CHAPTER 3

EXPERIMENTAL TECHNIQUES

In the study of the band spectra of molecules, experimental set up plays a vital role. This consists of the fabrication and assembly of the apparatus and the use of a suitable source to excite the molecule. In the following pages are given a brief report of the sources and their use to estimate the probability of appearance of the spectra under favourable conditions and the designing and assemblying of the apparatus required for this purpose.

SOURCES

In flames, the excitation is gentle and occurs mainly as a result of collisions between atoms and molecules and the band systems obtained in flame sources are due to transition between a few of the lowest levels of the molecule concerned. The energy

of the upper level involved is limited. Most of the band systems obtained with flame sources belong to molecules which are electrically neutral. Flame sources are suitable for those molecules which require gentle stimulus and which easily get dissociated in other sources.

The arcs are excited at higher temperatures and are therefore more suitable for substances which are not so volatile. Since sufficient energy is available in collision processes, comparatively larger number of band systems appear in arc spectra than in the flame spectra. There are however some limitations which arise from factors such as pressure, material of the arc etc.

Among the spark sources the uncondensed discharge is most common for the production of band spectra. The condensed discharge due to its violence is not suitable for production of band spectra because it also gives rise to a number of atomic lines. The bands obtained in uncondensed discharge contain less atomic lines and shorter branches. The appearance of shorter branches facilitates the vibrational analysis of the system under consideration.

The use of a discharge tube as a source for getting molecular spectra is very common. Its utility lies in offering a greater scope for the variations of conditions of excitation with an additional advantage of steadiness. Geissler tubes are best suited for use with gases or materials with appreciable vapour pressures at fairly low temperatures. In such tubes the most luminous parts are the positive column and the region of negative glow and the spectra are usually recorded from these two regions. The spectra obtained are usually of uncharged atoms and the number of excited states reached is greater than in the flame or an open arc in air. The excitation is mainly due to electron impacts. The higher stages of excitation are reached by lowering the pressure and increasing the intensity of the field. The detailed considerations of these factors will be considered later on.

Since the aim of the present investigation was to study the band spectra mainly in the visible region and because the bands are highly diffuse and appear on a continuum, it was therefore thought desirable to use a source in which these bands develop

better. In the beginning a few attempts were made to obtain these bands in a transformer discharge, but the continuum which accompanied them completely vitiated the bands. Since for obtaining the diatoms the triatomic compounds were available and on heating them the free Cl_2, Br_2 and I_2 vapours were expected, a very low vapour pressure discharge was therefore preferable to avoid the continuum and other impurity bands. Low vapour pressure high-frequency discharge was therefore selected for the purpose and the transformer discharge was not used. In what follows will be described,

(i) The evacuation system and design of the discharge tube.

(ii) Excitation unit - high-frequency oscillator.

(iii) Instruments etc. used for obtaining the spectra.

(i) THE EVACUATION SYSTEM AND DISCHARGE TUBES

With the applied voltages permissible a Geissler discharge generally ceases at pressures below 0.1 mm of mercury, whereas the high-frequency discharge

may persist down to a pressure of 10^{-5} mm. of mercury, if started at higher pressures. Since the bands under study appear better in low pressure conditions in a high-frequency discharge the evacuation system must be efficient enough to give that much order of pressure. Cenco-Hyvac 2 pump which can go upto a pressure of 10^{-4} mm. was therefore selected for the purpose. An absorption tower containing sodium pallets and one ice-cooled trap enabled the harmful vapours to be absorbed before they could go to the pump. The dimensions and shape of the joints were so adjusted that the pumping speed may not be appreciably affected.

