PHOTOFLUORESCENCE DECAY TIMES OF ORGANIC PHOSPHORS

by

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PREFACE.

The work reported in this thesis was carried out during the period March 1954 to August 1955 under the supervision of Dr.G.T.Wright. The general research program of the department was an investigation of the fluorescence and scintillation processes in organic phosphors, and it was considered necessary to obtain accurate values for the photofluorescence decay times in order to better understand the fluorescence process. This task was undertaken by the author using a method based partly on the previous work of Dr. W.A.Little in the same department, whose work, in turn, was based on that of Zmaeman (1941). Some results of this investigation have been published in two papers: Hamilton T.D.S. and Wright G.T., 1956, J.Sci.Instr., 33,36, and Hamilton T.D.S., 1957, Proc.Phys.Soc., B70,144. A number of difficulties necessitated the expenditure of a considerable amount of time in constructing the apparatus. These were mainly the lack of suitable electronic components which required considerable improvisation to overcome, and the time taken for the delivery of materials ordered from overseas.

All the apparatus, except the photomultiplier power supply, was built by the author. I would like to thank Dr. M.E.Szendrei for assistance in the field of electronics, Mr. F.van der Water, glassblower in the chemistry department, for the willing manufacture of various shapes of discharge tube, Mr. D.J.M.O'Sullivan and Mr. W.E.Campbell, research students in the chemistry department, for leading me through some of the intricacies of chemistry, and Mr. A.R.Scanlon for much assistance in the workshop.

I should also like to thank Prof. J.B.Birks, head of the department until July 1954, Dr. S.W.Watson, acting head until December 1954 and Prof.J.A. Gledhill, head from January 1955, for their kind interest and assistance.

I wish to acknowledge the financial support of the South African Council for Scientific and Industrial Research who provided maintenance grants and running expenses during the period of this work.

I hereby certify that, unless otherwise stated, the work reported here is, to the best of my knowledge, original.

PART I

1.1 Introduction.

The absorption and emission of energy is a fundamental property of any atomic system. When the emission occurs in the visible or near visible region the phenomenon is usually referred to as luminescence or fluorescence. This must be distinguished from thermal radiation as it does not follow Kirchoff's Law. The system may be excited in a number of ways e.g. by electromagnetic radiation, charged particles or by chemical action. The light given out during excitation and shortly afterwards is usually referred to as fluorescence, and that given out later as phosphorescence. There is, however, no dividing line between the two terms. It is to be expected that all substances will be luminescent, but in practice many are found not to be for a variety of reasons, e.g. thermal degradation of the energy or dissociation of the system. Those substances that do exhibit luminescence are generally referred to as phosphors.

A study of luminescent material is of interest, practically because of their use in many devices such as cathode ray tubes, scintillation counters, light amplifiers and the use of luminescence for chemical identification. From a theoretical point of view it is of interest since it gives information on the fundamental mechanisms and processes of the phosphor, and information on the state of aggregation of the phosphor. Phosphors may be divided roughly into two categories : inorganic and organic. In the first the occurence of fluorescence is usually due to the presence of impurities and the materials are classed as inorganic chemically. The latter category consists mainly of organic materials in which the fluorescence is an inherent property of the molecule.

The present work is concerned only with the organic phosphors and hereafter we will ignore the inorganic type. The interest in organic phosphors, except for some work on the fluorescence of dyestuffs, dates from the first use of

these materials in scintillation counters in 1947, when Kallman (1947) first used naphthalene. Much work was done on organic phosphors in the following years although Hofstadter (1948) showed that for general use an inorganic phosphor (sodium iodide, thallium activated) was more useful than organic types. However, since organic phosphors have much shorter lifetimes, they are used when this property is required.

In the development of the scintillation counter it has been of particular interest to measure those properties of the phosphor on which comparisons may be made, so as to obtain the most efficient phosphor for the particular application. These properties include the lifetime of the excited state, the spectral distribution of the emitted light, the efficiency, the stopping power for radiations, the energy resolution and the linearity of response.

Most of the measurements of these properties were originally made using ionising radiations for excitation and on phosphors which were not of the highest purity. It was much later that it was discovered that very small amounts of impurity produced large differences in the measured properties and also that the scintillation fluorescence mechanisms (excited by ionising radiations) were highly complicated compared with the photo-fluorescence mechanisms (excited by non-ionising photons). There are also the problems of the anisotropic crystalline properties of these phosphors in the solid state and of the spectral overlap of the absorption and the emission spectra. For these reasons nearly all early work is in error to some extent.

The general research program of the department was broadly 'An investigation of the fluorescence and scintillation processes in organic phosphors', and of the various properties to be investigated it was decided that the present work should be on the determination of the photofluorescence lifetimes of the excited states.

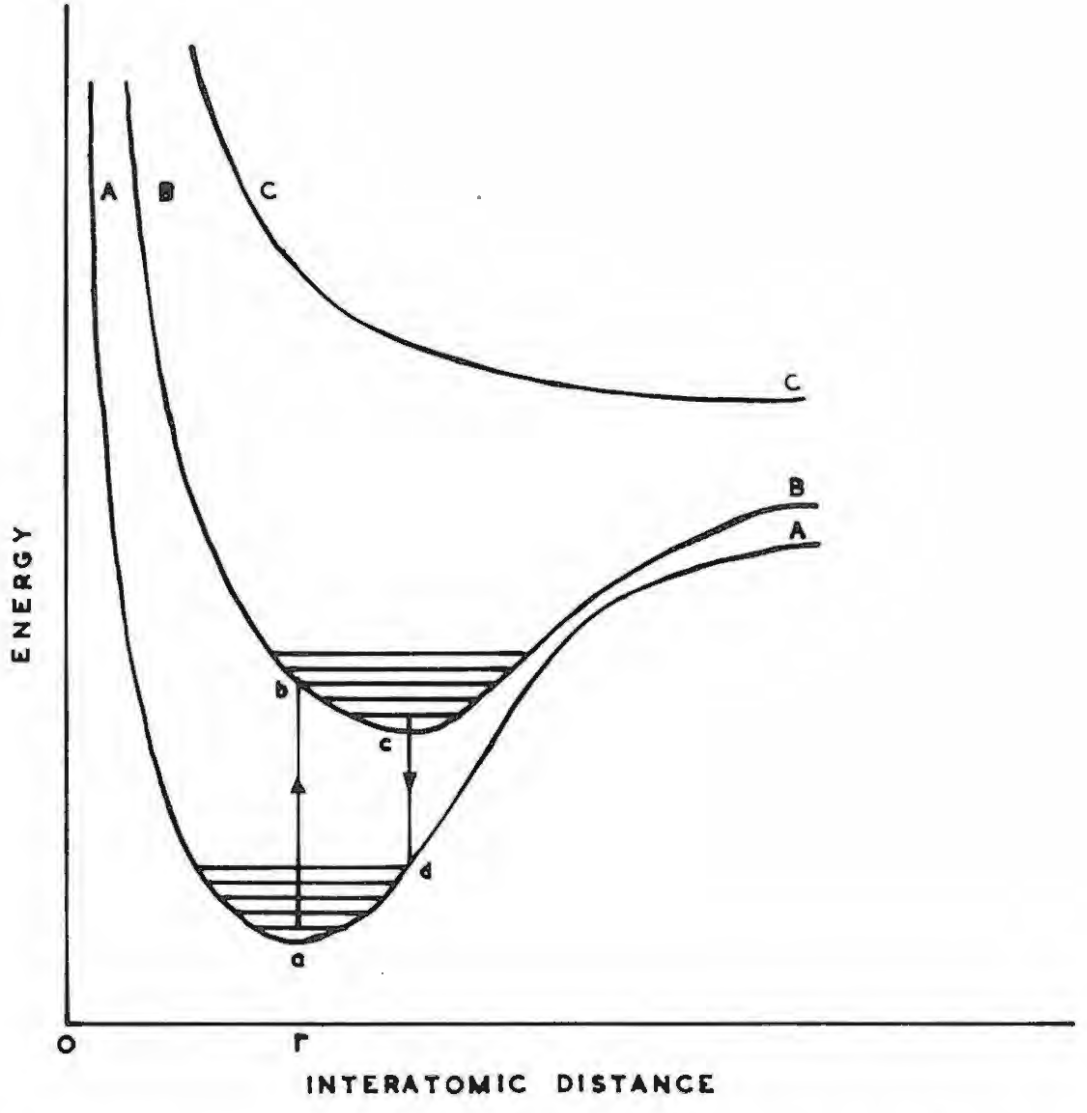

Figure I-1: Morse Diagram for a Diatomic Molecule.

There were a number of reasons for choosing this subject for investigation. Firstly, this is a fundamental property of the molecule and, together with measurements of the photofluorescence efficiency, enables the determination of the radiative and non-radiative transition probabilities, which may then be related to other physical characteristics of the π electrons and the molecule as a whole. Secondly, it is of importance when considering the problem of energy transfer in a phosphor from one molecule to another, as this occurs while the molecule is excited, so that it is necessary to know the time it spends in this condition if we wish to investigate transfer probabilities.

Practical phosphors are usually of such a thickness that there is some self-absorption of the fluorescence which will increase the observed decay time of the phosphor. Measurements of the increase in decay time due to self-absorption gives important information on the mechanisms of energy transfer.

We will now consider some of the more important aspects mentioned above in greater detail.

I.2 A Simple Model.

To gain an understanding of the fluorescence processes under investigation we will consider a simple diatomic model which leads to the familiar Morse diagram. Although this model is very simplified it suffices to discuss the various processes occuring in the organic phosphors with which we are concerned. If we have a diatomic molecule with an equilibrium separation r and in the lowest electronic state, then the potential energy - separation curve will be as in figure I.1 curve A. If the molecule is in the first excited electronic state the corresponding curve will be as shown at B, where the potential minimum will be at a greater equilibrium distance that r due to the expansion of the electronic orbit. There may be further electronic levels above this with stable configurations, but there

will eventually be a level with no minimum as at C and the molecule will dissociate if raised to this level. Superimposed on the electronic levels will be vibrational levels shown by horizontal lines within the electronic levels. As the atoms vibrate relative to each other, the total energy will remain constant but will alternate between kinetic and potential. At normal temperatures most of the molecules are in the lowest one or two vibrational levels of the ground state. This may be shown by noting that the energy difference between vibrational levels is about 0.16ev. and kT of the order of 0.04ev. (k = Boltzmann's constant, T = absolute temperature). Then from Boltzmann statistics we have

$$n_1 = n_0 e^{-\frac{E}{kT}} = n_0 e^{-8} = 0.0003 n_0$$

Thus we may confine our attention to molecules in the lowest vibrational level of the ground state. In organic crystals the simple Morse diagram should be replaced by one in many dimensions to allow for the interactions due to the neighbouring molecules. However, in these crystals, the molecules are relatively loosely stacked so that interactions are small and the simple diagram is found to lead to the prediction of results which are experimentally verified.

We now know in what levels the molecules are and to what levels they may go and can thus discuss the processes of absorption and emission of energy.

1.3 The Fluorescence Process.

The fluorescence process consists of raising the system to an excited electronic state by the absorption of a quantum of energy, with the subsequent reverse transition back to the ground state with the emission of a fluorescence photon. To follow the transition from the ground state to the excited state we must make use of the Franck-Condon principle. This states that the position and momentum of the constituent atoms of a molecule do not change appreciably

during the time of an electronic transition. (The vibrational period is of the order of 10^{-12} sec. and the time for an electronic transition about 10^{-15} sec.). Thus, the transition will be represented on the Morse diagram by a vertical line as at ab. In the excited state the molecule finds itself in a fairly high vibrational level. Since the vibrational period is much shorter than the lifetime of the state (10^{-12} cf. 10^{-9} sec.), the molecule usually dissipates this excess vibrational energy to its neighbours, and falls to the lowest vibrational level from whence it makes the transition back to the ground state. This transition occurs along cd, so that the molecule is now in a high vibrational level of the ground state. It then dissipates this vibrational energy to its neighbours and returns to the lowest levels. Not all molecules will start the return transition from the low vibrational levels of the excited state. There are two other possibilities; the molecule may return immediately to the ground state without dissipating vibrational energy, i.e. back along ba. This produces resonance radiation. The second possibility arises if the Morse curves for the two electronic states approach one another very closely at some point, so that the molecule may make a radiationless (or nearly so) transition to the ground state, all the energy being dissipated thermally. This evidently leads to a decrease in the efficiency of the fluorescence process.

1.4 Spectral Distribution of Absorbed and Emitted Radiation.

The possibility of transitions between various vibrational levels of the two electronic states and the thermal dissipation of energy determines the shape of the absorption and fluorescence spectra. In the case of absorption, we can have transitions from the lowest ground state vibrational level ($0'$) to a number of excited state vibrational levels ($0''$, $1''$ etc.) so that the spectrum appears as a broad band with a number of peaks, each peak corresponding to a transition

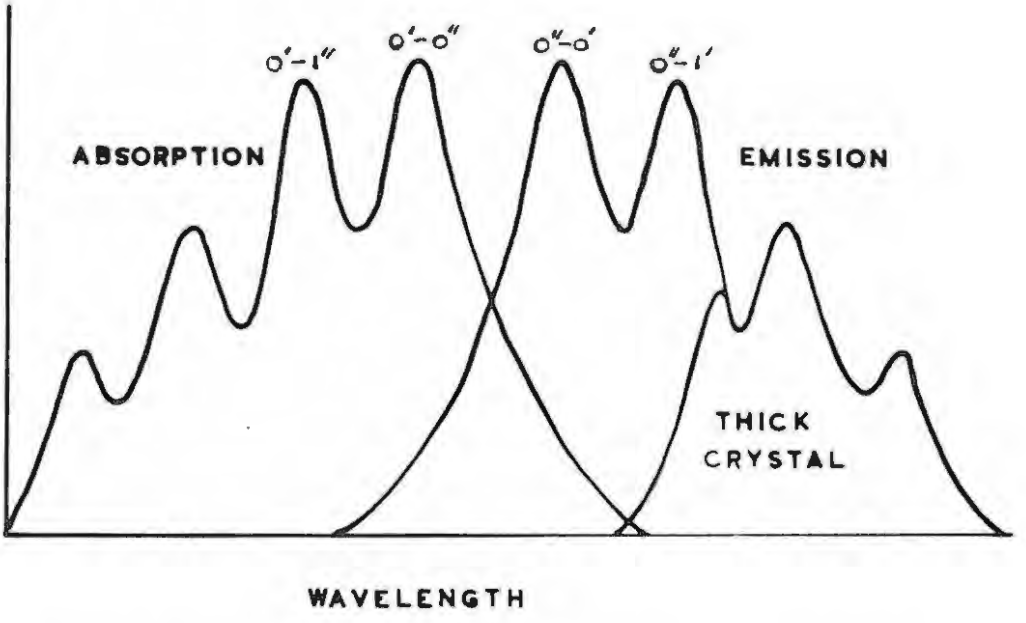

Figure I·2: Absorption and Emission Spectra of Organic Phosphors.

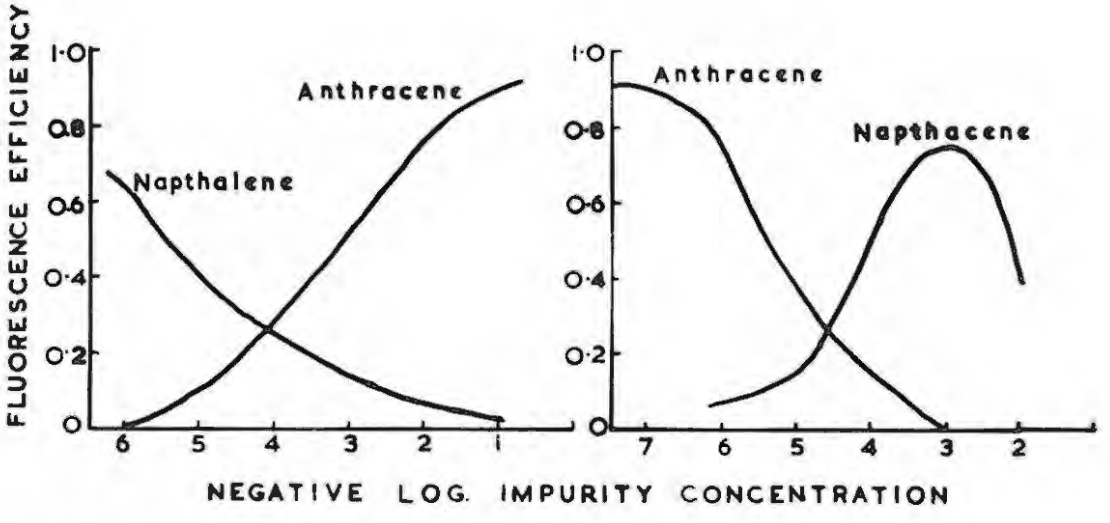

Figure I·3: Fluorescence of Mixed Organic Crystals.
(After Bowen, Mikiewicz and Smith.)

between two given vibrational levels. (Figure I.2). In the case of the fluorescence spectrum, the transitions begin in the lowest vibrational level (0') of the excited state, and end in various vibrational levels (0',1' etc.) of the ground state. Due to the shift of the potential minima and the thermal dissipation of energy before radiation, the energy of the emitted photons is, in general, less than that of the absorbed photons, so that the fluorescence spectrum is at longer wavelengths than the absorption spectrum. This shift of the fluorescent emission to a longer wavelength than the absorbed light agrees with the original observation of Stokes (Pringsheim 1949, p2). The two spectra usually overlap to a greater or lesser extent depending on the shape and relative position of the Morse curves. There is also the possibility that, after excitation, the molecule may absorb some vibrational energy from its neighbours and then return to the ground state, with emission of radiation of shorter wavelength than the exciting light. This is called anti-Stokes radiation. It has a much smaller probability of occuring than the other two processes of de-excitation, and is relatively unimportant in this work.

Excitation into the second and higher electronic states as well as the first has been observed in absorption, but in fluorescence only transitions from the first have been detected as yet. This is supposed to be due either to rapid thermal degredation from states higher than the first to the first, or to rapid transitions from the higher states with strong reabsorption until the energy is degenerated to the level of the first excited state. Thus the fluorescence spectrum is the same for excitation into any of the excited electronic states. For this reason, and due to the fact that the exciting light used in the present work would only excite to the first excited state, we will only consider this state.

1.5 Lifetime of the Excited State.

Once the molecule is in the excited state one of two things must occur: it will either radiate or the energy will be thermally degraded. Let p be the probability per unit time that it will radiate, and k the probability per unit time that it will make a non-radiative transition. If there were N_o molecules originally excited and at some time t later there are N, then the increase in the number of excited molecules in a further interval dt will be:

$$dN = -(p + k)N\,dt \qquad 1.5.1$$

$$\int_{N_o}^{N} \frac{dN}{N} = -\int_{o}^{t} (p + k)\,dt$$

$$\text{or} \quad N = N_o e^{-(p+k)t}$$

$$= N_o e^{-\frac{t}{\tau}} \qquad 1.5.2$$

$$\text{where } \tau = \frac{1}{p + k} \qquad 1.5.3$$

is called the fluorescence decay time. τ is also the average lifetime of the excited state, since this is given by:

$$\overline{\tau} = \frac{1}{N_o} \int_{o}^{\infty} N_o e^{-\frac{t}{\tau}}\,dt = \tau$$

The fluorescence decay is seen from 1.5.2 to be exponential, but this only necessarily holds where there is no reabsorption. The quantum efficiency q, defined as the ratio of the number of photons emitted to the number absorbed, may also be evaluated in terms of p and k. Since the total number of molecules returning to the ground state per unit time is proportional to p+k, and of these a fraction p give fluorescence photons, then we have :

$$q = \frac{p}{p + k} \qquad 1.5.4$$

Thus if we can measure the decay time and the quantum efficiency q experimentally, we may evaluate the two transition probabilities p and k. For an efficient phosphor (q=1) we find p to be of the order of 10^8 sec.$^{-1}$ and k very much smaller.

