General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

NASA CR-66112

W&S TR-39

POSSIBLE TECHNIQUES FOR OPTICAL MEASUREMENT OF TEMPERATURE AND CONCENTRATION PROFILES IN A SUPERSONIC RAMJET

by

BURTON KRAKOW
RICHARD H. TOURIN
GUNTER J. PENZIAS

N70-15082

FACILITY FORM 602

(ACCESSION NUMBER) 54 (PAGES) NASA-Cr# 66112 (NASA CR OR TMX OR AD NUMBER)

(THRU) 1 (CODE) 33 (CATEGORY)



PREPARED UNDER CONTRACT NO. NAS 1-5533 BY

THE WARNER & SWASEY COMPANY
CONTROL INSTRUMENT DIVISION
32-16 DOWNING STREET
FLUSHING, NEW YORK 11354

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA CR-66112

W&S TR-39

POSSIBLE TECHNIQUES FOR OPTICAL MEASUREMENT OF TEMPERATURE AND CONCENTRATION PROFILES IN A SUPERSONIC RAMJET

By Burton Krakow, Richard H. Tourin, and Gunter J. Penzias

Distribution of this report is provided in the interest of information exchange. Responsibility for the contents resides in the author or organization that prepared it.

Prepared under Contract No. NAS 1-5533 by

THE WARNER & SWASEY COMPANY
CONTROL INSTRUMENT DIVISION
32-16 Downing Street
Flushing, New York 11354

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LANGLEY RESEARCH CENTER
HAMPTON, VIRGINIA

ABSTRACT

The most likely possibilities of several spectroscopic methods for measurement of temperature and concentration profiles in a gas have been studied for possible application to an experimental hypersonic ramjet. The requirements and conditions of the ramjet restrict the solution of the measurement problem to a narrower range than would be considered for laboratory applications. The barriers to direct application of existing methods have been analyzed and new variations of these methods that may overcome these barriers have been devised. The discrepancy between available knowledge and that required by the new methods has been evaluated, the research needed to close the gap between them determined, and the effort involved estimated. Spectroscopic instrument technology is generally available for the optical measurements described in this report.

PRECEDING PAGE BLANK NOT FILMED.

TABLE OF CONTENTS

ABSTRACT		iii
SUMMARY		1
I.	INTRODUCTION	1
II.	OPTICAL TECHNIQUES FOR STUDY OF HOT GASES	2
	A. Inhomogeneous Gases	2
	B. Homogeneous Gases	11
	C. Instrumentation	18
III.	ADAPTATION OF OPTICAL MEASUREMENT TECHNIQUES TO RAMJET STUDIES	20
	A. Combination of Line Absorption and Spatial Scanning	20
	B. Development of a Method for Analyzing Spatial Scanning of Absorptance and Radiance of Flames	22
	C. Combination of Spatial and Spectral Scanning	25
	D. Seeding	25
	E. Crossed Beams	31
	F. Line-of-Sight Measurements	34
IV.	RESEARCH REQUIRED	37
	A. Evaluation of Working Molecules	37
	B. Spectroscopic Parameters	38
	C. Theory	38
	D. Testing	39
	E. Organization of Research	39
V.	CONCLUSIONS	39
APPENDIX		43
REFERENCES		46

PRECEDING PAGE BLANK NOT FILMED.

POSSIBLE TECHNIQUES FOR OPTICAL MEASUREMENT OF TEMPERATURE AND CONCENTRATION PROFILES IN A SUPERSONIC RAMJET

By B. Krakow, R. H. Tourin, and G. J. Penzias

SUMMARY

Spectroscopic methods have been used in the past to measure temperature profiles in hot gases in the research laboratory, and to measure combustion gas composition in situ. In the present work, we have studied the most likely possibilities among these methods for measurement of temperature profiles and composition profiles in an experimental hypersonic ramjet. This report discusses several such methods which illustrate techniques that are potentially applicable to the ramjet. The requirements and conditions of the ramjet restrict the solution of the measurement problem to a narrower range than would be considered for laboratory applications. We have analyzed the barriers to direct application of these methods to an operating ramjet, and have devised new variations of the methods that are potentially capable of overcoming these barriers. The discrepancy between available knowledge and that required by the new methods has been evaluated, the research needed to close the gap between them determined, and the effort involved estimated. Spectroscopic instrument technology is generally available for the optical measurements described in this report.

I. INTRODUCTION

Optical methods of gas temperature measurement are desirable for dynamic systems, because they do not disturb the system. Moreover, they may be the only feasible methods if the temperature is very high or the specimen inaccessible to sensing probes. However, in optical measurements of a gas with a temperature gradient along the line of sight, the temperature at a particular point cannot generally be determined optically without simultaneous consideration of the thermal structure of the entire optical path.

At present, there is no fully developed and tested optical method for measuring temperature and concentration profiles of the inhomogeneous hot gases (i.e. hot gases

having gradients of temperature, pressure, and/or composition) in a supersonic ramjet. In attempting to obtain one, two possible approaches are (1) the adaptation of methods used to obtain profiles of different types of hot gas systems and (2) extension of techniques for studying homogeneous gases with properties similar to those of the ramjet. We have explored both these approaches. In Section IIA methods are described that have been used for measuring gas temperature or composition profiles, and the barriers to their employment in ramjet studies are explained. Section IIB presents techniques for analyzing homogeneous gases that have possibilities for extension to the inhomogeneous case. Availability of instrumentation is discussed in Section IIC. Section III presents a number of ideas for adapting techniques described in Section II to the ramjet problem. Section IV discusses research that is needed to ascertain the practicability of the ideas in Section III and to pave the way for their application.

II. OPTICAL TECHNIQUES FOR STUDY OF HOT GASES

A. Inhomogeneous Gases

Three optical techniques have been used for extraction of temperature profiles of thermally inhomogeneous hot gases. They are:

1) Spectral scanning along a single line of sight.
2) Spatial scanning at a single wavelength.
3) Optical isolation of a local region in the line of sight.

(1) Spectral Scanning

Figure 1 shows a specimen as it is considered for line of sight spectral scanning. Spectroscopic measurements are made of the radiation that is emitted and transmitted along a line of sight through the body defined by the arrow I. The temperature profile along this line of sight is calculated from the spectroscopic measurements.

When temperature gradients exist in a gas, it is possible to consider the gas to consist of a series of zones, each of which is isothermal within the precision of measurement. If the gradients are steep the regions would have to be small, but, in principle, such a division always can be made. If we number these zones serially from 1 to n, with zone 1 nearest the detector, the irradiance of the detector, $H(\lambda_j)$, by radiation of wavelength λ_j, is given (ref. 1) by

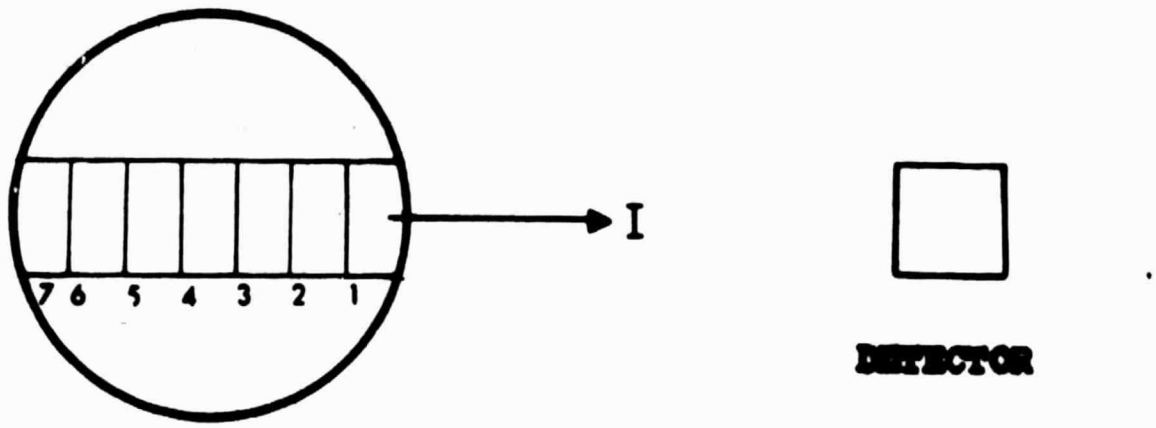


Fig. 1 Schematic for spectroscopic method of temperature profile measurements.

equation (1)

$$H_m(\lambda_j) = \sum_{i=1}^{n} W_{bm}(\lambda_j, T_i) \left[\bar{\tau}_{(i-1)}(\lambda_j) - \bar{\tau}_i(\lambda_j) \right] \quad . \qquad (1)$$

Physically, $\bar{\tau}_i(\lambda_j)$ is the transmittance of the section of the sample, composed of zones 0-i, and $W_{bm}(\lambda_j, T_i)$ is the spectral emittance of a blackbody at T_i and λ_j, where T_i is the temperature of the i zone.

For an isothermal temperature profile, n = 1, and equation (1) therefore contains only one transmittance $\bar{\tau}(\lambda_j)$, provided that the optical path outside the hot gas sample is free of absorbing gas, i.e. the path is evacuated or flushed with a non-absorbing gas so that $\bar{\tau}_o(\lambda_j) = 1$. Moreover, $\bar{\tau}(\lambda_j)$ can be measured directly, as can $H_m(\lambda_j)$. Equation (1) then reduces to

$$H_m(\lambda_j) = W_{bm}(\lambda_j, T) \left[1 - \bar{\tau}(\lambda_j) \right] \quad . \qquad (1a)$$

Equation (1a) has the form of Kirchhoff's law. It can be solved for the only remaining variable $W_{bm}(\lambda_j, T)$ from which the temperature can be determined. This is the emission-absorption method of temperature measurement. If equation (1a) is applied to a non-isothermal system, the wavelength dependent result is a weighted average of the temperatures in the sample with different weighting at each wavelength.

In applying equation (1) to a non-isothermal temperature profile, spectral emittance is measured at n different wavelengths, having n different sets of values of $\bar{\tau}_i(\lambda_j)$. This yields n independent simultaneous equations for calculating the n temperatures.

The infrared transmittances that appear in equation (1) are themselves somewhat temperature-dependent. Moreover, of the n transmittances that must be obtained, only one $\left[\bar{\tau}_n(\lambda_j)\right]$ can be measured directly. Therefore,

solution of equation (1) requires some a priori knowledge of the transmittances of the molecular species comprising the hot gas specimen, particularly a knowledge of how they vary with temperature. This knowledge may take the form of empirical data, theoretical formulas, or a combination of these. Once such information is available, the system of irradiance equations, equation (1), can be solved for the thermal structure of the specimen. Developed and tested iterative procedures for carrying out this solution are reported in references 2 and 3.

In applying this method to a hydrogen burning ramjet, the first problem is the choice of a good working molecule. The strongest infrared absorber present would be water vapor and this would not absorb very strongly in specimens of the size of the ramjet (see Appendix) unless (1) measurements are made at wavelengths where absorption is strong near the band center (introducing the problem of interference due to atmospheric water vapor absorption) and (2) the spectral slit widths are small. Meeting these requirements would involve eliminating atmospheric interference along the optical path and using a high resolution spectrometer. Moreover, this method has been used only when composition was a known function of temperature, not when the two are independent as they may be in the ramjet.

(2) Spatial Scanning

Figure 2 depicts the same specimen as figure 1 with the parameters that are useful for analysis of a spatial scan of its spectral radiance and transmittance. Such measurements are used extensively on optically thin plasmas, i.e. plasmas in which photons emitted from the inner regions are not absorbed before reaching the outer boundary.

a. Spatial scanning of optically thin cylindrically symmetric specimens.

