermodynamic properties of radiating gases.

The radiant energy emitted by a hot gas is the integral of contributions from all the spatial regions within the volume of the gas and all the spectral intervals over which it is active. Spatial integration is usually possible but spectral integration often is not. To predict accurately the radiation from hot gases, the spectral absorption coefficient, k_ν, as a function of frequency must be known. And so despite the efforts, there still exist many experimental situations in which it is not possible to obtain sufficiently well resolved spectra to determine the information desired. Furthermore even in those situations in which the resolution is sufficient to define the individual lines of a vibration-rotation band k_ν is a rapidly varying function of frequency and the computational task may become quite formidable and expensive when integrating over frequency even for a homogeneous gas of simple molecules and consequent simple spectrum. Both for interpreting measurements and computing numerical problems, it has therefore proved desirable to develop techniques for averaging over fine structure in the spectrum. The averaging process is intended to smooth out the lines without distorting the band contour and is thus referred to as a "band model". Band models provide the averaging processes by substituting for the true spectrum an infinite array of spectral lines of uniform statistical properties. Four types of band models are particularly useful and will be briefly discussed. These are the Elsasser model, the statistical model, the random Elsasser model, and the Quasi-random model.

These band models were designed to allow the prediction of the infrared spectral intensity of an homogensous gas when temperatures and pressures were known. The extent to which the averaging process could be applied to infrared measurements of inhomogeneous gases with gradients of temperature pressures and concentrations required investigation. The Curtis-Godson approximation provides a technique for calculating the radiance and transmittance of hot inhomogeneous gases by determining the necessary spectral parameters solely from homogeneous gas data. In the Curtis-Godson approximation the transmittance of the inhomogeneous path is obtained by substituting a hypothetical homogeneous path with the same transmittance. The homogeneous path can then be treated by established band model methods.

The objective of the present program was fourfold:

1. to acquire an understanding of band model theory and to present the information and and development of band model theory;
2. to study the applications of band model theory to various physical situations;
3. to examine the limitations and validity of band models as an averaging process for determining the emissivity and absorptivity of finite spectral bands containing many unresolved lines of water vapor and carbon dioxide in a radiating inhomogeneous gas; and
4. to determine the extent to which the accumulated knowledge of experimental techniques and spectral parameters of previous investigators could be used to develop a diagnostic method. That is a method based on band model theory for evaluating the temperatures and partial pressures of hot inhomogeneous gases from measured spectral intensities.

The present report is intended to be first of all an introductory handbook of band model theory and second a description of a band model diagnostic technique. Much of the pertinent literature was searched and reviewed. Information was compiled and evaluated and is presented as a guide to the literature in Section II. An exposition of the theory of band models beginning with the single spectral line and extending the development through the Curtis-Godson approximation to inhomogeneous gases is set forth in Section III. The extensive literature search led to a restricting and defining of the diagnostic problem and subsequently to the development of a mathematical inversion technique based on low resolution emission-absorption spectroscopy for determining temperatures and partial pressures of infrared active species. This is treated in Section IV. Section V describes the experiment designed to test the consistency and validity of the computational method.

The objective of the experiment was to seek spectral emission and absorption data at 2.7μ in the radiation spectrum of hot water vapor produced in flames. These experiments to provide the required line-of-sight radiance and transmittance data were carried out by UTSI personnel in cooperation with the ETF Special Projects Group utilizing the special burners and spectrometers available at AEDC. Section VI contains the concluding remarks.

SECTION II
LITERATURE GUIDE

A major phase of this report involved a compilation of information and critical evaluation as it pertains to the diagnostic problem. This information is gathered together in the bibliography and will be commented on in this section of the report and referred to at various points throughout the report. The bibilography is a collection of books, reports, and published articles which have been gathered together for study and evaluation. This subject is weighted down by a huge unpublished literature in the form of contract reports, such as this, which do not become readily available to the general scientific community. The present bibliography contains such reports because they sometimes contain information not available elsewhere, but the emphasis where possible is placed on books and articles appearing in the open literature. The present collection certainly does not exhaust the subject even in the English language and hardly touches on the foreign literature and yet it is believed to represent much of the major effort in this area. Although many approaches to a literature commentary suggest themselves, the present commentary will for the most part be directed to the efforts of groups of researchers working and reporting over a period of several years because that's how much of the work has been performed. However, the accomplishments of individuals often laid the groundwork.

The first physically satisfying band model was developed by W. M. Elsasser, in 1938 (Ref. 1) and in 1942 (Ref. 2) to aid in predicting the transmission of infrared radiation through the atmosphere. The principle of the random or statistical model was first published by R. M. Goody in 1952 (Ref. 3). These two models provide a starting point for understanding band model theory and remain basic to the study of many molecules.

The fundamental physical principles of band model theory are most completely developed in the very excellent book "Atmospheric Radiation" by R. M. Goody (Ref. 4). This book will be most satisfying to those who have some background in radiative heat transfer and spectroscopy although both of these areas are developed from basic concepts in the book.

The first four chapters are particularly informative and pertinent to radiation theory in general and band model theory in particular. Each chapter is capped off with a most complete bibliography wherein many references are accompanied by remarks suggesting their usefulness. Many excellent diagrams and graphs enhance the exposition in the text. There are fourteen appendices several of which are very useful tables.

A second book which provides considerable background in the theory and techniques of infrared radiation and the application of band models to radiative transfer problems is the Handbook of Military Infrared Technology (Ref. 5). As the title implies the book is exhaustive in coverage, containing hundreds of graphs and tables and references.

A very useful state-of-the-art report is "Band-Model Methods for Computing Atmospheric Slant-Path Molecular Absorption" written by David Anding (Ref. 6). This report contains a summary development of the band models together with many tables and graphs comparing the usefulness of the band models when applied to the constituents of the atmosphere. The report by Rochelle (Ref. 7) is similar in development although it emphasises the application to thermal radiation from rocket exhausts.

The theory of band models is based on parameters involved in describing individual spectral lines. The development of spectral line theory is described in many places but the present development is referred to the two papers by Benedict Herman, Moore and Silverman (Refs. 8 and 9) and the application by Mason and Nielson (Ref. 10). In extending the band model theories from homogeneous to inhomogeneous gases the contribution of Curtis (Ref. 11) and Godson (Ref. 12) are invaluable. These twelve references, together with the reported work of G. N. Plass provided the background from which the section of this report entitled Band Model Theory was written.

One need not look far into the literature before it becomes evident that band model theory was developed for and applied to radiative transfer through the atmosphere. A foremost worker in this area has been Gilbert N. Plass whose articles have spanned nearly twenty years (Refs. 13 through 20). Much of his effort has been devoted to refining band model theory and examining the criteria for the applicability and limitations of the different models. His reported work is sufficiently general that it is quite as pertinent to combustion problems as to atmospheric transmission problems. Plass proposed three approximations that can be used to give relatively simple analytical expressions for the absorptance predicted by the various band models for virtually any range of pressure and concentration of absorbing gas. These will be discussed in detail later in this report.

Plass also describes laboratory studies appropriate to the selection of the correct band and the correct approximation for the particular situation of interest.

A very active experimental group orginating at Ohio State consisting of D. E. Burch, D. Williams, D. Gryvnak, and R. R. Patty have published many papers on the results of extensive laboratory measurements of the total absorptance of the major near infrared absorption bands and lines of gases present in planetary atmospheres (Refs. 21 through 33). These gases, in particular carbon monoxide, carbon dioxide, and water vapor are often the gases of most interest in combustion phenomena and so the research of this group is of considerable interest to this report. In these experiments the total absorptance was measured as functions of absorber concentration and total pressure providing empirical relationships for a considerable range of these variables. Of particular import to band model theory is that Burch and Williams (Refs. 28) examine the possibility of experimental realization of the conditions leading to the Plass approximations and conclude that: (1) laboratory results give satisfactory approaches to the weak line approximation but not to the strong line approximation; and (2) it may often be necessary to introduce the results of high resolution studies to properly select appropriate band models.

There have been several groups active in the application of band model techniques to the problem of radiative transfer in rocket exhaust gases. Much of this work was performed under contract to the National Aeronautics and Space Administration. A summary and cross section of that work appears in a publication entitled "Molecular Radiation and Its Application to Diagnostic Techniques" edited by R. Goulard, Purdue University (Ref. 34). This is the record of the Proceedings of a Specialists Conference held at the Marshall Space Flight Center Huntsville, Alabama, October 5-6, 1967. Two research groups who were very much involved in the NASA effort and whose work provides the beginning point for the present UTSI-AEDC effort were the General Dynamics Convair Group and the Warner and Swasey Group.

The General Dynamics Convair Group consisted of C. C. Ferriso, (deceased), C. B. Ludwig, J. A. L. Thomson, and W. Malkmus. Several reports and journal articles (Refs. 35 through 51) document their research, which centered on the measurement of the absorption coefficients and fine structure parameters of water vapor and carbon dioxide at temperatures between 1200° and 3000°K. These data were then incorporated into a practical analytic procedure which could be used for the evaluation of the radiative base heating of rocket vehicles. Their experimental setup was quite unique providing a volume of high temperature water vapor above the combustion zone of a long three inch wide flat flame burner. Emission and absorption measurements were made with a path length of twenty feet. Also, nonisothermal measurements were made with four five-foot sections at different temperatures to test the nonisothermal radiance calculation procedure which was a modified Curtis-Godson method worked out independently by the General Dynamics Convair Group and the Warner and Swasey Group. This calculation was the basis for the computer program used by the NASA Marshall Space Flight Center to calculate the radiant heating of a rocket base. The most important consequence of the General Dynamics Program has been to generate tables of water vapor absorption coefficients covering the spectral region 50 to 9300 cm^{-1} and the temperature range 300° to 3000°K and tables of the reciprocal of the average line spacing, d, covering the interval 1150 to

9300 cm^{-1} in the temperature range from 600° to 3000°K.

William F. Herget, Rocketdyne Division, North American Rockwell Corporation, whose work (Refs. 52 through 55) is discussed later in the report, contributed smeared high resolution water vapor data to the generation of the above tables. Fredrick S. Simmons, Willow Run Laboratories, The University of Michigan has also been involved in the NASA effort to study the application of band models to nonisothermal radiating gases (Refs. 56 through 59) and provided comparison data for an independent check to the General Dynamics data for temperatures greater than 1000°K.

The Warner and Swasey Group composed of Harold Babrov, Richard Tourin, and Burton Krakow have made many contributions to the solution of the problem of utilizing spectroscopic techniques for the study of the radiant properties of hot flowing gases (Refs. 60 through 75). It is this group's development of the modified Curtis-Godson approximation utilizing a random band model with Lorentz lines of constant line strength and line width which provides the foundation for the determination of temperature and partial pressure profiles by the process described in this report.

There is also considerable interest in the spectral radiative properties of carbon dioxide as indicated by the work of Malkmus in the General Dynamics Group (Ref. 49 and 50). Among others who have been interested in developing useful band model techniques to molcules of the atmosphere and combustion are Oppenheim and Ben-Aryeh (Ref. 76). They have been particularly concerned with low resolution measurements to determine band model parameters for spectral emissivity calculations of the 4.3μ band of CO_2 (Ref. 77 and 78).Ellis and Schurin (Ref. 79) have also made integrated intensity measurements on CO_2 bands. The near infrared is not the only spectral region for which total band absorptances have been measured and for which band model calculations have been performed. The 15μ CO_2 band is of considerable interest Refs. (80 through 84). It was agreed that this band would not be investigated for this project because instrumentation is not available.

There are two reference monographs intended solely to provide fundamental information on the properties of the water vapor bands at 2.7μ (Ref. 85) and on the 1.9μ and 6.3μ water vapor bands (Ref. 86) in terms of line absorptions and integrated transmittance at any frequency for infinite resolution. Although the line parameters listed herein are vital for the interpretation of high resolution transmittance measurements they play no role in the work of the present report which is concerned only with low resolution band emission-absorption measurements.

Tables of line parameters such as the above Monographs depend for their development upon high resolution spectroscopic data. Considerable effort along these lines has been expended in the past few years by several capable researchers whose efforts are reported in the References 73 and 74 and 85 through 93. Although there was initial consideration in the present project to undertake high resolution experiments utilizing an instrument such as the Ohio State spectrometer for the purpose of preparing an atlas of heated water vapor, it was later recognized that such information was readily available in the open literature. Such high resolution spectra were to be used in selecting the most appropriate spectral region for further investigation and for ascertaining the validity of the various band models for the chosen spectral region. These things were accomplished on the basis of other considerations such as instrumentation availability, difficulty and expense of designing data acquisition systems for the test cell environment, and the relative ease of utilizing low resolution emission-absorption data for band model calculations. This appears to be a reasonable decision for the present effort but it is not intended to reject the usefulness and necessity of high resolution measurements for similar projects in the future.

The technique of total band absorptance and emittance measurements and the utilization of band models to predict radiance and transmittance are not limited to H_2O and CO_2 but have been applied to such molecules as $HC\ell$ (Ref. 94), CO (Refs. 95 and 96), and N_2O (Refs. 97 and 98). The Elsasser strong line approximation was found suitable for both CO and N_2O.

Theoretical examinations of the validity of such concepts as Beer's Law (Ref. 99), the Doppler Analog of the Elsasser Model, (Ref. 100), the Voight line profile (Ref. 101 and 102), the net interval for calculating spectra (Ref. 103), and the instrumental effects of slit functions (Ref. 104), are all important and continuing investigations supporting the efforts of experimentalist to acquire meaningful data and hopefully helping everyone to a better understanding of the physical processes taking place in radiating-absorbing gases.

The literature would not be complete without at least one comparision between a band model and line by line calculations. Such a comparison has been reported by A. Goldman and T. G. Kyle (Ref. 105)for the statistical band model and line by line calculation with application to the 9.6μ ozone and the 2.7μ water vapor bands. Their conclusion was that the agreement between the two types of calculation is much better than the agreement of either of them with experiment. Thus a refinement of the line parameters (high resolution data) is needed in order to obtain better agreement between the calculations and the experimental results. In general, however, the transmittance averaged over intervals greater than 10 cm^{-1} for the 2.7μ H_2O band is represented very well by the statistical model. This supports and correlates with the effort of the present project.

