AN INVESTIGATION OF THE SPECTRA AND DECAY TIMES OF SOME ORGANIC PHOSPHORS UNDER ULTRAVIOLET AND IONISING RADIATION

by

W.A. Little

Thesis presented for the Degree of
Doctor of Philosophy at
Rhodes University.

June, 1954.

INDEX

PART III

THE MEASUREMENT OF THE DECAY TIME OF FLUORESCENCE EMISSION FROM ORGANIC PHOSPHORS

PART IV

THE INVESTIGATION OF THE SPECTRA OF SOME ORGANIC PHOSPHORS UNDER IONISING RADIATION

Section B

PART V

PART VI

EXPERIMENTS WITH ELECTRON BEAM

PART VII

MEASUREMENTS OF THE DECAY TIMES OF ORGANIC PHOSPHORS UNDER IONISING RADIATION

PART VIII

ACKNOWLEDGMENTS

In work of this type one has to draw continually on the advice and experience of people only distantly connected with physics. These are the people I would first like to thank for their gracious help. I am indebted to most of the research students of the Chemistry Department for help and advice at one time or another on problems connected with cements, optics, solutions and chemicals. I wish to thank Mr. H.V. Eales of the Geology Department for invaluable help in early attempts to procure quartz for the optical apparatus, and for his help and advice in grinding some of the quartz blanks to optical tolerance.

In the construction of the apparatus I am indebted to Mr. A. Ross-Scanlen for much helpful advice on the use of materials and tools. I wish to thank him, too, for constructing much of the heavy apparatus and awkward pieces of precision engineering. I wish to thank Mr. F. van der Water for his patience and skill in glass-blowing.

Nearer home I would like to take this opportunity to thank Dr. S.W. Watson for his invaluable help on problems connected with optics and high vacuum, and Dr. M.E. Szendrei for advice on electronics. I am further indebted to Dr. M.E. Szendrei for his calibration of the transmission curves of the spectrophotelometer.

In the text I have made more specific reference to the help I have had from Dr.G.T.Wright. Here I would like to thank him for this help and for the many stimulating discussions I had with him during the period of this work.

Next I would like to acknowledge my gratitude and thanks to Professor J.B.Birks for the pleasure of working under him. I wish to thank him for his continued help, advice and criticism throughout the time this work was done. I must thank him, too, for suggesting the original problem and for safely leading me away from some of the interesting, but unimportant, cul-de-sacs en route. His initiative and enthusiasm continually instilled one with fresh interest in the problem under investigation and his ability of acquiring instruments from industry, government and even university departments made it possible for me to complete this work in a reasonable length of time.

I would like to thank Miss A.W.Smith M.A. for her care and patience in reading the proofs of the thesis and for correcting many of the grammatical errors in the English.

Finally, I wish to thank Mr.N.Baxter, acting on behalf of the Rotary Club of East London, for financial assistance during the lean years, since without it this work could not have been started; the South African Council of Scientific and Industrial Research for a maintenance bursary and for the purchase of major equipment; and the Shell Petroleum Company Pty., Ltd. for a Scholarship during the latter part of the work.

PREFACE

In this thesis I have given an account of the work carried out by me on the measurement of the spectra and decay times of a few selected organic phosphors under ultraviolet and ionising radiation. The purpose of the investigation has been to attempt to throw more light on the mechanism by which energy migrates within the crystalline lattice.

A general introduction is given to the process of fluorescence and the various proposed theories by which the excitation energy, which eventually appears as fluorescence light, is able to move about in the crystalline lattice. This constitutes Part I. In Part II I have recorded the investigation of the spectra of some of these phosphors under ultraviolet light. The rather interesting results which were obtained here were first presented in a paper read at the Jubilee Meeting of the South African Association for the Advancement of Science held at Cape Town in July 1952.[1] The inherent difficulties of this spectral method of approach led me to suggest, at this meeting, that it should be possible to determine the part played by photon-emission and re-absorption in the energy transfer process, if the decay time of the fluorescence emission was measured for large and small crystals. On returning from this Conference I started work on this project.