Experimentally a lateral intensity profile is obtained, giving H(x), the spectral radiance in the y direction at a distance x from the yz plane (in energy per unit time, unit area perpendicular to the y direction, unit frequency interval and unit solid angle) . At wavelengths where the specimen is optically thin, the brightness per unit depth (called "emission coefficient" by some authors) f(r) at the distance r from the origin (in energy per unit time, unit volume, unit frequency interval and unit solid

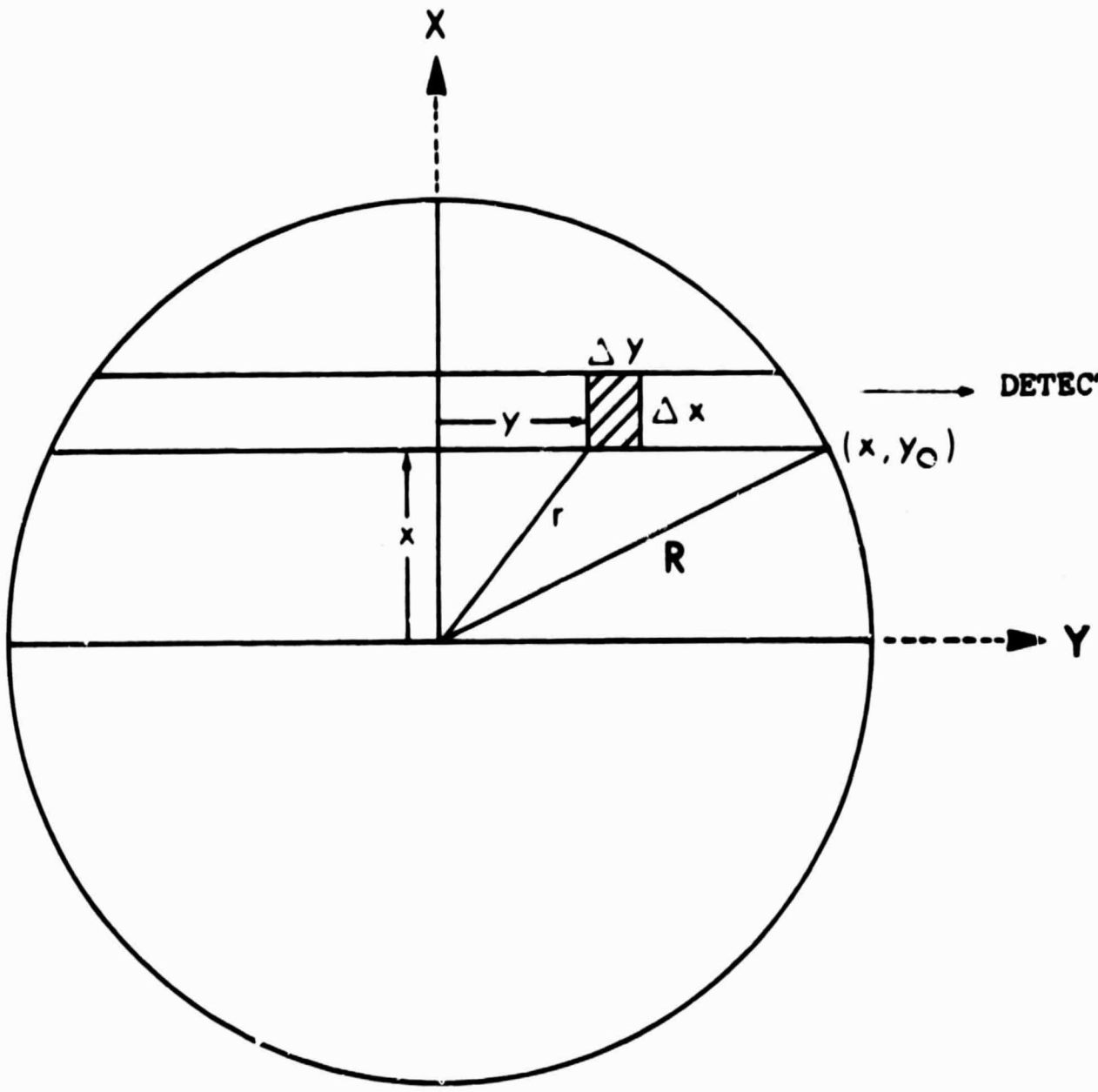


Fig. 2 Schematic for spatial scanning method of temperature profile measurement.

angle) is related to the spectral radiance from the plasma column of length $2\,y_o$ and cross section $\Delta x \wedge z$

$$H(x)\,\Delta x\,\Delta z = \sum_{-y_o}^{+y_o} f(r)\,\Delta x \wedge y \wedge z \quad .$$

Passing over to infinitely small volume elements, and by symmetry:

$$H(x) = 2\int_0^{y_o} f(r)\,dy$$

$$H(x) = 2\int_0^{(R^2-x^2)^{\frac{1}{2}}} f(r)\,dy \quad .$$

From the substitution $y = (r^2 - x^2)^{\frac{1}{2}}$

$$H(x) = 2\int_x^R \frac{f(r)\,r\,dr}{(r^2 - x^2)^{\frac{1}{2}}} \quad . \qquad (2)$$

By using Abel's transformation (for a proof see ref. 4, page 177)

$$f(r) = -\frac{1}{\pi}\int_r^R \frac{H'(x)\,dx}{(x^2 - r^2)^{\frac{1}{2}}} \quad . \qquad (3)$$

The boundary radius R of the source ($H = 0$ for $x > R$) and the x axis are divided into N equal increments of length $\wedge$. The data for the inversion are the radiances measured at $x = 0, .. k, .. (N-1)$ in units of $\wedge$.

$x_k = k\Lambda, \quad r_n = n\Lambda, \quad R = N\Lambda$

An abbreviated notation is used (H_o, H_k, ... f_o, f_k), thus H_o means the measured radiance across the origin. It has to be remembered, that H values are integrated over the optical path, and that the f values obtained by the inversion process refer to optical path unity.

Numerous authors (refs. 5 to 7, for example) have described mathematical procedures for extracting the profile of f(r) from the measured H(x) profile. Generally, in order to solve equation (3), an analytically integrable function J(x) is fitted to the H_k values obtained as a set of numerical data. The various methods differ by the way this is done.

Many workers have preferred not to use the Abel transformation. Instead, they have carried out numerical solutions of equation (2), treating f(r) as a step function of the radius (refs. 8 and 9).

b. Spatial scanning of cylindrically symmetric specimens with self-absorption.

In flames and many plasmas, self-absorption cannot be neglected at any wavelength at which radiance is appreciable. With such samples, lateral profiles of transmittance as well as of radiance are measured. However, currently available methods for mathematical analysis of such a system are only applicable if the Beer-Lambert absorption law holds, that is if local absorption coefficients are constant over the spectral slit width employed. In this case, the measured transmission $\tau(x)$ at the position x is given by

$$\ln \tau(x) = -2 \int_x^R \frac{k(r)\, r}{(r^2 - x^2)^{\frac{1}{2}}}\, dr \quad . \qquad (4)$$

This equation has the same form as equation (2) and may be solved for k(r) by any of the procedures used to solve equation (2) for f(r).

The spectral radiance at the position x is given by

$$H(x) = \int_{-y_o}^{+y_o} f(r) \exp\left[- \int_{y}^{y_o} k(r') \, dy' \right] dy \quad . \qquad (5)$$

Since k(r) is known, the exponential in equation (5) may be evaluated and equation (5) then solved for f(r) (refs. 9 to 11). The temperature profile may be obtained from the emission and absorption coefficients by using Kirchhoff's law, which says that their local ratio must be equal to the Planck function at that wavelength and at the local temperature.

Using this technique, Elder, Jerrick and Birkeland (ref. 11) have reported obtaining temperature profiles with 4 percent precision throughout the region where $r/R < 0.8$. The temperatures near the edge of their plasma were not reported at all. This was because the absorption was too small in this region to give adequately accurate results. This lack of information at the edge of the sample is not very important to plasma physicists but may be a serious gap in ramjet studies.

The requirement of applicability of the Beer-Lambert absorption law prevents direct adoption of this technique for ramjet measurements. All the lines in the ramjet spectrum will be so sharp (order of 0.1 cm^{-1} half width) that the absorption coefficient will vary very markedly over any practical spectral slit width.

(3) Optical Isolation

a. Crossed beams.

Figure 3 is a schematic illustration of a technique used by Muntz (refs. 12 and 13) to measure temperatures in a low pressure stream of nitrogen. An electron beam produces nitrogen ions as it passes through the sample. Radiation from these ions is then measured at frequencies where the un-ionized specimen is optically clear. All of this measured radiation comes from a small volume (which may be considered isothermal) about the intersection of the electron and optical beams.

The rotational temperature of a molecular emission may be obtained by measuring the relative intensities of the rotational line structure in the vibrational bands. The vibrational temperature may be obtained by measuring the relative intensities of various vibrational bands in the emission. In order to obtain this information, it is necessary to be able to predict the relative intensities in the

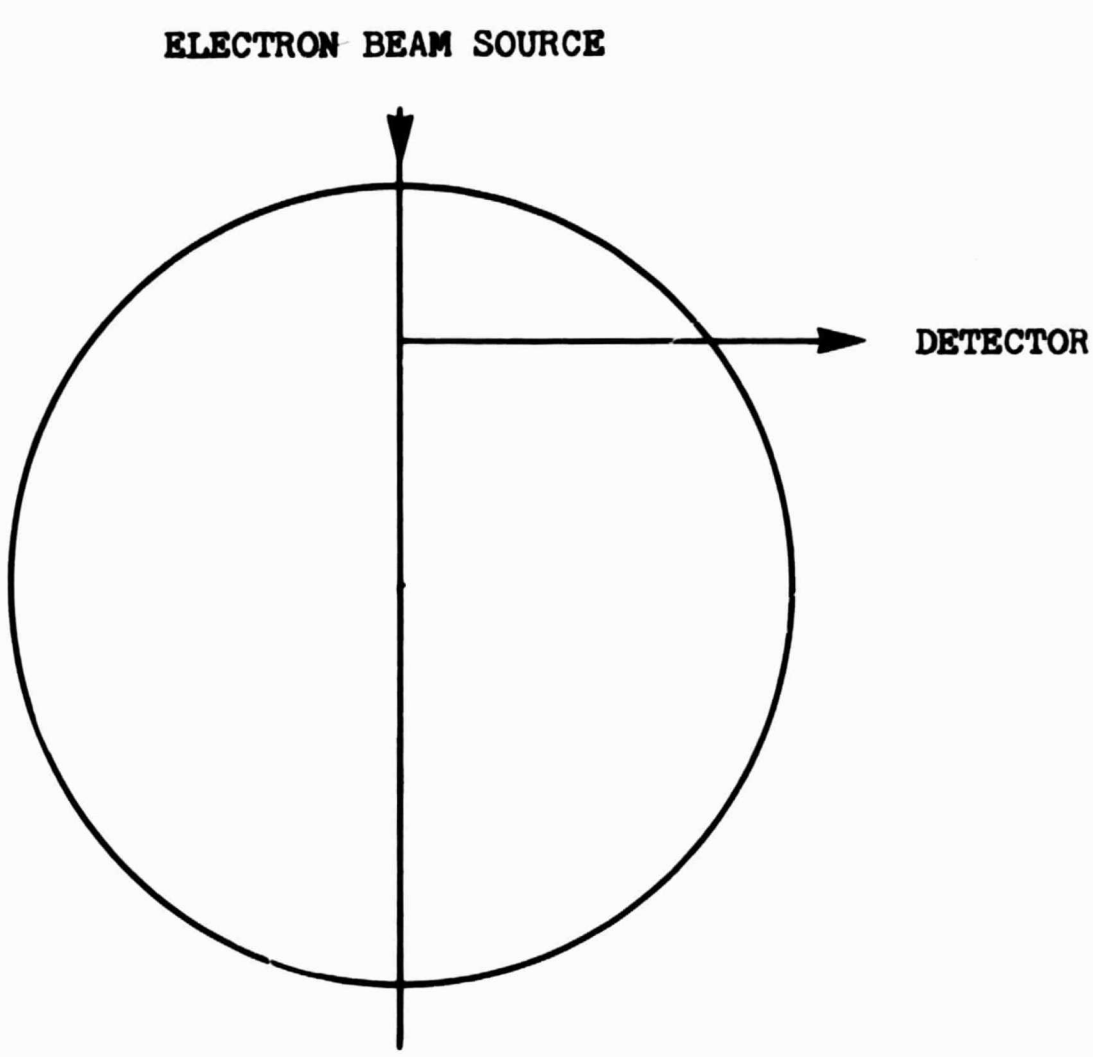


Fig. 3 Schematic for crossed beam method of temperature profile measurement.

emission for arbitrary population distributions in the neutral nitrogen molecules. The accuracy of the temperature determinations depends on the accuracy of the theoretical description of the excitation and emission process and, of course, on the accuracy of the actual measurements.