SECTION III
BAND MODEL THEORY

The radiant energy emitted by a hot gas is the integral of contributions from all the spatial regions within the volume of the gas and all the spectral intervals over which it is active. Spatial integration by numerical methods is feasible because spatial variations are usually gradual enough to allow utilization of large intervals. The spectral integration, however, is often not possible. To predict accurately the radiation from hot gases, the spectral absorption coefficient, k_υ, as a function of frequency must be known. In molecular band radiation k_υ is a rapidly varying function of frequency, and it is essential for numerical integration that k_υ be constant over each frequency interval. In many situations the frequency interval is so small that it has been desirable to develop techniques for averaging over spectral fine structure. Band models provide the averaging processes by substituting for the true spectrum an infinite array of spectral lines of uniform statistical properties. Four types of band models are particularly useful and will be briefly discussed: 1) The Elsasser model, a band composed of identical uniformly spaced lines; 2) The statistical model, a band composed of spectral lines with arbitrary intensity distribution and with random spacing between the lines; 3) The random Elsasser model, a band composed of several groups of lines, each of which forms an Elsasser band, but the groups are superposed with random spacing; and 4) The quasi-random model, a band composed of spectral lines whose intensities and variation of spacing from line to line are accurately simulated.

The band models lend themselves to further approximations in that there are three limits in which asymptotic forms of the equations defining each model can be obtained. These are: 1) The weak-line approximation, 2) The strong-line approximation, and 3) The non-overlapping-line approximation.

Band models were designed for and are successfully applied to the calculation of radiation of homogeneous gases. In many cases, however, the hot gases are no longer homogeneous but have gradients of temperature, pressure, and concentration. The Curtis-Godson approximation provides a technique for calculating the radiance and transmittance of hot inhomogeneous gases by determining the necessary spectral parameters solely from homogeneous gas data. In the Curtis-Godson approximation the transmittance of the inhomogeneous path is obtained by substituting a hypothetical homogeneous path with the same transmittance. The homogeneous path can then be treated by established band model methods.

The Single Spectral Line

This may be thought of as the most simple band model. It is the situation in which the spectral lines are so narrow and far apart that there is effectively no overlapping of lines and each line can be treated as an entity. This situation will be discussed in detail in order to introduce concepts, define parameters, and discuss limitations that are fundamental to band model theory.

In view of the complicated conditions that are often present in a source of radiation it is more fruitful to discuss spectral lines in terms of absorption rather than emission since conditions inside an absorption cell can be kept relatively simple and controllable. If parallel light from a source emitting a continuous spectrum of intensity I^o_υ is sent through an absorption cell containing a monoatomic gas, the intensity of the transmitted light, I_υ, may show a frequency distribution similar to that of Figure 1. When this is the case the gas is said to possess an absorption line at the frequency υ_o. Note that the spectral line has a definite width or spread of frequencies around υ_o.

The absorption coefficient, k_υ, of the gas is defined by the Lambert-Beer relation

$$dI = -k_\upsilon I d\ell$$

which is the flux absorbed from a beam of radiation of frequency υ of unit cross section as it traverses a path length $d\ell$ through the gas. When ℓ is measured in centimeters, k_υ is expressed in reciprocal centimeters. The spectral transmittance, τ_ν, is defined as the ratio of the transmitted flux to the incident flux at frequency ν and may be written in terms of the absorption coefficient as

$$\tau_\nu = I_\nu / I^o_\nu = e^{-k_\nu \ell} \tag{1}$$

From this equation and Figure 1 we may obtain k_ν as a function of frequency

$$k_\nu = -\frac{1}{\ell} \ell n \; I_\nu / I^o_\nu \tag{2}$$

and plot it as in Figure 2. The halfwidth of the line, γ, is shown in Figure 2 and is defined as the total width of the absorption coefficient curve at the point where the absorption coefficient is one-half its maximum value. In general the absorption coefficient of a gas is given by an expression involving a function of the frequency ν, a definite value of k_{max}, and the halfwidth γ all of which depend on the nature of the molecules of the absorbing gas, their motion, and their interaction with one another or with foreign molecules.

The intensity of a single line can be measured in absorption by determining the integrated absorption, S, defined as the integral of the absorption coefficient,

$$S = \int_0^\infty k_\nu d\nu \tag{3}$$

which is simply the area under the absorption coefficient curve, usually given in units of cm^{-2}. In general Beer's law does not hold, i.e., the absorption is not proportional to concentration. However for gas at densities sufficiently low that the mechanism for absorption is not altered, the integrated absorption is directly proportional to the number of molecules of the absorber in the optical path; thus,

$$S = S^o P \tag{4}$$

where S^o is the line strength in units of $cm^{-2}atm^{-1}$ and P is the pressure in atm of the absorber. The line strength is related directly to the theoretical transition probability.

The spectral absorptance, α_υ, which provides a useful way of expressing the absorption of radiation at frequency υ, is defined as the ratio of the difference between the incident flux and the transmitted flux to the incident flux at frequency υ. Thus

$$\alpha_\nu = \frac{I^o_\upsilon - I_\upsilon}{I^o_\upsilon} = 1 - \tau_\upsilon = 1 - e^{-k_\upsilon \ell} \tag{5}$$

When conditions are such that local thermodynamic equilibrium can be assumed, the spectral absorptance, α_ν, may be equated to the spectral emissivity, ϵ_υ, by Kirchhoff's Law. It is this assumption which makes possible the calculation of the radiant energy emitted by a hot gas utilizing the concepts of absorption spectroscopy.

The integrated absorptance, A, over a finite wavenumber interval, $\Delta\upsilon$, is defined as

$$A = \int_{\Delta\upsilon} \alpha_\nu d\upsilon = \int_{\Delta\upsilon} (1 - \tau_\upsilon) d\upsilon = \int_{\Delta\upsilon} (1 - e^{-k_\upsilon \ell}) d\upsilon \tag{6}$$

The integrated absorptance is also called the equivalent width, W. If k_υ is contributed to by one line only, then the integral of the spectral absorptance over all frequencies is finite and the equivalent width is given by

$$W = \int_0^\infty (1 - \tau_\upsilon) d\upsilon \tag{7}$$

which is simply the integral of the fractional flux removed from the incident flux, i.e., the area under the absorption curve. The equivalent width is a function of the amount of absorber and the relationship between the two is called the curve of growth.

Either the spectral absorptance or the spectral transmittance is the quantity ideally sought in single line absorption experiments. From the resulting absorption coefficient curve the integrated absorption S may then be measured and compared directly with theory. These preferred measurements, which require the techniques of high resolution spectroscopy, are very difficult partly because of undetermined effects of the instrument on the spectral line shapes. Consequently it is usually the equivalent width, W, which is actually measured because experimental conditions can in most cases be so chosen that the equivalent width is independent of the slit function of the spectrometer. The equivalent width is then related to the integrated absorption (and hence the theory) through an absorption coefficient curve. These curves have a shape and a halfwidth for each individual line which is determined by the interactions of the molecules in the gas. Thus the line shape and halfwidth are dependent on the temperature and pressure, i.e., upon the mechanisms responsible for broadening the line. These line broadening mechanisms can be categorized as natural broadening, Doppler broadening, and collision broadening. The natural width is inversely proportional to the finite lifetime of the excited states and compared to other processes can be neglected for the measurements in the infrared spectral region. For low pressure situations the principal line shape factor is the Doppler effect where the absorption coefficient is given by

$$k_{\nu,D} = \left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} \frac{S}{\gamma_D} e^{-\ln 2[(\nu - \nu_o)/\gamma_D]^2} \tag{8}$$

and the Doppler halfwidth is given by

$$\gamma_D = \frac{2\nu}{C} \left[\frac{2kT\ln 2}{M}\right]^{\frac{1}{2}} \tag{9}$$

where M is the molecular weight

As the pressure is increased the principal process responsible for determining the line shape is that of binary collisions. In this pressure regime a satisfactory representation for the line shape is given by the Lorentz line shape formula which in the infrared is

$$k_\nu = \frac{S}{\pi} \frac{\gamma_L}{(\nu - \nu_o)^2 + \gamma_L^2} \tag{10}$$

where γ_L is the Lorentz halfwidth. The Lorentz halfwidth is proportional to the number of collisions per second interrupting the radiation absorption process and so formulas can be obtained from kinetic theory for this halfwidth. To a good approximation one can simply say that γ_L is proportional to the total pressure of a pure gas, and write

$$\gamma_L \simeq \gamma^o P \tag{11}$$

Expressions are also available for lines which are broadened by a combination of Doppler and collision broadening.

These are variations of the Voigt Formula which is given by

$$k_\upsilon = k_o \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2}}{a^2 + (w - y)^2} dy \tag{12}$$

where

$$w = \frac{2\,(\upsilon - \upsilon_o)}{\gamma_D} \sqrt{\ell n 2}$$

$y = \frac{2\delta}{\gamma_D} \sqrt{\ell n 2}$ = an integration interval

k_o = maximum absorption coefficient when only Doppler Broadening is present

$$a \simeq \frac{\gamma_L}{\gamma_D} \sqrt{\ell n 2}$$

The mixed Doppler and Lorentz line shape is not amenable to an analytical solution but is solved by numerical techniques.

Three different theoretical expressions for the absorption coefficient, k_υ, have been given, each representing fairly accurately the shape of the spectral line if the appropriate conditions are satisfied. If the shape and strength of a line are known, its equivalent width may be calculated from Equation 7. For lines with the Lorentz line shape the equivalent width is given by the Ladenburg - Reiche equation

$$W = 2\pi\gamma_L f(x) \tag{13}$$

The function f(x) is defined by an expression in Bessel functions as

$$f(x) = xe^{-x}[J_o(ix) - i\,J_1(ix)] \qquad (14)$$

where

$$x = S\ell/2\pi\gamma_L = S^o\ell/2\pi\gamma^o \qquad (15)$$

For a pure gas x is independent of pressure and can be varied only by varying the path length, ℓ. For a gas mixture x can be varied for a particular line at a constant path length by varying the partial pressure of the absorbing gas. The importance of the variation of x becomes evident when it is recognized that in order to determine both the line strength S^o, and the halfwidth γ^o, for a particular spectral line from the measurement of equivalent width, it is necessary to determine W for more than one value of x. This becomes apparent when the limiting expressions for the equivalent width are examined. For small values of x

$$f(x) \simeq x\ (1 - x/2 + \ .\ .\ .) \qquad (16)$$

and the linear region of the curve of growth is approached where the equivalent width is given by

$$W^o = \frac{W}{P} \simeq S^o\ell[1 - W^o/4\pi\gamma^o + \ .\ .\ .] \qquad (17)$$

For large values of x the square root region is approached where

$$f(x) \simeq (\frac{2x}{\pi})^{\frac{1}{2}}\ [1 + 1/8x + \ .\ .\ .] \qquad (18)$$

and

$$W^o \simeq 2(S^o\ \overset{o}{\gamma}\ell)^{\frac{1}{2}}[1 - \pi(\gamma^o/W^o)^2 + \ .\ .\ .\ ] \qquad (19)$$

Thus there are two asymptotic approximations for the equivalent widths of isolated spectral lines:

Linear Approximation

$$W^o = S^o\ell \qquad x \ll 1 \qquad (20)$$

Square Root Approximation

$$W^o = 2(S^o\gamma^o\ell)^{\frac{1}{2}} \qquad x > 3 \qquad (21)$$

The determination of the spectral parameters of line strength and line width is important not only to the theory of isolated spectral lines but also to band model theory because the band model parameters may be determined from these more fundamental molecular quantities.

Approximations to Band Models

Before discussing the individual band models, a brief preview of the approximations to the models will be given because each model will be considered in the light of these general limiting cases.

Dr. G. N. Plass proposed three approximations (Ref. JOSA 50, 869 (1960)) that are intended to permit predictions of band absorptance for virtually any range of pressure and concentration of absorbing gas in terms of relatively simple mathematical expressions involving the parameters X and β. $X = S\mu/2\pi\gamma$, is a measure of the ratio of the line strength, S, to the line half-width, γ, for an absorber concentration, μ. $\beta = 2\pi\gamma/d$, is the ratio of the line halfwidth, γ, to the mean line spacing, d. The simple expressions for the band models apply to limiting curves on logarithmic plots giving absorptance as a function of X, or β, or various products of these two parameters. The three Plass approximations are the strong line, the weak line, and the nonoverlapping line approximation. Each of these approximations has a well defined region of validity discussed briefly below and curves are presented in the original paper which show these regions of validity for the different band models.

1. Strong Line Approximation

When the absorptance is virtually complete near the centers of the strongest lines in the band, the band absorptance is a function of the single variable β^2X where

$$\beta^2X = \left(\frac{2\pi\gamma}{d}\right)^2 \left(\frac{S\mu}{2\pi\gamma}\right) = 2\pi\gamma\ S\mu/d^2 \qquad (22)$$

The strong line approximation is defined to be this limiting absorption curve. This approximation is valid even when the spectral lines overlap and should not be confused with the square root approximation which is valid only when the spectral lines do not overlap. The absorption as calculated from the strong line approximation depends on the arrangement of the spectral lines in the band. It is different for a random spacing of the lines than for a regular spacing and so the shape of the experimental curve should serve as a guide to the selection of an appropriate band model. The strong line approximation is useful in extrapolating laboratory data to large values of absorber concentration, μ, and small values of pressure, ρ. Laboratory measurements in this approximation would be made in a long absorption cell at low pressure.

2. The Weak Line Approximation

When the spectral absorptance is small at all frequencies in a band including those near the centers of the strongest lines, the absorptance is a function of the single variable βX where,

$$\beta X = \left(\frac{2\pi\gamma}{d} \right) \left(\frac{S\mu}{2\pi\gamma} \right) = S\mu/d \tag{23}$$

This limiting absorption curve is called the weak line approximation and is valid even when the spectral lines overlap. Thus it should not be confused with the linear approximation which is valid only when there is no overlapping of the spectral lines. This approximation is independent of the particular arrangement of the spectral lines in a band and so is nearly the same for all models. The weak line approximation is useful in extrapolating to small values of absorber concentration and large pressures and laboratory measurements would be made in a very short cell.

3. The Nonoverlapping Line Approximation

When the value of β, which is proportional to the pressure, is sufficiently small that there is no overlapping of lines the band absorption is simply the sum of the absorptances of individual lines as given by the Ladenburg-Reiche expression. The only requirement for the validity of this approximation is that the spectral lines do not overlap appreciably. The nonoverlapping approximation is the limiting curve in a logarithmic plot of A/β for constant β values vs. X. This curve has a linear region for weak nonoverlapping lines and a square root region for strong nonoverlapping lines. The nonoverlapping approximation is useful in extrapolations to small μ and small p.