1.6 Energy Transfer in Organic Crystals.

It has been shown that in these crystals the molecule that finally emits a fluorescent photon is not necessarily the same one that originally absorbed the incident photon (Bowen 1949, Ganguly 1945, Bowen & Brocklehurst 1953). Thus the excitation energy must be capable of moving through the crystal until it finally escapes as a photon. Bowen et al. (1949) and Wright (1953) studied this using mixed crystals of the series naphthalene, anthracene, tetracene, pentacene. They used crystals with various known amounts of another member in solid solution. The two spectral components were isolated by filters and their intensities measured. It was found that even for very low concentrations of the impurity, of about 10^{-6} to 10^{-5} gm/gm, the fluorescence efficiency of the host was substantially decreased and that of the impurity correspondingly enhanced. Figure 1.3 shows some of the results. A number of energy transfer mechanisms have been suggested (Franck & Teller 1938, Franck & Livingston 1949, Bayliss 1951). These are:

(a) Electron transfer.

(b) Sensitised fluorescence (Cario & Franck 1923).

(c) Exciton transfer (Frenkel 1931).

(d) Photon transfer (Birks 1953).

Some organic compounds are found to be photoconducting and semiconducting, but these effects are thought to be due to triplet levels which have long

lifetimes and do not concern us here. As there are no other free electrons in these materials, we may eliminate electron transfer. We will discuss each of the others separately.

1.7 Energy Transfer by Photons.

In this mechanism it is supposed that the incident photon is absorbed by a host molecule which radiates a fluorescence photon. This photon may then escape from the crystal, be absorbed by another host molecule or by an impurity molecule. A necessary requisite for absorption by the impurity is that its absorption spectrum must overlap the emission spectrum of the host (Bowen 1949, Bowen & Lawley 1949, Birks 1953). The energy absorbed by the impurity molecules can now be emitted as their characteristic fluorescence. That absorbed by the other host molecules will just repeat the above process. Bowen and Lawley (1949) rejected this mechanism for a number of reasons, but Birks (1953, p73-74) showed that these objections were largely groundless. It seems fairly evident that if the spectra do overlap there must be some reabsorption and re-emission, but this does not exclude other processes from operating at the same time.

1.8 Energy Transfer by Exciton.

Exciton movement was first discussed by Frenkel (1931). It is a 'quick movement of excitation energy in crystals through a great number of building stones of the crystal' (Franck & Livingston 1949). The movement is supposed to be so rapid that the energy remains on one molecule for a time much shorter than that of an oscillation (i.e. $< 10^{-12}$ sec.). This implies a very strong coupling between the molecules in the crystal, so that the fluorescence spectrum of the crystal will be very different from that of the gas. For the organic crystals the two spectra are almost identical except for a small shift towards longer wavelengths in the solid (Garlick 1949, p205). The exciton may also be

considered as an electron and a positive hole bound in one another's field (Mott & Sneddon 1948, p227) which should give rise to a new narrow absorption band (Bayliss 1951, p69), but this band is not observed. From this and other evidence discussed in part IV it seems unlikely that this form of transfer occurs in the materials with which we are concerned.

1.9 Energy Transfer by Sensitised Fluorescence.

The process of energy transfer by sensitised fluorescence was discovered by Cario and Franck (1923) during a study of the optical resonance excitation in gases. The transfer may also be said to take place by collisions of the second kind (Klein and Rosseland 1921), the original idea having been worked out for collisions between electrons and atoms, and extended to aton-atom collisions by Franck (1922). When an excited and an unexcited atom collide in a gas, the excited atom may lose electronic energy non-radiatively and fall to a lower state. The energy lost by the excited atom may be utilised in increasing the kinetic energy with which the atoms separate after the collision, in electronic excitation of the unexcited atom, or in a combination of these. The probability of transfer of energy from one kind of atom to another has been shown experimentally (Arnot 1950, p36) to increase as the energy difference between the donating and accepting levels decreases i.e. the probability is high when there is close resonance between the two energy levels. One would thus expect energy transfer between identical atoms to be very likely as the energy levels will be in exact resonance. For molecules in the solid state, however, the resonance will not be exact due to the loss of vibrational energy. The original theory of the process was worked out by Kallman and London (1928), and recently an improved theory has been published by Förster (1948).

It appears that in gases and solutions the energy may be transferred over

linear distances of 50 to 100Å under optimum conditions. In solids the conditions are somewhat different due to the molecules having to remain at fixed points in the crystal lattice. Förster finds for anthracene that the exchange can only take place over a distance of about 8Å, which is just the diameter of one molecule, so that we may expect transfer to take place only to adjacent molecules. In the case of a mixed crystal (anthracene crystal containing naphthacene) Franck and Livingston consider that the transfer from anthracene to naphthacene occurs by sensitised fluorescence. Once the energy reaches a naphthacene molecule it remains there until radiated since the naphthacene energy level is lower than that of anthracene.

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PART II.

Theory of the Experimental Method.

2.1 Aim of the Present Work.

The aim of the present work has been to obtain accurate information on the properties of fluorescent organic compounds to aid in elucidating the fluorescence processes occuring in these materials. In particular, the author has been engaged in the measurement of the photofluorescent decay times of these materials when excited by photons in the near ultraviolet region of the spectrum. Closely allied to this has been the determination of the fluorescence spectra of the same compounds by Mr. A.J.W.Cameron, which give much useful information when used in conjunction with the decay times. All spectral measurements used in this thesis were made by Mr. Cameron unless otherwise specified.

2.2 Measurement of Photofluorescence Decay Times.

The first measurements of photofluorescence decay times in the region of 10^{-8}sec. appear to have been made by Gaviola (1927). The method used was a development of the original Becquerel phosphoroscope (1871), in which the rotating wheels are replaced by Kerr cells, to give the same effect of alternate excitation and observation. This method has been developed and used by a number of workers (Szymanowski 1933, Duschinsky 1933 & 1936, Oran 1936, Maercks 1938). The details are given in Pringsheim (1949) and will not be reproduced here. The results appear to be satisfactory and reproducible, but measurements have been made mainly on organic dye solutions.

2.3 Modulated Light Method.

A different method for the measurement of the decay time has been given by Tumerman (1941). He considered the excitation of a phosphor by light modulated at a high frequency (of the order of Mc/s). Due to the finite decay

time of the phosphor, there will be a phase difference between the exciting and fluorescent light. He showed that the phase difference ϕ was related to the decay time τ by the equation:

$$\tan \phi = \omega \tau \qquad 2.3.1$$

where ω is the angular frequency of modulation of the exciting light. The first use of this method appears to have been made by Liebson (1952) who used an 'ultrasonic diffraction grating' to obtain the modulated light. This 'grating' is produced in a liquid contained in a rectangular vessel with a quartz crystal on one side in the liquid, and a reflector on the opposite side. If the crystal is driven at its resonant frequency, and the distance to the reflector adjusted to an integral number of wavelengths of the sound waves in the liquid, a system of standing waves is set up which causes regular variations in the refractive index of the liquid. Light passed through the cell in a direction perpendicular to the standing waves will be periodically diffracted. By electrical measurement of the phase difference ϕ between exciting and fluorescent light, the decay time τ may be evaluated from 2.3.1. This method appears to be satisfactory and has more recently been used by Bailey and Rollefson (1953) to obtain very good results, but no measurements were made on organic crystals. Kavalicus et al. (1954), Hanle et al. (1951), Schmillen (1953), Schmillen, Schmillen and Rohde (1953) and Schmillen (1954) have also used this method with success.

2.4 Alternative Modulated Light Method.

Frey (1936) has shown that the light emitted from a gas discharge tube excited at a high frequency is partly modulated at the frequency of modulation. The degree of modulation will depend on the frequency used, since the gas molecules have finite lifetimes in the excited state, and on the pressure

in the tube, since collisions will decrease the lifetime of the excited state. The discharge tube method was tried by Birks and Little (1953) and found to work satisfactorily. The accuracy of their work depended mainly on the calibration of an electrical phase changer and the determination of phase difference minima, which were not sharp. The results differed from those of Liebson, and in view of the importance of the results (Birks 1953) and some criticism of the modulation of the first dynode voltage of the detecting photomultiplier, it was thought necessary to improve on the method and repeat the measurements, together with measurements on some other phosphors. In the improved method the modulated gas discharge tube was retained because of its simplicity, but the measurement of phase differences was discarded in favour of the measurement of relative modulation of the exciting and fluorescent light.

The action of the phosphor on the light is analagous to that of an electrical filter with a time constant equal to the decay time of the phosphor. The incident signal consists of, in general, a steady component on which is superimposed an alternating component. The filter, as well as introducing a phase shift as mentioned above, also produces a change in the degree of modulation of the signal. The change in the degree of modulation is related to the time constant of the filter as shown in section 2.5, and by measuring the degree of modulation of the input and output signals, the decay time may be determined. In practice this means measuring separately the amplitudes of both the input and output signals. The disadvantage of this is that although it is easy to calibrate an instrument to measure steady signals, it is difficult in the case of alternating signals at the frequencies used ($\approx 10^6$/s). One other major problem is that of transit-time spread in the photomultiplier used to detect the light, which introduces an added change in the degree of modulation (see Part V). This

effect would have to be measured and due allowance made. A simple method of overcoming both these difficulties is to arrange that the alternating amplitudes of the input and output signals are equal, so that all the corrections, which only apply to the alternating components, will cancel out and only a comparison of the steady components is necessary.

2.5 Theory of the Present Method.

We will now consider the theory of the method outlined above. We will consider a phosphor excited by light, the intensity of which will be represented by a Fourier series to allow for harmonic distortion in the light source. The basic assumption made in all measurements of photofluorescence decay times is that the decay is exponential. This was roughtly verified by Post (1952) and it is to be expected theoretically (Section 1.5). This has been further investigated in the present work as described in 2.6.

At a time t let there be N excited molecules. In an interval dt the number of excited molecules will increase by an amount dN given by (see 1.5) :

$$dN = -k_1 N \, dt \qquad 2.5.1$$

where k_1 is a constant, and is the reciprocal of the decay time. If the phosphor is being optically excited, new excited molecules are appearing. Let the number be dN' in the time dt. We now have for the increase in the number of excited molecules:

$$dN = -k_1 N \, dt + dN' \qquad 2.5.2$$

$$\frac{dN}{dt} = -k_1 N + \frac{dN'}{dt} \qquad 2.5.3$$

The rate of formation of excited molecules, dN'/dt, will be proportional to the intensity of the exciting light J(t) (which may be a funtion of time) i.e. to the rate of arrival of photons. Thus :

$$\frac{dN'}{dt} = k_2 J(t) \qquad 2.5.4$$

where k_a is some constant. The fluorescent intensity I at time t is proportional to the number of excited molecules at that time :

$$I = k_b N \qquad 2.5.5.$$

where k_b is some constant. From 2.5.3, 2.5.4 and 2.5.5 we then have:

$$\frac{1}{k_b}\frac{dI}{dt} = \frac{-k_1 I}{k_b} + k_a J(t)$$

or $$\frac{dI}{dt} = -k_1 I + k_2 J(t) \qquad 2.5.6$$

where $k_2 = k_a k_b$. This is the basic equation relating the time variation of the fluorescent light (dI/dt) to the time variation of the exciting light (J(t)). To take account of harmonic terms in the exciting light we represent the intensity of the exciting light by a Fourier series:

$$J(t) = a_o/2 + \sum_n \left[a_n \mathrm{Cos}(n\omega t) + b_n \mathrm{Sin}(n\omega t)\right] \qquad 2.5.7$$

where n=1,2,3,....., a_n and b_n are constants depending on n, and $a_o/2$ is the average intensity of the exciting light. From 2.5.6 and 2.5.7 we have :

$$\frac{dI}{dt} = -k_1 I + \frac{k_2 a_o}{2} + k_2 \sum_n \left[a_n \mathrm{Cos}(n\omega t) + b_n \mathrm{Sin}(n\omega t)\right] \qquad 2.5.8$$

This equation is solved in appendix VI and leads to the result:

$$I = \frac{a_o k_2}{2k_1} + k_2 \sum_n \left[\frac{a_n \mathrm{Cos}(n\omega t - \phi_n)}{(k_1^2 + n^2\omega^2)^{\frac{1}{2}}} + \frac{b_n \mathrm{Sin}(n\omega t - \phi_n)}{(k_1^2 + n^2\omega^2)^{\frac{1}{2}}}\right] + Ce^{-k_1 t} \qquad 2.5.9$$

The final term, $Ce^{-k_1 t}$, is an initial perturbation and becomes negligibly small as t becomes large compared with $1/k_1$, i.e. $tk_1 >> 1$. Since $1/k_1 = \tau$ is of the order of 10^{-8} sec. in the present work, the term will very soon vanish. The intensity I of fluorescence thus contains terms corresponding to each term in the expression for the exciting light J(t). The corresponding components differ in phase and amplitude. The phase difference is related to the decay time by the equation (see 6.1.7) :

$$\text{Tan } \phi_n = n\omega t \qquad 2.5.10$$

which corresponds to the equation 2.3.1 obtained by Tamarman. There is also a relation between the relative degree of modulation and the decay time. This is most easily seen if we simplify the expression for J(t). If we have a suitable detector we need consider only one frequency component i.e. for all terms with n 1, a_n and b_n=0, and, by a proper choice of time scale, either a_1 or b_1 can be made zero. We will then have :

$$J(t) = a_o/2 + b_1 \sin(\omega t) \qquad 2.5.11$$

$$\text{and} \qquad I = \frac{k_2 a_o}{2k_1} + \frac{k_2 b_1 \sin(\omega t - \phi)}{(k_1^2 + \omega^2)^{\frac{1}{2}}} \qquad 2.5.12$$

The degree of modulation of the exciting light m_e, (the ratio of the varying to the steady component), is given by:

$$m_e = \frac{2b_1}{a_o} \qquad 2.5.13$$

and of the fluorescent light by:

$$m_f = \frac{2b_1}{a_o} \frac{k_2}{(k_1^2 + \omega^2)^{\frac{1}{2}}} \qquad 2.5.14$$

If we have the means of detecting and measuring the varying and steady components of the exciting and fluorescent light, we can find the ratio:

$$M = \frac{m_f}{m_e} \qquad 2.5.15$$

which will always be less than 1, since the phosphor has a finite decay time. We now have from 2.5.13 and 2.5.14 :

$$M = \frac{k_1}{(k_1^2 + \omega^2)^{\frac{1}{2}}}$$

$$\text{or} \quad \tau = \frac{1}{k_1} = \frac{(1 - M^2)^{\frac{1}{2}}}{\omega M} \qquad 2.5.16$$

This formula is the basis of the present method for the measurement of τ. In practice the varying components of the exciting and fluorescent light are made equal, as this will avoid the necessity of calibrating a detector for the varying component, which is difficult to do.

2.6 Exponential Decay of Fluorescence.

In the case of a phosphor in which there is self-absorption of its own fluorescence, the decay is not necessarily exponential. Since the present as well as previous methods of measuring decay times depend on the assumption that the decay is exponential, this factor requires some investigation. It has been found by Holstein (1947, 1951) that in the case of gases the decay of resonance fluorescence is exponential. This case, however, concerns very narrow emission and absorption bands compared with those of organic phosphors, and a much larger overlap. This means that there will be many more absorptions and re-emissions in a gas, and it could be due to this that the gas decay is exponential. As As well as affecting the shape of the decay, re-absorption could lead to variations of the decay time over the emission spectrum, so that the measured value would only be some sort of average.

The problem could be analysed analytically if approximate spectra with known mathematical expressions were used. This is the approach used by Holstein. In this case it is of interest to find the actual value of the thick crystal decay time, the shape of its emission spectrum and the variation of decay time along the spectrum. This will help justify the correction to the microcrystal spectrum (see section 2.7), and will show what sort of average decay time is measured. For a practical case the only method appears to be the Monte Carlo method. The steps in this procedure are as follows. We assume a semi-infinite crystal and that the incident light is completely absorbed at the surface. We consider one photon at a time. The total solid angle is divided into ten equal parts and the

fluorescence photon will be emitted into any one of these with equal probability. This disregards the directional properties of the molecules in the crystal, which will favour certain directions of emission. In practice, however, decay time measurements on a crystal oriented in different directions gave identical results. It may also be emitted at any wavelength of the emission spectrum, and after a certain time, these two variables also being divided into equally probable intervals.

These three variables are fixed for a particular molecular process by following a table of random numbers (Kendall and Babington Smith 1951). Once the emission wavelength is fixed, the corresponding absorption coefficient is fixed, and this gives a mean free path for the photon. This mean free path, together with the direction of emission, fixes the co-ordinates of the new excited molecule in the crystal. We need only consider the co-ordinate in the direction in which the crystal is 1cm. thick, it being infinite in directions normal to this. This process is repeated until the photon escapes from the crystal. To obtain a good statistical accuracy a large number of photons are followed through the crystal, the wavelength of emission and the total elapsed time in the crystal being noted for each one.

In determining the absorption coefficient, the results of Korhum and Finckh (1942) were used. Since the absorption coefficient had large variations over the wavelength bands (of equal emission probability), a weighted average coefficient was obtained for each band by multiplying the absorption coefficient ε_λ at any wavelength λ, by the emission intensity I_λ at the same wavelength, and then taking the average by dividing the weighted area $\int \varepsilon_\lambda I_\lambda \, d\lambda$ by the area $\int I_\lambda \, d\lambda$ under the emission spectrum in the band. This also reduces the absorption coefficient to its original scale. The reciprocal of the absorption coefficient then gives the mean free path. The quantum efficiency of the

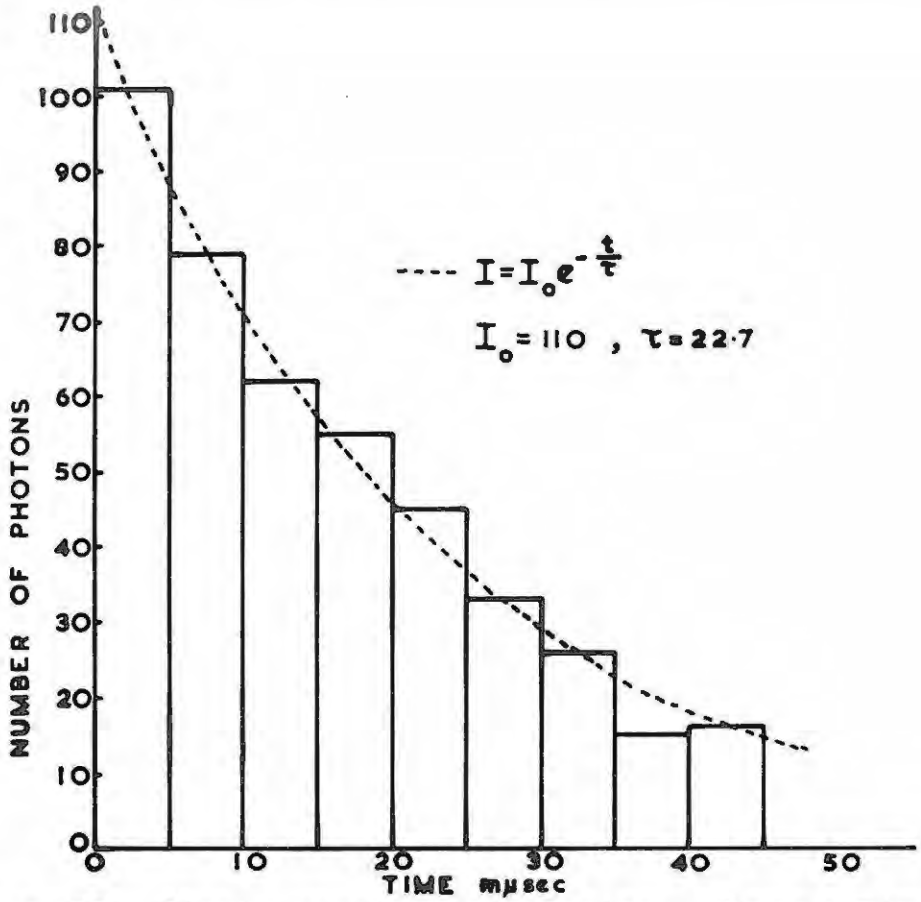

Figure II·1 : Monte Carlo Calculation : Decay Time.