Use of this method requires that the static pressure be within about an order of magnitude of 1 mm Hg.

b. Local seeding.

A spectral region in which the sample is optically clear may be made optically active locally by injecting a suitable material (e.g. sodium or cesium) from a probe (ref. 14). The probe should be located far enough upstream of the optical path so that the flowing gas is not appreciably disturbed or cooled, and allow the injected material to reach the gas temperature. The temperature of the injected material may be measured by the line reversal, emission-absorption, or the two-line method. The temperature measured is that existing at the intersection of the optical path and the stream of injected material.

B. Homogeneous Gases

(1) Application of Band Models

Penzias and Maclay (ref. 15) have determined H_2O and CO_2 concentrations in homogeneous gases from measurements of infrared absorptance.

As mentioned earlier, the absorption coefficients of the gases present in hydrogen-air flames all vary considerably over practical spectral slit widths. In fact, spectral slit widths of standard commercial spectrometers will usually contain many spectral lines. For such situations, band models represent good quantitative relationships between spectral transmittance and the temperature and composition of the sample.

The band model Penzias and Maclay chose to use was the random band model with constant line strengths and widths. According to this band model, the transmittance of a homogeneous gas over a spectral interval containing many lines can be expressed as follows

$$- \ln \tau = 2\pi \left[\gamma/d \right] f(x) \qquad (6)$$

in which τ is the transmittance, γ is the average line half width and d the average line spacing in the spectral interval considered. x is given by

$$x = \frac{\left[S/d \right] \ell}{2\pi \left[\gamma/d \right]} \qquad (7)$$

in which S is the average line strength and ℓ is the length of the optical path. The function f(x) is the Ladenburg and Reiche function, whose mathematical properties are well known and whose values have been tabulated (refs. 16 and 17).

The average line half-width γ varies with the partial pressure of the gases present as follows:

$$\gamma = \gamma_a{}^{\circ} P_a + \sum_i \gamma_{bi}{}^{\circ} P_{bi} \qquad (8)$$

where $\gamma_a{}^{\circ}$ is the half-width at unit pressure for self-broadening (i.e. for collisions between two absorbing molecules) and P_a is the pressure of absorbing gas. $\gamma_b{}^{\circ}$ is the half-width at unit pressure for foreign gas broadening (i.e. for collisions between absorbing molecules and other molecules in the gas mixture which do not absorb radiation at frequency ν) and P_b is the pressure of the non-absorbing line-broadening gas. The summation is over all species of non-absorbing molecules.

The line strength is directly proportional to the pressure of the absorbing gas, thus

$$S = S^{\circ} P_a \qquad (9)$$

P_a is the pressure of the absorber, and S° is the strength at unit pressure.

The following step-by-step procedures can be applied in determining the concentrations:

(1) Determine the geometrical path length ℓ in cm.

(2) Determine the static pressure, P_T, and the temperature of the phenomenon being investigated.

(3) Measure the absorptance of the species to be determined, at the specified frequency and spectral slit-width of the band model parameters to be used.

(4) From a knowledge of the gas temperature, the values of S^o/d and γ^o/d are determined from graphs similar to figures 4 and 5.

(5) Using the information obtained in steps (1) through (4), the following equations are solved for P_a, the pressure of the absorbing gas in atmospheres, which is the desired result.

$$\ln \frac{1}{\tau} = \frac{(S^o/d)\, P_a\, \ell\, f(x)}{x} \qquad (10)$$

$$x = \frac{(S^o/d)\, P_a\, \ell}{2\pi \left[P_a \frac{\nu_a^o}{d} + (P_T - P_a) \frac{\gamma_b^o}{d} \right]} \qquad (11)$$

The solution to the above equations requires iteration, however, the number of cycles may be reduced by a judicious first choice of P_a, based upon the theoretical concentrations expected for the gas phenomenon.

Equation (11) assumes that all the foreign gas broadeners in the specimen have the same γ_b^o. This is a good approximation for a hydrogen-air flame in which the foreign gas broadener is almost all nitrogen. Oxygen and hydrogen, which will be present in only small quantities anyway, do have broadening powers that are similar to that of nitrogen. In cases where a large amount of hydrogen or

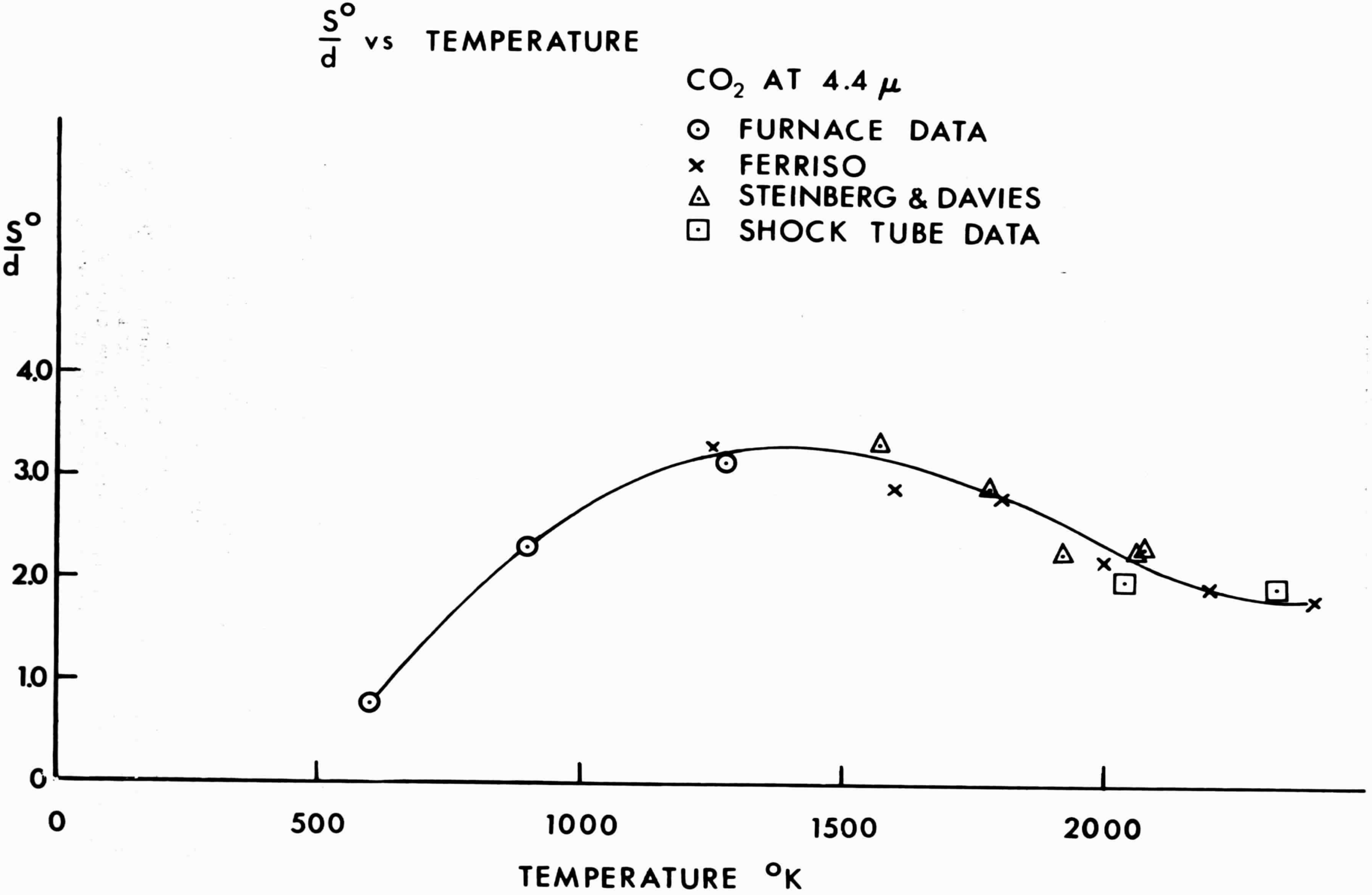


Fig. 4 Strength band model parameter $(S^*/d)_{CO_2}$ versus temperature.

$$\gamma = \frac{\left(\frac{\gamma}{d}\right)_{T\,^\circ K}}{\left(\frac{\gamma}{d}\right)_{1273\,^\circ K}}$$

$CO_2 - N_2$ AT 4.4 μ

⊙ FURNACE DATA

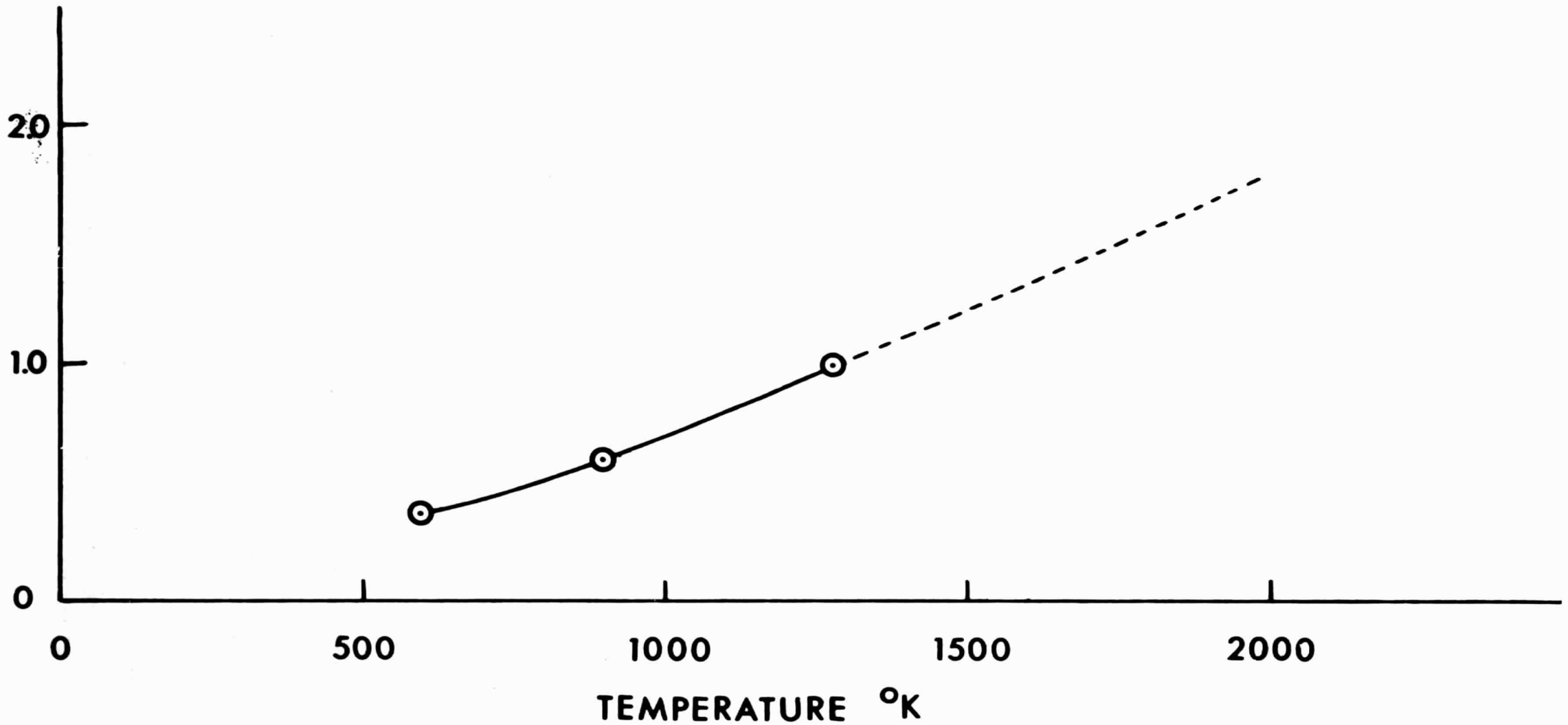


Fig. 5 Ratio of total half-width band model parameter $(\frac{\gamma^\bullet}{d})_T$, to half-width $(\frac{\gamma^\bullet}{d})_{1273}$ at 1273°K versus temperature.

oxygen is present, a suitably weighted average γ_b^o could be used.

