SAND82-8672
Unlimited Distribution
Printed April 1982

SAND--82-8672

DE82 015766

On the Application of Fourier-Transform Infrared (FT-IR) Spectroscopy to In-Situ Studies of Coal Combustion

D. K. Ottesen and L. R. Thorne
Sandia National Laboratories
Livermore, CA 94550

ABSTRACT

The feasibility of using Fourier transform infrared (FT-IR) spectroscopy for in situ measurement of gas phase species concentrations and temperature during coal combustion is examined. This technique is evaluated in terms of its potential ability to monitor several important chemical and physical processes which occur in pulverized coal combustion. FT-IR absorption measurements of highly sooting, gaseous hydrocarbon/air flames are presented to demonstrate the fundamental usefulness of the technique for in situ detection of gas phase temperatures and species concentrations in high temperature combustion environments containing coal, char, mineral matter and soot particles. Preliminary results for coal/gaseous fuel/air flames are given.

DISCLAIMER

INTRODUCTION

The problems associated with measuring the composition and properties of hot, luminous, and particle-laden flows have received increasing attention recently. The conflicting goals of reducing pollution while burning increasingly complex fuels, such as coal and synthetic fuels, require greater understanding of heterogeneous combustion processes such as coal devolatilization and oxidation (1) and soot formation (2).

Optical scattering techniques can be used in some cases to measure particle sizes and velocities. Particle temperature can often be measured by two color pyrometry. Gas phase information, however, is difficult to obtain in these harsh, particle-laden environments. The usefulness of spontaneous laser Raman and induced flouresence techniques is severely limited by the luminosity of the particles (3,4). Absorption measurements may also be hampered by the presence of particles, which can contribute a time varying background to the absorption signal of interest.

These difficulties can be largely overcome by the use of FT-IR spectroscopy in appropriately configured experiments (5). This paper reports results of our measurements of gaseous species concentrations and temperatures in hydrocarbon/air flames, demonstrating the usefulness of this technique for in situ measurements. We also give preliminary results for pulverized coal/gaseous fuel/air combustion environments.

GENERAL CONSIDERATIONS

Insight into the chemistry of pulverized coal combustion requires measurement of the concentrations and temperatures of the major chemical species and particulates under well controlled experimental conditions. Futhermore, the ability to determine the rates and mechanisms of chemical reaction requires measurement of the time evolution of these quantities. Laminar flow reactor techniques are currently in use at Sandia to obtain this kind of information for a wide range of heterogeneous fuels. These systems are designed so that reaction time is proportional to distance along the reactor. Thus, spatial resolution of the reactor composition and temperature becomes important. The Sandia reactors, which operate at atmospheric pressure, permit complete optical and sample probe access to the reacting fuel particles and also afford control of (a) the material properties of the unburned fuel, (b) the rate of addition of fuel to the reactor, (c) the high temperature environment to which the fuel is exposed, and (d) the relationship between reaction time and distance along the reactor.

Two reactors have been configured: one with injection of a single stream of solid fuel particles along the center line, and one which is specially designed to facilitate spectroscopic studies with fuel injection along the optical axis of the FT-IR system. In both reactors, spatial resolution of about 1 mm affords reaction time resolution of 1 msec. With these general considerations in mind, we summarize in Table 1 the more important measurement requirements.

Absorption spectroscopy is particularly well suited to many of these requirements as evidenced by the extensive literature on its application to homogeneous combustion (6). For in situ measurements of combustion processes, absorption spectroscopy has the advantage of being non-perturbing, since the light intensities used are far below those required to drive chemical reactions to any appreciable degree. Moreover, absorption spectroscopy can provide both quantitative and qualitative information.

Quantitative information is derived from the application of the Bouguer- Lambert Law of absorption from which the partial pressure of a particular chemical species can be determined.

$$A(\tilde{\nu}) = \ln\ [I(\tilde{\nu})/I_o(\tilde{\nu})] = -\beta(\tilde{\nu})PL \qquad (1)$$

where:

$A(\tilde{\nu})$ = the absorbance at frequency $\tilde{\nu}$.
$I(\tilde{\nu})$ = the intensity of the light transmitted through the sample at $\tilde{\nu}$.
$I_o(\tilde{\nu})$ = the intensity of the light at frequency $\tilde{\nu}$ before it enters the sample.
$\beta(\tilde{\nu})$ = the absorption strength of the chemical species at frequency $\tilde{\nu}$.
P = the partial pressure of the chemical species (atm).
L = the path length of the light through the sample (cm).

The shape of $\beta(\tilde{\nu})$ as a function of $\tilde{\nu}$ (spectrum) is unique for each chemical species, and so provides qualitative information. The strong temperature dependence of $\beta(\tilde{\nu})$ provides a means of determining the temperature of the absorbing species.

In the present study of flames we have used infrared spectroscopy (light in the frequency range $\tilde{\nu} = 400$ to $4000\ \mathrm{cm}^{-1}$, where $\tilde{\nu} = 1/\lambda$, and λ is the wavelength of the light in cm). Molecular absorption in this frequency region is due to interaction of the oscillating electric field of the incident beam with the oscillating dipole moment produced by internal vibrations of the molecule. Thus, atoms and homonuclear diatomic molecules, such as H_2, N_2, and O_2, do not absorb infrared radiation to any significant degree, and so they cannot be measured by this technique. However, heteronuclear diatomics and other polyatomics are strong infrared absorbers, and their presence can be detected easily. For mixtures of gases, as are produced in the combustion process, and $1\ \mathrm{cm}^{-1}$ resolution, the infrared absorption spectra of low molecular weight species (CO, NO, CO_2, SO_2, C_2H_2, C_2H_4, etc.) are sufficiently well resolved that they can be determined quantitatively. Higher resolution is required for H_2O. Only qualitative determinations are possible for hydrocarbons containing four or more carbons, even with high resolution. In addition to

Table 1

Measurement Requirements for in Situ Pulverized Coal Combustion Studies

Measurement Objective	Desired Value*	Values Typical FT-IR*
1. Quantitative Measure of Major Chemical Species	H_2, O_2, H_2O, CO, CO_2, C_mH_n > 10 ppm (10%)	H_2O, CO, CO_2, C_mH_n >10 ppm (20%) H_2, O_2, N_2 not detectable
2. Temperature of Chemical Species	300 - 2000 K (5%)	300 - 2000 K (5%)
3. Particle Size Distribution	0.5 - 150 Micron (30%)	Mean Particle Size (100%)
4. Spatial Resolution	< 100 Micron Thick, < 5 mm Wide, < 5 mm Long	< 2 mm Diameter, Flame Boundary Long
5. Large Dynamic Range	1000	1000
6. Intrinsically High S/N	300	300
7. Insentitive to Flow instabilities		S/N Reduced by a Factor of 1.25
8. Insensitive to Thermal Emision by Particles		S/N Reduced by a Factor of 5
9. Unique response to Chemical Species and Particulates		Chemical species give sharp features; particulates give increased background absorption
10. Nonperturbing	Does not alter any process by more than 1%	Does not alter any process by more than 1%

*Values in parentheses give typical uncertainties.

its distinctiveness (which is greatest for small molecules), the infrared spectrum of a molecule contains information about the presence of various molecular sub-units such as -CH_2-, CH_3-, -C=C-, etc. This is a significant aid in identifying combustion products and intermediates.

Small particles (100 Å to 100 μm diameter) absorb and scatter infrared radiation. However, unlike molecular absorptions, small particles do not produce sharp spectral features, but give rise to a noisy, slowly varying, background absorption.

Thus, in principle, infrared absorption spectroscopy provides a means of simultaneously measuring chemical composition, temperature and mean particle size and number density distribution in a combustion environment.

Currently, three types of infrared spectrometers are in wide use: grating, laser diode, and Fourier transform. Typical operating characteristics of these spectrometers are given in Table 2. Comparisons must be made with some caution, since a special-purpose instrument of any one of the types may be designed to have one or two characteristics a factor of 10 better than those listed, but other characteristics are then generally degraded.

