

AN EXPERIMENTAL STUDY OF FLASH HEATED
VAPOURS BY THE HOOK METHOD

by

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ABSTRACT

This thesis describes an investigation of the plasmas produced by flash heating of solids with the aims of determining their composition, density and temperature and their possible use in the measurement of oscillator strengths.

After preliminary experiments on the effects of varying such parameters as input energy, gas pressure and form of solid sample and on the time dependence of the vapour, the number densities of different types of atom in different states of excitation were investigated quantitatively by the hook method. For this purpose the pyrolysis tube was placed in one arm of a Mach-Zehnder interferometer and a background source of continuum was triggered at a pre-set delay time after the pyrolysis flash. The hooks formed by the interference fringes near an absorption line yield the product Nf of the population of the lower level of the transition N and the oscillator strength f of the line. Using lines of known f -value one can obtain relative number densities in the vapour of elements introduced in known proportion in the solid form. The results were not sufficiently reproducible for use in the determination of absolute f -values. However, the measurements on relative populations of different excited states for a single species of atom established that these followed a Boltzmann distribution at a temperature of about 5000°K . The technique may therefore be used to determine

relative f-values. A comparison of Nf values for atomic and ionic lines of the same species indicated that Saha's equation for ionization equilibrium is not applicable to this type of plasma, for which the electron density is of order 10^{13} to 10^{14} cm^{-3} .

Finally, the feasibility of determining relative f-values by the flash pyrolysis - hook technique was demonstrated in the case of yttrium. Results are given for six lines of Y I.

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CHAPTER 1

THE TECHNIQUE OF FLASH PYROLYSIS

1.1 Introduction

Atomic and molecular spectroscopy require atoms and molecules in gas or vapour form. Apart from the very high temperature devices for producing a high degree of ionization, the most usual sources are arcs, sparks, various forms of glow discharge, shock tube and furnace. The last source is more suited for absorption spectroscopy. The upper limits of temperature reached in a furnace are set by technical considerations, in particular the physical and chemical characteristics of the furnace materials, which have restricted the temperature to below 3000°K . For example, in the King's type high temperature vacuum furnace, owing to the rapid reaction of the vapour with the graphite tube to form carbide, the temperature cannot be raised above 2500°K . Within this limited range of temperature, many elements of low boiling point have been studied, but it is difficult to produce vapours of the refractory elements at sufficiently high concentration. With a shock tube, it is possible to reach very high temperatures, in excess of 10000°K , but there are often difficulties in vapourising powdered solids by this method.

Refractory elements can be vapourised with relatively modest equipment by the technique of flash pyrolysis. An energy of some thousands of joules is discharged through a helical flash lamp, in a time of order 1 m sec, producing an intense pulse of light which vapourises suitably prepared solids contained in a translucent cell within the helical flash lamp. The temperature of the vapours reaches several thousand degrees in a fraction of a milli-second. There already exist some studies of the general behaviour and temperature of flash heated vapours, but more quantitative information on vapourisation and excitation is required if the technique of flash pyrolysis is to be used to produce vapours for quantitative work, such as measurement of transition probabilities.

The aim of this work was to investigate the flash heated vapours by measuring their density, composition, temperature, etc, and to assess their suitability for determination of oscillator strengths. Among the experimental methods that are suitable for these tasks, the hook method of Rozhestvenskii was employed as it could be applied in many cases to obtain results on the concentration of atoms in different states with a much higher accuracy than other methods.

1.2 The Heating Effect of the Flash Lamp

There are many different types of flash lamp. The simplest form consists of a transparent tube, sealed at both ends by electrodes and

filled with an inert gas at about one-tenth of the atmospheric pressure. The tube may be bent into a U-shape or a helix. In flash pyrolysis work, the helical type is generally used and the tube is made of quartz and filled with Xenon gas. When a capacitor discharges through it, the energy stored in the capacitor is rapidly dissipated, producing an intense pulse of light.

The intensity, duration and spectral distribution of the light pulse depend on such factors as:

- (a) the design parameters of the flash lamp: the length, the diameter and the shape of the tube, and the type and pressure of the filling gas.
- (b) the power supply parameters: the capacitance of the capacitor and the voltage to which it is charged, and the inductance and resistance of the discharge circuit.

A number of investigations have been undertaken to study these factors (1, 2, 3, 4). The main conclusions may be summarised as follows:

- (1) At sufficiently high current density of the order of a few kilo ampere per sq cm the light pulse is mainly a continuum extending from the far infrared to the ultraviolet cutoff of the quartz tube. The intensity varies with both the wavelength and the time during the flash. The spectral distribution in the visible region corresponds approximately to a black body at a temperature between 6000°C and 7000°C .

- (2) The shape of the light pulse, or the brightness-time characteristic, as measured by a detector with a flat spectral response throughout the whole spectrum of the radiation, depends on both the input energy and the inductance of the discharge circuit. The peak brightness is proportional to the square of the voltage and tends to be independent of capacitance at higher values of capacitance.
- (3) Xenon is the most efficient of all inert gases. The total light output would at first increase monotonically with pressure and then remain constant, whereas the brightness, after reaching a peak value, would drop about 30% at higher pressure.
- (4) The duration of the light pulse depends on the values of capacitance and inductance. The dependence of duration on capacitance changes from $C^{\frac{1}{2}}$ to C^2 as the value of C increases. Increased inductance would reduce the magnitude of the peak brightness and lengthen the duration. However the total light output from the lamp is not significantly reduced if the corresponding increase in resistance in the discharge circuit is small.
- (5) The total radiant energy (integrated over the whole pulse), as measured by the amount of heat absorbed by a black body calorimeter, is proportional to the amount of input electrical energy. For the same amount of input energy but with different power supply parameters, the radiant energy is increased as the duration is shortened. The use of a reflector may increase its value by 50%.

- (6) The light pulse is reproducible to within 2-5% and the ageing of the lamp is slow, efficiency being reduced by about 5% after every 1000 discharges.

The flash lamp is one of the most efficient devices known for converting electrical energy into optical energy, with an efficiency of over 60%, over half of which is in the visible part of the spectrum (5). The uses of the flash lamp are extensive and applications include illumination in photography, flash photolysis, optical pumping for solid state lasers and many others.

The peak luminous energy emitted by a powerful flash lamp may be as high as 66kW/cm^2 which is at least an order of magnitude higher than that of the largest solar furnace (6), and the light pulse has been found to have a very strong heating effect on a light absorbing body with a high surface to mass ratio. The term flash pyrolysis is used to describe the vapourization of solid materials by a flash lamp.

1.3 A Review of Past Works on Flash Pyrolysis

Most of the original work on flash pyrolysis was done by L S Nelson and N A Kuebler. The flash evaporation of tungsten was investigated by kinetic absorption spectroscopy and high speed photography (6, 7, 8). The solid samples were black oxide coated wires of $13\ \mu$ diameter and bright strips of $14\ \mu$ thickness. A helical flash lamp was used which, when operated with a capacitor bank of $1300\ \mu\text{F}$ charged to 4 kV giving an input energy of 10400 J, had a radiant output of $32\ \text{J/cm}^2$. The brightness reached its peak about $400\ \mu$ sec after the start of the flash and its duration was about $1500\ \mu$ sec.

There was a threshold of input energy at about 5000 J (650 μ F at 4 kV) below which very little evaporation took place for the wire sample. The only effect was the removal of some surface oxide. The threshold was somewhat higher for the strip sample. At energies near the threshold, only part of the sample evaporated. Evaporation increased as the atomic weight of the surrounding gas was increased or its pressure was reduced.

At an input energy of 10400 J the wire and the strip evaporated completely, regardless of the type of the surrounding gas or its pressure. With nitrogen at atmospheric pressure, very little evaporation was detected in the first 300 μ sec. Near the peak of the light pulse at about 400 μ sec the sample expanded and tungsten lines appeared and increased steadily with time. At 750 μ sec droplets appeared, indicating that the solid sample had changed into a liquid phase and shortly after, at 900 μ sec, the most complex absorption spectrum was recorded. Absorption lines from states as high as 22000 cm^{-1} above the ground state were observed. Then absorption decreased steadily, with excited states depopulating more rapidly than lower states.

Impurities of lower boiling point appeared earlier and also remained longer in the vapour phase. Emission lines from states at 55000 cm^{-1} above the ground state were also detected.

The evaporation and excitation of the tungsten vapour was found to be predominantly a thermal process, although the photo-chemical and shock processes could play a secondary role. From the assumption that at any given time the number of atoms in a particular energy state is proportional to the number of detectable absorption lines from that state, the distribution of the energy levels was found to follow the Boltzmann law. The temperature of the vapour leaving the boiling tungsten was found to be about 7200°K .

The technique of flash heating had also been successfully applied to the evaporation of many other elements such as Al, Au, B, Dy, Eu, Pb, either as metals or salts deposited on thin graphite strip, provided the metal absorbers had a very high surface to mass ratio (9). As impurities present in other elements, some of the strongly absorbing elements like Al, Cu, Mg, were found to have limits of detection as low as 1 p.p.m. Hence the technique could be used for the detection of some elements difficult to obtain by other methods.

The vapours produced by flash heating have been compared with those produced by radiation from a ruby laser in the case of coal and differences have been found (10). Flash heated vapours were also found to differ from those produced by high temperature carbonization. For example, the vapours produced by a light flash contained 65% of H_2 and 16% of CO as compared to 45% of H_2 and 14% of CO with the laser beam. The corresponding figures for high temperature carbonization were 55% and 7%. However it was not certain whether the differences

were due to the different temperatures, ranging from 900°C by carbonization to an estimated temperature of over 1000°C by the light flash and 7000°C by the laser beam, or to differences in the nature of the radiation.

Under certain conditions the flash heated vapours may react with the surrounding gas. When a loose wool of tungsten or grids of carbonized rayon were flash heated in methane, a gas which does not absorb light of wavelength greater than $1200\text{ \AA}$, the gas decomposed into the methyl radical CH_3 and hydrogen. But when the gas was flash heated alone, it did not decompose (11). The orange A and B band systems of FeO were observed when Fe was flash heated in oxygen, by direct reaction of the metal with oxygen (12). Some hitherto unrecorded features in the spectra of copper and scandium hydrides were discovered when the metals were flash heated in hydrogen (13). The flash pyrolysis of BeH_2 in oxygen produced products like OH , BeH , BeH^+ and BeO , the relative proportions of which changed during the flash (14). The technique permits the preparation of molecular species that cannot be obtained by flash photolysis as it is basically thermal and not photo-chemical.

Flash pyrolysis can also take place in a liquid of a transparent solid (15).

The technique of flash heating has also been successfully applied to the study of combustion of liquid metal droplets (16, 17). This allows the study of phenomena that are purely thermal in the absence of strong electric fields, and in a well controlled atmosphere. The technique also seems to be a promising method in the study of any processes that may involve intense surface heating of solids such as re-entry into the atmosphere and the physics of comets and meteors.

1.4 The Use of Flash Heating in Spectroscopy

As a method of producing high temperature vapours, flash heating has many advantages over the conventional furnace method. It is possible to study temperature regions far beyond those attainable with static furnace techniques and the reaction of the flash heated vapour with the container is usually very small or negligible as the heated vapour comes into contact with the container for just a few milli-seconds. By flash heating it is also possible to study those species that are too reactive or too unstable to be observed in a furnace. For example, the absorption spectrum of sulphur I in the region 750-1500 Å has been recently obtained by flash heating (18), and the technique seems promising in the study of other non-metallic elements. The main disadvantages are the difficulty of knowing the temperature and the uncertainty of length of the vapour column.

Although the technique of flash heating employs essentially the same design of apparatus as flash photolysis (19) and enjoys many of the same advantages, there are fundamental differences. In flash photolysis only a selected wavelength band of the radiation from the flash lamp is used for photo-dissociation and photo-excitation, whereas flash heating is initiated by the absorption of the whole spectrum of radiation. Hence by the technique of flash heating it is possible to produce (eg: by thermal dissociation) species which do not occur in photo-chemical reactions.

CHAPTER 2

THE THEORY OF THE HOOK METHOD

2.1 Refractive Index and Nf-value

The refractive index of a transparent medium is a function of wavelength. The rate of change of refractive index with wavelength is normally small and negative except near regions of resonance where it undergoes a sharp variation of magnitude and slope. The existence of a large discontinuity in the dispersion curve as it crosses an absorption region is known as the anomalous dispersion. The general dependence of refractive index on wavelength can be derived from either the classical or the quantum theory of optical dispersion (20).

In the neighbourhood of an isolated absorption line of a gas, where the effects of other absorption lines can be assumed negligible, the refractive index can be expressed by Sellmeier's classical dispersion formula:

$$n-1 = \frac{r_0}{4\pi} \cdot \frac{\lambda_0^3}{\lambda - \lambda_0} \cdot N_j f_{jk} \quad (1)$$

where j refers to the lower state and k the upper state of the line λ_0 ,

and f_{jk} is its oscillator strength. N_j is the number of atoms per unit

volume in the lower state j and r_0 is the classical electron radius $\frac{e^2}{mc^2}$.

The dispersion formula obtained from the quantum theory differs from Sellmeier's formula by the addition of a negative dispersion term, giving rise to the factor:

$$1 - \frac{g_j}{g_k} \cdot \frac{N_k}{N_j}$$

where N_j and N_k are respectively the number densities of the atoms in the states j and k , and g_j and g_k are their statistical weights. At a temperature of a few thousand degrees, the negative dispersion term may be neglected as it is of the order of 10^{-4} .

Thus the product Nf , or one of them if the other is known, can be determined by measuring the magnitude of the anomalous dispersion in the vicinity of the absorption line.

2.2 The Hook Method

In the hook method of Rozhdestvenskii, the Nf -value is measured by an interferometer crossed with a spectrograph. The conventional experimental set-up uses a two-beam interferometer, such as a Mach-Zehnder, from which horizontal fringes are focussed on to the slit of the spectrograph. With zero path difference between the beams, the interference fringes observed in the focal plane of the spectrograph run horizontally across the spectrum. If, however, one of the beams passes through a gas with an absorption line, the interference fringes trace out hyperbolae on either side of the line (Figure 1a).

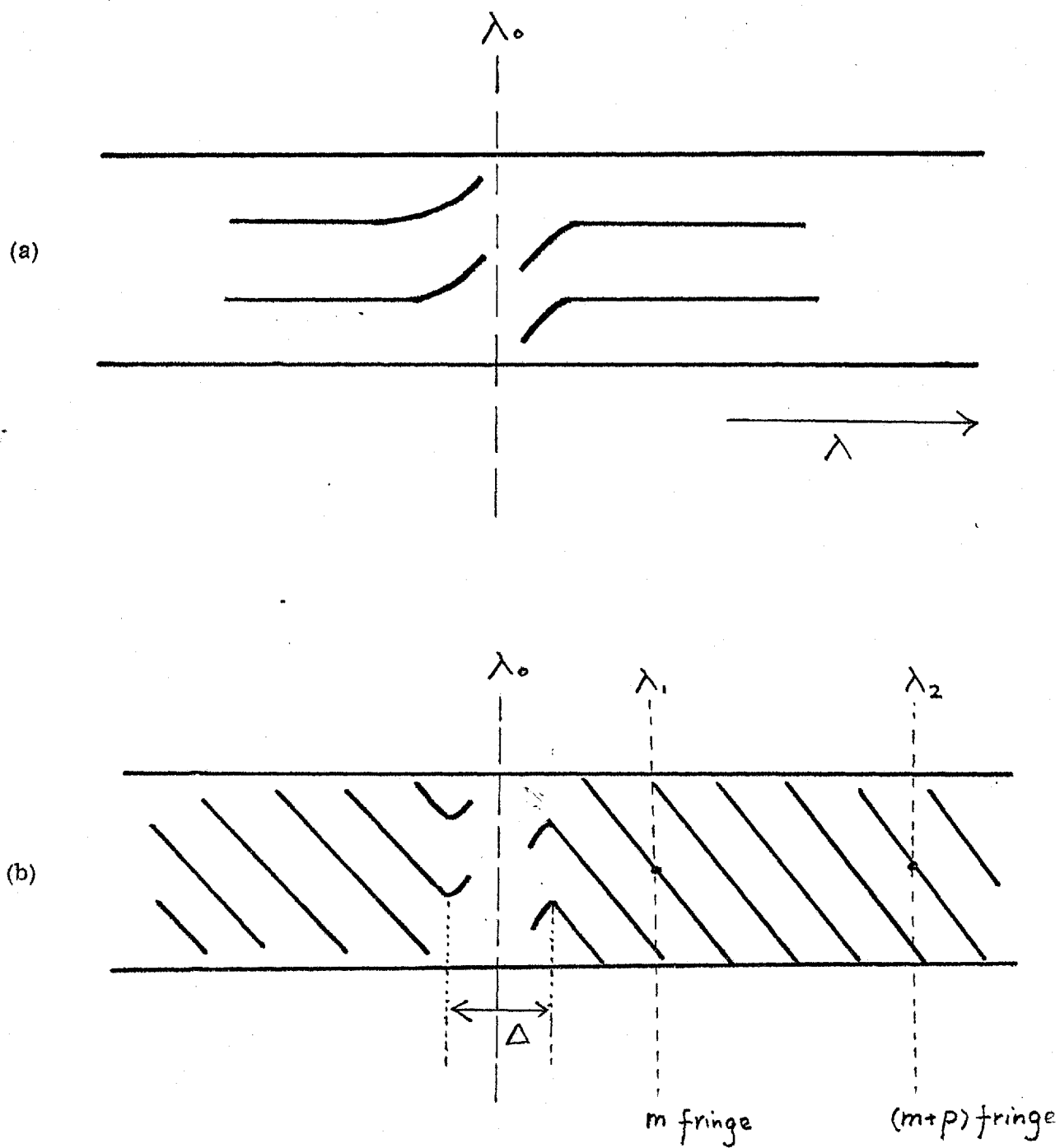


Figure 1: (a) Dispersion; (b) Hook

When the optical path in the second beam is increased, as by inserting a plane-parallel glass plate, the fringes are of a high order of interference and slope diagonally across the spectrum. The gradient of these fringes is opposite to the gradient due to anomalous dispersion so that a superposition of the two phenomena leads to the formation of a 'hook' on either side of the absorption line, at the places where the two effects cancel to give zero slope (Figure 1b). Theoretical analysis (21, 22) shows that the positions of the hooks are determined by the equation

$$L \frac{dn}{d\lambda} = -K \quad (2)$$

where L is the length of the gas column, and K is the fringe order, a constant which depends on the path difference between the two beams.

By combining the Sellmeier formula for the refractive index near a single line with the equation determining the hook positions, the Nf -value for a single line can be obtained immediately.

$$Nf = \frac{\pi}{r_0 L} \cdot \frac{K \Delta^2}{\lambda_0^3} \quad (3)$$

where Δ is the wavelength separation between the hooks defined as

$$\Delta = \lambda_+ - \lambda_-$$

The constant K is given by

$$K = \frac{P \lambda_0}{\lambda_2 - \lambda_1} \quad (4)$$

where ρ is the number of fringes crossing a wavelength range $\lambda_2 - \lambda_1$ centred on λ_0 , as shown in Figure 1b, and so may be determined experimentally from a region of undistorted fringes near the absorption line in question.

Thus the hook method reduces the measurement of Nf -values to a measurement of distances on the photographic plate, which can be done with great accuracy. This is the main advantage over the straightforward absorption methods. The other advantages are that there is no restriction on the resolving power of the spectrograph or the optical depth of the absorbing gas, and the accuracy is unaffected by scattered light or continuous absorption by impurities. The hook method permits easy measurement of the Nf -values of lines widely distributed over the spectrum and of greatly differing intensity.

However the hook method is about an order of magnitude less sensitive than the absorption methods. Another deficiency is its limitation to photographic detection. Recently it has been shown that the sensitivity of the hook method could be enhanced by using a series type interferometer in which multiple beam interference fringes of equal thickness were observed (23). A modification of the series type interferometer allowing the use of photo-electric detection has also been suggested (24), but neither of these modifications appear as yet to have been put to practical use.

The main applications of the hook method have been, in conjunction with a furnace, to the measurement of relative and absolute f -values of atomic transitions, and only recently, at Harvard College Observatory, has the method been used with a shock tube to measure f -values in the spectrum of iron. At Imperial College, the hook method has been extended to measure f -values of the (0,0) and (1,0) bands of the ultraviolet system of the hydroxyl radical and the (0,0) band of nitric oxide (25, 26). As a diagnostic tool, it has been applied in the investigations of the excitation and ionization processes in a King's furnace (27, 28), of stationary and non-stationary plasmas in a gas discharge (29, 30), and of gas dynamic processes in a shock tube (31, 32).

2.3 Some Computation Formulae

In the case of two neighbouring lines, both may contribute to the refractive index in the neighbourhood of either. There are two cases to consider (33).