(2) Absorption of a Line Source

Kaskan (ref. 18) has shown that OH can be determined by measuring the absorption in the ultraviolet $^2\Pi - ^2\Sigma$ band. This spectrum has been exhaustively analyzed (ref. 19) and a convenient reproduction is available (ref. 20). The f numbers of a number of lines in the 3064Å 0-0 band have been measured (ref. 21) and later corrected (ref. 22). Line shapes indicating some pressure broadening in a mixture of $2H_2O + O_2$ at 1473°K have been reported (ref. 21), but it has been shown, using the same data, that the pressure broadening under these conditions is actually very small (ref. 23). Consequently Kaskan assumed that the absorption lines have a pure Doppler shape. The most important consequence of this assumption is that with it the absorption coefficient becomes independent of pressure.

The method used to determine OH was the line absorption method in which a narrow emission line from a discharge in water vapor is absorbed by the broader absorption line in the flame. This method requires that the line shapes in emission and absorption be known; that the integrated absorption coefficient be known; that the resolving power of the spectrograph be high enough to separate the lines to be used from all other lines, but it need not be high enough to resolve the line shapes. This last requirement is easily met, but the other two are not.

This method becomes particularly simple if the source emission line is much narrower than the absorption lines, so that it can be assumed that only the peak absorption coefficient is measured. This assumption is made in the following development.

It can be shown that for those lines for which f numbers (corrected) were measured

$$f_i = 3.07 \times 10^{-4} \; A_K/(2J + 1) \qquad (12)$$

where A_K is the relative transition probability tabulated for all of the lines by Dieke and Crosswhite (ref. 19), and J is the rotational quantum number in the lower, $^2\pi$ state, both

for the level i. From the definition of the f number it follows that

$$\left[OH \right]_i = \frac{mc^2 (2J + 1)}{\pi e^2 \, A_K} \int k_\nu \, d\nu \times 3.25 \times 10^3 \qquad (13)$$

where $\left[OH\right]_i$ is the number of molecules per cm^3 in the rotational level i, m and e are the mass and charge of the electron, c is the velocity of light, k_ν is the absorption coefficient in cm^{-1} at the wave number ν. The integral is taken over the whole line. For a line with a Doppler shape the integrated absorption coefficient is

$$\int k_\nu \, d\nu = 1.065 \, k_o \, \Delta\nu_D \qquad (14)$$

where k_o is the peak absorption coefficient at the center of the line and $\Delta\nu_D$ is the width in cm^{-1} of the line at half intensity. Combining equations (13) and (14)

$$\left[OH\right]_i = \frac{mc^2 (2J + 1)}{\pi e^2 \, A_K} k_o \, \Delta\nu_D \times 3.46 \times 10^3 \quad . \qquad (15)$$

If rotational equilibrium exists

$$\left[OH\right]_i = \left\{ \left[OH\right] / Q_{r,v} \right\} (2J + 1) \exp(-E_i/RT) \qquad (16)$$

where $\left[OH\right]$ is the total concentration of hydroxyl in the $^2\Pi$ state, $Q_{r,v}$ is the rotation-vibration partition function and E_i is the rotational energy of the level i. Combining equations (15) and (16) and inserting the numerical value of the constants

$$\left[OH\right] = (Q_{r,v}\, k_o\, \Delta\nu_D/A_K) \exp(E_i/RT)\, 3.94 \times 10^{15} \quad . \quad (17)$$

Equation (17) as written can be used to calculate $\lfloor OH \rfloor$ from the results for any line. The partition functions were calculated (ref. 24) by the equation

$$Q_{r,v} = (kT/hcB) \sum_n \exp(-E_n/kT) \quad (18)$$

where k is the Boltzmann constant, h is Planck's constant, B is the rotational constant for OH taken as 18.51 cm^{-1}, and E_n are the energies of the vibrational levels.

Temperatures may be obtained (ref. 24) from two measured $\left[OH\right]_i$ values by using the formula

$$\frac{\left[OH\right]_i}{\left[OH\right]_j} = \frac{g_i}{g_j} \exp\,(E_j - E_i)/kT \quad . \quad (19)$$

g_i is the degeneracy of the energy level corresponding to E_i.

C. Instrumentation

Instruments and components are available for optical and spectroscopic studies of ramjet combustion gases, in ground tests and in flight. Commercial spectrometers can be used for the ground tests, with transfer optics designed according to well-known principles. Many such instrument setups have been built for application to similar problems. For example, spectrometer systems have been successfully applied to measure emission, to measure absorption, and to measure emission and absorption simultaneously, in shock tubes (refs. 25 to 29), transient solid propellant flames (refs. 30 and 31), liquid propellant flames (ref. 32), jet engine combustion gases (ref. 33), rocket exhaust gases (refs. 34 to 37), and plasmas (refs. 10, 11, and 38). In these various applications many of the same instrument problems as are involved in the supersonic ramjet application have been solved, in particular

the problems of short time for measurement (microseconds to milliseconds) and signal-noise ratio. Extending these same methods to the ramjet requires adaptation of instruments like those described in references 10, 11, and 25 to 38, rather than solving any essentially new instrument problems. The limitations on applicability of spectroscopic techniques to the supersonic ramjet have to do with the nature of the hot gas specimens themselves. Therefore, this study is concerned with methods and principles, in relation to the fundamental optical properties of the hot gases in a supersonic ramjet. When these problems have been solved, it will then be appropriate to consider instrumentation more specifically. In the light of experience, no significant limitation due to instruments is apparent. After a method is successfully developed, some instrument limitations may become apparent, but even then there is no evidence that a major instrument development effort will be required later. For example, the time required to make a measurement depends on the signal/noise of a particular specimen, not on how fast an instrument can operate. The speed capability of present instruments is already beyond what is practical to use for the ramjet application. Problems of access to the hot gases (e.g. windows) are likely to prove more significant obstacles than instrument problems, although here also, access problems of comparable difficulty have been solved (refs. 32, 39 and 40). Access problems will have to be considered later, in relation to the engine configuration to be used.

Consideration of limitations on flight instrumentation was specifically excluded from this study (cf. Appendix, paragraph #9). However, it is of interest to note that many spectroscopic devices have been built for in-flight measurements of radiation from rocket plumes and aircraft. These include instruments for mounting on board a ballistic missile in flight, to measure spectra of the exhaust plume. These are rugged, miniaturized instruments, with provisions for telemetering data to a ground station. Similar instruments have been built for use in research aircraft, to observe remote radiating phenomena. Examples of airborne spectroscopic instruments may be found in references 41 and 42.

III. ADAPTATION OF OPTICAL MEASUREMENT TECHNIQUES TO RAMJET STUDIES

A. Combination of Line Absorption and Spatial Scanning

1. Description of Method

In the line absorption method, with Doppler shaped OH lines, if the emission line is much narrower than the absorption line, it can be assumed that only the peak absorption coefficient is measured. In this case the measured peak absorptance should follow the Beer-Lambert absorption law. This is true even if the absorption coefficient of the absorbing gas varies widely over the spectral slit width of the spectrometer. The only requirement is that resolving power of the spectrometer be high enough to separate the line used from the adjacent lines.

As long as the Beer-Lambert law is applicable, a radial profile of k_o can be obtained for a radially symmetric specimen. This is accomplished by measuring a lateral profile of k_o by spatial scanning and putting the result into equation (4). This should be done with at least 2 lines having widely separated J values. Temperature and OH concentration can then be obtained at any radius with equations (19) and (17) respectively.

2. Output

a. Temperature profiles.

b. OH radical concentration profiles.

3. Specimen Requirement

a. Radial symmetry.

b. Temperature measurement requires local thermodynamic equilibrium in rotational or vibrational energy levels.

c. Temperatures that are high enough to allow sufficient concentrations of OH. Kaskan's specimens were at about 1500°K. The lower temperature limit has not been definitely established. For measurements of vibrational temperatures, this lower limit would be higher than for rotational temperature measurements because weaker bands would have to be used.

4. Accuracy

Errors in the local values of k_o produce equal fractional errors in $[OH]_i$ as can be seen from equation (15). In Kaskan's transmittance measurements, the noise levels were generally from one to five per cent of the discharge signal but he felt that the averaging times were sufficient to allow intensity measurements to one per cent of the source signal. Elder, Jerrick and Birkeland claimed 4 per cent precision in their determinations of local absorption coefficients by spatial scanning. Unfortunately they did not report the precision of the transmittance measurements involved in these determinations. If we assume that the precision of the transmittance measurements made by Elder, Jerrick and Birkeland was similar to that of Kaskan, we would conclude that 4 per cent precision in local $[OH]_i$ determinations would be obtained with such measurement precision.

Experimental errors become serious when the measured transmittance is high because the noise level becomes a large percentage of the absorption. On the other hand, when the transmittance is very low, the finite width of the source emission line becomes important leading to failure of the assumption that the measured absorption is the peak absorption of the OH line. Therefore, good results can only be obtained with lines whose transmittances are in the intermediate region.

Additional errors will stem from inaccuracies in the transition probabilities. The best OH transition probabilities that are currently available have an estimated accuracy of 15 per cent (refs. 43 and 44).

The accuracy of temperature measurements can be estimated by means of a differentiation of equation (19) which yields

$$\frac{d\,[OH]_i / [OH]_j}{[OH]_i / [OH]_j} = \frac{E_i - E_j}{kT} \qquad \frac{dT}{T}$$

where k is 0.6952 $cm^{-1}\ deg^{-1}$.

This shows that the percent error in the measured temperature is proportional to the percent error in $[OH]_i / [OH]_j$ and inversely proportional to $(E_i - E_j)/ kT$.

If E_j and E_i represent different rotational energy states of the same vibrational level, their difference will be of the order of 100 cm^{-1}. Vibrational state differences are about 3000 cm^{-1}. Therefore, vibrational temperatures will have smaller experimental errors and rotational temperatures greater experimental error than the $[OH]_i / [OH]_j$ ratio for the expected temperature range in the ramjet. This ratio, in turn, is likely to be a little more accurate than $[OH]_i$ because of cancellation of systematic errors.

5. Availability of Technology

a. Spectroscopic instrumentation technology is available.

b. Spectroscopic parameters.

At the present time f numbers have been measured for the 0 - 0 band of OH (refs. 43 and 44). These could be used for OH concentration and rotational temperature measurements. Determinations of transition probabilities for other bands would be needed for measurements of vibrational temperatures.

c. Theory.

In its simplest form, the necessary theory is just a consolidation of several theories that already exist and should require little development. However, profile measurements must be expected to be more sensitive to experimental or theoretical errors than are the measurements on homogeneous systems. Therefore, it may be desirable to work out corrections for the small amount of pressure broadening present and for the finite width of the emission line.

B. Development of a Method for Analyzing Spatial Scanning of Absorptance and Radiance of Flames

1. Description of Method

Available methods for analyzing spatial scans have been developed by plasma physicists who have found the Beer-Lambert law suitable for their media. As indicated earlier, this law is not applicable to combustion gases for practical

spectral slit widths. On the other hand, band models are available that do represent the absorptance of combustion gases fairly well. Development of methods for analyzing spatial scans of flames using absorption laws based on band models seems feasible.

Band models themselves apply to homogeneous specimens only. However, they can be extended to inhomogeneous systems by the Curtis-Godson method (ref. 45). Meteorologists use this method for inhomogeneous atmospheric gases and it has recently been proven suitable for hot combustion products (ref. 46).