There are several important advantages in using the Fourier transform spectrometer in the study of coal combustion. Its large frequency range makes possible measurement of many molecular species simultaneously, unlike diode lasers which are limited to one or two species due to their small frequency range. Since we are concerned here with time averaged measurements in a nominally steady-state experiment, the ability of a Fourier transform spectrometer to scan rapidly and average many scans is a substantial advantage. This permits improvement of the signal-to-noise ratio (S/N). Because of the frequency stability characteristic of FT-IR spectrometers, their ability to improve the S/N in this way is generally superior to that of a grating spectrometer.

Characteristics of Fourier Transform Spectroscopy Relevant to In Situ Combustion Studies

At the heart of the Fourier transform infrared spectrometer is a scanning Michelson interferometer, shown schematically in Figure 1 . Light from the source strikes a beam-splitter at Point O, resulting in two beams. One beam travels to the fixed mirror, F, then back through the beam-splitter to the detector; the other beam travels directly through the beam-splitter, is reflected first by the moveable mirror, M, then by the beam-splitter, and is imaged with the first beam at the detector. The path difference, δ, is called the retardation and is equal to 2(OM - OF). For polychromatic light and $\delta = 0$, a bright spot is produced at the detector, since the two beams interfere constructively at all frequencies. When $|\delta| > 0$, the path

Table 2

Typical Characteristics of Grating, Diode, and Fourier Transform Infrared Spectrometers

Characteristic	Grating	Diode Laser	Fourier Transform
Frequency Range (cm^{-1})	3500	100	3500
Spectral Resolution (cm^{-1})	1	0.0003	0.08
Frequency Repeatability (cm^{-1})	0.5	0.0003	0.03
Scan Rate (single scan) (cm^{-1}/s)	10	600	300
Signal/Noise	200	200	10,000

Table 3

Summary of the Relationship of Various Measurement Considerations*

Operation	1	2	3	4	5	6
1. Maximize Spectral Resolution		-	+	-	-	+
2. Maximize Signal-to-Noise	-		+	-	-	+
3. Maximize Detectability	+	+		-	-	+
4. Minimize Averaging Time	-	-	-		0	-
5. Minimize Computation Time	-	-	-	0		0
6. Maximize Temperature Accuracy	+	+	+	-	0	

*Optimizing a paramter given under the column heading results in either a desirable effect, + , no effect, 0, or an undesirable effect, - , on the other parameters (listed as 1, 2, 3, etc.)

length for each beam is different. If the two beams produced by the beamsplitter have different frequencies, separated by $\Delta\tilde{\nu}$, they will constructively interfere at a retardation of $n/\Delta\tilde{\nu}$, where n is an integer. Thus, when the moveable mirror is scanned, the light intensity at the detector oscillates, producing what is called an interferogram, I(δ):

$$I(\delta) = \int_0^{+\infty} B(\tilde{\nu}) cos(2\pi\tilde{\nu}\delta) \cdot d\tilde{\nu} \tag{2}$$

$I(\delta)$ is one half of a Fourier transform pair. The other half is:

$$B(\tilde{\nu}) = \int_0^{+\infty} I(\delta) cos(2\pi\tilde{\nu}\delta) \cdot d\delta \tag{3}$$

where $B(\tilde{\nu})$ is proportional to the frequency spectrum of the light source. With an absorbing sample between the source/interferometer and the detector,$B(\tilde{\nu})$ is proportional to the absorption spectrum of the sample. Because of the computational effort required to perform the Fourier transformation, most FT-IR spectrometers have a dedicated computer which calculates $B(\tilde{\nu})$ from $I(\delta)$. The computer also makes readily available powerful data reduction techniques such as spectrum smoothing, background subtraction, reference spectra subtraction and cross correlation.

Since light of differing frequencies, separated by $\Delta\tilde{\nu}$, constructively interferes at $\delta = 1/\Delta\tilde{\nu}$, the maximum retardation of δ_{max} determines the ultimate resolution: $\Delta, \Delta \approx 1/\delta_{max}$. For example, an interferometer scanned 10 cm could produce a spectrum having a maximum resolution of 0.1 cm^{-1}. In practice the resolution is slightly better than this.

Scanning the moveable mirror at a rate of V (cm/s) results in amplitude modulation of the optical frequency, $\tilde{\nu}$, at a frequency of $f_{\tilde{\nu}} = 2V\tilde{\nu}$. The scan rate is made fast enough so that the lowest modulation frequency can be amplified conveniently by an a.c. amplifier. For example: f(400 cm^{-1}) = 2 (1.2 cm/s)(400 cm^{-1}) = 960 Hz. The product of 1/V and δ_{max} determine the time required to obtain one interferogram, typically 10 seconds.

Since the wide range of optical frequencies emitted by the continuum source is not significantly reduced by the interferometer, the optical range is determined by the spectral cut-off of the detector and by electronic filtering, which passes only the desired frequencies, $f_{\tilde{\nu}}$. In addition, the range, $\tilde{\nu}_{max}$, is determined by the number of sample points, N_s, required for a resolution of $\Delta\tilde{\nu}$, $\tilde{\nu}_{max} = \Delta\tilde{\nu}N_s/2$.

An important theoretical advantage of Fourier transform spectroscopy is the Multiplex Advantage, or Fellgett's Advantage. It is equal to $N^{1/2}$, where N is the number of spectral elements: $N = (\tilde{\nu}_{max} - \tilde{\nu}_{min})/\Delta\tilde{\nu}$. This is the improvement in the S/N ratio of Fourier transform spectroscopy over a conventional, grating spectrometer operated over the frequency range $\tilde{\nu}_{max}$ to $\tilde{\nu}_{min}$ with resolution $\Delta\tilde{\nu}$.

In practice this advantage is achieved only approximately due to an imperfect beamsplitter, the time required to perform the Fourier transform, etc.

An important practical advantage of Fourier transform spectroscopy results from the excellent frequency accuracy from scan to scan. For applications to steady-state experiments such as the present one, this makes possible signal averaging where many scans are added together to improve the S/N ratio. This improvement increases as $t^{1/2}$, where t is the time spent acquiring scans. The S/N ratio can be improved further by smoothing. This is commonly done in two different ways: zero-filling the interferogram and convolution smoothing of the final spectrum. Zero-filling is accomplished by increasing the number of spectral elements from I to I + J, where the additional J points of the interferogram are given the value of zero. Zero-filling smooths the spectrum without reducing its resolution. Convolution smoothing is similar to a weighted moving average of K points and is equivalent to a p^{th} order polynomial fit through the K points. Generally $1 \leq p \leq 3$ and $3 \leq K \leq 15$. Convolution smoothing results in a S/N ratio improvement of $K^{1/2}$ but reduces the resolution. Clearly, smoothing procedures establish a trade-off between the time spent gathering data and the time spent computing.

APPLICATION OF FT-IR SPECTROSCOPY TO COMBUSTION ENVIRONMENTS

Pulverized coal combustion presents a particularly difficult measurement environment for absorption spectroscopy. The principal difficulties are due to instabilities in the flame geometry, thermal emission of the flame, flow instabilities, particle luminesence, and scattering and absorption of the infrared source beam by the particles. Further, to achieve good spatial resolution, the diameter of the source beam must be reduced. This reduces the optical throughput and thus the S/N ratio. Preliminary experiments to evaluate the technique have employed a simple laminar flow reactor heated and stabilized by a flat diffusion flame. The reactor is configured to permit introduction of a test fuel, coal particles or gases, into the post flame environment. The coal combustion environment is simulated by adjusting the fuel/air ratio to produce copious amounts of soot particles in the optical path or by direct injection of coal particles. Our preliminary results show that the S/N ratio is degraded by a factor of 1.25 for hydrocarbon/air flames relative to a static gas sample; the S/N ratio is further degraded by a factor of 5 for coal/gaseous fuel/air flames. For the hydrocarbon/air flames, the noise resulting from the flame itself was much greater than that due to soot particles. The S/N can be improved by averaging. But, for coal combustion, there is low freuqency noise which is difficult to reduce by averaging; for example, that produced from variation in the ignition time, particle size dispersion, particle velocities and so on. Table 3 summarizes the relationship of the various FT-IR measurement parameters; Table 1 shows the performance of FT-IR relative to the measurement requirements.

