AN INFRA RED STUDY OF FLAT FLAMES

Thesis
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by

Paul Davies, B.Sc., A.R.C.S.

Department of Chemical Engineering
and Chemical Technology,
Imperial College of Science & Technology,
London S.W.7.

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ABSTRACT

A non-interfering method of flame analysis employing infra-red absorption spectroscopy has been developed and studied in relation to a lean ethylene-air flame stabilized on a flat flame burner. Stabilization of a flame meeting the requirements of the method was possible over short periods of time. The optical system devised enabled the flame zones to be scanned throughout, with a higher spatial resolution than has previously been achieved, and absorption spectra obtained over the wavelength range 1 to 15 μ.

The method was not sufficiently sensitive to detect intermediate unstable species formed during the flame reactions. The disappearance of ethylene and the appearance of the stable products, carbon dioxide, carbon monoxide and water could be observed. It has been shown that by combining the spectroscopic observations with a measurement of temperature distribution by the beam deflection (refractive index) method the actual concentration distributions of the above stable species can be measured before and after the reaction zone. In the reaction zone excitation of the species makes this impossible. Particular attention has been paid in this connection to the product carbon dioxide and it has been shown that the calibration procedure

provides a useful method of measuring absorption coefficients at elevated temperatures, provided by the flame, for non-reacting species added to the reactant gases.

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CHAPTER 1. INTRODUCTION.

The study of flame requires investigations into both the nature of the species present, and the kinetic and equilibrium characteristics of their interactions. Experiments have been conducted to assist in this study and generally each gives information concerning both of these aspects. At the present stage considerable progress has been made in interpreting flame reactions in terms of overall kinetics but as to the detailed nature of the interactions little is known. This is not surprising considering the difficulties involved in the experimental study of flames. The inherent problems are lack of resolution, that is degree of separation of the species at the reacting stage, and the difficulties in taking samples or making measurements in flames at temperatures of the order of 1000°C and upwards. The first degree of control is that obtained by pre-mixing the fuel and air prior to its introduction to the flame. This allows calculation of reaction rates and the postulation of a reaction scheme if the products are analysed. Secondly it permits control of shape since it is found that the flame of pre-mixed reactants burns with a characteristic velocity dependent upon mixture composition, and using various types of burner, it can be satisfactorily stabilized in several geometric forms. The most suitable of these for detailed

analysis was that first obtained by Egerton and Powling[1] now known as the laminar flat flame. This was obtained, as its name implies, as a circular disc of flame produced parallel to the burner port, the essential feature being that the flow-rate was uniform across the whole flame and thus conditions prevailing at any part approach those in an infinite flame front. The theoretical treatment is consequently simplified, the equations used to describe the flame being expressed in terms of one distance variable only. The flame can only be stabilized in this manner with mixture compositions towards either of the composition limits. This means both that temperatures are not too high, and the spatial region over which reaction is proceeding is of the order of millimetres in thickness. An adequate spatial resolution using an optical probe can be expected in these circumstances.

Previous approaches have been by two kinds of method. Initially measurements of temperature were made using thermocouples of the smallest size to render detailed measurements possible . This was subject to criticisms concerning the effects of third bodies on the flame and the possibility of additional reactions occurring on the surface of the thermocouple, as well as conduction of heat through the material of the thermocouple. An ingenious method developed by Anderson

and Fein[2] enabled the calculation of temperature distribution from observations of particles of bentonite added to the reactant stream, the acceleration of which when approaching the flame front was observed by photographing their 'tracks' revealed when illuminated stroboscopically. However this procedure was once again subject to the criticism that particles added to the flame may be expected to interfere with it. Similarly Fristrom et al[3] have developed a probe technique for abstracting samples from small local volumes in flames of both this and spherical configurations, again subject to criticisms of interference with the reacting species. Thus 'non-interfering' methods were developed and principally these have been the observation of refractive index distribution[4,5], and observations of interference fringe displacements produced again by refractive index distributions[6]. These studies have led to the advances in structural knowledge of the flame, by means of calculations of temperature distributions and heat release rate distributions.

The present spectroscopic study was initially part of a three phase investigation into lean-limit laminar flames, the two remaining being those by Spokes[7] for the ultra-violet region, and Weinberg and Peacock[8] for the visible region. The somewhat diversified approaches in the three phases resulted from the different premises of their attacks and unfortunately a concerted summary of their results does not

appear to be practicable. The present work is intended as a further attempt to enlarge the field of knowledge upon both the natures and positions of the reacting species as revealed by the infra-red method, to gain further information regarding their physical properties, and as an evaluation of the infra-red method for these studies.

Statement of Aims.

The analysis of the flat flame by infra-red absorption had, in fact, two aims. The first was the continuation of a programme of studies for the detection of species found in flat pre-mixed flames and recording their spectra. The second was to investigate the possibility of using the flame as a source from which might be obtained the absorption coefficients, as a function of wavelength and temperature, for inert species added to the flame gases. These aims are, to some extent, interdependent.

The first must be further sub-divided into qualitative and quantitative aspects. The infra-red method is most commonly applied qualitatively but in the present case the two avenues were pursued. The first objective was to see if it was possible to detect the unstable intermediate chemical species which are produced during the process of conversion of fuel to final products and which are vital to

the chain reaction mechanism. It has to be emphasized straightaway that the work had to be confined to lean-limit flames for practical reasons, and a careful search for these unstable intermediates confirmed that their concentration was not sufficient for detection by this method, using the optimum experimental conditions.

The second qualitative objective was the recording of both their spectra and the location of the zones of disappearance of the fuel (ethylene), appearance and disappearance of carbon monoxide and appearance of carbon dioxide. As species these provide valuable information on the conditions prevailing through the flame and in the final products, and in addition serve as stable guides in the evaluation of the method in the light of the particular requirements of the second principal aim (see below).

The quantitative work initially envisaged was the measurement of the distribution of species concentration through the flame. This is potentially of considerable practical importance since it should enable the calculation of the dual dependency of concentration upon temperature and composition effects from one spectrum.

The second principal aim derives from considerations of the physical properties of the flame, and the opportunity presented of using it as a high temperature and constant pressure

source of spectra of inert species, which may be added to the mixture. It was considered possible to stabilize a flat flame without confining windows and in the absence, either upstream or downstream of the flame, of heat sinks in its immediate vicinity. If so, and assuming the non-accumulation of reaction products in its neighbourhood, the stationary and measureable temperature distribution it presents could be set up normal to an infra-red beam of appreciable path length. This would enable calibration of the spectra at the range of temperatures provided, of any inerts which might be added to the flame gases, the temperature distribution being maintained by removing volumes of the diluent nitrogen, equivalent to the volumes of inert added. This would, in turn, permit calculation of the absorption coefficients for these added inerts. To evaluate the potential use of the flame as such a source was the second principal aim of this work. The study of the fate of carbon dioxide was suited to this since when added to the reactants, it is present as an inert and the absorption at initial and final temperatures due to various amounts added, can be investigated to form the basis of a calibration. It was assumed that its presence would not affect the final flame temperature otherwise than can be compensated for by the removal of a quantity of nitrogen of equal thermal capacity.

The remaining sections of Chapter 1 include the relevant background theory, and some discussion on the method, serving to introduce Chapters 2 and 3.

Theoretical Background.

Flames can be very broadly divided into two types by the flow regimes which to a large extent govern their existence. These are flames of pre-mixed fuel/air from a single burner port and diffusion flames of fuel/air in separate but closely situated burner ports. Pre-mixed flames can be further sub-divided because they have a characteristic burning velocity dependent upon mixture composition, which enables the stabilization of flames with several configurations. Diffusion flames are dependent upon the diffusion of fuel and oxident together; and although several flames of this type have been closely examined[9] they are not as satisfactory for investigations into the fundamental chemical reactions in process. Analyses of the pre-mixed fuel/air flame have been achieved in both planar and spherical configurations by chemical sampling with a scavenger probe[3] and in planar flames by non-interfering methods. In the laminar configuration the flame's dependence upon mixture composition presents the possibility of controlling it in a steady position in space and sets the stage for observations of its chemical and

physical structures. Consequently both practical and theoretical attempts have been made to describe the flame's properties in both of these aspects. The theory discussed below is only that considered relevant to this work.

1.1. The Flat Flame.

The essential property of a flat flame is that it has a unique burning velocity, which is defined below; when the flame is freely stabilized this can be calculated by dividing the flow-rate of the reactants by the flame area.

Burning Velocity (S_u)

Consider a tube (Fig. 1) containing a mixture of fuel/air flowing left to right with velocity v; on igniting the mixture at the right hand . a flame will travel along the tube, assuming fuel/air ratio is within the required range, at an observable velocity V_f. The burning velocity (S_u) is defined from $|V_f - v| = S_u$, both velocities being taken orthogonally to the flame front.

Using the Egerton-Powling burner v may be adjusted so that $V_f = 0$ relative to the burner. Then $|v| = S_u$. The advantage of this method for finding burning velocities is that the existence of the steady flame ensures flame reproducibility, as the burner can only stabilize flames within a very narrow range of burning velocities. The question of flame

FIG. 1 SCHEMATIC DIAGRAM OF FLAME OF PRE-MIXED REACTANTS TRAVELLING ALONG CYLINDRICAL TUBE.

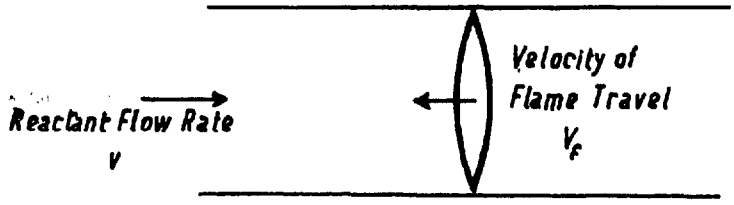
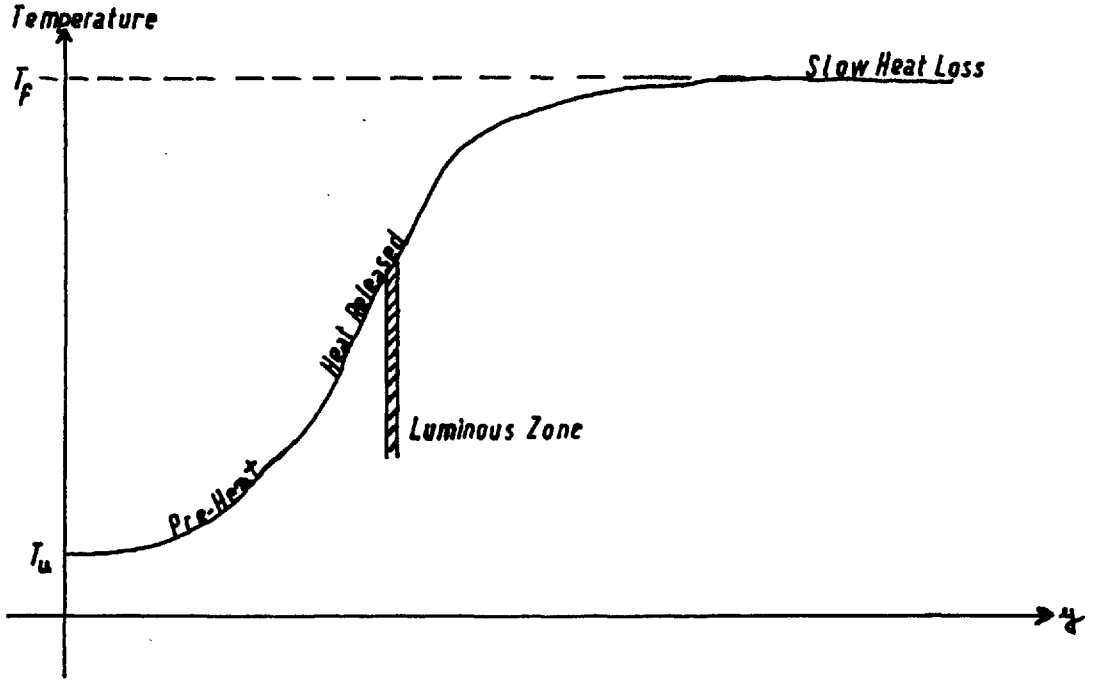


FIG. 2 TEMPERATURE DISTRIBUTION ASSOCIATED WITH FLAT PRE-MIXED FLAME.



reproducibility was to be slightly more complicated in the present case as for the absorption coefficient work some part of the mixture was to be replaced by an inert additive. The flame properties in the two cases would not be strictly reproduced, but the requirement that the temperature distribution be not varied could be met.

Factors influencing Burning Velocity.

The burning velocity of a flame has been found to depend upon pressure[10] and initial temperature[11] of the reactants as well as mixture composition. The present work was to be conducted at atmospheric pressure and small variations in it were disregarded.

The dependence upon the intial temperature of the reactants is illustrated by Fig. 2, the numerical values referring to a lean limit pre-mixed ethylene/air flame stabilized in the Egerton-Powling burner. Increasing the temperature of reactants results in early onset of reaction. In turn the onset of chemical reaction occurs some distance beyond the point where temperature rise is first observed. This is because energy feedback processes of diffusion and thermal conduction cause pre-heating of the reactants to ignition. Thus the onset of chemical reaction is to some extent masked by these effects as will be made more apparent from consideration of the steady state equations.

1.2. Steady State Equations.

Despite the rapidly changing values of the properties of the flame gases, both of physical characteristics such as temperature, density, and distribution of concentration of the various chemical species present, several parameters can be used to describe the flame, their derivation depending upon its 'steady state' overall condition. The first of these is the mass burning rate per unit area denoted by M and given by

$$M = \rho v = \rho_o v_o = \rho_f v_f \qquad \ldots\ldots\ldots 1.2$$

where ρ and v are the local density and velocity respectively, the suffix o denoting the steady values upstream, f the steady values in the final state. M is a constant throughout the flame-front.

Considering a unit volume of the flame, bounded by two plates at y and $(y + \delta y)$. Applying the principle of the 'Conservation of Heat' enables us to write

$$-\frac{\partial}{\partial y}\left(k \frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial y}(R) + \frac{\partial}{\partial y}(\rho v c T) - Hw = 0 \qquad \ldots\ldots 1.3$$

where T is temperature, k = thermal conductivity, R = flow of radiant energy per unit area, c = specific heat at constant pressure, H = heat of reaction, w = rate of reaction per unit volume such that Hw = heat release rate per unit volume. In view of the relative transparency of gases to

visible radiation $\frac{\partial}{\partial y}(R)$ is generally taken = 0 and we have

$$-\frac{\partial}{\partial y}(k.\frac{\partial T}{\partial y}) + M.\frac{\partial}{\partial y}(cT) - Hw = 0 \qquad \ldots\ldots\ldots 1.4$$

Similarly by applying 'Conservation of Species' to the same volume we can state for the j^{th} species

$$-\frac{\partial}{\partial y}\left(D_j\frac{\partial c_j}{\partial y}\right) + \frac{\partial}{\partial y}(vc_j) \pm w_j n_j = 0 \qquad \ldots\ldots\ldots 1.5$$

where $w_j n_j$ is the local rate of creation or destruction of the j^{th} species, vc_j is the rate at which new material is being transported into the volume by natural flow and the first term represents material lost to the volume by diffusion. This is proportional to $\frac{dc_j}{dy}$ where c_j is the local concentration of the j^{th} species, the constant of proportionality being the local diffusion coefficient D_j. The solution of this equation and the subsequent construction of a concentration profile for the j^{th} species would thus require a knowledge of both the temperature dependence c_j (or ρ) and D_j's. In fact, as will be seen in Chapter 4, the calculation could not be proceeded with to this stage. A theoretical treatment is included to introduce the features of the analysis relevant to the infra-red method.

A theoretical summary of the flame comprises

(a) the heat conservation equation, 1.4,

(b) one equation of species conservation like 1.5 for each species,

(c) expressions for the rates of creation or destruction of species as functions of temperature and concentration,

(d) an equation describing the variation in density with temperature and mole number,

(e) equations relating k, c and D to temperature and composition,

(f) the boundary conditions for these equations.

Experimental Methods.

The physical model of the flame is of a horizontal distribution in the pre-flame region of non-reacting species heated initially by energy "feed-back" processes to an ignition temperature at which the onset of reaction takes place. Proceeding with a given volume through the flame exothermic reactions continue, heat released is dissipated in several ways, species concentrations build up and decay and the temperature rapidly increases. The processes continue until all exothermic reactions cease once more, the final products reach steady state equilibrium values, convecting away much of the heat released, and the products eventually cool again.

1.3. Temperature Measurement.

The analyses to be conducted were (a) temperature distribution through the flame, (b) qualitative appreciation

of absorption peaks for identifiable species, (c) concentration of a species through the flame if possible.

A method enabling the measurement of temperature through the vertical section of a flame enables the construction of curves of heat release versus position in the flame for these reactions. The one adopted was the "inclined slit" optical method described in some detail in Chapter 3[4,5].

1.4. Qualitative Infra-Red Analysis.

Under this heading falls the programme of work discussed in Chapter 4. It includes scans at all levels in the flame, identification of peaks observed and noting the wavelength at which they arise. It was required to make analyses of the flame across as many horizontal zones as possible. The width of the infra-red beam of radiation used for this is the beam's "spatial resolution". This width is dependent upon both the beam configuration adopted and possible distortion of this produced by the flame. Both these factors are discussed fully in Chapter 3.