Since all the halides under investigation melt and evaporate at higher temperatures (ranging from 700°C to 900°C) it was necessary to use quartz glass as the material of the discharge tube. Transparent silica tubes were used for the purpose. To avoid much of the blowing a straight tube was selected. A quartz or a glass window was sealed at one end by Apiezon Q.wax. Tubes of length of about 30 cm. and internal diameter of about 1.5 cm were found highly convenient. At the other end of the tube was sealed a pyrex attachment which was provided with a side

tube for connection to pumping system. The adaptor was sealed on the tube by Apiezon Q.wax. The substance was kept at the centre of the tube in quartz boats made from small diameter silica tubes. Two thin foils of copper about 1.5 cm. in length were wrapped outside the main tube for connection to the output of the oscillator. The design of the tube is shown in fig. (1).

(ii) EXCITATION UNIT

The unit of the high frequency oscillator for obtaining electrodeless discharge was assembled in the laboratory and is described here in detail. fig. (2) shows the schematic diagram of the arrangement of the high frequency oscillating system. V is a variac to regulate the voltage out put of high tension. The variac is capable of delivering voltages of the order of 220-230 at 4 amp. The high tension is supplied to the oscillator O, the resulting high frequency voltage is then applied to the evacuated discharge tube at E_1 and E_2 by using short pieces of lead wires. The component parts of the circuit are described below.