Once such a method is developed, optical, chemical and thermal analyses of radially symmetric flames should become possible as a general rule. In applying this method, it would probably be necessary to know S^o/d and γ^o/d as a function of temperature for the working molecule.

2. Output

a. Temperature profiles.

b. Concentration profile of the working molecule.

3. Specimen Requirements

a. Radial symmetry.

b. Presence of a working molecule with adequate optical activity.

c. Local thermodynamic equilibrium for working molecule.

4. Accuracy

Accuracy of spatial scan analysis would depend on the accuracy of the absorption law and on the wavelengths studied. The wavelength affects the accuracy of the result in two ways:

(1) The relative variation of the Planck function with temperature is different at each wavelength and the accuracy of temperature determinations increases with this relative variation.

(2) Also, the limiting accuracy of spectral measurements varies with wavelength.

Again let us use the sodium D line (.59μ) measurements of Elder, Jerrick and Birkeland for comparison. The

slope of the Planck function at 2000°K and 0.59μ is 0.62 per cent per degree. At the same temperature it is 0.15 percent per degree at 2.5μ where water vapor is optically active and 1.27 percent per degree at 0.3μ where OH is optically active. On this basis alone the 4 percent precision in temperature measurements reported by Elder, Jerrick and Birkeland should become about 16 percent for measurements made at 2.5μ and 2 percent for measurements made at 0.3μ.

Instrumental errors are greater in the ultraviolet and infrared than in the visible. Consequently, temperature profiles extracted from measurements at 0.3 and 2.5μ would be somewhat less precise than indicated in the preceding paragraph.

5. Availability of Technology

a. Spectroscopic instrumentation technology is available.

b. Working molecules.

The ramjet may or may not contain a suitable working molecule. H_2O and OH are possibilities. According to the information in the appendix of this report, the specimen size may vary from 1/2-inch to 24 inches and the static pressure will be generally in the range from 3 to 0.1 atmospheres, with the largest path and lowest pressure corresponding to conditions at the nozzle exit. For a specimen at 5000°R with a pressure of 3 atmospheres and 5 inch path, which may be representative of conditions somewhere in the combustor, current available data indicate that enough H_2O and OH should be present so that either one might serve as the working molecule. For a specimen at 2800°R with a pressure of 0.1 atmospheres and 24 inch path, representative of conditions at the nozzle exit, indications are neither H_2O nor OH would have enough optical activity. At this time our knowledge of the requirements of the method and the spectra of the molecules are inadequate for a definite determination. If both these molecules prove inadequate, seeding should be considered.

c. Spectroscopic parameters.

Band model parameters for the working molecule would have to be obtained.

d. Theory.

A considerable amount of development of mathematical techniques is required.

C. Combination of Spatial and Spectral Scanning

1. Description of Method

It was noted in Section II that spatial scanning results are very inaccurate at the edge of the specimen. On the other hand, the results of spectral scanning are best at the edge of the specimen. Therefore, a combination of the two techniques should give good picture of the entire system.

2. and 3. Output and Specimen Requirement

Same as Method B.

4. Accuracy

As stated above, adding spectral to spatial scanning should improve the already analyzed accuracy of the latter. The extent of this improvement depends on the suitability of the working molecule or molecules.

5. Availability of Technology

The technology for this method is very similar to that of Method B. Here we will only consider requirements that have not already been given for Method B.

a. Spectroscopic instrument technology is available.

b. Spectroscopic parameters would be needed at many wavelengths.

c. Theory.

Once the theoretical development of Method B is complete, combining it with available spectral scanning techniques should be a fairly straightforward problem.

D. Seeding

1. Description of Method

Local seeding is accomplished by injecting a suitable optically active material (e.g. cesium or sodium) from a probe into the gas stream. The probe should be located

far enough upstream of the optical path so that the flowing gas is not appreciably disturbed or cooled, and to allow the injected material to reach the gas temperature.

In the emission-absorption method, emission and absorption of the sample are measured for one spectral interval. This interval may contain any number of lines and involve any amount of self absorption without damage to the measurement accuracy. In the two-line method, only emission is measured but it must be done for two wavelength intervals. Moreover, a single line must be isolated in each of these intervals and self absorption must be carefully avoided.

Sodium is the most popular seeding material. Buchele (ref. 14) introduced sodium into hot gas streams, in the form of sodium bicarbonate powder, for line reversal measurements. At pressures below 20 atm. his injection rate w was

$$w \approx C_1 \, My/p$$

where $C_1 = 0.16$ g atm in^{-1} min^{-1}, M is Mach number, p static pressure; and y, the diameter of the cylindrically shaped stream of sodium vapor. With p equal to 1 atm and y equal to one inch this formula yields a molar density of 1.5×10^{-10} moles/cc of sodium or a sodium mole fraction of 0.25×10^{-4}. This would be a reasonable concentration for line reversal or emission-absorption measurements with resonance lines of any alkali metal. The concentration can vary quite widely without affecting the accuracy of these measurement techniques.

When the two-line method is used, the quantity of optically active material is much more critical. Tables I, II, and III list emission intensity ratios of lines of lithium, iron, and sodium, respectively, that are suitable for two-line measurements. The proportionality constant needed to calculate absolute line intensities from the data given in these tables is the same for all lines of a given element. It cancels in the ratio. These ratios are valid only when there is no self absorption. The importance of self-absorption can be illustrated by considering the line ratio for sodium given in Table III. The resonance line has been used in computing the ratios. Although the ratios are theoretically possible, they may not be achievable in practice because self-absorption cannot be eliminated and the ratio will approach unity. In order to limit self-absorption as much as possible, the concentration of lithium or iron

TABLE I

Emission Intensity Ratio for 2 Lithium Lines

$$A = 1.2 \times 14904 \exp\left[\frac{-14904}{0.6952T}\right]$$

α Intensity of line at 14904 cm^{-1}

$$B = 13 \times 16379 \exp\left[\frac{-31283}{0.6952T}\right]$$

α Intensity of line at 16379 cm^{-1}

T(°K)	A	B	A/B
1500	13.8×10^{-3}	2.01×10^{-8}	6.87×10^{5}
2000	39.9×10^{-2}	3.64×10^{-5}	10.9×10^{3}
2500	33.7×10^{-1}	3.28×10^{-3}	10.3×10^{2}
3000	14.1	6.58×10^{-2}	2.14×10^{2}

TABLE II

Emission Intensity Ratio for 3 Iron Lines

$$C = 0.0031 \times 23711 \exp\left[\frac{-23711}{0.6952T}\right]$$

$$D = 27 \times 23694 \exp\left[\frac{-52514}{0.6952T}\right]$$

$$E = 38 \times 23648 \exp\left[\frac{-50523}{0.6952T}\right]$$

T(°K)	C	D	E	C/D	C/E
1500	97.8×10^{-10}	86.0×10^{-18}	81.6×10^{-17}	1.13×10^{8}	1.19×10^{7}
2000	28.9×10^{-7}	24.3×10^{-12}	14.8×10^{-11}	1.14×10^{5}	1.95×10^{4}
2500	87.5×10^{-6}	48.0×10^{-9}	21.3×10^{-8}	1.82×10^{3}	4.11×10^{2}
3000	84.7×10^{-5}	74.1×10^{-7}	27.2×10^{-6}	1.14×10^{2}	3.11×10^{1}

TABLE III

Emission Intensity Ratio of 3 Sodium Lines

$$F = 0.90 \times 16956 \exp\left[\frac{-16956}{0.6952T}\right]$$

α Intensity of line at 16956 cm^{-1}

$$G = 1.8 \times 16973 \exp\left[\frac{-16973}{0.6952T}\right]$$

α Intensity of line at 16973 cm^{-1}

$$H = 1.8 \times 17576 \exp\left[\frac{-34549}{0.6952T}\right]$$

α Intensity of line at 17576 cm^{-1}

T(°K)	F	G	H	F/H	(F+G)/H
1500	1.324×10^{-3}	2.609×10^{-3}	1.293×10^{-10}	1.024×10^{7}	3.042×10^{7}
2000	7.715×10^{-2}	1.526×10^{-1}	5.115×10^{-7}	1.508×10^{5}	4.492×10^{5}
2500	8.843×10^{-1}	1.753	7.366×10^{-5}	1.201×10^{4}	3.580×10^{4}
3000	4.495	8.928	2.023×10^{-3}	2.222×10^{3}	6.635×10^{3}

should be adjusted so that the weaker of the two lines used has the minimum intensity necessary for accurate measurement. Self-absorption by the stronger line would then be minimized, and the large size of the thermal variation of the intensity ratio might overcome it. In the spectra of lithium and sodium, the lines are widely spaced and generally easy to separate by filters. However, the two lines to be used are in different regions of the spectrum and would require different detectors with consequent calibration difficulties. In iron the lines are close enough so that they could both be measured with the same detector but this element has such a rich spectrum that a spectrometer should be used.

Discussions with NASA personnel led to the suggestion that the large difference in the intensities of the two lines used in the two-line method (and the consequently large self absorption of the stronger one) could be decreased if two seed materials in different concentrations were used and one line of each material were measured. Suppose the 16379 cm^{-1} lithium line and the 16956 and 16973 cm^{-1} sodium line intensities were measured in a sample in which the ratio of lithium to sodium concentration was 10^4. The ratio of the radiances of the lithium to the sodium lines would be of the order of unity at 2000°K and would vary by about three orders of magnitude between 1500°K and 3000°K. It should be possible to segregate the lines used by means of filters and their frequencies are close enough together to allow making both measurements with the same detector. However, the proportionality factor for line intensities is not the same for lines of different elements and does not cancel in the ratio because the partition functions is different in each element. Therefore, their ratio must be determined experimentally.

Of all the optical methods for obtaining temperature profiles, local seeding is the simplest in concept and probably the most accurate. I can be used on any system in which the mechanical introduction of the seeding material can be managed and which would not be altered by the presence of the seeding material.

In some cases, total seeding may be possible where local seeding is not. If the specimen could be seeded with a molecule whose absorptance follows the Beer-Lambert Law, its temperature profile may be sought by the available spatial scanning procedures. If the concentration of seed material could be controlled, spectral scanning might yield the temperature profile.

2. Output

Temperature profiles.

3. Specimen Requirement

Seedability.

4. Accuracy

a. Local seeding.

With reasonable care, temperatures can be measured within about 20°K by the emission-absorption or the line reversal method. The two-line method is less reliable.

b. Total seeding.

Spectroscopic measurements of totally seeded specimens may be made by methods B, C or F. The accuracy that may be expected of the resulting temperature profiles is that described for these methods.

5. Availability of Technology

a. Spectroscopic instrument technology is available.

b. Sound choices of materials for local seeding can be made with available information.

c. Adequate estimates of the required quantity of additive can be made for emission-absorption or line reversal measurements of a locally seeded specimen.

d. Two-line method temperature measurements require an exacting determination of the optimum amount of local seeding. It may prove best to make this determination experimentally.

e. In the case of additives to be used for total seeding, the presence of the special optical and chemical properties desired must be sought and proven.

E. Crossed Beams

1. Description of Method

Crossing the optical beam with an electron beam, as described in Section II A, 3a, may be useful for plume

measurements under high altitude conditions. The pressure range within which an electron beam is operable is too small to make it generally valuable.

If the local ionization were produced by light or X-ray beams, the crossed beam technique could be used at much higher pressures. However, the increased pressure would not only require a change in the excitation method but would involve a completely different overall excitation-emission process. For his low pressure-low temperature specimens, Muntz (refs. 12 and 13) was able to assume that the excited particle experienced no gas kinetic collision during the process of excitation and emission. He was able to justify this assumption in the following manner:

For room temperature, number densities of the order of $1.5 \times 10^{16}/cm^3$ (pressure 470μ Hg, the maximum existing in Muntz's experiments) and assuming the diffusion collision cross-section of 4.8×10^{-15} cm^2, the time required to traverse a mean free path at the mean speed of 475 m/s is approximately 2×10^{-7} sec. Bennet and Dalby (ref. 47) have measured the mean life of the excited state of the (0,0) band of $N_2 + B^2\sum$ (the transition used in Muntz's measurements) as $6.53 \pm 0.22 \times 10^{-8}$ sec. Thus, molecular collisions will produce little interference with the electron excited emission of the $N_2 + B^2\sum$ state. This description of the excitation-emission path holds good until the average free flight time of an excited particle compares with the mean life of the excited state.