1.5. Quantitative Infra-Red Analysis.

The principles of gas analysis by infra-red absorption are well known. When infra-red radiation passes through an absorbing medium the linkage between it and the various polar

species present enables them to absorb. The energy flux at any wavelength (λ) and temperature (T) has been related to the concentration of species present, and the pathlength by the Lambert-Beer formulation

$$\frac{I}{I_o} = e^{-\alpha.C.L}$$

$\frac{I}{I_o}$ = ratio of transmitted to incident energy

where C is the concentration, L the path length, and α a constant which when C is in grams/ml., L is in cms., is the absorption coefficient. It must be immediately made clear that for a particular species α is a function of both temperature and to a lesser degree pressure as well as over the small wavelength band(s) for which it is significant, the wavelength.

During the quantitative work undertaken in the present study, the intention was to establish a relationship of the form above, and use this to obtain absorption coefficients at the temperatures and wavelengths available.

Requirements of the Equipment.

The implementation of the several aims of this study assumed the development of a number of new techniques and the adaptation of some existing ones. Two of these concern the burner and associated gas supply system, and the optical system for the infra-red beam. Optical systems previously developed were not considered to meet the requirements of the present work.

At the outset the ability to control the shape of the flame had not been completely explored. The flame requires a pre-mixed supply of fuel/air in precise ratio and at a flow-rate determined by consideration of its position. To obtain gas mixtures of the required composition presented two problems. The first concerns the correction of flow gauge calibration customarily made for variation in atmospheric temperatures and pressures. This was not considered a convenient procedure. The second is the effect produced by variations in downstream pressures upon the flow-gauges in general use. The position of the flame was to be controlled by a final valve, and variations in its setting corresponding to desired flow-rates cause these consequent pressure changes. One solution would be to bleed off any excess mixture, enabling the downstream pressures to be unaltered. This again presents problems when a large number of lines are to be connected. A device was built into the system and achieved the aim of allowing for changes of atmospheric pressure and making flow-rate changes less tedious. It is described in Chapter 2 together with the whole gas supply system, burner and criteria for the best flat flame for this work.

From considerations of the qualitative and quantitative procedures introduced in Sections 1.4 and 1.5, the following points concerning the requirements to be made of the optical

system will be apparent. Firstly, the background signal level I_o must be maintained at the level required to obtain a full scale recorder signal. The noise level on this should for quantitative analysis be not $>$ 5% of the total signal. Secondly the spatial resolution must be a maximum, i.e. the beam must permit scanning across as narrow a vertical section of the flame as possible. Thirdly the zone from which absorption spectra have been derived must be located. This might be difficult if the beam suffered vertical deflections while in the flame. Full discussion of these problems within the context of the two beam configurations which were considered possible alternatives for these analyses is contained in Chapter 3.

Scope of the Present Work.

The proposed analyses were aimed at elucidating the physicochemical structure of a flame, i.e. the distribution of temperature and species concentration throughout the reaction zone. The possibility of employing infra-red absorption spectroscopy satisfactorily for the measurement of : species concentrations would depend upon the spatial resolution obtainable. It would also depend upon the feasibility of proper calibration of the infra-red spectra. Calibration would involve, for example, the comparison of absorption bands

between 4.2 and 4.6 μ due to product CO_2 and to CO_2 added to the reactants. Additional information might be obtained on the progressive disappearance of the fuel (ethylene) and the fluctuating concentration of carbon monoxide.

The bearing ofthe results on the flame structure is discussed in Chapter 4. In Chapter 5 consideration is given to the use of the flame to determine absorption coefficients of inert species as a function of temperature and wavelength and so to establish a law relating absorption with species concentration.

CHAPTER 2. FLOW SYSTEM AND BURNER ASSEMBLY.

Introduction.

A flame suitable for this work must have the following properties.

It must be flat over an appreciable part of its area, or at least linear along one dimension, in order that the infra-red beam can be made parallel to it over a sufficient distance to absorb a useful fraction of the incident radiation which can thus be attributed to as homogeneous a 'zone' of the flame as possible.

It must be stabilized in a fixed position to permit scans through the full range of wavebands under investigation.

It must be freely stabilized against the approaching gas stream, i.e. it must be separated from any solid heat sinks by a distance large in comparison with the thickness of its normal temperature profile.

It must not be surrounded by "windows" which absorb infra-red radiation, or could become clouded owing to exposure to flame products, especially hot water vapour.

It must not contaminate the surrounding atmosphere with infra-red absorbing gaseous products.

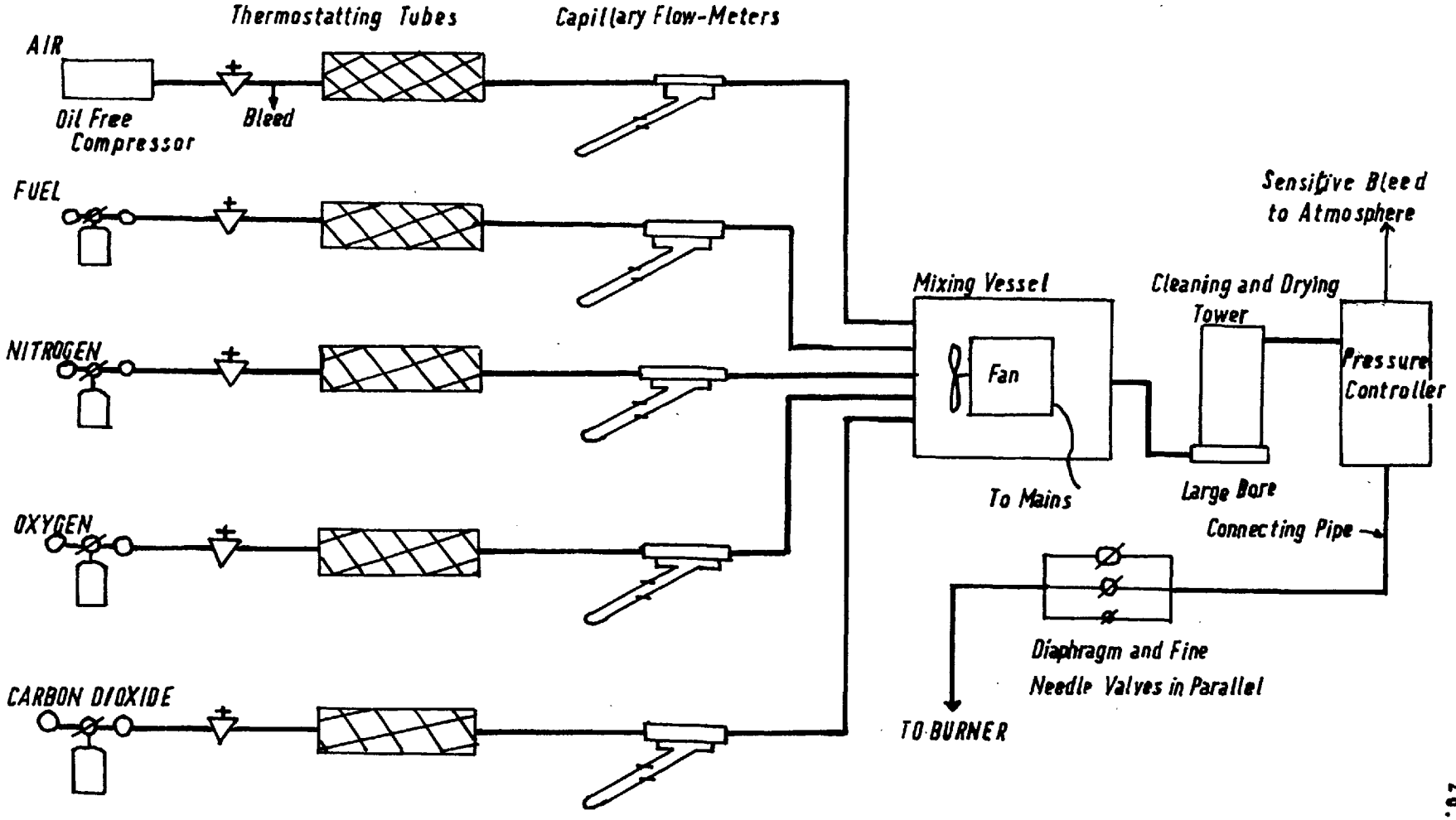
A discussion of the flow and burner systems and the difficulties to be overcome in implementing these aims occupies Chapter 2.

The Flow System.

2.1. Introduction to Flow System Components.

The flow system supplying the burner was somewhat more elaborate than is usual in combustion studies. The flat flame requires a pre-mixed supply of fuel and air in precise ratio and at a flow-rate determined by the position of the flame and, to a lesser extent, by its shape. The gas supply system in the preliminary experiments was to provide for a range of burning velocities to be readily obtained, the position of the flame being controlled by the operation of the final total flow controlling valve, no control on shape being possible, or required, at this stage. The pressure change which arises upstream from the final valve when its setting is altered produces a corresponding change in the flow-rates of the constituent gases, i.e. the composition of the mixture changes by an uncontrollable amount. To prevent this pressure effect a controller was designed permitting variations in flow beyond the individual flow-meters while presenting their downstream sides with a constant pressure. The next step was the thermostatting of the flowing gases before passing through their flow-meters. The remaining components of the flow system were the supply cylinders and associated reducing valves, the fine flow control valves

FIG. 3 BLOCK DIAGRAM OF THE SYSTEM FOR PREPARING AN UP TO FIVE COMPONENT GAS MIXTURE.



before each flow-meter, the flow-meters, a mixing vessel through which the gas mixture is driven by a fan (power supplied by an induction motor built in to the vessel), cleaning and drying towers, and finally three valves of varying capacities mounted in parallel comprising the total flow-controlling valve. In addition for introducing particles into the stream for particle-track photography a test-tube of bentonite was mounted on the connecting tube to the burner. A flow-sheet (Fig. 3) illustrates the system and its various components will now be discussed.

2.2. Gas Supply.

The diagram shows five individual lines. These provided for a mixture of fuel and air, oxygen and nitrogen to be mixed in the same ratio as in air, and carbon dioxide to be substituted for some part of the nitrogen when calibration was required. Air was provided by an oil free compressor, the remainder from standard cylinders.

2.3. Flow-Meters.

Reference was made to the literature[12] for information on metering devices. Two meters in common use were considered. The flow-meters chosen were of the capillary type, provided with inclined manometers, and operating between 15 cms and 30 cms manometric head to an accuracy of $\pm \frac{1}{2}\%$. The capillary

flow-meter has one distinct advantage over the rotameter. It is desired to use the devices at settings known beforehand. Capillary tubes can be easily interchanged and selected to minimize the error in settings, i.e. give the maximum change in pressure drop over the flow-rate range around the required value.

2.4. Thermostatting.

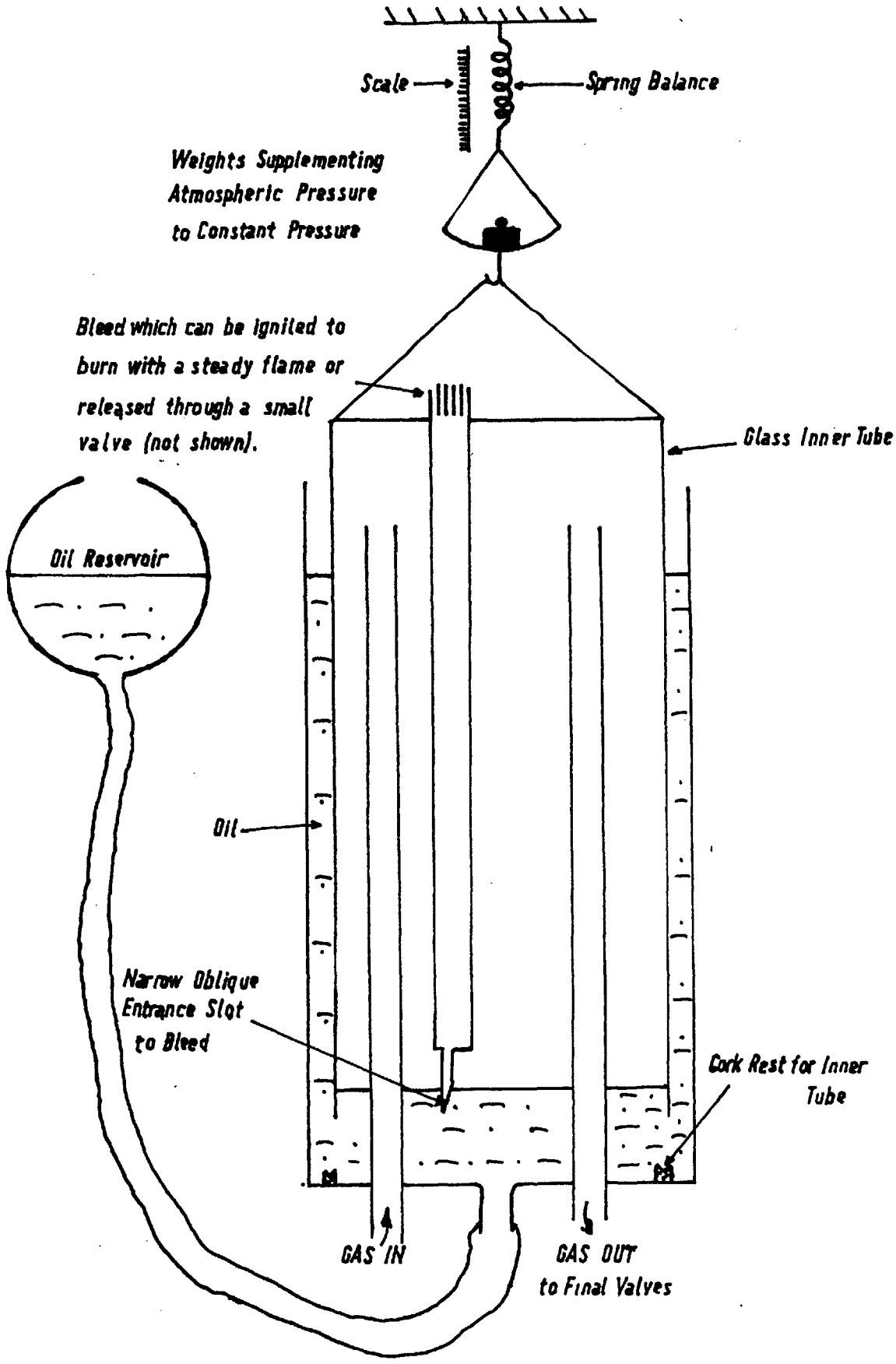
Each gas flow was passed through a thermostat before entering its flow-meter. Temperatures were maintained constant by means of heat exchangers, each made of two co-axial tubes, the gas carrying annulus being packed with copper flame trap material and the whole being inserted in a thermostatically controlled water bath.

2.5. Pressure Controller.

The object of the pressure controller was to allow the total reactant flow to be varied by the final valve, while presenting the flow-meters with a constant pressure to their downstream side, thus maintaining a constant mixture composition and hence burning velocity. This was achieved by the apparatus illustrated in Fig. 4 in which the flow-lines communicate with the space under a low-inertia, partially submerged bell provided with a leak aperture which increases steeply with upward displacement. Loading variation was used

FIG. 4

PRESSURE CONTROLLER.



to compensate for day to day variations in barometric pressure. The controller was set to present the capillary tubes with a pressure of 785 mms, which slightly exceeds the maximum atmospheric pressure likely to be experienced.

2.6. Final Valve.

The valve controlling the total flow to the burner was to provide a fine control setting and if possible require a small back pressure to maintain the required flow-rate since both flow-rate control and pressure controller performance became less satisfactory with increased pressure throughout. The characteristic of throughput versus pressure drop for valves of various designs were examined and no satisfactory single valve was obtained. A large capacity diaphragm valve, a small diaphragm valve fitted with a finely threaded control screw, and a needle valve were mounted in parallel as a single unit. These were found satisfactory, pressures being automatically minimized by this arrangement, flow through the large valve at all times being far in excess of that through the smaller ones.

The pressure controller, final valve and burner were connected with rubber tubing of $> \frac{1}{2}$" bore to minimize the pressure drop across this section.

The Burner.

Introduction.

The establishment of a satisfactory flame demands three things. Firstly evaluating the extent to which physical controls enable selection of the required flame properties to be made, second determining settings of these controls providing the best flame, and lastly the methods to be used to test that the settings are maintained during infra-red scanning must be determined (see 2.9). This involves in the first instance both burner design and exploration of possible controls on flame shape and position.

2.7. Burner Design.

Two types of burner have been described on which premixed flames approaching the desired geometry can be stabilized. In one, due to Botha and Spalding[13], the flame is stabilized above a porous disc to which it loses heat. This flame is therefore stabilized only in part by the recirculatory energy loss to the approach stream and is thus unsuited to the present study. The other burner, due to Powling and Egerton[1], is free from this shortcoming, in that its packing of glass beads and a flame trap matrix is used only to rectify and streamline the reactant flow, the flame being stabilized well above the burner port. This appeared

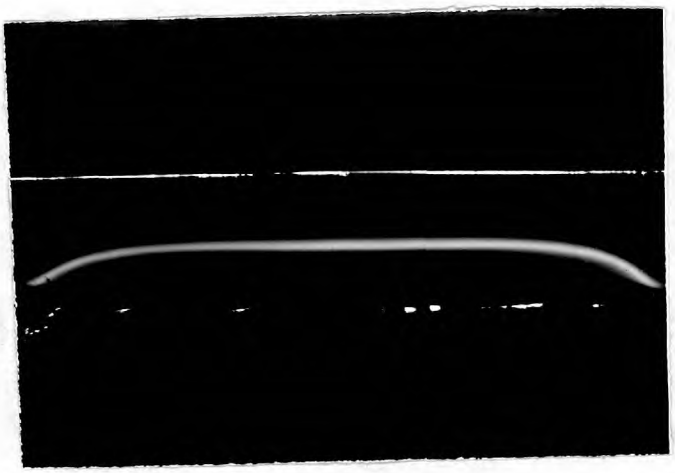
to be an ideal medium in which to conduct detailed investigations, conforming closely to the 'steady state' conditions postulated in the theoretical treatment of the flame, together with the relative simplicity in construction of the burner.