Plass has shown that the approximations should be valid over practically all ranges of X and β for the Elsasser model and over most ranges of X and β for the statistical model and that predictions of absorption to within ± 10% are possible. Plass also describes laboratory studies appropriate to the selection of the correct approximation for the particular situation of interest.

The Elsasser Model

The Elsasser band model consists of an infinite array of spectral lines of equal intensity and equal halfwidths spaced at equal intervals. It has been shown to be most suitable for linear molecules. This model is based on the Lorentz line shape and is indeed simply an infinite repetition of a Lorentz line so that the absorption coefficient is given by

$$k_\upsilon = \sum_{n=-\infty}^{\infty} \frac{S}{\pi} \frac{\gamma_L}{(\upsilon - nd)^2 + \gamma_L^2} \tag{24}$$

where d is the line spacing

It is possible to express this infinite sum in terms of periodic and hyperbolic functions,

$$k_\upsilon = \frac{S}{d} \frac{\sinh \beta}{\cosh \beta - \cos z} \tag{25}$$

where

$$\beta = 2\pi\gamma_L/d \qquad z = 2\pi\upsilon/d$$

If the averaging interval $\Delta\upsilon$ is taken as one period of the band ($\Delta\upsilon = 2\pi$) the exact expression for the integrated absorptance or equivalent width of an Elsasser band is

$$A = \frac{1}{2\pi}\int_{-\pi}^{\pi}(1 - e^{-k_{\upsilon}\ell})dz$$

$$= 1 - \frac{1}{2\pi}\int_{-\pi}^{\pi} \exp\left[(-\beta x)\frac{\sinh\beta}{\cos\beta - \cos z}\right]dz \quad (26)$$

where $\beta x = s\ell/d$

This integral cannot be evaluated in closed form and must be integrated numerically. Several solutions based on expansions of the integrand have been developed; however, it is often quite useful to work with the asymptotic approximations which are valid for certain conditions.

The weak line approximation is the asymptotic limit as $\beta \rightarrow \infty$. Then $\sinh\beta \rightarrow \infty$ and the integrated absorptance becomes

$$A = 1 - e^{-\beta x} = 1 - e^{s\ell/d} \quad (27)$$

Since the parameter β measures the ratio of the line width to the distance of the neighboring line, in this limit lines overlap and there is no fine structure. The transmission is now independent of pressure (Beer's Law). This approximation is good whenever the absorption at the line centers is small, i.e., when the ratio of the line strength to the line halfwidth is small and for this reason is referred to as the weak line approximation.

The strong line approximation is the asymptotic limit to equation 26 when $x > 1$. Under this condition the absorption at the line center is usually complete, the halfwidths are narrow and the lines do not overlap strongly (β small). The integral becomes,

$$A = \operatorname{erf}(\tfrac{1}{2}\beta^2 x)^{\frac{1}{2}} \quad (28)$$

where the error function is given as,

$$\mathrm{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-t^2} dt$$

This approximation is particularly useful for long path lengths and small values of pressure. It differs from the square root approximation in that here the lines may overlap.

The Statistical Model

The statistical or Mayer-Goody model of a band assumes a random spacing of spectral lines and an intensity that varies from line to line in any manner which can be represented by a distribution function. An expression for the integrated absorptance for this model can be developed from the following considerations.

Let $\Delta\upsilon$ be a spectral interval in which there are n lines of mean distance d,

$$\Delta\upsilon = nd$$

where it is assumed that any line has equal probability of being anywhere in the interval.

Let $P(S_i)$ be the probability that the i^{th} line will have an intensity between S_i and S_i+dS_i. The probability is normalized so that

$$\int_0^\infty P(S_i)dS_i = 1$$

The mean transmittance is found by averaging over all positions and all intensities of the lines, thus

$$\tau = \frac{1}{(\Delta\upsilon)^n}\left[\int_{\Delta\upsilon} d\upsilon_1 \ . \ . \ . \int_{\Delta\upsilon} d\upsilon_n\right]$$

$$\left[\int_0^\infty P(S_1)e^{-k_{\upsilon_1}\ell}dS_1 . \ . \ . \int_0^\infty P(S_n)e^{-k_{\upsilon_n}\ell}dS_n\right]$$

But since all the integrals are alike we may write

$$\tau = \left[\frac{1}{\Delta\upsilon}\int d\upsilon \int P(s)e^{-k_\nu \ell}dS\right]^n$$

which may be rewritten as

$$\tau = [1 - \frac{1}{\Delta\upsilon}\int d\nu \int P(s)(1 - e^{-k_\upsilon \ell})ds]^n$$

or interchanging the order of integration

$$\tau = [1 - \frac{1}{\Delta\upsilon}\int P(s)ds \int (1 - e^{-k_\upsilon \ell})d\upsilon]$$

The integral over the frequency in this equation is equal to the equivalent width of a single line evaluated over the frequency interval $\Delta\upsilon$. Thus the transmittance can be written

$$\tau = [1 - \frac{1}{\Delta\upsilon}\int_0^\infty W_{s\ell,D}P(S)dS]^n$$

The average value of the equivalent width over the distribution of line strengths is

$$\bar{W}_{s\ell,D}(S_o,\gamma) = \int_0^\infty W'_{s\ell,D}(S,\ \gamma)P(S)dS$$

where S_o indicates some mean line intensity that occurs in the distribution function P(S). Since $\Delta\upsilon$ = nd the transmittance becomes

$$\tau = [1 - \bar{W}_{s\ell,D}/nd]^n \qquad (29)$$

If the number of lines in the band is allowed to approach infinity while the mean spacing is held constant, this last expression approaches an exponential

$$\tau = \exp[-\bar{W}_{s\ell,D}/d] \qquad (30)$$

In terms of average integrated absorptance for the band equations (29) and (30) become respectively

$$A = 1 - [1 - \bar{W}_{s\ell,D}/nd]^n \qquad (31)$$

the absorption from a finite number of spectral lines, n; and

$$A = 1 - \exp[-\bar{W}_{s\ell,D}/d] \qquad (32)$$

the absorption from an infinite number of randomly spaced spectral lines.

The equations are often examined for two special intensity distributions: lines of equal intensity and line strength by

Poisson distribution.

Where all the lines have equal intensity equation (21) reduces to

$$A = 1 - \exp\left\{- \beta x e^{-x}[J_o(ix) - i\, J_1(ix)]\right\} \qquad (33)$$

If each of the lines absorbs weakly so that x is small then we have the weak line approximation to the statistical model with all lines equally intense given by

$$A = 1 - e^{-\beta x} \qquad (34)$$

If the lines absorb strongly then we have the strong line approximation to the statistical model with all lines equally intense given by

$$A = 1 - \exp[-(\tfrac{2}{\pi}\, \beta^2 x)^{\frac{1}{2}}]$$

Many spectral bands may be simulated by assuming an exponential distribution of line intensities, namely,

$$P(S) = S_o^{-1}\exp(- S/S_o) \qquad (35)$$

With this distribution, Goody developed the following formula for the integrated absorptance

$$A = 1 - \exp[\, - \beta x_o/(1 + 2X_o)^{\frac{1}{2}}] \qquad (36)$$

where $X_o = S_o \ell/2\pi\gamma$

The weak line approximation to equation (36) is obtained when $X_o \ll 1$

$$A = 1 - \exp(- \beta X_o) \qquad (37)$$

The strong line approximation to equation (36) is obtained when $x_o \gg 1$

$$A = 1 - \exp[-(\tfrac{1}{2}\beta^2 X)^{\frac{1}{2}}] \qquad (38)$$

The Random Elsasser Model

The predicted absorption for the Elsasser and statistical models agree at small values of x because the absorption is determined by the total strength of all the spectral lines. However, as x increases the results calculated from these two models begin to diverge, with the Elsasser theory always predicting more absorption than the statistical model for a given value of x. Thus another model which is a generalization of these two models is suggested. The spectral lines of an actual absorption band are not arranged either completely at random or at regular intervals. The actual line pattern is formed by the superposition of many systems of lines.

The random Elsasser band model simulates this actual pattern by assuming that the absorption may be characterized by the random superposition of Elsasser bands, each of which may have a different line intensity, halfwidth, and spacing between the lines. As many different Elsasser bands as desired may be combined by multiplication in this model and thus the weak spectral lines that contribute to the absorption can be included in the calculations.

The absorptance of N randomly superimposed Elsasser bands is

$$A = 1 - \prod_{i=1}^{N} [1 - A_{E,i}(x_i, \beta_i)] \tag{39}$$

where $A_{E,i}$ is the absorptance of an Elsasser band with a halfwidth of γ_i, a line spacing d_i, and a line strength S_i so that

$$X_i = S_i \ell / 2\pi\gamma_i \text{ and } \beta_i = 2\pi\gamma_i / d_i$$

The weak-line approximation for the absorptance in the random Elsasser model is given by

$$A = 1 - \prod_{i=1}^{N} \exp[-\beta_i x_i] \tag{40}$$

The strong-line approximation is

$$A = 1 - \prod_{i=1}^{N} \left[1 - \operatorname{erf}\left(\tfrac{1}{2}\beta_i{}^2 x_i\right)^{\frac{1}{2}}\right] \tag{41}$$

As the number of randomly superimposed Elsasser bands increases the absorptance approaches that of the statistical model.

The Quasi-Random Model

The quasi-random model does not require that the spectral lines be either uniformly nor randomly spaced but is sufficiently flexible to simulate the complex spacing and intensity distributions of lines which are actually observed in practice. It provides for calculating the effect of wing absorption from spectral lines whose centers are outside the frequency interval of interest, as well as including the contributions of the weak lines in the interval. This is the most accurate of the band models but it may approach line by line calculations in complexity. In this model the general transmittance cannot be expressed in terms of elementary functions and an a priori knowledge of the band structure is required. However, because of its greater sophistication this band model provides the most realistic but perhaps unnecessarily complicated treatment for calculating the temperature and concentration profiles of hot gases from measurements of the radiant energy.

In the quasi-random model the absorptance is calculated first for a frequency interval that is much smaller than the interval of interest. This localizes the stronger lines to a narrow interval around their actual positions and prevents the introduction of spurious overlapping effects. The absorptance for each of the N spectral lines in the interval is calculated separately and the results combined by assuming a random placing of the lines within the small interval. The absorptance values for all of the small intervals that fill the large interval of interest are averaged to obtain the final value for the absorptance. The absorptance for the quasi-random model is

$$A = \frac{1}{L} \sum_{j=1}^{L} A_j \qquad (42)$$

where A_j is the absorptance of each of the L smaller intervals and is calculated from

$$A_j = 1 - \prod_{i=1}^{N} \left\{ 1 - A_{s\ell,D}(S_i, d_i) \right\} \tag{43}$$

where $A_{s\ell,D}$ is the single line absorptance over the finite interval D and N is the number of lines in the frequency interval j.

The weak-line approximation for the quasi-random model is given by

$$A = \frac{1}{L} \sum_{j=1}^{L} \left\{ 1 - \prod_{i=1}^{N} (1 - e^{-\beta_i x_i}) \right\} \tag{44}$$

the strong line approximation is,

$$A = \frac{1}{L} \sum_{j=1}^{L} \left\{ e^{-\zeta i^2} - \pi^{\frac{1}{2}} \zeta i [1 - \mathrm{erf}(\zeta i)] \right\} \tag{45}$$

where

$$\zeta i^2 = 8\gamma_i^2 X_{i/D^2}$$

The quasi-random model is developed and discussed in detail by Wyatt, Stull, and Plass (Ref. 17).

The Curtis Godson Approximation

Band models have been applied with considerable success to calculate the transmittance of homogeneous gas sample. In many practical situations, however, hot gas specimens have gradients of temperature, pressure and concentration. It then becomes necessary to extend the band model considerations to the calculation of the transmittances of inhomogeneous gases. There are a number of possible ways of developing the required approximation but perhaps the most useful is the Curtis-Godson approximation. (Ref.4) In the Curtis-Godson approximation, the non-homogeneous path is approximated by an homogeous path by assigning an effective amount of absorbing gas and an effective pressure referred to a standard temperature so that the two paths will absorb exactly the same. This implies that a single line absorbing along a non-homogeneous path can be simulated by a line, whose intensity and width can be adjusted, absorbing along a homogeneous path. The adjustment of intensity and width is made to give the correct absorption in the strong and the weak line regions. Since the interest here is in the application to combustion phenomena the development followed will be that of the Warner and Swasey group who utilized a finite difference scheme to modify the Curtis-Godson method. This simplification allowed the use of inhomogeneous paths that were composed of a series of smaller homogeneous zones.

The optical path is divided into r isothermal zones as shown in Figure 3. The spectral radiance of this inhomogeneous column of gas is then given by

$$N(\upsilon_j, \Delta\upsilon_j) = \sum_{i=1}^{n} N_b(\upsilon_j, T_i)\epsilon_i \qquad (46)$$

in units of $W[cm^2 cm^{-1} str]^{-1}$

where

i ≡ labels an isothermal zone in the line of sight; i increases with the distance of the zone from the detector.

j ≡ labels a spectral interval.

υ_j ≡ frequency of the midpoint of the spectral interval

$\Delta\upsilon_j$ ≡ frequency spread of the spectral interval

$N_b(\upsilon_j, T_i)$ ≡ spectral radiance of a Black Body at the frequency υ_j and temperature T_i (Planck's Function)

$\epsilon_i(\upsilon_j, \Delta\upsilon_j)$ ≡ spectral emissivity at the freq. υ_j of zone i.

Under conditions such that local thermodynamic equilibrium can be assumed, the spectral emittance may be equated to the spectral absorptance by Kirchhoff's Law

$$\epsilon_i(\upsilon_j, \Delta\upsilon_j) = \alpha_i(\upsilon_j, \Delta\upsilon_j) - \alpha_{i-1}(\upsilon_j, \Delta\upsilon_j) \qquad (47)$$

or since $\alpha_i = 1 - \tau_i$

$$\epsilon_i(\upsilon_j, \Delta\upsilon_j) = \tau_{i-1}(\upsilon_j, \Delta\upsilon_j) - \tau_i(\upsilon_j, \Delta\upsilon_j) \qquad (48)$$

Here $\tau_i(\upsilon_j, \Delta\upsilon_j)$ is the transmittance of the column of gas from the beginning of the first zone (the zone nearest the detector) to the end of zone i. Similarly $\tau_{i-1}(\upsilon j, \Delta\upsilon_j)$ is the transmittance from the beginning of the first zone to the end of zone i - 1. τ_o is taken as unity.