When there are hooks between the lines (Figure 2a), the two Nf -values are given by:

$$N_1 f_1 = \frac{4\pi K_1}{\gamma_0 L_1 \lambda_1^3} \cdot \delta_1 \delta_2 \cdot \left[1 + \frac{\delta_3 \delta_4}{\epsilon^2 - \delta_1 \delta_2 - \delta_3 \delta_4} \right]^{-1} \quad (5)$$

$$N_2 f_2 = \frac{4\pi K_2}{\gamma_0 L_2 \lambda_2^3} \cdot \delta_3 \delta_4 \cdot \left[1 + \frac{\delta_1 \delta_2}{\epsilon^2 - \delta_1 \delta_2 - \delta_3 \delta_4} \right]^{-1}$$

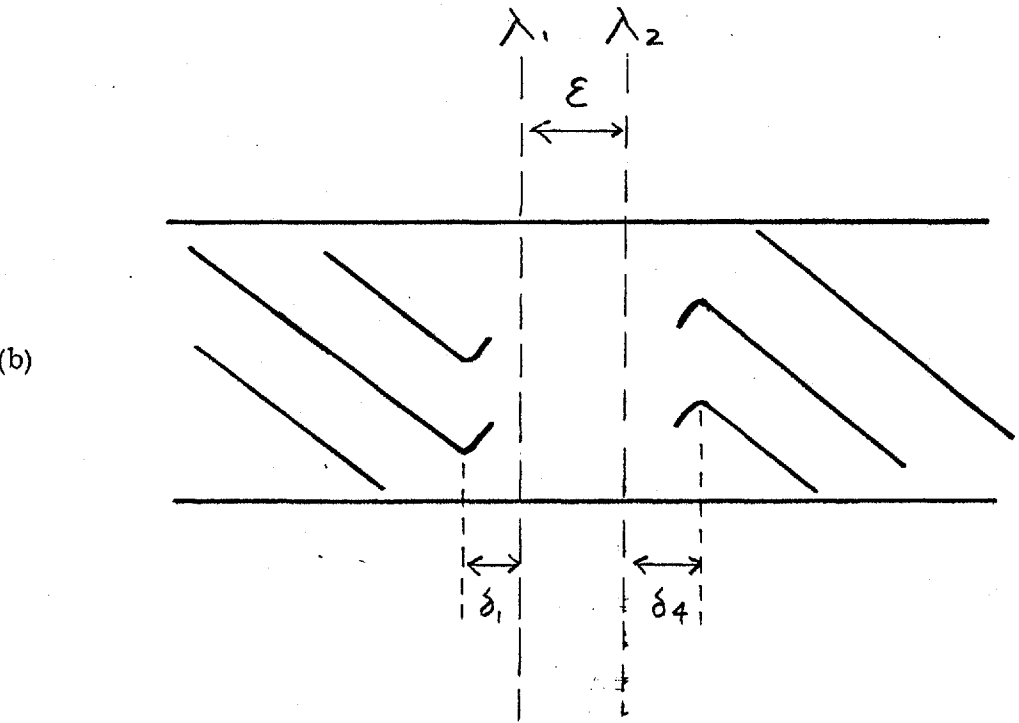
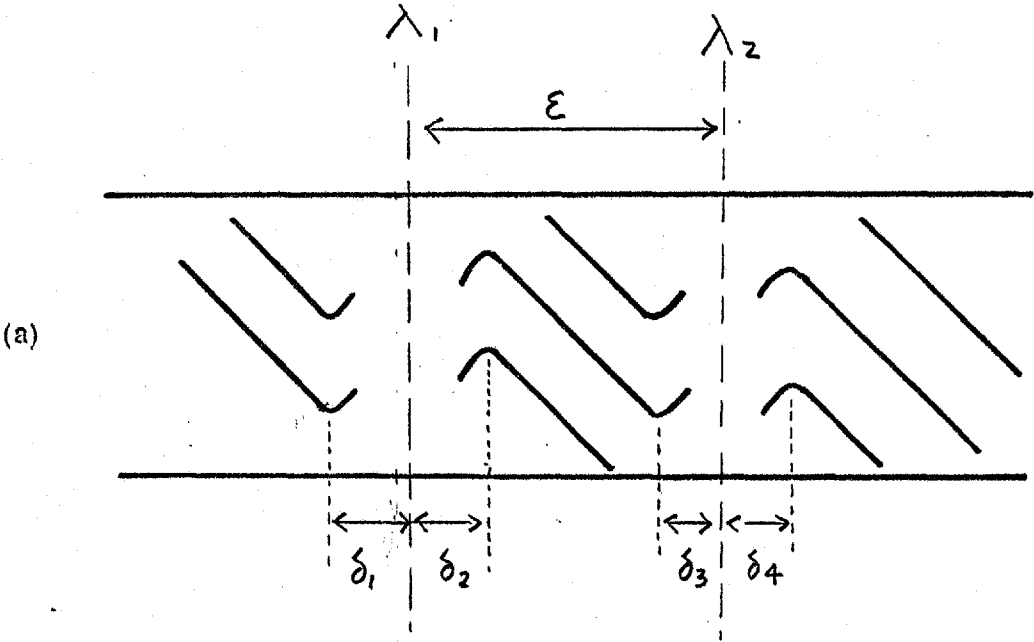


Figure 2: Hooks of Two Close Lines

where all quantities not previously defined are indicated in Figure 2a.

When only the outer hooks are measurable (Figure 2b) as is often the case in a close doublet, the Nf -values are given by:

$$N_1 f_1 = \frac{4\pi K_1}{\gamma_0 L_1 \lambda_1^3} \cdot \frac{(1 + \delta_1/\epsilon)^2 - (\delta_4/\epsilon)^2}{(1 + \epsilon/\delta_1)^2 - (1 + \epsilon/\delta_4)^2} \cdot \epsilon^2$$

$$N_2 f_2 = \frac{4\pi K_2}{\gamma_0 L_2 \lambda_2^3} \cdot \frac{(1 + \delta_4/\epsilon)^2 - (\delta_1/\epsilon)^2}{(1 + \epsilon/\delta_4)^2 - (1 + \epsilon/\delta_1)^2} \cdot \epsilon^2$$
(6)

The accuracy of measuring Nf -values of two close lines by the hook method has been discussed (34), and the solutions for three close lines and for an arbitrary number of lines has also been given (35). The practical application to a molecular band spectrum requires a lengthy re-iterative procedure (25).

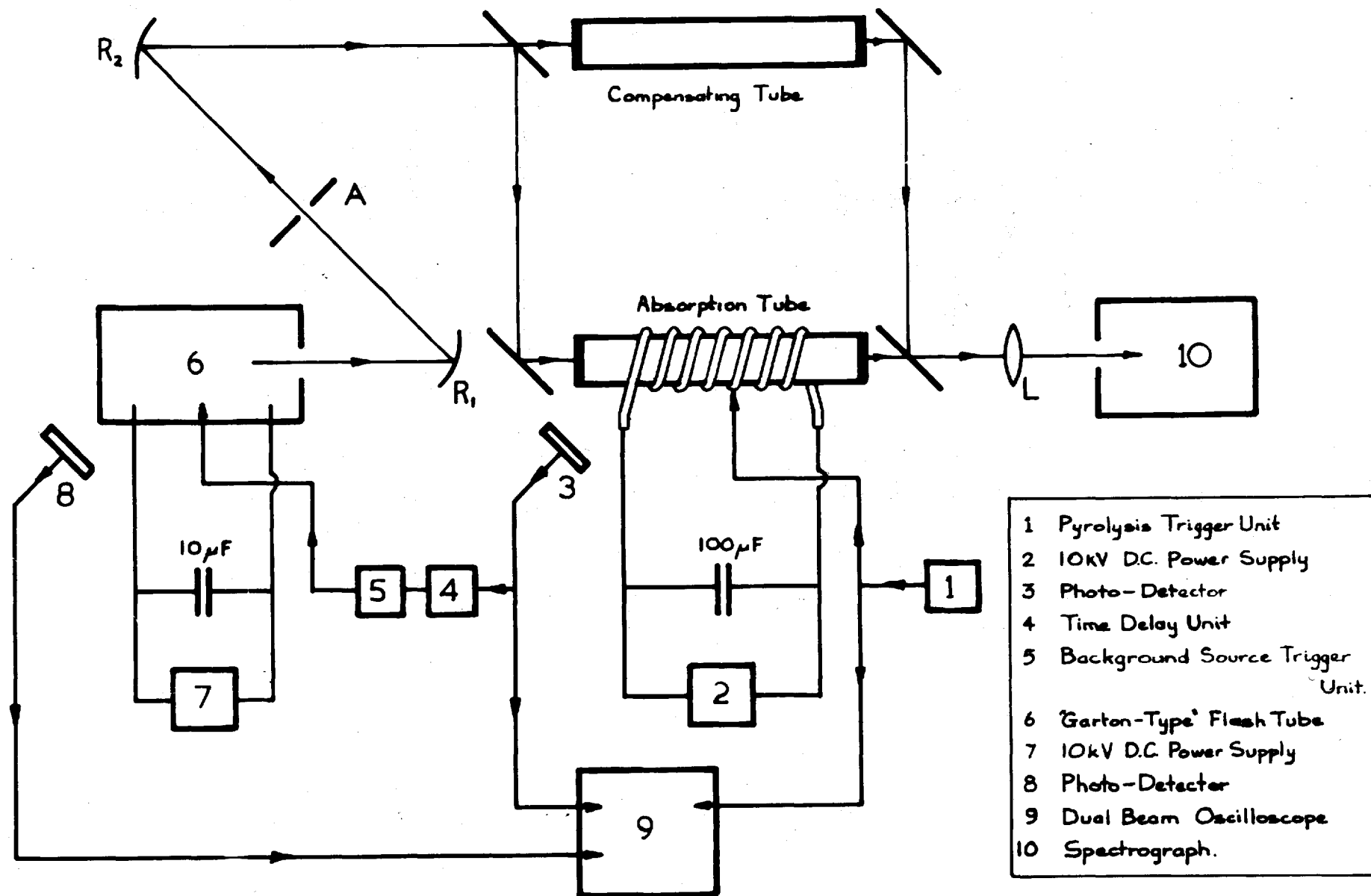
CHAPTER 3

EXPERIMENTAL: APPARATUS AND TECHNIQUE

A schematic diagram of the arrangement of the apparatus is shown in Figure 3. Light from a source of background continuum (6), collimated by the two mirrors R_1 and R_2 , passed through the interferometer to the spectrograph (10). In one arm of the interferometer, the helical flash lamp was placed concentrically around the absorption tube which contained the solid material to be vapourised; the flash lamp in its turn was surrounded by a cylindrical reflector coated with aluminium oxide. In the other arm was the 'compensating tube'. Both tubes were closed by identical plane parallel quartz windows.

The helical flash lamp was fired by applying a high voltage triggering pulse to a wire running along the surface of the flash lamp. A photo-diode pick-up circuit (3) detected the light from the pyrolysis flash and initiated the delay pulse generator (4), the output of which triggered the continuum background light source (6) after any desired time delay (eg: a few hundred micro-seconds). The interference fringes from the recombined light beams were then focussed by the lens (L) on the slit of the spectrograph.

Fig.3 SCHEMATIC DIAGRAM OF APPARATUS



In this chapter a detailed description of the apparatus and the method of its operation will be given.

3.1 The Optical System

(a) The Mach Zehnder Interferometer

The interferometer consisted of two beam splitters and two total reflectors, arranged at the four corners of a rectangle with the planes of all four parallel and inclined at 45° to the sides of the rectangle.

Both the beam splitters were 7.64 cm diameter discs, 1.91 cm thick, made of Spectrosil 'A'. The surfaces were finished to a flatness of one-tenth of a wavelength of green light, parallel to 0.5 second of arc and matched to 2 micron thickness. One surface of each beam splitter was coated with aluminium, to give 50% transmission at $2000 \text{ \AA}$ and 45° incidence. The reflectors were finished to the same specifications except that their surfaces were aluminised to be opaque to that wavelength.

The whole interferometer was mounted on an anti-vibration chassis. However in this experiment vibration was not a problem as the spectrum was recorded in a few micro-seconds.

A detailed description of the construction of the interferometer and the procedure for setting it up, using a laser and a high pressure mercury lamp, has been given by F P Banfield (36).

The stability of the interferometer was very good and no major adjustment was needed to obtain the white light fringes after the first alignment more than five years previously.

(b) Background Light Source and Auxiliary Optics

The background source of continuous radiation was a 'Garton-type' flash tube (37). This consists basically of a ceramic tube of about 5 mm ID, through which a high voltage low inductance capacitor is discharged. The plasma is contained by a magnetic pinch resulting in negligible wear of the tube and a long term reproducibility.

The flash tube operates at a pressure of between 5 and 24 microns in air and can be triggered anywhere in this range. The upper limit, at 24 microns, is approximately the Paschen breakdown of the tube in air for a voltage of 7 kV. The tube does not trigger reliably at less than 5 microns pressure. A rotary pump with a cold trap is used to maintain the pressure in this range. Changing the filling gas to argon, helium, etc, has no effect on the radiation from the flash tube except that of decreasing the opacity of the system in the far ultraviolet.

The flash tube is connected to a 10 μ F rapid discharge capacitor (supplied by Hivotronic Ltd, Basingstoke, England) by means of a parallel plate transmission line to reduce the inductance of the discharge circuit. In operation, the capacitor is charged to 8 kV by a 100 milli-ampere DC power supply (7 in figure 3) and the flash tube is fired by a triggering pulse of 8-10 kV negative.

Radiation from the flash tube consists of a continuum extending from the visible to about $400 \text{ \AA}$, overlaid with emission lines which are faint in the visible and become more and more dominant in the vacuum ultraviolet region. The duration of the light pulse is about $2 \mu\text{sec}$ and the flash tube can be fired with an accuracy of $1 \mu\text{sec}$.

Debris from the discharge is ejected on to the window of the flash tube, and as a result regrinding and polishing of the window is needed after about every ten discharges.

The two collimators R_1 and R_2 were aluminised spherical mirrors of focal length 12.5 cm. An advantage of using reflectors was their freedom from chromatic aberration. It was, however, necessary to keep the angles of incidence small to reduce astigmatism. R_1 focussed an image of the source at the aperture (A in figure 3) where a 4 mm stop was used to limit the angular spread of the collimated beam formed by R_2 . With the interferometer adjusted for fringes at infinity (one pair of parallel plates slightly inclined to the other pair of parallel plates), the lens (L) focussed both the source and the interference pattern on the slit of the spectrograph. This lens was an f/12 quartz-fluorite achromat whose focal length (from the visible to about $3000 \text{ \AA}$) was 25.5 cm.

(c) The Spectrograph and Plate Measurement

The accuracy of the hook method depends primarily on the measurement of the quantity Δ , the wavelength separation between the hooks on the photographic plate. Since the accuracy of setting a

microscope cross wire on the hooks (see below) is limited, it is necessary to use a spectrograph of reasonably high linear dispersion which is also stigmatic.

The instrument used was a Hilger and Watt E1 f/20 automatic glass/quartz prism spectrograph, of the Littrow type.

The reciprocal dispersion of the spectrograph varied from about 4 Å/mm at 2800 Å to 12 Å/mm at 4000 Å with the quartz optics, and from about 4 Å/mm at 3900 Å to 20 Å/mm at 6500 Å with the glass optics. An accurate value in each relevant wavelength range was determined from iron lines. In general the value of the reciprocal dispersion could be determined with an accuracy of 0.1 % to 0.2%.

It was desirable to use a fine grain emulsion for measuring distances accurately on the photographic plate, but as the background light source had a duration of only about 2 micro-seconds, a fast emulsion was required. Although Ilford XK plate was somewhat faster than HP3 plate in the ultraviolet region, the grain size was too coarse. So only HP3 plate was used.

The plates were measured with a Zeiss comparator on which readings could be taken to the nearest micron. The uncertainty of setting the cross wire exactly on the turning point of a two beam interference fringe was of the order of 20 microns. Errors of setting on spectral lines were negligible by comparison. This error in determining Δ will be discussed in Chapters 5-7.

(d) The Alignment of the Optical System

The alignment of the optical system was carried out in two stages, the first stage being without the four quartz windows in position.

An He-Ne laser was first used to define the optical axis of the whole system: the beam was sent backwards, first through the spectrograph, then the interferometer and finally after reflections by the two mirrors, through the centre of the Garton-type flash tube.

As the continuum light source was a long discharge tube, viewed end-on, of pulsed operation, its position relative to the mirrors R_1 and R_2 for optimum collimation had to be determined by trial. The far end of the flash tube was first focussed on to the slit of the spectrograph. Then a sodium lamp was placed immediately behind it. By adjusting the positions of the mirrors R_1 and R_2 , but keeping their separation constant, a well collimated beam of light of about 1.5 cm diameter was obtained in the region between R_2 and the interferometer, and interference fringes could be observed on the slit of the spectrograph. The sodium lamp was then replaced by a high pressure mercury lamp, which gave off a strong continuum when it had warmed up. This allowed a check that the fringes were near zero order and that their spacing was approximately correct. Finally, a series of plates was taken of the near zero order fringes from the (background) flash tube for various positions of the mirrors R_1 and R_2 . It was found that the 'best' position for the mirrors as indicated by observing the fringes obtained from the flash tube was about 0.5 cm. from that indicated by

the high pressure mercury lamp. From then on the positions of the mirrors and the flash tube remained unchanged.

The second stage was to place the four quartz windows in the two arms of the interferometer. The quartz plates, in their 'window holder' were held in position by a structure of metal rods. This structure was so constructed that no one plate could move independently from the others and the absorption tube could be taken in and out without disturbing the windows, as described in the next section.

To start with, one quartz window was introduced in each arm and adjusted so that fringes were obtained with the sodium lamp and then with the high pressure mercury lamp. Then the second pair was added and the process of adjustment repeated. It was found necessary to use the controls of the interferometer for some fine adjustments of the fringes, such as their spacing.

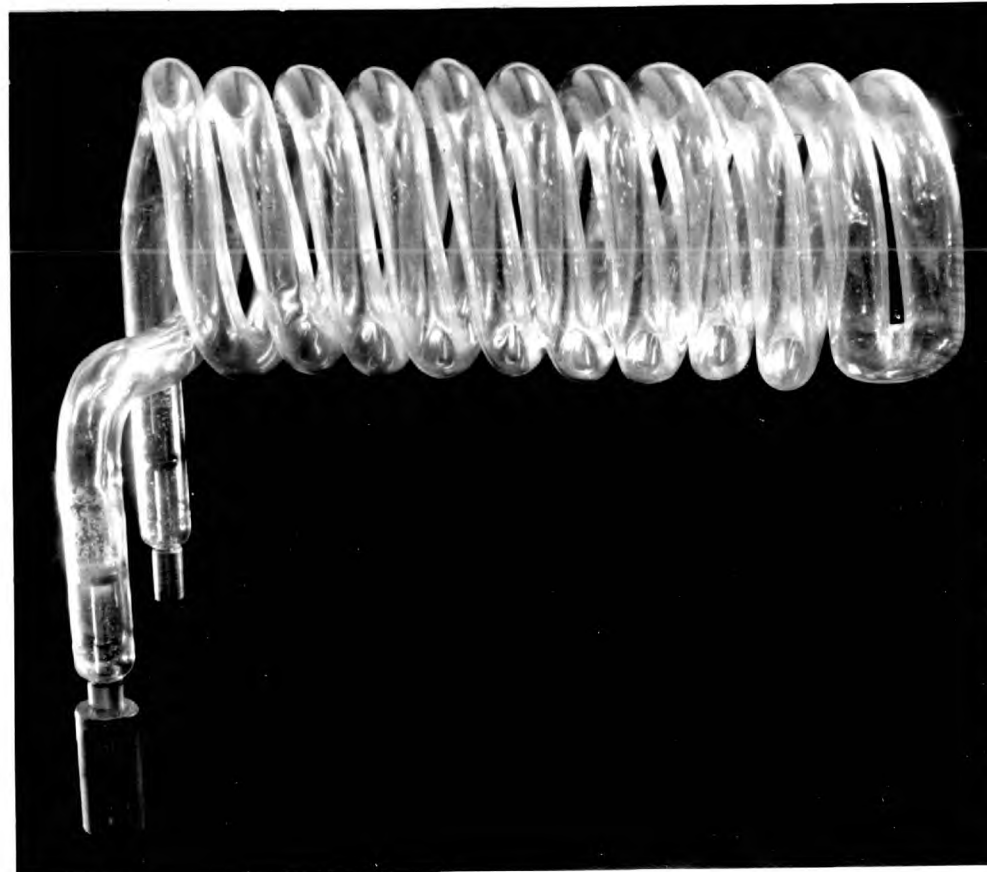
The high order fringes were produced by introducing high pressure argon into the compensating tube. This had an advantage over the use of a conventional compensating plate in that the order of interference could be varied continuously. The pressure of the argon varied from about 30 lb/sq in to 75 lb/sq in.

