CHAPTER III

EXPERIMENTAL TECHNIQUES

Experimental technique of excitation of band spectra and recording them plays a vital role in the investigations on the spectra of molecules. The probability of obtaining an expected band system depends upon the proper selection of the source to excite it and hence a knowledge of the various spectral sources employed in the production of band spectra is essential. Various types of sources have been known to excite the molecules to give rise to their band spectra in emission. They extend from a gentle open flame to a large variety of electric discharges. Among the latter electric arcs, electric sparks and a variety of ionic discharges at low pressures are frequently employed.

The flames are known to yield band systems since very long. The band spectra of C_2, CH and OH are readily excited in flames which are due to the direct combustion of inflammable substances. The analyses of these band spectra have shown that only low-lying electronic states are involved in the transitions. The lowest electronic state is usually the ground state of the molecule and the upper state energy rarely exceeds 5 e.v. Excitation in flames takes place as a result of the collisions between atoms and molecules. The main disadvantage of a flame source in the production of band spectra is that the substance should be kept in the gaseous state within the flame.

As the electric arcs produce higher temperatures they are more suitable for the excitation of spectra of the substances whose melting points are very high. The arcs can impart more energy to the molecules and as a result higher energy levels are excited and consequently more number of band systems appear in arcs than in the flames. The current density and the material of the electrodes producing arc are the major factors for the proper excitation of the spectra.

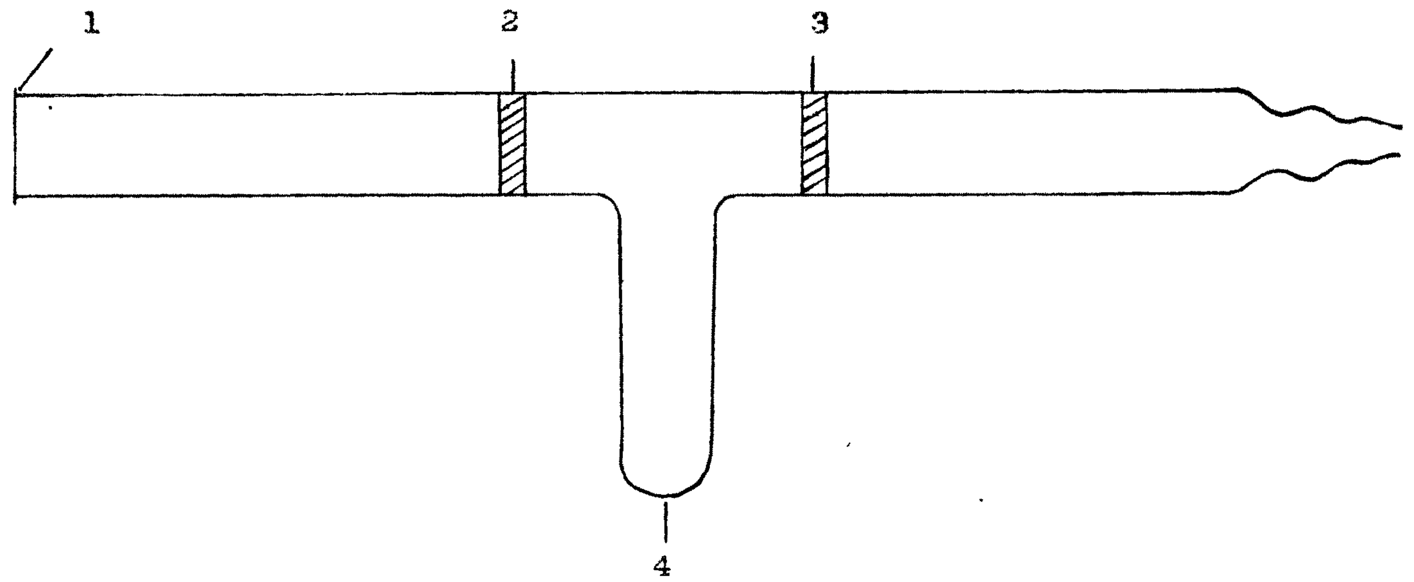
Among the spark sources the uncondensed discharge is commonly used for exciting the band spectra. The condensed discharge is usually not preferred as it also gives rise to a number of atomic lines.