However, two undesirable features of it in its conventional form were the cylindrical window which confines the expanding column around its edge and the recirculating torroidal vortex of products CO_2 and H_2O, both strong infra-red absorbers, extending beyond the flame carried from the region above it to the region below by convection. It has even been suggested that this vortex is necessary for flame stabilization[5]. However whilst the Botha and Spalding burner is irreconcilable in principle with present aims, it was thought possible that the Egerton-Powling burner might be modified to overcome its shortcomings. For instance the replacement of the cylindrical window by an annular flow of an inert and non-absorbing gas nitrogen might remove both of the difficulties associated with the Egerton-Powling burner. This would combine the function of confining the flame with that of sweeping away the products, thus providing a gaseous "window" through which the infra-red beam could be passed. Experiments were carried out using a glass housing carrying a peripheral stream of nitrogen into which circular burners with diameters of up to 12 cms could be inserted. These

showed that the effects of the nitrogen sheath were most satisfactory at the smallest possible separation from the reactants. The burner tube proper was thus constructed on the principle of the conventional flat flame burner, that is with a bed of glass beads to randomize reactant flow, followed by a stream-lining matrix constructed of adjacent plane and corrugated metal strips wound into a spiral with an outer matrix wound directly to it for the annular nitrogen sheath.

Using this burner the next step was to investigate possible control of the shape and position of the flame. The effects of variation in individual and total flows of reactants and sheathing nitrogen upon flame shape and position were extensively investigated. It was found that fast flow-rates of the nitrogen sheath resulted in rigid localization of the flame and improved flatness at the centre extending to some 3/5th of the area. Due to mixing of nitrogen into the edge of the reactant stream, however, the flame periphery curved upwards, causing a serious departure from the required uniform horizontal section. At lower flow-rates the edge-effect was thereby lessened but so was the overall increase in flatness towards the centre. An attempt to correct for edge-effects at large flow-rates was made by the addition of circumferential heater coils, these being readily mounted round the nitrogen sheath matrix. The effects of the heaters

Fig. 5: Flame Shape Produced using Circumferential Heaters without Nitrogen Sheath.



was mainly to assist in flame stabilization, by pre-heating a small circumferential area of both nitrogen sheath and burner matrix with consequent pre-heating of the gases round the edge. The effect illustrated in Fig. 5 obtained using heaters without the nitrogen sheath flowing, shows the local increase in burning velocity obtained round the edge of the flame by heating the mixture.

A further modification to the top plate of the burner was found to give an additional degree of control. In the conventional design, the top gauze, supported by the chimney, gives rise to a pressure drop which is believed to play an important part in stabilizing the flame. In order to produce a similar but controlled effect, an annular matrix was inserted in a tube much larger in cross-section than the burner or flame together with a centrally mounted top plate supplied with water cooling, and the whole mounted well above the flame was connected to the intake of an exhaust system. The exhaust fan operated at various speeds so that the rate of extraction and to some extent the divergence of the gas stream could be controlled. It appeared, furthermore, that with this arrangement flame stabilization with a minimum in pressure drop across the top plate was obtainable.

On the bases of the observed effects of these modifications to the burner on the position and shape of the flame

FIG. 6a DIAGRAM OF BURNER CONFIGURATION .

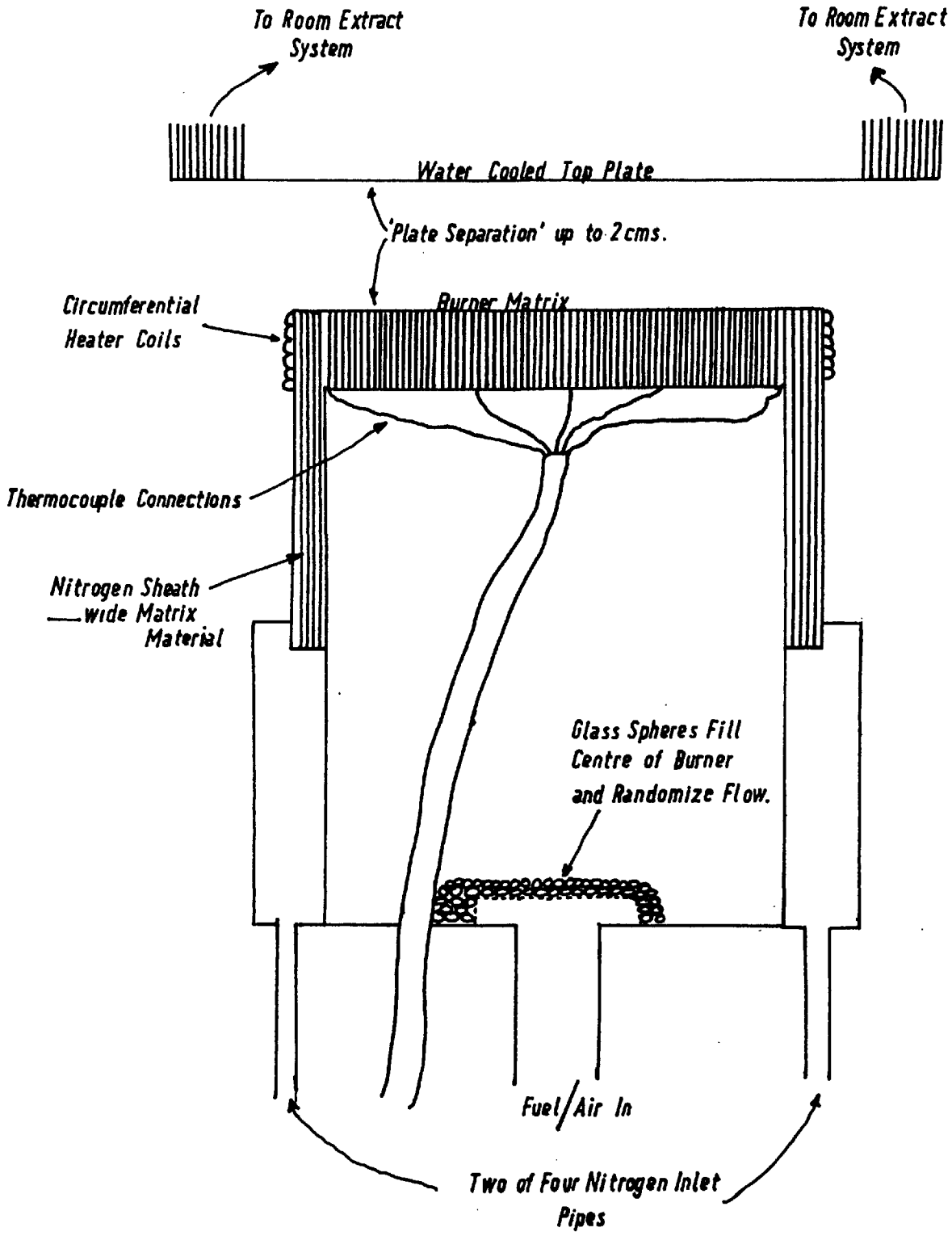


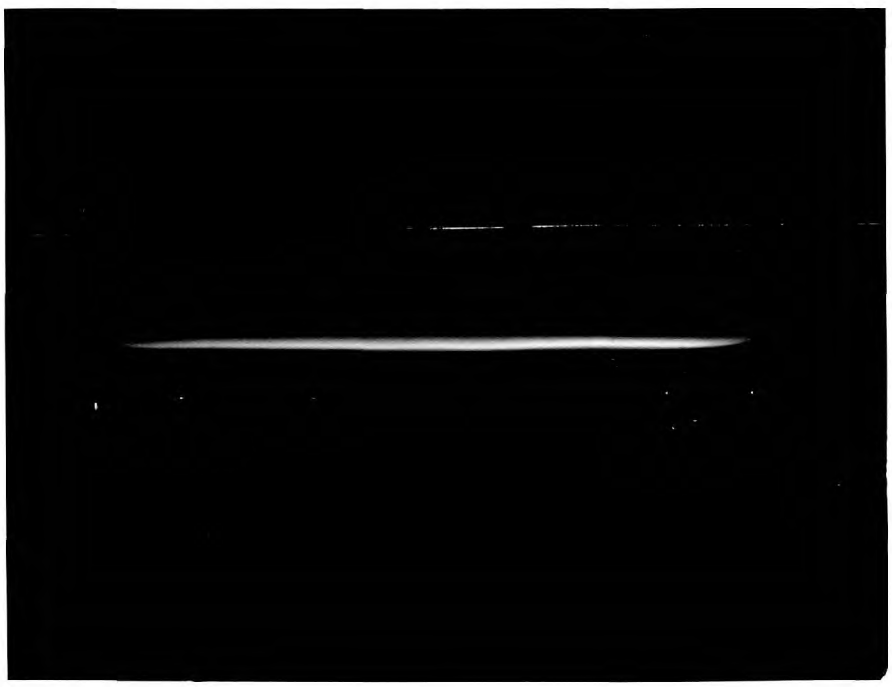
Fig. 6b: The Burner.

the next step was to determine the various flow rate settings, top plate and burner separation and nitrogen sheath/circumferential heater balance required to produce a flame most closely approaching the needs of this work. The burner and extract system are illustrated in Fig. 6a, and Fig. 6b is a photograph of the assembled burner.

2.8. Discussion of the Flame Problem.

The practical problems presented by flames developed so far was in adequate stabilization in the vertical plane and the shape of the edge of the luminous zone. "The position of the flame" is generally defined as being that of the luminous zone and this definition was used in the present work. The position depends upon the aerodynamic balance between the volume of mixture introduced from the burner, the burning velocity of the mixture (which is limited in range) and the removal of the products. The 'shape' of the luminous zone can be regarded as a burning velocity profile and the factors influencing this are more involved. For example if a flame of slightly rich composition is allowed to become stabilized on the bottom matrix, the subsequent rise in matrix temperature and pre-heating effect upon the reactants is characterized by the dip in the luminous zone towards the centre of the burner which can be observed when the flame lifts. To satisfy the requirements of this work it was necessary therefore to stabilize the flame off the matrix to

Fig. 7: The Unconfined Flat Flame.



enable a uniform temperature to be established across it as soon as possible.

Some experimentation enabled flames satisfactory for the aims of this work to be obtained. The flow-rate settings were subject to slight variations owing to the ambient nature of the atmospheric pressure. However a flame satisfactory in shape and stabilized in a suitable if not identical position each time was produced. Corrections for the effects of the nitrogen sheath mixing into the edge of the flame were not completely to be made. The effects were to produce a small upward curvature, not extending inwards for more than 1% of the flame's diameter, and the more serious apparent decrease in flame stability. This was attributed to variations in the aerodynamic balance at the extract annulus between the convecting product and the relatively cold nitrogen. An example of the flame shape and position relative to the burner finally accepted in shown in Fig. 7.

Flames on the apparatus cannot be recommended against those using the conventional flat flame burner when the window problem does not arise, on the grounds that as regards long term stability they are much more sensitive to small fluctuations of local pressure and matrix temperature. Again although the use of circumferential heaters permits control of the shape of the edge of the flame with a nitrogen sheath

flowing, the exact settings of both are interdependent, and the desired balance difficult to maintain successfully for longer than 2 mins, a relatively short time for the present infra-red work.

2.9. Maintenance of the Flame during Infra-Red Scanning.

In section 1.4 the importance of a narrow beam when making infra-red scans was emphasized. In addition any detailed work requires stabilization of the flame to within the narrowest limits to allow the beam to pass horizontally across as narrow a 'zone' of the flame as possible.

The position of the flame was constantly checked throughout infra-red scans by viewing the position of the luminous zone against a cathetometer graticule. Non-movement against this ensured maintenance of both burning velocity and hence mixture composition.

Additional records were kept of

(1) Matrix Temperature, the circumferential heater current being maintained at its pre-set value throughout. Nitrogen Sheath Velocity as read off a Rotameter to ensure steady environmental conditions.

(2) The Extract Velocity as indicated by an ammeter in the d.c. circuit to the extract fan.

(3) Regular Readings of Atmospheric Pressure (not $< \frac{1}{2}$ hr. intervals). This was accompanied by re-setting the pressure controller and bleed if necessary. The fuel/oxygen/diluent + added inert ratio was maintained to $\pm \frac{1}{2}\%$ of each constituent, i.e. for five components $2\frac{1}{2}\%$ of total flow.

CHAPTER 3. OPTICAL SYSTEMS.

SECTION A. INFRA-RED BEAM SYSTEMS.

The design of a suitable optical system was the second practical requirement of this method. Previous workers have used narrow beam systems[14] and a review of features of optical system design pertinent to the problems arising when producing narrow beams and of the practical limitations previously experienced was thought necessary. Of particular interest were features concerning two design aspects, the choice of beam configuration to provide the most detailed analysis, and the corrections to be applied to the results due to flame effects on the beam. These corrections depend upon beam configuration to a great extent and in the following discussion both of the aspects are considered jointly.

3.1. Focused or Parallel Beam Configuration?

Comparisons of the advantages of parallel and focused beam configurations were made. These alternatives were in the use of a focused image at the centre of the flame or of a horizontal section of a parallel beam. A theoretical comparison of their relative merits brought out the following points.

While an image of the narrow line source focused at the centre of the flame would encompass a larger section of the

flame, the use of a parallel beam would permit scanning with a beam of uniform intensity, having the added merit that the region of the flame being scanned could be changed at will be simple movement of the slit. In addition, the corrections to be applied for flame effects on the parallel beam were understood for the visible region, and should be so with minor modifications for infra-red wavelengths. The flame could affect the shape and vertical position, and cause curvature of an initially horizontal beam, thus changing the spatial resolution. Secondary effects arising from turn-up at the edge of the flame on a parallel beam had been calculated and found to be significant. Corrections to be made for possible similar effects upon the focused beam had not been made.

On the other hand, it could be shown that a laminar flat flame appeared to focus an initially parallel beam, the emerging rays appearing from a virtual image at the centre of the flame. Thus the distortion produced in a beam initially focused might be expected to be insignificant. Also the secondary effects at the edge of the flame might not be so significant for the extreme rays, since on passing through a wider flame section both would traverse comparable paths of absorption (assuming no distortion) either before or after passing the focus. Lastly, the additional advantage

of more accurate spatial resolution and location of the beam's path might be realized because of the elimination of diffraction effects on the beam. This had been a source of trouble using the parallel beam system in the visible region and would be more prominent at infra-red wavelengths.

In view of the possible use to be made of either system the ability to examine both had to be built into the final optical system design adopted.

3.2. Possible Infra-Red Optical Systems.

The criteria to be used to examine the performance of an optical system were:-

(a) spatial resolution at the flame,

(b) ability to define the path through the flame,

(c) provision of a beam satisfying the requirements of the spectrometer to provide resolved spectra,

(d) construction of a practical system, i.e. one which minimizes the time required in lining up mirrors and which in all respects is manageable.

The Source.

The infra-red source was a Nernst filament (1 mm x 5 cms) mounted horizontally in a non-reflecting water-cooled housing and maintained by an a.c. stabilized current

supply of 0.7 ± 0.05 amps. Provision was made in the front of the housing for mounting slits of fixed width and one of these comprised the required line source.

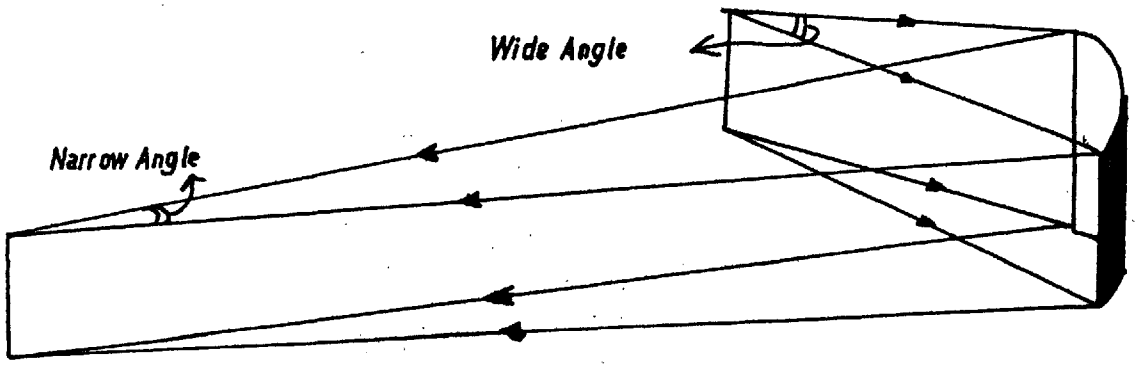
Preliminary Considerations.

The need for a small image at the flame involves at first sight very long light paths. For instance a concave cylindrical mirror of short focal length (say 5 cms) could be used to convert a narrow angle at the flame to a wider angle at the monochromator slit (Fig. 8a). Although achieving the desired angle conversion (see 3.3) an alternative would be preferred because of the large noise levels unavoidably incurred with long path length systems due to local disturbances. This was particularly important as the signal "level" in the ultimate design would be bound to be small.