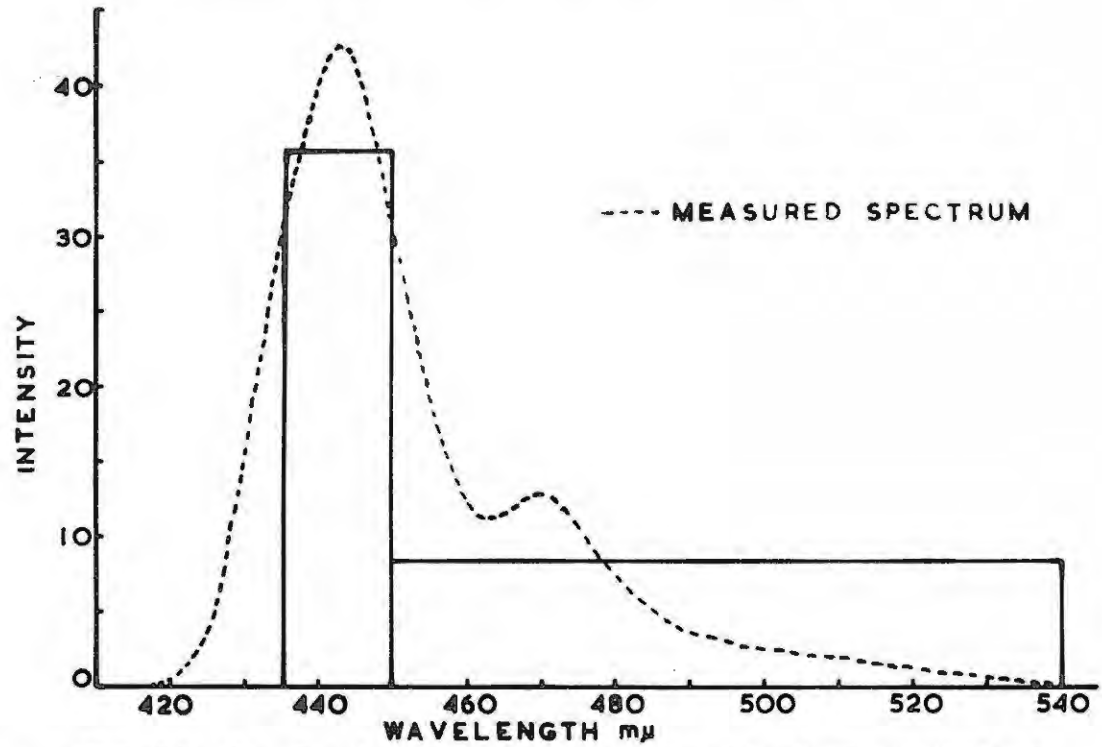

Figure II·2 : Monte Carlo Calculation : Spectral Distribution.

processes does not concern us here, since we are only interested in the lifetimes of those photons that escape from the crystal, and not those that would be quenched internally.

The result of this investigation is shown in figures II.1 and II.2, which show the decay and spectral output from a 1cm. thick anthracene crystal. A total of 920 photons were followed, of which 500 escaped after passing through the crystal, and the remainder escaped on the same side as the light was incident. The decay times of the 500 group were divided into 5mμsec. intervals and the result plotted as a histogram (Figure II.1). The exponential curve is given by $I = I_o e^{-t/\tau}$ where the adjustable constants, I_o and τ, were obtained as follows: τ is given by the mean of all the calculated lifetimes, and I_o is obtained by equating the area under the histogram between t = 0 and t = 45 mμsec. (above this the numbers of photons per division is rather small) to that under the exponential between the same limits. The curve has a decay constant of τ = 22.7 mμsec., which, in view of the approximations made in the calculation, is in very good agreement with the measured value of 24.1 mμsec..

The fit of the exponential to the histogram is close enough for the decay to be taken as exponential as required for measurement by the present method. It should be noted that the thick crystal emission spectrum is somewhat sensitive to the shape of the tail of the absorption spectrum on the long wavelength side. This tail was not measured by Kortum and Finckh, and the spectrum was, therefore, somewhat arbitrarily extended as a smooth curve to become zero where the emission spectrum indicated that reabsorption was absent. The various spectra are shown in figure II.3. That some error was introduced here is indicated by a comparison of the ratio of the two long wavelength spectral areas as actually measured (0.97) and the ratio of the numbers of photons emitted in these two regions according to the Monte Carlo calculation (0.70).

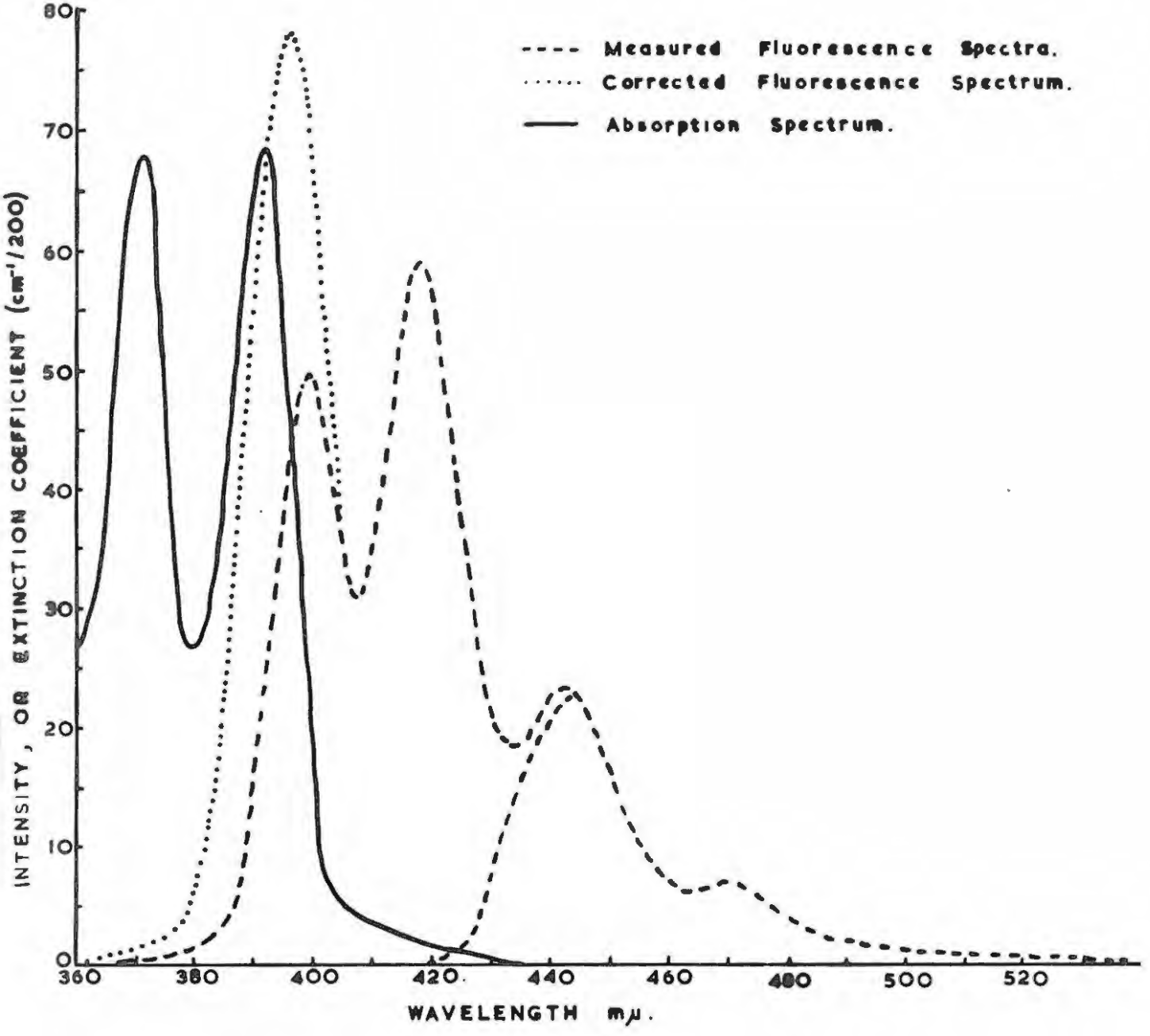

Figure II·3 : Absorption and Emission Spectra for Anthracene.

The decay of the photons emitted in the two long wavelength regions, shown in figure II.2, were each found to be exponential with decay times of 23.6 and 22.0 μsec., the shorter being for the longer wavelength region. These results are equal considering the accuracy of the calculation, so that we may say that there is no variation of τ along the spectrum. The average number of emissions before escaping from the crystal, n, was also determined and found to be 4.03. Since we have $n\tau_m = \tau_0$, and for anthracene in particular $K\tau_e = \tau_m$ (see 4.5.2), where K is the probability of escape from the crystal, then we have $n = 1/K$. K is found from table E (under K_3, specimen A) to be 0.234 i.e. $1/K = 4.27$, which shows reasonable agreement with the calculated value of n.

The agreement of theory with experiment would be improved if the absorption spectrum was shifted to longer wavelengths as suggested by Wright (1955b) on the basis of his measurements on the excitation spectrum of anthracene. The shift amounts to only 50Å, but since we are concerned with the overlap of two peaks, this will have a considerable effect as may be seen from figure II.3. The magnitude of the effect is difficult to determine without a repetition of the complete calculation.

2.7 Fluorescence Efficiencies.

In order to evaluate the quantum efficiencies of the compounds under investigation using the method of Wright (1955a), it is necessary to know the fluorescence spectra as well as decay times of microcrystalline specimens. Once the absolute efficiency of one compound is determined, these two factors are sufficient to evaluate the remaining efficiencies. According to Wright the quantum efficiency q is given by:

$$q = \frac{1 - \tau/\tau_0}{1 - (\delta + K - \delta K)} \qquad 2.7.1$$

where τ_m and τ_c are the micro and thick crystal decay times, K the escape coefficient in thick crystals and δ a correction factor depending on crystal constants. The decay times may be measured directly, K is given by the ratio of the areas of the thick to microcrystalline fluorescent spectra and δ has been evaluated by Wright in the case of anthracene. Once the efficiency of anthracene is established, the efficiencies of the other compounds are determined as follows. Since the area α of the microcrystalline spectrum is proportional to the radiative transition probability p, we have using 1.4.4:

$$\frac{q_1}{q_2} = \frac{p_1 \tau_{m1}}{p_2 \tau_{m2}} = \frac{\alpha_1 \tau_{m1}}{\alpha_2 \tau_{m2}} \qquad 2.7.2$$

so that if q_1 is known q_2 may be determined.

In using the fluorescence spectrum as a measure of the radiative transition probability p a serious difficulty arises as pointed out by Wright. In his paper he shows that the factor δ strongly influences the proportion of the fluorescence from a specimen that is collected by the detector. He points out that the absorption would be a better measure of p. Since the absorption spectra were unfortunately not measured by Cameron, use had to be made of the spectra published for solutions (Friedel and Orchin 1951). It was thought that these should be similar to those measured for the solid except for a wavelength shift.

For the absolute determination of q for anthracene the fluorescence spectra can be used since the thick and micro spectra are normalised at long wavelengths where there is no reabsorption, so that light collection variations are eliminated. Figure II.3 contains examples of the spectra obtained by Cameron, and shows the effects of reabsorption on the spectra. The absorption spectrum is taken from Kortum and Finckh (1942). Even for the microcrystals used (estimated from the known concentration of the solution and the area of the glass slip to be about 1/10μ thick), there is still some reabsorption, and an attempt has been made

to correct for this.

The correction is based on a comparison of the spacing and relative heights of the vibrational peaks of the fluorescent spectrum among the compounds studied (Cameron 1957). A plot is made of the relative intensities of the $0' - 0'$ to the $0' - 1'$ peak versus the peak separation for a number of compounds, such as anthracene and the benzanthracenes, that have allied structures and similar spectra. The points obtained are found to lie on a well defined curve which has a maximum at the point 2224 spacing and 1.33 intensity ratio. Points for different specimens of the same compound fell at different positions on the curve due to variations in thickness, indicating that there was still some reabsorption even with the thin specimens used.

It is suggested that all the compounds of similar type should have similar peak spacing and intensity ratio, so that the correction for anthracene has been made on the basis of the maximum figures given above. The corrected $0' - 0'$ peak is now obtained by plotting a gaussian curve with the requisite intensity ratio and peak to peak spacing, and with a half-width equal to that of the $0' - 1'$ peak. This is shown in figure II.3 where the corrected peak, shown dotted, is seen to fit in well with the measured spectrum.

The basis of the correction described above is not very satisfactory, but it gives some indication as to the order of the correction. The question is discussed further in section 4.4, where it is shown that the correction applied as detailed above, is, in fact, quite satisfactory.

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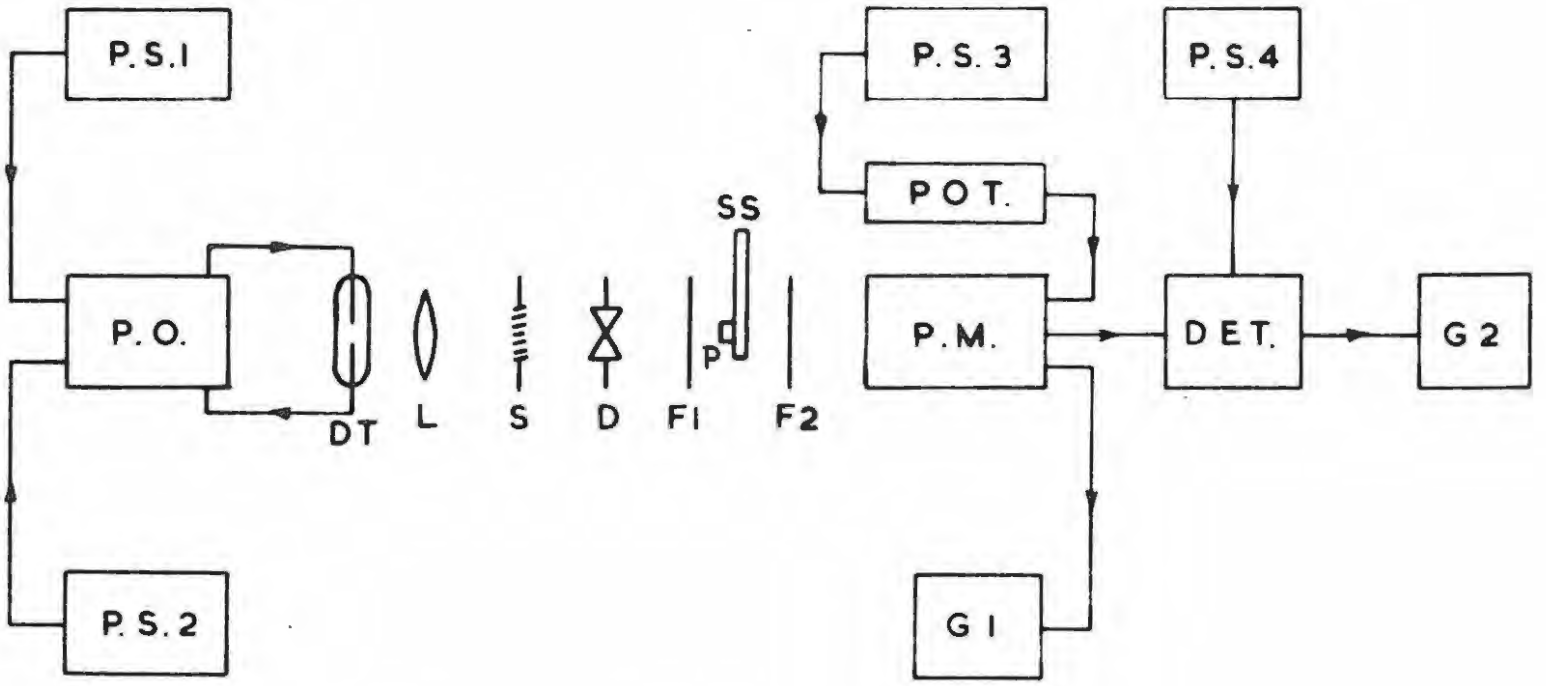


Figure III : Block Diagram of the Apparatus.

PART III.

Apparatus and Experimental Technique.

3.1 Introduction.

A block diagram of the apparatus is shown in figure III. The general outline of the experimental arrangement is as follows. Light from a modulated source (ST) illuminates the phosphor (P) being investigated and excites it to periodic fluorescence. The modulated fluorescence is detected by a photomultiplier (PM) and converted into electrical signals. These signals are rectified (RET) and measured on indicating meters (G_1 , G_2).

The apparatus is conveniently divided into four parts:

(i) A modulated light source. This source was required to produce the alternating excitation of the phosphor under examination as indicated in equation 2.5.7. This source consisted of a gas discharge tube driven by a high frequency power oscillator.

(ii) An optical detector-transducer. This served to detect the light from the source or the phosphor, convert it into an electrical signal and amplify it.

(iii) A light filter. This filter, which was in two parts, one between the light source and the phosphor, and the other between the phosphor and optical detector, was required to stop any of the exciting light from reaching the detector while it was receiving the fluorescent light from the phosphor. In this part may be included a shutter that could cut off all light from the optical detector, and an iris diaphragm to adjust the intensity of the light reaching the detector.

(iv) An electrical detector. This received the signal from the optical detector, selected the desired frequency component, rectified it, and recorded the result on a suitable meter.

The individual units are described in more detail in the following sections.

The most difficult part of the construction was building a suitable detector. A fairly high sensitivity was required which made pick-up from the discharge tube oscillator and important consideration. The first unit constructed for the detection of the varying component of the multiplier output was a three stage tuned r.f. amplifier with diode crystal rectification. This unit was found to be liable to pick-up and oscillation, and was replaced by a two stage amplifier and heterodyne unit. This unit also gave a lot of trouble and was finally replaced by a compact and very well shielded heterodyne unit with no amplification before mixing, which proved entirely satisfactory.