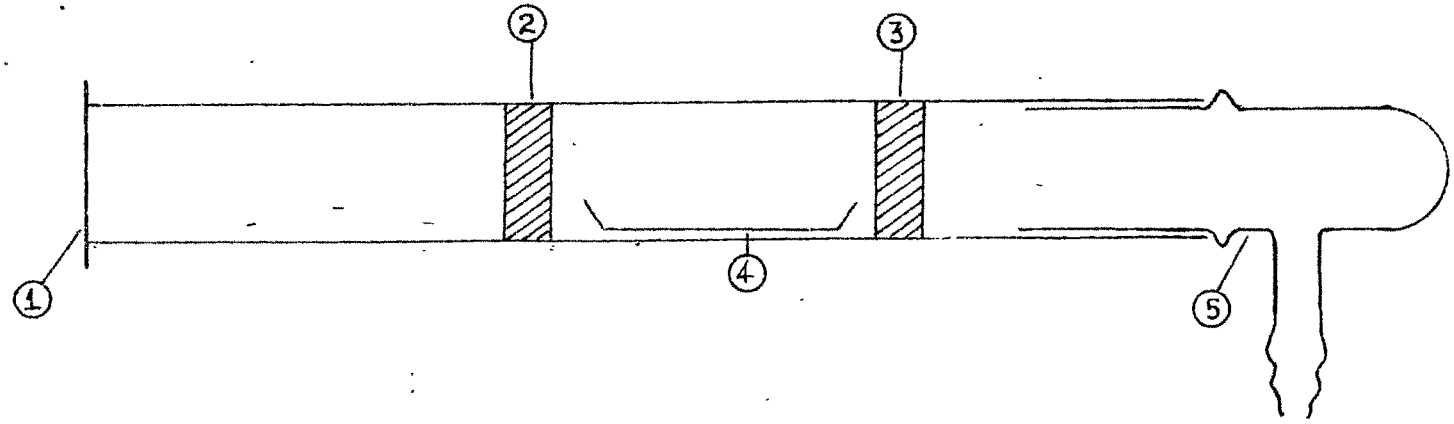

FIG. (1) QUARTZ - PYREX DISCHARGE TUBE

① QUARTZ WINDOW

②-③ COPPER FOILS

④ QUARTZ BOAT

⑤ PYREX ATTACHMENT

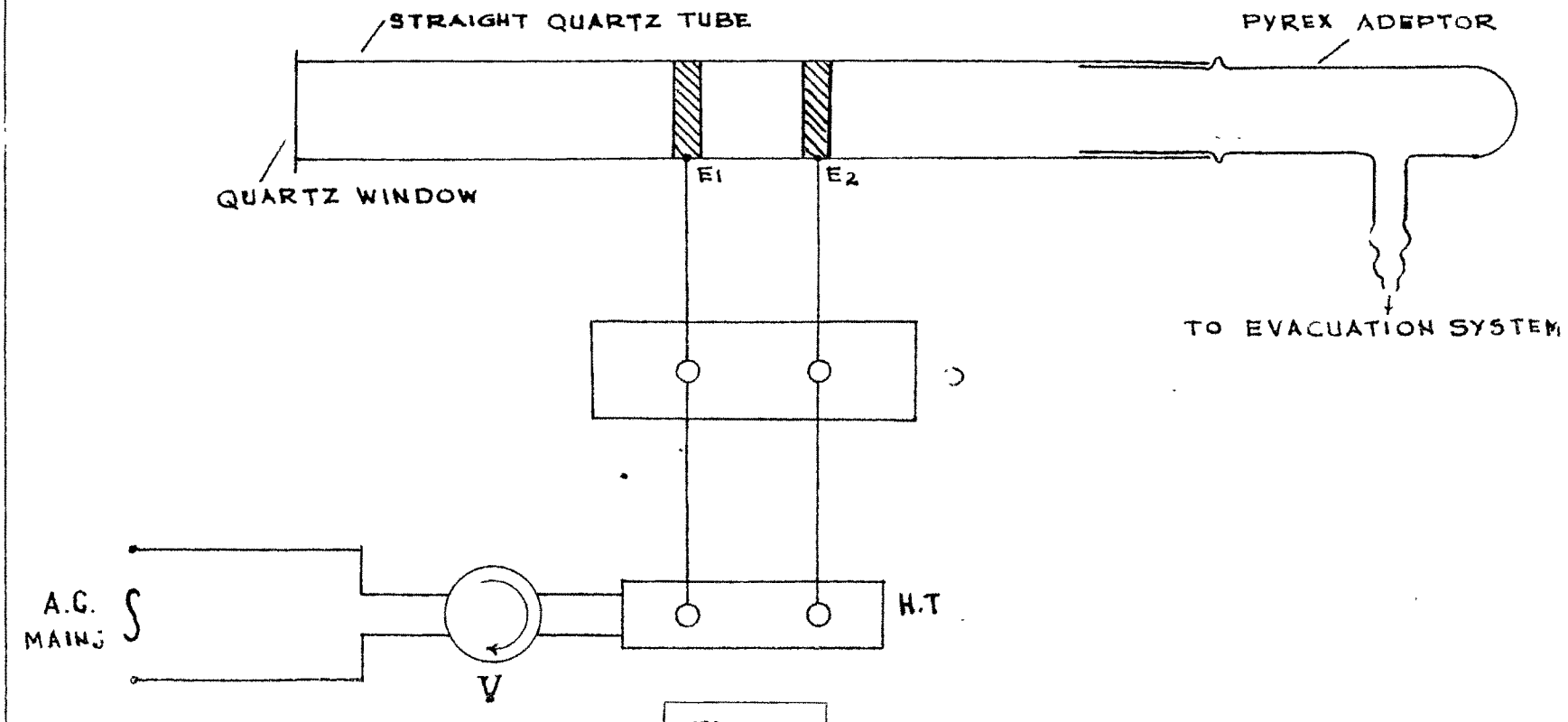
STRAIGHT QUARTZ TUBE
PYREX ADEPTOR
QUARTZ WINDOW
E1
E2
TO EVACUATION SYSTEM
A.C. MAINS
V
H.T

Fig. 2.