It is well known for several years that discharge tubes can be used very conveniently as a source of exciting the molecular spectra. It offers a larger scope for varying the conditions of excitation and also can be maintained steady for any desired length of time. Geissl~~a~~er discharge tubes are most suitable for gases or substances having appreciable vapour pressure at low temperatures. The positive column and negative after-glow in such discharge tubes are responsible for most of the emission of light and they are utilized for production of the spectra. In such sources the spectra result due to uncharged atoms and greater number of excited states are possible as compared to arcs and flames. In the present investigation on the spectra associated with the halides of mercury, the high frequency oscillatory discharge sources were found to be most suitable and in what follows the techniques adopted are described in detail.

(i) THE DISCHARGE TUBE AND VACUUM SYSTEM:

The discharge tubes of conventional type were used as the source. The substances under investigation are having low melting points (< 300°C) and hence pyrex discharge tubes could be employed with a cavity at the centre. Discharge tubes having length 30 cms. and internal diameter 1.5 cms. with a central cavity of 4.0 cms. length and the diameter as that of the main tube were found most convenient. One end of the tube was provided with a knurling to connect it to the vacuum pump with rubber tubes and the other end was closed by fixing a thin quartz window to allow the transmission of ultraviolet radiations. Apiezon wax was used in sealing the window. Fig.1 represents a schematic diagram of the pyrex discharge tube.

The substance under study was kept in the central cavity of the discharge tube. Continuous evacuation of the discharge tube was done till the steady conditions of the source were attained by means of a Cenco-Hyvac pump which can give an ultimate vacuum of 0.1 micron. A tower containing sodium hydroxide pellets and an ice-cooled trap were kept intermediate between the discharge tube and the vacuum pump to minimise the contamination of the pump oil caused by the vapours from the discharge tube. The connections by rubber tubing in the evacuating system were kept as small as possible to increase the vacuum. Both the ends of the discharge tube were kept water-cooled by keeping water-soaked cotton-wool near them to cool down the vapours of the substance before reaching the transmitting window or the pump line of the



1. QUARTZ WINDOW
2.&3. COPPER FOILS
4. CENTRAL CAVITY

Fig. 1

PYREX DISCHARGE TUBE

evacuating system. As mentioned earlier the substances are having low melting points and hence the heat of the discharge itself was found sufficient to vapourise them. However, intermittent heating with a burner was necessary to maintain the characteristic colours and conditions of the discharges.

(ii) THE HIGH FREQUENCY OSCILLATOR:

The high frequency oscillator employed in the present work was fabricated in this laboratory. Fig. 2 shows a schematic diagram of the arrangement used. A variac which could work at 220 volts at 4 amps. is used to regulate the voltage applied to the high tension unit (H.T.). The output voltage is applied to the oscillator (O) and the high frequency current is generated which is then fed to the discharge tube by means of external electrodes E_1 and E_2.

(a) The High Tension Unit:

The circuit diagram of the power supply for the oscillating unit is shown in Fig. 3. The power transformer T_2 delivers 1500-0-1500 volts in its secondary. This output voltage is then rectified by means of two RCA 866 A high vacuum mercury rectifiers. The rectified voltage is filtered using a choke input filter system. A bleeder resistance R_B ($R_1 = R_2 = R_3 = 25{,}000$ ohms) is connected across the output of the high tension.