The discharge tube oscillator (or power oscillator) unfortunately grew in stages as new demands were realised, and does not represent an efficient overall design. The two multipliers available - (R.C.A. 5819's rated 1250volts overall) - were both found to become unstable above 1000volts overall, which reduced the gain available. Below 1000 volts, however, the tubes worked very well. Mains supply variations were very troublesome and necessitated the construction and use of regulated power supplies throughout. It was originally thought that the frequency of modulation of the light source should be twice the driving frequency since the tube would fire twice for each cycle. With the tube design and connection as used here, however, it was found that the tube fired only once in each cycle as shown by the concentration of the discharge around one electrode. The frequency of detection was nevertheless kept at twice the driving frequency since,there was a large amount of second harmonic present in the light modulation. This arrangement had the advantages that the detector worked at a different frequency from the power oscillator, which reduced pick-up very substantially, and that the discharge was well concentrated, which made light collection and focussing much easier.

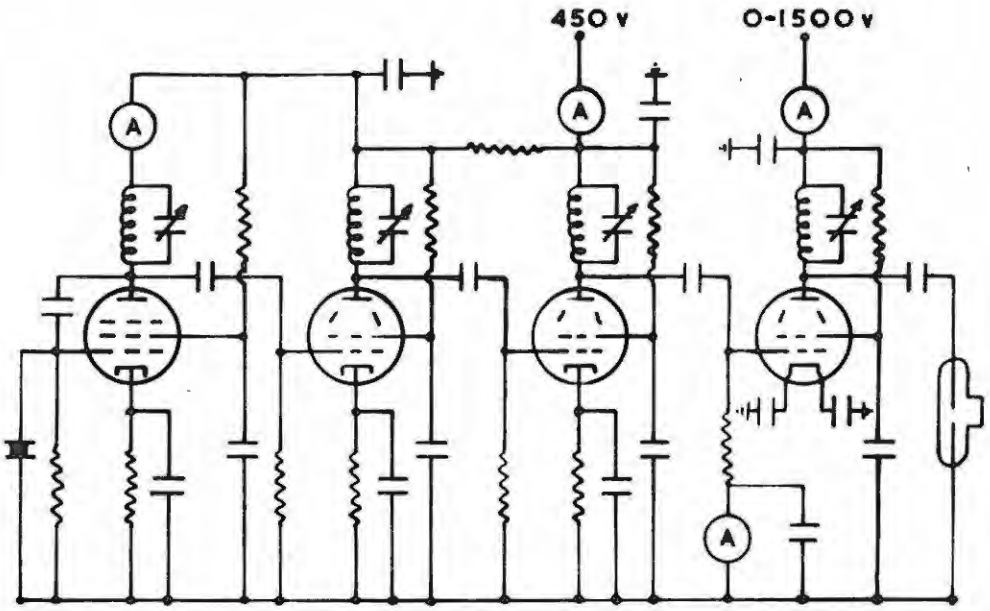
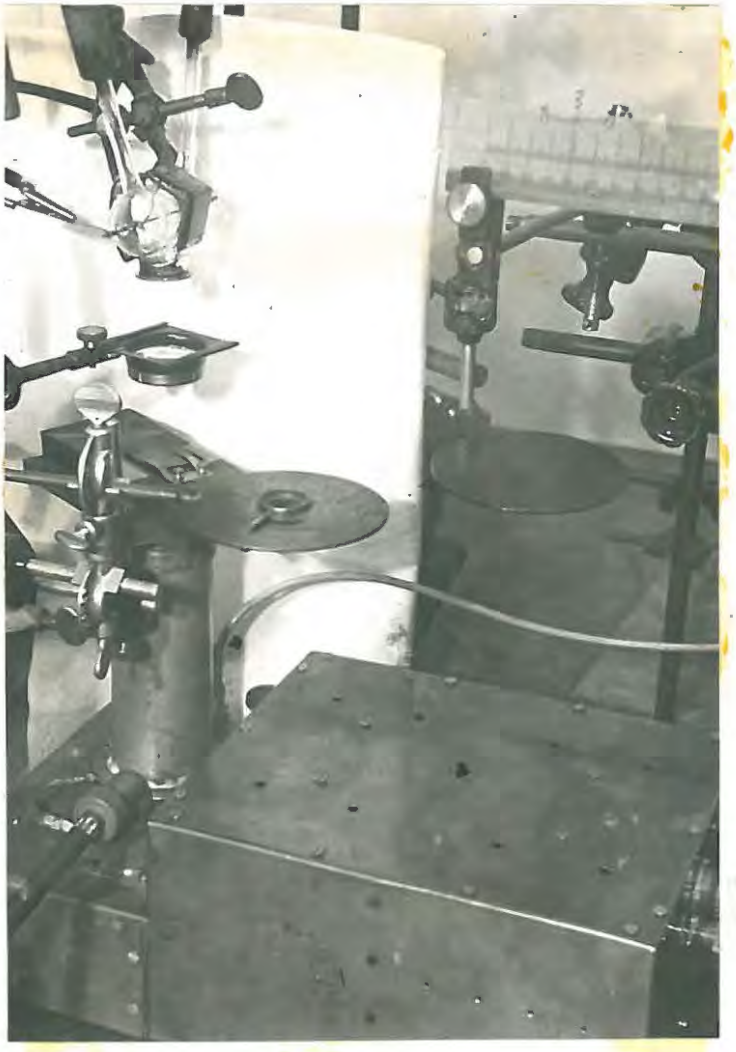


Figure III·1 : Power Oscillator.



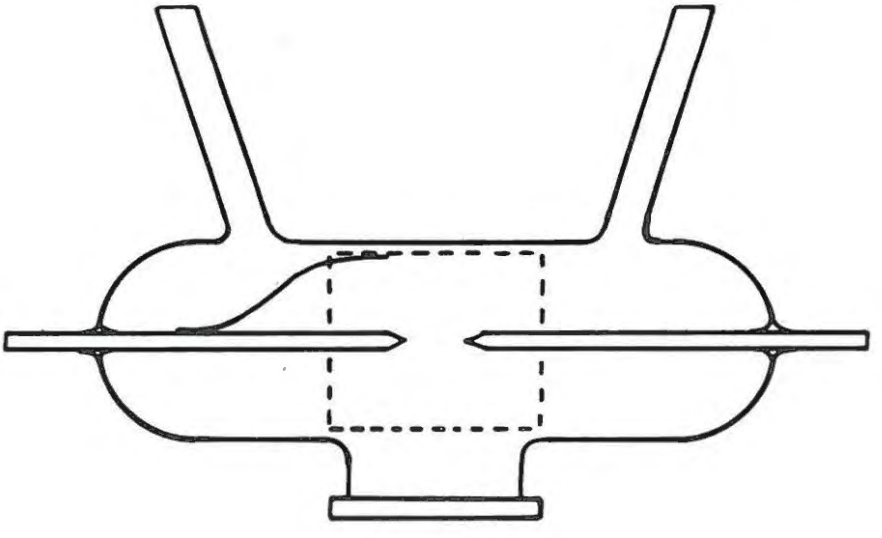


Figure III·2 : Discharge Tube

3.2 The Power Oscillator (P.O. in figure III)

The circuit of the power oscillator is shown in figure III.1 . V_1 is a Pierce oscillator, crystal controlled to ensure frequency stability with respect to the detector which is also crystal controlled. This type of circuit was used since it has the desirable property that it will operate with crystals of widely differing frequencies (Edson 1953, p 213), as were used in this work.

On the crystal fundamental, V1 could drive the output tube V4 adequately, but since it was required to work on crystal harmonics as well, the amplifiers V2 and V3 were necessary. The unit was capable of driving the discharge tube on harmonics up to the fourth at least, which was more than enough. To obtain a large voltage swing at the output, which is necessary to fire the tube at the pressures used, an output valve of fairly high voltage rating is required. The most suitable of those available was found to be an 813 beam tetrode which is rated at 2000 volts plate voltage, and may be used up to 30Mc/s at full ratings. As explained in 3.3, it was necessary to vary the plate voltage of the 813 so that two power supplies were necessary for the power oscillator.

3.3 Discharge Tube. (DT in figure III)

The design of the tube was influenced by the original tube used by Little (Thesis 1953). This was rather small, with an electrode separation of about 2cm. A much bigger tube was required to get a bigger discharge and to dissipate heat more effectively. The tube is shown in figure III.2. Pointed electrodes were favoured since they kept the discharge confined to the point of the 'hot' electrode, and so made light collection easier. With a point separation of 1cm. and pressures of 5cm. of mercury, it was found difficult to initiate the discharge. The pressure was therefore reduced until the tube did strike and then increased to the required value, at the same

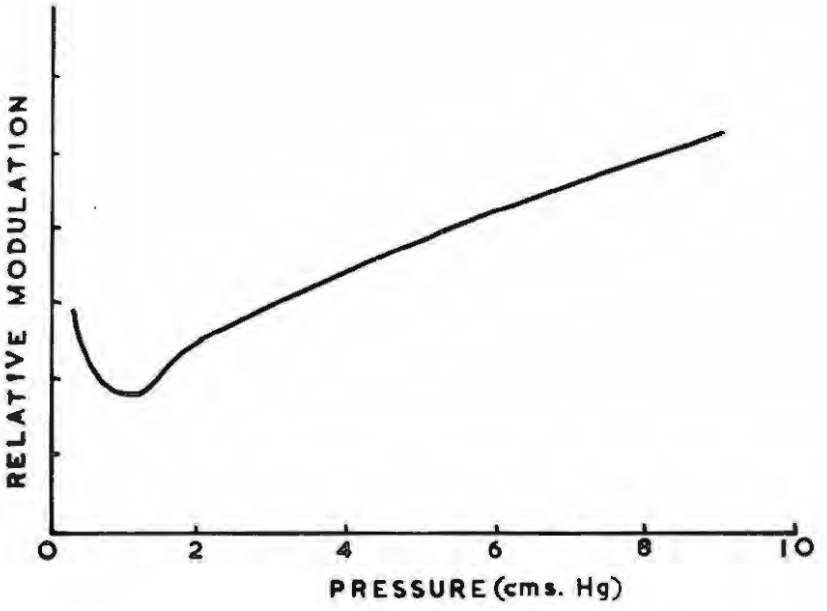


Figure III·3: Variation of Modulation with Pressure.

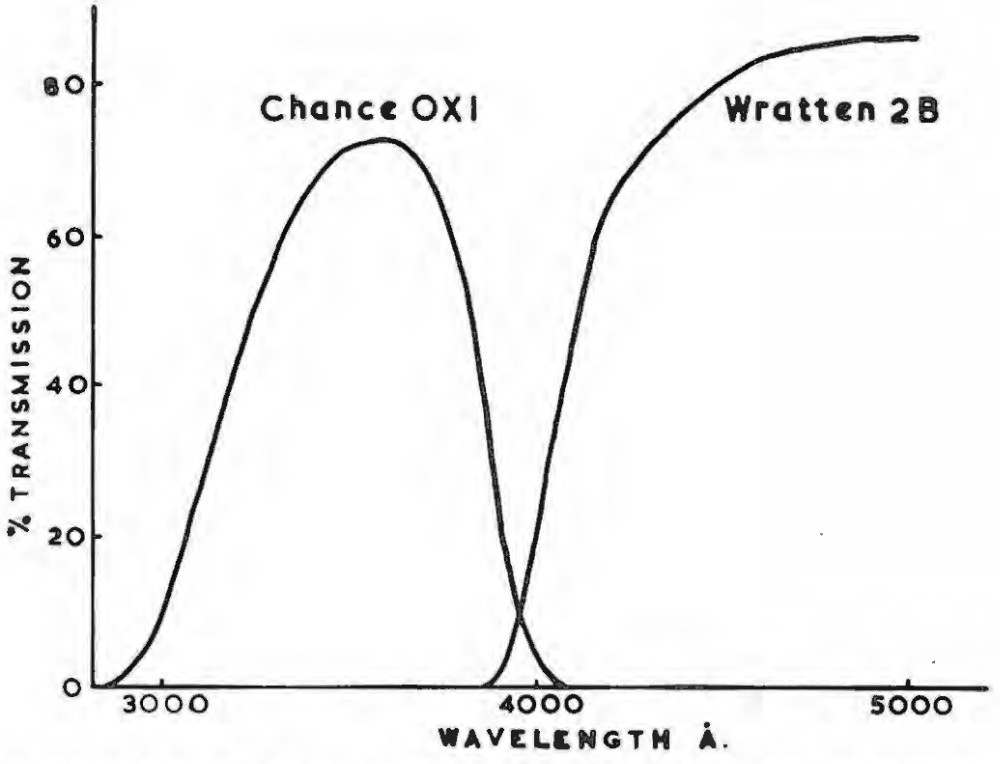


Figure III·4: Filter Transmission Characteristics.

adjusting the G13 voltage to keep the discharge alive. An aluminium cylinder surrounding the points and connected to the earthy electrode made the tube strike less violently, and also served as a reflector. A piece cut from the cylinder allowed the light to emerge through the plane window cemented to the tube. Two side tubes allowed for the evacuation and inlet of air. The working pressure of 5cm. of mercury was found to be a suitable compromise between degree of modulation, which increases, and light output, which decreases with increase of pressure. Figure III.3 shows the variation with pressure of the light modulation as measured by the steady component of the light output with the varying component kept at a fixed value. The light from the tube was focussed onto the specimen by a lens of fairly large aperture (focal length about 10cm) to collect as much light as possible.

3.4 Filters and Specimen Holder. (F_1F_2 and SS in figure III)

It is necessary that none of the exciting light should reach the multiplier while it is looking at the fluorescent light. Since, in general, the fluorescent light is at longer wavelengths than the exciting light (Stokes' law), this may be achieved by the use of suitable optical filters, one before the specimen to transmit wavelengths up to a certain value, and one after to transmit only above this value. The only suitable combination available consisted of a Chance OG1 and a Wratten 2B. Figure III.4 shows the transmission characteristics of these two filters as determined with a Beckman model DU spectrophotometer. The overlap of the two transmission bands is seen to be small, and in practice the light leakage was found to be negligible. The filters were tested to see if they were themselves fluorescent. This was done by comparing the degree of modulation of the exciting light when seen by the multiplier directly and through the two filters in turn. No significant difference was found, but it should be noted

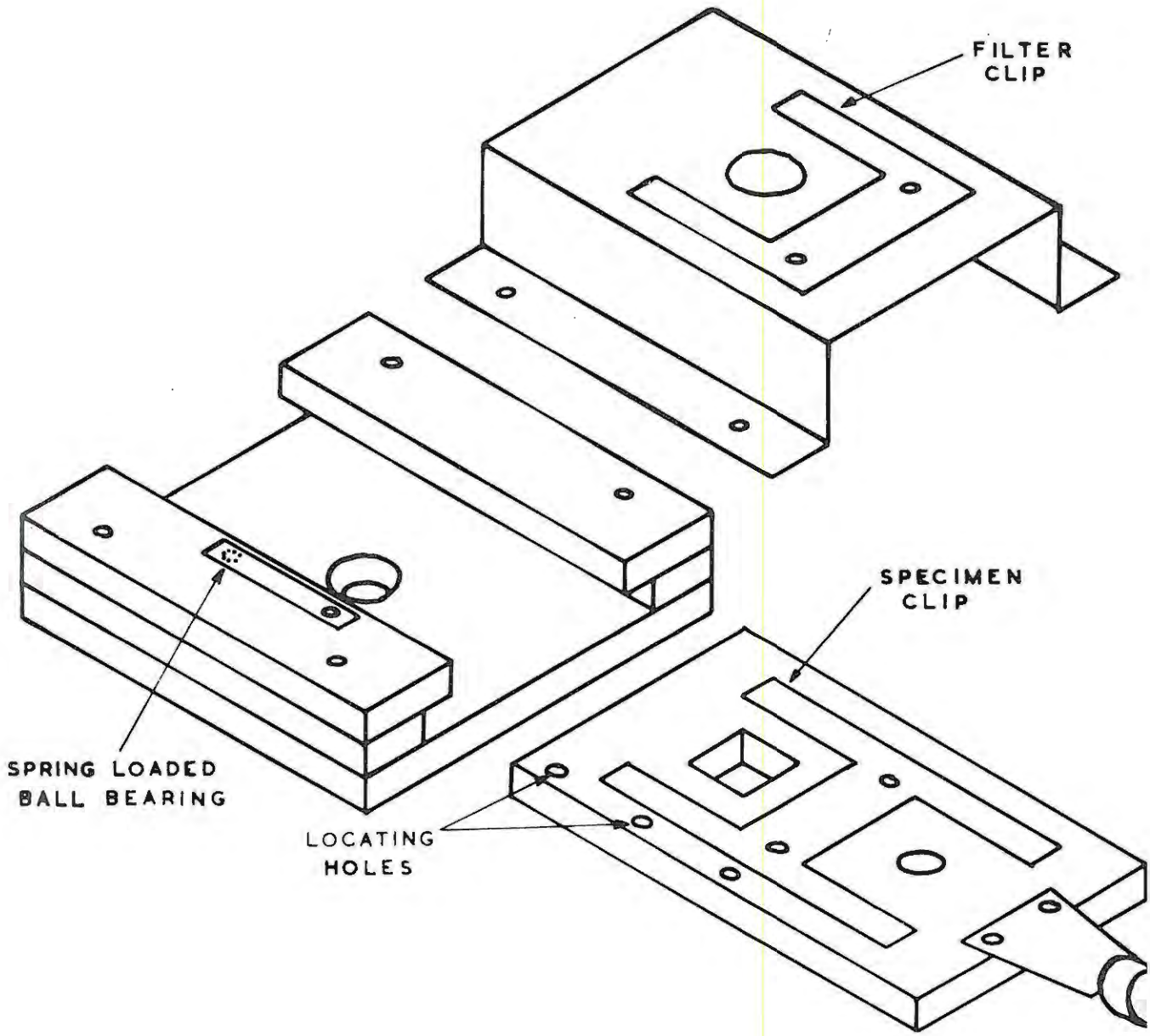


Figure III·5: Specimen Holder.

that a number of other filters tested, particularly those heat treated to obtain the required characteristics, were strongly fluorescent.

The specimens were mounted on a sliding stage (SS in figure III) so that alternate readings could be taken on the fluorescent and exciting light. The stage was enclosed in a box which fitted onto the top of the multiplier casing (figure III.5): two holes allowed the exciting light in and the fluorescent light out. Between the discharge tube and the specimen holder is a shutter (S in figure III) and an iris diaphragm (D in figure III), both of which could be swung into and out of position. The shutter served to cut off the exciting light from the specimen to give a zero reading due to any stray light. The iris diaphragm was used to adjust the intensity of the exciting light when this was being looked at by the multiplier directly, since this intensity had to be adjusted until the varying component was identical with that obtained with the fluorescent light (see 2.4).

3.5 Photomultiplier (P.M. in figure III).

For an optical detector-transducer a photomultiplier was used, as it combines the functions of light detector, conversion to electrical signals and amplification. It is also a wide band device so that signals of complex shape will be accurately reproduced, and the output is proportional to the input for the range of currents used.