3.2 The Flash Heating System

The flash pyrolysis lamp used was a five turn 're-entry' helix (Figure 4), wound from 12 mm OD quartz tube (ID 9 mm). The diameter

Fig 4 RE-ENTRY TYPE HELICAL FLASH LAMP

15cm



of the helix was 4 cm and the linear length was about 15 cm. The active length between the electrodes was 150 cm. The tube was filled with Xenon gas at a pressure of 10 cm of mercury, as supplied by T W Wingent Ltd, Cambridge.

The capacitor bank for flash heating consisted of five 1 kilo-joule (20 μ F, 10 kV) rapid discharge capacitors (manufactured by Hivotronic Ltd, Basingstoke). The capacitors were connected in parallel by co-axial cable and powered by a 10 kV 100 milli-ampere DC supply (2 in Figure 3). The applied voltage could be controlled to an accuracy of 0.1 kV.

The pyrolysis flash was fired by applying a high voltage (about 15 kV) triggering pulse to a thin wire spiralling round the whole length of the helix from the manually controlled pyrolysis triggering unit (1 in Figure 3).

Occasionally the flash lamp had a spontaneous breakdown while the capacitor bank was being charged up. The frequency of spontaneous breakdown increased with use but rarely occurred before the charging voltage reached 8 kV.

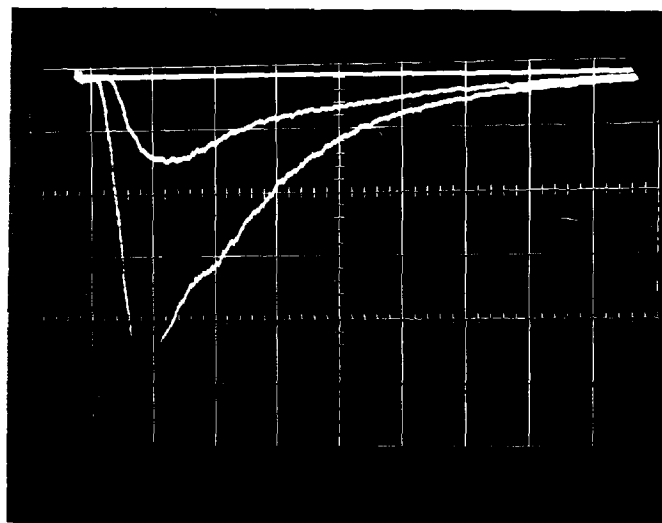
The duration of the light pulse of the 're-entry' type flash lamp is about an order of magnitude shorter than that of an otherwise similar 'single-coil' type, because of lower inductance. This is of paramount importance in flash pyrolysis work as, other conditions being equal, the shorter the duration of the light pulse, the greater the heating effect.

The light emission from the flash lamp was investigated in a subsidiary experiment, using a grating monochromator with an EMI type 9783 photomultiplier. The signals were recorded on a dual-beam oscilloscope, the signal from the pyrolysis trigger unit (1 in Figure 3) being used to trigger the oscilloscope.

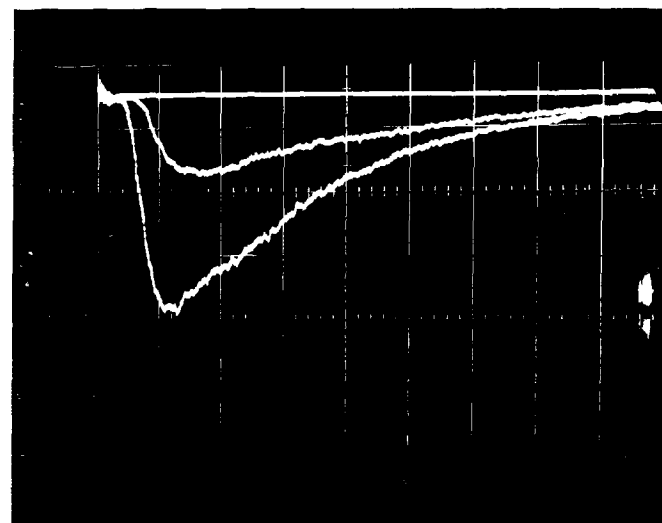
Figures 5a and 5b show the emission of the flash lamp at $3000 \text{ \AA}$ and at $6000 \text{ \AA}$. In each case, the upper curve represents the emission at 6 kV and the lower one at 8 kV, and the time scale is 100 μsec per division. The intensity at $3000 \text{ \AA}$ cannot be directly compared with that at $6000 \text{ \AA}$ because of the change of sensitivity of the photomultiplier and the different slit widths used. The ultraviolet end and the red end of the emission show nearly similar time dependence. In each case, the time taken to initiate the discharge of the flash lamp was shortened from about 60 μsec to 40 μsec when the applied voltage to the capacitor bank was increased from 6 kV to 8 kV. At 8 kV the intensity of the light pulse reached its peak value about 60-80 μsec after the start of the discharge and then decayed slowly. 500 μsec after the discharge, the intensity had dropped to about one-quarter of its peak value, with the ultraviolet end decaying more rapidly than the red end of the emission.

The absorption tube was made of thin wall quartz tube of 30 mm OD, allowing plenty of clearance when inserted along the axis of the helix. Its length was about 30 cm. As it was necessary to reload the solid material after every pyrolysis flash, the window holder had to be constructed in such a way that the absorption tube could be easily detached

Fig 5 RELATIVE INTENSITY OF THE EMISSION OF THE HELICAL FLASH LAMP.



A
3000 Å

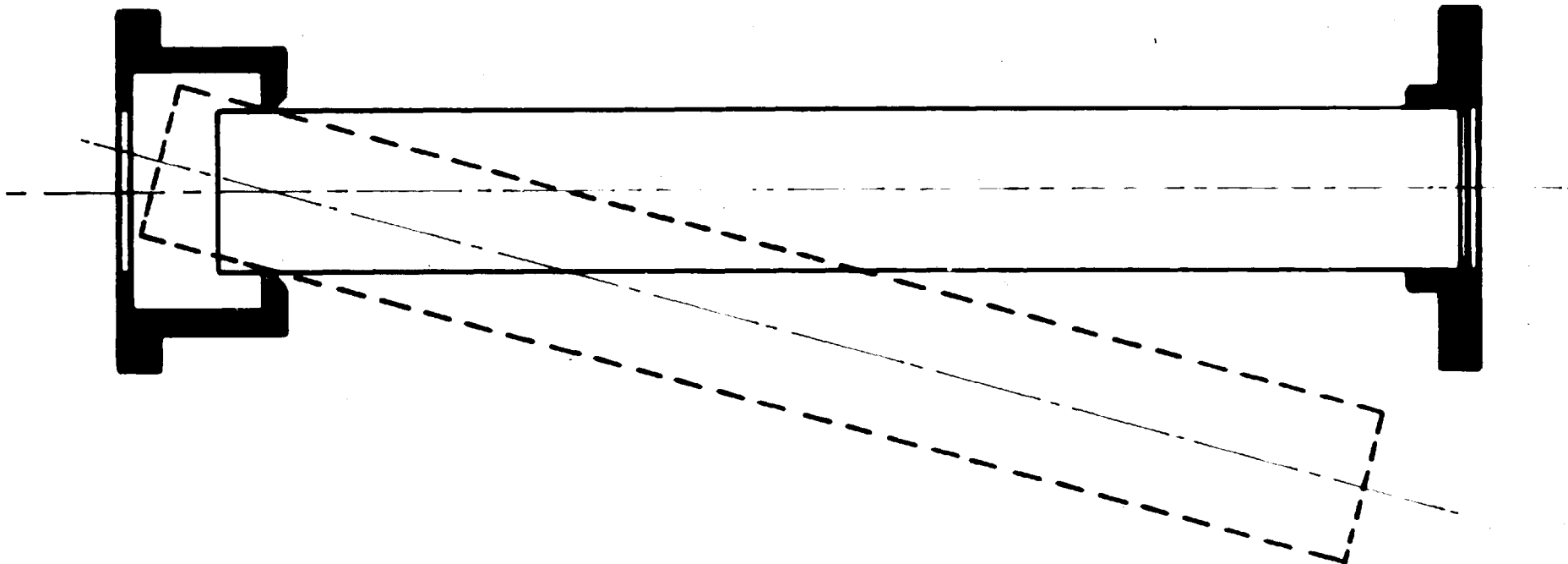


B
6000 Å

UPPER CURVE:- INPUT ENERGY $100\mu F$ 6kV.
 LOWER CURVE:- ———"——— $100\mu F$ 8kV.

TIME SCALE:- $100\mu \text{ sec./cm.}$

Fig.6 WINDOW HOLDERS OF THE ABSORPTION TUBE



from the holder without disturbing the orientation of the windows and hence the interference fringes. This was done by allowing sufficient space for one end of the tube to be slid through the O-ring and pivoted slightly until the other end had sufficient clearance to be inserted into the second holder, as shown in Figure 6.

In the absorption experiment, the background light source was fired at a pre-set time after the pyrolysis flash. This was achieved by using the signal from a photo-diode (of rise time less than 1 micro-second) to trigger the delay pulse generator (3 and 4 respectively in Figure 3).

Another photo-diode (8 in Figure 3) was used to detect the flash from the background light source, and delay between the signals from the two photo-detector circuits was checked on a dual-beam oscilloscope. In Figure 7, the lower trace is the signal from the pyrolysis flash and the upper one that from the background light source, with a delay of 500 μsec . In general the delay was accurate to 2% of the pre-set value.

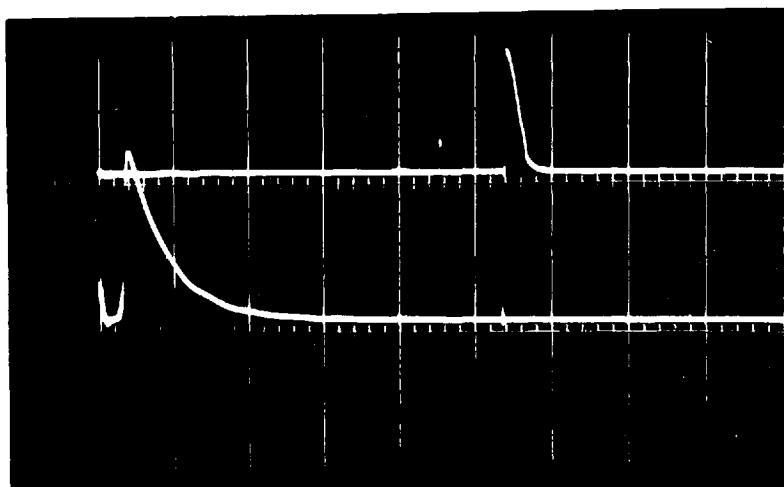


Figure 7 - Delay Signals. Lower trace: signal from the pyrolysis flash. Upper trace: signal from the continuum flash. Time scale: 100 $\mu\text{sec}/\text{cm}$. Delay: 500 μsec .

CHAPTER 4

THE PRELIMINARY EXPERIMENTS

One feature of the flash heated vapour is the very short time of its duration, of the order of a few milliseconds. The preliminary experiments attempted to establish the feasibility of applying the hook technique to the investigation of flash heated vapours, the only other comparable application being the recent work on shock heated plasmas. The experiments also investigated the effects on the vapour density and the formation of hooks of the various experimental parameters, such as the input energy, the pressure of the buffer gas, the delay time, the form and the method of introducing the solid material and its quantity, etc.

Some of the preliminary experiments (on gold) were performed with a medium quartz spectrograph. The spectral region from $2300 \text{ \AA}$ to $6800 \text{ \AA}$ could be covered in one single experiment. However the dispersion was not adequate for quantitative work, so the large quartz/glass instrument was used thereafter.

4.1 Some Qualitative Experiments with Different Elements

The effectiveness of flash pyrolysis depends, among other things, upon the form of the solid sample and the methods of introducing it into the absorption tube. The main requirement is that the material should be in the form of a very thin wire or foil or a very fine powder. The substrate on which the material is supported also plays an important part. This is not surprising when one considers that the pyrolysis process requires either the material or the substrate to be an efficient absorber of ultraviolet radiation. Moreover, if the energy is absorbed via the substrate, its heat capacity must be kept low (see section 4.2a).

In the experiments discussed in this section, various methods of introducing each element were actually tried, but only the most successful method is actually described.

In all the experiments the slit of the spectrograph remained open throughout the whole duration of the pyrolysis flash. The effect of the emission from the pyrolysis flash could reduce the contrast of the fringes in some cases, but not seriously enough to necessitate a high speed shutter synchronized to the firing of the background source. The pressure of the buffer gas (argon) in the absorption tube was about 100 microns for the reasons discussed in section 4.2c and the delay time was 400-500 μ sec (see section 4.2d).

Figures 8-12 show hooks obtained with indium, gold, tungsten, bismuth and ^amixture of Ba-Ca-Sr fluorides respectively.
A

Fig. 8. ANOMALOUS DISPERSION AND HOOKS IN THE SPECTRUM OF InI

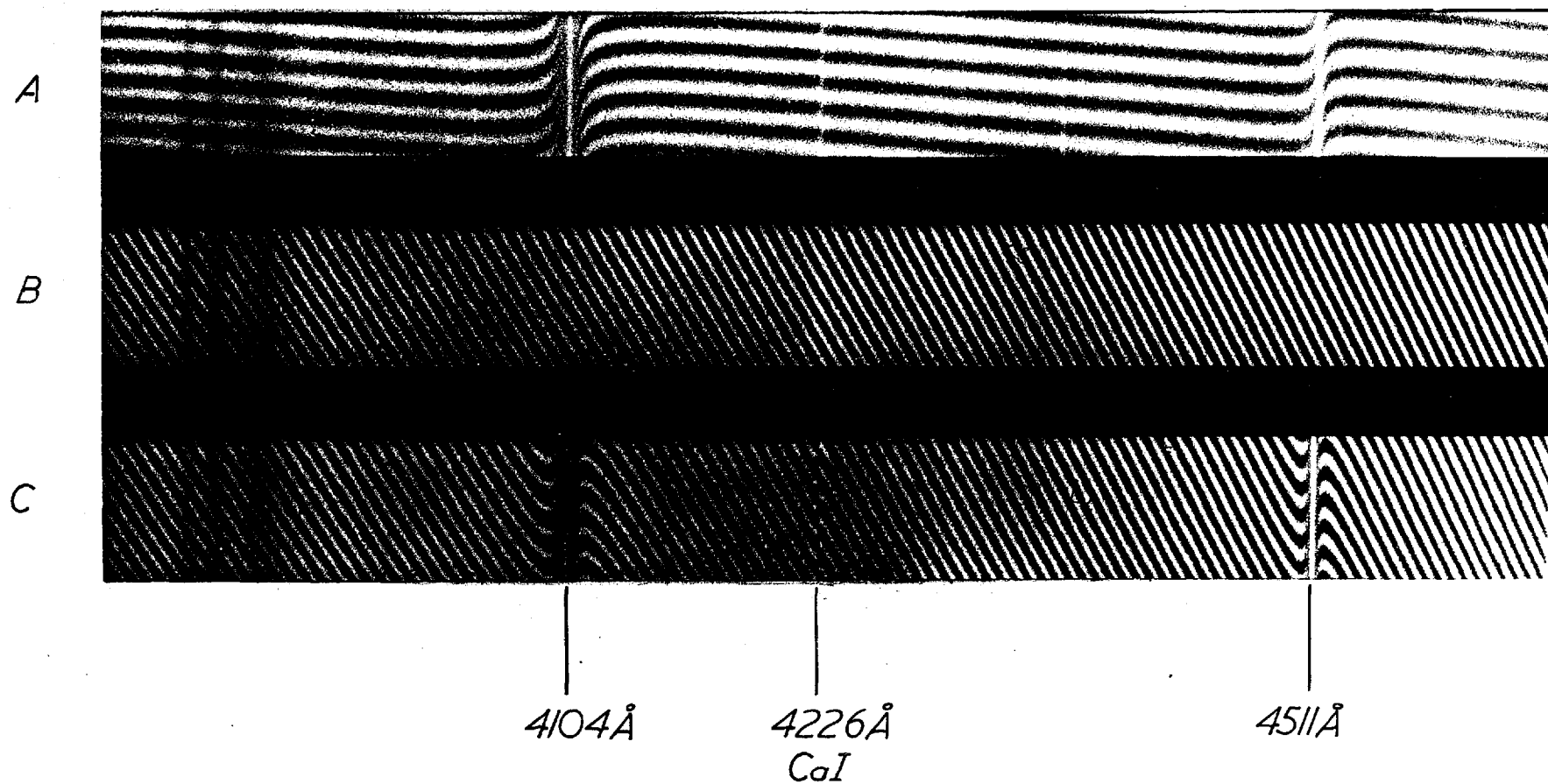


Fig.9 Gold

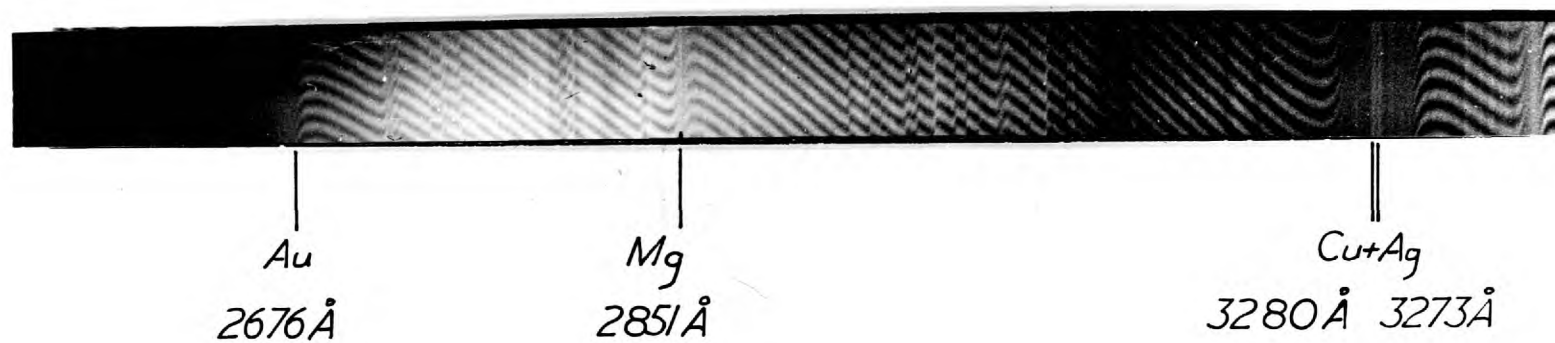


Fig 10 TUNGSTEN

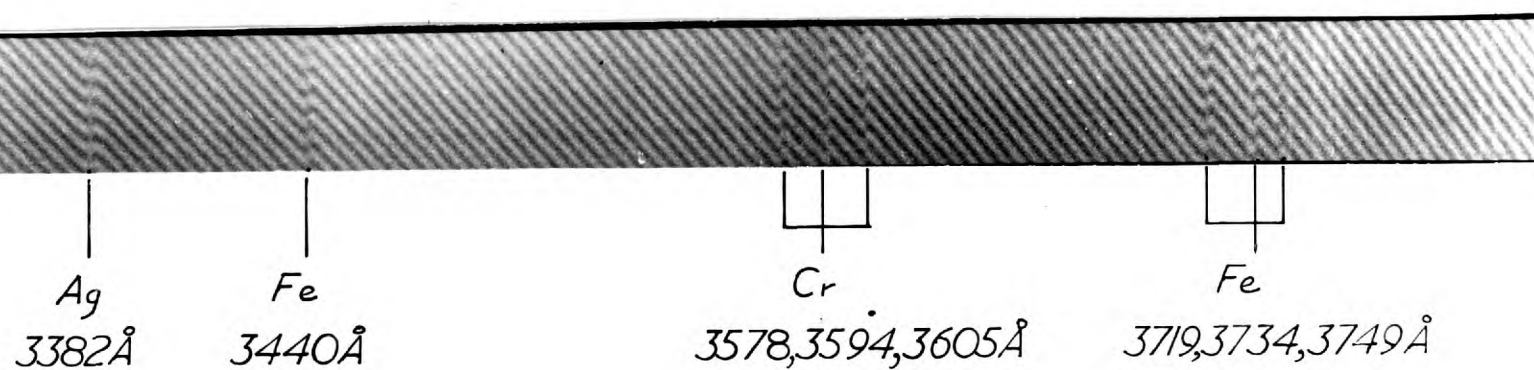


Fig.11 Bismuth

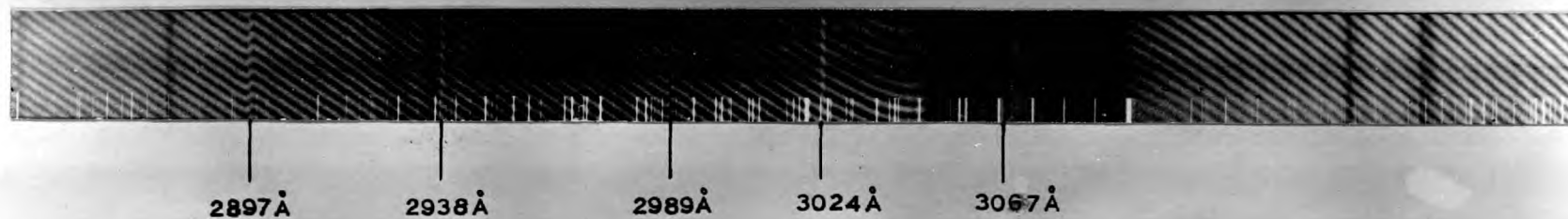
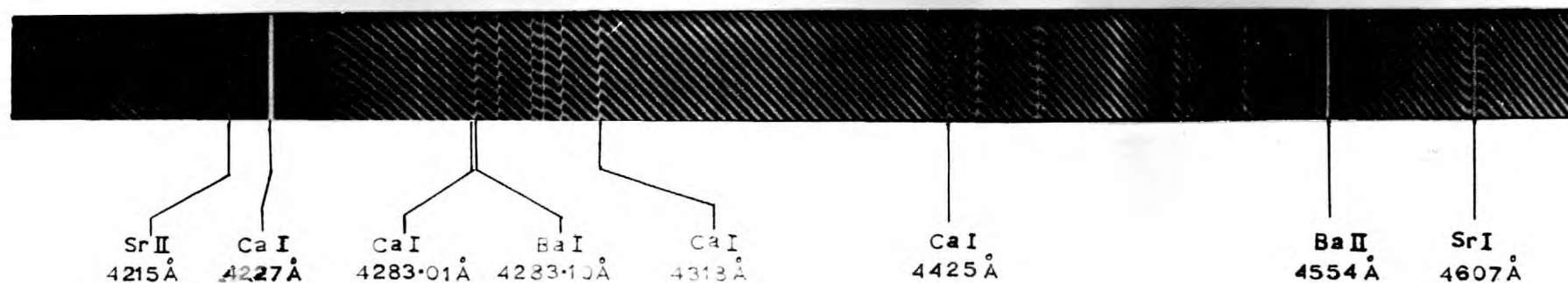


Fig.12 Ba-Sr Mixture



(a) Indium Powder on Carbon Foil

The indium powder had a grain size less than 45 microns and a purity of 99.99%. The carbon foil was 100 microns thick and measured 1 cm x 5 cm (supplied by Ultra-Carbon Corporation, Bay City, Michigan). The foil was coated with a thin layer of glue (a compound containing water and carbon) to adhere the powder. Acetone could also be used to 'wet' the carbon foil but it was more difficult to control the amount of powder adhered. No detectable difference was observed in the spectrum from the two ways of adhering the powder.