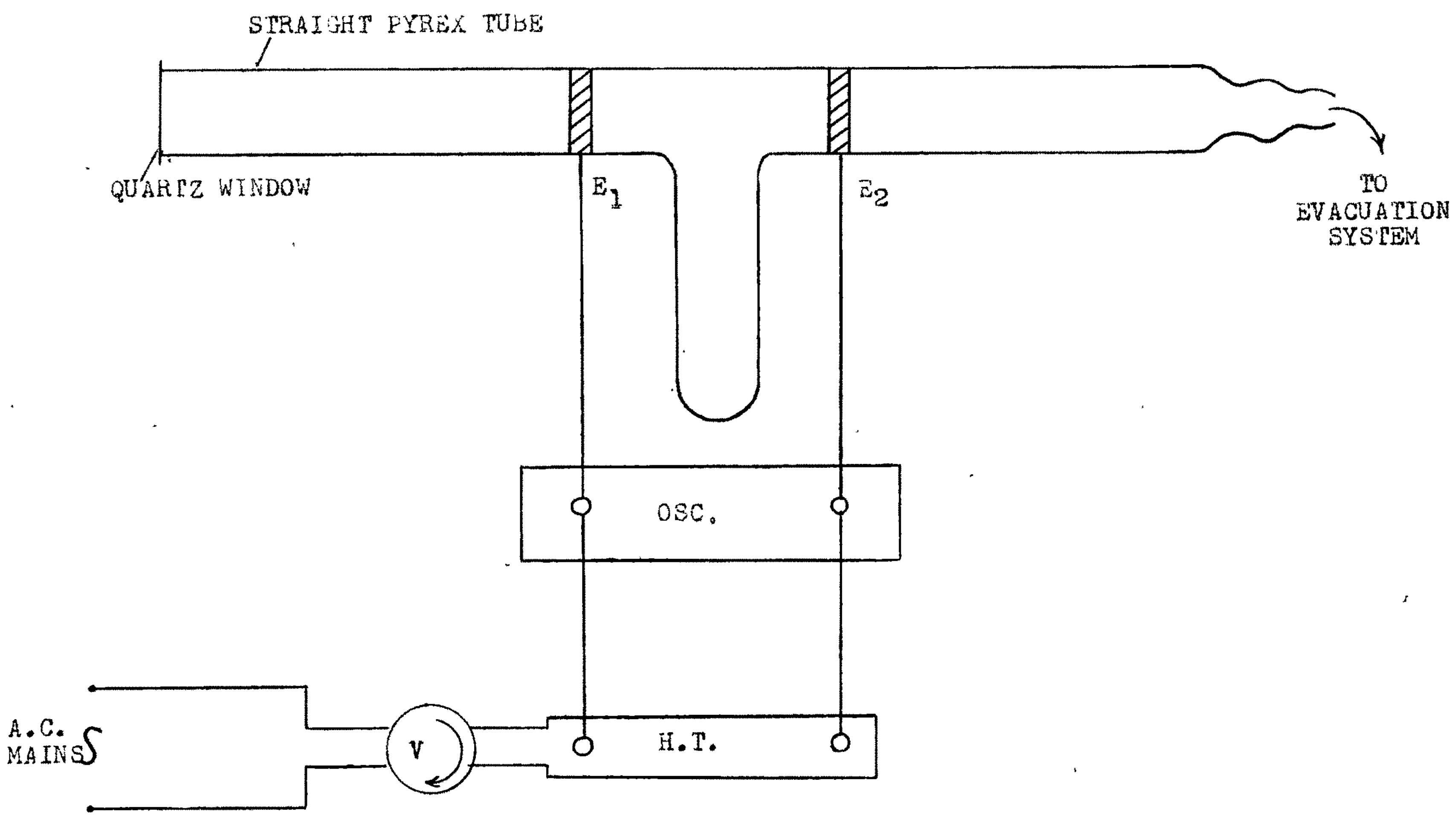

STRAIGHT PYREX TUBE
QUARTZ WINDOW
E_1
E_2
TO
EVACUATION
SYSTEM
OSC.
H.T.
V
A.C.
MAINS

Fig. 2

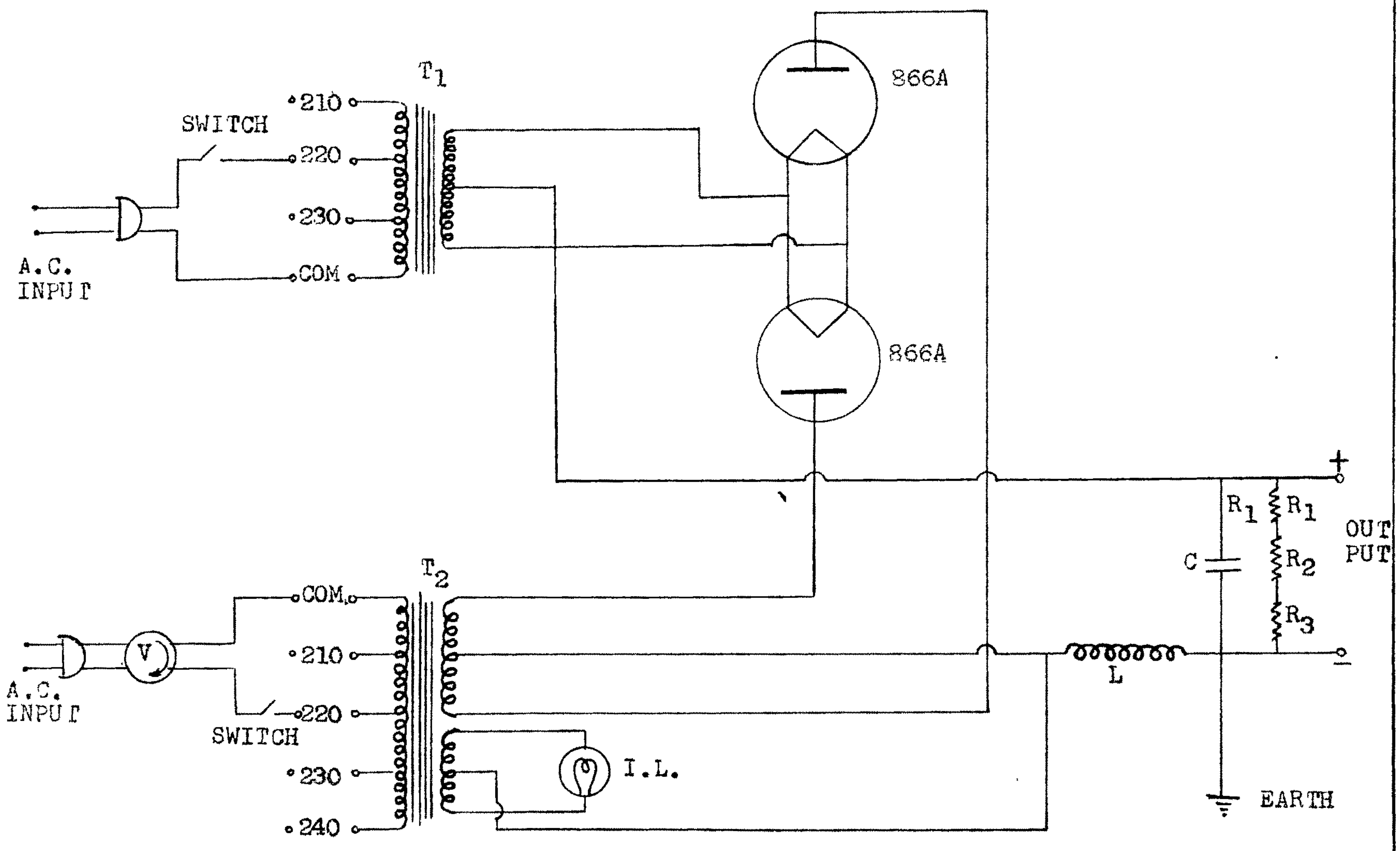

T1
210
220
230
COM
SWITCH
A.C. INPUT
866A
866A
T2
COM.
210
220
230
240
SWITCH
A.C. INPUT
V
I.L.
+
R1
R1
R2
R3
C
OUT PUT
L
−
EARTH

Fig. 3

(b) The Oscillator:

The series fed push-pull type of Hartley oscillator is shown in Fig. 4. The two power tubes 811 are connected in push-pull circuit as shown in the figure. A low voltage transformer T_3 delivers 6.3 volts at 4.0 amps. suitable for the filaments of the valves. A tank circuit consisting of a transmitting type variable air condenser and an inductance coil generates oscillations. The desired range of the frequency of oscillations was obtained by preparing coils with different number of turns and with various diameters. and the maximum output power was obtained by the proper matching of the coil with the condenser. The output from the tank circuit was fed to R.F. chokes r_1 and r_2. Thus the oscillator unit is fabricated to give an output power of 125 watts at the frequency range 6.5-20 Mc./sec. The oscillator is coupled to the discharge tube at E_1 and E_2 by short leads.

It will be appropriate at this stage to mention some of the salient features of the high frequency discharge for the study of band spectra.