The best multiplier available for this work was an electrostatically focussed R.C.A. 5819. This was mounted vertically on the detector chassis and screened by a light-tight brass cylinder which also supported the specimen holder (figure III.5). It was unfortunately found that the two tubes of the above type available were both unstable when overall applied voltages in excess of 1000 volts were applied. Since these tubes are rated up to 1250 volts, this imposed a serious limitation on the gain available. This instability was

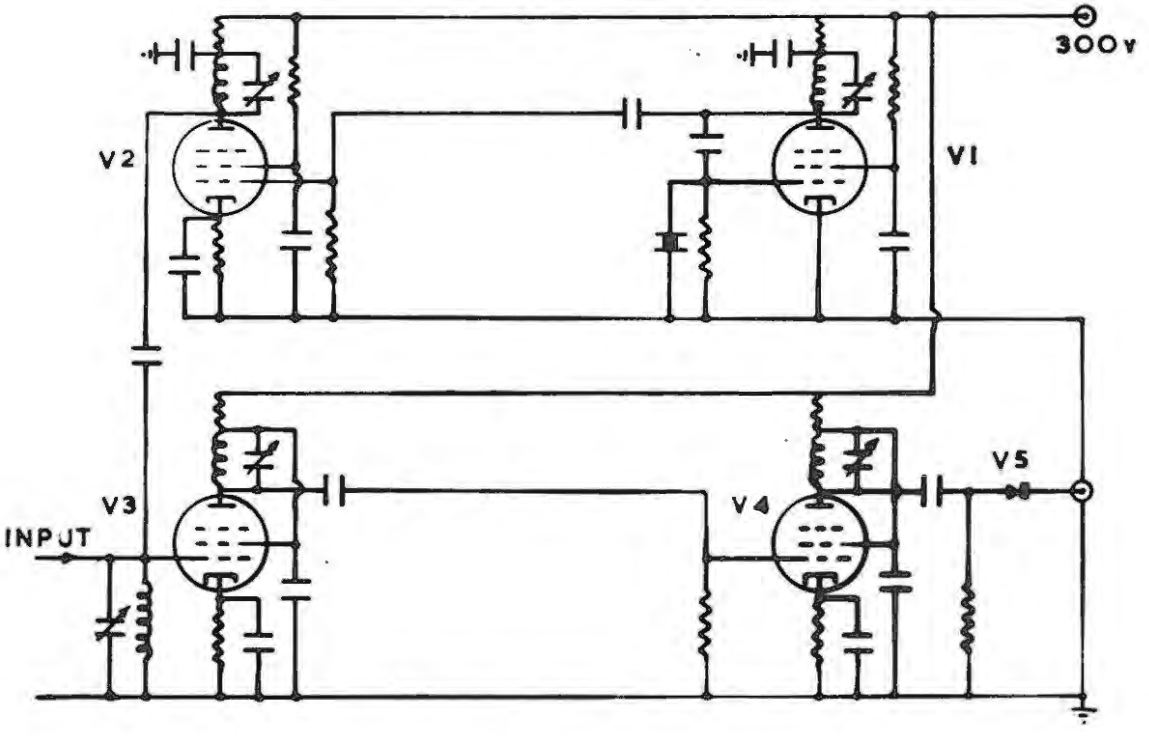


Figure III·6: Detector Circuit.

probably due to some sort of internal breakdown or to regenerative feedback effects (Stump and Talley 1954). Since it was convenient to adjust the multiplier gain by varying the applied voltage, and somewhat inconvenient to stabilise the individual voltages, the situation was tolerated and increased detector sensitivity used. The usual mumetal magnetic shield was not used as this increased the tendency to instability, and its absence did not affect the operation in any way.

3.6 Detector (DET. in figure III).

The circuit of the heterodyne detector is shown in figure III.6. The oscillator V_1 is a tuned-grid-tuned-plate circuit with the crystal as the grid tuned circuit (Terman 1951, p 429). Various crystals could be used, the value being chosen to give a suitable intermediate frequency with the light modulation frequency. The output from the oscillator is fed into a tuned amplifier V2 that can be tuned to one of the crystal harmonics to give a suitably high frequency for mixing. This was necessary as the only crystals obtainable were in the range 6-9Mc/s and it was desired to work in the range 15-30Mc/s. The local oscillator and multiplier signals were then fed onto the control grid of a pentode mixer V3, whose anode circuit was tuned to the intermediate frequency. The i.f. was then amplified by V4 and rectified by the crystal diode V5. The whole unit was built into a very well shielded copper box and the internal parts individually shielded. The unit was found to be stable and reliable in operation.

For a deflection of 25cm. on the output galvanometer (a typical value) an input to the mixer of 10mv. was required. This corresponds to a multiplier current of $\approx 2\mu$amp. compared to a steady current value of about 25 μamp. The selectivity of the unit is illustrated by the curves of figure III.7 which give an overall Q of about 100 which is quite satisfactory, although image

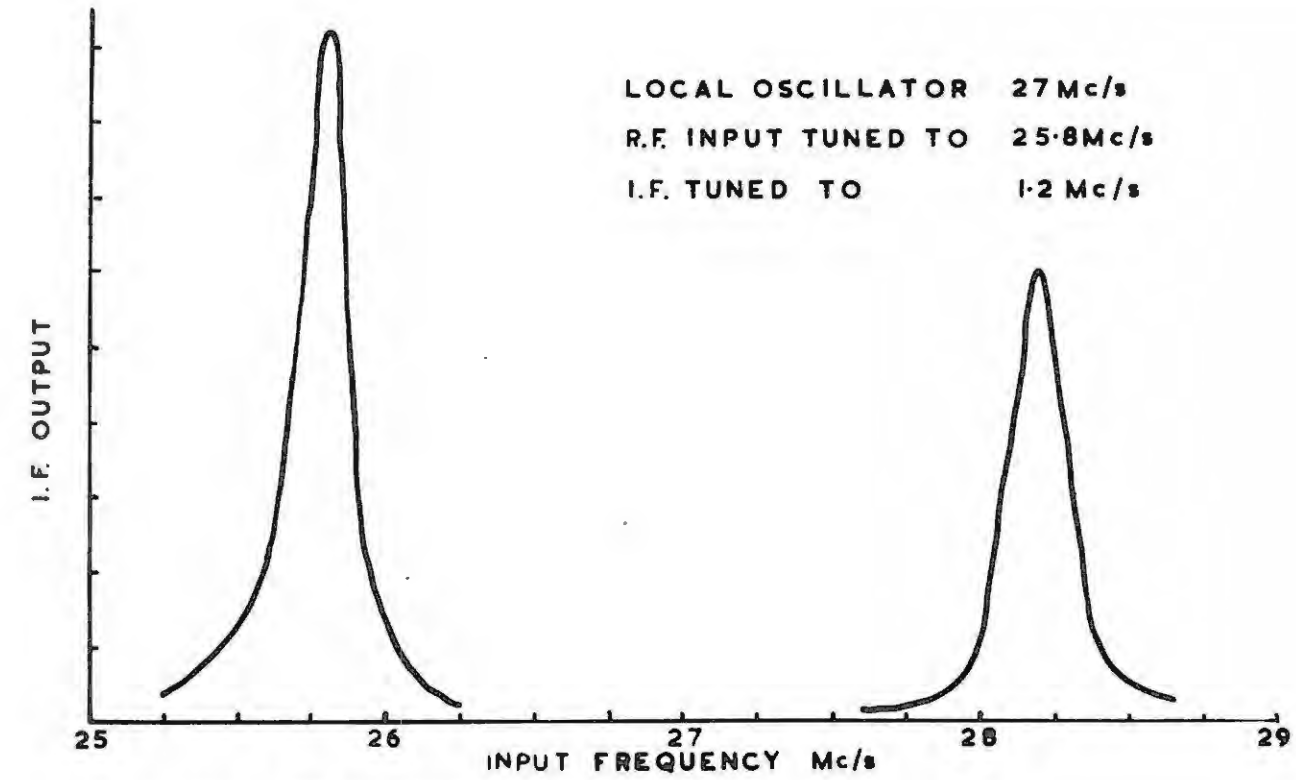


Figure III·7: Detector Selectivity.

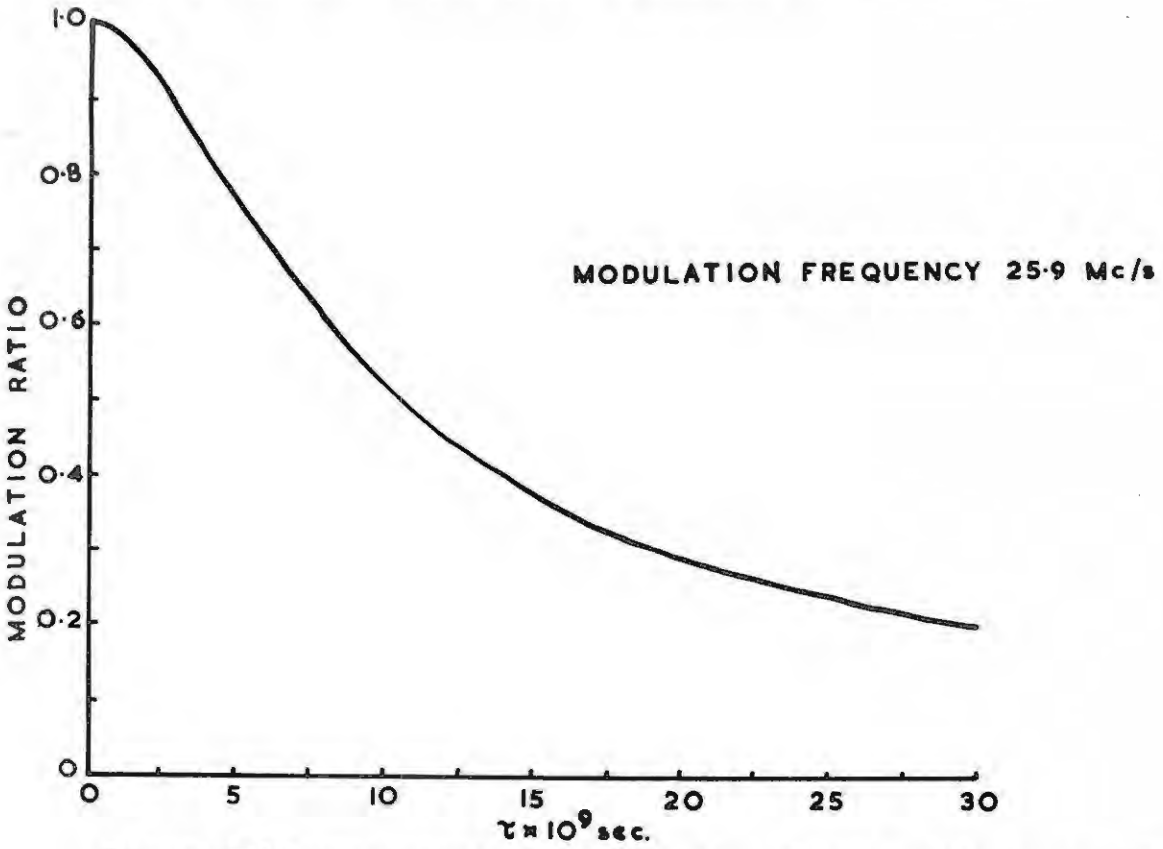


Figure III·8: Variation of Modulation Ratio with Decay Time.

rejection is not very good. The choice of discharge tube modulation frequency for a particular order of decay time was made on the basis that if in equation 2.5.16 we make $(1 - M^2)^{\frac{1}{2}} = M$, i.e. $M = 0.707$, then τ will be least sensitive to errors in measurement of M and will depend mainly on ω which is accurately known. This is shown by the plot of M vs. τ (figure III.8) for a particular frequency (25.8Mc/s) where it is easily seen that the curve is steepest in the region where $M = 0.707$. Towards either end the curve is rather flat, and small variations in M give large variations in τ. For the range of τ encountered ($3-30.10^{-9}$ sec.) this gives a frequency range of 6.6 to 30 Mc/s. The crystals available, however, limited the lower frequency to about 13 Mc/s.

3.7 Power Supplies. (P.S.1,2,3,4 in figure III).

Due to mains fluctuations and the need for good stability over a fair period, all the power supplies used were electronically stabilised. Four units were required, one of which - the multiplier supply - was constructed by Mr. A.R.Scanlen, and was a copy of the A.E.R.E. Harwell type 1007 unit (P.S.3). The others were as follows:

(i) a 300 volt, 100 ma. supply for the detector to a standard laboratory design (P.S.4).

(ii) a 450 volt, 150 ma. supply for the power oscillator (except output tube) from Elmore and Sands (1949, p 375) (P.S.2).

(iii) a 500-1500 volt, 200 ma. supply for the power output tube of the power oscillator (figure III.9) (P.S.1).

With the material available, the design of this unit proved somewhat difficult. Since the discharge tube would extinguish if the 813 plate voltage was even momentarily removed, the output had to be continuously variable. The only series regulator tubes available, however, were type 807 (maximum plate voltage 750), so that it was necessary to use a variac on the transformer

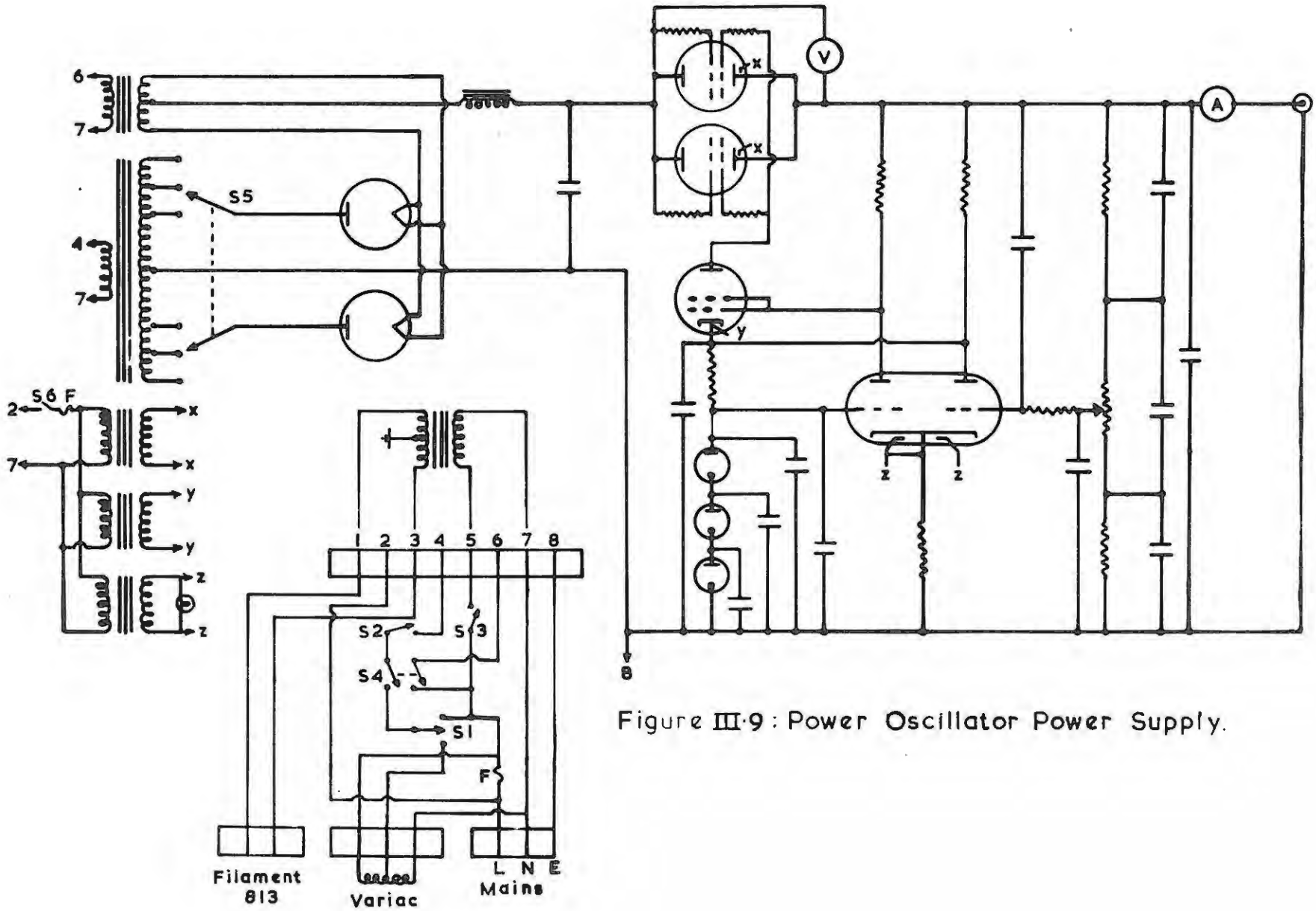


Figure III·9 : Power Oscillator Power Supply.

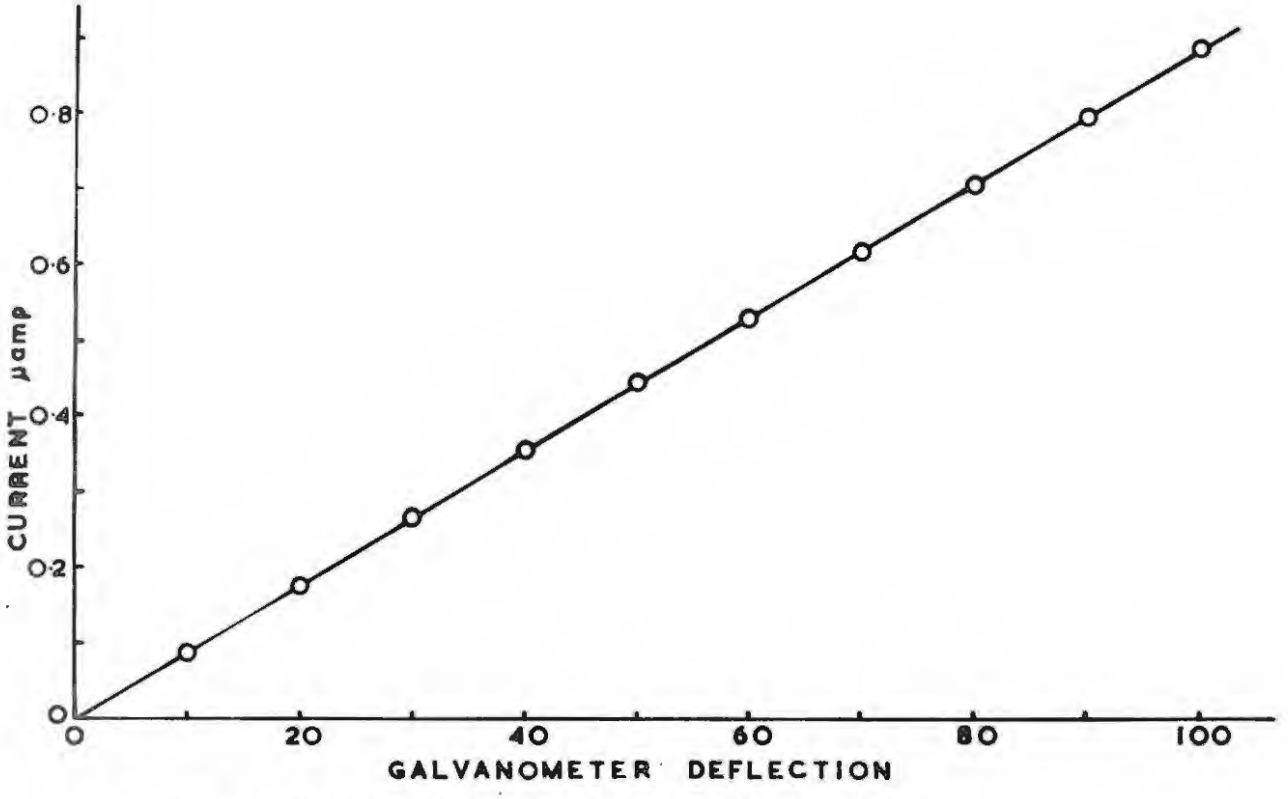


Figure III·10 : Galvanometer Calibration.

input as well as the normal means of output variation (variation of the grid tap of the first stage of the feedback amplifier). Then, using both controls, it was possible to keep within the ratings of the series tube.