In figure 8, (a) shows the anomalous dispersion near the components of the leading doublet of the sharp series of In I (4513.31 and 4101.76 Å); (b) shows the high order fringes obtained with the background source only; and (c) hooks near the 4513 and 4101 Å lines. Both (a) and (c) were obtained with an input energy of 3000 J. Evaporation of the carbon foil was very little, of the order of 0.1 mg.

(b) Gold Foil on Copper Mesh

Penkin and Slavenas had reported difficulty in obtaining hooks of the longer wavelength component (2675.59 Å) of the resonance doublet of Au I with vapour from a furnace at 1700°K (38). By the technique of flash pyrolysis, measurable hooks of the line were easily obtained with a few milligrams of the metal (figure 9). In this case the solid sample was

in the form of foil of about 0.1 microns thick supported on copper mesh made of wire of about 1mm diameter. The hooks were obtained with an input energy of 2500 J. In this particular case the delay time was 800 μ sec, because at 400 μ sec the vapour pressure was too high to give sharp fringes (see section 4.2).

Using the known f-values of the gold resonance lines the number density of gold atoms in the vapours was found to be of the order of 10^{17} cm^{-3} .

The resonance lines of copper and silver also appear strongly in the spectrum. Chemical analysis of the gold foil showed that it contained less than 0.1% of silver and 0.5% of copper. Resonance lines of magnesium, sodium and calcium also appeared in the vapour.

After the pyrolysis flash, the wall of the absorption tube and the quartz windows were coated with a layer of gold, and visual inspection showed that very little gold remained on the copper mesh.

(c) Tungsten Wire

The tungsten wire was of 10 microns diameter and was wound around a cylindrical grid made of quartz rods and constructed in such a way that when inserted in the absorption tube, light could pass through the absorption tube without obstruction. With an input energy of 4000 J, only part of the tungsten wire vaporized. At 5000 J the tungsten wire vaporized completely, and figure 10 shows the spectrum obtained.

Hooks appeared around the strong lines of iron, copper, silver, magnesium and chromium impurities, but none around the tungsten lines, although very faint emission lines of tungsten could be seen at the appropriate wavelengths. The failure to obtain tungsten hooks was probably due to the low vapour pressure of tungsten. Although Nelson and Kuebler (6) succeeded in obtaining the absorption spectrum of tungsten by flash pyrolysis, they used twice as great an input energy (10 400 J) and a buffer gas pressure of one atmosphere.

(d) Bismuth Powder on Copper Foil

The copper foil used was 5 microns thick and had a purity better than 99.99%. It was coated with a thin layer of glue and the bismuth powder was sprayed on to it. With an input energy of 4000 J, the copper foil vaporized completely. Figure 11 shows hooks in the bismuth spectrum. The 3067 Å line is the resonance line of bismuth. Both the 2989 and 2897 Å lines are from an excited state with an energy of about $11 \times 10^3 \text{ cm}^{-1}$ above the ground level. The emission lines at 2938 and 3034 Å are clearly visible in the spectrum. The lower states of these two lines are about $15 \times 10^3 \text{ cm}^{-1}$ above the ground level.

(e) Ba-Ca-Sr Fluorides on Carbon Foil

If an element cannot be obtained in the form of suitable foil, wire or powder, a salt can be used. In the case of the alkaline earths, the mixture of salts was stuck to the carbon foil by a thin layer of glue. Acetone could also be used.

Figure 12 shows the spectrum obtained in the range 4100-4700 Å with an input energy of 4000 J. The resonance lines of the neutral atom and the ion of all three elements showed sharp hooks, although the Ca II lines have too short a wavelength and the Ba I line too long a wavelength to appear on this print. The other lines are from excited states of both Ca and Ba; for example, the 4318 and 4225 Å lines have a lower state about $15 \times 10^3 \text{ cm}^{-1}$ above the ground level.

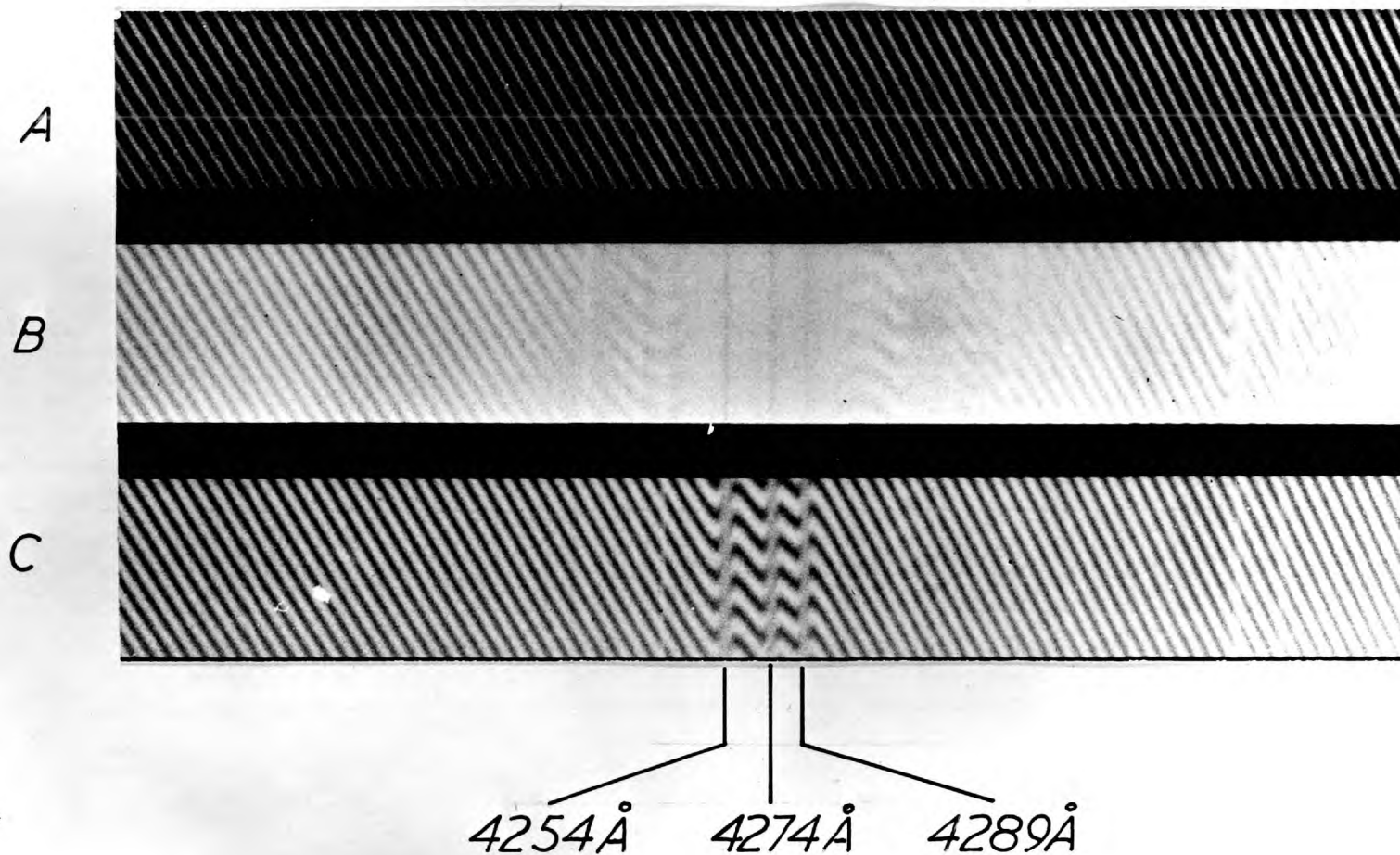
Another method of introducing the solid sample that has not been mentioned above, but has been tried and found successful, includes salt solution deposited on a carbon foil or on metal mesh. One other possible method is to evaporate a thin layer of the element on to a substrate in vacuum, but this has not been fully investigated because of lack of time.

The preliminary experiments established that the application of the hook technique to the study of flash heated vapours is a feasible operation.

4.2 Experimental Parameters Affecting the Vapour Pressure and the Formation of Hooks

In general, it was desirable to attain as high a vapour pressure as possible in any experiment so that the hook separation would be large and weak lines could be studied. However, too high a vapour pressure could lead to a blurring of the interference fringes, and sometimes to complete loss of fringe contrast. In figure 13, (a) shows the high order

Fig.13 CHROMIUM SPECTRUM WITH DIFFERENT AMOUNT OF SAMPLE



fringes obtained from the background flash only; (b) and (c) are two successive flashes using the same filling of chromium powder, supported on a carbon foil. In each case the input energy, buffer gas pressure and delay time were the same.

The vapour pressure in a particular experiment depends on (i) the method of introducing the solid sample to the absorption tube and the quantity used; (ii) the input energy; (iii) the buffer gas pressure; and (iv) the delay time. The effect of each of these experimental parameters will now be discussed.

(a) The Sample Amount

In the case of foil and wire, and to some extent salt solution, the amount of sample inserted could be controlled, but with powder samples it was difficult to control the amount so that the experimental results were difficult to reproduce.

The effect of the thickness of the substrate was investigated by studying carbon foils of 100 microns and 1.5 mm thickness coated with a saturated solution of sodium acetate. Using foils of the same surface area, flashed under identical conditions, the vapour pressure of sodium obtained with the 100 micron foil was found to be about 20-30% higher than that obtained with the 1.5 mm foil. The thermal capacity of the 1.5 mm foil was at least an order of magnitude larger than that of the 100 micron foil. It was also found that sodium acetate vaporized more readily than sodium chloride. However, when a powder sample was substituted the

evaporation seemed to be less dependent on the thickness or the type of the substrate.

(b) Input Energy

In general, evaporation increases as input energy is increased. The threshold energy required to vaporize a solid sample depends on the physical dimensions (thickness, diameter, grain size) and is different for different elements. For example, only 2000 J of energy was required to vaporize cadmium foil 4 microns thick, but 4000 J of energy was required to vaporize magnesium foil of the same thickness. In the case of a salt, the energy required also depends on the type of compound used.

For a given flash lamp, the variation of the input energy is rather limited, due to the lamp design and power supply parameters. There is an upper limit to the input energy, above which the flash lamp may explode. In this experimental setup the input energy could be varied between 2000 J and 5000 J.

(c) Buffer Gas Pressure

Previous experiments on flash pyrolysis were all conducted with high buffer gas pressure (up to one atmosphere pressure) to reduce the rate of diffusion of the flash heated vapour from the absorption path. In these experiments the effect of the buffer gas pressure was investigated using copper foil. Two 1 cm x 5 cm foils 5 microns thick were flashed at the same input energy of 4000 J and the hooks were photographed at the same delay time of 500 μ sec, but

with different argon pressures in the absorption tube.

Figure 14 shows a series of hooks near the copper resonance doublet (3273.96; 3247.55 Å) with the argon pressure increased from 500 microns to about 10 cm. A high buffer gas pressure led to a loss of fringe contrast, an effect similar to that observed when the vapour pressure was too high. So a buffer gas pressure of 100-200 microns was chosen for all future experiments.

(d) Time Delay

The time dependence of the density of the flash heated vapour was investigated using gold foil. Very little evaporation was detected in the first 200 μ sec after the start of the pyrolysis flash, which reached its peak about 100 μ sec after the discharge of the helical flash lamp. The most fully developed spectrum was recorded at a delay time 400-600 μ sec. Then the concentration of the vapour decreased, remaining detectable for as long as 3000 μ sec. Using the known f -values of the gold resonance lines, the number density of gold atoms in the vapour was found to be of the order of 10^{17} cm^{-3} at a delay time of 500 μ sec. This decreased to about 10^{16} cm^{-3} at 1000 μ sec and to 10^{15} cm^{-3} at 2000 μ sec. The total quantity of gold present at 1000 μ sec was about 0.1 mg, about 10% of the amount of gold foil inserted.

The blurring of fringes also occurred when the hooks were photographed at too short a delay time. Figure 15 shows the hooks near the sodium resonance doublet obtained from

Fig/4. COPPER SPECTRUM AT DIFFERENT BUFFER GAS PRESSURE.

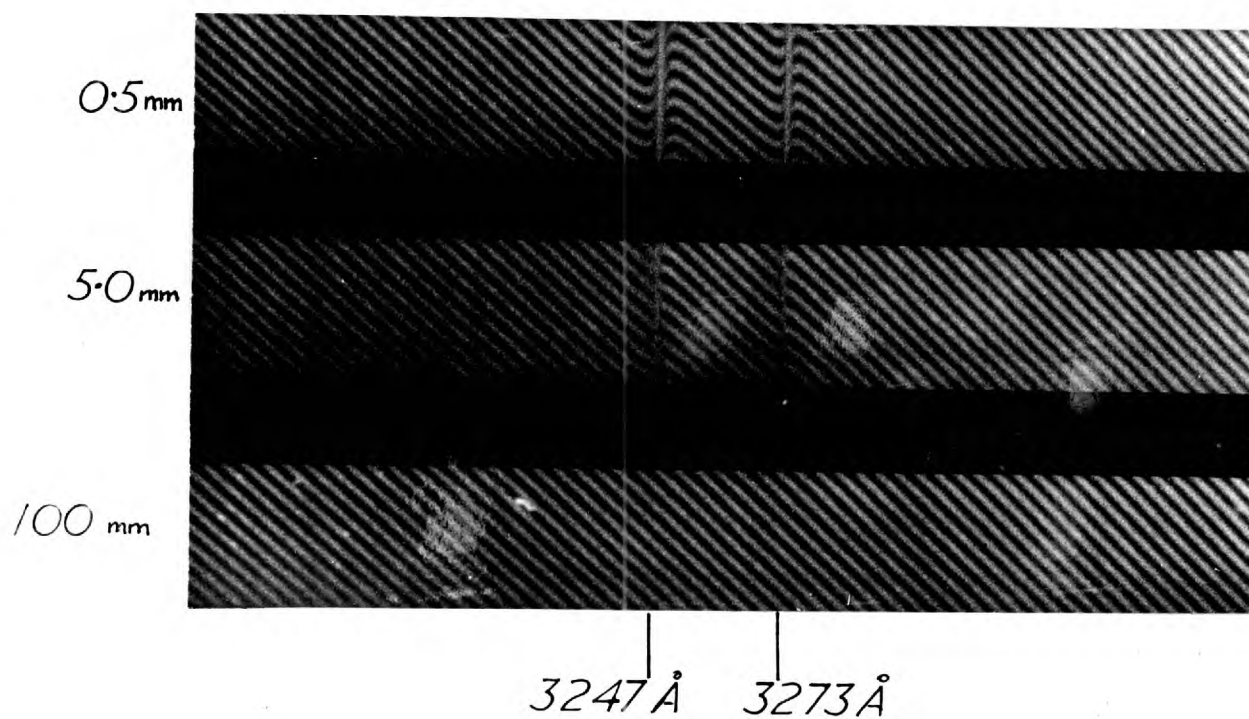
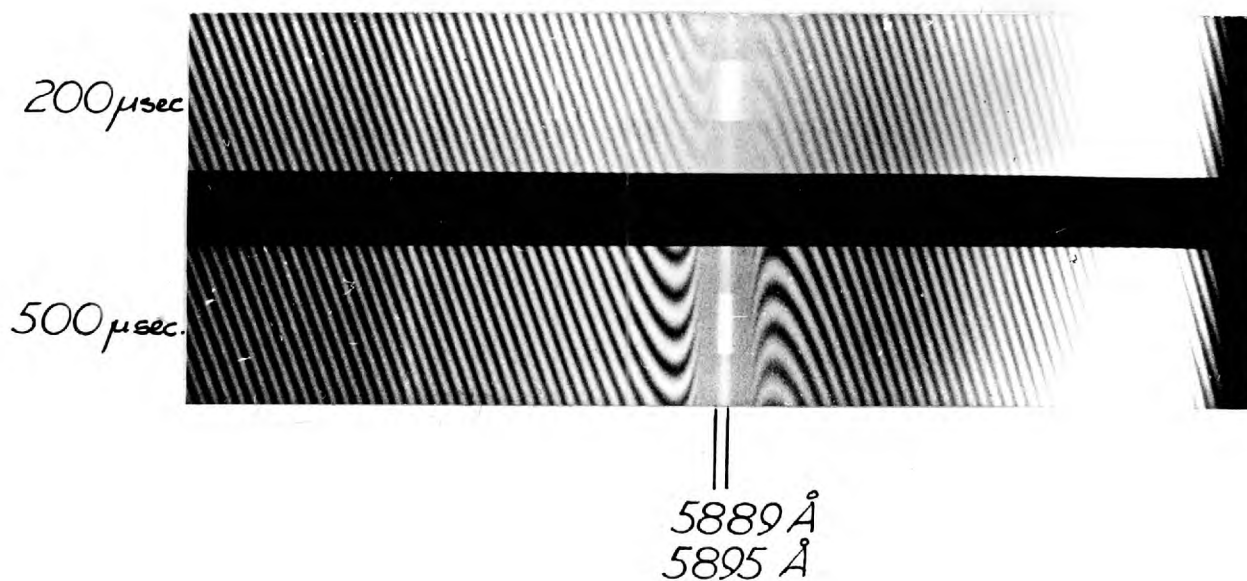


Fig.15 SODIUM SPECTRUM AT DIFFERENT DELAY TIME



acetate solution deposited on carbon foil. (a) was taken at a delay time of 200 μ sec and (b) at 500 μ sec, having refilled the tube with an approximately equal amount of salt. The input energy and buffer gas pressure were the same.

4.3 The Time Resolved Emission Spectra of Flash Heated Vapours

Owing to the difficulty of obtaining hooks at a delay time less than 300 μ sec (see section 4.2(d)) and the possible error from flash-to-flash variation, the time dependence of flash heated vapour was investigated in a subsidiary experiment by studying the emission from the vapour using a photo-electric detection method.

A grating monochromator (Monospek 1000, Hilger and Watts) was used in conjunction with an EMI type 9783 photomultiplier. The signal was recorded on an oscilloscope. Although the emission at only one wavelength could be studied at one time, it had the advantage that the complete time-dependence could be studied in one single experiment.

The emission from the flash heated barium vapour was studied at 5535.48 and 4934.09 $\text{\AA}$. These two wavelengths correspond to the resonance lines of the barium neutral atom and its ion.

The barium vapour was produced from the fluoride salt as described in section 4.1. Figure 16(a) and (b) show a typical emission spectrum obtained at 5535 Å and 4934 Å respectively. In each case, the time scale is 100 usec per unit length; curve I represents the emission from the pyrolysis flash only (without the barium sample) and curve II represents that of the excited barium (after deduction of the emission from the pyrolysis flash). The relative intensity of the emission in (a) and (b) cannot be compared directly as the sensitivity of the photomultiplier changes with wavelength.