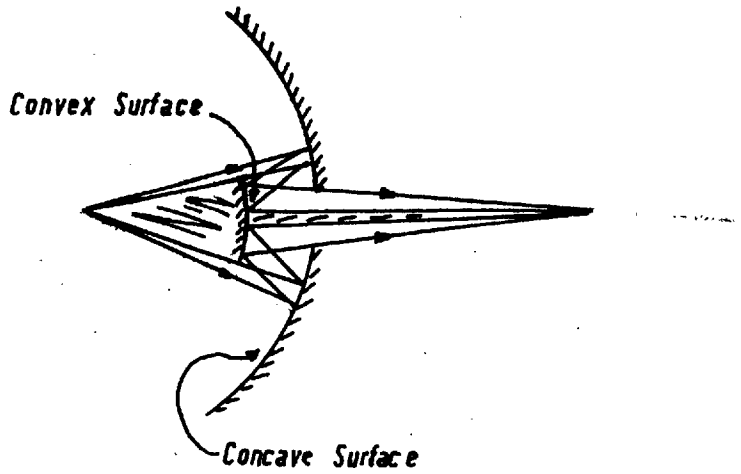
The second system discussed provided the basic idea used in the design finally adopted. The infra-red microscope objective is illustrated in Fig. 8b. The interesting feature is the use of a concave surface followed by a convex one in providing a narrow beam from a wide one with a much shorter path length. Further details of this device are found in Ref. 15. Its disadvantage, which is unavoidable, is that the small convex mirror mounted behind a hole behind the centre of the concave one results in a central obstruction,

FIG. 8 OPTICAL SYSTEMS PRODUCING NARROW BEAMS.

a) Cylindrical Mirror with long light path off-axis.



b) Infra-Red Microscope Objective



causing loss of not less than 30% of the light transmitted by the system.

The design finally adopted is discussed after details of criterion (c), the particular requirements of the spectrometer have been outlined.

3.3. The Perkin-Elmer 12C Spectrometer and its Optical Properties.

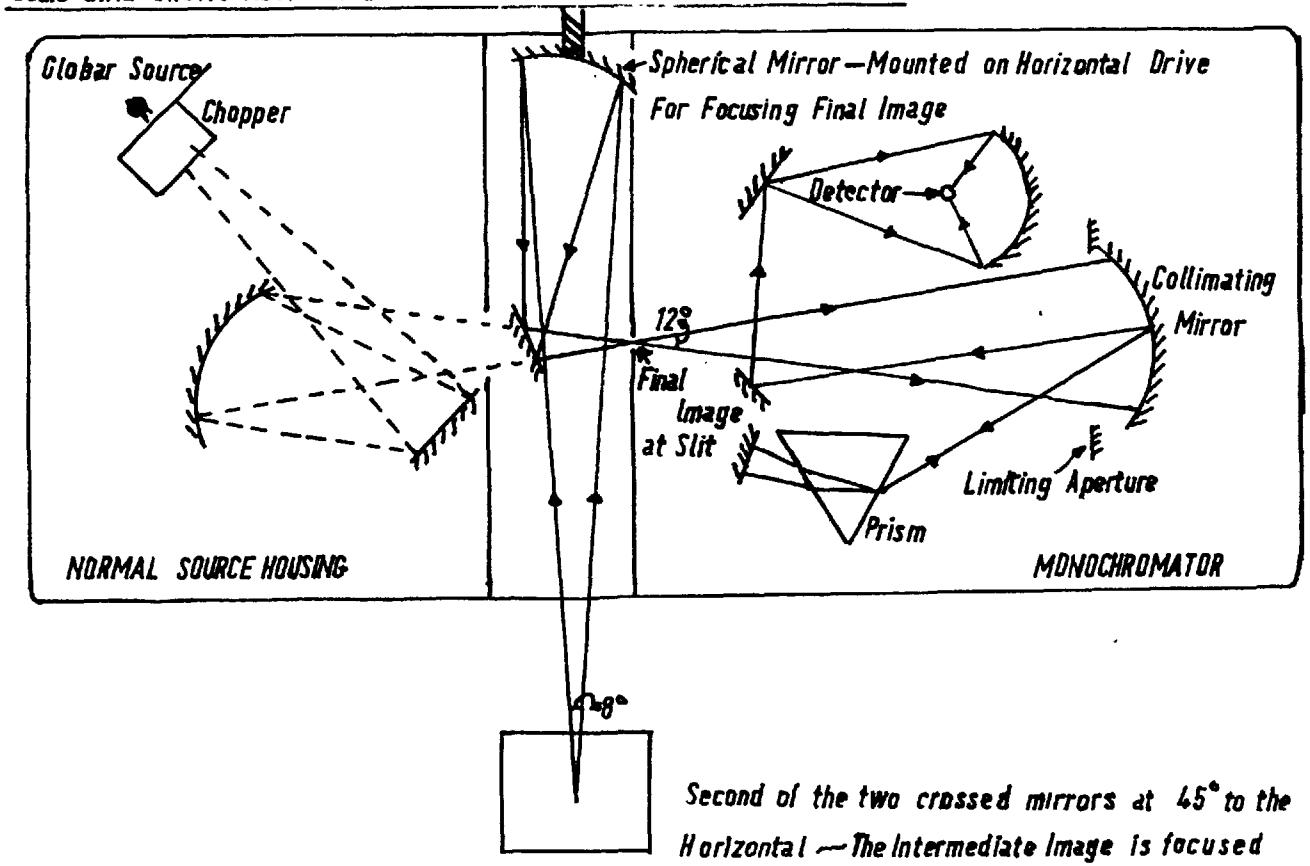
The spectrometer was of the single beam type and was provided with interchangeable calcium fluoride or sodium chloride prisms permitting the recording of spectra from 0.2 - 15μ . The design of the optical system had to provide a beam suited to the requirements of the spectrometer in addition to those for traversing the flame. These are:-

(i) that an image of the test region is focused on the entrance slit, longer than its length and wider than the slit width;

(ii) that the extreme rays forming that image shall diverge from the slit at an angle large enough to fill the limiting aperture of the monochromator optical system;

(iii) the energy flux to the detector unit must be adequate to provide a signal/noise ratio from the recorder amplifier at not less than 20:1.

FIG. 9 DIAGRAM OF PERKIN ELMER 12C SPECTROMETER — DOTTED LINE SHOWS OPTICAL PATH FOR NORMAL USE, SOLID LINE SHOWS ADDITIONAL PATH SUBSEQUENT TO CROSSED MIRRORS.



Second of the two crossed mirrors at 45° to the Horizontal — The Intermediate Image is focused at its surface.

The limiting aperture (see ii) of the system is a screen mounted in front of a concave parabolic mirror (see Fig. 9) of surface area 30 sq. cms (height 6 cm, width 5 cm). To fill this, the angle subtended by the extreme rays at the slit must be 12^{o}. Fig. 9 illustrates the conversion of a beam focusing at 8^{o} at an intermediate image to the required 12^{o}. This intermediate image is formed by the optical system adopted for the narrow infra-red beam and consequently that system must produce a focused image, the extreme rays converging at 8^{o}. Furthermore, this image is horizontal and the image at the monochromator slit is required to be vertical. Fig. 9 also illustrates the positions of two plane mirrors at right angles to each other and both at 45^{o} to the horizontal, the function of which is to cause the intermediate image to become vertical.

The Perkin-Elmer detector was unmodified and the monochromator working was according to standard practice.

3.4. Final Optical System Design.

As emphasized in the discussion of spatial resolution (1.4) the fundamental requirement of the infra-red beam is that it shall probe the flame through as narrow a vertical section as possible. Secondly the path through the flame must be known, to ensure satisfactory location of the flame

zone. It was decided to compare the relative merits of a parallel and a narrow focused beam configuration from these viewpoints using a system quickly adaptable from one to the other.

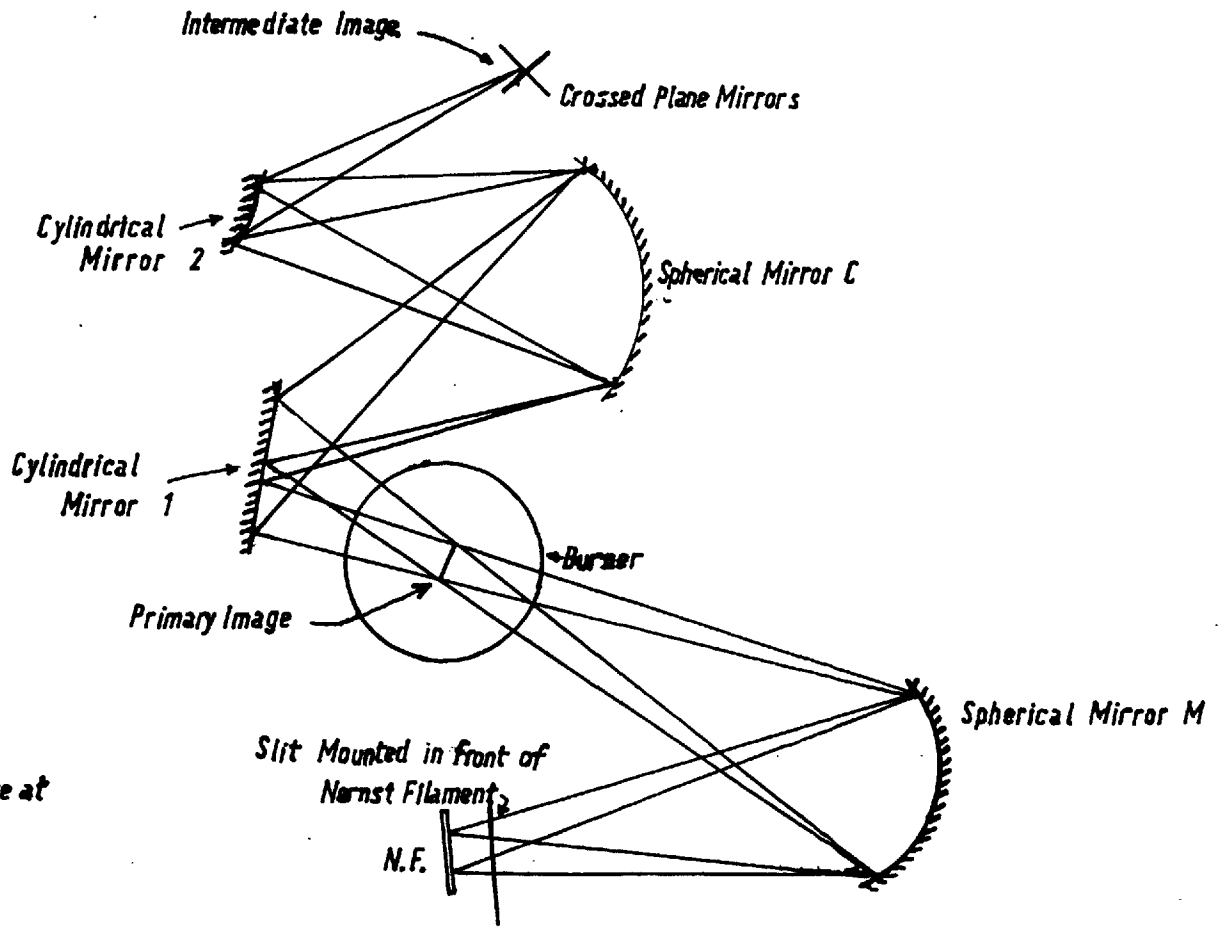
It was decided to design first a system with a narrow focused beam which provides a strong signal, and for the comparison work modify it to give a parallel beam. The second important factor was to minimize path lengths. Apart from advantages in minimizing space required, and vibrations of surfaces being magnified, giving rise to an adverse noise level, this would ensure that when the system was used to provide the parallel beam, a maximum beam intensity would be obtained, enabling a fair comparison to be made. When the mirrors for the focused beam system had been mounted, it was found that only small mirror displacements were required to test the system when used with the parallel beam. The two arrangements of mirrors, slits and etc., for obtaining the beams, are discussed below with reference to Figs. 10 and 11.

(a) Focused Beam System (Fig. 10).

The Nernst filament is placed at twice the focal length of spherical mirror M from mirror M which is also placed at twice its focal length from the centre of the burner. Thus

FIG. 10

HORIZONTAL SECTION OF OPTICAL SYSTEM FOR FOCUSED BEAM.



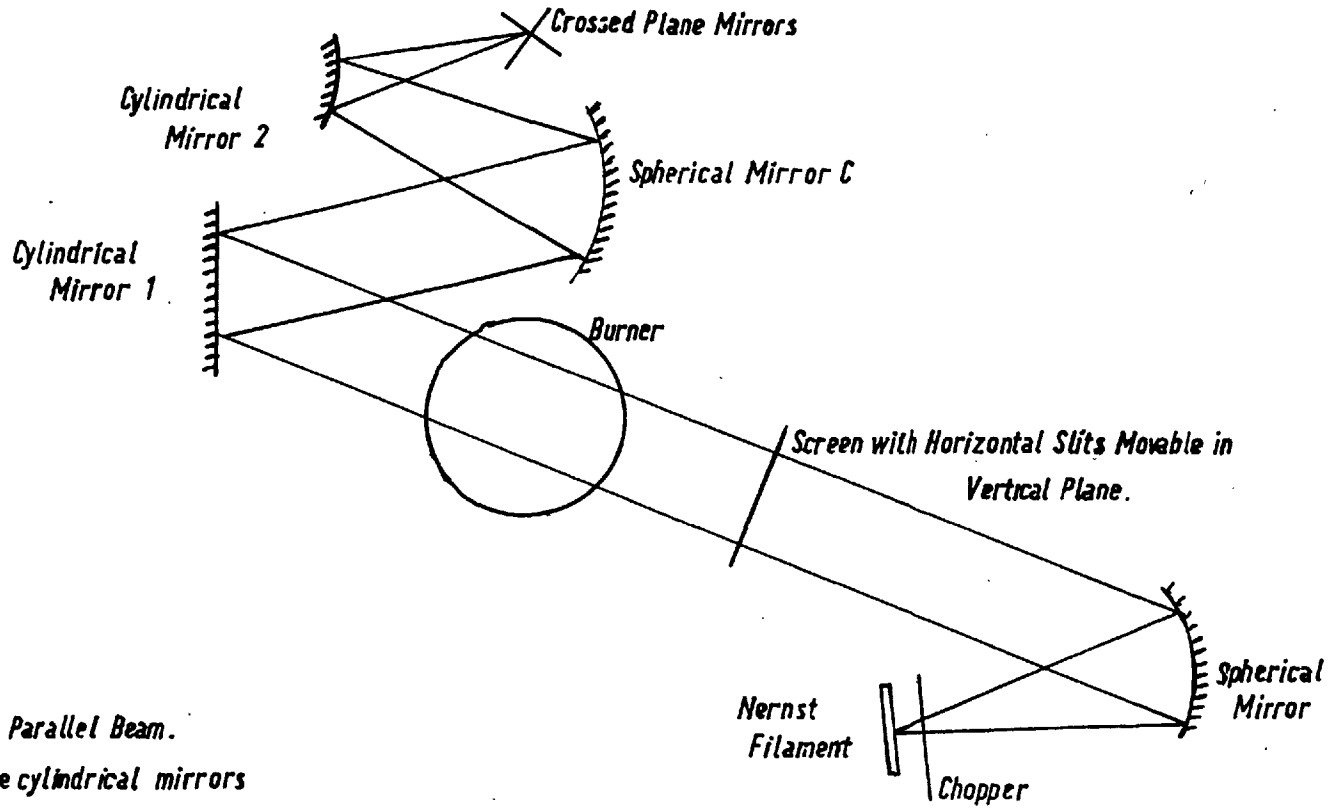
ARRANGEMENT 1

Slit at 2f to M producing 1:1 image at Centre of Burner.

a 1:1 image of a slit at the filament is produced at the centre of the flame. The vertical dimension of the beam was limited in addition by apertures mounted on M_1, the image being formed by beams, the extreme rays forming which converge at $\frac{1}{2}^{o}$ or 2^{o}. Accurate focusing of the slit at the centre of the burner was achieved by locating the image of a piece of thin wire stuck at one end of the slit. The location of the two convex cylindrical mirrors C_1 and C_2 to produce the desired angle conversion was very critical. The beams diverge from the primary image and on reflection from C_1 the vertical angle of divergence is increased while the horizontal one stays constant. Should the resulting beam be focused on the slit, two positions of focus corresponding to these two sections would result. To correct for this, the angle of convergence of the horizontal section was artifically decreased (see diagram), the whole beam having been reflected by a large 'collecting' mirror C, by reflection upon convex cylindrical C_2. Positioning C_1 and C_2 was achieved by viewing the image formation at the intermediate image position with a piece of white card. The intention of the design was that beams in both sections come to focus at twice the focal length of C, this being 19.9 cms, thought to be a distance sufficiently large for convenient mirror positioning and small enough to satisfy the short path

FIG. II

HORIZONTAL SECTION OF OPTICAL SYSTEM FOR PARALLEL BEAM.



ARRANGEMENT 2

Filament at f to M producing a Parallel Beam.

For correct image formation the cylindrical mirrors were set to give maximum signal from the Spectrometer

length required. At this position they were to converge at 8^{o}. From these data the desired focal lengths of C_1 and C_2 for conversion of the $\frac{1}{2}^{o}$ and 2^{o} beams were calculated.

(b) Parallel Beam System (Fig. 11).

The use of the system with a parallel beam traversing the flame was investigated using the modification shown in the diagram. The change from the focused to the parallel beam configuration was achieved by moving the Nernst filament to the focus of mirror M and confining the beam by a movable horizontal slit before its traversal of the flame. The required positions for C_1 and C_2 for correct formation of an 8^{o} beam from a parallel one could be calculated according to geometrical optics but the diffraction effects on the beam required C_1 to be slightly moved, and the desired positions were achieved by setting the mirrors to give the maximum signal from the recorder.

The optical system subsequent to the intermediate image was common to both systems and has been explained in 3.3 in connection with Fig. 9. The entire spectrometer/external mirror and burner assembly was enclosed in an airtight perspex box and is illustrated by Figs. 12 a and b.

Fig. 12a: Optical System Showing Position of The Burner Relative to Mirrors.