3.8 Calibration of Steady Component Galvanometer. (G1 in figure III).

The galvanometer used to measure the steady component of the multiplier output was a Cambridge spot galvanometer giving full scale deflection for 1 amp. The response was claimed by the makers to be linear to better than 1%. This was checked using a simple circuit with standard resistances, and the results are shown in figure III.10. It is seen that the deflection is linear to better than 1%.

3.9 Phosphors, Solvents and Preparation of Specimens.

The phosphors used were obtained from four sources. The 1cm. cube crystals were obtained from the Large Nuclear Instrument Co., Palisades Park, New Jersey. The other phosphors, in powder form, were obtained by Prof. J.B. Birks from Prof. J.W.Cook of Glasgow University, and from Prof. M.S.Newman of Ohio State University, to whom we are much indebted. A dye (eosin) used for checking the operation of the apparatus was supplied by Distillation Products Industries-Eastman Kodak Co. The 1cm. cube crystals were used as such. The powdered phosphors were used for the preparation of microcrystalline layers deposited on glass slips by evaporation from solution. The solvents used were the purest obtainable commercially (spectroscopically pure) and were supplied by Hopkin and Williams Ltd. and Eastman Kodak Co. The preparation of the specimens was done mainly by Mr. A.J.M.Cameron with whom the author was collaborating.

3.10 Decay Time Measurement.

The procedure for measuring the decay time of a phosphor was as follows.

The apparatus was run up and allowed to run for one hour before measurements were started. This allowed all initial fluctuations, mainly due to thermal effects, to disappear. The specimen was then inserted in the sliding stage and exposed to the exciting light, the two meter shunts being set to suitable ranges. When the two meters were settled, both readings were taken and then the shutter closed to give the zero readings. The sliding stage was then moved to the 'direct' position, the iris diaphragm inserted in the light path and the shutter opened. The diaphragm was quickly adjusted to give the same reading on the meter indicating the varying component as had been noted with the phosphor, and then the reading of the direct component meter noted. The shutter was again closed and the zero readings taken. The time taken between the two sets of readings was of the order of one minute so that no serious drifts were likely to have occurred. The procedure was repeated five times at least.

From the readings the factor M (see 2.5.15) was evaluated, it being now the ratio of the two steady component readings, as the varying components were adjusted to be identical. The factor $(1-M^2)^{\frac{1}{2}}$ is conveniently found by means of a slide rule with trigonometrical scales relating sines and cosines. Since ω is known from the crystal frequency, τ may be evaluated.

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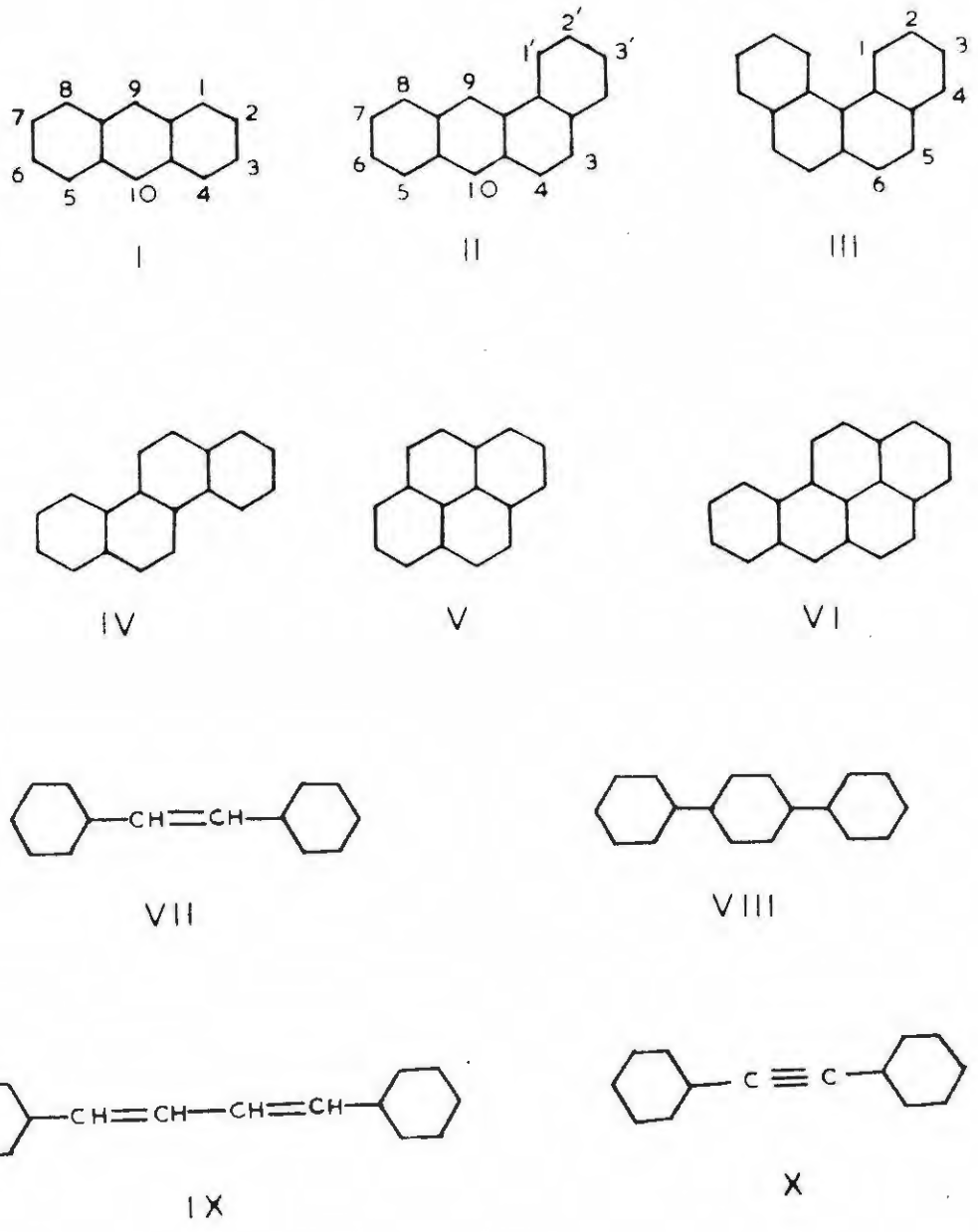

Figure IV: Molecular Structures.

TABLE A.

Photofluorescence Decay Times.

Phosphor	1	2	3	4	5	6	7
Anthracene	6.4(a)	24.2(c)	3.5(g)	14.0(g)	17.0(g)	15.0(e)	13.0(g)
Anthracene	3.1(b)	12.6(d)	3.5(g)	14.0(g)	17.0(g)	25.0(f)	13.0(g)
p-Terphenyl	5.5	5.5	-	3.8	11.0	-	-
t-Stilbene	3.9	4.8	1.7	3.0	3. 1	6.0	-
Diphenyl Acetylene	-	4.9	-	3.0	2.5	15.0	-
Anthracene	5.1(h)	-	-	-	-	-	-

	8	9	10	11	12
Anthracene	15.6,30.0	12.8,30.0	103	75	I
Anthracene	25.9	25.9	5	60	I
p-Terphenyl	15.6,30.0	25.9	15	22	VIII
t-Stilbene	15.6	25.9,15	5	53	VII
Diphenyl Acetylene	-	25.9	-	15	X

1. Microcrystal decay time, present work.
2. Thick crystal decay time, present work.
3. Microcrystal decay time, Birks and Little (1953)
4. Thick crystal decay time, Birks and Little (1953).
5. Thick crystal decay time, Liebson et al (1950).
6. Thick crystal decay time, Hanle et al. (1951).
7. Thick crystal decay time, Schmillen et al. (1953).
8. Light modulation frequencies for microcrystals, present work.
9. Light modulation frequencies for thick crystals, present work.
10. Number of determinations for microcrystals, present work.
11. Number of determinations for thick crystals, present work.
12. Reference to structure in figure IV.

a) Microcrystal deposited from pure solvent.
b) Microcrystal deposited from impure solvent.
c) Freshly cleaved surface.
d) Surface long exposed to the atmosphere.
e) Pure specimen.
f) Commercial Grade (Merck).
g) State of crystal unspecified.
h) Final value corrected for reabsorption.

TABLE B.

Microcrystalline Photofluorescence Decay Times.

Phosphor	τ_m	f	S
1:2 Benzanthracene	11.6	25.7	II
2' Methyl 1:2 Benzanthracene	11.1	25.7	II
3' Methyl 1:2 Benzanthracene	10.1	15.6	II
4' Methyl 1:2 Benzanthracene	13.7	15.6	II
3 Methyl 1:2 Benzanthracene	15.3	15.6	II
4 Methyl 1:2 Benzanthracene	10.1	15.6	II
5 Methyl 1:2 Benzanthracene	125.0	15.6	II
6 Methyl 1:2 Benzanthracene	12.9	15.6	II
7 Methyl 1:2 Benzanthracene	8.8	15.6	II
8 Methyl 1:2 Benzanthracene	99.1	15.6	II
9 Methyl 1:2 Benzanthracene	10.1	15.6	II
9:10 Dimethyl 1:2 Benzanthracene	5.2	15.6	II
2':6 Dimethyl 1:2 Benzanthracene	15.2	15.6	II
2':7 Dimethyl 1:2 Benzanthracene	13.1	15.6	II
3':6 Dimethyl 1:2 Benzanthracene	11.5	15.6	II
2 Methyl Benzo (c) Phenanthrene	17.7	15.6	III
3 Methyl Benzo (c) Phenanthrene	18.3	15.6	III
4 Methyl Benzo (c) Phenanthrene	19.9	15.6	III
5 Methyl Benzo (c) Phenanthrene	20.9	15.6	III
6 Methyl Benzo (c) Phenanthrene	20.6	15.6	III
1:2:3:4 Dibenzanthracene	7.9	15.6	I
1:2:5:6 Dibenzanthracene	14.7	15.6	I
3 Methyl 1:2:5:6 Dibenzanthracene	12.4	15.6	I
9:10 Dimethyl Anthracene	6.1	15.6	I
3:4 Benzpyrene	8.6	15.6	VI
Pyrene	46.5	15.6	V
Chrysene	17.6	15.6	IV
1:4 Diphenyl Butadiene	5.4	15.6	IX

τ_m in μsec.

f = Light modulation frequency in Mc/s.

S = Reference to structures in figure IV.

Five determinations for each compound.

PART IV.

Results and Discussion.

4.1 Results.

The final results obtained (Hamilton 1957) are given in tables A and B. In every case at least five measurements were made, and on some phosphors many more using a number of different specimens in these cases. The total number of determinations in each case is shown. The results shown are just the average of all the individual determinations. The temperature of the phosphors during measurements was within the range $20 \pm 3^{\circ}C$. Measurements on different specimens gave quite significant variations as illustrated in table E. These variations are considered to be due to crystal variations and not to errors or inaccuracy in the apparatus since measurements on the same specimen could be reproduced. Possible reasons for these differences are discussed in 4.4 and 4.5. An example of one set of readings is shown in table C. This is an average example and illustrates the random fluctuations obtained in a set of measurements on one particular sample.

4.2 Check Result and Accuracy.

A convenient check on the operation of the apparatus is the measurement of a decay time that is already accurately known. In the past, most work has been done on organic dye solutions and for some of these the decay times appear to be well known. One immediately available in pure form was eosin, and this was used as the check. The result of this measurement, together with the results of other investigators, is shown in table D. The agreement is very satisfactory and indicates that the apparatus was working correctly.

For a phosphor on which a large number of determinations were made, the statistical error was about 1% which is thought to be due mainly to fluctuations of the discharge tube light source. The other sources of error were the frequency

TABLE C.

Example of Actual Experimental Readings.

Steady Signal		Alternating Signal	M=d/p	$(1-M^2)^{\frac{1}{2}}$	$\tau .10^9$ sec.
Direct(d)	Phosphor (p)				
24.6	53.2	21.4	0.463	0.886	23.8
24.4	52.6	21.6	0.464	0.886	23.7
22.9	49.9	19.7	0.459	0.888	24.0
21.8	47.8	18.3	0.456	0.890	24.2
23.4	50.5	20.8	0.454	0.891	24.3
22.4	48.7	19.2	0.460	0.888	24.0
21.8	47.6	18.7	0.458	0.889	24.1

Modulation frequency = 12.850 Mc/s.

Angular frequency = $8.072 \cdot 10^7$ rad/s.

$$\tau = \frac{(1 - M^2)^{\frac{1}{2}}}{\omega M}$$

TABLE D.

Decay time of eosin.

Phosphor	Author ($\tau .10^9$ sec.)		
	Present	Kirchoff (1940)	Macrakis (1938)
Eosin (10^{-4} gm/cm^3 solution in water)	4.73	4.70	4.70

of modulation and the linearity of the detector. The frequencies were all crystal controlled and known to better than 1 part in 10^3, so that errors from this source were negligible. For the detector the linearity of the galvanometer was checked (see 3.6) and found to be linear to better than 1%. The photomultiplier was more difficult to check, and reliance had to be placed on the manufacturers data that the response was linear within specified limits. From these considerations it was deduced that the error was of the order of 2%.

It was also considered necessary to determine whether the modulation of the light from the discharge tube varied with wavelength. If it did, erroneous results would be obtained due to the wavelength dependence of crystal absorption, filters, and multiplier response. To test this, the modulation was measured using filters which admitted different spectral regions to the multiplier. Some very small variations were found, but good agreement between the direct light and that through the usual filter (Chance OX1) was obtained. It would seem that there is a small variation at very long wavelengths, but under the present experimental conditions, the variations are negligible.

4.3 Results of Previous Investigators.

The results obtained by other investigators are given in table A. The two rows for anthracene at the top of the table give results for pure (upper) and for contaminated specimens (lower), except in the cases marked (g). For these the state of the specimen was unspecified, so that the same value had been entered in both rows. There are few published results on the photofluorescence decay times of organic phosphors, but even among these, differences are very evident. The reasons for these differences are not known for certain, but are most probably due to impurities. If the impurities

are non-fluorescent, or have a shorter decay time than the host, they will reduce the overall decay time. The converse holds for impurities with a longer decay time. The case of anthracene is a good example. Using the same lot of anthracene and solvent (xylene) as used by Birks and Little (1953) the same decay time was obtained (3.1 mμsec). Using spectroscopically pure solvent the decay time was found to be 6.4 mμsec. Since the spectral characteristics of the impure specimen were the same as those of a pure specimen, it is evident that the impurity was non-fluorescent. In the case of thick crystals, the decay time for anthracene is given as 14 mμsec. by Birks and Little. In the present work the value was found to be 12.6 mμsec. for a crystal long exposed to the atmosphere, and 24.2 mμsec. for a newly cleaved surface. Crystals having intermediate exposures gave values between these limits, and correspond, for example, to the value 17.0 mμsec. obtained by Ibbsen et al (1950). These differences are probably due to surface oxidation. This effect has been studied by Bowen and Williams (1939) and by Bowen (1953), although only for solutions. The oxide formed is probably non-fluorescent (since the fluorescence spectrum is unaltered), but due to energy transfer, it removes the energy from the excited anthracene molecules and dissipates it non-radiatively, thus reducing the effective decay time. Differences in the values for other phosphors are probably due to the same causes as discussed for anthracene. The results of Henle et al (1951) for anthracene (column 6, Table A) appear to be almost the inverse of our results in column 2. A reasonable explanation may be based on the fact that their measurements were made by examining the 'reflected' fluorescence from a thick crystal. It is known that the 'reflected'fluorescence spectrum is considerably different from the transmitted spectrum (Birks and Wright 1954), due to decreased self-absorption. This will diminish the effective decay time of the crystal. Taking rough measurements of the relative areas of the

spectra from the paper of Birks and Wright, we find the ratio of the 'reflected' to transmitted to be 0.5. Using the relation 4.5.2 with τ_0 = 24.2 n sec. and K = 0.5, we find the decay time for the reflected fluorescence to be 12.1 n/sec. Since the exact value will depend on the angles of incidence and 'reflection', this calculated value agrees well with the value of Hanle et al. The commercial anthracene may be expected to contain some impurity which causes its decay time to be longer than that of the pure material. It cannot be considered to be in agreement with our value of 24.2 n/sec., since it was also measured by 'reflection', and so underestimated. The difference in the values for diphenylacetylene (tolan), can only be attributed to impurities as the self-absorption in this material is very small.

4.4 Discussion of Present Results: Reabsorption.

The effects of reabsorption are clearly shown by the results for para-terphenyl, trans-stilbene and anthracene. These three phosphors have respectively no overlap, a small overlap, and a large overlap of their absorption and emission spectra (Birks and Wright 1954, Cameron 1957). This is reflected in the ratio of the respective thick and microcrystal decay times, which is unity for terphenyl and 3.8 for anthracene. The decay time ratio for anthracene (3.8) is fairly close to the microcrystal-thick crystal spectral ratio of 3.2. This approximate agreement is to be expected on the photon cascade theory (see 4.5) which holds that the increase in decay time is due to repeated absorption and re-emission. The agreement should be exact if the fluorescence efficiency is 100%, and since anthracene has a very high efficiency (see 4.6), it is evident that there was still some reabsorption in the microcrystals used. This was evident from another point of view as discussed in section 2.7. In the case of anthracene, then, we may use equation 4.5.1 to obtain a corrected molecular decay time. We will consider the four

TABLE E.

Corrections to Anthracene Decay Times.

Spec.	K_1	τ_{m1}	K_2	τ_{m2}	K_3	τ_o	τ_{m3}	τ_m
A	0.293	6.55	0.796	5.22	0.234	24.1	5.64	5.43
B	0.340	6.85	0.792	5.42	0.233	22.5	5.25	5.34
C	0.331	6.64	0.755	5.02	0.228	23.9	5.45	5.24
D	0.311	6.58	0.761	5.01	0.236	23.3	5.50	5.26
Means	0.319	6.65	0.776	5.17	0.233	23.5	5.46	5.31

K_1 = ratio of thick to uncorrected micro spectra.

τ_{m1} = measured micro decay time.

K_2 = ratio of uncorrected to corrected micro spectra.

$\tau_{m2} = \tau_{m1} \times K_2$

K_3 = ratio of thick to corrected micro spectra.

τ_c = measured thick decay time.

$\tau_{m3} = \tau_c \times K_3$

τ_m = mean of τ_{m2} and τ_{m3}.

specimens whose spectra as well as the decay times were measured. The figures obtained are shown in table 8.

We have obtained two sets of corrected decay times (τ_{m2} and τ_{m3}) by working from the measured micro values and from the measured thick values, and using the corrected micro spectrum discussed in 2.7. That we obtain substantially the same result in each case is added confirmation for the micro spectrum correction, as is the improved agreement of the K values as shown under K_3 compared with the measured values shown under K_1. The crystal A value for τ_m was used in the Monte Carlo calculation (see 2.6) together with A spectra to yield a thick crystal decay time of 22.7 which agrees well with the measured value, 24.1, giving added confidence in the corrected micro value. The effects of reabsorption on the micro decay times of phosphors other than anthracene are difficult to determine due to the lack of the necessary data on the absorption spectra in the solid state. Terphenyl is unaffected and stilbene only slightly, and all the benzanthracene series have less reabsorption than anthracene as may be seen from the plot of 0-0 to 0-1 peak spacing against the relative heights of these two peaks (Cameron 1957). From the low τ_o value for diphenylacetylene, it appears likely that this also has little reabsorption. For the other compounds no information is available except their extinction coefficients in solution (Friedel and Orchin 1951), which can give only a rough indication as to the possibility of reabsorption.