The time resolved spectrum shows the time dependence of the population of the $6s6p\ ^1P_1^0$ level of the neutral atom and the $6p\ ^2P_{3/2}$ level of the ion (whereas the hook measurements are concerned with the ground level in each case). The shape of the emission in the first two to three hundred microseconds depends on the amount of the sample present. However it is possible to deduce the following general conclusions about the vapour:

- (i) the vapour density reaches its peak value at a time after the peak of the pyrolysis flash and which appears to vary between 200-400 μ sec.
- (ii) After reaching the peak density the vapour density decreases slowly over a period of two to three milliseconds.
- (iii) No significant difference in the behaviour of the atom and its ion was detected although the ion appears to reach its peak and to decay more rapidly.

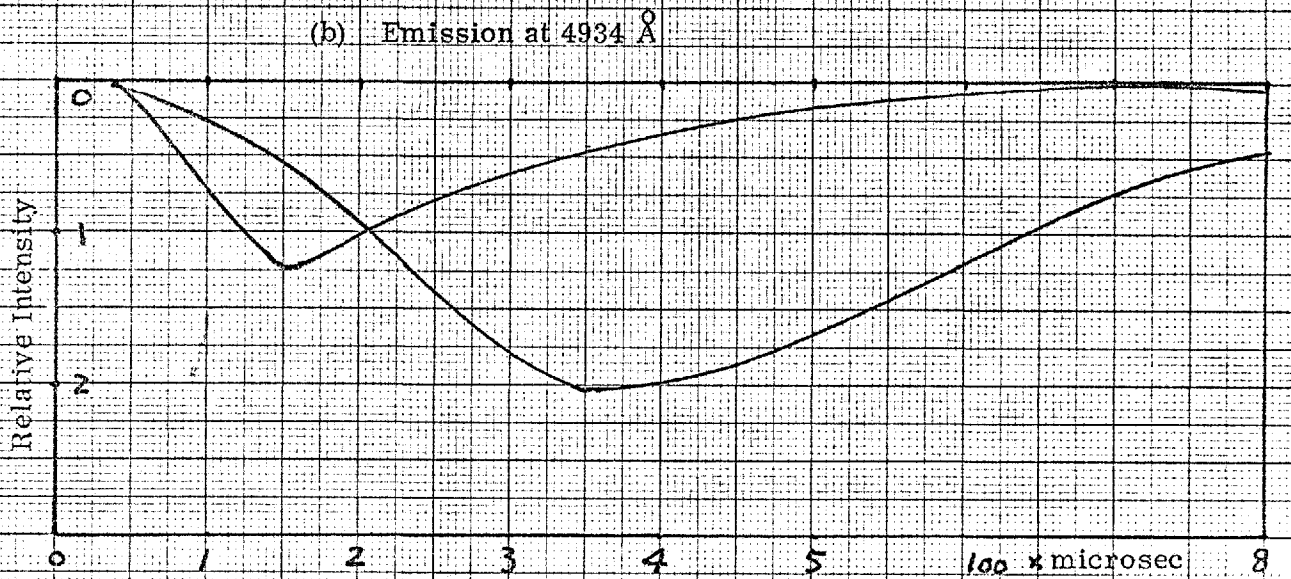
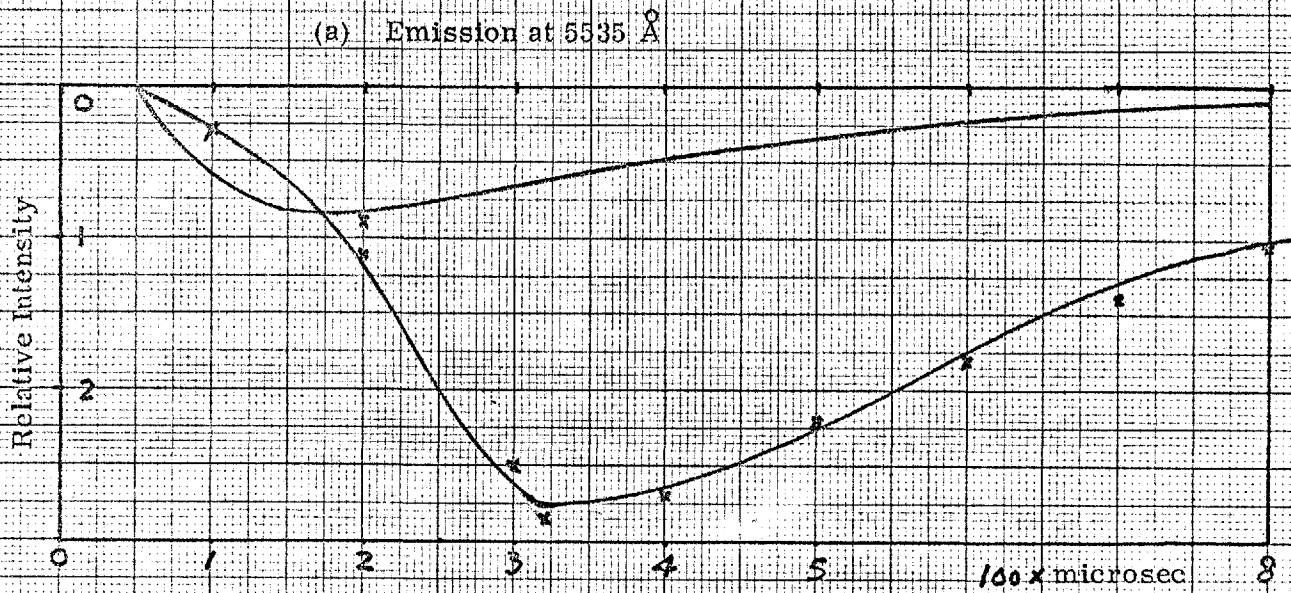


Figure 16: Emission from Flash Heated Ba Vapour

CHAPTER 5

FLASH PYROLYSIS OF MIXTURES OF KNOWN COMPOSITION

5.1 Introduction

Apart from lifetime techniques, which do not require a knowledge of the number density, measurements of oscillator strengths are carried out for the most part by (i) the method of emission; (ii) the method of absorption; and (iii) the hook method of Rozhdestvenskii. The product Nf can be measured with an accuracy of a few per cent by any of the methods, provided the conditions that assure the applicability of the given method are fulfilled. In going over from the Nf -values to the f -values, it is necessary to know the concentration of the absorbing or emitting atoms, and the determination of the number density is the chief source of error in the measurement of f -value by these methods. For example, the concentration of the absorbing atoms in a furnace can be calculated from the vapour pressure data if the temperature is known. However, many of the available vapour pressure data are not reliable, especially for those elements that require high temperature for evaporation, and revised vapour pressure data have led to f -values that differ by an order of magnitude (39).

The experiments on the flash pyrolysis of mixtures of different elements were designed to investigate the relative number densities in the vapours of these elements in order to determine whether the method could be used to measure an unknown f-value of one element in terms of a known f-value of another element, if the two were introduced in a known proportion.

5.2 Experiment

Potassium-Sodium tartrate was chosen for study for the following reasons: the first three members of the principal series of sodium and the second and third members of potassium are suitably situated in the spectrum so that they can be photographed in the same plate for the determination of number densities; the f-values of these lines are fairly well known; and the atomic ratio of these two elements in the compound is one which would favour the formation of hooks suitable for comparison. Table 5.1 contains the wavelengths and f-values of these lines. The absolute values of the oscillator strengths are from Marr and Creek (40), summarising the results of earlier work.

Table 5.1

	Wavelength	Transition	f-value
Na	5890, 5896 Å	$3^2S_{\frac{1}{2}} - 3^2P_{\frac{1}{2}, \frac{1}{2}}$	0.975
Na	3302, 3303 Å	$3^2S_{\frac{1}{2}} - 4^2P_{\frac{1}{2}, \frac{1}{2}}$	0.14×10^{-1}
Na	2852, 2853 Å	$3^2S_{\frac{1}{2}} - 5^2P_{\frac{1}{2}, \frac{1}{2}}$	0.205×10^{-2}
K	4044, 4047 Å	$4^2S_{\frac{1}{2}} - 5^2P_{\frac{1}{2}, \frac{1}{2}}$	0.868×10^{-2}
K	3446, 3447 Å	$4^2S_{\frac{1}{2}} - 6^2P_{\frac{1}{2}, \frac{1}{2}}$	0.846×10^{-3}

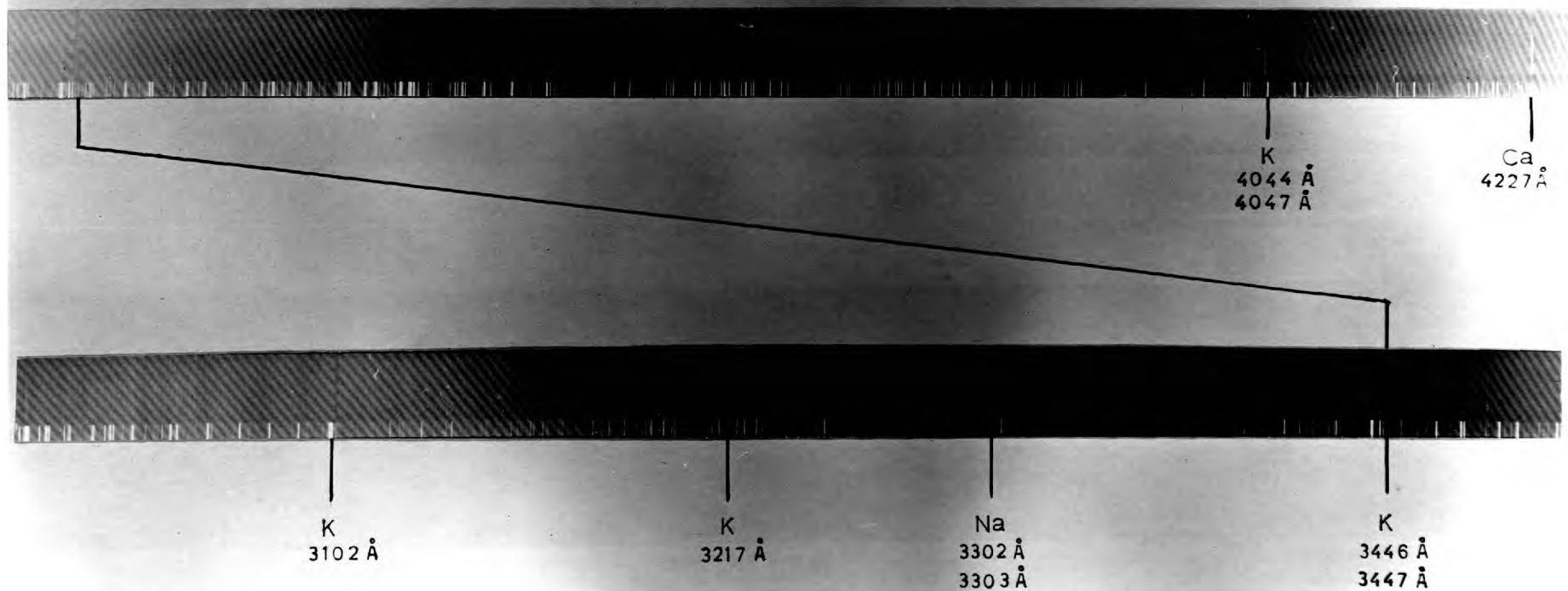
The compound used was supplied by Johnson and Matthey Ltd, England, and its maximum limits of impurities were: calcium group 0.0065%, iron 0.0005% and lead 0.0005%.

A saturated solution of the salt was deposited on carbon foil 100 microns thick and dried in air. The pyrolysis flash voltage was 8 kV and the delay time was varied from 300 μ sec to 700 μ sec. The argon pressure in the absorption tube was maintained at 100 millitorr. Emission from a carbon arc containing Na and K was superimposed on the interference fringes so that the distances from the outer hooks to the line centres could be measured accurately.

With the quartz optics of the spectrograph, it was possible to study either the sodium 5890 $\text{\AA}$ and 3302 $\text{\AA}$ doublets or the 3302 $\text{\AA}$ and 2852 $\text{\AA}$ doublets with the potassium 4044 $\text{\AA}$ and 3446 $\text{\AA}$ doublets in one experiment. With the glass optics, it was only possible to study the sodium 5890 $\text{\AA}$ and the potassium 4044 $\text{\AA}$ doublets. But as the f -value of the potassium 4044 $\text{\AA}$ doublet is about two orders of magnitude smaller than that of the sodium 5890 $\text{\AA}$ doublet, it was not always possible to obtain hooks of both lines at the same time. So effort was concentrated on the sodium 3302 $\text{\AA}$ and the potassium 4044 $\text{\AA}$ doublets.

In all, about 100 sets of interferograms were obtained, out of which 20 were chosen for measurement. Figure 17 shows the hooks at the doublets 4044 $\text{\AA}$ and 3302 $\text{\AA}$.

Fig.17 Sodium-Potassium



5.3 Reduction of Data

In the case of a close doublet, the two inner hooks are not formed and only the distances from the outer hooks to the doublet

δ_1 and δ_4 , can be measured (figure 2b). The total Nf-value of the doublet is given by

$$Nf = \frac{\pi}{r_0 L} \cdot \frac{K}{\lambda^3} \cdot 4(\beta' + \beta'') = \frac{\pi}{r_0 L} \cdot \frac{K}{\lambda^3} \cdot 4\beta \quad (7)$$

where β is the sum of the quantities β' and β'' , which refer to the short and long wavelength component of the doublet, and are related to δ_1 , δ_4 and the doublet separation (ϵ) by

$$\beta' = \frac{(1 + \delta_1/\epsilon)^2 - (\delta_4/\epsilon)^2}{(1 + \epsilon/\delta_1)^2 - (1 + \epsilon/\delta_4)^{-2}} \cdot \epsilon^2$$

$$\beta'' = \frac{(1 + \delta_4/\epsilon)^2 - (\delta_1/\epsilon)^2}{(1 + \epsilon/\delta_4)^2 - (1 + \epsilon/\delta_1)^{-2}} \cdot \epsilon^2$$

The ratio of the ground state populations of the two elements is then given by

$$\frac{N_1}{N_2} = \frac{f_2}{f_1} \cdot \frac{\lambda_2^3}{\lambda_1^3} \cdot \frac{K_1}{K_2} \cdot \frac{\beta_1}{\beta_2} \quad (8)$$

where the indices 1 and 2 refer to sodium and potassium respectively.

5.4 Results of Measurement and Discussion

The results for the ratio of the ground state populations of sodium and potassium, obtained from 15 sets of experiments on the sodium 3302 Å and the potassium 4044 Å doublets are summarised in Table 5.2. The indices 1 and 2 refer to sodium and potassium respectively. Δ is the separation between the outer hooks (ie: $\Delta = \delta_1 + \epsilon + \delta_4$), η is the ratio of the ground state population calculated as $\eta(\Delta)$ without allowing for the effect of the doublet separation and as $\eta(\beta)$ allowing for the effect by the use of the above equation (7). These equations are exact, and $\eta(\beta)$ is therefore the most accurate value of the ratio; $\eta(\Delta)$ is included to show the decrease in the ratio due to neglecting the doublet structure.

The fringe order (K) was determined with an accuracy of 1-2%. The magnitudes of δ_1 and δ_4 varied from about 0.4 mm to 0.7 mm and could be determined with an accuracy of about 4-6%. This leads to an error of about 12% in the ratio of the populations.

The 15 sets of data were obtained under the same experimental conditions (all at a delay time of 500 μ sec). The mean value for the ratio of the ground state populations is found to be 0.75 ± 0.05 .

The number density of the atoms in the ground state (N_{a0}) is related to the total number density (N_a) by the Boltzmann Law:

$$N_{a0} = \frac{g_{Na}}{Q(T)}$$

Table 5.2

Plate No	K_1	Δ_1	β_1	K_2	Δ_2	β_2	$\eta(\Delta)$	$\eta(\beta)$
45.3	877	1.382	78.1	684	1.129	162.0	0.61	0.71
45.4	877	1.423	80.0	684	1.110	160.2	0.67	0.73
45.5	877	1.229	59.14	684	0.971	113.46	0.65	0.76
45.6	877	1.189	55.47	684	0.976	117.26	0.61	0.70
45.7	877	1.132	49.94	684	0.895	91.68	0.65	0.80
45.8	877	0.969	34.73	684	0.783	63.79	0.62	0.80
50.3	926	1.376	77.80	743	1.059	141.3	0.69	0.78
50.4	926	1.458	89.96	743	1.104	164.0	0.69	0.78
50.5	926	1.623	108.6	743	1.188	187	0.73	0.82
50.6	926	1.554	96.98	743	1.174	193	0.65	0.69
43.5	973	1.075	44.50	768	0.803	82.08	0.73	0.80
43.6	973	1.064	39.80	768	0.975	70.24	0.74	0.83
51.5	926	1.408	79.86	743	1.064	146.0	0.72	0.81
51.6	926	1.240	62.52	743	0.934	109.3	0.72	0.84
51.7	926	1.377	79.34	743	1.027	138.9	0.73	0.85

where g is the statistical weight of the ground state of the atom and $Q(T)$ is the partition function of the atom at temperature T . However, the ratio of the ground state populations of the atoms is not significantly different from that of the total numbers of the two atoms, as the statistical weights are the same and the partition functions also came in as a ratio which is close to one. The use of N_{ao} instead of N_a would not have led to more than 1-2% difference in the ratio at a temperature up to 5000°K.

The conclusion therefore is that in the flash heated vapour, the concentration of the potassium vapour was about 25% higher than that of the sodium.

The ratio of the ground state populations was also calculated from the Nf -values of the sodium 3302 Å and the potassium 3446 Å doublets for six sets of data and the results are given in Table 5.3.

The anomalous dispersion of the potassium 3446 Å doublet was too small for the distances δ_1 and δ_4 between the two outer hooks and the doublet to be measured with sufficient accuracy and so only the separation Δ between the two outer hooks were measured. The Nf -values of the 3446 Å doublet were calculated without taking into account its doublet structure, while for the sodium 3302 Å doublet the doublet structure was allowed for as in the data of Table 5.2. The hook separation was measured to an accuracy of 4% and this led to an error of about 8% in the Nf -value.

TABLE 5.3

Plate No:	Δ in mm	K	$\eta(\Delta)$	$\frac{f(4044)}{f(3447)}$
50.3	0.429	915	0.60	7.9
50.4	0.415	915	0.69	9.1
50.5	0.493	915	0.62	8.7
45.3	0.435	840	0.58	8.2
45.4	0.483	840	0.57	8.3
45.5	0.372	840	0.55	7.5

The mean ratio of the ground state populations from the six sets of data is 0.61 ± 0.05 , compared with 0.75 ± 0.05 calculated from the $3302 \text{ \AA}$ and $4044 \text{ \AA}$ doublet. The ratio of the f-values of the potassium $4044 \text{ \AA}$ and $3446 \text{ \AA}$ doublets (the second and third members of the principal series), deduced from the measured Nf-values, is given in the last column of Table 5.3 and the mean is found to be 8.3 ± 0.7 .

In the case of the $3446 \text{ \AA}$ doublet, where the hook separation is about 4-5 times that of the doublet separation, first order approximation shows that the Nf-values, calculated without taking into account the doublet structure, would be at least 11-17% too low. Applying this correction would raise the ratio of ground state populations calculated from the $3302 \text{ \AA}$ and $3446 \text{ \AA}$ ^{lines} to about 0.71.

Applying the correction for the doublet structure, the ratio of the f-values of the two potassium doublets would be raised to about 9.7 close to the value of 10.3 given in Table 5.1.

The experiments results show consistently that the ratio of sodium to potassium in the flash heated vapours was between 0.7 and 0.8, compared to the ratio of 1 in the compound.

The discrepancy may have been due to one of the following reasons: the absolute f-values of the lines used; the impurities present in the compound; chemical reactions among the species in the flash heated vapours; and different vapour pressure of sodium and potassium.

The absolute values of the sodium 3302 Å doublet and the potassium 3446 Å and 4044 Å doublets in Table 5.1 are based on the relative f-values obtained by Filippov and Prokof'ev (41,42), with an accuracy of 5%, together with the absolute f-values of the resonance doublets of sodium and potassium, which are estimated by Marr and Creek to be accurate to 2%. So the error in the absolute f-values could at most lead to an error of about 15% in the ratio, compared to the present 20-30% in the measured values. However, it is by ^{no} means _Λ impossible that the accuracy of the f-values has been over-estimated.

Although the compound contains less than 0.0065% of all the elements of the calcium group, the dispersion around the calcium resonance line (4227 Å) was appreciable and hooks of the lines were obtained in every experiment. So the effect of impurities was looked into. The following lines appear in the regions of interest. ^(Table 5.4) _Λ The number behind each line is just a rough value of its relative intensity (obtained from the NBS Table of Spectral Line Intensities).