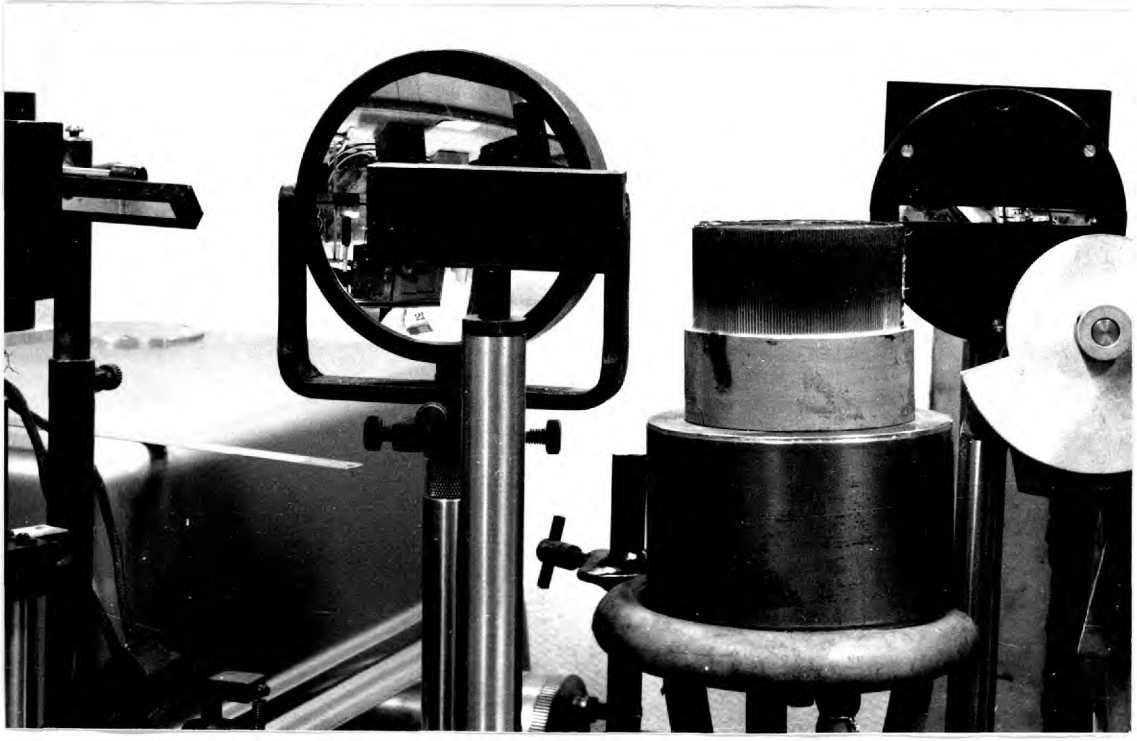
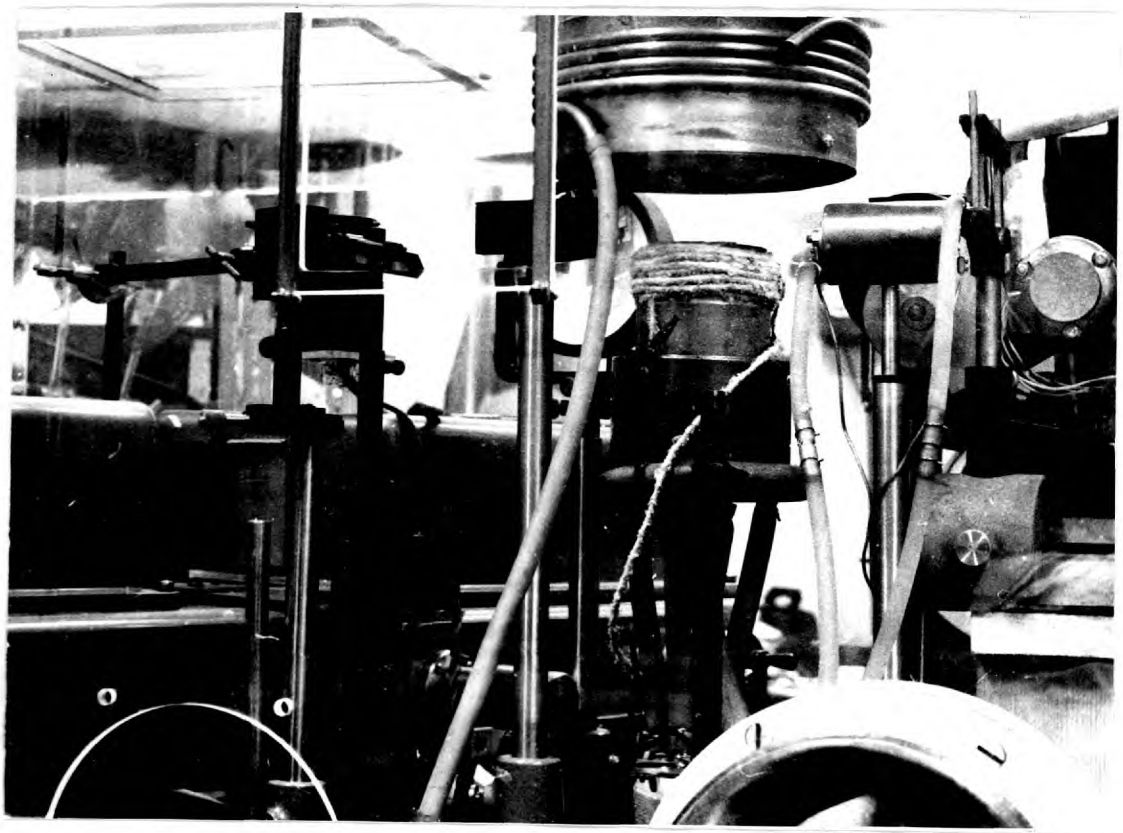


Fig. 12b: The Spectrometer, Optical System, Burner and Perspex Box Assembly.



3.5. Comparison of the Two Systems in Practice.

The two optical systems were extensively compared on four points. Firstly, the spatial resolution each provides, secondly the definability of path of the beam, thirdly the intensity each passes from the source through to the spectrometer, and lastly the effects observed of the refractive index field of the flame on the beam. The outstanding advantage of the parallel beam system is that the beam width is constant across the flame and the spatial resolution appears at first sight to be determined entirely by the width of the traversing slit before the flame. This, however, is true only insofar as the laws of geometric optics are applicable. In fact, the spreading of the beam due to diffraction at the slit is so appreciable, at these long wavelengths, that the improvement in the determinancy of "ray trajectories" is not very great. The advantage of the focused system is that it is much less affected by ray deflections in the flame. These deflections, caused by the refractive index gradient, vary from point to point across either beam but focusing at the centre of the flame assists in eliminating this effect. In addition, for comparable degrees of spatial resolution, the focused system provided more intensity. These two assets ultimately proved decisive and the focused system was used in the majority of investigations. Using the mirror arrangement for converting

$\frac{1}{2}^{o}$ to 8^{o} the 'zone of scanning' in the flame could be reduced to a rectangle of 0.14 x 2 cm, giving absolutely no overlap for centres approximately 2 mm apart. Since the effect of different, but known ray trajectories can be corrected for by successive approximations, it is possible to obtain infra-red absorption peaks at 6 - 10 points across the flame thickness.

SECTION B. THE OPTICAL SYSTEM FOR INLINED SLIT METHOD.

The foregoing discussion concerns the optical systems purely suitable for the infra-red method. Some time was spent upon the problems attached to producing narrow beams of visible radiation. This was undertaken partly with reference to the other work, but became important for measuring the temperature distribution for calibration purposes at intermediate positions between the initial and final stages. The method is based on the variation of refractive index with temperature gradient and the consequent distribution of ray deflections which can be produced across the flame. The subsequent theoretical treatment of these deflections to enable the calculation of refractive index and temperature is according to Burgoyne and Weinberg[4] and only that part of the theory relative to the present work is included.

FIG 13a

OPTICAL SYSTEM FOR INCLINED SLIT METHOD.

Source Filter | Long Focal Length (70 cms.) Achromatic Combination Lens | Slit Screen | Burner and Flame | Beam Deflected by Flame, $\propto \frac{d\mu}{dy}, d, D$ | Photographic Record

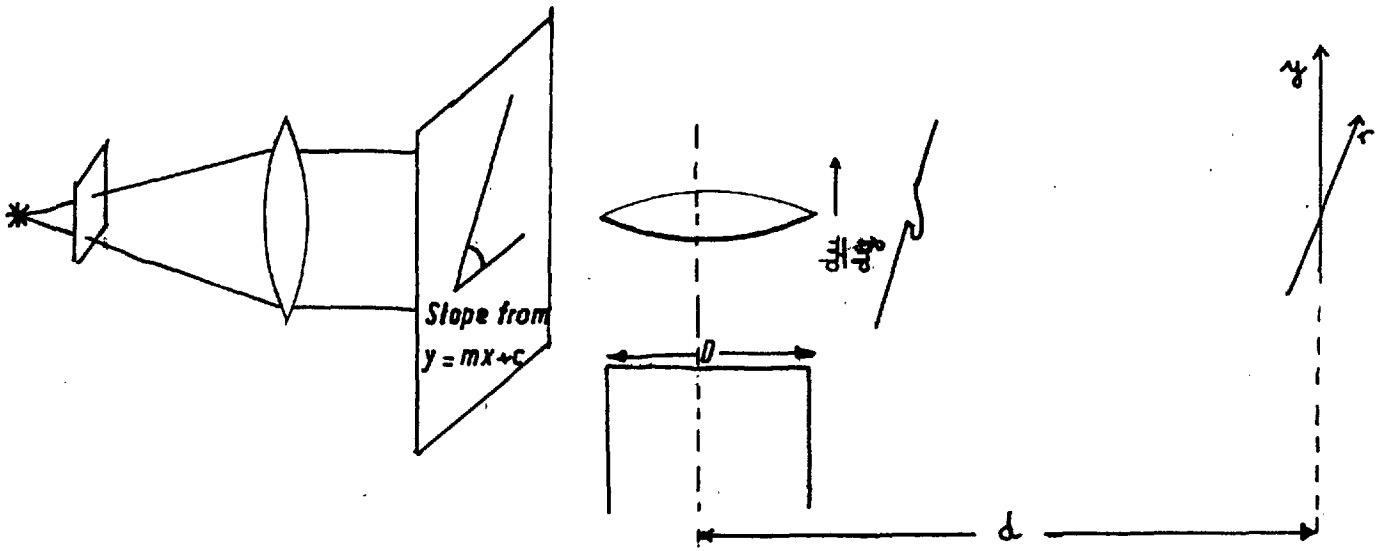


Fig. 13b: Typical Photographic Record.

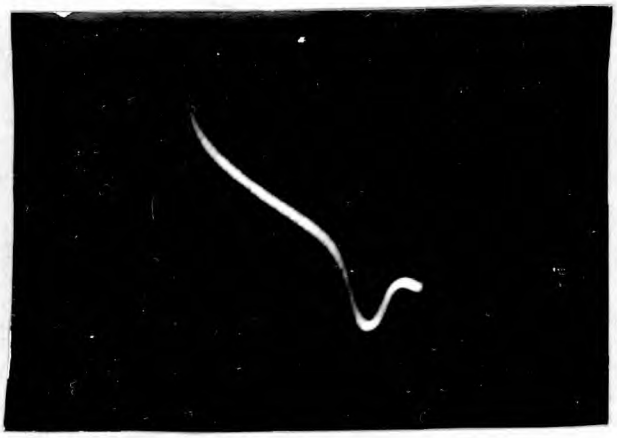
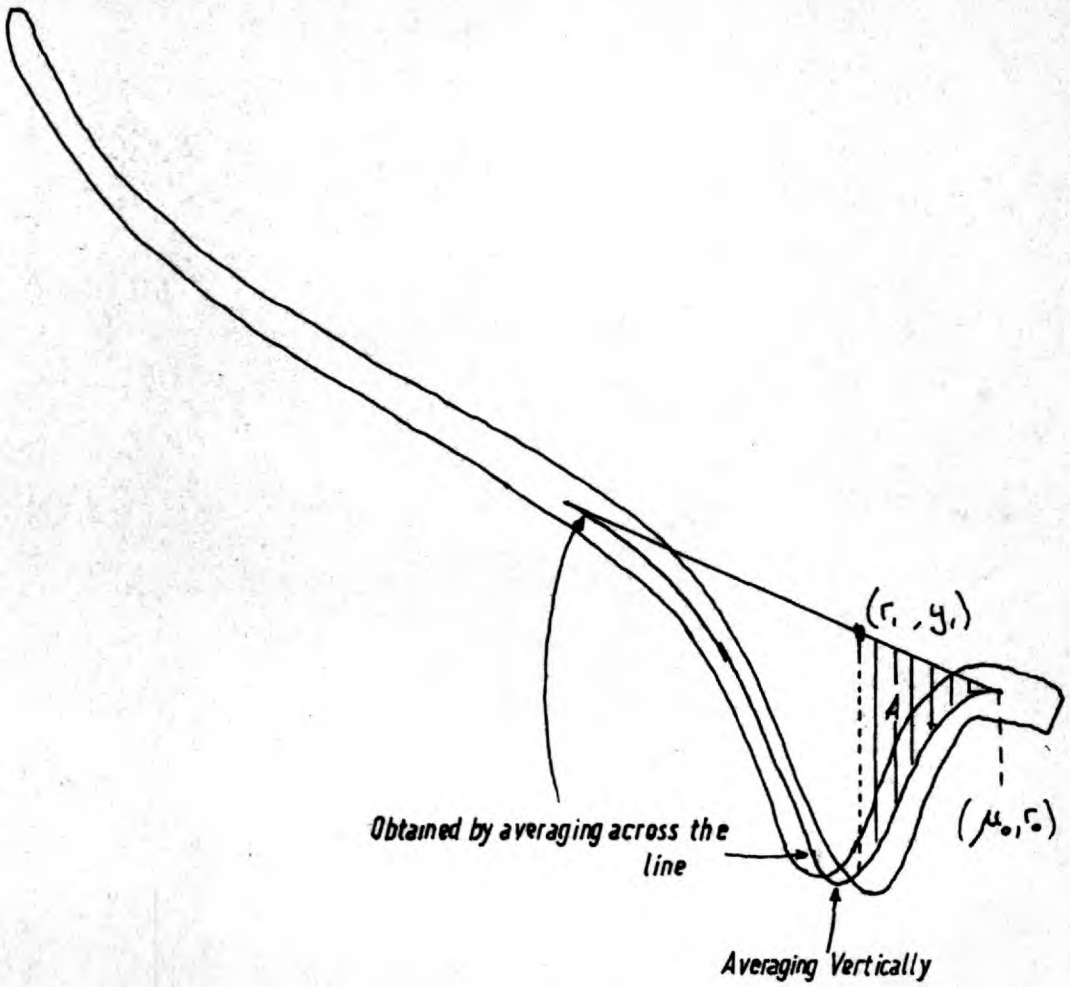


Fig. 13c: The Deflection Enlarged.



Optical System and Method.

Fig. 13a illustrates the system, Fig. 13b illustrates a typical photographic record, Fig. 13c illustrates the same record enlarged using the plate with a photographic enlarger and tracing round the profile.

The photographic record illustrates the best slit image obtained. The slit width was 25/1000", the light was the mercury green 5461 Å line. Narrower slits produce secondary diffraction maxima which complicated the observation of the primary maximum with no real increase in spatial resolution.

The source was a high pressure mercury vapour arc lamp mounted in a cooled housing with a restricted aperture. The effective source was an image of this aperture, again restricted by a pin-hole (optical system for this not included in the figure). This was situated at the focus of an achromatic combination convex lens, 70 cms focal length and diameter 15 cms. Setting this in the desired position was achieved using a plane mirror and observing the reflected beam against the incident one in the usual manner.

The deflections produced by the flame were observed at their maximum useful values by using a large path length (D) in the flame, and observing the deflected beam some distance (d) beyond the flame - this cannot be increased indefinitely owing to rays spreading out causing loss of

of definition of the record. At 150 cms, this was not sufficient to justify the use of an additional lens. Some advantage was gained by using plates sensitive to green light thus minimizing exposure times.

Theory.

For convenience the symbols used in the previous statement of this work are adhered to. With reference to the enlarged deflection illustrated in Fig. 13c, it can be shown that for a flat flame the displacement h is given by

$$h = d.D.\frac{d\mu}{dy} \qquad \ldots\ldots\ldots\ldots 1$$

where d, D are as defined above, $\frac{d\mu}{dy}$ is the local refractive index (μ) gradient perpendicular to the flame, and higher derivatives of refractive index have been neglected.

Using this, together with the formulae for the area of the shaded portion, a value for the local refractive index at point (r_1, y_1) in terms of the refractive index at the initial temperature, μ_o, can be calculated. Since

$$A = \int_{r_o}^{r_1} h \, dr \qquad \ldots\ldots\ldots\ldots 2$$

$$\therefore \quad A = d.D. \int_{r_o}^{r_1} \frac{d\mu}{dy}.dr \qquad \ldots\ldots\ldots\ldots 3$$

For the undeflected slit, of known gradient $(\frac{dy}{dr}) = m$,

$$y = mr + c \quad \text{always} \qquad \ldots\ldots\ldots 4$$

$$\therefore \quad dr = \frac{1}{m}\, dy \qquad \ldots\ldots\ldots 5$$

$$\therefore \quad A = d.D. \int_{r_o}^{r_1} \frac{d\mu}{dy}.\frac{1}{m}.dy = \frac{dD}{m}(\mu_r - \mu_o).$$

Taking into account the negative sign of $\frac{d}{dr}$ we have the general equation for the refractive index at (r_1, y_1)

$$\mu_r = \mu_o - \frac{m}{D.d} A \qquad \ldots\ldots\ldots 6$$

To calculate the temperature at point (r_1, y_1), it can again be shown that for a gas i.e. when $\mu - 1$ is very small,

$$(\mu - 1)T = \text{constant} = (\mu_o - 1)T_o = (\mu_f - 1)T_f.$$

From these relationships, it is evident that, after a small correction for composition effects, both refrative index and temperature distribution can be found by assuming either μ_o, T_o or μ_f, T_f, and measuring h's and A's accordingly.