4.5 Discussion of Present Results: Energy Transfer.

The various possible mechanisms of energy transfer were discussed in Part I. In the past it has been difficult to decide between the various mechanisms, but the position is now more clear and the present results have helped to elucidate some of the difficulties. We will first discuss exciton transfer since it is believed that this mechanism is not operative in molecular crystals, as the

strong coupling necessary is not present. Also, according to Pringsheim, (1949, p 289), 'the total lifetime corresponding to exciton migration becomes shorter in the same ratio as the number of identical crystal elements which take part in the resonance process becomes larger'. We would expect, therefore, that if this process was the only one occuring, the decay time of a microcrystal (with no reabsorption) would, if anything, be smaller than that of a free molecule (usually measured in solution). In practice, the lifetime is longest for the microcrystal. It is difficult, however, to evaluate the effect of deactivating collisions in solutions which shorten the lifetime, but the evidence seems to be against excitons. The argument used by Franck and Livingston (1949) against excitons is unconvincing. They claim that, since the fluorescence spectrum indicates that thermal equilibrium is reached before emission, then every molecule stays excited for longer than one atomic oscillation which would thus exclude exciton migration. However, if the coupling is strong enough, there may be a quick exciton movement through a number of molecules in a time less than one oscillation until the energy is trapped on one molecule by the loss of some vibrational energy, after which thermal equilibrium is reached. In all, the most convincing evidence against excitons is the lack of the strong coupling between molecules which is vital to their existence.

To decide between radiative (photon) and non-radiative (sensitised fluorescence) transfer, we must consider whether there can be photon transfer between adjacent molecules. The situation appears analagous to the case of an electromagnetically radiating dipole. The surrounding field has two components, an inductive field and a radiative field. At small distances the inductive, and at large distances the radiative field, is predominant. Sensitised fluorescence may be likened to the transfer of energy to another dipole through the inductive field where the transfer probability depends on

the wave functions of both molecules simultaneously. Photon transfer may be likened to the transfer of energy through the radiative field, where the transfer probability does not depend on the two wavefunctions simultaneously. These two processes merge into one another and cannot really be separated. For example, Förster(1948) has shown that in anthracene, sensitised transfer can occur over distances of about 8A which is of the order of the size of one molecule, so that transfer over larger distances as found experimentally, are due to photon transfer.

The theory of energy transfer by photons has been given by Birks (1953). He showed that the ratio of microcrystal to thick crystal decay times should be given by :

$$\frac{\tau_m}{\tau_c} = \frac{pK + k}{p + k} \qquad 4.5.1$$

where K is the ratio of the thick crystal spectral area to that of the microcrystal i.e. the escape coefficient. If the efficiency is high then p $\gg$ k and we may neglect k. From 4.5.1 we then have:

$$\frac{\tau_m}{\tau_c} = \frac{pK}{p} = K \qquad 4.5.2$$

The confirmation of this formula by the results of Birks and Little (1953) was rather fortuitous. The ratio of their measured decay times, τ_m/τ_c = 3.5/14 = 0.25, was by chance close to the correct value, 5.1/24 = 0.21, as obtained in the present work. Their value of 0.23 for K was also rather fortuitous as their spectra are considerably different from those obtained later by Cameron (1957), with K = 0.23.

Wright (1955a), in later work in which he considers the effects of the refractive index on the escape of photons from the crystal, gives the approximate formula:

$$\frac{\tau_m}{\tau_c} = \delta + K - \delta K \qquad 4.5.3$$

where δ is an optical escape coefficient. Since, however, δ is small (0.04 for anthracene), this is very little different from 4.5.2.

From the discussions in 4.4 and 2.6 it is evident that photon transfer alone is responsible for the lengthened decay time of thick crystals. The differing decay times for long exposed and new anthracene surfaces (see 4.3) is evidence that photon transfer is not, however, the only energy transfer mechanism operating. This has been discussed by Wright (1955b) on the basis of the present measurements. From measurements of the fluorescence excitation spectrum of anthracene, the thickness of the surface quenching layer is shown to be less than 10^{-4} cm. thick. A comparison of the excitation spectrum with the absorption spectrum shows that most of the incident light is absorbed by the host molecules. The low efficiency found is explained by the quenching action of a low concentration of impurity molecules which will also affect the decay time. This is shown by the results given in Table A. Now, unless the quenching takes place before radiation, at least 23% of the photons will escape from the crystal (K = 0.23: see 4.5), and even if all the other photons were absorbed by impurity molecules, the efficiency would be greater that that found experimentally. Thus the quenching occurs before radiation and so must be due to a non-radiative mechanism. From the evidence it appears then that photon and sensitised transfer both occur in the systems we are considering.

We may thus think of the excitation energy as moving around from molecule to molecule in a random manner (sensitised transfer) until a fluorescence transition occurs. The emitted photon can travel over a considerable distance to be reabsorbed at some other point in the lattice to repeat the above process until it escapes from the crystal. This conclusion agrees with conclusions of Wright (1955b) and Northrop and Simpson (1956), except that the latter consider that the short range transfer is due to 'excitons'. What they term exciton transfer is, however, identical with what we have designated sensitised

transfer.

There are a number of criticism of Northrop and Simpson's paper which are important to note as they affect their conclusions to some extent. The spectra were not measured below 3600Å, which results in a small part of the fluorescence not being recorded, as most spectra are still significant at this wavelength (Cameron 1957). Their specimens were too thick (5μ), as we have shown in 4.4 that there was still considerable reabsorption in some materials for specimens of the order of 1/10μ thick. Thus the spectra are very much reduced in intensity due to reabsorption in that region where the overlap with the impurity molecule absorption spectrum occurs, and so the measured overlap is reduced. They do not state the source of their data on the absorption spectra of the various compounds, and this appears to be almost non-existent in the case of the solid state. That available is for the absorption in solution, but if this was used, it would lead again to reduced overlap, as the absorption in the solid state always occurs at longer wavelengths than in the liquid. Thus the assertion that their quenching factor Q is independant of the overlap, is open to question and may be quite erroneous. The alignment of impurity molecules in the host lattice, which they consider for sensitised transfer, is also important from the point of view of photon transfer due to the polarisation of the emitted light as shown by Birks (1953), and makes photon transfer much more effective in solids. They dismiss photon transfer for the reason that the extinction depth is only of the order of one micron. It is just the existence of photon transfer that extends the excitation to the whole of the crystal and their dismissal of the mechanism, except in the case of deep excitation, is unjustified.

In general, our conclusions are also supported by the work of Swank and Buck (1953), Krems (1955) and Cohen and Weinreb (1956) although they have worked with

TABLE F.

Photofluorescence Quantum Efficiencies.

Phosphor	q(F)	q(A)
Anthracene	1.01	-
1:2 Benzanthracene	2.39	-
3:4 Benzpyrene	2.24	5.32
p-Terphenyl	1.54	4.91
1:4 Diphenyl-Butadiene	4.13	0.61

For q(F) $\propto$ is measured from the fluorescence spectra.
For q(A) $\propto$ is measured from the absorption spectra.

solutions in liquids or plastics and so decreased the photon transfer efficiency compared with solid solutions.

4.6 Quantum Efficiencies.

The theory of the quantum efficiency measurements has been discussed in section 2.7. In using 2.7.1 it is best to use a material for which τ_m/τ_e and $(\delta + K - \delta K)$ are small so that q is less sensitive to errors of measurement. These conditions imply a large overlap of the absorption and emission spectra and are well met by anthracene. Therefore we will first consider the results for the absolute efficiency of anthracene. Using the mean of the corrected results given in table E (i.e. K=0.23, τ_m=5.31, τ_e=23.5) and taking δ=0.04 from Wright's paper (1955a), we find q=1.05. Since the value of δ is rather uncertain it may be better to take δ=0, which gives q=1.01. The value given by Wright is in error mainly due to the use of a value of 18.0 m sec. for τ_e and 6.4 m sec. for τ_m. These values were obtained before the effects of surface oxidation and residual reabsorption were fully realised. In the present work the identical specimens were used for the decay time and the spectral measurements and correction has been made for residual reabsorption. The present result is therefore more accurate than the value given by Wright even considering the errors in the decay times. In view of the present work the accuracy given by Wright (2%) appears to be optimistic and should be more like 10%, which should cover variations of q with as shown above.

Some examples of the quantum efficiencies of other compounds found by the comparison method using 2.7.2 and both absorption and fluorescence spectral areas for α are shown in table F. It is evident that this method is not suitable for measuring q. The direct method appears to be more reliable but only for compounds where the spectral overlap is substantial. The main reason for the failure of the comparison method is the effect of different refractive indicies on the light

collection efficiency in measuring fluorescence as well as absorption spectra. Also, since the compounds are fluorescent, the measured absorption spectrum is only the effective absorption and not the true absorption spectrum so that the area is not strictly proportional to the transition probability p.

4.7 Decay Times, Fluorescence Spectra and Diamagnetic Anistropy.

The very long decay times of 5 and 8 methyl 1:2 benzanthracene ($\simeq$100 mμsec.) appear to be too great to class as normal fluorescence and could be due to transitions from a triplet level instead of the normal singlet level (Garlick 1949, p228; Pringsheim 1949, pp256 & 439). These transitions, direct from the triplet level to the ground singlet level, are forbidded by the selection rules, which accounts for the long decay times. They are usually referred to as slow fluorescence or β transitions (Lewis and Kasha 1944) to distinguish them from the phosphorescence transitions which are due to thermally activated transitions from the triplet state to the excited singlet state with subsequent fast normal fluorescence (α transitions).

The fluorescence spectra of these two compounds are diffuse (i.e. show no vibrational structure) and are shifted to longer wavelengths relative to the other methyl derivatives. β transitions in other compounds are known to produce similar spectra, so that both decay times and spectra point to β transitions. If this is true, then these compounds should be of interest from the point of view of photoconductivity and semiconductivity as the triplet level appears to be concerned in both these processes (Northrop & Simpson 1956a).

The molecular diamagnetic anistropy ΔK is the difference between the average susceptibility in the two perpendicular directions in the plane of the molecule and the susceptibility in a direction normal to that plane. Since the molecules under consideration are essentially planar, the anistropy is a measure of the effective electron mobility in the plane of the molecule. Various

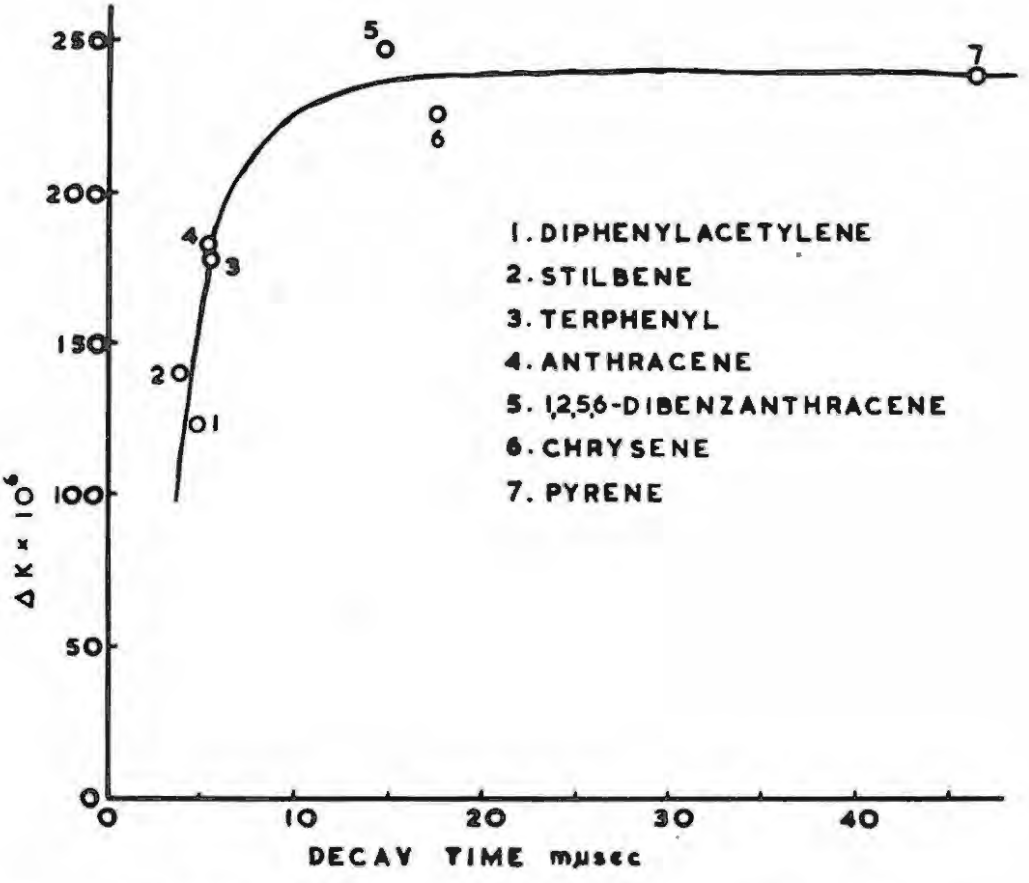

Figure IV·1: Decay Time vs. Diamagnetic Anisotropy.

correlations with ΔK have been found by Sangster and Irvine (1956) and it appeared that there should be a good correlation between ΔK and the photofluorescence decay times, since photofluorescence is a more fundamental process than any scintillation processes. Unfortunately, only a few of the compounds used in the present work have known anistropies. Some calculations have been made by McHenry (1953 and references there) but only for molecules for which there are experimental results or for which we have not measured τ. The available results are shown plotted in figure IV.1. The curve drawn would indicate that a limiting anistropy is attained at large decay times. This indication is, however, based on only one point (pyrene) and may be quite misleading. It may be expected, however, that molecules with very mobile electrons (high ΔK) will have long decay times, as there will be less perturbation of the electron configuration and so less liklihood of a transition.

4.8 Scintillation Decay Times.

It is of interest to compare the photofluorescence decay times with the scintillation decay times. In the scintillation case, the decay time depends on the type of excitation used. Anthracene, for example, has the following decay times:

Table 6.

Excitation	τ (μsec)	Difference.	Reference.
U.V. photons	24.2	-	Present Work.
γ or X-rays	30.1	5.9	Brooks (1956).
Electrons	31	6.8	Wright (1956).
α-particles	53	28.8	Wright (1956).

Under the heading 'Difference', the figures show the difference between the scintillation and the photofluorescence decay times. The general mechanism of scintillation decay has been discussed by Wright (1955c) and must account for the

longer scintillation decay times. The incident particle loses its energy to molecules along or near its path to form a 'primary excitation column' consisting of ionised molecules and excited molecules, the excited molecules predominating. The excitation density depends on the type of incident particle and is greatest for α-particles. There is a considerable amount of quenching due to various causes, such as non-radiative interaction between molecules and the presence of permanently or temporarily damaged molecules. This would tend to shorten the observed decay time, but the diffusion of negative ions back into the excitation column overshadows this and results in a lengthening of the decay time. The lifetimes of excited states other than the first are thought to be very short ($\approx 10^{-11}$ sec.) so that the time taken for the electron, once recaptured, to return to the first excited state is fairly small. Thus the difference between the photofluorescence and the scintillation lifetimes will give a figure for the effective diffusion time modified by quenching.

For electrons and γ-rays this time is of the order of the molecular photofluorescence decay time, while for α-particles it is about four times this. Since the rate of energy loss is proportional to the square of the charge (i.e. α-particles lose energy at four times the rate of electrons), there appears to be a proportional relation between excitation density and effective diffusion time. The rate of energy loss also depends theoretically on the velocity of the particle which would destroy the proportionality. The decay time does not seem to depend much on the velocity, however, as measurements with particles of different energies give essentially the same results. This is probably due to the fact that the particles are stopped in the phosphor, so that they have a wide range of velocities as they are slowed down. Also, the maximum rate of energy loss occurs when the particle is moving slowly, so that the initial velocity is not so important. It is unfortunately not possible to test these ideas on other

phosphors as there are no results for their decay times with electron or α-particle excitation.

4.9 Conclusion.

It has been shown that the method used in the present work is capable of giving reliable and accurate photofluorescence decay times. The method has the advantage over the ultrasonic cell of being easily convertible to different time ranges. The results obtained are considered more reliable than those previously published for the particular compounds concerned, and have elucidated some of the reasons for previous discrepancies. The variations in decay times have helped to substantiate proposals for non-radiative energy transfer process in organic crystals, which has been shown to be sensitised fluorescence, and have demonstrated the very important effects of self-absorption in phosphors.

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PART V.

Transit-Time Spread in Photomultipliers.

5.1 Introduction.

Due to the variations in path length for electrons passing through a photomultiplier, there is a certain spread of the transit times. Thus, a sharp electron pulse at the photocathode will be somewhat smeared out on arrival at the collector. Transit-time spread depends on the number of stages, the degree of focussing and the applied voltage. It is of some interest to know the transit-time spreads in multipliers of various types, since this factor is of importance when the question of time resolution arises, usually in coincidence scintillation work (Birks 1953, Chap.4). In fast coincidence work it is desirable to increase the time resolution as much as possible. The light pulse produced in a phosphor by the passage of an ionising particle is broadened by the finite time of emission and collection of the photons. The spread is still further increased by the spread in the multiplier. To determine what resolutions may be expected for any system, it is necessary to determine the magnitude of both spreads. In preceding parts we have determined the lifetimes of various phosphors, from which the phosphor contribution to the spread may be obtained, and below we will describe our measurements of the multiplier spread. It was pointed out by Dr.G.T.Wright that the apparatus used for measuring decay times, already described, could also be used to measure transit-time spreads, by examining the modulation variation of the output signal from the multiplier with variation of applied voltage and a fixed modulated input.

5.2 Theory of the Method.

To work out the theory of the method, we assume that the 'single electron pulse' from the cathode arriving at the anode is given by:

$$y = te^{-bt} \qquad 5.2.1.$$

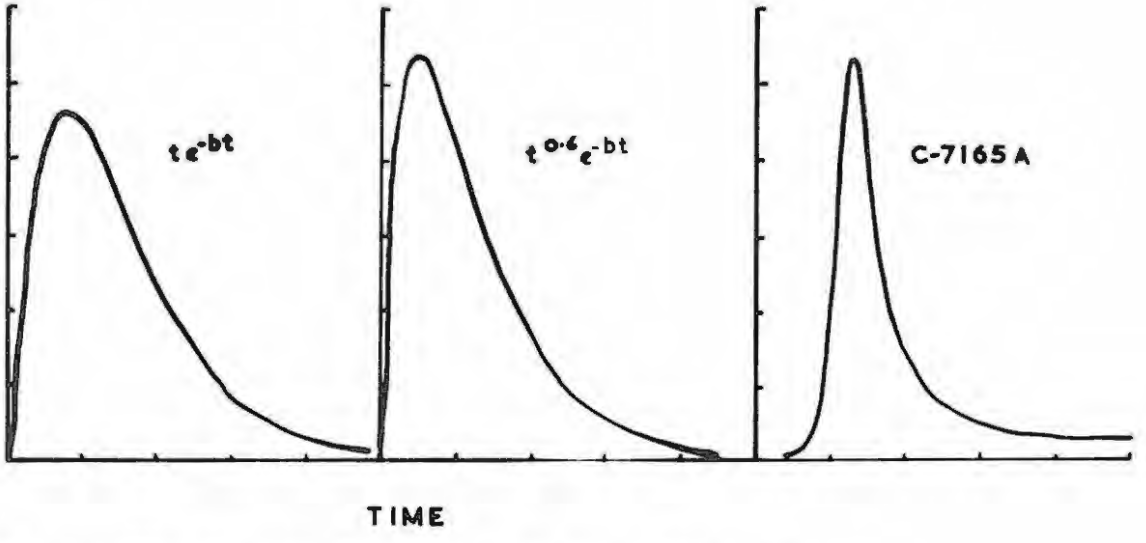

Figure V-1: Single Electron Pulse Shapes.