PRELIMINARY EXPERIMENTS AND EVALUATION

We have conducted a series of preliminary experiments for the purpose of demonstrating the application of FT-IR spectroscopy to in situ measurement of species concentrations and temperature in luminous, particle-laden combustion environments. To our knowledge these are among the first of such studies to employ FT-IR absorption spectroscopy. However, similar studies have been carried out by Solomon and coworkers (7) using FT-IR to investigate coal devolatilization at temperatures somewhat lower than practical flame temperatures.

In this section, the results of these experiments are summarized. While we emphasize that our objective has been to quantify species detectabilities, sources of error, and to identify potential system improvements, the reader will note that we at times infer mechanistic information about the sequence of combustion events on the basis of our data. The very fact that such seemingly sensible and self-consistent inferences can be made is, we believe, encouraging for the future application of FT-IR to in situ combustion studies.

All of our experiments utilized an FT-IR spectrometer, transfer optics, flame source with associated gas handling system, and an infrared detector. This system has been described elsewhere (7-9); a top view of the optical path through the flame is shown in Figure 1. Almost all of the data presented in this paper were collected at 2 cm^{-1} spectral resolution and computed in double precision using a 32 bit word length. Preliminary data for coal combustion experiments were collected at 8 cm^{-1} spectral resolution. Interferogram files were enlarged by zero-filling, by a factor of two.

Our transfer optics produced a beam whose maximum diameter in the flame was 2.5 mm. Flame sources could be translated vertically, and we thus were able to measure the infrared absorption of the flame gases along a horizontal axis with a vertical spatial resolution of 2.5 mm. Although effort is being made to determine the minimum practical diameter required to obtain an acceptable S/N, it is not clear that a substantial reduction in beam diameter will lead to more detailed information about the combustion process. In practice, some reduction in spatial resolution may serve to improve the S/N by spatial averaging, which, in the flow reactor, is equivalent to time averaging.

The experiments to be described in this paper were made with three flame sources: an ordinary kerosene lantern; a flat flame surface-mixing burner to study

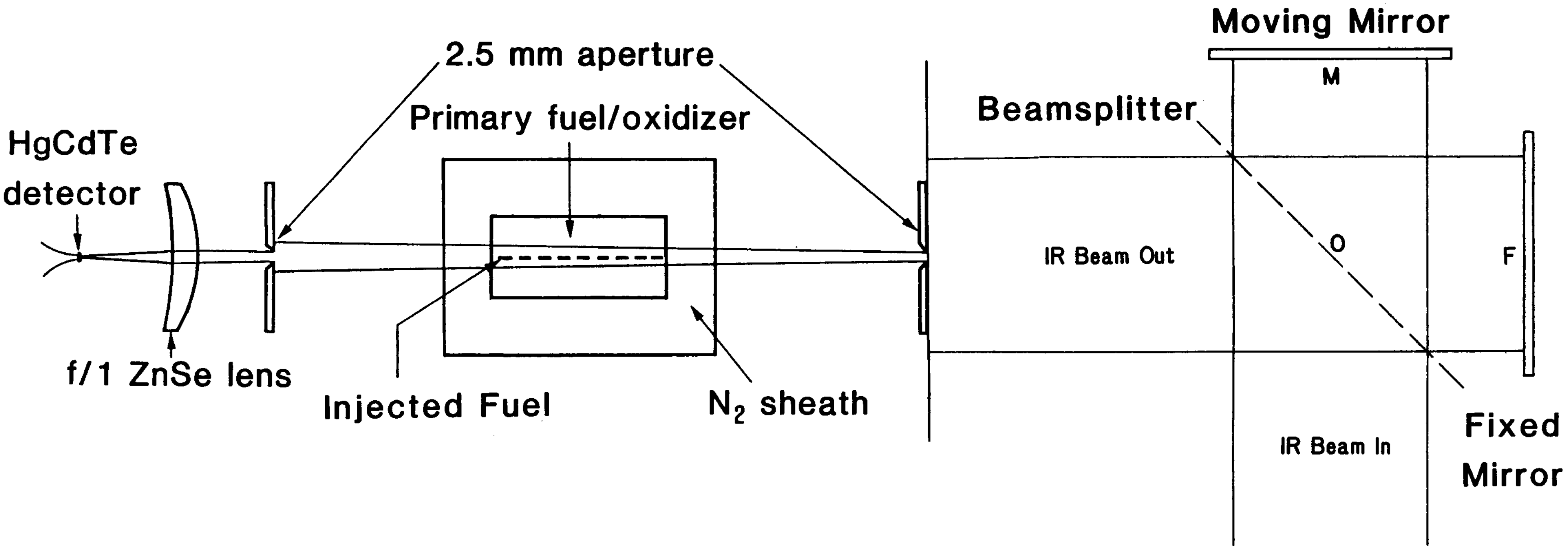


Fig. 1. Top view of Michelson interferometer and flow reactor.

the combustion of gaseous hydrocarbon fuels in air; and a modification of this, a flat flame burner designed to inject coal particles into the flame along the optical line of sight (Figure 1). This latter configuration closely approximates the laminar flow reactor which we hope to apply to our subsequent studies of pulverized coal combustion.

Test Fuel: Kerosene

Commercially available kerosene was used as the fuel; it was predominantly a mixture of aliphatic hydrocarbons. It produced a highly luminous, sooting flame having about 25 mm maximum optical path length. The infrared absorption spectrum of this flame, 2 mm above the lantern wick, is shown in Figure 2. Vibration-rotation lines of water were observed from 1250 to 1900 cm^{-1} (ν_2) and from 3400 to 4000 cm^{-1} (ν_1 and ν_3). The very intense ν_3 band of CO_2 is centered near 2330 cm^{-1}, and the P and R branches of the ν_1 band of CO are centered around 2145 cm^{-1}. In addition to these expected lines, a larger number of lines were observed from the lower limit of the detector, 720 cm^{-1}, extending to about 1000 cm^{-1}. These result from excited higher rotational levels in hot H_2O molecules (2).

The moderately intense absorption at 2930 cm^{-1} and the weaker band at 950 cm^{-1} are presumably due to gas phase hydrocarbons. Further examination of the band at 2930 cm^{-1} reveals a partially resolved shoulder at about 2860 cm^{-1}, and a much weaker peak at 3010 cm^{-1}. The bands at 2860 and 2930 cm^{-1} can be assigned to C-H stretching modes in aliphatic -CH_2- groups; it is not obvious what fraction of these bands is due to hot, unburned components of kerosene. It is clear, however, that the bands at 950 and 3010 cm^{-1} cannot be attributed to unreacted fuel. These bands are typical of C-H in-plane bending and stretching modes of longer chain olefinic hydrocarbons. Their presence in a series of spectra for this flame suggests that pyrolytic dehydrogenation of the hydrocarbon fuel takes place in a zone immediately above the wick and extending upward some 10 mm.

These very luminous, highly sooting flames posed no insurmountable difficulties in our absorption measurements. The most severe problems arose from instability in the flames resulting in low signal-to-noise ratios. The stability of the flame was increased by surrounding the wick housing with a chimney. Remaining instabilities were further compensated for by time averaging 400 interferograms. This greatly improved the S/N ratio.

Test Fuel: Gaseous Hydrocarbons.