The relatively large value of the measured Nf-value of the potassium 4044 Å doublet could have been due to iron impurity, and that of the 3446 Å doublet due to nickel. The ratio of the f-values of these two doublets, however, agrees well with the experimental values determined by Filippov. The ratio of the f-values of the sodium 3302 Å doublet and the 2852 Å doublet was found to be 25% smaller than Filippov's experimental value as to be expected if the magnesium resonance line were blended with the latter, the ratio would indeed be reduced, but the very small percentage of impurity made such a large effect unlikely.

Table 5.4

Wavelength	Element	Intensity
4044.14	K	32
4045.82	Fe	300
4047.20	K	16
3446.26	Ni	400
3446.72	K	-
3447.70	K	-
3302.32	Na	30
3302.59	Zn	90
3302.94	Zn	28
3302.99	Na	15
2852.13	Mg	6000
2852.83	Na	-
2853.03	Na	-

The compound Na-K tartrate contains, besides potassium and sodium, also hydrogen, oxygen and carbon. At a temperature of a few thousand degrees, the compound may have dissociated completely, but the atoms may also react with each other to form compounds like NaOH, KOH, etc. The similarity of the chemical properties of sodium and potassium would rule out any large effect on the ratio of the concentrations due to any chemical reaction that may take place. This uncertainty could, however, be avoided by studying an alloy of two metals.

An attempt was made to study the ratio of zinc and copper in the vapour formed by flash heating an alloy in the form of a foil 25 microns thick, but this was too thick to be vaporized completely with the maximum input energy available (100 μ F at 10 kV). As no other suitable alloys were available, this investigation was pursued no further.

The present experiments are therefore somewhat inconclusive and further investigations are needed.

CHAPTER 6

THE EXCITATION AND IONIZATION PROCESSES IN

THE FLASH HEATED VAPOURS

6.1 Introduction

In measuring either absolute f -values or relative f -values of transitions that originate from different levels of an atom, it is necessary to know how the population is distributed over the levels. The pertinent information in the literature as regards flash-heated vapours is rather fragmentary. Only two papers have dealt with the subject.

In an experimental investigation of flash vaporization of tungsten (8), Nelson and Kuebler cited evidence suggesting that the vaporization and excitation processes were mainly thermal. The evidence includes:

- i) the progressive increase of the excited state populations with time as the absorption of energy by the solid tungsten was taking place;
- ii) the existence of a threshold for the input energy above which the vaporization was independent of the type and pressure of the surrounding gas;
- iii) the fact that shielding the absorption cell from any ionic or field induced processes had no effect on the observed spectra.

They also attempted to measure the electronic temperature of the tungsten vapour from the relative intensities of the absorption lines obtained by photoelectric microdensitometry, but the data scattered very badly and meaningful interpretation was not possible. Instead, by making the assumption that the number of atoms in a particular state was proportional to the number of observed absorption lines originating from that state, they were able to conclude that a Boltzmann distribution of energy levels occurred in the flash heated vapours and to obtain an approximate estimate of the temperature of the tungsten vapour. The temperature of the vapour was found to be approximately 7200°K , compared to the boiling point of tungsten at 6300°K .

The other known attempt to measure the temperature of the flash heated vapour was made by Petrella and Spink (14). From the absorption spectrum of iron obtained by flash heating graphite strips that were coated with an 0.02% solution of ferrocene (dicyclopentadienyl-iron), the relative intensity of two iron lines was determined by a microdensitometer. The temperature of the iron vapour was found to be at $2477 \pm 20^{\circ}\text{K}$ at a delay time of $17.5 \mu\text{sec}$. In this experiment the pyrolysis flash reached its peak value $6 \mu\text{sec}$ after its start and had a decay time of $35 \mu\text{sec}$. It was also found that the relative intensity of the two lines was independent of the amount of material deposited on the strips.

There was clearly a need for a more systematic investigation of excitation processes in the flash heated vapours to see whether any form of thermal equilibrium exists among the populations of different states of an atom; and if so what is its dependence on the experimental parameters. The method adopted was to determine Nf -values by the hook method for lines originating on a number of excited states, lying within a few electron volts of the ground state, choosing lines whose relative f -values were already known, so that the relative populations could be obtained from the hooks.

The degree of ionization was likewise investigated by measuring hooks from lines of the ion and the neutral atom to see whether the degree of ionization followed that predicted by the Saha theory of thermal ionization.

The hook method was employed by Penkin to study the excitation and ionization processes in a King's furnace (27, 28). The relative populations of chromium atoms in the levels $7S_3$ and $5S_2$, whose energy separation is 7539 cm^{-1} , were determined by measuring the hooks of the $7S_3 \rightarrow 7P_{4,3,2}$ lines (4254.3; 4374.8; 4289) and the $5S_2 \rightarrow 5P_{1,2,3}$ lines (5204.5; 5206.2; 5208.4) at furnace temperatures from 2100 to 2700°K. The linear dependence of $\log (N_1 f_1 / N_2 f_2)$, (where the index 1 and 2 refer to the levels $7S_3$ and $5S_2$ respectively) on the reciprocal temperature ($1/T$) was used to establish that the atoms follow the Boltzmann law of distribution over the energy levels.

In the case of ionization, Penkin determined the relative number densities of barium atoms and ions at different furnace temperatures from 2100 to 3000°K. The barium vapour was produced either from the metallic element or its chloride. The ratio $N_i^2 f_i^2 / N_a f_a$ (where i and a refer to the ion and atom respectively) was then compared to the value predicted by the Saha theory at the relevant temperature. The degree of ionization was found to be the same whether the vapour was produced by the metal or by the chloride, and also agreed well with the Saha theory of thermal ionization.

Preliminary experiments with our apparatus showed that the dispersion of the spectrograph was too low to disperse the chromium green triplets sufficiently. In this case to obtain the Nf -values would involve lengthy numerical calculations. So chromium was not a suitable element for our purpose.

Experiments on the alkaline earth elements showed that hooks of the lines from the ground state and excited states of the atoms as well as from the ground state of their ions were readily obtained. In this case the relative populations of more than two states of the atoms could be studied at the same time. This would enable the distribution of the atoms over the energy levels to be studied without an explicit knowledge of the temperature of the vapour. The degree of ionization of the vapour could also be studied at the same time.

The relations describing the populations of excited states and ionized states in LTE are given in section 2 of this chapter, and the experiments and results are described in the remaining sections.

6.2 Theoretical Formulation

(a) The Boltzmann Distribution

Under conditions of thermal equilibrium, the ratio of the number densities of atoms in two levels j and k , N_j and N_k , is given by the Boltzmann law

$$\frac{N_k}{N_j} = \frac{g_k}{g_j} \cdot e^{-(E_k - E_j)/kT} \quad (9)$$

where g_j and g_k are the statistical weights of the two levels, and E_j and E_k are their energies, k is the Boltzmann constant, and T is the electronic excitation temperature.

The ratio of the number densities, as described by the hook method for lines of wavelength λ_j and λ_k and oscillator strengths f_j and f_k starting from these levels, is given by

$$\frac{N_k}{N_j} = \frac{K_k}{K_j} \cdot \frac{\Delta_k^2}{\Delta_j^2} \cdot \frac{\lambda_j^3}{\lambda_k^3} \cdot \frac{f_j}{f_k} \quad (10)$$

where in each case Δ is the hook separation and K the fringe order near the line.

Combined with the Boltzmann law, this gives

$$\frac{K_k}{K_j} \cdot \frac{\Delta_k^2}{\Delta_j^2} \cdot \frac{\lambda_j^3}{\lambda_k^3} \cdot \frac{f_j}{f_k} = \frac{g_k}{g_j} e^{-(E_k - E_j)/KT}$$

or after re-arranging the terms

$$\left(\frac{K \Delta^2}{g f \lambda^3} \right)_k \cdot \left(\frac{g f \lambda^3}{K \Delta^2} \right)_j = e^{-(E_k - E_j)/KT} \quad (11)$$

Let j be the ground level and k any excited level E , so that $E_j = 0$ and $E_k = E$. If E is measured in 10^3 cm^{-1} and T in absolute degrees, then changing into logarithmic form (base 10), equation (11) becomes

$$\log \left(\frac{K \Delta^2}{g f \lambda^3} \right) - \log \left(\frac{K \Delta^2}{g f \lambda^3} \right)_0 = - \frac{625}{T} \cdot E$$

where the suffix 0 refers to a line starting from the ground state.

Therefore, if the relative populations of different levels follow the Boltzmann law, the plot of $\log (K \Delta^2 / g f \lambda^3)$ versus E is a straight line, and the intercept of the straight line on the ordinate is $\log (K \Delta^2 / g f \lambda^3)_0$. The corresponding electronic excitation temperature can be obtained from the slope of the straight line:

$$T = - \frac{625}{\text{slope}} \quad (12)$$

(b) The Saha Equation

According to the Saha theory for a single state of ionization in LTE at temperature T , the number densities of the atom and its ion, N_a and N_i , are related by

$$\frac{N_i}{N_a} \cdot N_e = \left(\frac{2\pi m k}{h^2} \right)^{3/2} \cdot \frac{g_e \cdot Q_i(T)}{Q_a(T)} \cdot T^{3/2} \cdot e^{-E_i/kT} \quad (13)$$

where N_e is the number density of electrons, g_e is the internal partition function of the electrons, numerically equal to 2, and E_i is the ionization energy of the atom. $Q_a(T)$ and $Q_i(T)$ are the internal partition functions (or state sums) for the atom and ion respectively and are given by

$$Q(T) = \sum_n g_n e^{-E_n/kT}$$

From the Boltzmann law, we have

$$N_a = \frac{N_{a0}}{g_{a0}} \cdot Q_a(T) \quad ; \quad N_i = \frac{N_{i0}}{g_{i0}} \cdot Q_i(T)$$

where N_{a0} and N_{i0} are respectively the number densities of atoms and ions in their respective ground states, with statistical weights g_{a0} and g_{i0} respectively. If the electrons are due solely to the ionization of this one species of atom, then

$$N_i = N_e$$

and equation (13) becomes

$$\frac{N_{io}^2}{N_{ao}} = \left(\frac{2\pi mk}{h^2} \right)^{3/2} \cdot \frac{2g_{io}^2}{g_{ao}} \cdot S(T) \quad (14)$$

where

$$S(T) = \frac{1}{Q_i(T)} \cdot T^{3/2} \cdot e^{-E_i/kT}$$

The function $S(T)$ can be calculated from energy level tables. This has been done for barium, calcium and strontium in the temperature range 2500-4000°K, and the curves are plotted in figure 18.

From the hook experiment, the ground state number densities of atoms and ions are given by

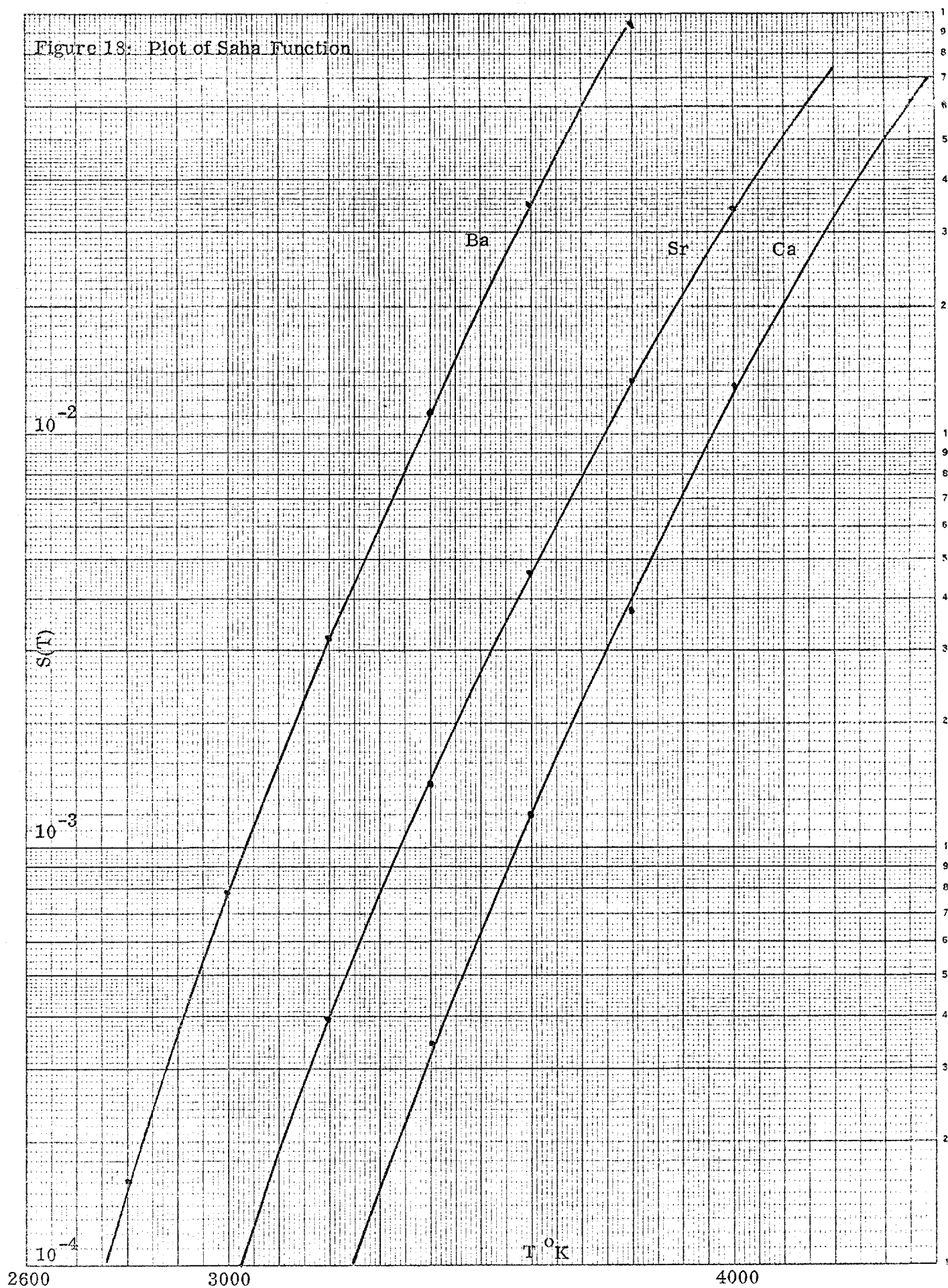
$$N_{io} = \left(\frac{\pi mc^2}{e^2} \right) \cdot \left(\frac{\Delta^2 K}{L f \lambda^3} \right)_i$$

$$N_{ao} = \left(\frac{\pi mc^2}{e^2} \right) \cdot \left(\frac{\Delta^2 K}{L f \lambda^3} \right)_a$$

where the suffixes i and a refer to the resonance lines of ion and atom respectively. Substituting these values into equation (14), we obtain

$$S(T) = \left(\frac{2\pi mk}{h^2} \right)^{3/2} \cdot \left(\frac{e^2}{\pi mc^2} \right)^{-1} \cdot \frac{g_{ao}}{2g_{io}^2} \cdot \frac{L_a}{L_i^2} \cdot \frac{\Delta_i^4}{\Delta_a^2} \cdot \frac{K_i^2}{K_a} \cdot \frac{f_a}{f_i^2} \cdot \frac{\lambda_a^3}{\lambda_i^6} \quad (15)$$

Figure 18: Plot of Saha Function



For alkaline earth elements and their ions, $g_{20} = 1$ and $g_{10} = 2$. Assuming that the length of vapour column is the same for the ions as for the atoms, $L_i = L_a = L$ (a condition not always fulfilled in a furnace under prolonged operation), and using the following numerical values for the fundamental constants

$$\begin{aligned} m &= 9.109 \times 10^{-28} \text{ gm} \\ k &= 1.38 \times 10^{-16} \text{ erg deg}^{-1} \\ h &= 6.625 \times 10^{-27} \text{ erg sec} \\ e &= 4.803 \times 10^{-10} \text{ esu} \\ c &= 2.998 \times 10^{10} \text{ cm/sec} \end{aligned}$$

we obtain finally

$$S(T) = 5.776 \times 10^{-4} \cdot \frac{1}{L} \cdot \frac{\Delta_i^4}{\Delta_a^2} \cdot \frac{K_i^2}{K_a} \cdot \frac{f_a}{f_i^2} \cdot \frac{\lambda_a^6}{\lambda_i^3} \quad (16)$$

Hence, if L is known, $S(T)$ can be obtained from the hooks and the corresponding value of T can then be read off from the appropriate curve.

The main assumption made in equation (16) was that the electrons were due solely to the ionization of a single species of atom and there was no other source of electrons, such as photoionization, thermal emission, etc. Another uncertainty was the length of the vapour column. These difficulties could be avoided by studying the ionization of mixtures. Saha's equation can be applied to each species of atom present, with

N_e now representing the total concentration of electrons resulting from the ionization of all components present.

Consider the case of a mixture of two types of atoms, 1 and 2: from equation (13) we obtain the following expression for the number densities of atoms and ions

$$\frac{N_{i1}}{N_{a1}} \cdot \frac{N_{a2}}{N_{i2}} = \frac{Q_{i1}(T) \cdot Q_{a2}(T)}{Q_{a1}(T) \cdot Q_{i2}(T)} \cdot e^{-(E_{i1} - E_{i2})/kT}$$

where E_{i1} and E_{i2} are the ionization energies. Using the Boltzmann law, we obtain from the number densities of atoms and ions at ground level the equilibrium temperature

$$T = - \frac{E_{i1} - E_{i2}}{K \log Z} \quad (17)$$

where

$$Z = \left(\frac{\Delta_{i1} \Delta_{a2}}{\Delta_{i2} \Delta_{a1}} \right)^2 \left(\frac{K_{i1} K_{a2}}{K_{i2} K_{a1}} \right) \left(\frac{f_{a1} f_{i2}}{f_{a2} f_{i1}} \right) \left(\frac{\lambda_{a1} \lambda_{i2}}{\lambda_{a2} \lambda_{i1}} \right)^3$$

In this case the main error in the calculation of the equilibrium temperature comes from the measurement of hook separation.

6.3 Barium

The barium vapour was produced from barium fluoride, supported on 100 microns thick carbon foil coated with a layer of glue. The barium salt had a purity of 99.98% and detectable impurities were sodium, magnesium and calcium.

At an input energy of 4000 J (100 μ F at 10 kV), measurable hooks were obtained for lines originating from the ground level and several excited levels of both the neutral atom and the ion. With the glass optics of the spectrograph, the spectral range 4100-6800 Å could be covered in one single experiment. Figure 19 shows the spectrum taken at a delay time of 500 μ sec. Table 6.1 contains the wavelengths, classifications and f-values of the observed Ba I lines and the energy of the lower state of each transition. Apart from the resonance line, there are 20 lines originating from six excited states with energies ranging from 9000 cm^{-1} to 13000 cm^{-1} above the ground state. The Ba II lines observed in this spectral range are, the two resonance lines 4934.09 and 4554.93 Å and three lines (6496.90, 6141.72 and 5853.68 Å) from two excited levels.