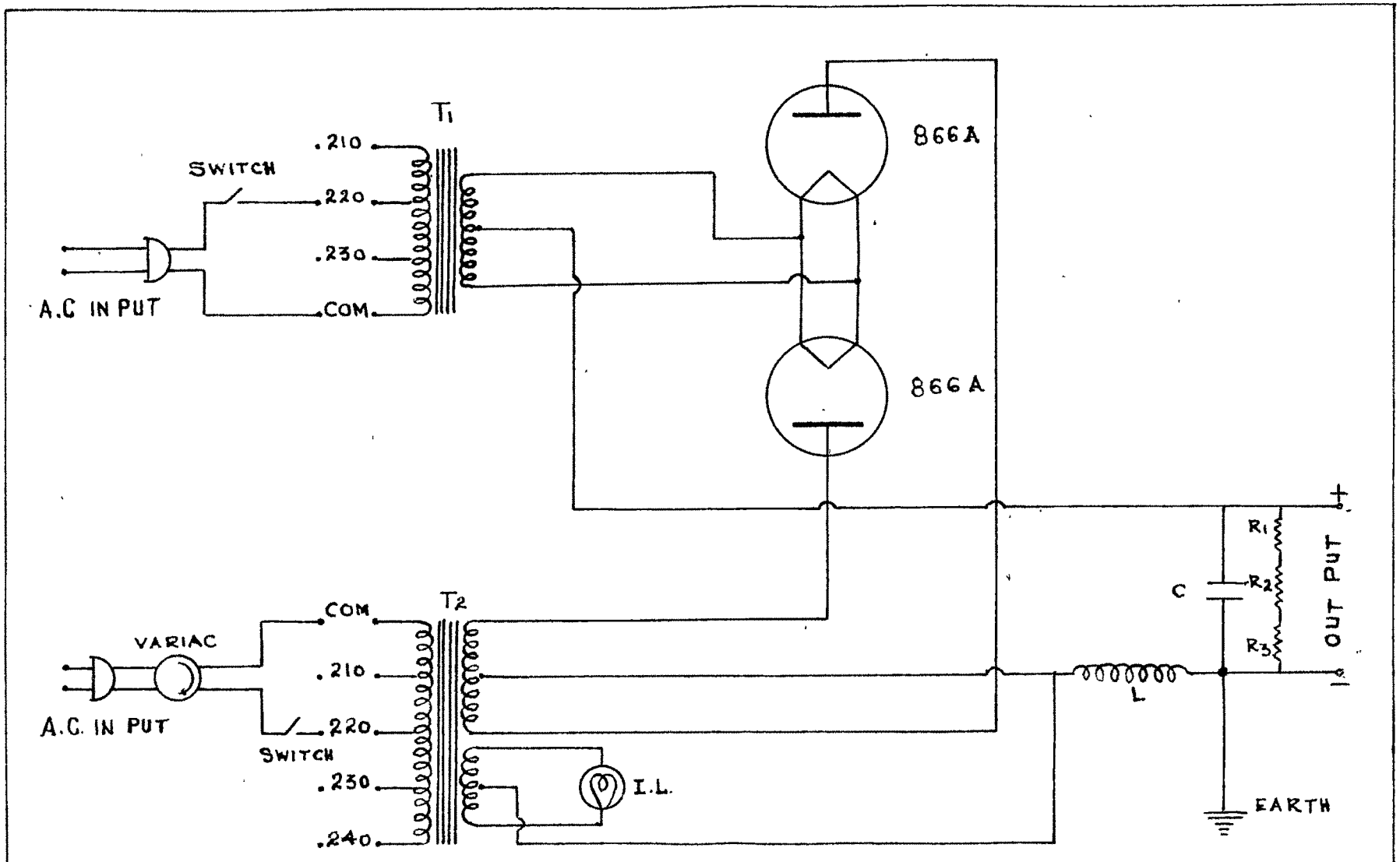
T1
.210
SWITCH
220
.230
COM
A.C IN PUT
866A
866A
T2
COM
VARIAC
.210
A.C. IN PUT
220
SWITCH
.230
.240
I.L.
L
C
R1
R2
R3
+
OUT PUT
-
EARTH

Fig. 3.