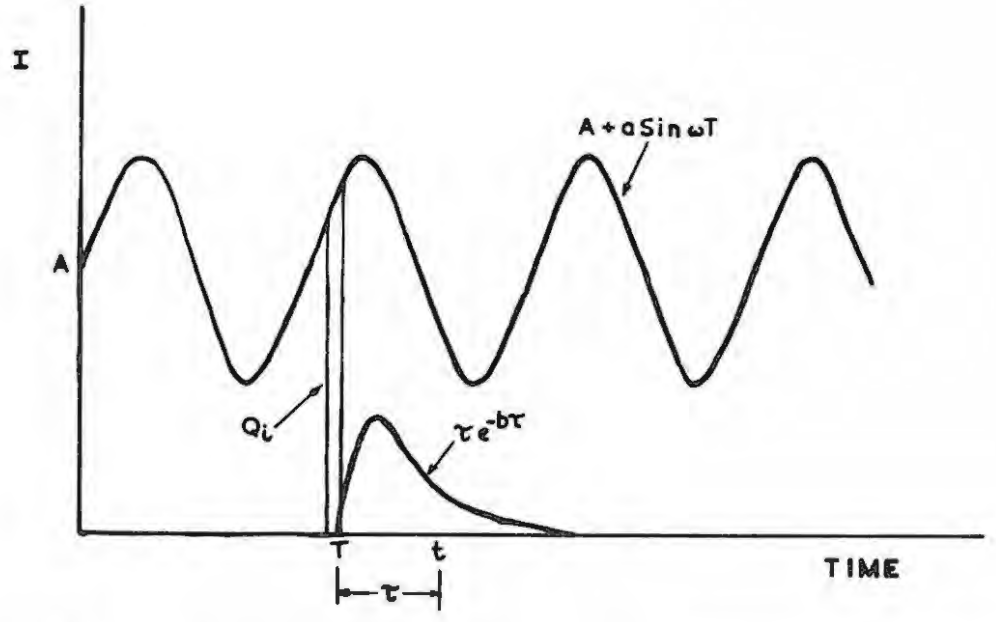

Figure V-2 : Illustrating Transit Time Spread Calculation.

where t is the time and b a constant. This pulse shape agrees well with that found by Swank (1954) for the R.C.A. type of multiplier, and with that found by Meltzer et al. (1955) for the E.M.I. type of multiplier. These three shapes are shown in figure V.1 . As was seen in the theory of the decay time method, it is only necessary to consider the particular harmonic of interest in the exciting light. Thus we will use a simple expression for the intensity of the exciting light I_i at time T :

$$I_i = A + a\sin \omega T \qquad 5.2.2.$$

which will also be the rate of production of photoelectrons at the photocathode. In an interval dT the number of electrons produced will be :

$$Q_i = I_i dT = (A + a\sin \omega T)dT \qquad 5.2.3$$

The total number of electrons that arrive at the anode due to these Q_i is :

$$Q_o = Q_i G = G(A + a\sin \omega T)dT \qquad 5.2.4$$

where G is the average multiplication factor of the multiplier. (This is unimportant as it does not affect the final result). The probability that any one of these electrons arrive at the anode at a time τ later (see figure V.2) is from 5.2.1 :

$$p = \tau e^{-b\tau} \qquad 5.2.5$$

so that the number arriving at this time is:

$$Q_\tau = Q_o p = G\tau e^{-b\tau}(A + a\sin \omega T)dT \qquad 5.2.6$$

The total number of electrons arriving at the anode at time t due to all the previous intervals 'dT' will be :

$$Q = \sum_o^t Q_\tau = \int_o^t G\tau e^{-b\tau}(A + a\sin \omega T)dT \qquad 5.2.7$$

This integral is evaluated in section 6.2 where the result is found to be:

$$Q = \frac{GA}{b^2} + \frac{Ga}{(b^2 + \omega^2)}\sin(\omega t + \phi) \qquad 5.2.8$$

This equation shows how the transit-time spread modifies the modulation of the input signal.

We must now investigate the effect of varying the applied voltage V. For an electron emitted from a certain point on a dynode, the same path will be followed to the next dynode whatever the interstage potential. Since the field distribution remains the same, increasing the potential will merely increase the velocity of the electron. The time for secondary emission to occur is of the order of 10^{-11} sec. (Oroemblat and Miller 1947, Diemar and Jonker 1950), so that even for a ten stage multiplier the time involved is about 10^{-10} sec., which is much less than the actual transit time (about 3-5 $.10^{-8}$ sec.). If s is the path distance for an electron, f the acceleration and t the transit time, then, assuming that secondary electrons are emitted with zero velocity, we have :

$$s = \tfrac{1}{2}ft^2 \qquad 5.2.9$$

Now the force acting on an electron is proportional to the applied voltage V and the force is proportional to the acceleration f. Thus, since s is a constant, we have:

$$V \propto \frac{1}{t^2} \qquad 5.2.10$$

This is confirmed by the results of Smith (1956). It was found by Morton (1949) that the spread in transit time Δt was proportional to the square root of the number of stages n. Also we have $n \propto s$ for equally spaced stages, (which is usual for commercial multipliers), and s t. We have then $\Delta t \propto n^{\frac{1}{2}} \propto s^{\frac{1}{2}} \propto t$ and thus:

$$\Delta t \propto t \propto \frac{1}{V^{\frac{1}{2}}} \qquad 5.2.11$$

As a measure of the spread we will take the half-width of the distribution te^{-bt}. It is not possible to calculate this explicitly, but by trial substitution it is found to be:

$$\Delta t = \frac{2.446}{b} \qquad 5.2.12$$

where b is dependent on applied voltage. We will put b = B when V = 1Kv. i.e.

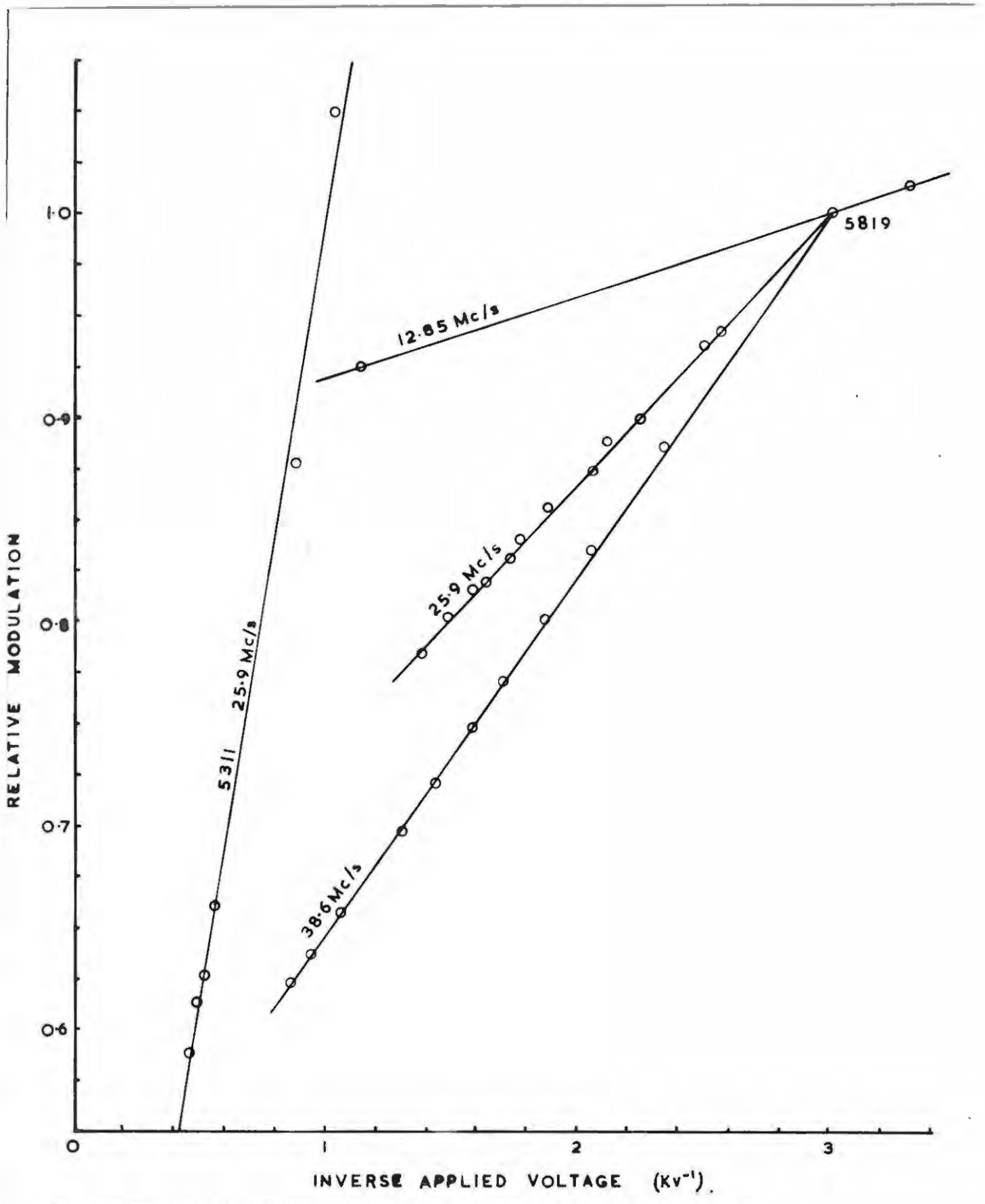

Figure V·3: Multiplier Modulation vs. Applied Voltage

$$\Delta t = \frac{2.446}{B V^{1/2}} \qquad 5.2.13$$

From 5.2.8 the modulation of the output signal at $V = V_1$ is :

$$m_1 = \frac{AB^2 V_1}{A(B^2 V_1 + \omega^2)} \qquad 5.2.14$$

and a similar expression for $V = V_2$. If we consider V_1 as a constant C such that $m_1 = 1$ and put $V_2 = 1/R$ we get :

$$D = \frac{1}{m_2} = \frac{C(B^2 + R\omega^2)}{CB^2 + \omega^2} \qquad 5.2.15$$

$$= kR + P$$

$$\text{where } k = \frac{C\omega^2}{CB^2 + \omega^2} \quad \text{and} \quad P = \frac{CB^2}{CB^2 + \omega^2} \qquad 5.2.16$$

which is the equation of a straight line. Thus if we plot the inverse of the applied voltage against the inverse of the modulation we will get a straight line from which B may be determined.

5.3 Results.

The results obtained are shown in figure V.3. Each curve, for a particular multiplier, is for a different modulation frequency. The points were obtained by varying the applied voltage and noting the steady component of the multiplier output, the varying component being kept at a constant value by varying the intensity of the incident light. Measurements were made on two different sorts of multiplier - an E.M.I. 5311 'venetian blind' type and an R.C.A. 5819 electrostatically focussed type. The results have been normalised and the lines for each set of points obtained by a least-squares fit. The final numerical results are given in table II. The transit times are those measured by Rhoderick and McWhirter (1954) for the 5311 and by Smith (1956) for the 5819.

TABLE II.

Tube	Voltage (Kv).	t(n sec).	Transit Time (n sec).
E.M.I. 5311	2.0	20	55
R.C.A. 5819	1.25	5.9	30

Transit-Time Spreads in Photomultipliers.

The transit times are those measured by Rhoderick and McWhirter (1954) for the 5311, and by Smith (1956) for the 5819.

Transit-time spreads at other applied voltages may be found by using 5.2.13 with B= 0.0865 for the 5311 and B= 0.371 for the 5819.

5.4 Discussion.

The straight lines obtained for the variation of modulation with applied voltage show that the assumptions made in the theory are justified. We may compare our results with those obtained by previous workers. From the work of Allen and Engelder (1951) we can find roughly from the 'single' electron pulse shown, that the spread is of the order of 10^{-8} sec., and Owen (1951) gives a value of $3 .10^{-8}$ sec., both for an E.M.I 5311 tube as we have used. Our value of $2 .10^{-8}$ sec. is not inconsistent with these results. For the 5819 tube, Morton (1952) quotes $5 .10^{-10}$ sec. as the spread per stage so that the total spread will be of the order of $1.5 .10^{-9}$ sec. It would appear, however, that this should be taken as a minimum value, as the results of Smith indicate that it should be somewhat longer. (The area illuminated in the present measurements was a circle of about 1cm. diameter in the centre of the photocathode). Using results published earlier by Morton (1949) we find a spread of $6 .10^{-9}$ sec. for a ten stage multiplier, which is in better agreement with our results.

5.5 Conclusion.

Comparison of the present results with those of previous investigators shows that the method of measuring transit-time spreads described above is accurate, and experience has shown it to be quick and convenient. The statistical error in the results obtained is about 2% and it is estimated that the absolute error is about 5%.

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PART VI.

Evaluation of Integrals.

6.1 Decay Time Integral.

From 2.5 we have the equation 2.5.8 :

$$\frac{dI}{dt} = -k_1 I + \frac{k_2 a \rho}{2} + k_2 \sum_h \left[a_n \mathrm{Cos}(n\omega t) + b_n \mathrm{Sin}(n\omega t) \right] \qquad 6.1.1.$$

This equation may be integrated by standard methods, there being two parts, a complementary function and a particular integral. The first is found from the equation ($D = d/dt$) :

$$DI_1 + k_1 I_1 = 0 \qquad 6.1.2$$

Assuming a solution of the form $I = Ce^{mt}$, where C and m are constants, and $C = 0$, we get on substitution in 6.1.2 an equation for m :

$$Cme^{mt} + Ck_1 e^{mt} = 0$$

from which $m = -k_1$ and :

$$I_1 = Ce^{-k_1 t} \qquad 6.1.3$$

The particular integral is given by :

$$I_2 = \frac{1}{(D + k_1)} \left[\frac{k_2 a \rho}{2} + k_2 \sum_n \left[a_n \mathrm{Cos}(n\omega t) + b_n \mathrm{Sin}(n\omega t) \right] \right] \qquad 6.1.4$$

The operator $1/(D + k_1)$ may be transformed by a binomial expansion:

$$\frac{1}{(D + k_1)} = \frac{1}{k_1} - \frac{D}{k_1^2} + \frac{D^2}{k_1^3} + \ldots$$

which operates on the first part of the square bracket to give :

$$I_2' = \frac{k_2 a \rho}{2k_1} + 0 + 0 + \ldots \qquad 6.1.5$$

To evaluate the second part we will consider only one term of the summation:

$$I_2'' = k_2 a_n \frac{1}{D + k_1} \operatorname{Cos}(n\omega t)$$

$$= k_2 a_n \operatorname{Re.} \frac{1}{D + k_1} e^{in\omega t} \qquad \text{(Re. = real part)}$$

$$= k_2 a_n \operatorname{Re.} e^{in\omega t} \frac{1}{(in\omega + k_1)} 1$$

$$= k_2 a_n \left[\frac{k_1 \operatorname{Cos}(n\omega t) + n\omega \operatorname{Sin}(n\omega t)}{n^2\omega^2 + k_1^2} \right] \qquad 6.1.6$$

If we introduce the angle β, such that:

$$p\operatorname{Cos}\beta_n = \frac{k_1}{(n^2\omega^2 + k_1^2)}$$

$$p\operatorname{Sin}\beta_n = \frac{\omega n}{(n^2\omega^2 + k_1^2)} \qquad 6.1.7$$

$$p^2 = (n^2\omega^2 + k_1^2)^{-1}$$

Then 6.1.6 becomes:

$$I_2'' = \frac{k_2 a_n}{(n^2\omega^2 + k_1^2)^{\frac{1}{2}}} \operatorname{Cos}(n\omega t - \beta_n) \qquad 6.1.8$$

All the Cos terms will be similar to 6.1.8, and the Sin terms will be similar to:

$$I_2''' = \frac{k_2 b_n}{(n^2\omega^2 + k_1^2)^{\frac{1}{2}}} \operatorname{Sin}(n\omega t - \beta_n) \qquad 6.1.9$$

Thus from 6.1.3, 6.1.5, 6.1.8, and 6.1.9 we have:

$$I = \frac{a_0 k_2}{2k_1} + k_2 \sum_n \left[\frac{a_n \operatorname{Cos}(n\omega t - \beta_n)}{(k_1^2 + n^2\omega^2)^{\frac{1}{2}}} + \frac{b_n \operatorname{Sin}(n\omega t - \beta_n)}{(k_1^2 + n^2\omega^2)^{\frac{1}{2}}} \right] + Ce^{-k_1 t} \qquad 6.1.10$$

which is the required expression.

6.2 Transit Time Spread Integral.

From 5.2 we have the equation 5.2.7 :

$$Q = \sum_0^t q_\tau = \int_0^t G\tau e^{-b\tau}(A + a\sin\omega T)dT \qquad 6.2.1$$

This may be divided into two integrals: The first:

$$Q_1 = \int_0^t G\tau e^{-b\tau} A \, dT \qquad 6.2.2.$$

$$= GA\left[\frac{1}{b^2} - \frac{e^{-bt}(bt+1)}{b^2}\right] \qquad 6.2.3$$

Since e^{-bt} decreases more rapidly than bt increases, and in the cases under investigation b is of the order of 10^8 sec.$^{-1}$, the second term becomes negligible after a short time. For the second part of 6.2.1 :

$$Q_2 = \int_0^t G\tau e^{-b\tau} a\sin\omega T \, dT$$

$$= \text{Im.}Ga\int_0^t \tau e^{-b\tau} e^{i\omega T} \, dT \qquad (\text{Im.} = \text{imaginary part})$$

$$= \text{Im.}Ga\, e^{i\omega t}\int_0^t \tau\, e^{-(b+i\omega)\tau} \, d\tau \qquad (T = t-\tau)$$

$$= \text{Im.}\frac{Ga(b-i\omega)^2}{(b^2+\omega^2)^2}\left[e^{i\omega t} - e^{-bt}\left[(b+i\omega)t + 1\right]\right] \qquad 6.2.4$$

This may be multiplied out and the imaginary terms picked out. Certain of these may be eliminated using the argument applied to 6.2.3 above, and we eventually arrive at:

$$Q_2 = \frac{Ga}{(b^2+\omega^2)^2}\left[(\omega^2-b^2)\sin\omega t - 2\omega b\cos\omega t\right] \qquad 6.2.5$$

This may be simplified by introducing the variable ϕ such that:

$$\sin\phi = \frac{2\omega b}{(b^2+\omega^2)} \quad ; \quad \cos\phi = \frac{\omega^2-b^2}{(b^2+\omega^2)} \qquad 6.2.6$$

so that 6.2.5 becomes:

$$q_2 = \frac{Ca}{b^2+\omega^2} (\cos\beta \sin\omega t - \sin\beta \cos\omega t)$$

$$= \frac{Ca}{b^2+\omega^2} \sin(\omega t-\beta) \qquad 6.2.7$$

From 6.2.3 and 6.2.7 we get :

$$q = \frac{Cb}{b^2} + \frac{Ca}{(b^2+\omega^2)} \sin(\omega t-\beta) \qquad 6.2.8$$

which is the required expression.

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PART VII.

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