Rewriting equation 46, the spectral radiance of the inhomogeneous column of gas is

$$N(\upsilon_j, \Delta_j) = \sum_{i=1}^{n} N_b(\upsilon_j, T_i)[\tau_{i-1}(\upsilon_j, \Delta\upsilon_j) - \tau_i(\upsilon_j, \Delta\upsilon_j)] \quad (49)$$

The radiant flux, or the irradiance, is the power per unit area at an element of the detector and is given by

$$H = \int_w \sum_{j=1}^{m} N(\upsilon_j, \Delta\upsilon_j)\Delta\upsilon_j \cos\theta dw \quad (50)$$

in units of Wcm^{-2}.

These radiance equations provide a satisfactory means of developing the calculation whenever it is possible to identify isothermal zones. The integral over the solid angle can be carried out by numerical integration. The zonal transmittances, $\tau_i(\upsilon_j, \Delta\upsilon_j)$, are the unknowns and are to be determined by utilizing a suitable band model together with the Curtis-Godson approximation. Each line in the spectral interval $\Delta\upsilon_j$ is characterized by its position υ its strength S and its halfwidth γ. The band model parameters are the effective line strength S/d and the effective halfwidth γ/d where d is the frequency spacing between lines for the interval $\Delta\upsilon_j$.

In applying the Curtis-Godson approximation one first determines the values of the band model parameters $(S/d)_h$ and $(\gamma/d)_h$ for each of the isothermal zones constituting the inhomogeneous sample. The subscript h identifies any individual zone. The band model parameters of the equivalent hypothetical homogeneous path are then defined in terms of the parameters of the individual zones by the equations

$$(S/d)\ell = \sum_{h} (S/d)_h \ell_h \tag{51}$$

$$(S/d)\ell(\gamma/d) = \sum_{h} (S/d)_h \ell_h (\gamma/d)_h \tag{52}$$

where ℓ is the length of an optical path.

It is important to observe that there is a different inhomogeneous path through the gas sample for each transmittance $\tau_i(\upsilon_j, \Delta\upsilon_j)$. This is because $\tau_i(\upsilon_j, \Delta\upsilon_j)$ is defined as the transmittance of the inhomogeneous column of gas from the beginning of the first zone to the end of zone i. Hence there must be an equivalent homogeneous path hypothesized for each transmittance $\tau_i(\upsilon_j, \Delta\upsilon_j)$ and its band model parameters are defined by the equations,

$$[(S/d)\ell]_i = \sum_{h=1}^{i} (S/d)_h \ell_h \tag{53}$$

$$[(S/d)\ell(\gamma/d)]_i = \sum_{h=1}^{i} (S/d)_h \ell_n (\gamma/d)_h \tag{54}$$

The transmittance through a given non-homogeneous sample is calculated by choosing a particular band model. This may be done on the basis of the known character of the spectrum of the gas under examination. For gases of particular interest in this study, namely, hot water vapor and carbon dioxide it has been shown that transmittances can be predicted satisfactorily using the statistical band model with constant line widths. According to this band model, the transmittance of a homogeneous gas over a spectral interval containing many lines can be expressed as

$$-\ell n\ \tau = 2\pi(\gamma/d)f(x) \tag{55}$$

where x is given by

$$x = (S/d)\ell/2\pi(\gamma/d) \tag{56}$$

The form of f(x) depends on the probability distribution function used for the line strengths. f(x) is the Ladenburg-Reiche function for a delta function distribution where all the lines are assumed to have equal intensity. The present development will be based on this type of line strength distribution.

To determine the transmittance $\bar{\tau}_i(\nu_j, \Delta\nu_j)$ of an inhomogeneous column of gas consisting of i isothermal zones one calculates the transmittance of the equivalent hypothetical homogeneous column whose band model parameters are given by equations 53 and 54. Thus,

$$-\ell n\ \bar{\tau}_i(\nu_j, \Delta\nu_j) = 2\pi(\gamma/d)_i\ f(\bar{x}_i) \tag{57}$$

The expression for $(\gamma/d)_i$ in terms of the band model parameters of the isothermal zones is obtained by diving equation 54 by equation 53

$$\left(\frac{\gamma}{d}\right)_i = \frac{[(\bar{S}/d)\ell(\gamma/d)]_i}{[(\bar{S}/d)\ell]_i} \tag{58}$$

and $\bar{x}_i$ is

$$\bar{x}_i = \frac{[(\bar{S}/d)\ell]_i}{[2\pi\bar{\gamma}/d]_i} \tag{59}$$

Substituting, we have the transmittance in terms of zonal band model parameters.

$$-\ell n\ \bar{\tau}_i(\nu_j, \Delta\nu_j) = 2\pi \frac{\sum\limits_{h=1}^{i} (S/d)_h \ell_h (\gamma/d)_h}{\sum\limits_{h=1}^{i} (S/d)_h \ell_h}\ f\left[\frac{\left[\sum\limits_{h=1}^{i} (S/d)_h \ell_h\right]^2}{\sum\limits_{h=1}^{i} (S/d)_h \ell_h (\gamma/d)_h}\right] \tag{60}$$

We now return to Ladenburg-Reiche expressions to obtain the band model parameters of the isothermal zones in terms of transmittances within those individual zones. Thus,

$$(\gamma/d)_h = \frac{-\ell n\ \tau_h}{2\pi f(x_h)} \tag{61}$$

and

$$(S/d)_h\ \ell_h = x_h\ 2\pi \left(\frac{-\ell n\ \tau_h}{2\pi f(x_h)}\right) \tag{62}$$

The Transmittance $\tau_i(\upsilon_j, \Delta\upsilon_j)$ of the inhomogeneous path can now be determined in terms of the zonal transmittances and zonal x's

$$-\ell n\ \tau_i(\upsilon_j, \Delta\upsilon_j) = \frac{\sum\limits_{h=1}^{i} x_h \left(\frac{-\ell n\ \tau_h}{f(x_h)}\right)^2}{\sum\limits_{h=1}^{i} x_h \left(\frac{-\ell n \tau_h}{f(x_h)}\right)}\ f\left\{\frac{\left(\sum\limits_{h=1}^{i} x_h\ \frac{-\ell n \tau_h}{f(x_h)}\right)^2}{\sum\limits_{h=1}^{i} x_h \left(\frac{-\ell n \tau_h}{f(x_h)}\right)^2}\right\} \tag{63}$$

This equation can be used for any value of x but x must be known. f(x) is tabulated for numerical values of its argument.

Since there are two asymptotic limits on the Ladenburg-Reiche function the above equation reduces to forms in which τ_i is independent of x_h. For low values of x, $f(x) \simeq x$ and Eq. 63 reduces to

$$-\ell n\ \tau_i(\upsilon_j, \Delta\upsilon_j) \simeq \sum_{h=1}^{i} -\ell n\ \tau_h \tag{64}$$

If all the x_h's are high, $f(x) \simeq (2x/\pi)^{\frac{1}{2}}$ and Eq. 63 reduces to

$$-\ell n\ \bar{\tau}_i(v_j, \Delta v_j) \simeq \left[\sum_{h=1}^{i} (-\ell n\ \tau_h)^2\right]^{\frac{1}{2}} \tag{65}$$

Equations 64 and 65 are valid in the low x and high x regions respectively and the x value need not be known for these calculations.

The parameters $(\bar{\gamma}/d)_i$ and $\bar{x}_i$ are written in Eq. 58 and Eq. 59 in terms of the zonal band model parameters which are dependent on the pressure and temperature in the following way.

$$(s/d)_h = (s^o/d)_h p_h^a \tag{66}$$

and

$$(\gamma/d)_h = (\gamma_a^o/d)_h\ p_h^a + (\gamma_b^o/d)_h\ p_h^b \tag{67}$$

where p_h^a and p_h^b are the pressure of the absorbing gas the pressure of the broadening gas respectively in the isothermal zone h of path length ℓ_h. The quantities $(s^o/d)_h$ and $\gamma^o/d)_h$ are functions of temperature. The parameters $(\bar{\gamma}/d)_i$ and $\bar{x}_i$ may now be written in terms of partial pressures and temperature dependent band model parameters as,

$$\left(\frac{\bar{\gamma}}{d}\right)_i = \frac{\sum_{h=1}^{i} p_h^a (s^o/d)_h \ell_h \left[(\gamma^o{}_a/d)_h\, p_h^a + (\gamma^o{}_b/d)_h\, p_h^b\right]}{\sum_{i=1}^{i} (s^o/d)_h\, p_h^a\, \ell_h} \tag{68}$$

and

$$\bar{x}_i = \frac{\left[\sum_{i=1}^{i} (s^o/d)_h\, p_h{}^a\, \ell_h\right]^2}{2\pi \sum_{i=1}^{i} (s^o/d)_h\, p_h{}^a\, \ell_h \left[(\gamma^o{}_a/d)_h\, p_h{}^a + (\gamma^o{}_b/d)_h p_h{}^b\right]} \tag{69}$$

For the case of several broadening gases the single terms $(\gamma^o{}_b/d)_h\, p_h{}^b$ for a given zone are replaced by sums over species in that zone, namely, $\sum_s (\gamma^o{}_s/d)_h\, p_h{}^s$.

For the spectral region where two gas species both absorb radiant energy, the transmittance is first computed for each gas separately and then the product determines the effective transmittance. For example, the case of overlapping H_2O and CO_2 bands near 2.85 μm would be calculated by

$$\bar{\tau}_i(\nu_j,\Delta\nu_j) = \bar{\tau}_i{}^{H_2O}(\nu_j,\Delta\nu_j)\ \bar{\tau}_i{}^{CO_2}(\nu_j,\Delta\nu_j) \tag{70}$$

In a case like this the second gas is always treated as a broadening agent when the first is treated as the absorber, and vice versa.

The Equation of Transfer

The infrared brightness method of obtaining information about the temperature distribution in a hot gas from its emission and absorption spectra was suggested by Silverman (Ref. 107) and has been developed and verified by numerous investigators. The technique is based on the recognition that radiation is both emitted and absorbed in a hot gas in local thermodynamic equilibrium and that the spectral irradiance by a one dimensional beam of monochromatic radiation varies according to the equation of transfer.

$$dH(\nu_j,s) = -k(\nu_j,s)\ p(s)\ [\ H(\nu_j,s) - N_b(\nu_j,T_s)\ ]\quad ds. \quad (71)$$

$H(\nu_j,s)$ is the irradiance; $N_b(\nu_j,T_s)$ is the Planck function; $k(\nu_{j,s})$ is the spectral absorption coefficient; $p(s)$ and T_s are the partial pressure and temperature of the gas at the frequency ν_j and the position s. The left hand side of this equation is the change in irradiance on going from a point s to a point s + ds. The first term on the right hand side is the decrease in irradiance due to absorption along the path ds; the second term is the increase in irradiance due to the emittance of the hot gas within ds. The formal solution of the equation of transfer may be written

$$H(\nu_j,s) = H(\nu_j,0)\ \exp[-\int_0^s kpds] + \int_0^s N_b(\nu_j,T_{s'})\exp[-\int_{s'}^{s} kpds]kpds \quad (72)$$

where the optical thickness between s and s′ is

$$t = \int_{s'}^{s} k\ p\ ds \quad (73)$$

SECTION IV
EMISSION-ABSORPTION METHOD

At this point it was increasingly evident that the mathematical tools and experimental techniques were available for predicting the radiances of hot gases, even with temperature, pressure, and concentration gradients, provided these gas parameters are known for the physical situation under investigation and provided sufficiently accurate data on the spectral parameters of line strength and line width are available to use in the band model. It was also quite evident that very little was known regarding the inverse problem, namely, determining the temperature, pressure, and concentration gradients in a hot inhomogeneous gas from spectroscopic data and a suitable band model. A very pertinent effort in this direction was that of Dr. William F. Herget and associates (Ref. 52-Ref. 55) who extended the spectroscopic emission-absorption method to obtain information about both temperature distribution and concentration distribution. To determine these quantities the spectral radiance and spectral transmittance of the infrared active species in the hot gas must be measured spectroscopically along a series of coplanar chordal lines of sight. These data allow the calculation of the radial distributions of temperature and partial pressure of the species of interest by inversion methods. The method is best explained by first considering media homogeneous in temperature and pressure, and then extending the technique to heterogeneous media.

The partial pressure of the gaseous medium may be determined by its absorptive properties which are expressed by the spectral transmittance of the gas

$$\tau(\nu) = e^{-k(\nu,T)\ p\ell} \tag{74}$$

where $k(\nu,T)$, the spectral absorption coefficient, is a unique property of the absorbing gas for a given frequency and temperature. $k(\nu,T)$ can be completely determined for a particular species by performing laboratory absorption measurements over a range of temperatures.

The spectroscopic determination of partial pressures makes use of the fact that once $k(\nu,T)$ has been determined for various species by laboratory measurements then the partial pressure of an active gas can be determined from Eq. 74 by a measurement of $\tau(\nu)$, T and ℓ.

The temperature may be determined by a measurement of the spectral radiance which is the power of the radiation per unit frequency interval emitted from a unit area of the gas surface filling a given solid angle and is expressed in units of $W[cm^2\ cm^{-1}\ str]^{-1}$. Spectral radiance is measured by comparing the brightness of the hot gas with the brightness of a standard source such as a blackbody at a known temperature. The optical system is arranged to insure that the detector views the same solid angle, frequency interval, and source area whether viewing the hot gas or the blackbody. Because of this arrangement the ratio of the spectral radiance of the gas to the spectral radiance of the blackbody is the same as the ratio of the spectral irradiance of the gas to the spectral irradiance of the blackbody. That is

$$N(\nu)/N_b(\nu) = H(\nu)/H_b(\nu) \tag{75}$$

Also with this optical arrangement the spectral radiance of the hot gas will be equal to that of the blackbody if the detector produces the same output signal no matter which source is viewed. The spectral radiance of a blackbody $N_b(\nu,T)$ is a unique function of frequency and temperature given by the Planck formula

$$\begin{aligned} N_b(\nu,T) &= 2c^2h\nu^3[\exp(hc\nu/kT)-1]^{-1} \\ &= 1.1909 \times 10^{-12}\nu^3[\exp(1.439\ \nu/T)-1]^{-1} \end{aligned} \tag{76}$$

The spectral radiance of a homogeneous gas $N(\nu)$ is related to the spectral radiance of a blackbody at the same temperature by

$$\begin{aligned} N(\nu) &= N_b(\nu,T)\ \epsilon(\nu) \\ &= N_b(\nu,T)[1 - \tau(\nu)] \end{aligned} \tag{77}$$

Thus once $N(\nu)$ and $\tau(\nu)$ have been measured, $N_b(\nu,T)$ can be calculated from Eq. 77 and the gas temperature is then uniquely determined by the Planck formula since the temperature is then the only unknown quantity in that expression and is equal to the gas temperature.