The hook measurements on the Ba I lines were used to calculate the quantity y , where $y = \Delta^2 K / g f \lambda^3$. The results of measurements on one set of experimental data are summarised in Table 6.2. The fringe order (K) was determined to an accuracy of 1-2%. The accuracy in the measurement of the hook separation depended on the magnitude of the separation. For the 5535 Å resonance line, the accuracy was ± 0.08 mm or about

Fig. 19 Barium I & II

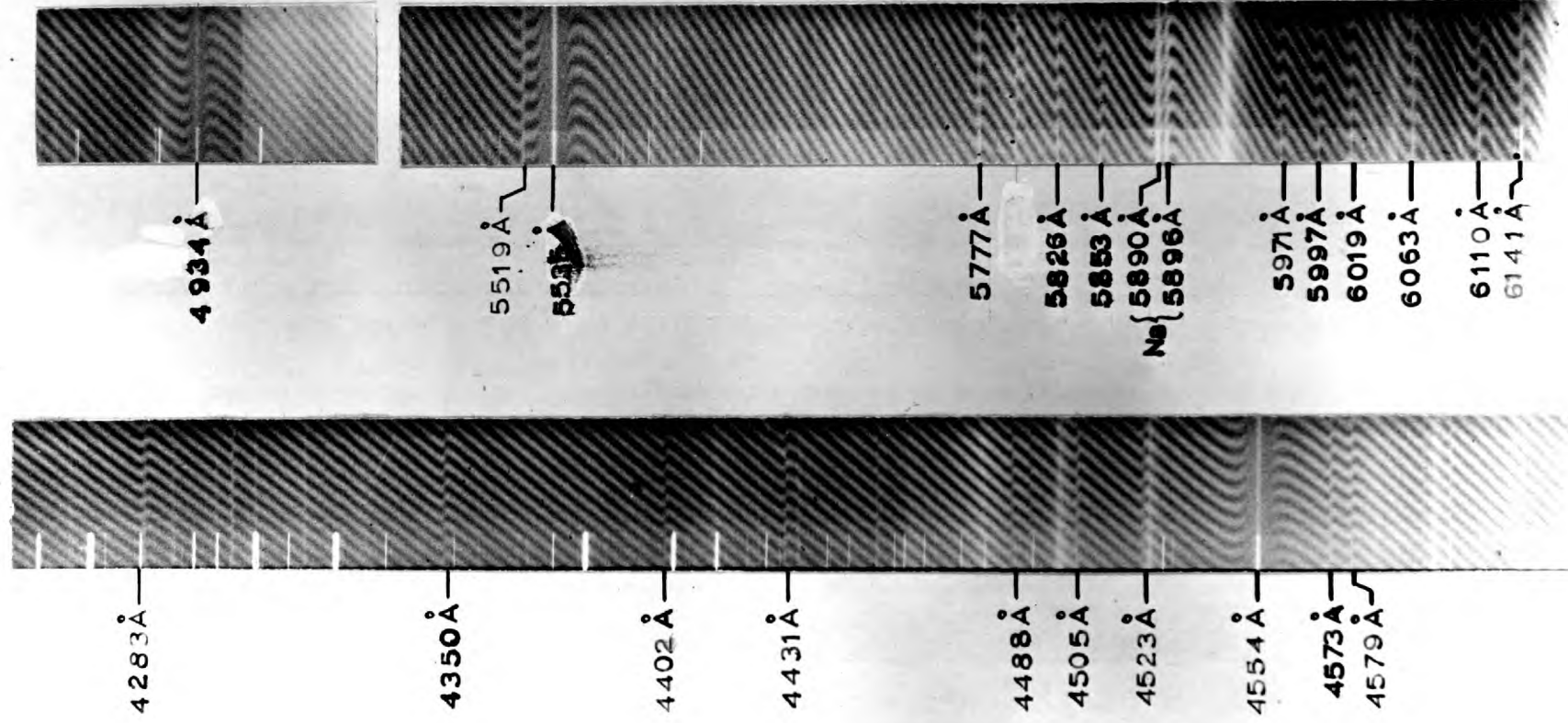


Fig. 19 Barium I & II

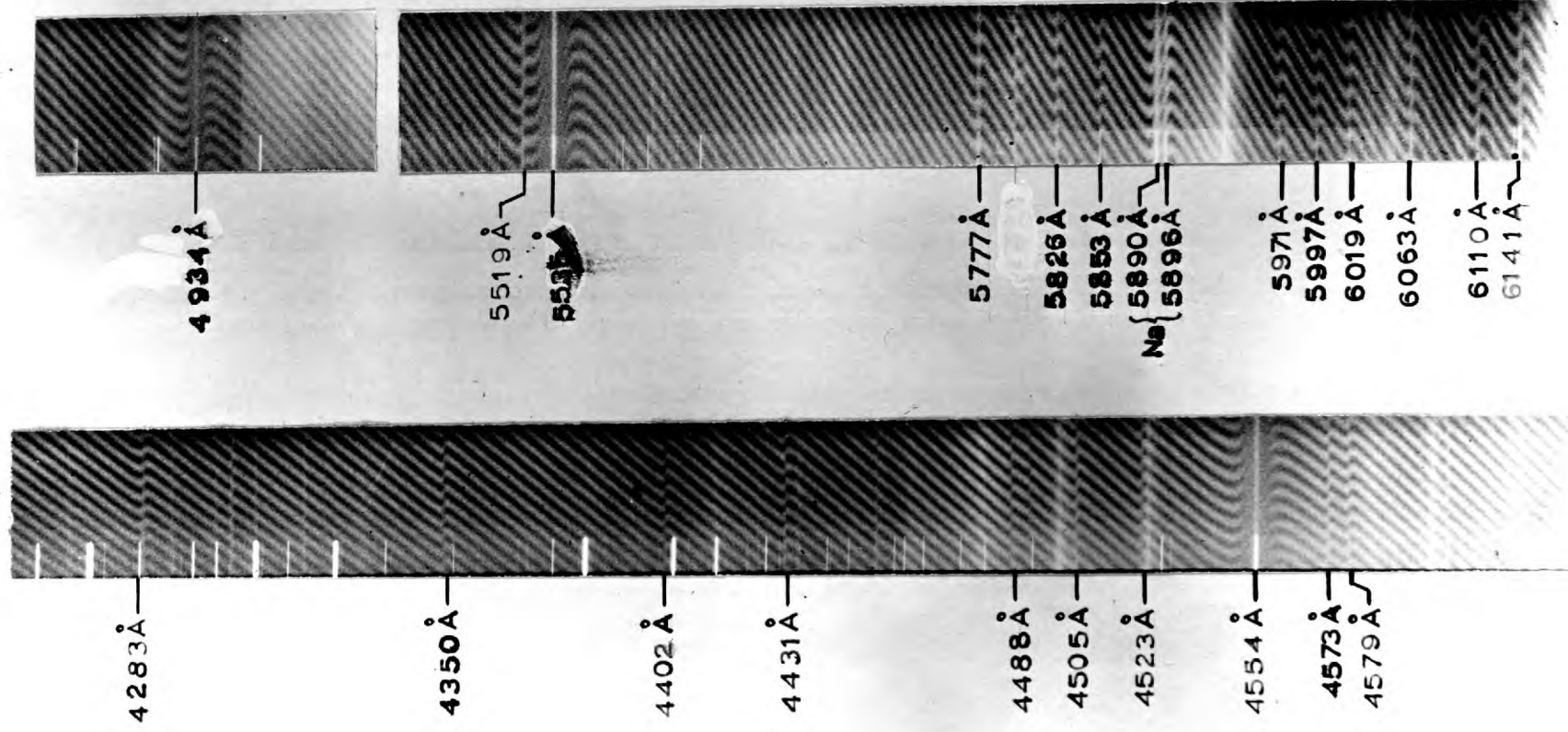


TABLE 6.1

Wavelength	Transition	J-J	$E_{10^3\text{cm}^{-1}}$	g	f
6595.32	$5d\ ^3D - 6p\ ^3D$	1-1	9.034	3	0.47
6527.31	$5d\ ^3D - 6p\ ^3D$	2-2	9.216	5	0.38
6482.91	$5d\ ^1D - 6p\ ^1F$	2-3	11.395	5	0.39
6450.85	$5d\ ^3D - 6p\ ^3D$	1-2	9.034	3	0.11
6110.78	$5d\ ^3D - 6p\ ^3P$	3-2	9.597	7	0.40
6063.12	$5d\ ^3D - 6p\ ^3P$	2-1	9.216	5	0.32
6019.47	$5d\ ^3D - 6p\ ^3P$	1-0	9.034	3	0.26
5997.09	$5d\ ^3D - 6p\ ^3P$	1-1	9.034	3	0.25
5971.70	$5d\ ^3D - 6p\ ^3P$	2-2	9.216	5	0.15
5826.28	$5d\ ^1D - 6p\ ^1P$	2-1	11.395	5	0.30
5777.62	$6p\ ^3P - 6d\ ^3D$	2-3	13.515	5	1.0
5535.48	$6s\ ^1S - 6p\ ^1P$	0-1	0	1	1.59
4726.45	$5d\ ^1D - 7p\ ^1P$	2-1	11.395	5	0.14
4691.62	$6p\ ^3P^0 - 6p^2\ ^3P$	2-1	13.515	5	0.33
4579.64	$6p\ ^3P^0 - 6p^2\ ^1D$	2-2	12.637	5	0.56
4523.24	$6p\ ^3P^0 - 6p^2\ ^3P$	2-2	13.515	5	0.30
4505.92	$6p\ ^3P^0 - 6p^2\ ^3D$	1-1	12.637	3	0.32
4488.97	$6p\ ^3P^0 - 7d\ ^3D$	2-3	13.515	5	0.18
4431.89	$6p\ ^3P^0 - 6p^2\ ^3P$	0-1	12.266	1	1.1
4402.54	$6p\ ^3P^0 - 6p^2\ ^1D$	1-2	12.637	3	0.34
4350.33	$6p\ ^3P^0 - 6p^2\ ^3P$	1-2	12.637	3	0.28
4283.10	$5d\ ^1D - 4f\ ^1F$	2-3	11.395	5	0.25

TABLE 6.2

Wavelength in Å	K	Dispersion in Å/mm	Δ in mm	$y = \frac{\Delta^2 K}{g f \lambda^3}$	$\log_{10}(y)$
6595	651	23.18	0.426	15.83	1.199
6527	653	22.60	0.464	13.77	1.139
6450	662	21.78	0.330	13.15	1.410
6341	675	20.73	0.358	18.22	1.260
6110	704	18.49	0.580	12.70	1.110
6063	710	18.05	0.464	13.97	1.145
6019	715	17.67	0.340	15.17	1.181
5997	718	17.47	0.451	27.54	1.440
5971	723	17.25	0.433	25.24	1.402
5826	742	15.98	0.407	10.58	1.025
5777	750	15.51	0.514	4.94	0.694
5535	786	13.56	2.301	283.8	2.453
4726	938	7.94	0.304	7.45	0.872
4691	947	7.70	0.334	3.67	0.564
4579	975	7.08	0.508	4.65	0.667
4505	994	6.69	0.348	6.14	0.788
4488	999	6.60	0.297	4.37	0.640
4431	1014	6.31	0.431	7.83	0.893
4402	1022	6.16	0.357	5.68	0.754
4350	1037	5.90	0.366	6.99	0.844
4283	1056	5.58	0.459	7.05	0.848
4934	891	9.22	2.206		
4554	984	6.95	3.618		

4%; for the other lines, it was between ± 0.02 - 0.03 mm or about 5-8%. This leads to an error of about 3% for the $\log(y)$ value of the 5535 Å line and about 8-10% for that of the other lines. The relative f -values of the lines are stated to be known to an accuracy of 10-15% (43) and this itself leads to an error of 2-3% in the $\log(y)$ value. So the uncertainty of the $\log(y)$ values was 6% for the 5535 Å line and 10-12% for other lines.

A plot of $\log(y)$ versus E (in 10^3 cm^{-1}) for one set of data is shown in Figure 20. For those cases when there is more than one measured $\log(y)$ value for a given E , the mean value is used. The plot shows a linear dependence of the $\log(y)$ values on E , indicating that the relative populations of different levels follow the Boltzmann law of distribution, and hence an electronic excitation temperature can be defined.

From the linear plot, the electronic excitation temperature can be calculated using equation 12. The results of calculation for 10 sets of experiments are given in Table 6.3. The uncertainty in determining the slope is about 6%, corresponding to an accuracy of about $\pm 300^\circ \text{K}$ in the temperature.

The mean value of the temperature at a delay time of 400 μsec is 5435°K and that at 500 μsec is 4950°K , showing a decrease of about 400°K in 100 μsec . It was difficult to use significantly shorter or longer delay times as at too

Figure 20 Plot of $\log \frac{\Delta^2 K}{g f \lambda^2}$ v.s. E

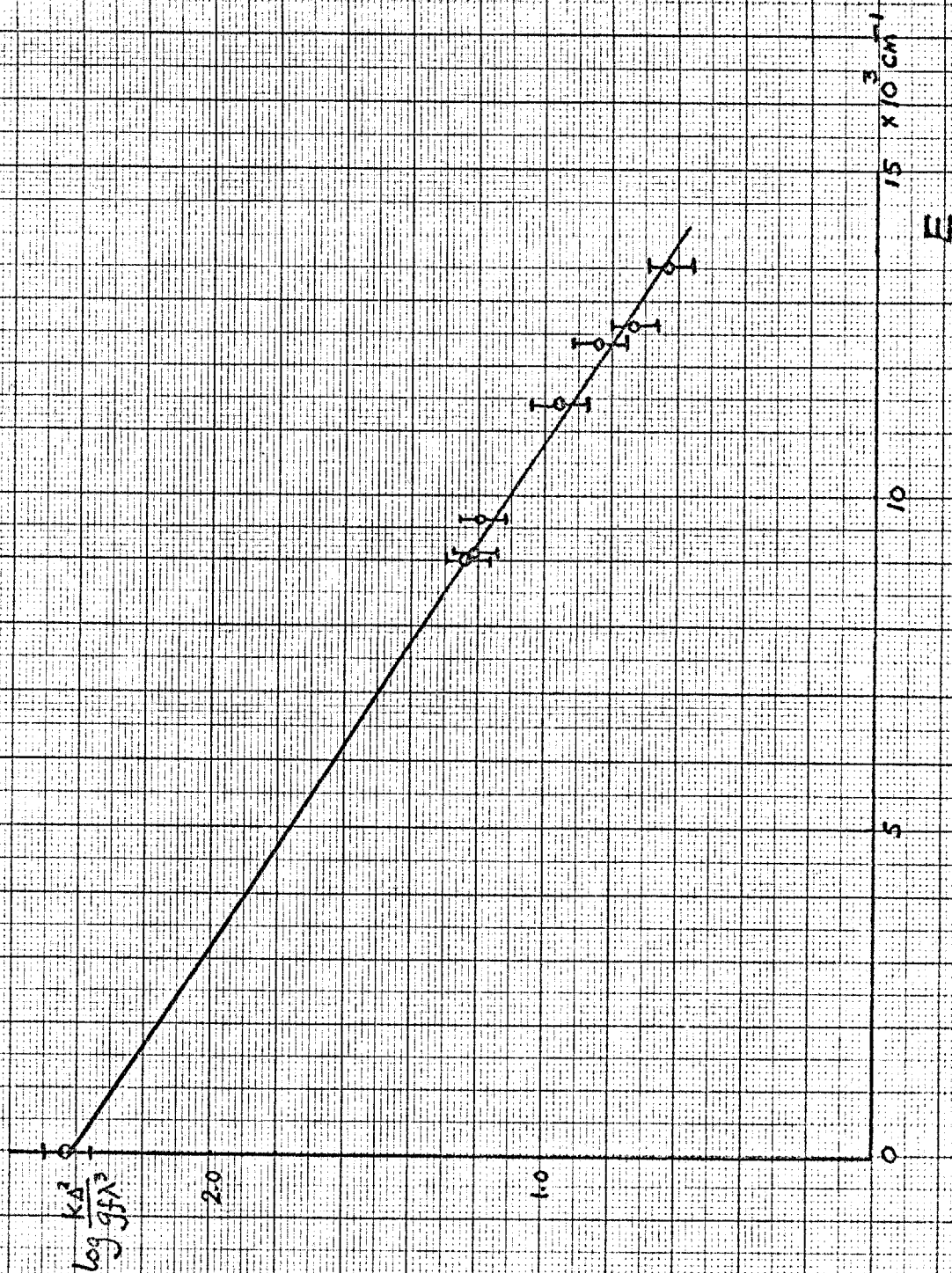


TABLE 6.3

Plate No:	Delay Time μ sec	Excitation Temperature $^{\circ}$ K	$S(T)$ $\times 10^{-2}$	Ionization Temperature $^{\circ}$ K
41.4	400	5540	5.02	4240
41.6	400	5760	4.75	4220
50.1	400	5190	1.12	3870
51.3	400	5250	2.04	4020
32.3	500	4860	5.67	4270
32.4	500	5116	4.32	4220
32.5	500	4993	2.65	4070
32.6	500	5000	1.53	3950
32.7	500	4971	0.88	3820
37.3	500	4800	3.91	4180

short a delay time the hooks were blurred and at too long a delay the hook separations for the lines originating on the excited states were too small.

For both the delay times used the scatter of results is around $\pm 150-200^{\circ}\text{K}$. As this is within the error limits, it appears that the shot-to-shot reproducibility of the temperature in these conditions is $\pm 200^{\circ}\text{K}$ or better.

The degree of ionization in the barium vapour is calculated using equation 16, and the ionization temperature corresponding to the calculated function $S(T)$ is given in the last column of Table 6.3.

In the calculation of the function $S(T)$, the length of the vapour column, which is unknown, is taken to be equal to that of the absorption tube (35 cm). This is based on the considerations that in the experiment two carbon foils measuring 1 cm x 5 cm were used end on, making a total length of 10 cm; and from the mobility of the barium atoms at a temperature of 5000°K the vapour would have filled the whole length of the absorption tube in about 100 μsec .

Assuming for the moment that equation 16 is valid, the error in determining the function $S(T)$ arises from (i) measurement of the hook separation and (ii) the absolute f -value used. The hook separations of the resonance lines are relatively large and can be determined to an accuracy of about 4-5% and this leads to an error of about 25-30% in the

calculated value of the function $S(T)$. Equation 16 contains the f -values in the form f_a/f_i^2 - ie: an absolute f -value as well as a ratio, in contrast to the Boltzmann relation where only the ratio is involved. Assuming 10% and 20% errors for the relative and absolute values respectively, this will add another 30% uncertainty to the calculated value of $S(T)$. However, a large variation in the function $S(T)$ results from a fairly small change in temperature, and a 50% error in the value of $S(T)$ will lead to an error of only about 100°K in the corresponding ionization temperature.

The values of the function $S(T)$ vary by a factor of 5 and this cannot be due to error in the determination of hook separations alone, nor to the value assumed for L . It is likely that the assumption ($N_e = N_i$) made in the derivation of equation 16 is not valid. Impurities like sodium, calcium and BaF^+ etc could contribute to the total density of the electrons. A high electron density depresses the number of ions and so leads to too low a value for the equilibrium temperature as calculated from equation 16. On the other hand, a shot-to-shot variation of a factor of 5 or so in electron density seems improbable, particularly since the fluctuations in ionization temperature do not correlate with those in the Boltzmann temperature. It seems likely that true ionization equilibrium does not exist and this point will be discussed further in section 6.6.

6.4 Calcium

The calcium vapour was produced from calcium fluoride with a purity of 99.9% ; detectable impurities were barium, strontium and sodium. The input energy and buffer gas pressure were the same as those in the experiment on barium. In the spectral range 3900-5800 Å, hooks were obtained for about 10 lines originating at the 4^1S and 4^3P^0 levels of the neutral atoms and the two resonance lines of the ion. Figure 21 shows a photograph of the spectrum and Table 6.4 contains the wavelengths, classifications, lower state energies and f-values of the lines.

The results of measurements of one exposure are given in Table 6.5. The uncertainty in the determination of the hook separations varies from about ± 0.1 mm (or about 3%) for the 4226 Å resonance lines of Ca I to $\pm 0.02-0.03$ mm (or about 7-10%) for other lines.

From the relative populations of the 4^1S and 4^3P^0 levels, the electronic excitation temperature of the calcium vapour can be calculated:

$$T = - 625 \times (0-15.2)/(2.668 - 0.839) = 5200^\circ\text{K}$$

where the value 15.2 is the mean of the energies of the 4^3P^0 levels in 10^3cm^{-1} , and 0.839 is the mean of the $\log(y)$ values of the six lines originating from these levels. The accuracy of the temperature depends on the relative f-values of the

Fig. 21 Calcium

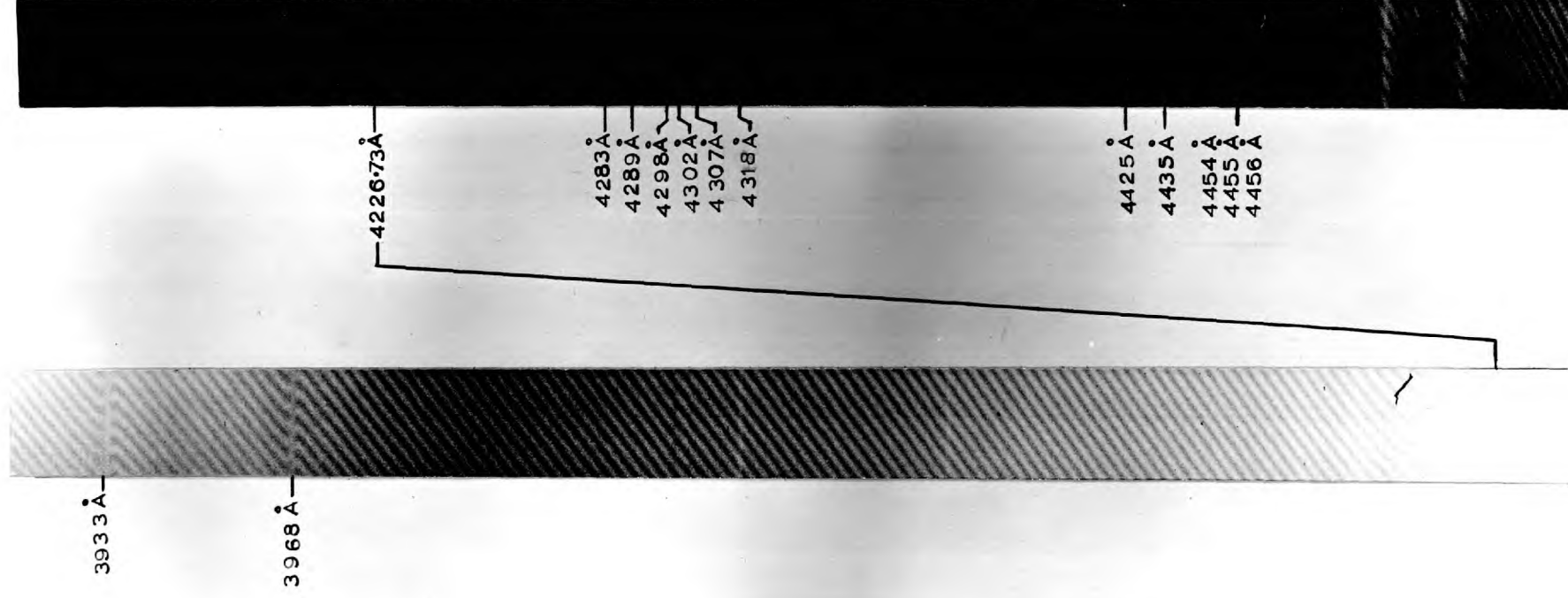


TABLE 6.4

f-values of Calcium Lines

Wavelength	Transition	J-J	g	E	f
4226.73	$4^1S-4^1P^0$	0-1	1	0	1.49
4283.01	$4^3P^0-4p^2^3P$	1-2	3	15.21	0.17
4289.36	"	0-1	1	15.16	0.40
4298.99	"	1-1	3	15.21	0.11
4302.53	"	2-2	5	15.32	0.29
4307.74	"	1-1	3	15.16	0.14
4318.65	"	2-1	5	15.32	0.10
4425.44	$4^3P^0-5^3D$	0-1	1	15.16	0.32
4434.96	"	1-2	3	15.21	0.27
4454.78	"	2-3	5	15.32	0.26
3933.67	$4^2S-4^2P^0$	$\frac{1}{2}-\frac{3}{2}$	2	0	0.83
3968.47	$4^2S-4^2P^0$	$\frac{1}{2}-\frac{1}{2}$	2	0	0.43

TABLE 6.5

Wavelength	Hook Separation	Dispersion	K	$\gamma = \frac{\Delta^2 K}{g f \lambda^3}$	$\log(\gamma)$
4226.73	3.778	5.33	1300	4.66	2.668
4283.01	0.249	5.58	1290	6.61	0.820
4289.36	0.234	5.60	1285	6.99	0.845
4307.74	0.219	5.71	1265	5.89	0.770
4318.65	0.268	5.76	1255	7.40	0.872
4425.44	0.215	6.25	1250	7.69	0.886
4434.96	0.361	6.34	1240	6.43	0.808
3968.47	0.530	4.18	1400	-	-

lines and the error in the measurement of the hook separations. The relative f -values were known to an accuracy of 10-15% (41) and this, added ^{t_0} _{Δ} the error in the hook separation, leads to an uncertainty of about 8%, or about $\pm 400^\circ\text{K}$, in the value of the temperature.