The molecule in the gaseous state may be excited in a low pressure discharge tube either by electrode or electrodeless discharge. The presence of electrodes within the tube causes the 'life' of a gaseous ion to be short-lived

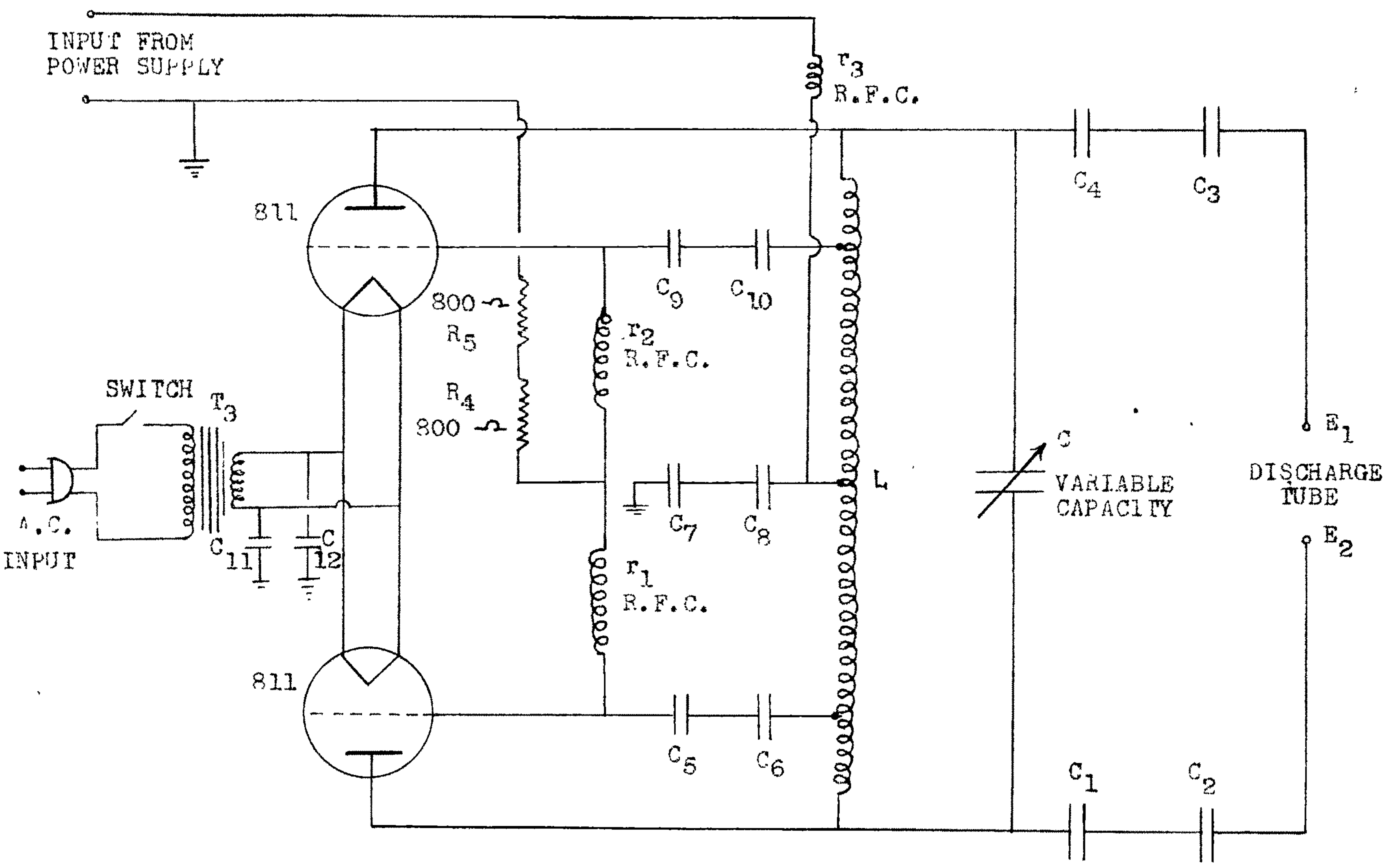

INPUT FROM
POWER SUPPLY
r_3
R.F.C.
C_4
C_3
811
800 Ω
R_5
R_4
800 Ω
C_9
C_{10}
r_2
R.F.C.
SWITCH
T_3
A.C.
INPUT
C_{11}
C_{12}
C_7
C_8
L
C
VARIABLE
CAPACITY
E_1
DISCHARGE
TUBE
E_2
r_1
R.F.C.
811
C_5
C_6
C_1
C_2

Fig. 4

on account of the constant difference of potential between the electrodes. This can be minimised by using the alternating potentials or it may be almost entirely removed by applying the radio frequency oscillations to the discharge tube by means of external electrodes. The external electrodes are connected to a coil which carries a high frequency current generated by a thermionic oscillator valve. The high frequency electric field provides enough electron velocity to excite the molecules of a gas at low pressure. Electron velocity which can be varied by adjusting the field strength and the pressure inside the discharge tube enables the conditions for excitation of higher energy levels of the molecules. In fact, the energy available for excitation is governed by the factors such as the pressure inside the tube, the frequency of oscillations and the voltage across the electrodes. In the main process of excitation only the normal states of the emitter are involved, the excitation by collisions of other types appears to be too feable.