More systematic evaluation followed our encouraging preliminary results. In this section we summarize data presented elsewhere (8-10) for very stable methane/ air, propane/air, and methane/ propane/ air combustion. These studies made use

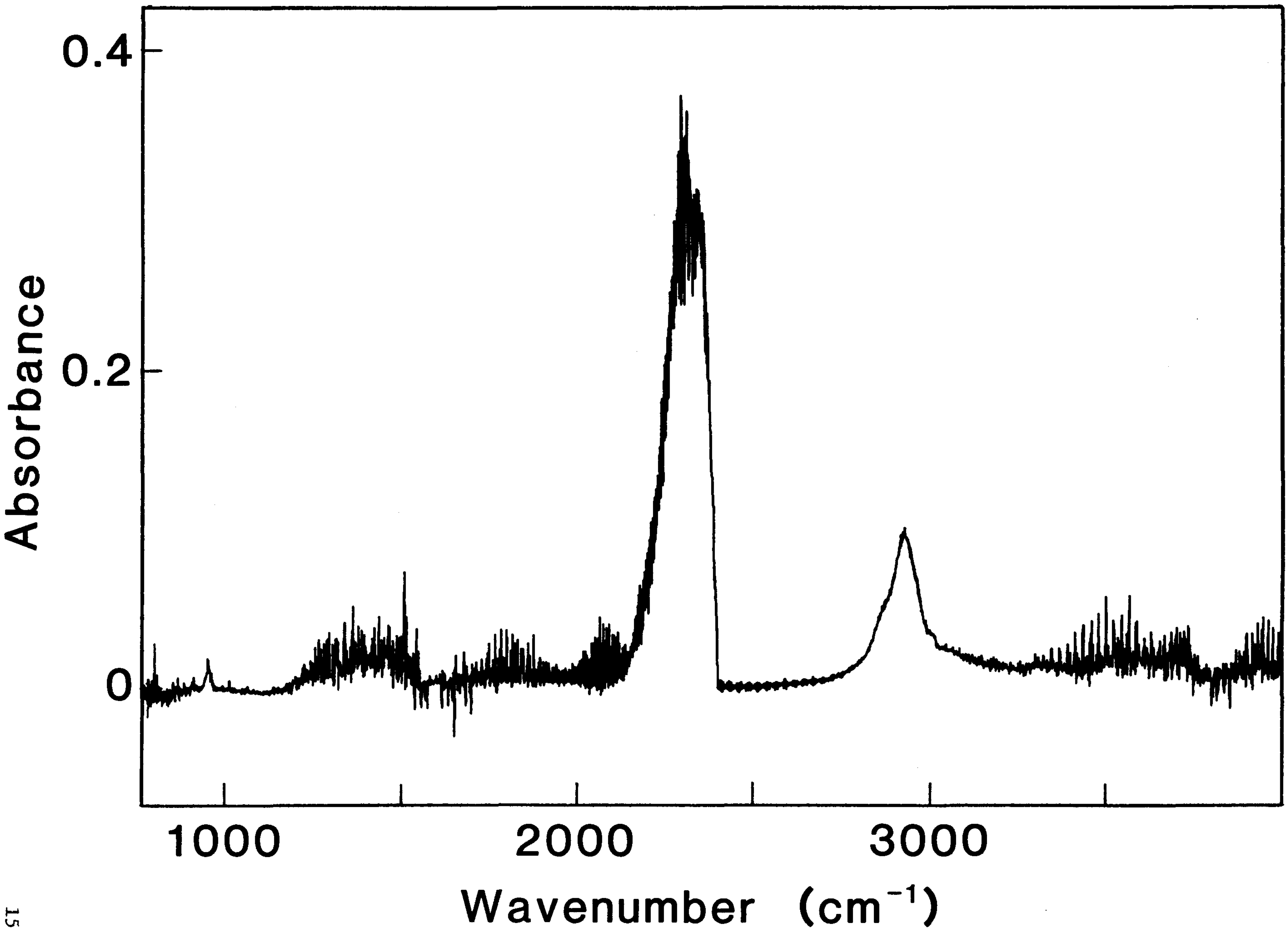


Fig. 2. FT-IR spectrum of kerosene flame, 2 mm above wick.

of the laminar flow reactor shown schematically in Figure 1. In the reactor, a multi-element diffusion flame surrounds and stabilizes the combustion of a secondary fuel which is injected along the center line of the burner to be coincident with the FT-IR optical axis. Using this arrangement, combustion of the secondary fuel (test fuel) can be monitered as a function of combustion time by raising or lowering the reactor relative to the IR beam.

We have calculated an axial temperature profile for the methane and methane/propane test fuels using measured peak absorbances of vibration-rotation lines in the P branch of the CO fundamental (Figure 3). Since our spectral resolution is some 10 times broader than the expected line widths, we relied on an isointensity method which compares lines of equal intensity for a given temperature rather than attempting to calculate accurate integrated intensities. Lines due to the $\nu(2\text{-}1)$ hot band are clearly observed in our data. Comparing $\nu(1\text{-}0)$ lines of calculated isointensity which are best resolved from the hot band lines, we arrived at the temperature profiles shown in Figure 4. Uncertainties in each point are an average of 12.5 smooth curve is shown solely to connect the data and has no theoretical basis. In spite of these large uncertainties, the calculated maximum temperatures are quite reasonable for flames of this type.

Signal-to-noise ratios in these experiments follow a $t^{1/2}$ dependence (where t is the data collection time) as shown in Figure 5 for a methane/air flame. Noise generated by flicker in the test fuel combustion caused a reduction in S/N by a factor of 1.25 from a condition with no flame present. We have measured S/N ratios for two different sets of transfer optics differing in peak detector signal by a factor of 2.45, and we observe that the slopes of the two lines differ by a factor of 2.25. This is good experimental agreement for these measurements and is the behavior expected for detector limited conditions.

Using methane as the primary and test fuels, the reactor produced a very lightly sooting flame, and no infrared absorbing species were observed other than H_2O, CO, CO_2 and unburned CH_4.

When propane was used as the primary and test fuels, we identified CH_4, C_2H_4, and C_2H_2 as decomposition products in addition to H_2O, CO, CO_2 and unburned propane. These first three species appear to peak at a flame temperature of 1000 K; these bands gradually decrease (those due to methane and ethylene more rapidly than acetylene) as the flame temperature and distance above the burner surface continue to increase.

Several bands were observed which had peak absorbances at 1400 K, and were similar to the broad, unresolved hydrocarbon species found in the kerosene/air flames discussed above. Bands at 955 and 3005 cm^{-1} were assigned to bending and stretching modes of gas phase -CH=CH- groups. A much broader band was centered at 2995 cm^{-1} and was assigned to the unresolved symmetric and asymmetric C-H stretching modes of aliphatic $-CH_2-$ groups. All of these broad hydrocarbon