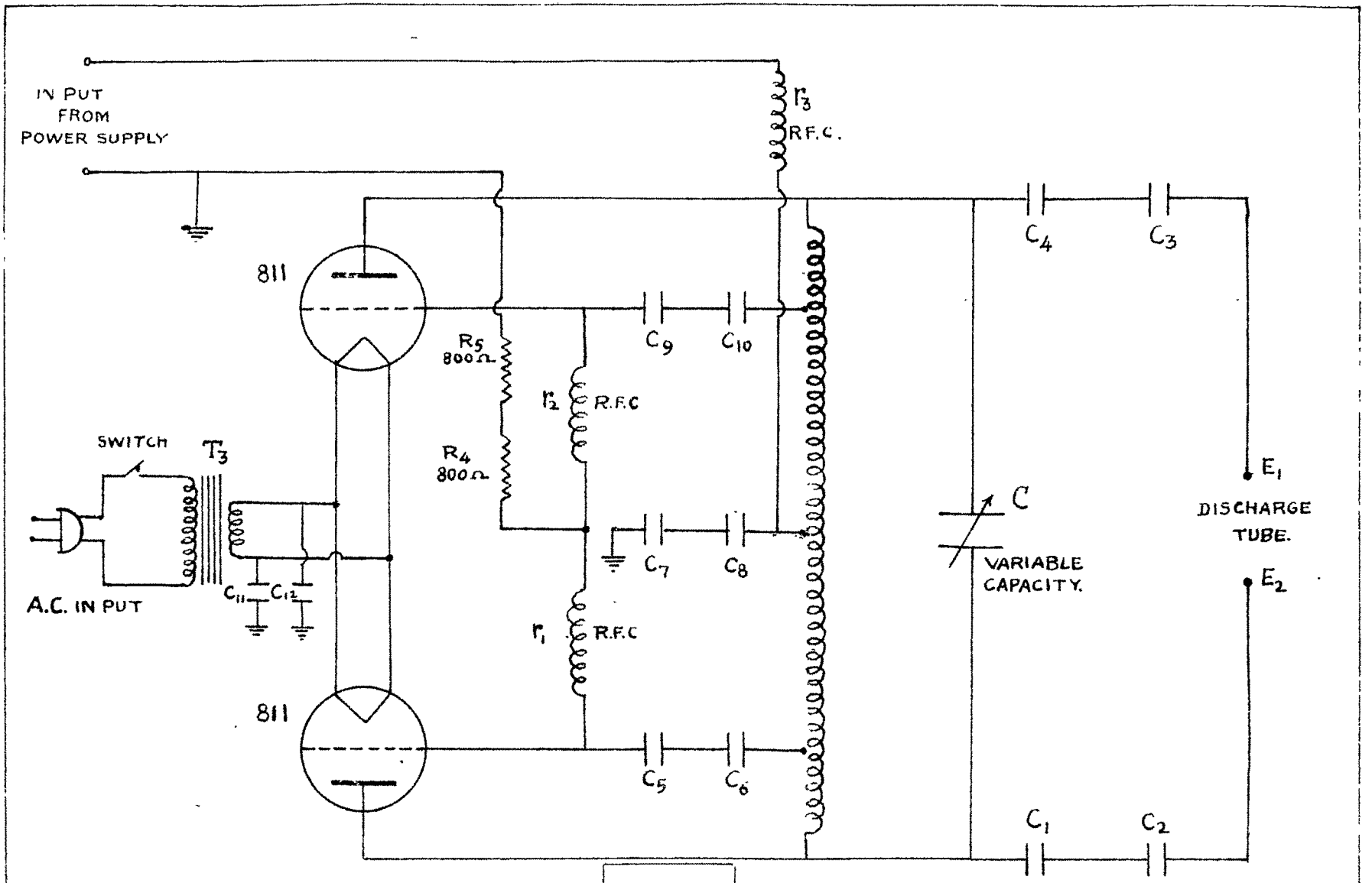
IN PUT
FROM
POWER SUPPLY
r3
R.F.C.
811
C4
C3
C9
C10
R5
800Ω
r2
R.F.C
R4
800Ω
SWITCH
T3
C
E1
DISCHARGE
TUBE.
C7
C8
VARIABLE
CAPACITY.
E2
A.C. IN PUT
C11
C12
r1
R.F.C
811
C5
C6
C1
C2

Fig. 4.