(iii) SPECTROGRAPHS:

Two different types of spectrographs were employed for recording the spectra of the molecules under investigations. As the present work was confined to the ultraviolet region a Hilger medium quartz spectrograph having a dispersion of about 10 A°/mm. at 2650 A° was used for the preliminary survey of the band systems of mercury chloride, mercury bromide and mercury iodide. A two-metre Carl Zeiss plane grating spectrograph was employed to photograph the spectra of these molecules at high dispersions for detailed study. The grating spectrograph has a fine slit which can be narrowed upto nine microns with the attachments provided for adjustment of the tilt and the height of the spectrum to be recorded. The grating used in the plane grating spectrograph has got a saw-tooth profile and concentrates the radiations in a preferred angular direction, the position of which depends upon the rake angle of the grating grooves. This special property of the grating is known as the 'Blaze property' and the rake angle of the grating grooves as the 'Blaze angle' of the grating. The grating having a blaze angle = 5.6° which concentrates most of the radiations around 3000 A° in the first order was used. However, to record the second order spectra at higher dispersion, the grating with a blaze angle = 10.7° which is capable of throwing maximum radiations around 3100 A° in the second order was employed. Both the gratings were having 651 number of grooves per mm. and were readily interchangeable. They were rotatable and can be set very easily for desired wavelength regions and different orders of the spectrum. These gratings provide dispersions of about 7.3 A°/mm. and 3.69 A°/mm. in the first and second order respectively. The optical principle of the spectrograph is the Ebert mounting of the plane grating with mirror optics. The rays travel from slit to a deflecting mirror and to the lower section of a large concave mirror where they are aligned in parallel and reflected towards the grating. After diffraction at the reflection grating the dispersed rays strike the upper section of the concave mirror which after recombination of the parallel rays produces a well focussed spectrum in the plane of the photographic plate above the grating. The spectrograph is equipped with a supplimentary device that enables the rays to impinge on the grating twice, thereby offers double the dispersion produced previously. Thus with the use of double passage equipment the spectrograph has a dispersion of 3.69 A°/mm. and 1.85 A°/mm. in the first and second order respectively. While recording the spectra it was found necessary to introduce appropriate filters to avoid the overlapping of other different order spectra.

(iv) COMPARISON SPECTRUM AND MEASUREMENT OF BANDS:

For obtaining the wavelength data of the spectrum under investigation a comparison spectrum of iron arc running at 110 volts at 4 amps. was recorded in juxtaposition with it. The iron spectrum is extensively used for comparison because of the convenience and simplicity associated with it in addition to the fact that it gives large number of lines in the visible and ultraviolet regions of the spectrum. The iron electrodes of the arc tend to form a bead of oxide at the anode and hence the lower electrode was connected to the positive terminal.

The iron secondary standards adopted by the International Astronomical Union in 1928, 1932 and 1938 (Sawyer, 1951) were selected from the Hilger charts (Hilger & Watts, London). The M.I.T. Wavelength table (Harrison, 1939) was also occasionally used.

The measurements of the plates were carried out on a comparator with a screw accurate upto 0.001 mm. In the analysis of the prism spectrograms the Hartmann interpolation formula was used for the determination of wavelengths. For wavelength determinations of the grating spectra, a standard line λ_1 in the reference spectrum was selected and by utilizing it in the following formula, wavelength (λ) of an unknown line or band can be found as follows:

$$\lambda_m(x) = \lambda_m(x_1) \pm \Delta x \, D_m\left(\frac{x_1+x}{2}\right)$$

where $\Delta x = x_1 - x$ is the distance between the two lines $\lambda_m(x_1)$ and $\lambda_m(x)$ and $D_m\left(\frac{x_1+x}{2}\right)$ is the reciprocal linear dispersion midway between the two lines. The formula is accurate for the distance $\Delta x = 20$ mm. and a correction was applied for larger distances. The wavelengths reported in the thesis are the averages of the three different sets of observations and the measurements are accurate upto 1 cm^{-1} or sometimes better.