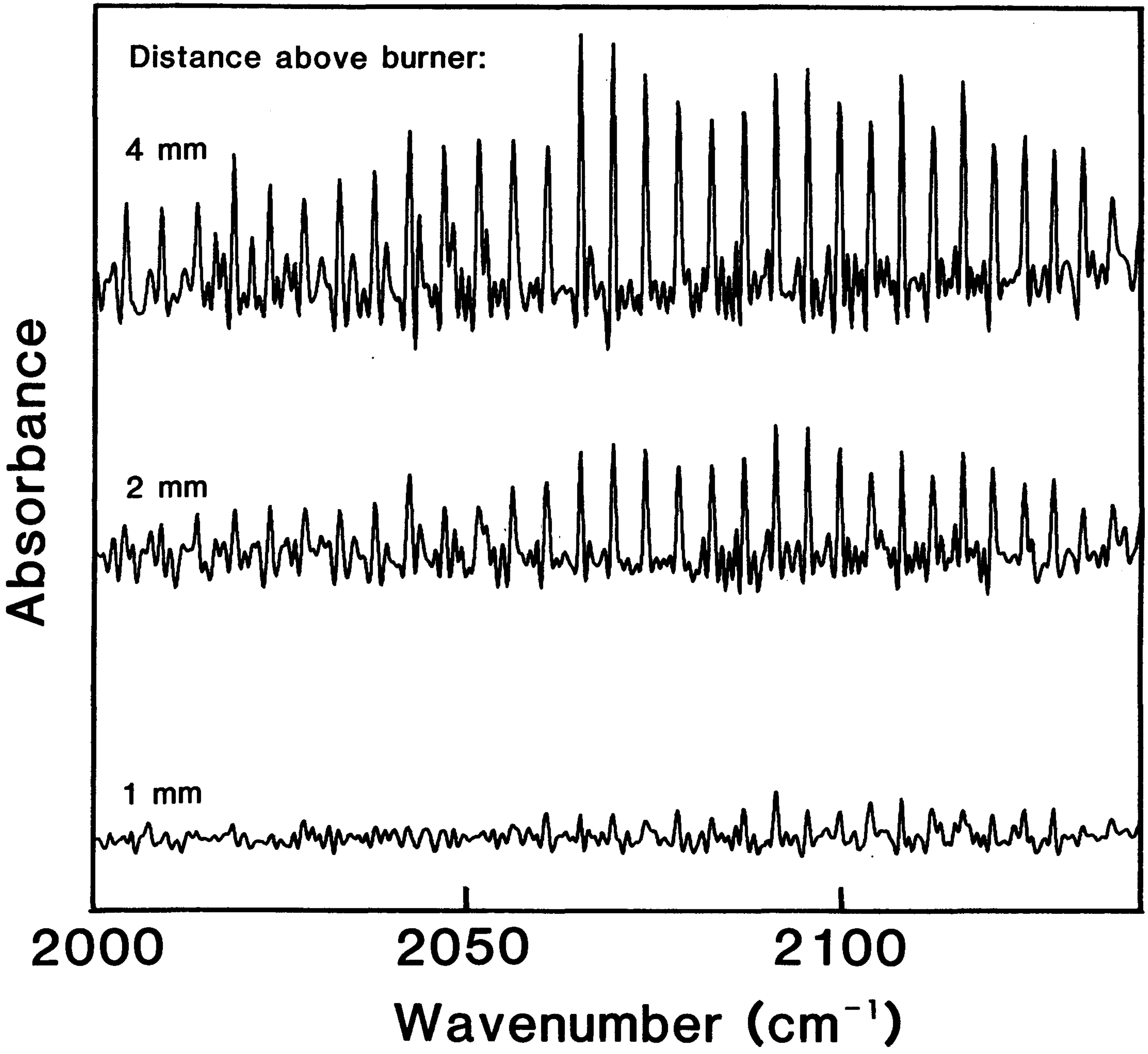


Fig. 3. Carbon Monoxide P branch for propane injected into mathane/air post-flame gases.

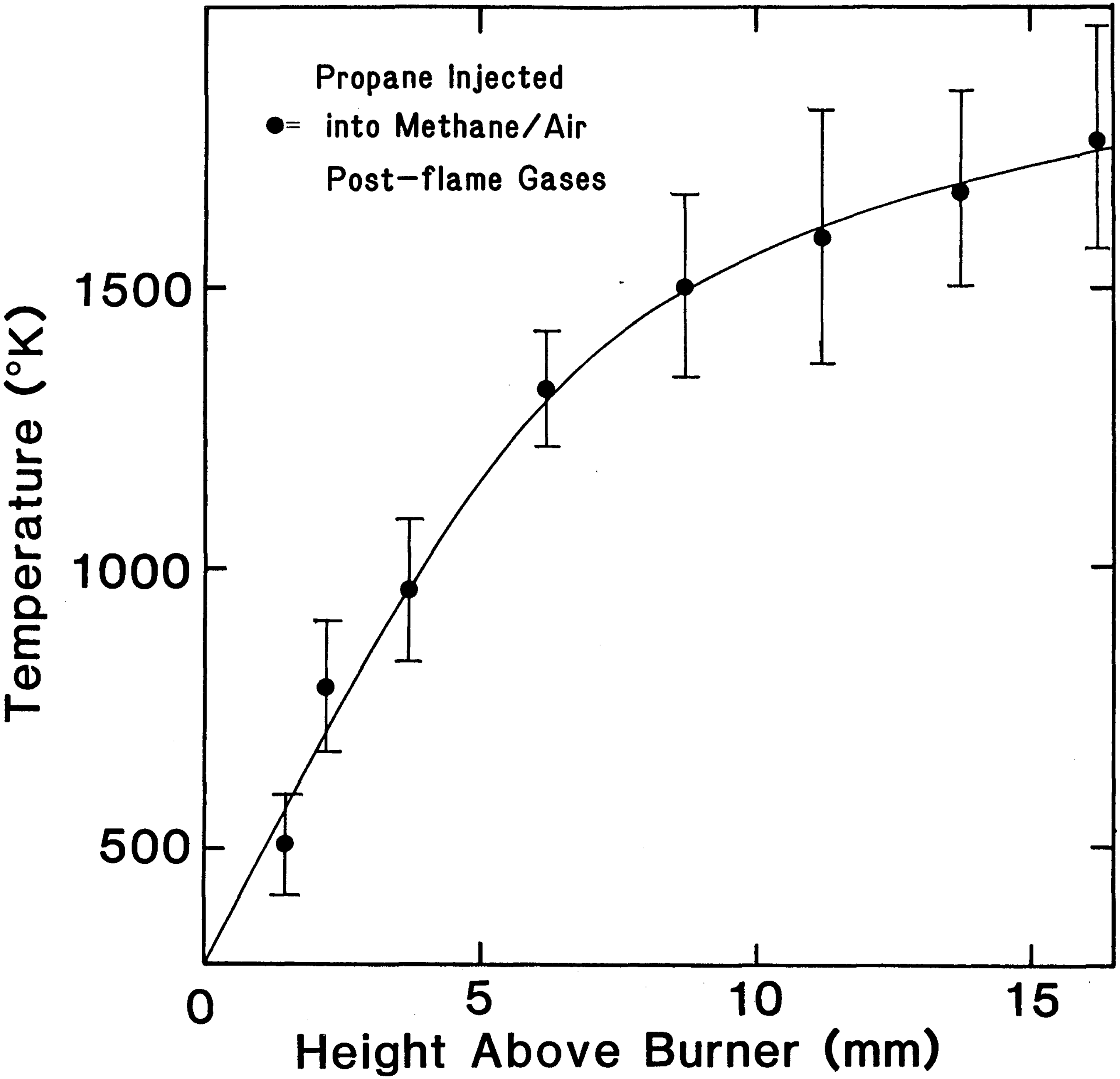


Fig. 4. Axial temperature profile for hydrocarbon/air flames.