The electronic excitation temperature, calculated from 6 sets of experimental data all obtained at a delay time of 500 μsec are given in Table 6.6. The six sets of results give a mean value of 5180°K with a scatter similar to that for barium.

The degree of ionization in the calcium is calculated using equation 16. The function $S(T)$ obtained from the 4226 Å and 3968 Å resonance lines (the 3933 Å line was not used as in general the contrast of the fringes was too poor), is given in the last column of Table 6.6.

The accuracy in the determination of the hook separations in this case varies from about 3% for the 4226 Å lines to about 5% for the 3968 Å line, and this leads to an error of about 25% in the value of $S(T)$. The derived ionization temperature will also depend on the absolute f -values used, giving another 30% uncertainty to the value of $S(T)$ as in the case of barium.

The average value of the function $S(T)$ obtained for the six sets of experimental data is 2.5×10^{-5} , corresponding to an ionization temperature of 3200°K . As with barium, large changes in $S(T)$ reflect only small changes in T and an uncertainty of 100% in $S(T)$ leads to an uncertainty of less than 200°K in the derived ionization temperature.

TABLE 6.6

Calcium

Plate No:	Δ (4226 Å)	Δ (3968 Å)	Excitation Temperature	S(T)
7.3	3.778	0.530	5220	2.29×10^{-5}
8.3	3.408	0.466	5280	1.68×10^{-5}
8.7	3.356	0.471	5051	1.81×10^{-5}
10.4	4.100	0.592	4953	3.03×10^{-5}
11.7	3.822	0.585	4990	3.32×10^{-5}
12.4	4.121	0.598	5530	3.09×10^{-5}

The electronic excitation temperature in the calcium vapour agrees with that in the barium vapour within experimental errors. The degree of ionization shows a similar trend that is the ionization temperature is lower than that of the excitation temperature and in this case the difference reaches about 2000°K . This could not have been due to errors in Δ , f -values or the length of the vapour column. The arguments about electron density and ionization equilibrium apply as in barium, and the question will be further discussed in section 6.6.

6.5 Mixture of Ba-Ca-Sr Fluorides

The experiment on a mixture of alkaline earth elements was to investigate the degree of ionization in the flash heated vapour without an explicit knowledge of the electron density and the length of the vapour column, both of which are required in the study of the degree of ionization in the vapour of a single element.

The barium and calcium salts were as described in sections 6.3 and 6.4. The strontium fluoride used was of 99.95% purity, and impurities included calcium and magnesium. The experimental conditions (input energy, buffer gas pressure, method of introducing the solid sample and type of carbon foil used) were the same as those in the experiments on barium and calcium fluorides so that the results are directly comparable. The spectral range of the spectrograph was set from 3900-5800 Å.

The number of measurable hooks varied from experiment to experiment although attempts were made to standardize the relative amount of each element used. The variations were probably due to the different grain sizes present in one type of salt. The total vapour pressure was relatively high, which reduced the accuracy in the measurement of the hook separations.

Figure 12 shows one of the spectra obtained. Because of blending of lines of different elements, such as the $4283.10 \text{ \AA}$ line of barium and the $4283.01 \text{ \AA}$ line of calcium, the number of sufficiently isolated and measurable lines was greatly reduced.

The results of measurements of one set of experimental data are given in Table 6.7. E is the energy of the lower state of transition of the line in 10^3 cm^{-1} and $y = \frac{A^2 K}{g f \lambda^3}$ as before. The electronic excitation temperature is calculated from the relative populations of different levels as in section 6.4, using both the Ba I and the Ca I lines. The results of seven sets of measurements are given in columns 2 and 3 of Table 6.8. A blank indicates that the hooks for lines originating on excited states were too weak for reliable measurements. In two cases it was also possible to derive an excitation temperature from strontium (column 4), using the $4811.88 \text{ \AA}$ and $4783.32 \text{ \AA}$ lines originating from the 5^3P^0 level at 14504 cm^{-1} together with the resonance line $4607 \text{ \AA}$.

The ionization temperature is calculated via the functions $S(T)$ for Ba and Ca separately from equation 16 (columns 5 and 6) and for Ba/Ca, Ca/Sr and Ba/Sr mixtures from equation 17 (columns 7, 8 and 9). In using equation 17 the main error comes from the

TABLE 6.7

Ba-Ca-Sr Mixture

Element	Wavelength	E in 10^3 cm^{-1}	Δ in mm	$\gamma = \frac{\Delta^2 K}{g f \lambda^3}$	$\log_{10}(\gamma)$
Ba I	5535	0	1.576	1.60	2.161
	4350	12.64	0.212	2.78	0.444
	4402	12.64	0.232	2.84	0.453
	4505	12.64	0.214	2.76	0.443
Ba II	4554	0	2.477	-	-
Ca I	4226	0	3.280	3.52	2.547
	4289	15.16	0.225	6.32	0.801
	4307	15.21	0.215	5.64	0.751
	4318	15.32	0.237	5.79	0.763
	4425	15.16	0.269	5.57	0.746
Ca II	3968	0	0.769	-	-
Sr I	4607	0	0.827	-	-
Sr II	4077	0	0.529	-	-

TABLE 6.8

Plate No:	Excitation Temperature			Ionization Temperature				
	Ba	Ca	Sr	Eq 16 Ba	Eq 16 Ca	Eq 17 Ba/Ca	Eq 17 Ca/Sr	Eq 17 Ba/Sr
11.7	4940	5042	-	3400	3100	4500	4900	4400
21.4	4581	5300	-	3580	3100	3670	3790	3920
29.3	-	5013	-	3560	2950	3270	-	-
29.5	-	4992	-	3610	2950	3600	-	-
31.5	4948	5016	-	3600	2900	3590	3780	3850
21.6	4480	-	5250	-	-	3600	3800	3560
21.7	4800	-	5480	-	-	4070	3450	3750
Mean Value	4750	5070	5360	3550	3100	3760	3940	3900

measurements of the hook separations (in this case for four lines). A 5% error for each line will lead to an error of 40% in the value of z in equation 17. Assuming the relative f -values of the resonance line of the neutral atom and its ion to be known to an accuracy of 10% for each element, one must add another 20% error to the value of z . This leads to an overall uncertainty of about 20% in the value of the derived ionization temperature.

The excitation temperatures obtained from the three different elements in the mixture agree with each other within experimental error and also with the temperatures obtained in the vapour of the single elements Ba and Ca (Tables 6.3 and 6.6). The tendency for the calcium measurements to yield somewhat higher temperatures than the barium is again apparent, the mean discrepancy in this case being about 300°K .

The ionization temperatures calculated from the mixtures are some 500° higher than those calculated from the single elements but are still about 1000° lower than the excitation temperatures. In comparison with the results of the two previous sections, the calcium ionization temperature is virtually the same while the barium ionization temperature is some 400° lower.

6.6 Summary and Conclusions

The experiments with barium and calcium show that in the flash heated vapour the relative populations of the energy levels within a couple of electron volts of the ground state follow the Boltzmann law of distribution, and therefore a state of at least partial LTE prevails among the moderately excited states of the atoms. For an input energy of 4000 J and a delay time of 500 μ sec, the excitation temperature was about 5000^oK. There was no evidence of shot-to-shot variation and, within the experimental error, the same temperature was obtained from calcium, barium, and a mixture of the two. There appeared to be no difference in behaviour for metastable and non-metastable levels - for example the $^3P_1$ level did not differ from $^3P_2$ and $^3P_0$.

The number density of ions can be calculated directly from the hooks on the ion resonance line and its absolute f-value, if the length L of the vapour column is assumed known. This number turns out to be about $2 \times 10^{13} \text{ cm}^{-3}$ and may be taken as a lower limit for the electron density since (i) L may have been over-estimated by taking it equal to the tube length and (ii) additional electrons may be produced by the ionization of BaF_2 and impurities such as sodium. The criterion for LTE is given by McWhirter (45) as $N_e \geq 1.6 T_e^{\frac{1}{2}} (\Delta E)^3$ where ΔE is the excitation energy in volts. For levels of order 1 eV above the ground state this criterion requires $N_e > 10^{14} \text{ cm}^{-3}$,

but since the criterion may be relaxed if the gas is not optically thin the existence of LTE for these fairly low states seems quite reasonable.

Ionization equilibrium, on the other hand, seems much less likely, because if ΔE is set equal to the ionization potential the minimum value of N_e is raised by a factor of order 200.

In fact, the ionization temperatures found in the vapours of single elements had a rather wide scatter of value, possibly because of variations in the electron density. The ionization temperatures calculated from the mixtures which should be independent of N_e if Saha's equations are valid, were found to be closer to the electronic excitation temperature but still about 1000°K below it. Ionization equilibrium at 5000°K with the known number density of ions ($2 \times 10^{13}\text{ cm}^{-3}$) would require an electron density about 20 times the ion density, which is extremely unlikely.

The experiments therefore show that the flash heated vapour may be used for determinations of relative f -values of lines from different moderately excited states of an atom (and probably also of an ion) but it is not possible without further investigation to relate populations of atomic states to those of ionic states.

CHAPTER 7

MEASUREMENT OF RELATIVE OSCILLATOR STRENGTHS IN THE SPECTRUM OF YTTRIUM

The experiment described in this chapter demonstrates the feasibility of applying the flash pyrolysis - hook technique to the measurement of relative f -values. For this purpose it is desirable to choose an element whose vapour pressure is too low for ordinary furnace techniques and whose f -values are of intrinsic interest. For use with this particular apparatus it was also necessary that it have reasonably well-separated lines in the blue-violet and near ultra-violet part of the spectrum. These conditions are fulfilled by yttrium.

Yttrium is an astronomically important element. 47 lines of Y I have been identified in the solar spectrum. No experimental determinations of oscillator strengths have been carried out for either the Y I or Y II lines. The only theoretical determination is by Krueger, Aller and Czyzak (45), using the Hartree-Fock self-consistent field wave functions to obtain the transition probabilities of the permitted lines involving the $5s^2$, $4d5s$, $4d^2$, $4d5s$, and $5s5p$ configurations of Y II. The derived gf -values were then used to calculate the solar abundance of yttrium, which was found to be about two orders of magnitude smaller than that calculated from empirical gf -values of Y I.

The theoretical gf-values of Y II were also found to be an order of magnitude different from the empirical gf-values obtained by curve of growth methods for Sirius and a number of A stars with Y II lines. There is thus a clear need for accurate experimental f-value determinations.

7.1 Experiment

As no suitable solid samples in the form of foil or powder were available, yttrium oxide was used. This was in powdered form, and had a purity of 99.99%. The sample was supported on 100 microns thick carbon foil by a thin layer of glue.

Figure 22 shows some of the spectra obtained. (a) (i) (ii) and (iii) show the spectrum in the wavelength range from 3500-4200 Å in order of decreasing vapour density at a delay time of 500 usec and an input energy of 4000 J (100 uF at 9 kV). The number of observable lines varies greatly with the vapour density. The six lines indicated in (a)(iii) are transitions from the ground and the first excited states of Y I, $4d\ 5s^2\ ^2D_{3/2, 5/2}$, and are the lines actually measured in this pilot experiment. (b) and (c) show the spectrum in the range from 3200-3500 Å and 2900-3100 Å. In (b) the 3216, 3242 and 3327 Å lines are transitions from excited states of the ion with energies between 1000 and 3300 cm^{-1} above the ground state. The complications arising from blends are illustrated by the lines at 3549 Å and 3552 Å, one of

Fig. 22 Spectrum of Y I and Y II

a(i)

a(ii)

a(iii)

3592Å

3620Å

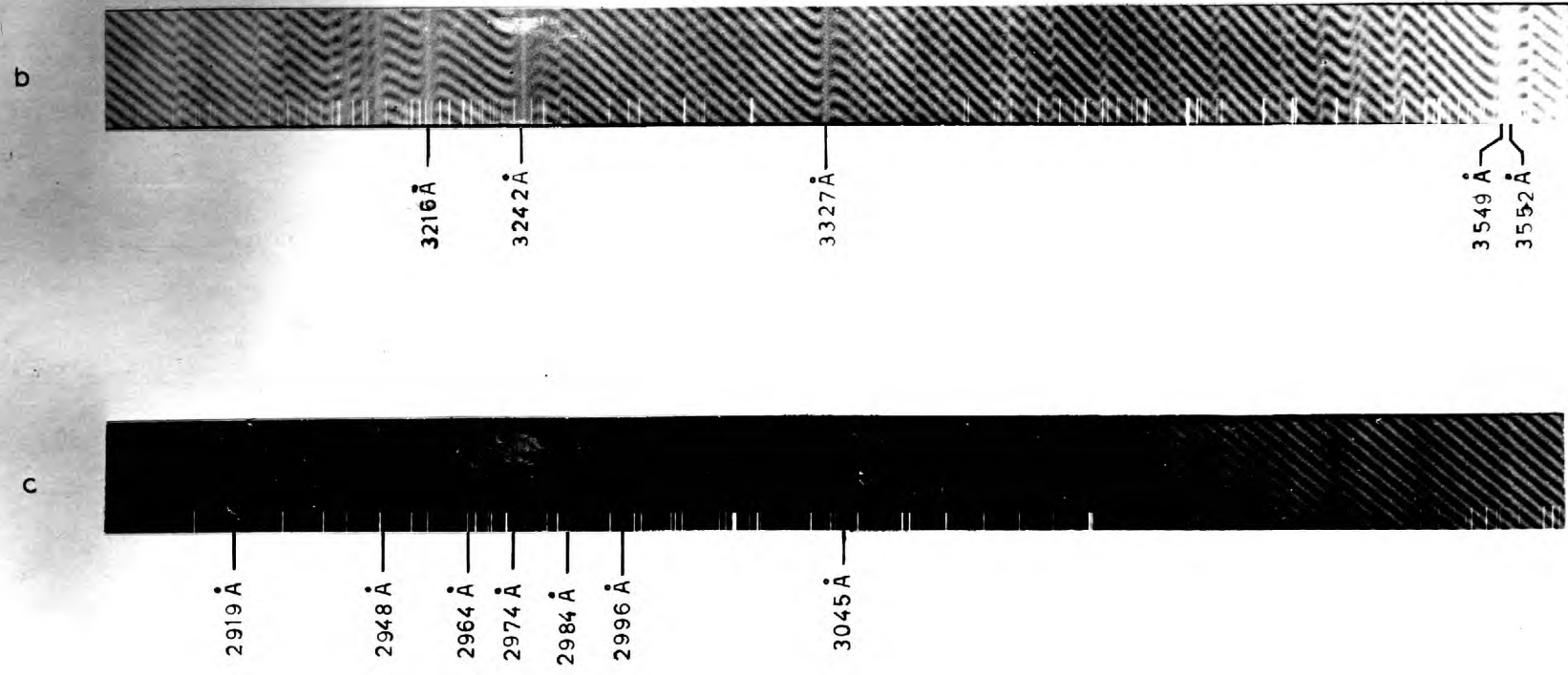
4077Å

4102Å

4128Å

4142Å

Fig 22 Spectrum of Y I and Y II



which belongs to Y I and the other $\lambda_{\bar{0}}$ Y II. In (c) the seven lines indicated are from the ground state doublet, $^2D_{3/2, 5/2}$ of Y I (doublet splitting 530 cm^{-1}). The spectra (b) and (c) were obtained at different vapour densities. Spectrum (c) corresponds to the vapour density of the second spectrum in (a).

With the quartz optics of the spectrograph, the spectral range $3500\text{--}4200 \text{ \AA}$ is covered on 7 cm of a 25 cm long photographic plate and it is estimated that in this spectral range there are well over 60 lines of Y I and Y II, including nearly all the strong lines. A complete and accurate experimental determination of f-values for all these lines must await the use of a spectrograph of larger dispersion.

7.2 Results

The six strongest accessible lines of Y I were chosen for measurement. The results of ten sets of experimental data are given in Table 7.1. Column 1 gives the wavelengths of the lines measured. Columns 2 and 3 give the term designations and the energy of the lower state transition in cm^{-1} . In column 4 the relative f-values of lines with the same lower state are given. Column 5 gives all the f-values relative to the strongest line, $4102 \text{ \AA}$, after taking into account the relative populations of the ^2D levels, assuming an electronic excitation temperature of 5000°K .

TABLE 7.1

λ in Å	Terms Designation	Energy cm ⁻¹	f/f ₄₀₇₇	f/f ₄₁₀₂
4077.38	$4d^1 5s^2 {}^2D_{3/2} - 4d^1 5s^1 5p^1 {}^2F_{3/2}^0$	0	100	98 ± 7
4142.85	$4d^1 5s^2 {}^2D_{3/2} - 4d^1 5s^1 5p^1 {}^2D_{3/2}^0$	0	88	91 ± 11
3592.92	$4d^1 5s^2 {}^2D_{3/2} - 4d^1 5s^1 5p^1 {}^2P_{1/2}$	0	58	61 ± 8
			f/f ₄₁₀₂	
4102.38	$4d^1 5s^2 {}^2D_{5/2} - 4d^1 5s^1 5p^1 {}^2F_{5/2}^0$	530	100	100
4128.31	$4d^1 5s^2 {}^2D_{5/2} - 4d^1 5s^1 5p^1 {}^2D_{5/2}^0$	530	89	89 ± 7
3620.94	$4d^1 5s^2 {}^2D_{5/2} - 4d^1 5s^1 5p^1 {}^2P_{1/2}$	530	56	56 ± 4

The errors given in the last column are the r.m.s. deviations from the ten results.

The magnitude of the hook separations was of the order 0.4-0.6 mm, and this was measured to an accuracy of 5-7%. This leads to an error of about 10-15% for the f -value of a line relative to the "standard" from the same lower level. The reduction of the two sets of f -values to the same standard by the Boltzmann distribution would add at most another 5% to the uncertainty in the relative f -values. Since the levels are separated by only 530 cm^{-1} , the population distribution is not very sensitive to uncertainties in the temperature when $kT \sim 3500 \text{ cm}^{-1}$.

It should be emphasized that it is possible to obtain f -values for many more of the Y I lines that appear on the present exposures. Because of the time involved in making the measurements, however, it was necessary to limit the pilot experiment to the above six lines, which suffice to establish the feasibility of the method. Furthermore, relative f -values for a large number of Y II lines could also be obtained from these same exposures. The results of Chapter 6 have shown, however, that it is not possible at present to relate relative f -values in YII with those in Y I. Further research into this problem is needed, it might, for example, be possible to mix yttrium with an element of closely similar ionization potential and use a procedure similar to that in section 6.5.

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