CHAPTER 4. DETECTION AND LOCATION OF SPECIES.

The spectra to be presented under this heading are concerned with two aspects discussed in the Introduction; the test of the method as a means of detecting species in the flame and the location of the points of appearance and disappearance of these species. In this context discussion of the purely physical effects of high temperatures and other instrumental effects upon the form of the spectra is included. Discussion of the extent to which these and other factors bear upon quantitative analyses and the applicability of the method in finding absorption coefficients of inerts added to the flame is deferred until Chapter 5.

4.1. Unstable Species.

Before being concerned with the detection of the stable species a few comments are required on the non-detection of the unstable ones, a fact which provides information on the potentialities of this method. For their interest value it was hoped that some of the unstable intermediates would be present in sufficient concentration to enable their spectra to be recorded. To this end scans of from 1 - 15μ were made at all levels in the flame under what were considered the optimum experimental conditions. No significant amounts of any unstable intermediates could be observed. However,

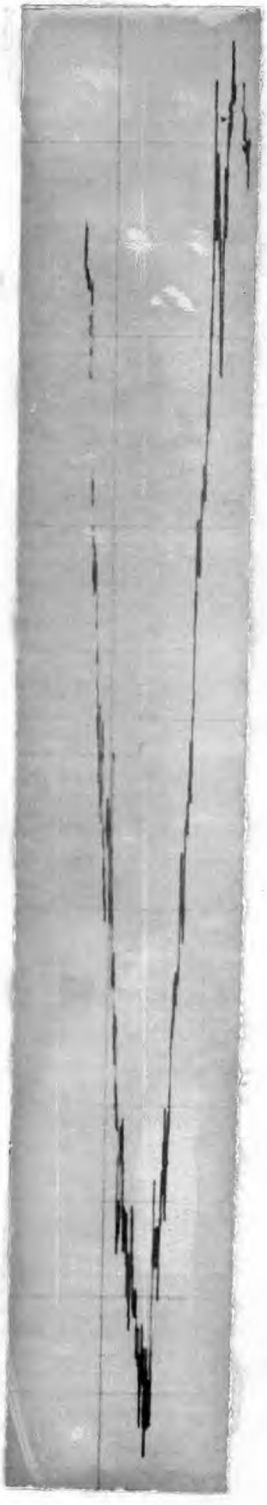
it would have been possible to detect the unstable species by changing the nature of the flame, or by increasing the fuel concentration to the rich limit. Although detection of these species under such conditions would be of value, the information to be obtained was considered as only of secondary interest for the following reasons. The present picture we have of the overall reaction scheme is of a set of horizontal zones of uniform species concentration populated by as yet unknown chain reactions being carried on in parallel as well as in series. Intermediates present in appreciable concentration are unlikely to play a significant role in the rate controlling reaction mechanism because of the rapid reaction rates of the processes involved. Furthermore, the impossibility of maintaining and examining these in isolation and under normal conditions precludes any quantitative calibration, and possibly even identification. Thus although these species play an important part, detection of their infra-red absorption would not lead to useful information concerning flame structure, and their non-detection has not the significance which might be attached to it at first sight.

4.2. Stable Species.

The spectra recorded were those due to the initial reactant C_2H_4, the intermediate CO and final products CO_2,

Fig. 14a:

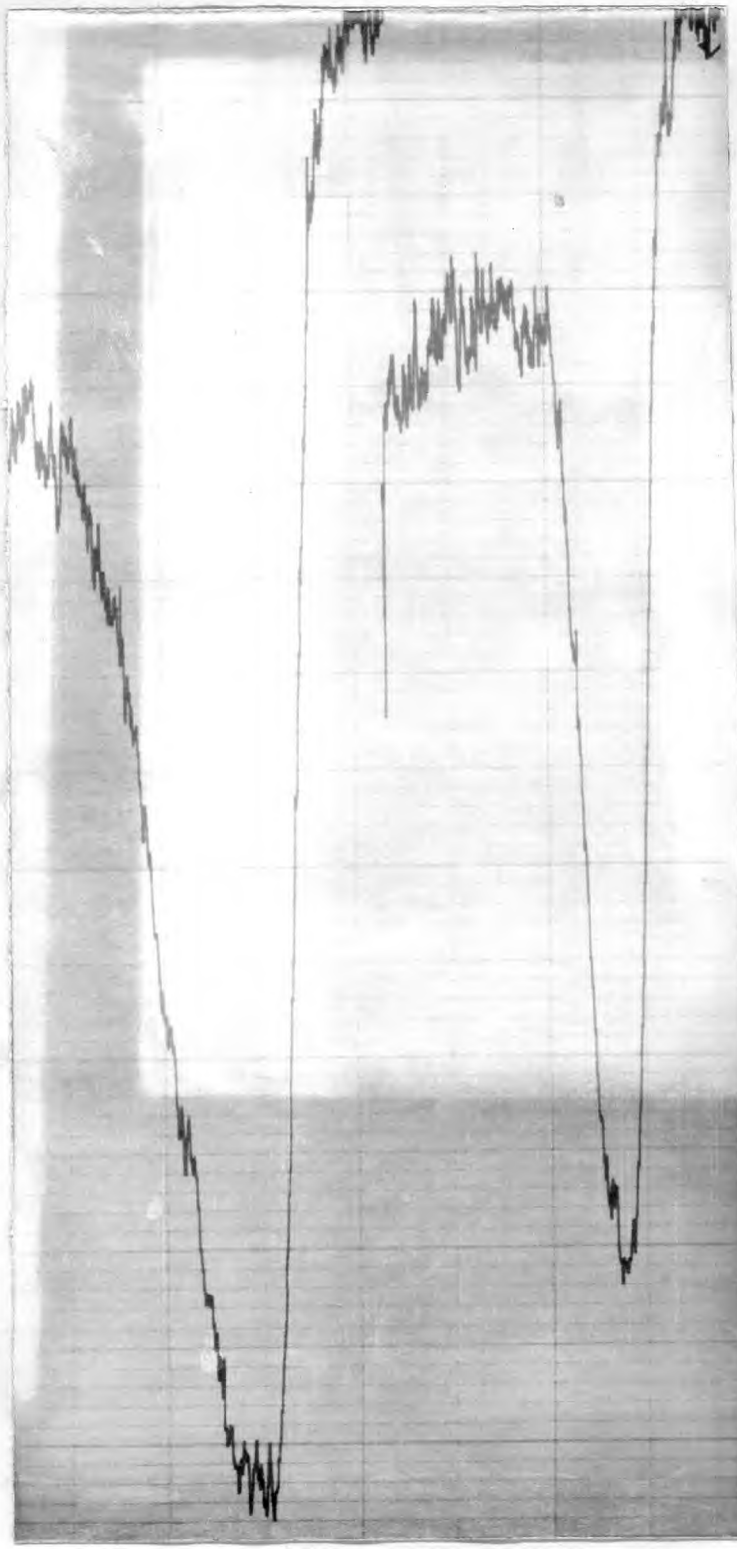
Ethylene Peak at 10.6 μ scanning well below luminous zone.



Figs. 14 b and c: Carbon Dioxide 14.8μband at two scanning speeds.

Fig. 15: Carbon Dioxide at 4.4μ.

(a) Hot (1200°K) (b) Cold (355°K)



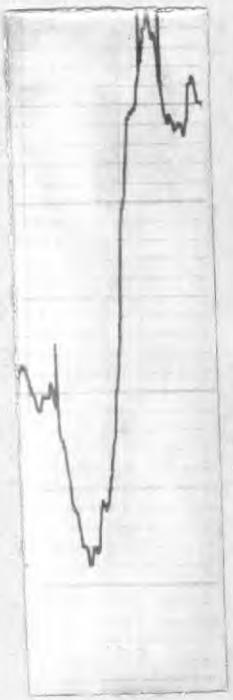
H_2O. Significant amounts of intermediates other than CO could not be observed against a background signal which was sufficient to be amplified to the maximum range of the recorder, viz. 10 mV, at all wavelengths up to 15 μ. The flame spectra discussed below were obtained using the focused beam system at minimum aperture, providing a spatial resolution at the centre of the flame of 0.5 mm with maximum beam width at the edge of the flame of 1.66 mm. (Image Mirror Distance = 180 mms, Mirror Aperture = 5 mms, Diameter of Flame = 136 mms).

Typical records of the ethylene 10.6 μ (Fig. 14a) and carbon dioxide bands at from 4.2 - 4.6 μ (Fig. 15a), and at 15 μ (Figs. 14 b and c) are illustrated by 1:1 replicas. The majority of such scans, i.e. traces of absorption versus wavelength for one level in the flame, were taken on the rock-salt prism up to 15 μ. Identification of peaks was made by using calibration curves of the monochromatic dispersion system of wavelength versus prism position as indicated by the vertical "blips". These correspond to drum readings on the screw thread directly connected to the prism drive mechanism. Comparison of resolution of peaks can be made with those supplied with the instrument (cold), with some found in the literature (cold)[16,16a] and, for CO_2, with some work by Tourin et al[17] for temperature effects. Up

Fig. 16: Background Absorption.

(a) With Box Unwashed

(b) With Box Washed



to 9 μ, peaks with the rock salt prism could be compared with those using the calcium fluoride prism.

4.3. Comments on Spectra with Reference to Perkin-Elmer 12C Spectrometer.

The advantages in signal strength and resolution of peaks obtained by 'filling' the monochromator are illustrated both by the quality of the spectra and the ability to detect flame absorption above background absorption in the regions of atmospheric interference. Although this could be eliminated (see Fig. 16) by continual 'washing-out' of the perspex box with oxygen-free nitrogen, the effect of adding 5 cc/sec at N.T.P. of CO_2 to the unlit reactants and the background level of absorption due to normal room concentration levels of CO_2 show this to be unnecessary. This also demonstrates that the use of a double-beam spectrometer, to eliminate background absorption, would have no additional advantages.

Purely instrumental effects to be observed from the spectra are better appreciated after a discussion of the controls of the electric signal from detector to recorder. The pen trace is the output voltage of the thermocouple suitably amplified to millivolt level. This thermocouple signal is due to infra-red energy incident upon the thermo-

couple and rotation of the prism permits a true record of wavelength of the infra-red energy transmitted through the entrance slit from the external system to be made. Thus amplification of the signal level occurs at the following stages.

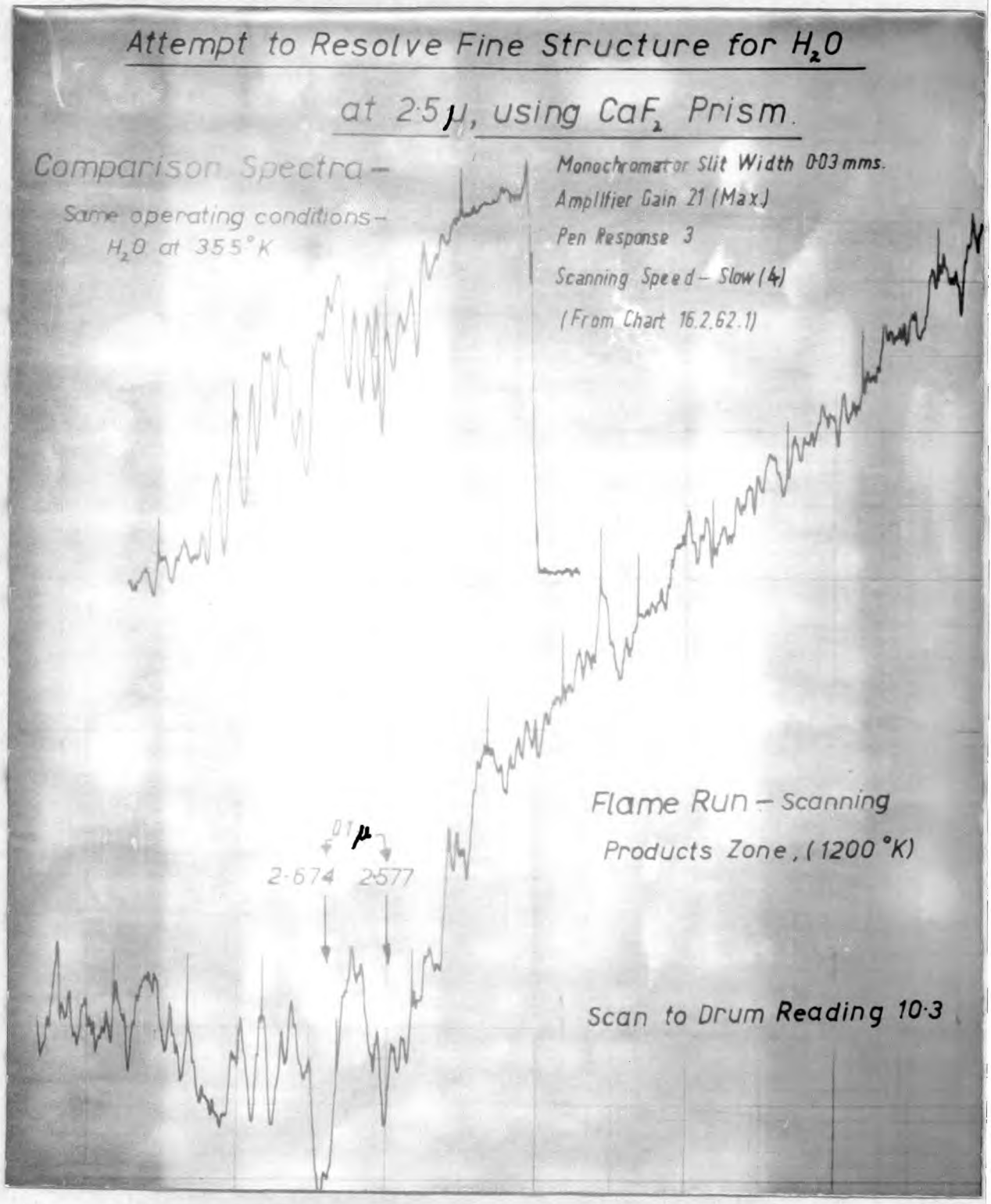
1. On incidence at the detector with a built-in pre-amplifier.
2. Subsequent amplification and filtering stages.
3. An amplifier in the recorder pen circuit.

The initial signal can be increased by increasing monochromator entrance slit width (this can be increased to 2 mms if necessary), and the scanning time, i.e. rate of rotation of prism. The electric signal can be amplified to a level in practice limited only by the noise level incurred. Under 3 isthe response time of the pen which is determined by the signal/noise ratio, and finally the pen trace can be modified by 4 variations in pen response time.

Discussion of the Spectra.

The chief feature of spectra of species at elevated temperatures, which is illustrated in Fig. 17 relating to water vapour is the apparent lack of fine structure to be observed. Both the broadening of bands, the overall increase in absorption (or emission) and the apparent lack of fine structure can be attributed to increased transitions occurring

Fig. 17: Comparison of Water Peaks at 2.5 μ - Resolution of Fine Structure.

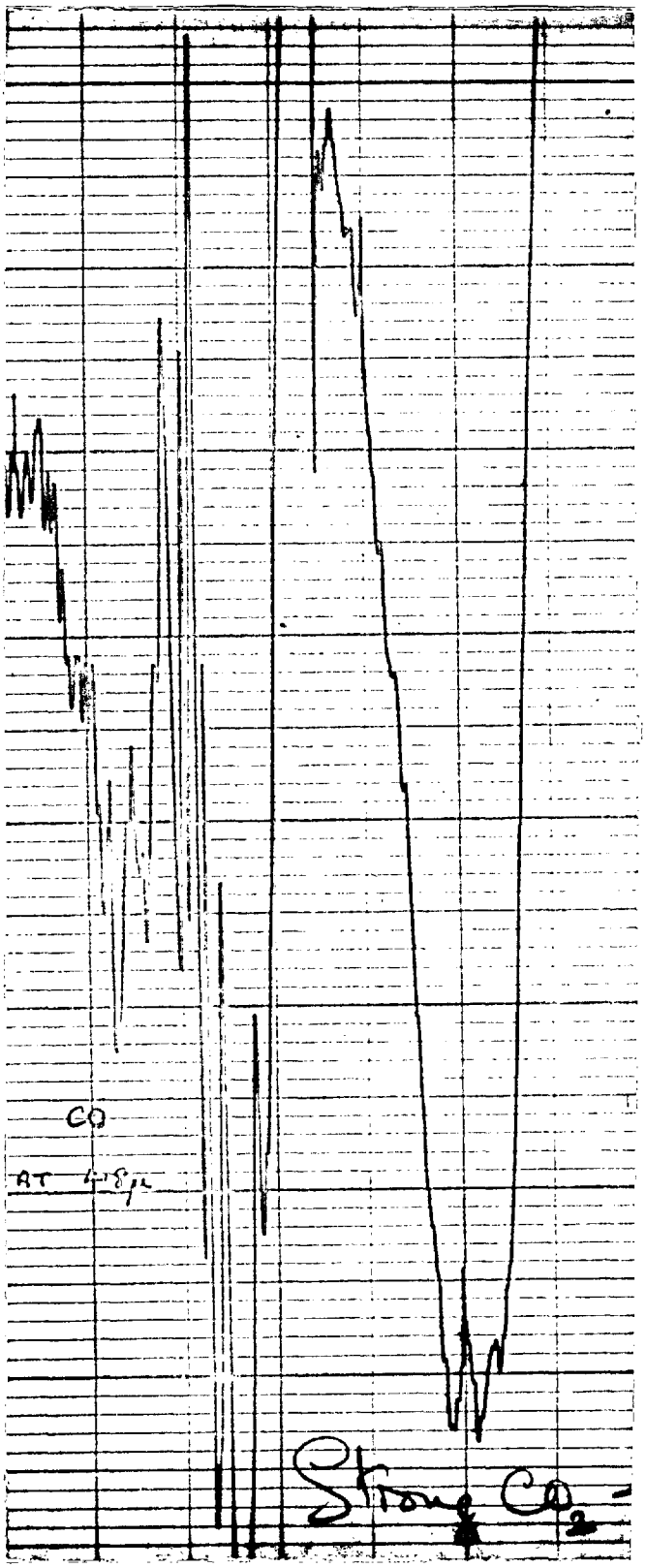


between higher vibrational levels of the species concerned. The H_2O band, Fig. 17, illustrates this and it is consequently apparent that spectra at room temperature convey more information on the geometry of the molecule and its modes of vibration. The lack of fine structure limits the estimation of vibrational temperatures, through which, it had been thought that information might be obtained regarding conditions prevailing in the flame. The increase in peak height and overall broadening of a band with temperature are illustrated by Fig. 15 a and b. The CO_2 concentration for both is the same, made up of 0.19 gm/l produced from the flame (Fig. 15a) or added to the unlit reactant stream (Fig. 15b), over and above the background concentration in the case enclosing the apparatus.