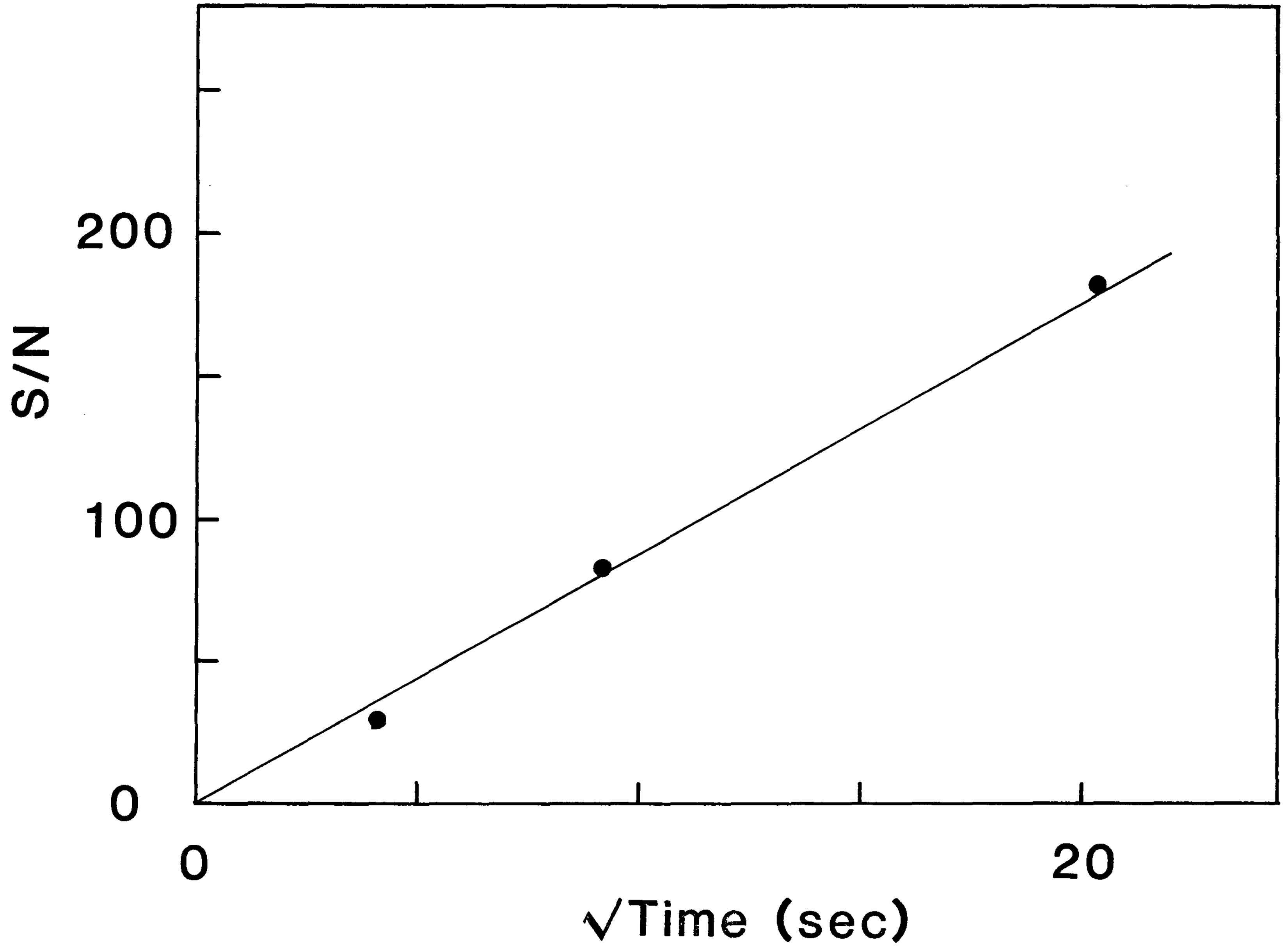


Fig. 5. Signal-to-Noise ratio as a function of data collection time for hydrocarbon/air flames.

bands rapidly decreased in intensity as the flame temperature increased, and were essentialy absent in the luminous, sooting reigon.

Using methane as the primary fuel and propane as the test fuel, resulted in a very rich, soot-laden region along the center of the burner with a sharp onset of intense yellow incandescence about 20 mm above the burner surface. Nevertheless, the detector signal remained fairly stable well into the luminous zone. We did,however, observe a slow variation in the baseline of each interferogram due to flicker.

Our data for methane(primary)/propane(test) fuel clearly show a lack of the C_2H_4 and C_2H_2 which was formed when propane was the exclusive fuel. Any production of CH_4 would be masked by the presence of unburned CH_4 from the primary fuel. Since these unsaturated species were also not detected in the methane/ air flame, one might infer that these small hydrocarbons arise mainly from the pyrolytic decomposition of propane. Oxidative attack on the propane molecule is probably more strongly favored in the methane/propane/air flame due to the more rapid increase in temperature near the base of the burner observed in our experiments.

We do observe three broad infrared bands in these flames (Figure 6) which are located at the same frequencies as those observed in propane/air flames. Peak absorbance values for the bands at 955 and 3005 cm^{-1} show the same dependence on temperature for both propane/air and methane/propane/air flames with a peak in olefin concentration occurring at about 1400 K as shown in Figure 7. It is quite tempting to infer from this information that these olefinic species are gas phase soot precursors since Dyer and Flower have recently demonstrated the important role of temperature in the production of soot (11). Comparison of our data with the literature (12) indicates that these unsaturated hydrocarbons are probably unconjugated, noncyclic secondary olefins. Our data also show approximately equal intensities for the two modes which is consistent with an equimolar mixture of both isomers of a given olefin.

Test Fuel: Pulverized Coal

Preliminary experiments to evaluate FT-IR absorption spectroscopy as a diagnostic technique for in situ detection of gas phase species during coal devolitization and oxidation are currently underway. The flat flame burner shown in Figure 1 is used to provide a hot, oxidizing environment, and pulverized coal particles are injected into the lean, primary flame along the optical axis in a fashion similar to that described earlier for the methane/ propane/air flames. Pittsburg Seam #8 bituminous coal milled to produce a broad size distribution with a mean diameter of about 60 μm was used in this study. A fluidized bed feeder permits entrainment of the particles into the combustion gases and distribution to the burner through a

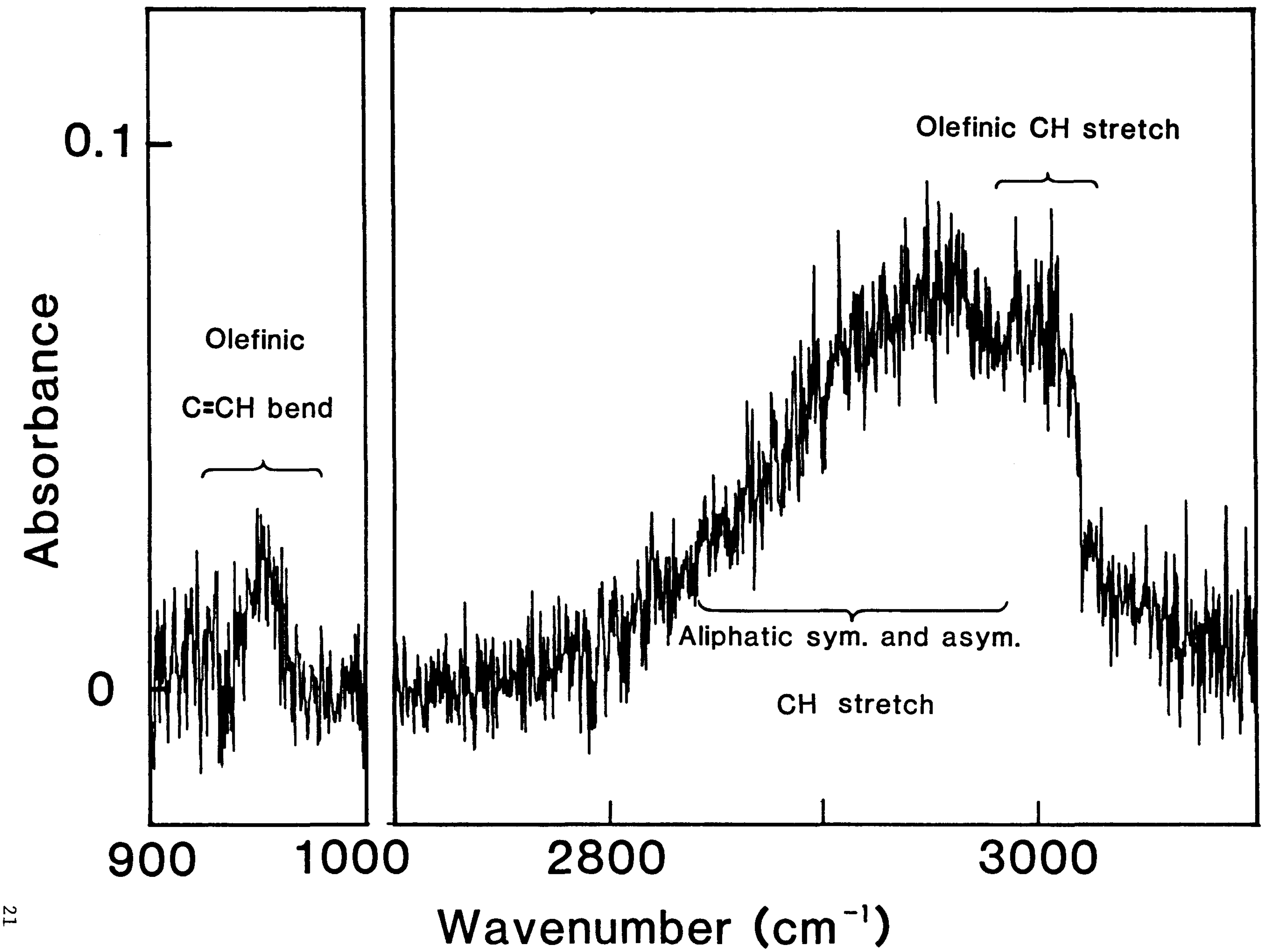


Fig. 6. FT-IR spctrum of propane injected into methane/air post- flame gases, 6mm above the burner surface.