To the hard sphere approximation, the free flight time of a molecule varies inversely with pressure and directly with the square root of temperature. Therefore, at 470 mm Hg and 1200°K the time required to traverse a mean free path should be $2 \times 10^{-3} \times 2 \times 10^{-7}$ or 4×10^{-10} sec. The average excited ion would then undergo over 100 collisions during its lifetime and its radiation should be thermal.

Many other extensions of the crossed beam idea may be possible. Radiation from beam excited states of the neutral molecule may be as useful as that of ions. Also, measurement of light from the beam after it is scattered by the sample may yield information about the scattering molecules. For instance, if Raman scattering is studied, the intensities of single lines should lend themselves to

analyses similar to that presented in Section II B for absorption of single OH lines. Detecting the small amounts of energy produced by Raman scattering may be a problem but this might be overcome by using a laser source. Rayleigh scattering provides more energy and may prove useful for measuring molecular densities. However, severe interference with measurements of Rayleigh scattering could be produced by small amounts of dust. Preliminary tests of this Rayleigh scattering technique have been made with pure gases (refs. 48 and 49).

2. Output

Profiles of temperature and density of the working molecule.

3. Specimen Requirement

a. Presence of suitable working molecule.

b. Suitable pressure. This is below 1 mm Hg for studies that neglect collisions and of the order of one atmosphere or more if collision induced equilibrium is assumed. Intermediate pressures are not suitable for either case.

4. Accuracy

Muntz has claimed accuracies of 2 percent, 10 percent and 8 percent for rotational temperature, vibrational temperature and nitrogen concentration respectively in measurements made on rarefied gas at about room temperature using electron beam excitation.

Recent papers on photoionization coefficients of N_2 by Cook and Ogawa (ref. 50) and of H_2O by Metzger and Cook (ref. 51) did not give the accuracy of the results. This precludes estimates of the accuracy of concentration measurements based on this data.

If measured ionic radiation is thermal, the accuracy of temperature measurements obtainable by local seeding may be considered an upper limit to the accuracy obtainable from measurements made on photoionized species.

5. Availability of Technology

a. Spectroscopic instrument technology is available.

b. Theory.

For measurement of nitrogen density and temperature at low pressure by means of electron beam ionization, the technique has been developed and used.

c. Spectroscopic parameters.

Nitrogen and water vapor cross sections for photoionization by ultraviolet radiation have been measured. Information about Raman intensities of gases is sparse.

F. Line of Sight Measurements

1. General Description

This method can be used as described in Part I if the specimen requirement given below is met. Whether or not this is so must be decided, for each experiment, by the investigator.

In order to obtain a detailed picture of the temperature and composition profile along a line of sight through a hot gas from measurements made only along that line of sight, the present state of the art requires that the composition be a known function of the temperature. However, when this condition is not fulfilled it is still possible to obtain some information about the temperature profile from line of sight measurements. This is done by applying equation (1a). As stated in Section II A, this formula gives a weighted average of the temperatures along the line of sight with different weighting distributions at each wavelength. Using an estimate of the wavelength dependence of the weighting distributions and a suitable set of such weighted average temperatures measured at several wavelengths, an estimate of the line of sight temperature profile can be made. By such a procedure, Tourin and Krakow were able to detect a small cold spot in a propane-air flame and to estimate its location (ref. 1).

There is another possible approach when only a finite number of possible profiles exist. The emission and absorption spectrum of the sample can be measured and compared with the pre-determined spectra for each of the possible profiles. If there is a substantial difference in the various possible profiles there should be enough difference in the corresponding spectra to allow matching of the measured spectrum to the proper pre-determined one.

2. Output

Profiles of temperature and concentration of the working molecule.

3. Specimen Requirement

a. Concentration must be a known function of temperature.

b. Presence of a working molecule with sufficient optical activity.

4. Accuracy

The accuracy of line of sight temperature determinations depends so strongly on the detail desired, slope of the Planck function, slope of temperature vs. transmittance curves, accuracy of temperature vs. transmittance curves, accuracy of temperature vs. concentration curves, stability, and measurement accuracy that general statements cannot be made. Therefore, the discussion will be confined to a few specific cases. First, the accuracy of line of sight temperature profiles that have been obtained from measurements of CO_2 at 4.3μ will be discussed. Consideration will then be given to how this accuracy is likely to change when the input data are changed to measurements of water vapor at 2.5μ or to measurements of OH radicals at 0.3μ.

At 4.3μ and 2000°K, the relative slope of the Planck function is only 0.10 percent per degree. However, CO_2 transmittance varies so strongly with temperature and wavelength that the small Planck function slope could be overcome by judicious choices of wavelengths. In the demonstrations of the method that have been made, measurement precision was characterized by mean transmittance deviations of .01 and relative mean radiance deviations of 2 percent in typical measurements. The transmittance curves used were prepared from data of similar precision. Also, in these tests very stable laboratory specimens were used and errors in concentration curves were of negligible importance. In two and three zone examples involving temperatures between 1400°K and 2800°K, zonal temperatures were determined with errors of less than 100°K (ref. 3).

Accuracies comparable to those of the CO_2 measurements just described may be expected for temperatures determined from measurements made at 2.5μ using H_2O as the working molecule. As far as the spectroscopic measurements themselves are concerned, an improvement that might be brought about by the better detectors available for the 2.5μ region would probably be nullified by greater atmospheric interference and need for higher resolution. In calculating temperatures from the spectroscopic data we would be helped by a slightly larger Planck function slope

but hindered by a smaller variation of transmittance with temperature. In short, the wavelength is slightly better but the working molecule worse. In fact, for small specimens, the optical activity of H_2O may prove too weak to allow its use.

The molecule OH is active near 0.3μ. The relative Planck function slope at 2000°K is over twelve times as steep at 0.3μ as at 4.3μ. This fact should dominate the comparison of accuracies. Detectors at 0.3μ are much better and may overcome the lower radiances, greater amounts of stray light, greater calibration difficulty, and the increased light scattering at this wavelength to make the spectroscopic data as good as at 4.3μ. Therefore, if all chemiluminescence has decayed before the gas reaches the point of measurement, temperature profiles obtained from spectral radiances in the 0.3μ region should be much more accurate than studies using measurements at around 4.3μ because of the larger relative Planck function slope.

Of course, this greater ultimate accuracy could be traded for greater detail, roughness in temperature vs. transmittance curves, or sample instability.

Estimates of the line of sight temperature profile made in the absence of temperature vs. transmittance curves are quite rough. Only a general idea of the nature of the profile can be obtained in this case.

5. Availability of Technology

a. Spectroscopic instrument technology is available.

b. Working molecules:

H_2O and OH may be suitable.

c. Spectroscopic parameters.

These would have to be obtained for the working molecule.

d. Theory.

Mathematical techniques are available.

IV. RESEARCH REQUIRED

A. Evaluation of Working Molecules

1. OH Chemiluminescence

Of all the molecules produced by hydrogen-air flames, OH is the one whose optical activity has the most favorable wavelength and intensity for analysis of its thermal radiance. In fact, it may prove to be the only suitable working molecule in many specimens. However, before making such analyses, one must ascertain that the measured radiance is indeed thermal.

The rate at which OH chemiluminescence decays is uncertain. All studies that have been made on the subject have involved temperature gradients along the line of sight and been based on assumptions about line shapes, f-numbers, vibration-rotation interaction and rate constants that have made the results inconclusive. The differences of opinion on the subject are illustrated by the results of Kaskan (ref. 18), Zinman and Bogdan (ref. 52), and Zeegers and Alkemade (ref. 53). Kaskan's line absorption measurements using the f numbers of Dieke and Crosswhite indicated that non-equilibrium persisted for a long distance downstream of a hydrogen-air flame. Zinman and Bogdan found that the radiance of the gas above hydrogen-air flames was consistent with thermal equilibrium if the f numbers were corrected for vibration-rotation interaction as directed by Learner but this was not true if James' corrections for vibration-rotation interaction were used. Recent kinetic calculations by Zeegers and Alkemade indicated considerable OH chemiluminescence above acetylene-air flames. While the majority of papers on this subject indicate that chemiluminescence produces serious distortions of OH radiance measurements, the results are still questionable. Because of the potential power of OH radiance as a thermometer, this question should be resolved.

Estimated Effort: 4 man years

2. Molecules for Total Seeding

Molecules to be used for total seeding should have a high spectral absorptance at a suitable wavelength and this absorptance should vary in accordance with the Beer-Lambert absorption law for measurements made with practical spectral slit widths. The optimum spectral region for the measurement of temperatures of about 2000°K would be the

visible or near infrared. The presence of these properties should be sought and proven in selected materials.

Estimated Effort: 4 man years

3. The practicability of producing optical isolation by means of radiation probes needs further investigation.

B. Spectroscopic Parameters

There is a general need for research into the spectroscopic properties of working molecules that may be used in spectroscopic studies of hot combustion products. Data of this type required for the techniques described in Part III are:

1. f numbers for OH bands other than the O-O band.

Estimated Effort: 6 man years

2. OH band model parameters.

Estimated Effort: 2-4 man years

3. H_2O band model parameters.

Estimated Effort: ½ man year per interval for temperatures below 1300°K; 1 man year per interval for temperatures above 1300°K

4. Seed material line strengths for 2 line method measurements.

Estimated Effort: 2 man years

C. Theory

Theoretical studies needed for methods A, B, and C described in Part III are:

1. Development of techniques for analyzing spatial scans of radiance and absorptance of radially symmetric specimens when the Beer-Lambert absorption law does not apply to the working molecules.

Estimated Effort: 2 man years

2. Combination of spatial and spectral scanning.

Estimated Effort: ½ man years

3. Development of machinery for correcting the line absorption method for the finite width of the emission line and for pressure broadening of the absorption line.

Estimated Effort: 3 man years

D. Testing

Each method should be tested in the laboratory.

Estimated Effort: 1 man year per method. Possibly more for crossed beam methods.

E. Organization of Research

Figures 6 and 7 illustrate a reasonable organization of research programs and show how they lead to final evaluation of the measurement methods proposed in this report. Figure 6 deals with studies of OH and H_2O which are natural products of hydrogen-air combustion. This figure centralizes two pivotal tasks: (1) determination of OH equilibrium, and (2) development of the theoretical techniques required to apply spatial scanning methods and to combine spatial and spectral scanning. What follows these two tasks depends on the results of the OH equilibrium investigation. If reason is found for believing that OH radiance in a ramjet specimen will be thermal, then the OH studies on the left side of figure 6 should be the first application of the new theories for spatial scanning developed in task 2. On the other hand, if the results of task 1 indicate that OH radiance in a ramjet will be substantially chemiluminescent, then the new theories would be applied first to H_2O in the manner indicated on the right side of figure 6. The OH line absorption test should be done in either case. Figure 7 shows research concerned with molecules that are artifically introduced into the sample. Three distinct programs are outlined -- one for each of three introduction techniques.

V. CONCLUSIONS

The natural products of hydrogen-air combustion include two molecules, H_2O and OH, that are optically active at suitable wavelengths for spectroscopic study. Temperature and composition profiles of these molecules may be sought through measurement of their spectral absorptance or radiance.