In extending measurements to an unhomogeneous gas in which temperature and pressure gradients exist it is generally assumed that the gas consists of a series of regions each of which is isothermal and isobaric within the precision of measurement. If the gas under investigation is in an axially symmetric flow field as is often the case for engine exhausts then the zones of constant temperature and pressure are chosen as shown in Figure 4. If the temperature and concentration gradients are steep the regions would have to be small but in principle such a division can always be made. The medium between the sample and the detector is considered zone zero. Spectroscopic measurements are made along lines of sight as shown in the diagram.

Herget made line of sight measurements of medium resolution of spectral radiance and spectral transmittance at small frequency intervals centered about 3 specific frequencies in the infrared for gaseous carbon dioxide in a rocket exhaust. The partial pressures and temperatures for each radial zone were determined by solving appropriate spectral radiance and transmittance equations utilizing an "onion peel" or back substitution calculation. This means that the partial pressure and temperature for the outermost zone are determined directly from line of sight data taken through that zone alone. These results are then used with the data taken along the next innermost line of sight to obtain temperatures and pressures for the next innermost zone. This method is repeated until the problem is solved.

Progress in developing a low resolution band model method for determining the temperature, pressure, and concentration gradients in a hot inhomogeneous gas required that selections be made among the band models, the available approximations, the spectral region and the experimental techniques. The decision was made to concentrate on the work of two groups which have been very active in the development and application of band model methods to predicting radiative heat transfer where the concentrations and temperatures of combustion gases are known. These are the General Dynamics Convair Group of C. B. Ludwig, J.A.L. Thomson, and W. Malkmus, and the Warner and Swasey Group of H. Babrov, R. Tourin, and B. Krakow. The data of the General Dynamics group on band model parameters in the infared at 2.7μ were to provide a computional base. The Warner and Swasey development of the Curtis-Godson approximation utilizing the statistical band model with Lorentz lines of equal width and intensity provided the mathematical model. This band model and intensity distribution were chosen because they have been shown to satisfactorily and conveniently represent the water vapor band spectra and because much of the available band model data were based on the statistical model. A different band model, for example the quasi-random model, would possibly provide an even better representation of the water vapor spectra but the computational complexity appeared unnecessary for the precision of the measurements contemplated. Although several approximations are available for dealing with mixtures of gases only the Curtis-Godson approximation was given serious consideration in the present work because the mathematical development of this approximation had been well advanced and its representation of inhomogeneous gases under operating conditions similar to those encountered in a test cell environment had been experimentally verified by the Warner and Swasey group.

The task of "inverting" the equations of the Warner and Swasey group was undertaken by Mr. LeRoy Brewer, ETF Special Projects Branch, Arnold Engineering Development Center. The equations referred to are those derived in this report in the section on the Curtis-Godson approximation. The equations were originally developed to predict radiance knowing temperature and concentration profiles of inhomogeneous gases. The "inversion" required determining temperature and concentration profiles from measured values of spectral radiance and spectral transmittance. This was achieved by a back substitution computational technique utilizing data obtained from spectroscopic emission-absorption experiments. The band model development by Brewer requires the tabulated values of the band model parameters S^o/d and γ^o/d as functions of temperature compiled by the General Dynamics group for various temperatures ranging from 300 to 3000°K. In the development which follows the geometry of the problem is shown in Figure 4 which was discussed above in the section on emission-absorption measurements.

INVERSION OF THE CURTIS-GODSON EQUATIONS FOR STATISTICAL MODEL

Given the following expression for the spectral radiance

$$N(\nu_j,\Delta\nu_j) = \sum_{i=1}^{n} N_b(\nu_j,T_i)[\bar{\tau}_{i-1}(\nu_j,\Delta\nu_j) - \bar{\tau}_i(\nu_j,\Delta\nu_j)] \qquad (49)$$

SECTOR A.

I. In sector A, this equation becomes simply the equation for Zone 1 and thus,

$$N_A(\nu_j,\Delta\nu_j) = N_1(\nu_j,\Delta\nu_j) = N_b(\nu_j,T_1)[1 - \bar{\tau}_1(\nu_j,\Delta\nu_j)]$$

where the transmittance of zone zero is considered to be unity. Once $N_A(\nu_j,\Delta\nu_j)$ and $\tau_1(\nu_j,\Delta\nu_j)$ have been measured, $N_b(\nu_j,T_1)$ can be calculated directly from this equation and the gas temperature in zone 1 is then uniquely determined by the Planck function

$$N_b(\nu_1 T) = 2c^2h\nu^3\,[\exp(hc\nu/kT)-1]^{-1} \qquad (76)$$

Result: T_1

II. The band model parameters $(S^o/d)_h$ and $(\gamma^o/d)_h$ are tabulated fuctions of temperature and can now be determined for zone 1.

Result: $(S^o/d)_1$ and $(\gamma^o/d)_1$

III. Given the definition of x_h for the h^{th} isothermal zone

$$x_h = \frac{(S/d)_h \ell h}{2\pi(\gamma\ /d)_h} = \frac{(S^o/d)_h\ P_h \ell_h}{2\pi(\gamma^o/d)_h P_h}$$

The pressure term cancels; For zone 1 the pathlength is measured and the values of $(S^o/d)_1$ and $(\gamma^o/d)_1$ are known.

Result: X_1

IV. Given: f(x), the Ladenburg and Reiche function the values of which are tabulated.

Result: $f(x_1)$

V. Given: The transmittance of a homogeneous gas for a statistical band model with constant line widths

$$-\ell n\ \tau = 2\pi(\gamma/d)\ f(x)$$

Then for Sector A which is zone 1

$$-\ell n\ \tau_1 = 2\pi(\gamma^o/d)_1\ P_1 f(x_1)$$

Here everything is known except P_1 for which a direct solution is obtained

Result: P_1

For zone 1 we now know the temperature and the partial pressure of the absorbing gas

Sector B

I. Measure $N_B(\upsilon_j, \Delta\upsilon_j)$, $\bar{\tau}_B(\upsilon_j, \Delta\upsilon_j) = \bar{\tau}_{1,2,1}(\upsilon_j, \Delta\upsilon_j)$

and the path length for the various zones

The equation for the spectral radiance becomes

$$\begin{aligned} N_B(\nu_j, \Delta\nu_j) = {} & N_b(\nu_j, T_1)[1 - \bar{\tau}_1(\nu_j, \Delta\nu_j)] \\ & + N_b(\nu_j, T_{1,2})[\bar{\tau}_1(\nu_j, \Delta\nu_j) - \bar{\tau}_{1,2}(\nu_j, \Delta\nu_j)] \\ & + N_b(\nu_j, T_1)[\bar{\tau}_{1,2}(\nu_j, \Delta\nu_j) - \bar{\tau}_{1,2,1}(\nu_j - \Delta\nu_j)] \end{aligned}$$

There are two unknowns in this equation $N_b(\upsilon_j, T_2)$ and $\tau_{1,2}(\upsilon_j, \Delta\upsilon_j)$

II. The transmittance of the inhomogeneous path in terms of the zonal parameters is given by Eq. 60 and for the present case takes the form,

$$-\ell n\ \tau_B = \frac{2x_1\left(\frac{-\ell n\ \tau_1}{f(x_1)}\right)^2 + x_2\left(\frac{-\ell n\ \tau_2}{f(x_2)}\right)^2}{2x_1\left(\frac{-\ell n \tau_1}{f(x_1)}\right) + x_2\left(\frac{-\ell n\ \tau_2}{f(x_2)}\right)}$$

$$X\ f\left\{\frac{\left(2x_1\,\frac{-\ell n\ \tau_1}{f(x_1)} + x_2\frac{-\ell n\ \tau_2}{f(x_2)}\right)^2}{2x_1\left(\frac{-\ell n\ \tau_1}{f(x_1)}\right)^2 + x_2\left(\frac{-\ell n\ \tau_2}{f(x_2)}\right)^2}\right\}$$

The unknowns in this equation are $(-\ell n\ \tau_2)$, x_2, and $f(x_2)$ where $f(x_2)$ is determined from x_2 by the Ladenburg and Reiche function.

III. These two equations for sector B contain the information for determining the pressure and temperature of zone 2. However the equations cannot be written in terms of these unknowns, P_2 and T_2, and solved simultaneously because of the Ladenburg and Reiche function and because S^o/d and γ^o/d are tabular functions of T. Therefore as an initial step in an iterative solution assume one of the approximations, either the low x or the high x approximations to equation 60 is valid. For example, assume the validity of the low x or Beer's law approximation; then,

$$-\ell n\ \bar{\tau}_B = -\ell n\ \bar{\tau}_{1,2,1} = -\ell n\ \tau_1 - \ell n\ \tau_2 - \ell n\ \tau_1$$

and

$$-\ell n\ \bar{\tau}_{1,2} = -\ell n\ \tau_1 - \ell n\ \tau_2 \quad .$$

The first of these equations can be solved for $-\ell n\ \tau_2$ since $-\ell n\ \bar{\tau}_{1,2,1}$ is measured and $-\ell n\ \tau_1$ is known from sector A. The second of these equations then yields $(-\ell n\ \tau'_{1,2})$ where the prime indicates an approximate value for the transmittance through zones 1 and 2.

IV. Substituting $-\ell n\ \bar{\tau}'_{1,2}$ equation 78 is solved for $N_b(\upsilon_j, T_2')$ and the temperature of zone 2, T_2', is obtained directly from the Planck radiation expression.

V. Following the routine of sector A, the band model parameters $(S^o/d)'_2$ and $(\gamma^o/d)'_2$ are obtained for the temperature T'_2 and lead to a value for x'_2 through Eq. 56, and thence to $f(x'_2)$ by the tabulated Ladenburg and Reiche function.

VI. Now substitute $(-\ell n\ \tau'_2)$, x'_2, along with the known zone 1 parameters and calculate $(-\ell n\ \bar{\tau}'_B)$. There are two possible consequences of this procedure:

  a) If $\tau'_B = \tau_B$, then Beer's law is valid and we move on to Step VII.

  b) If $\tau'_B \neq \tau_B$, then adjustments must be made in the values of $(-\ell n\ \tau'_2)$, x'_2, and $f(x'_2)$. The adjustment in these parameters may be accomplished by examining the other approximation to Eq. 60, for example, the high x approximation.

VII. Agreement between the calculated and measured transmittance of Sector B is taken to imply the correctness of the parameters of zone 2, in particular the temperature T_2 and the transmittance τ_2. The correct temperature yields correct $(S^o/d)_2$ and $(\gamma^o/d)_2$ from tables. These in turn provide correct x_2 and $f(x_2)$. The partial pressure of the infrared active gas in zone 2 is now determined from

$$-\ell n\ \tau_2 = 2\pi(\gamma^o/d)_2\ P_2\ f(x_2)$$

Sector C.

I. Measure $N_C(\nu_j,\Delta\nu_j)$, $\tau_C(\nu_j,\Delta\nu_j) = \tau_{1,2,3,2,1}$ and the path lengths for the various zones. The equation for the spectral radiance becomes

$$\begin{aligned} N_C(\nu_j,\Delta\nu_j) = {} & N_b(\nu_j,T_1)[1 - \bar{\tau}_1(\nu_j,\Delta\nu_j)] \\ & + N_b(\nu_j,T_2)[\bar{\tau}_1(\nu_j,\Delta\nu_j) - \bar{\tau}_{1,2}(\nu_j,\Delta\nu_j)] \\ & + N_b(\nu_j,T_3)[\bar{\tau}_{1,2}(\nu_j,\Delta\nu_j) - \bar{\tau}_{1,2,3}(\nu_j,\Delta\nu_j)] \\ & + N_b(\nu_j,T_2)[\bar{\tau}_{1,2,3}(\nu_j,\Delta\nu_j) - \bar{\tau}_{1,2,3,2}(\nu_j,\Delta\nu_j)] \\ & + N_b(\nu_j,T_1)[\bar{\tau}_{1,2,3,2}(\nu_j,\Delta\nu_j) - \tau_{1,2,3,2,1}(\nu_j,\Delta\nu_j)] \end{aligned} \tag{79}$$

There are three unknowns in this equation:

$$N_b(\nu_j,T_3),\ \bar{\tau}_{1,2,3}(\nu_j,\Delta\nu_j),\ \text{and}\ \bar{\tau}_{1,2,3,2}(\nu_j,\Delta\nu_j)$$

II. The transmittance of the inhomogeneous path in terms of the zonal parameters takes the form shown on the following page.

$$-\ell n\ \bar{\tau}_C = \frac{2x_1\left(\frac{-\ell n\ \tau_1}{f(x_1)}\right)^2 + 2x_2\left(\frac{-\ell n\ \tau_2}{f(x_2)}\right)^2 + x_3\left(\frac{-\ell n\ \tau_3}{f(x_3)}\right)^2}{2x_1\ \frac{-\ell n\ \tau_1}{f(x_1)} + 2x_2\ \frac{-\ell n\ \tau_2}{f(x_2)} + x_3\ \frac{-\ell n\ \tau_3}{f(x_3)}}$$

$$f\left\{\frac{\left(2x_1\frac{-\ell n\ \tau_1}{f(x_1)} + 2x_2\frac{-\ell n\ \tau_2}{f(x_2)} + x_3\frac{-\ell n\ \tau_3}{f(x_3)}\right)^2}{2x_1\left(\frac{-\ell n\ \tau_1}{f(x_1)}\right)^2 + 2x_2\left(\frac{-\ell n\ \tau_2}{f(x_2)}\right)^2 + x_3\left(\frac{-\ell n\ \tau_3}{f(x_3)}\right)^2}\right\}$$

There are three unknowns in this equation:

$(-\ell n\ \tau_3)$, x_3, and $f(x_3)$

III. As before one assumes an approximation to Eq. 60 as an initial step in an iterative solution for the pressure and temperature in zone 3. Assuming Beer's law, for example, gives,

$$-\ell n\ \bar{\tau}_c = -\ell n\ \bar{\tau}_{1,2,3,2,1}$$

$$= -\ell n\ \tau_1 - \ell n\ \tau_2 - \ell n\ \tau_3 - \ell n\ \tau_2 - \ell n\ \tau_1$$

and

$$-\ell n\ \bar{\tau}_{1,2,3,2} = -\ell n\ \tau_1 - \ell n\ \tau_2 - \ell n\ \tau_3 - \ell n\ \tau_2$$

$$-\ell n\ \bar{\tau}_{1,2,3} = -\ell n\ \tau_1 - \ell n\ \tau_2 - \ell n\ \tau_3$$

The solution of these equations leads to approximate values,

$-\ell n\ \bar{\tau}'_{1,2,3}$ and $-\ell n\ \bar{\tau}'_{1,2,3,2}$

IV. Substitute $-\ell n\ \bar{\tau}'_{1,2,3}$ and $-\ell n\ \bar{\tau}'_{1,2,3,2}$ into Eq. 79 and solve for $N_b\ (\upsilon_j,\ T'_3)$. The approximation to the temperature of zone 3, T'_3, is obtained from the Planck radiation expression. Following the routine of sectors A & B yields an approximate value for x'_3 and for the

Ladenburg and Reiche function $f(x'_3)$. Substituting $(-\ell n\ \tau'_3)$, x'_3, and $f(x'_3)$ together with previously determined quantities into Eq. 80 yields the approximate transmittance for Sector C, $\bar{\tau}'_C$.