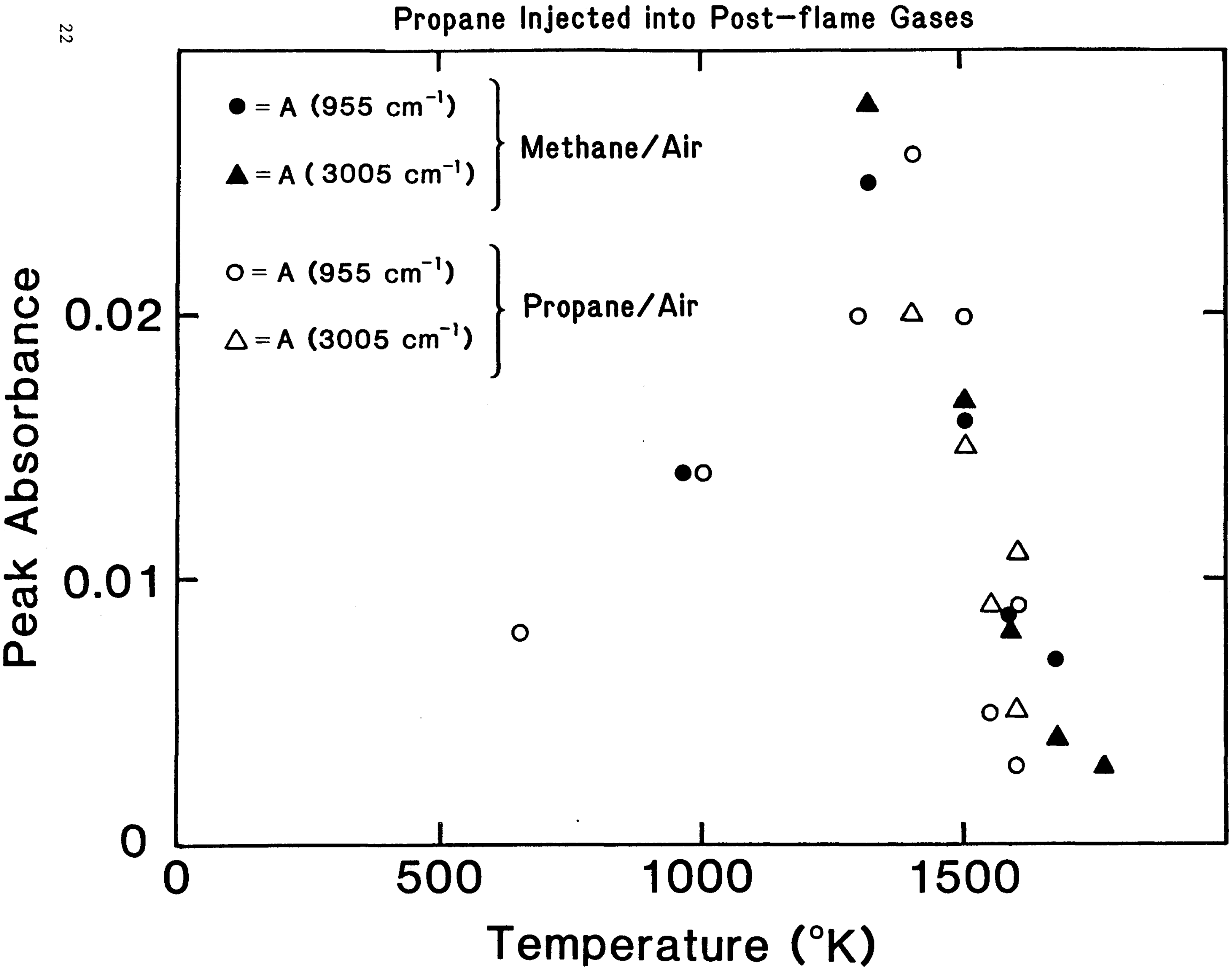


Fig. 7. Olefin peak absorbance values for hydrocarbon/air flames.

manifold with 29 tubes of 0.38 mm diameter. Particle flow along the optical axis is relatively steady on average as evidenced by the visible luminosity of the combusting coal. Some end effects are noticeable and are probably due to a combination of manifold pressure and post-flame gas temperature differences along the burner axis.

Thermal emission, scattering and adsorption due to the low number density, burning coal particles caused a severe time variation in the interferogram baseline – much more than was observed for the high number density soot particles produced in the gaseous fuel/air flames. These fluctuations could be satisfactorily reduced by time averaging interferograms, and the improvement in S/N ratio followed the same $t^{1/2}$ behavior as was observed in our previous experiments. We compare S/N ratios for methane/air post-flame gases, with and without coal particles injected, at 2500 cm^{-1} in Figure 8. The presence of coal particles reduces the S/N ratio by a factor of 5 under our present conditions.

In Figure 9 we present low resolution spectra of these post-flame gases from 800 to 4000 cm^{-1}. In these spectra the presence of H_2O and CO_2 are clearly observed despite the noisier data for the gases containing coal particles. These spectra are intended to demonstrate the feasibility of obtaining useful infrared absorption of gas phase species in coal-laden flames using FT-IR spectroscopy. No quantitative interpretation of these spectra was made, since the greater part of the gases observed are produced by the combustion of methane in the primary flame. Nevertheless, the technique has been unambiguously demonstrated. Work is currently underway to quantify the detectability of low molecular weight gases and their temperatures during coal combustion using non-carbon or non-hydrogen containing fuels in order to remove interferences from the primary fuel. A preliminary estimate of the typical detectability for 2 cm^{-1} resolution, 5 cm sample path and 10 min averaging time per reactor position is 20 ppm.

FUTURE DEVELOPMENTS

At the moment we are progressing in three, related directions in these studies.

(1) We are improving and enlarging the capabilities of our flow control system and burner design to allow a greater variety of solid fuels to be studied and to achieve greater control of the chemical environment in which they are pyrolyzed and oxidized.

(2) Our FT-IR spectrometer and data processing system have been recently upgraded to achieve a maximum spectral resolution of 0.08 cm^{-1} (compared to our previous limitation of 0.5 cm^{-1}). The new intereferometer has been placed on an optical table with a central access hole to accommodate a flow reactor source and