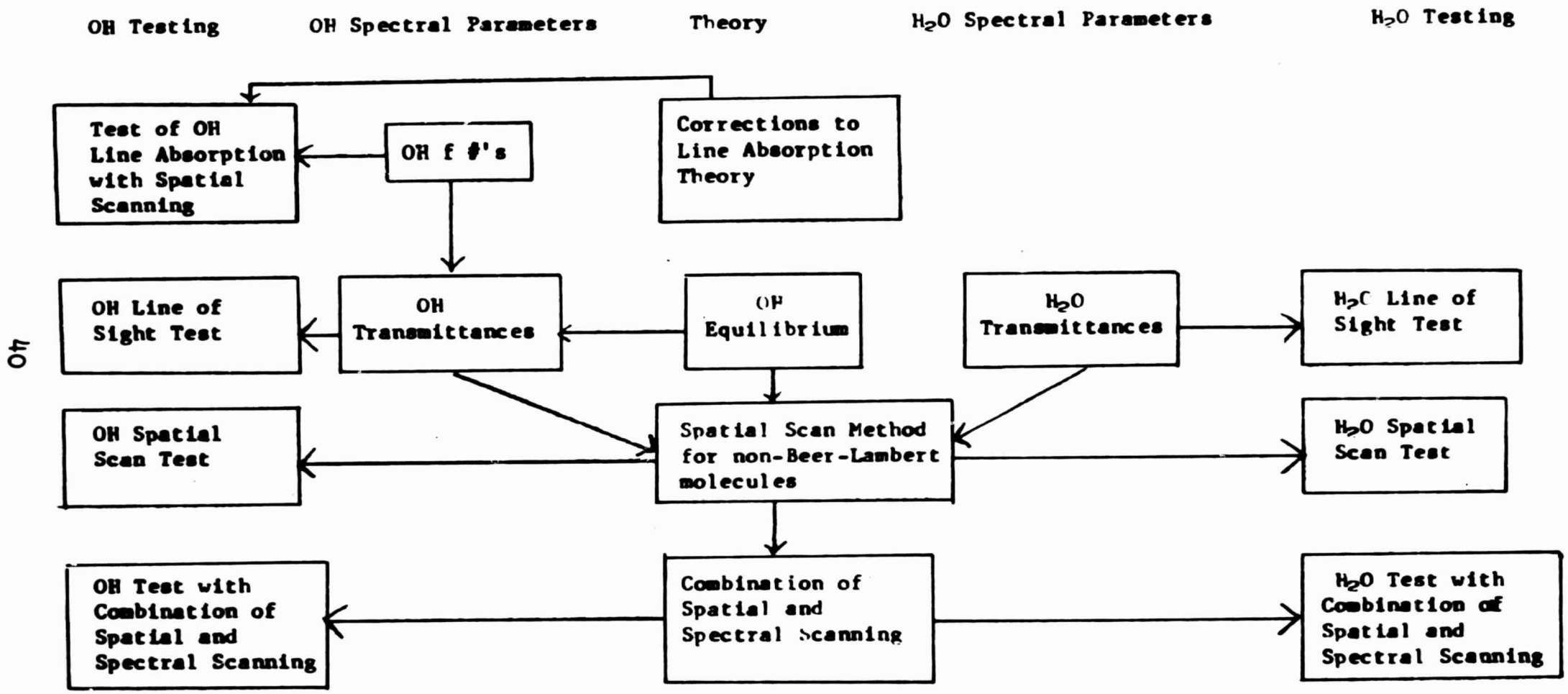


Fig. 6 Schematic diagram of organization of research program dealing with natural products of hydrogen-air combustion OH and H_2O.

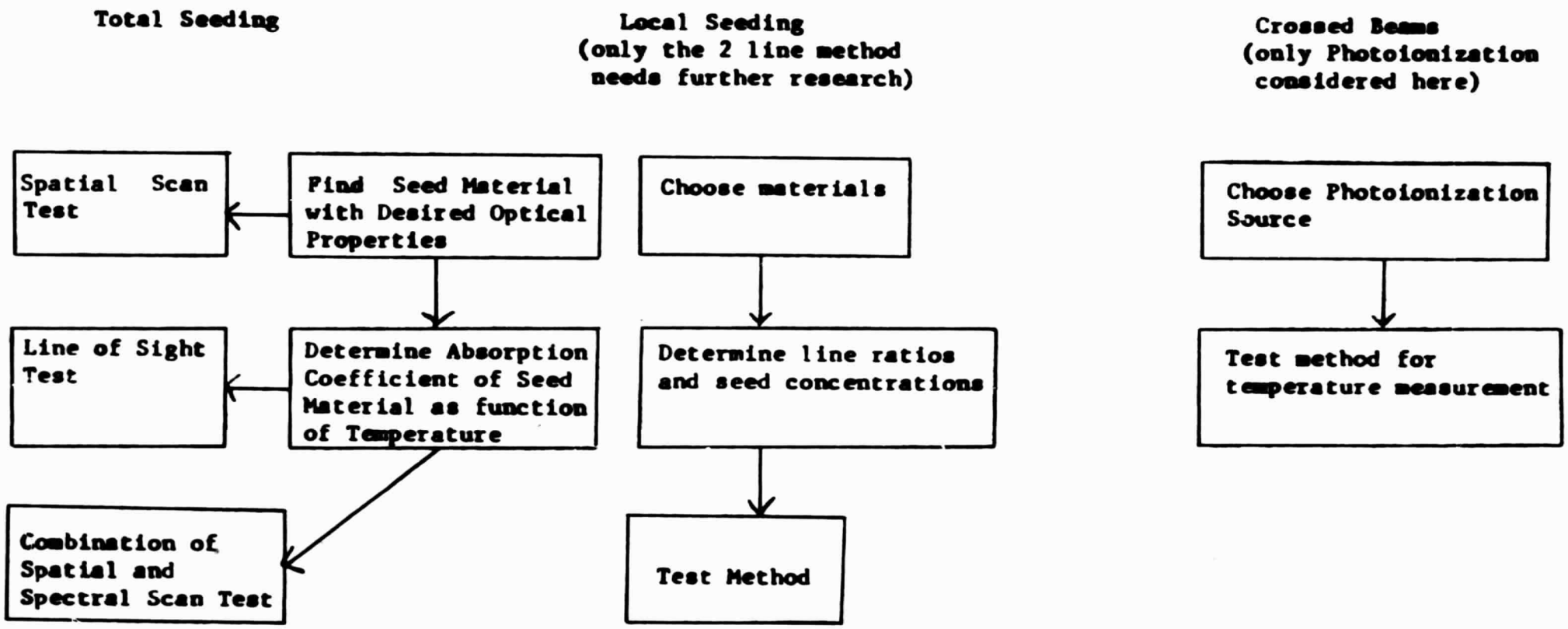


Fig. 7 Schematic diagram of organization of research programs dealing with molecules that are artificially introduced into the sample.

Spectral lines of OH display an extraordinary resistance to pressure broadening. This quality opens possibilities for analysis of line absorption measurements of OH. OH concentrations and temperatures have been determined in this way in homogeneous gases. Methods have been developed to extend this technique to obtain profiles of OH concentration and temperature in radially symmetric inhomogeneous samples.

It is difficult to measure and interpret either the OH or the H_2O thermal radiance of the ramjet. In the case of OH, chemiluminescence might interfere with the measurements. For H_2O the emissivity is low, hence hard to measure accurately and hard to find sufficient variation of emissivity. For temperature measurements based on thermal radiance, the optical activity of OH occurs at a much more favorable wavelength than that of H_2O. Interpretation of measurements of spectral radiances of natural components of the specimen in terms of thermodynamic parameters requires either radial symmetry in the sample or a knowledge of the composition as a function of temperature. For working molecules like H_2O and OH whose spectra consist of narrow, well-spaced lines, utilization of radial symmetry would require some further development of the available theories, which are designed for continuous spectra. Guidelines for such a development have evolved from this project.

Introduction of a better working molecule than OH or H_2O into the specimen could facilitate temperature profile measurements greatly, especially if it can be accomplished locally. Techniques for achieving this introduction involve simple addition or production through interaction between a natural constituent of the sample and an electromagnetic beam crossing the line of sight of the optical measurement. The crossed beam technique might also provide an avenue to chemical analysis of optically inactive components of the sample. This report describes several extensions of currently used techniques that might help adapt them for ramjet study.

Research that is needed to increase capabilities for optical measurement of temperature and composition profiles of hot gases is of the following 3 types: (1) determination of spectroscopic properties of potential working molecules, (2) advancement of techniques for theoretical analysis of optical measurements and (3) experimental studies of new measurement techniques.

Spectroscopic instrument technology is generally available for the optical measurements described in this report.

APPENDIX

The following information was received from NASA in response to questions regarding the nature of the specimens to be studied. This information and information obtained from informal conferences with NASA personnel guided the selection of approaches to the study problem.

1. The specimen size may vary from as small as a passage height of 1/2-inch to as large as a diameter or height of 24 inches depending upon the location along the engine axis or station and the engine configuration.

2. The static pressure within the engine will vary with conditions (altitude, Mach number, engine station, etc.) but will be generally in the range of 0.1 to about 3.0 atmospheres with the lowest pressure occurring at the nozzle exit.

3. Static temperatures of the flow within the engine will vary with conditions and the engine station. Generally speaking, the static temperature will vary from about 1000°R at the entrance to the combustor to a maximum of about 5000°R at the exit of the combustor. The static temperature at the exit of the nozzle will be about 2600°R depending upon flow conditions. The maximum total temperature of the engine flow will be about 5900°R. Hydrogen gas will be introduced into the combustor at a temperature in the range of 1000°R to 3000°R.

4. The composition of the burned gases will of course depend upon state conditions of the hydrogen-air mixture before combustion and upon flow conditions during and after combustion. However, an order of magnitude indication of the gas composition after combustion in the ramjet engine in mole fractions would be H_2 - .037467, H_2O - .284133, N_2 - .627622, OH - .018113, O_2 - .011467, NO - .006787, H - .010481, O - .003928, and N - .000001. These values were taken from NACA TR 1383, "Survey of Hydrogen Combustion Properties", for equilibrium adiabatic conditions, an equivalence ratio of 1, a static pressure of 1 atmosphere, and an initial mixture temperature of 1800°R. Also, air was assumed to consist of oxygen and nitrogen only in the molar ratio of 1:3.7572. Operation of the ramjet engine is not restricted to an equivalence ratio of 1 but may operate at equivalence ratios less or greater than 1.

5. It is expected that temperature profiles across the flow near the fuel injectors will be irregular and lack

symmetry because of the introduction of fuel at discrete radial and axial locations. Further irregularities and asymmetry may occur from flow distortions caused by the engine inlet. Profiles may become "smoother" and more symmetrical as the flow leaves the combustor and passes through the nozzle depending upon whether or not operation of the engine at angles of attack or yaw produces adverse effects in this part of the engine.

6. It is expected that temperature and composition profiles will be stable over the time period available for measurements. Reports on supersonic combustion experiments do not indicate any combustion instability.

7. For flight tests, the time for measurements will be restricted to 1 second or less because of nonsteady flight conditions (accelerating or decelerating flight). Ground tests will permit measurement times of up to 1 minute for certain test conditions. However, it is required that measurement time in ground tests be of the same order of magnitude as that for the flight tests.

8. Departure from equilibrium conditions within the engine should be small. However, since the engine design will not be optimized, the effect of small departures from equilibrium on engine performance may be significant for certain flight conditions.

9. Both ground and flight tests will be made on the ramjet engine. It is preferred that the method or technique of measurement be the same for both ground and flight tests. However, the instrument itself need not be the same for both flight and ground tests. The contractor should note that ground tests will permit more detail testing procedures than flight tests and that the primary use for an instrument whose design is based on a feasible method for measuring temperature and composition profiles by optical techniques will be in the ground tests. Consequently, restrictions (such as size, weight, etc.) imposed by flight measurements should not unduly influence the choice of technique or the instrument design. It is felt that once a probeless technique for measuring temperature and composition profiles in a hypersonic ramjet becomes a reality, it is only an engineering problem to adapt this technique to flight testing. The answers to certain remaining questions should be viewed with the above in mind.

10. The temperature and composition across the hot gas path is to be considered.

11. The main interest is in measurements within the engine, although measurements in the exhaust plume are also of interest. In ground tests "boilerplate" models of the engine or engine components will be tested which will permit measurements similar to that which can be made across the exhaust plume. That is, measurements of the flow exiting from an engine component, such as the combustor, will be made.