The oscillator is coupled to the discharge tube at E_1 and E_2 by leads taken from tank coil L. These leads are brought on the top of the oscillator using good insuator blocks.

It was possible to obtain a power of about 100 to 125 watts with the above arrangement of the oscillating unit.

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

The R. F. discharge is considered to be a very good source for the excitation of molecular spectra. It allows one to obtain within the gases intense currents with relatively weak electric fields and that the molecule can be excited without dissociating it significantly.

Two aspects of the high frequency discharge need a mention. In one aspect we try to study the mechanism of discharge by knowing the electrical quantities which control the discharge, the composition of plasma and the chemical reaction which take place in it. The

other aspect deals with use of discharge mainly as a source of light and its spectroscopic analysis. In reality both these aspects are complimentary because the spectrum emitted is dependent on the electric parameters. When the second aspect is to be investigated it is desirable to use damped oscillations of high frequency.

It has been observed that the chlorides and bromides emit band spectra easily in the arcs but the iodides easily get destroyed in these conditions. On the other hand in a discharge of high frequency it has been observed that the bands of iodides appear with fairly good intensity and purity. This gentle excitation favours the production of molecular spectra in certain cases, since there is little tendency to violent dissociation.

For high frequency discharge no internal electrodes are required. This considerably simplifies the tube design especially when quartz tubes are used. This simplicity of design enables very high vacuua to be obtained with little difficulty. This factor is of importance especially when very low vapour pressure discharge is to be maintained. Also when chemically

active vapours are under examinations, grave complications are introduced when they attack the metal electrodes. To maintain the proper condition of the discharge heating of the salt was done by strong burners. The colour of the discharge was different with different compounds. In case of CdCl and CdBr it was bright white in colour while in the case of CdI it was golden yellow. These conditions were maintained by careful heating throughout the course of exposure.

(iii) INSTRUMENTS USED FOR OBTAINING THE SPECTRA

Having selected the source for producing the spectrum, it is necessary to utilise an appropriate instrument for recording the spectrum. The choice of the instrument depends upon the region under investigation, dispersions required and the stability of the source.

The laboratory was equipped with only three instruments viz. (a) Hilger medium quartz spectrograph (b) A Hilger E_2 - Glass spectrograph and (c) a Hilger constant deviation spectrograph. The medium quartz spectrograph had a dispersion of about 10 A.U./mm at 2650 A.U. This was mainly used for the investigation

of spectra in the ultra-violet region. Since the study involved a comparison of the various systems of the allied molecules regarding their positions in different spectral regions, the dispersion in any way was not a serious drawback. The major aim of the study in this region was to examine if any additional systems appear and to establish correlations between the various systems of CdCl, CdBr and CdI. An accurracy of $\sim 1 cm^{-1}$ can easily be achieved depending however upon the sharpness of the heads and the grain size of the plate. Wherever speed was essential Ilford Zenith plates were used for photographing the spectra. The final exposures however were taken on Ilford N. 40 plates.

For the investigation of the spectra in the visible region Hilger constant deviation and Hilger E_2 glass spectrographs had to be used. The constant deviation spectrograph had a dispersion of about 38 A.U./mm at 4000 A.U. The E_2 - glass spectrograph had a dispersion of 16 A.U./mm at 4000 A.U. The accuracy of measurement with the latter instrument was of the order of $1\ cm^{-1}$. Ilford Zenith, N. 40 and R. 40 plates were mainly used for this region. Wherever sharpness was needed N. 40 and R. 40 plates were preferred.

For calculation of wavelengths of band heads standard methods and interpolation formulae were used with a proper choice of the standards from the iron arc spectrum (Sawyer 1944, Lord et. al. 1948; Pearse and Gaydon 1963). Measurements reported in the thesis are the averages of the three different sets.