V. As before, if the calculated transmittance for Sector C, $\bar{\tau}'_c$, equals the measured transmittance for Sector C, $\bar{\tau}_c$, then the Beer's law approximation is valid. If however, $\bar{\tau}'_c \neq \bar{\tau}_c$ then adjustment in the parameters is necessary. When sufficiently precise agreement is reached between calculated and measured transmittance of Sector C the parameters of zone 3 may be assumed correct and the temperature and partial pressure of the gas may be determined for that zone.

Other Sectors.

The complete problem is solved by repeating the above procedure for each sector until all chosen sectors have been evaluated.

Presence of Foreign Gases

In the inversion process described above no provision was made for the presence of any gas other than the one whose radiance and transmittance is being observed. In most combustion processes of interest this situation is not obtained. There are usually broadening agents present in appreciable concentrations and the foreign-gas broadening effects and band overlap effects must be considered. The band model halfwidth which enters into the radiance equations for a given isothermal, isobaric, zone within the inhomogeneous gas can be written

$$(\gamma/d)_h = (\gamma_a^o/d)_h\ p_h^{\ a} + (\gamma_b^{\ o}/d)_h\ p_h^{\ b} \qquad (81)$$

where the index a indicates the absorbing-emitting gas and the index b indicates the non-absorbing or broadening gas; $p_h^{\ a}$ and $p_h^{\ b}$ are the partial pressures of the absorbing and broadening gases respectively in zone h. The band model halfwidth for the foreign gas can be approximated in terms the band model halfwidth of the absorbing-emitting gas by writing

$$(\gamma_b{}^o/d) = K\ (\gamma_a{}^o/d) \tag{82}$$

where K is a constant which differs for each broadening gas but which is assumed in this approximation to be independent of temperature and frequency. Also observe that if only two gases are present the partial pressure of the broadening gas may be expressed in terms of the absorbing-emitting gas as

$$p^b = 1 - p^a \tag{83}$$

The band model halfwidth parameter then takes the form,

$$(\gamma/d)_h = (\gamma_a{}^o/d)_h[K + (1 - K)\ p_h{}^a] \tag{84}$$

For the case of several broadening gases the term $(\gamma_b{}^o/d)_h p_h{}^b$ is replaced by $\sum\limits_s (\gamma_s{}^o/d)_h\ p_h{}^s$ where the summation over the index s indicates that one should sum the product of partial pressure and broadening parameter for each species for each zone h. Although this additional complication can be incorporated into the equations, it is in most cases not necessary to consider the effect of more than one broadening gas. The case of interest here is that in which the absorbing-emitting gas is water vapor and the broadening gas is carbon dioxide or perhaps nitrogen. There a few experimental data from which a value of K may be obtained. Babrov (Ref. 73) estimated that for water vapor lines broadened by nitrogen K_{N_2} is approximately 0.2. This is in agreement with the General Dynamics Group (Ref. 44) who give a value $\gamma_{N_2} = 0.09$ when the water vapor parameter is $\gamma_{H_2O} = 0.44$ for nitrogen broadening water vapor lines. In exhaust gases CO_2 is the primary foreign gas in H_2O absorption studies and has a much greater broadening ability than N_2.

Rusk (Ref. 106) found CO_2 to be 1.6 times as effective as nitrogen in broadening water vapor lines. The data of the General Dynamics group support this value also. On the basis of these findings it is suggested that an initial value of 0.32 be assigned to K_{CO_2}.

Very little experimental information is actually available regarding halfwidths. This is true not only for band models but for the basic spectral parameter single line halfwidths for pure homogeneous gases as well. The self broadening and foreign gas broadening parameters as functions of frequency and temperature are not known for most molecules and should be measured for those molecules of importance in combustion.

The spectral region where the measurements of interest to this report are made, namely, the 2.7μ infrared region is a region where both water vapor and carbon dioxide are absorbing and emitting radiation. When this is the case for two gas species, more accurate values of the spectral radiance and the spectral transmittance are obtained if one first computes $\bar{\tau}_i(\upsilon_j, \Delta\upsilon_j)$ for each absorbing gas separately, and then multiplies the two $\bar{\tau}_i(\upsilon_j, \Delta\upsilon_j)$ s to obtain the effective transmittance. In this case for example,

$$\bar{\tau}_i(\upsilon_j, \Delta\upsilon_j) = [\bar{\tau}_i{}^{H_2O}][\bar{\tau}_i{}^{CO_2}] \qquad (85)$$

In these calculations the second gas is treated as the broadening gas when the first is the absorbing gas and vice versa. This refinement can be incorporated into the calculations for temperatures and partial pressures, but the additional complication is not warranted at this time by the precision of the experiments.

Another point which should be considered with care in the development and utilization of the inversion process is the transfer of the zonal spectral transmittance, $\tau_h(\upsilon_j, \Delta\upsilon_j)$, from one sector to another. The optical depth for a given zone differs from sector to sector as is seen by examining Fig. 4.

It is possible that the path length in zone 1 sector A may be greater than the combined path lengths through both pieces of zone 1 in sector B. A similar situation exists for the other zones although it becomes less pronounced as the center zone is approached. Perhaps the simplist way to account for this situation is to observe that the logarithm of the spectral transmittance may be written

$$-\ell n\ \tau = k(\upsilon_1 T)\ p\ell \tag{86}$$

where ℓ is the optical path length in the medium. Then if ℓ is reduced to one-half, the $\ell n\ \tau$ is also reduced to one-half, provided pressure is not changed appreciably.

Calculations

An examination of the utility of the inversion procedure was initiated using a desk calculator. Calculations were made for a two zone situation in which the temperature and partial pressure differ for the two zones. The data input for the calculation were taken by the Warner and Swasey group who measured transmittance as a function of temperature and pressure using furnaces under controlled laboratory conditions. Applying these data to the inversion procedure utilizing a statistical band model with the Curtis-Godson approximation the temperature and pressure of each zone are obtained. For zone one the calculated pressure is within 2% of the measured pressured and the calculated temperature within 1% of the measured temperature. For zone 2, the agreement was within 4% for pressure, 1% for temperature, and 3% for transmittance. This indicates self consistency of the inversion process. When the band model parameters S_o/d and γ_o/d as functions of temperature are taken from tables compiled by the General Dynamics group. The error in pressure calculations is slightly higher than 50%. This discrepancy was traced to a difference in the value of γ^o/d determined by averaging and by direct measurement over a small wavelength interval.

Two other points of interest were brought out by the hand calculations. Because the Beer-Lambert law is not valid, the calculation requires an iteration. The calculation verified that this iteration process converges very rapidly to acceptable values of pressure and temperature. The calculation also revealed that the high x approximation, namely,

$$-\ln \tau \approx \left[\sum_h (-\ln \tau_h)^2\right]^{\frac{1}{2}}$$

provides more correct values to the transmittance and thus more rapid convergence than does the low x approximation for gas samples in the temperature and pressure range of interest. (600 to 1200°K and 100 torr)

SECTION V
EXPERIMENTAL

Two types of experiments were designed in cooperation with the Special Projects Group, ETF, Arnold Engineering Development Center for obtaining data under controlled laboratory conditions. The first of these had the objective of assessing the utility and validity of the previously formulated band model inversion technique as a diagnostic tool for determining temperatures and partial pressures from spectroscopic measurements of radiance and transmittance. The second experiment was designed for measuring the effect of foreign gas broadening on the band model halfwidth parameter.

Only a few comments will be made regarding the second experiment because there was not time to carry it out under the auspices of the present contract. This would be an absorption experiment in which band-width measurements are made as a function of temperature and partial pressure on hot water vapor mixed with such gases as carbon monoxide, carbon dioxide, or nitrogen. These measurements can be accomplished satisfactorily with an instrument of low resolution such as a Perkin-Elmer Model 12 infrared spectrometer fitted with a prism or grating. The difficulties of such measurements are not optical but are associated with the gas handling system and with the removal of atmospheric water vapor from the optical path. The later difficulty is most satisfactorily solved by placing the entire experiment in a vacuum. This is probably not possible in the existing test cell environment and so the purging of the system with an inert gas would be required. The problems associated with the gas handling system for such an absorption experiment are more restrictive. An absorption cell is required which remains vacuum tight as temperatures range from 300°K to 1200°K and back to 300°K. The overall gas handling system must provide for the mixture of two or more gases at elevated temperatures, the accurate measurement of their partial pressures, and the transfer of the mixture to the absorption cell. Because of these problems consideration is being given to design of a combustion experiment for measuring foreign gas broadening of the molecular band.

The objective of the first experiment was of more immediate concern and the decision was made to seek emission and absorption data at 2.7μ in the spectrum of hot water vapor produced in flames. These experiments were carried out by UTSI personnel in cooperation with the ETF Special Projects Group utilizing the special burners and spectrometers available at AEDC.

To provide the required line-of-sight radiance and transmittance data the infrared instrumentation system must be capable of the following experiments:

1. Measurement of flame spectral radiance is made by comparing flame intensity with blackbody intensity; radiation is optically chopped between the flame and the detector.
2. Measurement of flame spectral transmittance is made by observing the radiation from a greybody source after passage through the flame; greybody radiation is optically chopped between the greybody and the flame.
3. The line of sight must be varied by spatially scanning the flame image across the entrance slit of the spectrometer.

Figure 5 shows the emission-absorption experimental arrangement.

The experiment was set up in the RTF test area of the Arnold Engineering Development Center. A burner whose characteristics were well known from earlier experiments was made available. The selection of a burner with known characteristics was necessary to provide a comparison standard for the spectroscopic measurements. Temperature, partial pressure, and velocity profiles had been mapped for this burner for several different fuel-oxidizer ratios and inlet pressures. The burner was placed in position so that a vertical flame would be obtained. Traversing mechanisms were installed so that the flame could be moved across the optical path in both a horizontal and a vertical plane. Measurements can consequently be made at various stations downstream of the flameholder and transversely at each station. A hood and exhaust system were designed and placed in position above the flame. This is necessary because the major portion of the exhaust gas will be water vapor and this must be removed from the vicinity of the spectroscopic measurements. The gas handling apparatus was designed for burning hydrogen premixed in either air or oxygen. The initial measurements were made of hydrogen burning in air. The flame was surrounded by a shroud gas of nitrogen. On occasion argon or helium was used as the shroud gas.

A Perkin-Elmer model 112 double pass prism spectrometer for the infrared was acquired and positioned for obtaining spectral data. This instrument utilizes a lead sulfide detector, a 13cps chopper, a preamplifier, and a Perkin-Elmer model 107 amplifier for receiving emission radiation directly from the flame. Across the flame directly opposite the spectrometer a graybody radiation source has been placed for making the absorption measurements. This radiation source is a water cooled Globar which has high emissivity throughout the near infrared and is operated at about

1200°K. A movable shutter between the Globar and the flame allows the Globar to be isolated so that its radiation is not received at the spectrometer when it is desired to look only at the flame. The signal detection system for the Globar consists of a 300 cps chopper together with a lock-in amplifier. The entrance slit of the spectrometer is about 18 inches from the flame on one side and the Globar is the same distance from the flame on the other side. An optical system external to the spectrometer connects the two, placing a one-to-one image of the Globar on the center line of the flame and then a one-to-one image of the Globar image onto the entrance slit.

The optical paths between the Globar and the flame and between the spectrometer and the flame are enclosed in transparent plastic boxes. When measurements are being made, the spectrometer and much of the optical path is flushed with an inert gas to reduce absorption by atmospheric water vapor. This flushing gas will generally be the same as the shroud gas, that is, nitrogen, argon, or helium.

Preliminary measurements of the emission spectra of the hydrogen-air flame were made in the spectral region 1.5μ to 2.8μ, showing a strong molecular band at approximately 2.5μ and a weaker band in the neighborhood of 1.8μ. The structure at 2.5μ consists of the water vapor band of interest and the first overtone band of CO_2. The band at 1.8μ is also water vapor.

Preliminary absorption measurements were also made on the flame center line throughout this spectral region using the Globar as a greybody source. These measurements showed a very weak absorption in the region of the water vapor band at 2.5μ.

Following these preliminary emission-absorption measurements the instrument was calibrated using a secondary standard tungsten ribbon source. This together with the emission-absorption data gave an estimate of the flame temperature which was within 20% of the previously determined probe values under similar burning conditions.

Emission-absorption measurements were then performed at 5mm intervals across the flame to obtain more detailed information. These data provide the input to the band model inversion program from which temperature profiles and water vapor partial pressure profiles across the flame could be calculated.

Table 1 through Table IV present typical sets of data for four different stations downstream of the burner base. At each station the flame was scanned transversely from edge to edge at 5 mm intervals resulting in twenty-one measurements of radiance and transmittance at each station. These data were then inverted to provide temperatures and water vapor partial pressures for each of ten zones for every station downstream.

Figure 6 presents typical spectral radiance and transmissivity curves across the flame from centerline to edge. In Figure 7 typical profiles are shown of temperature and water vapor partial pressure. The temperature and pressure profiles obtained from a chemical equilibrium calculation and previous probe measurements are also shown in Figure 7. This profile is distinguished from those determined spectroscopically in two respects. First, it is flat showing an cylindrical isothermal region of 3/8 inch radius about the centerline of the flame. Second, its value differs from the spectroscopic value in the zone of maximum value by approximately 12%. It should be observed, however, that the spectroscopic values are fairly high but show gradients in the region shown by the probe to be isothermal.