12. The best possible accuracy is, of course, desirable but it is realized that the accuracy attainable in practice will be less than that for ideal or laboratory conditions. An accuracy of $\pm$ 5 percent or less for temperature measurements over the range of 2000°R to 5000°R should be a design goal if the present state-of-the-art is less accurate than this.

13. The accuracy of the composition profile data should be sufficient to permit determination of small departures from equilibrium conditions.

14. The use of solid probes in the engine flow passages cannot be tolerated.

15. An electron beam may not be feasible in view of the pressures existing within the engine.

16. An instrument that does not require seeding is preferred over one that does since introduction of alien species, especially radicals, will adversely affect hydrogen-air reaction and recombination times.

17. Since probes cannot be tolerated within the engine passages, local seeding by this method cannot be used.

18. Spatial scanning across the specimen is possible.

19. It may or may not be possible to evacuate or flush the optical path. The fewer "complications" involved in the application of the measurement technique, the more desirable the technique becomes.

REFERENCES

1. Tourin, R. H., and Krakow, B.: Applicability of Infrared Emission and Absorption Spectra to Determination of Hot Gas Temperature Profiles. Appl. Optics, vol. 4, 1965, pp. 237-242.

2. Krakow, B.: Determination of Hot Gas Temperature Profiles from Infrared Emission and Absorption Spectra. AIAA Jour., vol. 3, 1965, pp. 1359-1360.

3. Krakow, B.: Spectroscopic Temperature Profile Measurements in Inhomogeneous Hot Gases. Appl. Optics, vol. 5, 1966, pp. 201-209.

4. Griem, H. R.: Plasma Spectroscopy. McGraw Hill Book Co., 1964.

5. Nestor, O. H., and Olsen, H. N.: Numerical Methods for Reducing Line and Surface Probe Data. SIAM Review, vol. 2, 1960, p. 200.

6. Bockasten, K.: Transformation of Observed Radiances into Radial Distribution of the Emission of a Plasma. J. Opt. Soc. Am., vol. 51, 1961, pp. 943-947.

7. Barr, W. L.: Method for Computing the Radial Distribution of Emitters in a Cylindrical Source. J. Opt. Soc. Am., vol. 52, 1962, p. 885.

8. Maecker, H.: Z. Physik, vol. 136, 1953, p. 119.

9. Pearce, W. J.: Plasmajet Temperature Measurement. In: Optical Spectrometric Measurements of High Temperatures. University of Chicago Press, 1961, p. 125.

10. Freeman, M. P., and Katz, S.: Determination of a Radiance Coefficient Profile from the Observed Asymmetric Radiance Distribution of an Optically Thin Radiating Medium. J. Opt. Soc. Am., vol. 53, 1963, p. 1172.

11. Elder, P., Jerrick, T., and Birkeland, J. W.: Determination of the Radial Profile of Absorption and Emission Coefficients and Temperature in Cylindrically Symmetric Sources with Self-Absorption. Appl. Optics, vol. 4, 1965, pp. 589-592.

12. Muntz, E. P.: Measurement of Rotational Temperature, Vibrational Temperature, and Molecule Concentration in Non-Radiating Flows of Low Density Nitrogen. UTIA Report #71, 1961.

13. Muntz, E. P.: Static Temperature Measurements in a Flowing Gas. Phys. Fluids, vol. 5, 1962, pp. 80-90.

14. Buchele, D.: A Self-Balancing Line-Reversal Pyrometer. In: Temperature, Its Measurement and Control in Science and Industry. Reinhold Pub. Corp., 1962, vol. III, pt. 2, pp. 879-887.

15. Penzias, G. J., and Maclay, G. J.: Analysis of High Temperature Gases in Situ by Means of Infrared Band Models. NASA CR-54002, W&S TR-28 - Final report on NAS 3-1542 - phase III, Dec. 1963.

16. Ladenburg, R., and Reiche, F.: Ann. Physik, vol. 42, 1911, p. 181.

17. Kaplan, L. D., and Eggers, D. F.: Intensity and Line-Width of the 15-Micron CO_2 Band, Determined by a Curve-of-Growth Method. J. Chem. Phys., vol. 25, 1956, p. 876.

18. Kaskan, W. E.: Hydroxyl Concentration in Rich Hydrogen-Air Flames Held on Porous Burners. Combustion & Flame, vol. 2, 1958, pp. 229-243.

19. Dieke, G. H., and Crosswhite, H. M.: The Ultraviolet Bands of OH. J. Quant. Spectrosc. Radiat. Transfer vol. 2, 1962, pp. 97-199.

20. Bass, A. M., and Broida, H. P.: Circ. U.S. Bur. Stand. No. 541, 1953.

21. Oldenberg, O., and Rieke, F. F.: Kinetics of OH Radicals as Determined by Their Absorption Spectrum III. A Quantitative Test for Free OH; Probabilities of Transition. J. Chem. Phys., vol. 6, 1938, pp. 439-446.

22. Dwyer, R. J., and Oldenberg, O.: J. Chem. Phys. vol. 12, 1944, p. 351.

23. Kaskan, W. E.: Line Shape in the OH $^2\Pi - ^2\Sigma$ Transition. J. Chem. Phys., vol. 28, 1958, pp. 729 - 730.

24. Herzberg, G.: Spectra of Diatomic Molecules. Van Nostrand Pub. Co., 1950, 2nd ed., p. 125.

25. Wurster, W. H.: Measured Transition Probability for the First-Positive Band System of Nitrogen. J. Chem. Phys., vol. 36, 1962, p. 2111.

26. Treanor, C. E., Wurster, W. H., et al.: Shock Tube Measurements of Transition Probabilities for Oxygen and Nitric Oxide. Cornell Aeronautical Laboratory, Inc. Report No. QM-1209-A-2, 1960.

27. Penzias, G. J., Dolin, S. A., and Kruegle, H. A.: Spectroradiometric Pyrometry of Shock-Heated Gases by Infrared Emission and Absorption Measurements. Appl. Optics, vol. 5, 1966, p. 225.

28. Young, L. E.: Infrared Temperature Measurement of the Laminar Wake of a Hypersonic Sphere. AIAA Jour., vol. 3, 1965, p. 610.

29. Steinberg, M., and Davies, W. O.: High-Temperature Absorption of Carbon Dioxide at 4.40 Microns. J. Chem. Phys., vol. 34, 1961, p. 1373.

30. Penzias, G. J., Liang, E. T., and Tourin, R. H.: Infrared Radiation and Temperature Measurements in Solid Propellant Flames. I. Preliminary Study of Arcite 368. W&S TR-22 on Contract Nonr 3657(00), Advanced Research Projects Agency, 1962.

Penzias, G. J.: Infrared Spectra of Solid Propellant Flames from 1.4μ to 4.8μ. W&S TR-35, Confidential on Contract Nonr 3657(00), Advanced Research Projects Agency, 1964.

31. Povinelli, L. A.: Study of Composite Solid-Propellant Flame Structure Using a Spectral Radiation Shadowgraph Technique. NASA TM X-52071, 1964.

32. Penzias, G. J., Gillman, S., Liang, E. T., and Tourin, R. H.: An Atlas of Infrared Spectra of Flames, Part Two. Hydrocarbon-Oxygen Flames 4-15μ, Ammonia-Oxygen 1-15μ, Hydrazine-Oxygen 1-5μ, and Flames Burning at Reduced Pressures. AFCRL-848(II) - W&S TR-17, 1961.

Babrov, H. J., Henry, P. M., and Tourin, R. H.: Methods for Predicting Infrared Radiance of Flames by Extrapolation from Laboratory Measurements. AFCRL-1070 - W&S TR-18, 1961.

Penzias, G. J., Gillman, S., Liang, E. T., and Tourin, R. H.: An Atlas of Infrared Spectra of Flames. Part III.

Nitrogenous Liquid Propellants. W&S TR-26 on Contract Nonr 3657(00), Advanced Research Projects Agency, 1963.

33. Hornbeck, G. A., and Olsen, L. O.: Emission and Absorption Studies of Jet Engine Hydrocarbon Combustion Products. WADC TR 57-516, 1958.

34. Ferriso, C. C., Ludwig, C. B., and Boynton, F. P.: A Band-Ratio Technique for Determining Temperatures and Concentrations of Hot Combustion Gases from Infrared-Emission Spectra. In: Tenth Symposium (International) on Combustion. The Combustion Institute, 1965, pp. 161-175.

35. McGregor, W. K., and Brewer, L. E.: Experimental Determination of a Rocket Exhaust Gas Temperature at Altitude by Infrared Spectroscopy. AEDC-TN-61-94, 1961.

36. Dolin, S. A., Penzias, G. J., and Tourin, R. H.: Determination of Rocket Exhaust Gas Temperatures and Emissivities by Infrared Spectral Methods. AFCRL-881 - W&S TR-16, 1961.

37. Simmons, F. S., and DeBell, A. G.: Spectral Radiometry and Two-Path Pyrometry of Rocket Exhaust Jets. In: Temperature, Its Measurement and Control in Science and Industry. Reinhold Pub. Corp., 1962, vol. III, pt. 2, pp. 437-447.

38. Tourin, R. H.: Infrared Techniques for Temperature Measurement in Plasmajets. J. Heat Transfer, vol. 84, 1962, p. 164.

39. Hett, J. H., and Gilstein, J. B.: Indicated Instantaneous Temperatures of Liquid Rocket Exhaust and Combustion Chambers. J. Am. Rock. Soc., vol. 25, 1955, p. 119.

40. Calingaert, G., Heron, S. D., and Stair, R.: Sapphire and Other New Combustion Chamber Window Materials. SAE Jour., vol. 39, 1936, p. 448.

41. Tourin, R. H.: Letter to Mr. W. E. Hutcheson, Contracting Officer, NASA Langley Research Center.

42. Dolin, S. A., and McHenry, T.: Notes on the Feasibility of an Airborne Spectrometer. Perkin-Elmer Report at WADC Briefing, March 1958.

43. Golden, D. M., Del Greco, F. P., and Kaufman, F.: Experimental Oscillator Strength of OH, $^2\Sigma^+ \rightarrow {}^2\Pi$, by a Chemical Method. J. Chem. Phys., vol. 39, 1963, p. 3034.

44. Bennet, R. G., and Dalby, F. W.: Experimental Determination of the Oscillator Strength of the Violet System of OH. J. Chem. Phys., vol. 40, 1964, p. 1414.

45. Goody, R. M.: Atmospheric Radiation. Oxford University Press, 1964.

46. Krakow, B., Babrov, H. J., Maclay, G. J., and Shabott, A. L.: Use of the Curtis-Godson Approximation in Calculations of Radiant Heating by Inhomogeneous Hot Gases. NASA TM X-53411, 1966.

47. Bennet, R. G., and Dalby, F. W.: Experimental Determination of the Oscillator Strength of the First Negative of N_2^+. J. Chem. Phys., vol. 31, 1959, p. 434.

48. Newton, J. F., and Walsh, M. J.: AIAA Jour., vol. 3, 1965, p. 2335.

49. Camac, M., Locke, E. V., and Rose, P. H.: A Technique to Measure Wake Densities by Rayleigh Scattering. Avco Everett Research Lab., AMP 181, 1965.

50. Cook, G. R., and Ogawa, M.: Can. J. Phys., vol. 43, 1965, p. 256.

51. Metzger, P. H., and Cook, G. R.: On the Continuous Absorption, Photoionization and Fluorescence of H_2O, NH_3, CH_4, C_2H_2, C_2H_4, and C_2H_6 in the 600 to 1000A Region. J. Chem. Phys., vol. 41, 1964, p. 642.

52. Zinman, W. G., and Bogdan, S. I.: Influence of Vibration-Rotation Interaction on the Rotational "Temperature" Determined from an Electronic OH Transition. J. Chem. Phys., vol. 40, 1964, p. 588.

53. Zeegers, P. J. Th., and Alkemade, C. The. J.: Chemiluminescence of OH Radicals and K Atoms by Radical Recombination in Flames. In: Tenth Symposium (International) on Combustion. The Combustion Institute, 1965, p. 33.