Evidence for the existence of Excited Species.

Before discussing the more unusual effects observed, it must be pointed out that the spectra presented were, apart from that of ethylene which was found up to 1 mm from the luminous zone, derived from the region where reaction had ceased and where sufficient collisions can be assumed to have taken place to ensure that equilibrium existed. Ethylene was not observed to exhibit other than the normal vibrational structure of the 10.6μ band. However both CO

Fig. 18: Spectra of Product CO_2 in Luminous Zone showing Excited Levels and Product CO_2 in Equilibrium at Final Flame Temperature.



and CO_2 were found to exhibit other than 'normal' spectra in the flame region where reaction took place. Abnormalities were of two kinds as illustrated in Fig. 18. This record was obtained when scanning 1 mm beyond the luminous zone. It shows abnormally large absorption peaks which characterize an apparent re-distribution of energy among the states. The two indicate very strongly that product CO_2 close to and probably at its point of origin exists in an excited condition as is understood by such variations in population of the vibrational states. The requirement of obtaining CO_2 in equilibrium in this region was vital to the quantitative work and as subsequent spectra indicated a build up in concentration of excited species in the flame such a project was unavoidably eliminated.

Location of Species.

The four species which were found present in the infra-red absorption spectra of the ethylene-air flat flame were ethylene (10.6 μ), carbon monoxide (4.8 μ), carbon dioxide (4.4 and 15 μ) and water-vapour bands (extensive absorption from 2.5 - 2.8 μ). Characteristic bands of each of these have been used to illustrate the previous ~~components~~ on the form of the spectra records under various experimental conditions. It became apparent that the scope of what was originally the recording of their characteristic spectra at various positions through the flame could be extended if the various zones of appearance of disappearance of absorption peaks could be satisfactorily localized. Using the optical system at its maximum spectral resolution, the spectra of each absorbing species were recorded as close to their zones of appearance or disappearance as possible. For these measurements some data pertinent to previous studies of the flame by other means can be verified. It has been suggested previously[18] that a discrete stage in hydrocarbon combustion is that giving rise to carbon monoxide, and that the further oxidation of this intermediate is inhibited by the hydrocarbon or one of its immediate products. Fig. 19 illustrates the decay of ethylene with formation of carbon monxide until the ethylene has vanished. Following the formation of carbon

Fig. 19: Series of Scans through 10.6 μ showing location of zone of disappearance of ethylene.

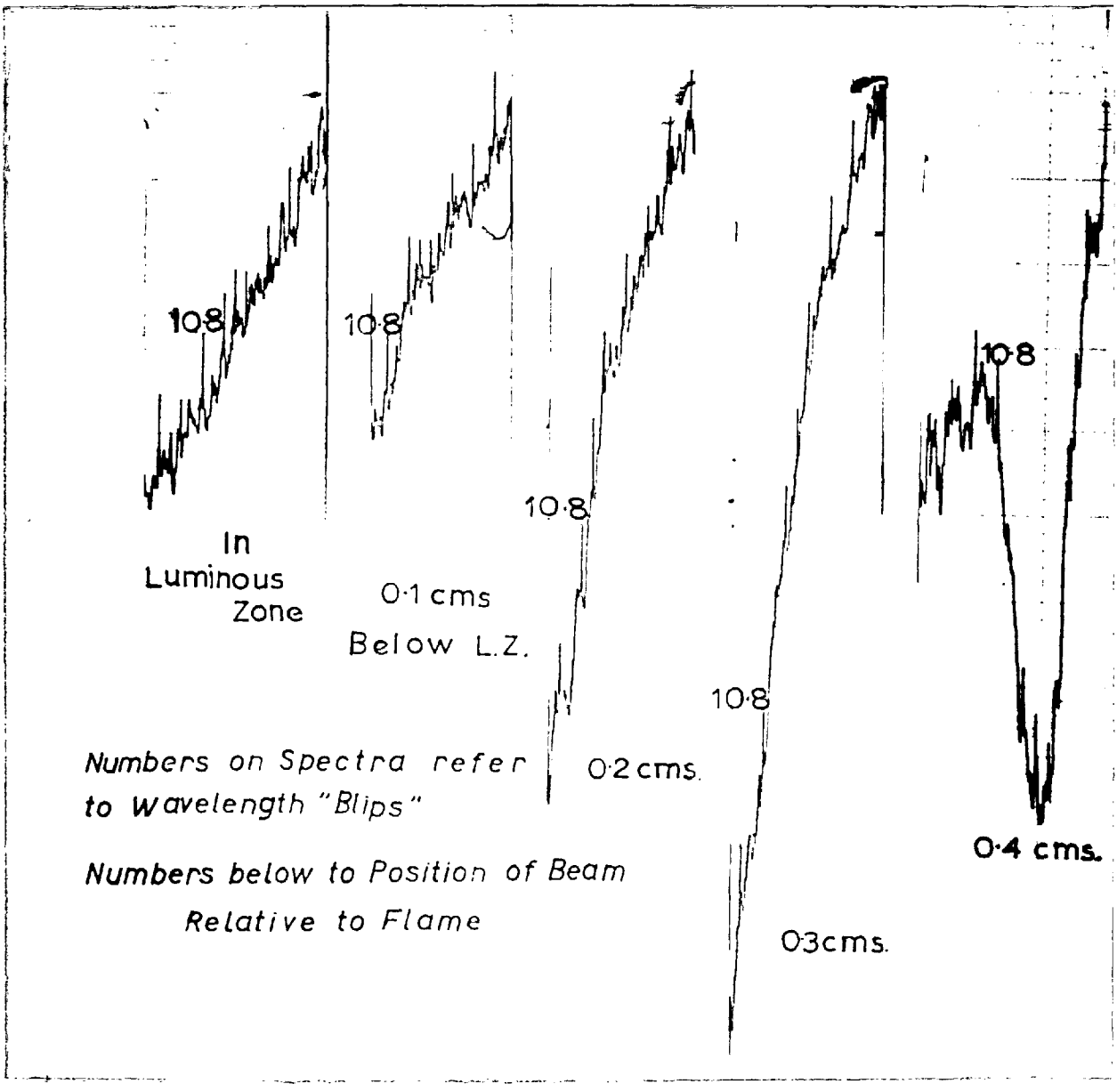


FIG. 20 SET OF CURVES RELATING ABSORPTION PEAK HEIGHT WITH ZONE POSITION FOR THE SPECIES LISTED.

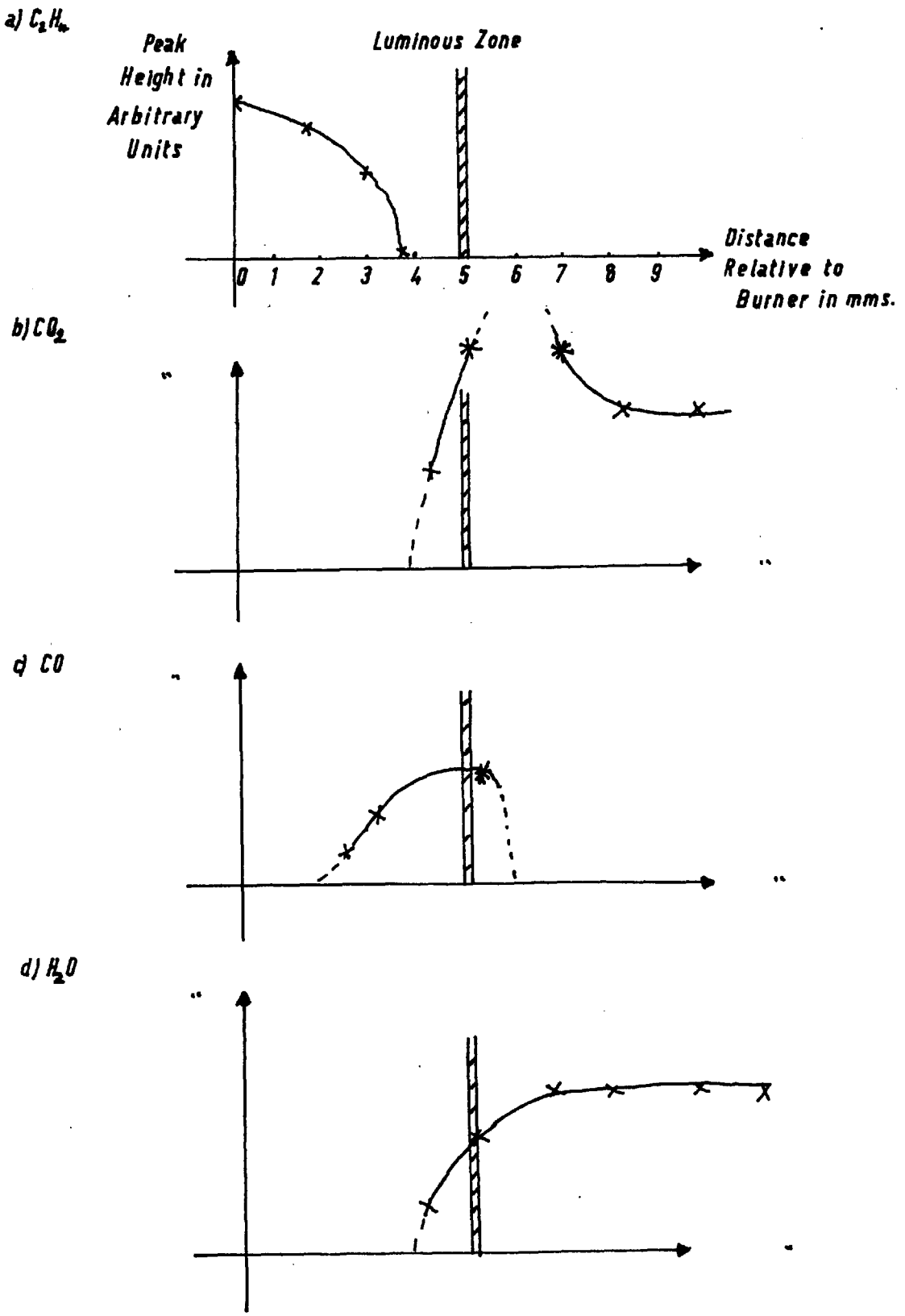
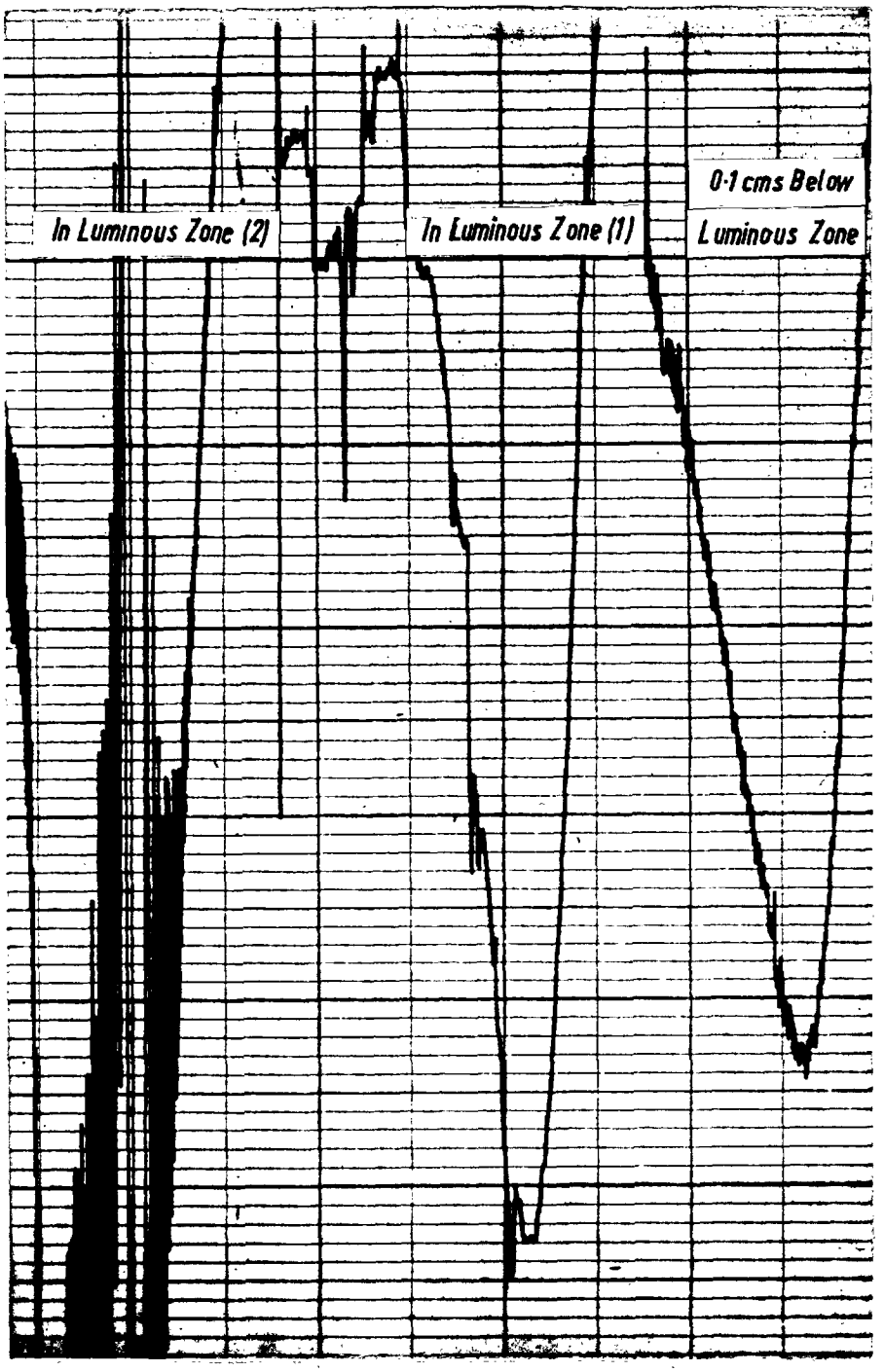


Fig. 21: Three scans through 4.4μ showing first detection of Carbon Dioxide in Flame.



monoxide and carbon dioxide was made more difficult by the appearance of anomolous peak heights although, of course, these enabled accurate location of the actual point of observation. The abscissa of Figs. 20 a, b, c and d are only to be taken as qualitative and do not refer one to the other for two reasons. One, the temperature shift ensures that the wavelengths at which the comparison of peak heights is made are different, and absorption coefficients there must be different also (this refers in particular to the water bands), secondly where anomolous absorption has taken place (indicated by *'s) the value plotted is an average for the entire band.

For the two critical species the spectra [redacted] obtained when approaching the zone have been reproduced in Figs. 19 and 21.

CHAPTER 5. QUANTITATIVE DETERMINATION OF CARBON DIOXIDE IN THE FLAME.

Earlier research on flame analysis has been directed principally towards the determination of the thermo-chemical properties of the flat flame. The field of visible, ultra-violet and infra-red absorption was left, possibly because of difficulties in experimentation incurred in the methods. A literature survey reveals little on the subject. Gaydon and Spokes[7] on ultra-violet work, Weinberg and Peacock on visible absorption in the Bromine-Hydrogen flat-flame[8], Tourin and Babrov (ref. 19 concerning absorption coefficients of CO_2 at 4.4 μ) and Minkoff et al[14] for some preliminary infra-red investigations, are contributions of interest. The present aim was to proceed as far as possible along the lines of the investigation suggested by Cole and Minkoff and to attempt a quantitative measurement of concentration of a species in the flat flame by infra-red absorption. The study of the fate of carbon dioxide was particularly suitable to this because the procedure to be adopted would involve the addition of carbon dioxide, an inert for calibration purposes. The results could be used simultaneously to test the suitability of the flame as a source for absorption coefficients of inerts.

The stages involved in undertaking this work were: selection of a suitable absorption band, chosen by virtue of the minimum to maximum peak height values corresponding to the zero and maximum concentration of the inert; selection of the most suitable peak within the band from which to obtain the actual values of I_o/I; using these results to verify a suitable law relating absorbtivity with concentration. Section 5.2 contains details of the factors to be considered when establishing a suitable formulation.