The reason for these discrepancies is not known. The fault may rest with the experiment or in the computer program and efforts are continuing to determine which.

SECTION VI
CONCLUDING REMARKS

The investigation of the feasibility of applying the theory of band models to the diagnostic problem of determining temperatures and concentrations has lead to the development of a mathematical inversion technique based on low-resolution emission absorption spectroscopy. Band model theory and much of its literature is summarized in this report. The inversion of the Curtis-Godson approximation of a statistical band model with Lorentz lines of constant width is presented in detail. Experiments were performed to verify the technique but are inconclusive at this time.

The present work is not complete and its goal will be reached only if it stimulates further effort in the application of spectroscopic band models to the diagnostic problem. The present band model inversion needs to be refined and the utility of other band models should be investigated. The application to molecules other than H_2O, in particular CO_2, and to other spectral regions, such as the 15μ region, should be pushed. Both foreign gas broadening and self broadening are too little understood and available data all too meager. The band model parameters are not known for enough molecules, over an adequate spectral range, with sufficient accuracy for really satisfactory solution of the diagnostic problem. Much fundamental work needs to be done in these areas. It is not unreasonable to expect the final goal of band model diagnostics to be on-line instrumentation functioning automatically to provide instantaneous temperature and concentration profiles for the gases of interest.

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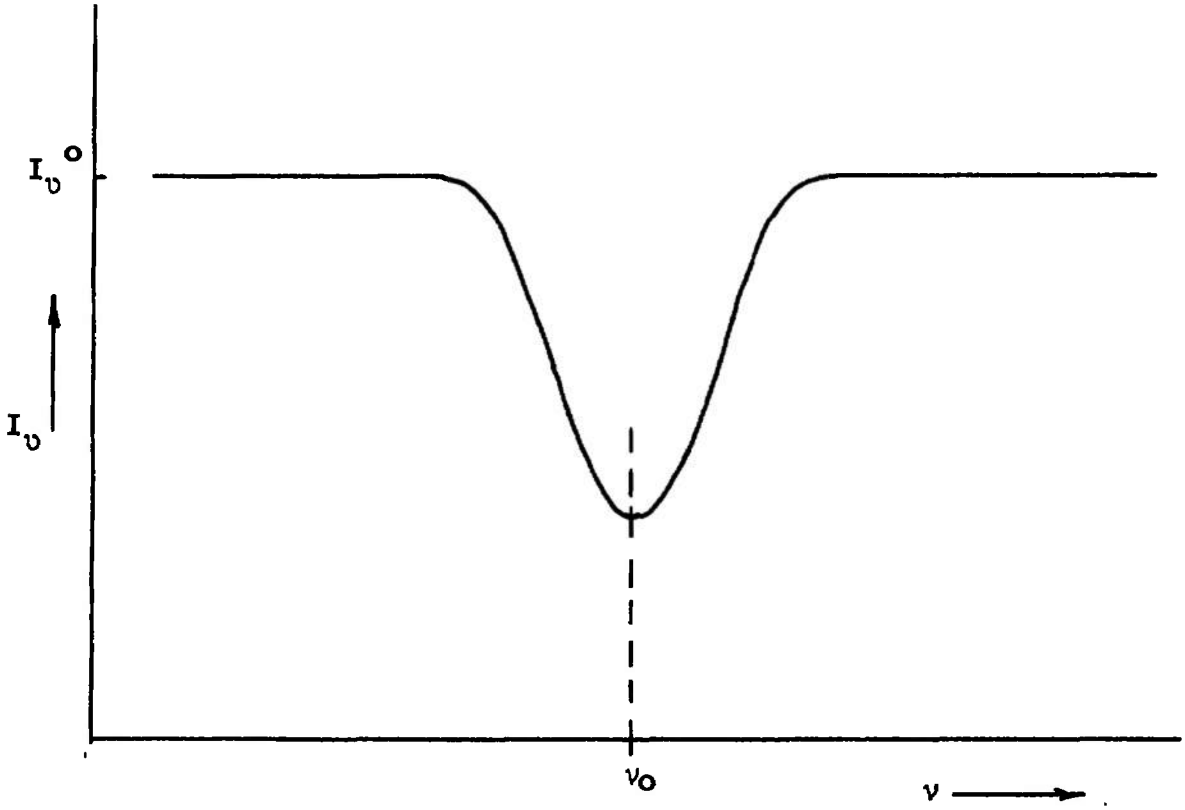


Fig. 1 An Absorption Line at ν_o

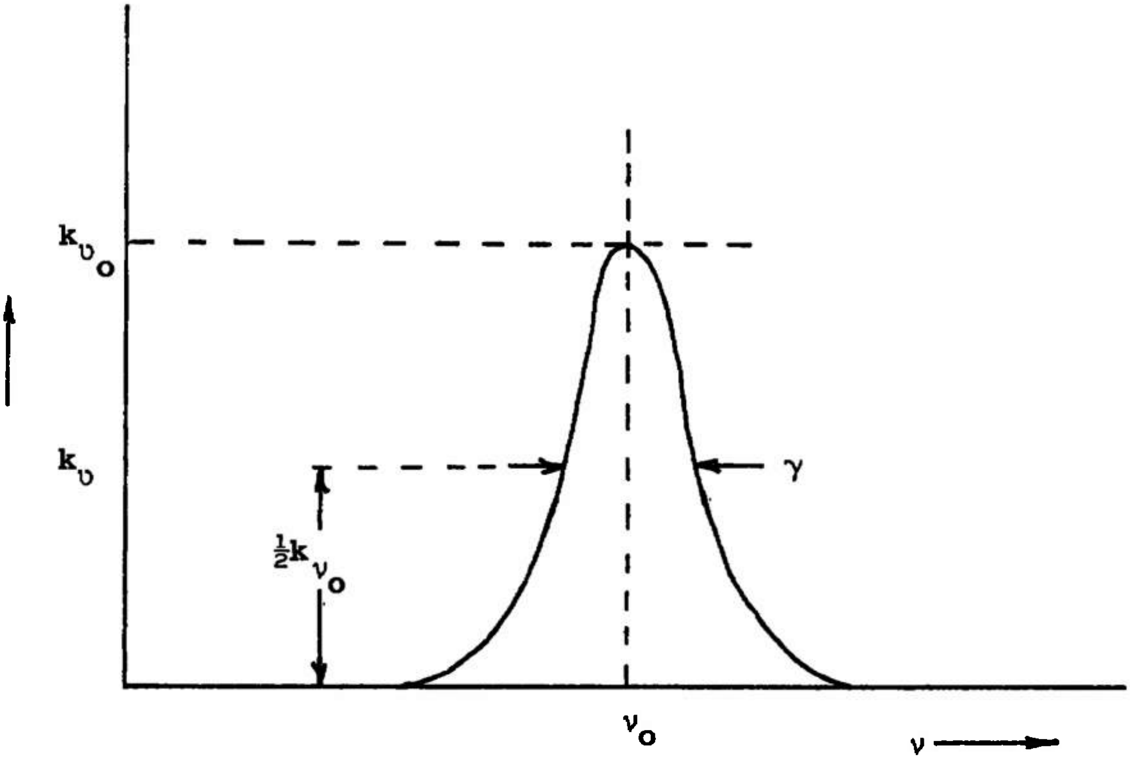


Fig. 2 An Absorption Coefficient Curve at ν_o

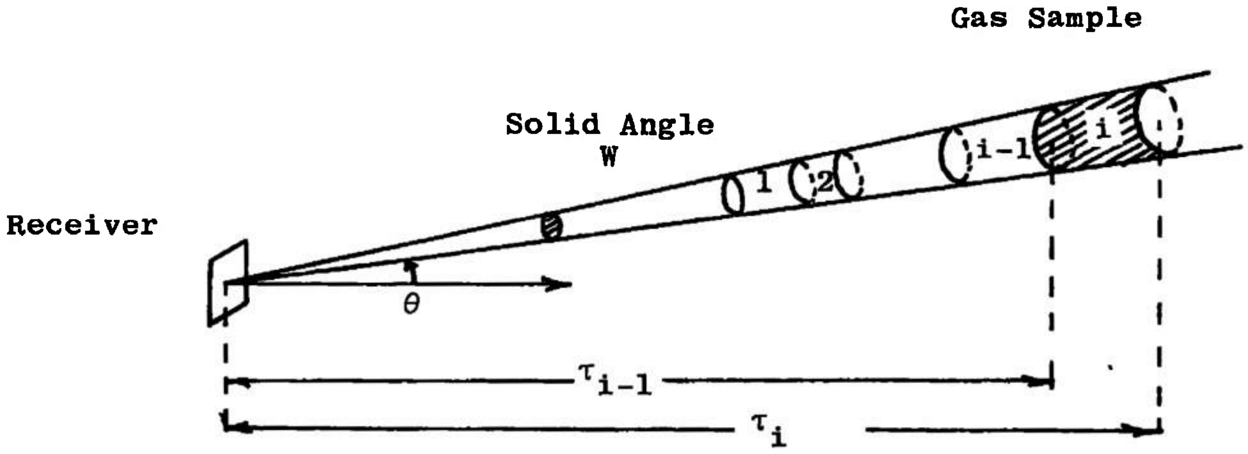


Fig. 3 Optical Path Through the Inhomogeneous Gas

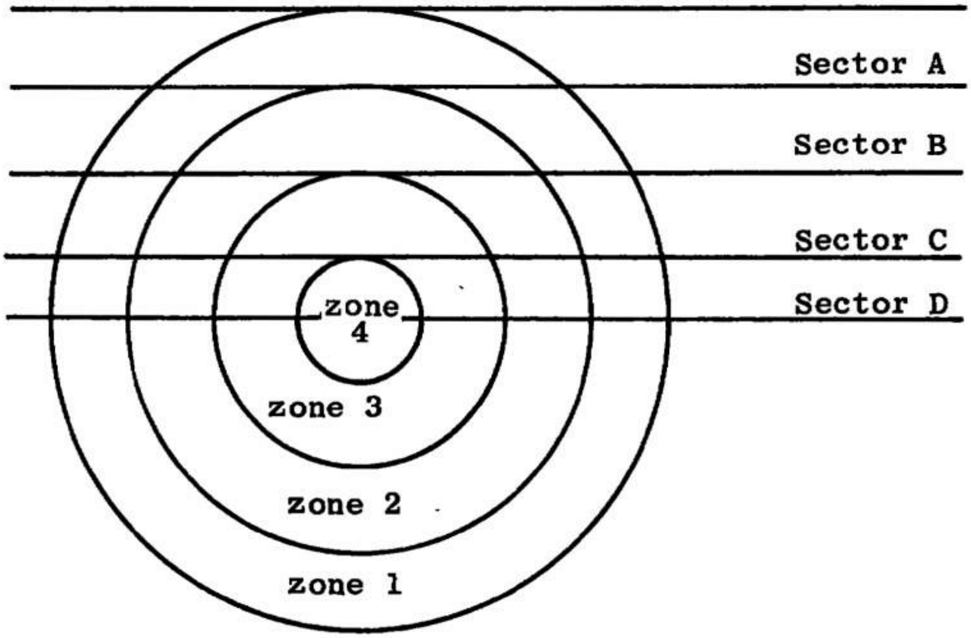
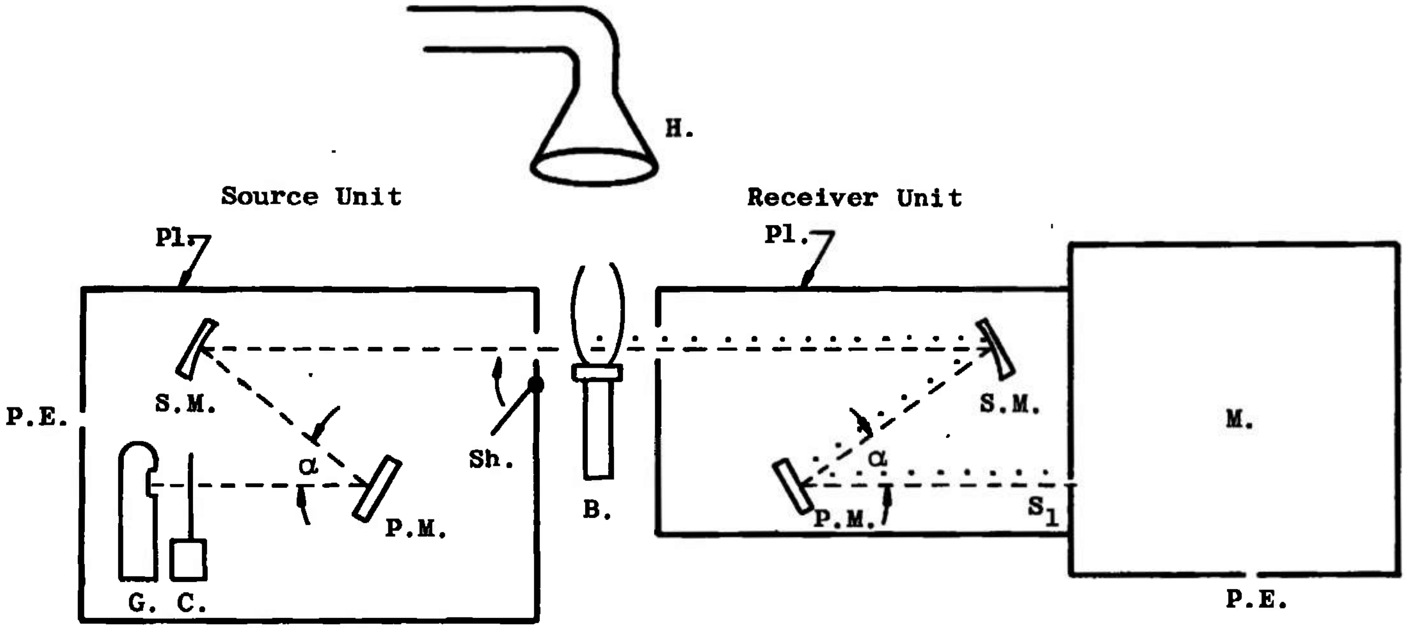


Fig. 4 Geometry of Lines of Sight for Radially Symmetric Flame



Pl. - Plexiglass Enclosures
P.E. - Purge Gas Entrance (Ar)
G. - Globar (Continuum Source)
C. - Chopper (300 cps)
S_1 - Entrance Slit