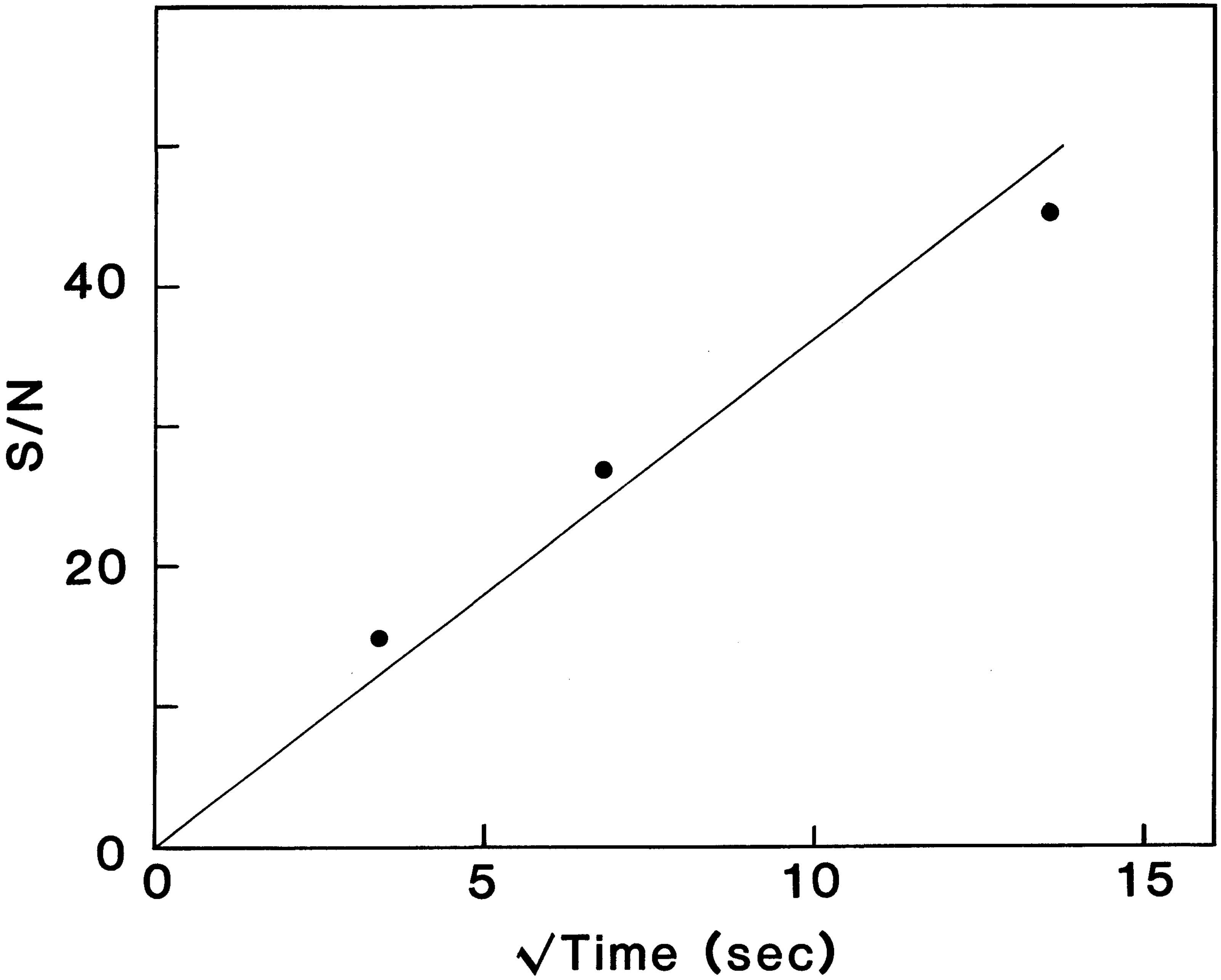
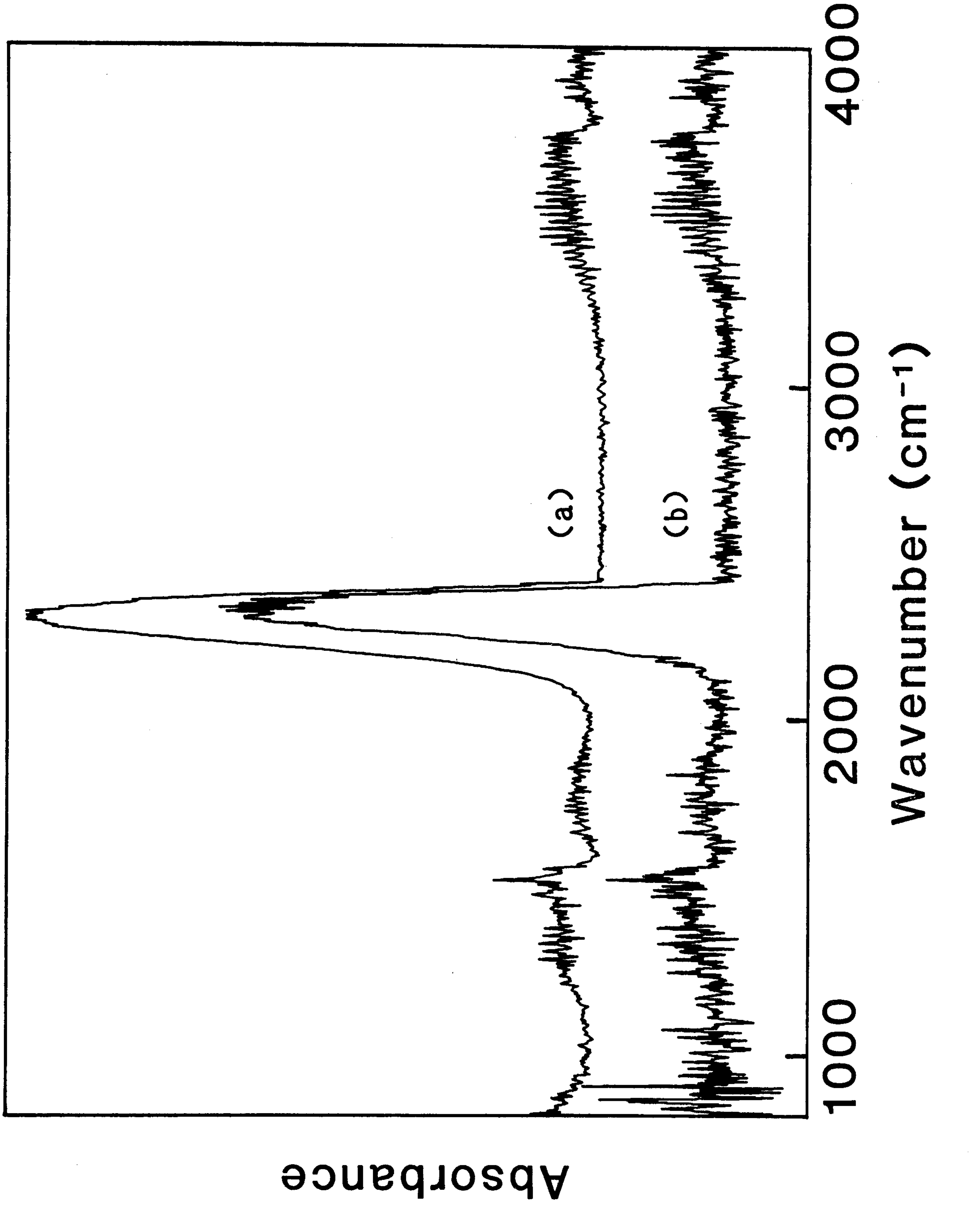


Fig. 8. Signal-to-Noise ratio as a function of data collection time for coal injected into laminar flow reactor.

Fig. 9. Low resolution FT-IR spectrum of post flame gases in a methane/air combustion evvironment, 20 mm above burner surface; (a) no coal injected, (b) coal injected.



to allow other experiments, such as optical particle sizing, optical pyrometry, and physical sampling, to be conducted concurrently with the infrared measurements. Computer memory in the FT-IR system has been expanded, and a vector processor has been added in order to calculate Fourier transforms of the very large, high resolution data files in a matter of minutes (rather than hours). The design of transfer optics is being improved continually to increase throughput of the modulated infrared beam while increasing the spatial resolution within the flame.

(3) Computer codes are being developed in order to fit the observed spectral lines to calculated band shapes as a function of temperature, number density and total pressure. Correlation techniques will be used to identify and measure quantitatively, species whose band intensities are on the order of the noise level. Qualitative identification of unresolved, broad-band hydrocarbon intermediate species will continue in a fashion similar to the studies of gaseous fuel/air flames. Some quantitative estimates of particle size can be made from measurements of infrared scattering and can be compared with visible particle sizing studies.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. D. R. Hardesty for many helpful suggestions and Mr. K. Hencken for construction of the burners. This work was supported by the Department of Energy.

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