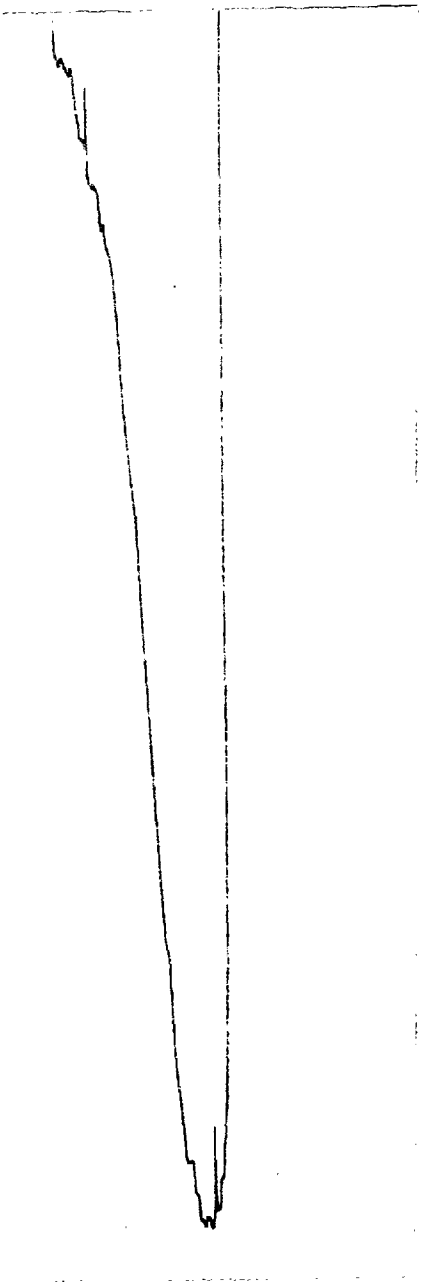
The results for two peaks corresponding to 4.2μ and 4.4μ and at the final flame temperature (1200°C), together with, for comparison purposes, the same plot at the initial flame temperature (355°K) at 4.2μ, and the calculation leading to values of the absorption coefficients for these are presented (Sections 5.3 and 5.4).

5.1. Comments on Spectra, calibrated by adding Carbon Dioxide.

Calibrations were conducted by the addition of carbon dioxide into the pre-mixed stream at known volumetric flow-rate. The pre- and post-flame regions were scanned, these being at steady states of composition and pressure and at temperatures of 355°K and 1200°K respectively. The effects upon the absorption band of carbon dioxide in the 4.2 - 4.4μ

Fig. 22a: Scan at 4.4 μ, through Equilibrium Zone with Max. Concentration of CO_2 added to Flame.

Fig. 22b: Repeat Scan with Flame Out.



band at the two temperatures was different. A comparison of the two spectra derived when the maximum concentration of carbon dioxide was added (Fig. 22 a and b) illustrates that at the higher temperature absorption by the two branches at about 4.2μ and 4.4μ is favoured. The side-peak at 4.4μ varies more rapidly with changes in carbon dioxide concentration and thus provides a more sensitive indication of absorption.

5.2. Relationship between Absorption and Concentration of a Species.

To carry out accurate analyses from the measurements of infra-red absorption requires the formulation of a relationship between the absorption peaks and concentration of the species. Such a formulation is mentioned in Chapter 1, and although its applicability has been under question[20] as a first approximation it proved useful in this case. As indicated in Chapter 4 the possibility of obtaining quantitative results must be limited to the regions where product carbon dioxide is in equilibrium with that added for a calibration. Results were plotted in the form suggested by the Lambert-Beer Law as $\log_e \frac{I_o}{I}$ against $C_F L_F$ where C_F is the carbon dioxide concentration and L_F the path length in the flame. The formulation of this law assumes the reality of

an absorption coefficient α which takes into account factors other than concentration, such as temperature and pressure effects upon the absorption. The analytical procedure was therefore to examine the law under known conditions, finding α's as a function of temperature and/or pressure. Although there are a number of reasons why the law is only applicable to infra-red spectroscopy in special cases, it is convenient to plot the results in this form because (1) the complex variations with pressure and temperature are more amenable when treated in terms of deviations of α from constancy and (2) α may approximate to constancy at one wavelength and temperature at the great dilutions and over the small pressure ranges involved in the present work.

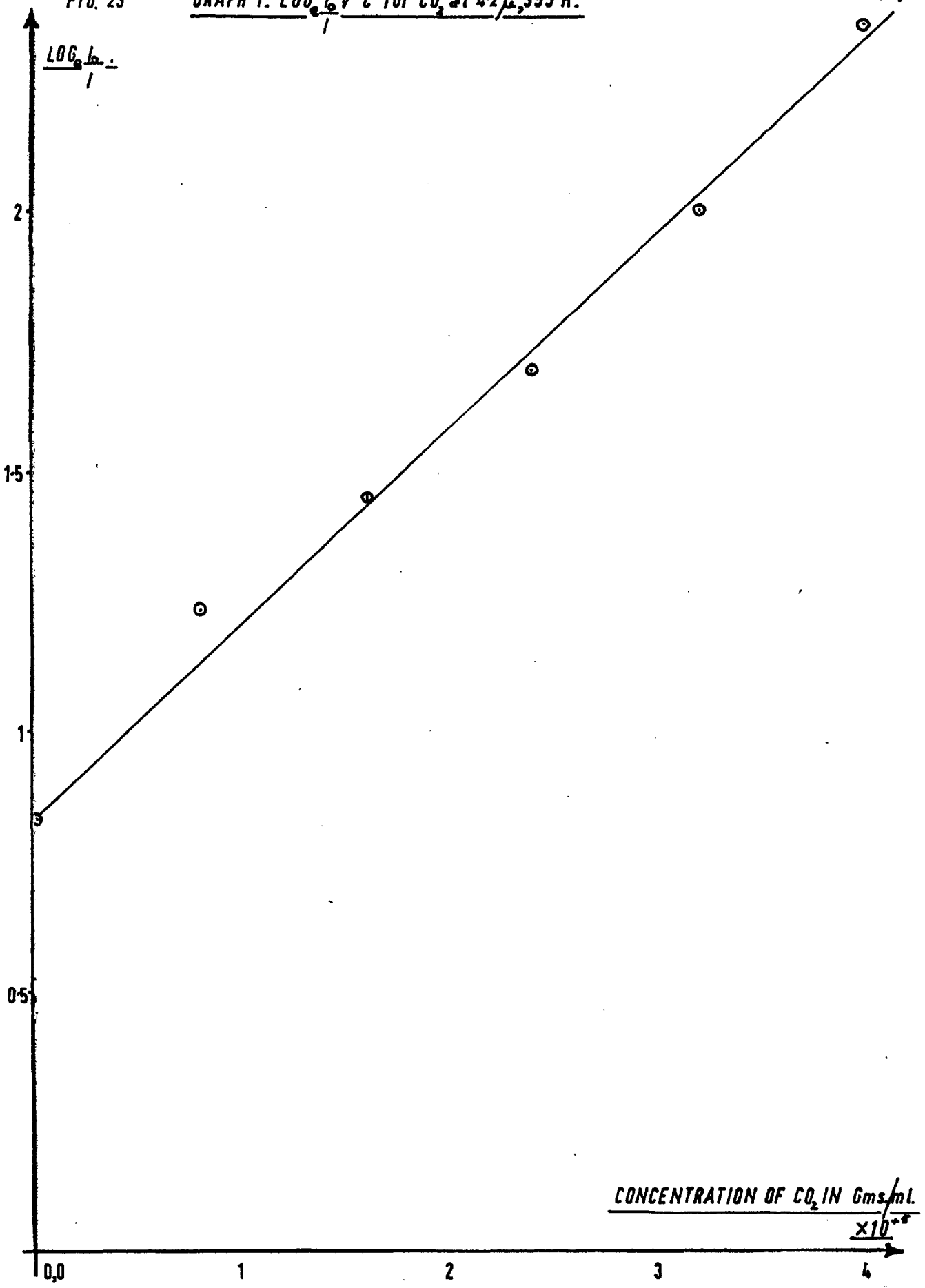
5.3. Absorption Coefficient of Carbon Dioxide at 355°C and approximately 4.2 μ.

We have $\frac{I_o}{I} = e^{+\alpha_o C_R L_R + \alpha_o \bar{C} . L_B}$

α_o = absorption coefficient for carbon dioxide at 4.2 μ and the temperature of the reactants upon entering flame, and other symbols are as denoted earlier (Section 1.5)

$$\therefore \log_e \frac{I_o}{I} = \alpha_o C_R L_R + \alpha_o . \bar{C} . L_B$$

FIG. 23 GRAPH 1. $\log_e \frac{I_0}{I}$ v $\bar{C}$ for CO_2 at 4·2 μ, 355°K.



Plotting $\log_e \frac{I_o}{I}$ versus $\bar{C}$, we have GRAPH 1 (Fig. 23) and assuming a linear relationship, slope = $\alpha_o L_B$, y-intercept is $\alpha_o C_R L_R$. We know L_B, L_R the relative path lengths in the flame and in the laboratory, hence α_o, C_R can be found.

Results.

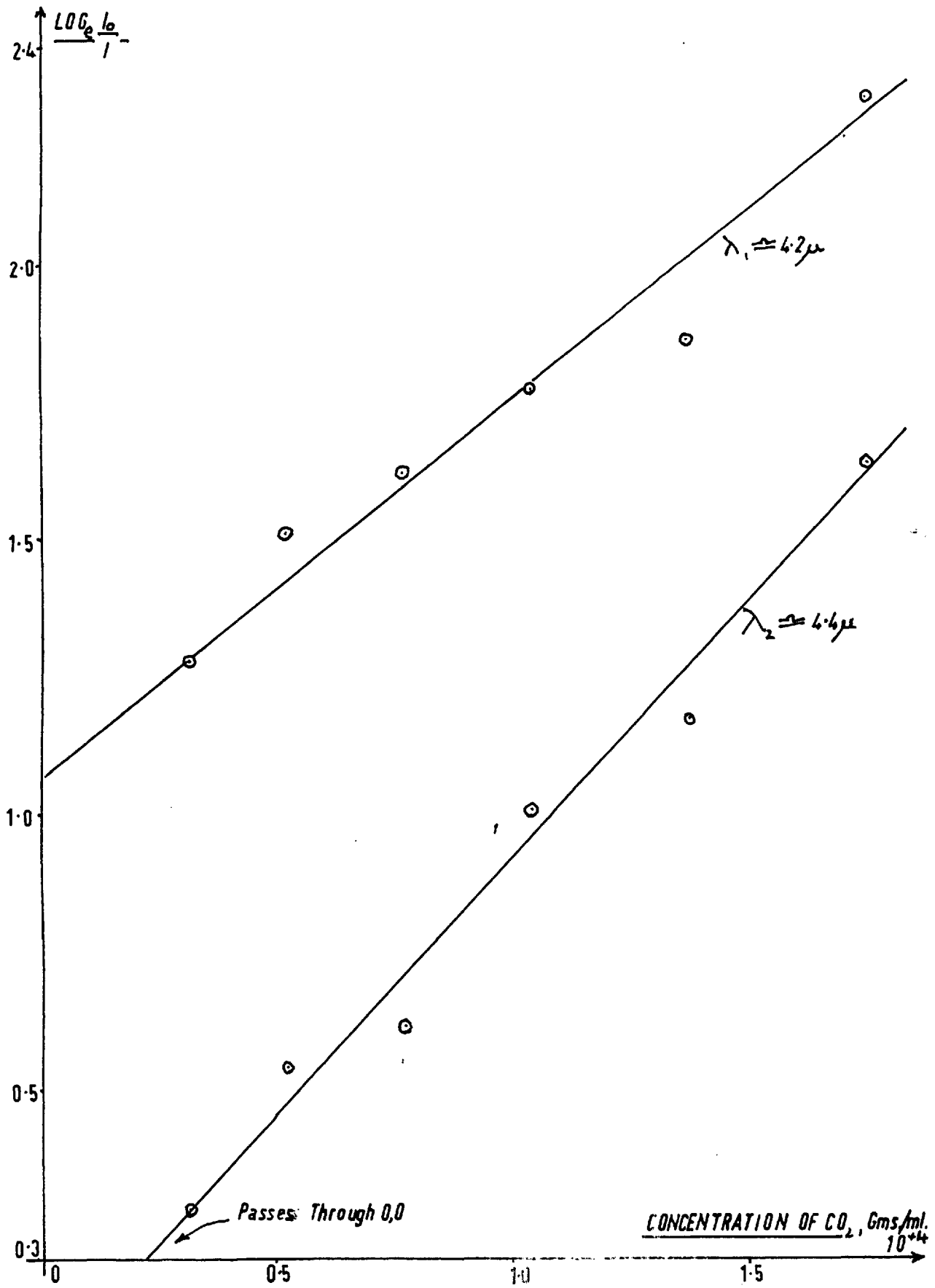
Fig. 23 shows the results at the initial temperature and at 4.2μ, scanning well below the flame. The graph approximates quite closely to a straight line, as predicted by the Lambert-Beer Law. The amount of CO_2 in the comparatively very long path outside the flame can readily be deduced from the intercept. It is equivalent to 0.5% CO_2 in the flame gases.

5.4. Absorption Coefficient of Carbon Dioxide at 1200°K and approximately 4.2μ, 4.4μ.

We have $\log_e \frac{I_o}{I} = \alpha_o L_R C_R + \alpha_T L_B (\overline{C_F + C})$

where C_F is concentration of carbon dioxide in product gases, $\bar{C}$ is the concentration added to reactants. The first term refers to the background absorption. Again plotting $\log_e \frac{I_o}{I}$ versus $\overline{(C_F + C)}$ we have GRAPH 2 (Fig. 24). We can examine the form of this corresponding to two wavelengths and it was found that the graph for the 4.4μ peak passed

FIG. 24 GRAPH 2. $LOG_e \frac{I_o}{I}$ v $\overline{C_F + C}$ for CO_2 at 4·2, 4·4 μ, 1200°K



through the origin, indicating α_0 at that wavelength to be zero. From the two graphs the values of the absorption coefficients at the two wavelengths and at the temperature concerned were calculated.

Results.

The two graphs (Fig. 24) are again reasonable straight lines (i.e. the deviations from linearity are without trend and appear to be due to error alone). The values of the absorption coefficients vary for the two wavelengths and also denote a significant change with temperature. Calibration at several temperatures would be necessary to establish the dependence of α upon temperature. The further conclusions concerning this work are summarized in Chapter 6, Section 1.

CHAPTER 6. CONCLUSIONS.

This study was undertaken from the viewpoint of developing techniques for probing the flat flame in the infra-red region. Principal objectives were the stabilization of a wall-less flame and the design and construction of a mirror system providing the optical probe.

After some preliminary investigations into the means of controlling both flame shape and, as subsequently became clear, to a lesser extent the equilibrium position, a burner was developed with which it is possible to obtain a flat flame with a configuration meeting the requirements of analytical work. With an optical probe it is possible to record absorption bands at various wavelengths and at all heights in the flame, that is absorption versus the temperature over the range provided by the flame gas.

New approaches in optical system design aimed to provide increased spatial resolution while shortening path lengths. These objects were achieved by varying the aperture of a focused beam system using cylindrical mirrors, and shortening the path length to the limit set by the incidence of off-axis abberations.

Using the spatial resolution to the maximum advantage several series of infra-red scans were recorded with a view to circumscribing the range of potential applications of the

technique. It was found that:

1. A flame can be used as a stationary temperature distribution at constant pressure for the purpose of establishing the relation between the infra-red absorption and species concentration, provided the species examined is an inert component and remains in equilibrium with local temperature. Thus the absorption by carbon dioxide at 4.2 and 4.4 μ was derived as a function of composition, in the former case at temperatures of 355°K and 1200°K and in the latter case at 1200°K only.

   The values of the absorption coefficients obtained were

$$\alpha_{355^{\circ}K,4.2\mu} = 3.7 \times 10^{3} \text{ grms}^{-1}\text{cm}^{2}$$

$$\alpha_{1200^{\circ}K,4.2\mu} = 1.06 \times 10^{4} \text{ grms}^{-1}\text{cm}^{2}$$

$$\alpha_{1200^{\circ}K,4,4\mu} = 1.42 \times 10^{4} \text{ grms}^{-1}\text{cm}^{2}$$

2. Free radicals and other unstable species are not present in lean limit flames in sufficient concentration to be detectable by infra-red absorption spectroscopy with about 12 cms optical path.

3. The method can be used to follow the disappearance, or first appearance of major species such as reactants, products or stable intermediates. This makes possible the location of boundaries beyond which such species no longer exist, to an accuracy limited by the resolving power of the optical system. This system, using the degree of intensity presented by conventional sources, is considered to present the maximum resolving power to be obtained. Thus the conclusions concerning ethylene and carbon dioxide, where it was found that the change in peak height with position extrapolates to zero at the same point for the two gases, confirmed the earlier work of Burgoyne and Hirsch[18]. Curves correlating these changes with the appearance and disappearance of carbon monoxide and with the accumulation of water to its final level have been presented.

4. Although it is possible to calibrate absorption quantitatively for the determination of species concentration under equilibrium conditions, such calibrations cannot be applied to the species while it is undergoing reaction. Thus CO_2, whilst being formed by reaction, manifests greater absorption, and gives absorption peaks which differ in appearance as well as height from those obtained under conditions of both higher and lower

temperature. The spectra obtained under conditions of disequilibrium of translational and vibrational energy states appeared of unusual interest arising from their novelty. However, it seems clear that the application of this technique to gain information concerning disequilibrium excitation would be of little practical advantage. The consideration of such disequilibrium states is as yet in an elementary stage and the quantitative interpretation of these spectra does not seem possible at present.

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