S.M. - Spherical Mirror
P.M. - Plane Mirror
B. - Burner (1-1/16" diam.)
Sh. - Shutter (Employed for Emission Only)

H. - Exhaust Hood
M. - Monochromator
——— Absorption Optical Path
.... Emission Optical Path
α - 20 deg

Fig. 5 Schematic of the Optical System

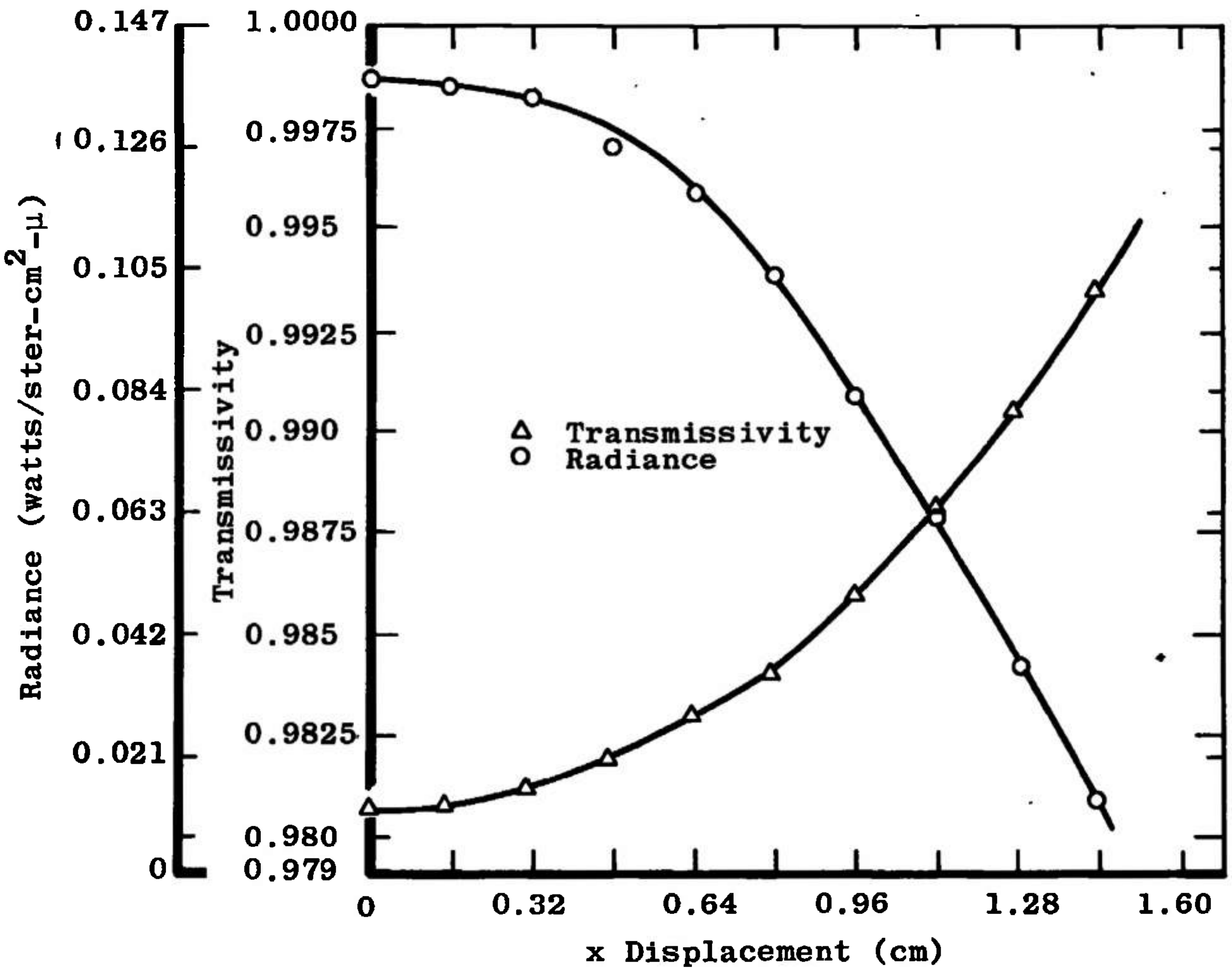


Fig. 6 Measured Spectral Radiance and Transmissivity Profiles for a Hydrogen-Air-Carbon Dioxide (4%) Flame

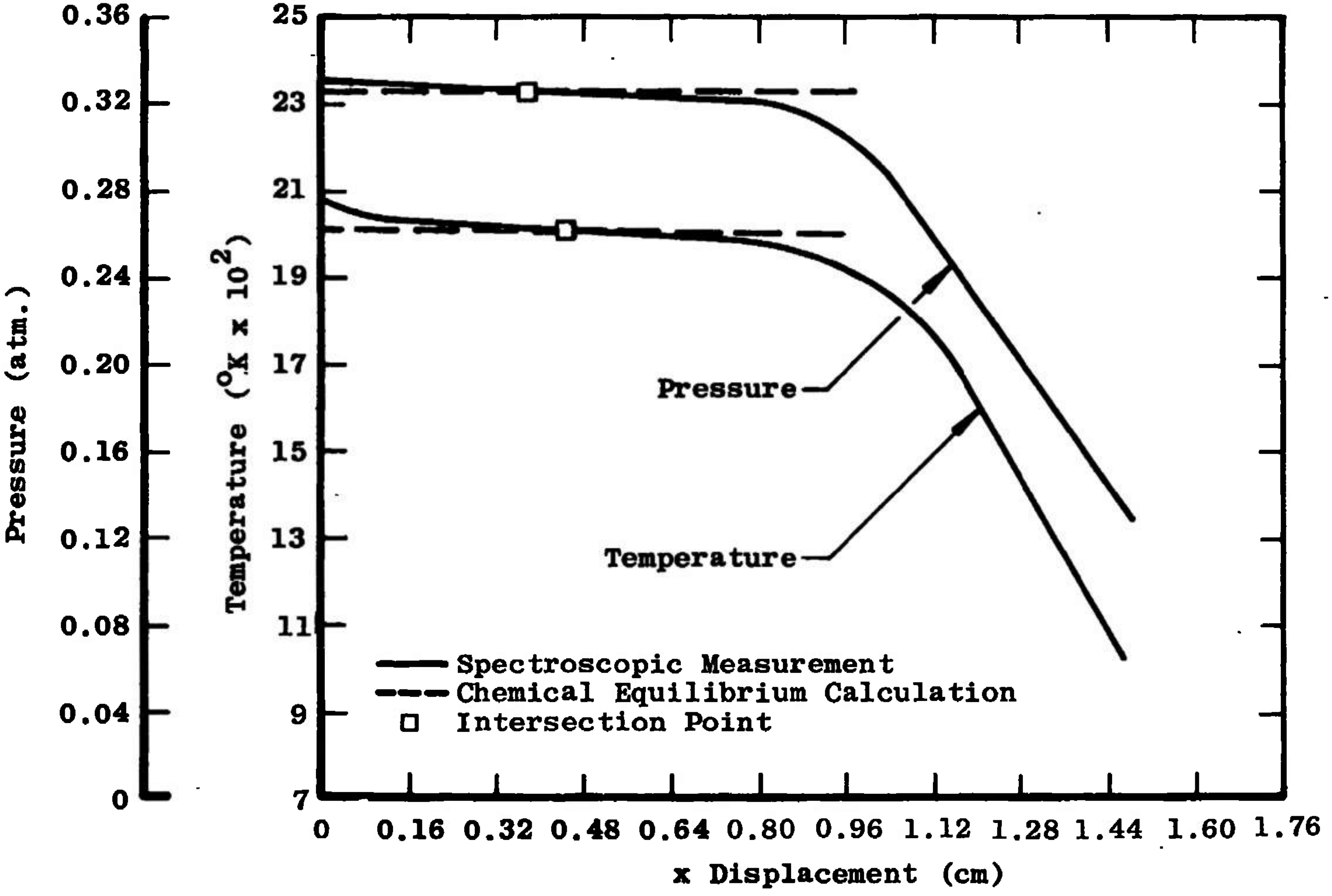


Fig. 7 Temperature and Water Vapor Partial Pressure Profiles for Hydrogen-Air-Carbon Dioxide (4%) Flame (Neglecting Foreign Gas Broadening)

TABLE I
STATION 0. HEIGHT ABOVE BURNER BASE 1/2"

Minus side of flame

Zone	H_i	τ_i	T_h	p_h
1	0.0088	0.9946	1329.768	0.160144
2	0.0235	0.9908	1598.593	0.1912517
3	0.0439	0.9884	1830.329	0.2416925
4	0.0683	0.984	1766.159	0.3725197
5	0.0964	0.9816	2042.532	0.3851425
6	0.113	0.9822	2415.941	0.2547318
7	0.126	0.9802	1973.946	0.4243071
8	0.1334	0.9788	1976.341	0.3987573
9	0.134	0.9782	1868.96	0.3734008
10	0.134	0.9761	1425.101	0.7195553

Plus side of flame

Zone	H_i	τ_i	T_h	p_h
1	0.0072	0.9929	1199.679	0.1040097
2	0.0202	0.9929	1633.923	0.1072218
3	0.0439	0.9891	1765.506	0.1960801
4	0.0675	0.9864	1881.406	0.2533221
5	0.0952	0.9826	1914.978	0.3425443
6	0.1098	0.9812	1961.568	0.3467113
7	0.1204	0.9795	1939.124	0.3689625
8	0.1286	0.9787	1968.003	0.3739443
9	0.134	0.9778	1950.502	0.3966639
10	0.134	0.9761	1743.325	0.4711858

TABLE II
STATION 1. HEIGHT ABOVE BURNER BASE 3/4"

Minus side of flame

Zone	H_i	τ_i	T_h	P_h
1	0.004	0.9959	1190.162	0.06572864
2	0.0138	0.9931	1522.641	0.1345853
3	0.0333	0.9917	2039.2	0.1599885
4	0.0577	0.9886	1914.87	0.2729758
5	0.0817	0.9823	1704.095	0.4321557
6	0.109	0.9819	2399.626	0.2897842
7	0.12	0.9805	1918.579	0.3646834
8	0.137	0.9788	2116.154	0.4257887
9	0.14	0.9788	1870.317	0.3706299
10	0.14	0.9778	2008.301	0.3253451
11	0.138	0.9784	2556.197	0.1313624

Plus side of flame

Zone	H_i	τ_i	T_h	P_h
1	0.004	0.9948	1134.789	0.07272909
2	0.0162	0.9917	1434.445	0.1245156
3	0.0389	0.9889	1710.057	0.1905522
4	0.0667	0.9826	1700.995	0.3211193
5	0.0928	0.9812	1898.645	0.3441612
6	0.1098	0.9809	2045.449	0.3298195
7	0.1254	0.9802	2132.306	0.3394778
8	0.1344	0.9798	2172.490	0.3376801
9	0.1376	0.9784	2005.149	0.3855848
10	0.1384	0.9784	2027.117	0.3704518

TABLE III
STATION 2. HEIGHT ABOVE BURNER BASE 1"

Minus side of flame

Zone	H_i	τ_i	T_h	P_h
1	0.0040	0.9932	1078.085	0.1008756
2	0.0121	0.9889	1308.032	0.1804165
3	0.0292	0.9864	1667.921	0.2097130
4	0.0517	0.9846	1883.424	0.2570956
5	0.0777	0.9828	2048.448	0.3065125
6	0.1017	0.9806	2041.374	0.3651089
7	0.1266	0.9799	2386.426	0.3304918
8	0.1353	0.9792	2126.313	0.3350262
9	0.1388	0.9774	1874.469	0.4126021
10	0.1416	0.9767	1957.927	0.3834246
11	0.1418	0.9765	1849.66	0.3792502

Plus side of flame

Zone	H_i	τ_i	T_h	P_h
1	0.0113	0.995	1436.612	0.08800917
2	0.0276	0.9918	1623.908	0.1455148
3	0.0483	0.9903	1879.595	0.1799156
4	0.0737	0.9889	2110.551	0.2159047
5	0.1017	0.9853	2059.729	0.3108270
6	0.1196	0.9849	2229.696	0.2931871
7	0.1298	0.9824	2047.16	0.3532553
8	0.1364	0.9799	1907.419	0.4071964
9	0.1392	0.9788	1865.414	0.4166042
10	0.1408	0.9785	1869.995	0.4215534

TABLE IV
STATION 3. HEIGHT ABOVE BURNER BASE 1¼"

Minus side of flame

Zone	H_i	τ_i	T_h	P_h
1	0.008	0.9942	1281.014	0.09960471
2	0.017	0.9893	1348.209	0.1967253
3	0.03	0.986	1536.079	0.2175365
4	0.0521	0.9847	1933.05	0.2439525
5	0.0781	0.984	2212.649	0.2597838
6	0.1046	0.9821	2157.58	0.3459801
7	0.1242	0.9808	2227.028	0.3393879
8	0.1364	0.9788	2005.548	0.4149947
9	0.1404	0.9785	2130.546	0.3201958
10	0.142	0.9778	1919.647	0.3823121
11	0.1426	0.9762	1535.344	0.6208833

Plus side of flame

Zone	H_i	τ_i	T_h	P_h
1	0.0088	0.9883	1129.815	0.1636166
2	0.0243	0.988	1487.810	0.1630804
3	0.0475	0.984	1638.096	0.2439516
4	0.0765	0.9834	1957.051	0.2689019
5	0.1005	0.9821	2084.923	0.2968581
6	0.1148	0.9817	2177.459	0.2881885
7	0.1262	0.9804	2127.871	0.3184034
8	0.1348	0.9798	2153.448	0.3254421
9	0.1384	0.9765	1826.465	0.4465935
10	0.1416	0.9762	1873.864	0.4548999

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13 ABSTRACT

A major phase of this report involved a compilation of information and critical evaluation of that information as it pertains to the diagnostic problem. The information is gathered together in a bibliography of books, reports, and published articles and is discussed in Section II. The investigation of the feasibility of applying the theory of band models to the diagnostic problem of determining temperatures and concentrations has led to the development of a mathematical inversion technique based on low-resolution emission-absorption spectroscopy. Band model theory and much of its literature is summarized in this report. The inversion of the Curtis-Godson approximation of a statistical band model with Lorentz lines of constant width is presented in detail. Experiments were performed to verify the technique but are inconclusive at this time.

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