At first progress was very slow. This was due to the fact that at this time the laboratory was very poorly equipped for research. In particular, quartz optical components were urgently needed for the fluorimeter and could not be obtained. For this reason the geologists were consulted and several plates and lenses were eventually ground, in their department, from odd pieces of quartz and some home-grown crystals of alum. The optical plates were ground by Mr. H.V. Eales and myself and the lenses by a local optician. The second reason for the apparent lack of progress during these first few months was my inexperience of research - especially in the fields of electronics, ultrasonics and gaseous discharges. Thirdly, Professor J.B. Birks' illness at this time left me somewhat to my own devices. However, by December 1952 all the individual units of the fluorimeter had worked and in January 1953 the first decay time results were obtained. A report on the construction of the fluorimeter and the results obtained with it have been published in a paper in the "Proceedings of the Physical Society".[2]

After completion of this work two lines of development lay open; either the "pilot" fluorimeter could be improved, on the experience gained on working with it, or the suggestions of Birks' photon theory could be followed up. The latter choice was taken. A technique was developed whereby the fluorescence of a range of phosphors could be photographed under excitation by an intense beam of electrons. This work is described in Part IV.

After obtaining results from this section I wanted to derive an expression for the time a molecule takes to reach thermal equilibrium in a lattice when excited thermally in the electronic ground state. Dr. G.T. Wright suggested that a consideration of the thermal conductivity might give a method of finding this, as the dimensions of a thermal conductivity contain the inverse of a time. By considering this and the other thermal coefficients I have worked out the problem theoretically in a fairly simple manner, and the results obtained are presented in Part V together with a discussion.

Part VI describes some other experiments performed with the electron beam on quartz and on glass. Part VII gives the results obtained with thin metal foils. The results of this section have been published in "Nature".

At this time in the laboratory it was realised that a great deal could be learned about the part played by molecular structure in determining properties of fluorescence if a systematic investigation of the decay times and spectra was conducted ~~into~~ on a large variety of different phosphors. In this programme I was allocated the job of finding a suitable method of measuring the decay times of phosphors under ionising radiation. A technique developed by Liebson was used and an original method devised whereby a calibrating parameter 'n' could be found without the use of elaborate equipment. The results obtained here are presented in a summarised form and their implications are discussed. It is concluded that this technique is suitable for a rapid but approximate survey of many phosphors. It is suggested that a pulsed or modulated X-ray technique would give more accurate results.

Part VIII is the Conclusion. Here I have discussed the two theories of the mechanism of energy transfer. One is due to Professor J. B. Birks, and the other to Dr. G.T. Wright. My own ideas on the subject are given at the end of this section together with some experiments which I consider might throw more light on the transfer mechanism.

In the appendix I have put all matter which has no rightful place in the main body of the text. Appendix I concerns the art of crystal growing; appendix II the stabilisation of the high voltage supply for the photomultiplier; and appendix III an integral which appears in the text.

I hereby certify that, unless otherwise stated, the work done here is original.

WJLittle.

PUBLICATIONS

(1) Scintillation Counting III. "Energy Exchange Processes in Mixed Organic Crystals" by W.A. Little and J.B. Birks. S.A.A.A.S. Congress, Cape Town, July 1952.

(2) "Photofluorescence decay times of organic phosphors" by J.B. Birks and W.A. Little. Proc. Phys. Soc. A 66, 921-928, October, 1953.

(3) "Simple scintillation crystal growing technique" by W.A. Little, Journal of Scientific Instruments, Vol. 30, p.253, July 1953.

(4) "Cathodoluminescence of Air, Quartz and Metal Films" by J.B. Birks and W.A. Little. Nature (London) 174, 82-3, July 10, 1954.

PART I. GENERAL INTRODUCTION

Section A.

The Process of Fluorescence

For an understanding of the process giving rise to fluorescence in organic crystals we will consider first the behaviour of a simple fluorescent diatomic molecule. (Bowen 1949).

A(a) Molecular Model

Let such a molecule consist of two atoms X and Y separated by a distance 'r'. If we plot the potential energy of the configuration against the separation we obtain the familiar Morse curve as shown in Figure I. The curve of lowest energy corresponds to the ground state of the molecule and has a position of equilibrium at the point of minimum potential energy 'a'. At higher electronic energies we obtain the first electronically excited level at B' also with a position of equilibrium. This position of equilibrium will be, in general, at a different separation to that of the ground state because the molecule may have here a higher rotational energy causing a centrifugal broadening. Thus the excited molecule will interact with the environment to an extent depending upon its electronic energy. Above the first level are the second, third, ... etc., excited electronic levels extending up to the curve dd' which has no minimum except at infinity. At this energy the molecule will

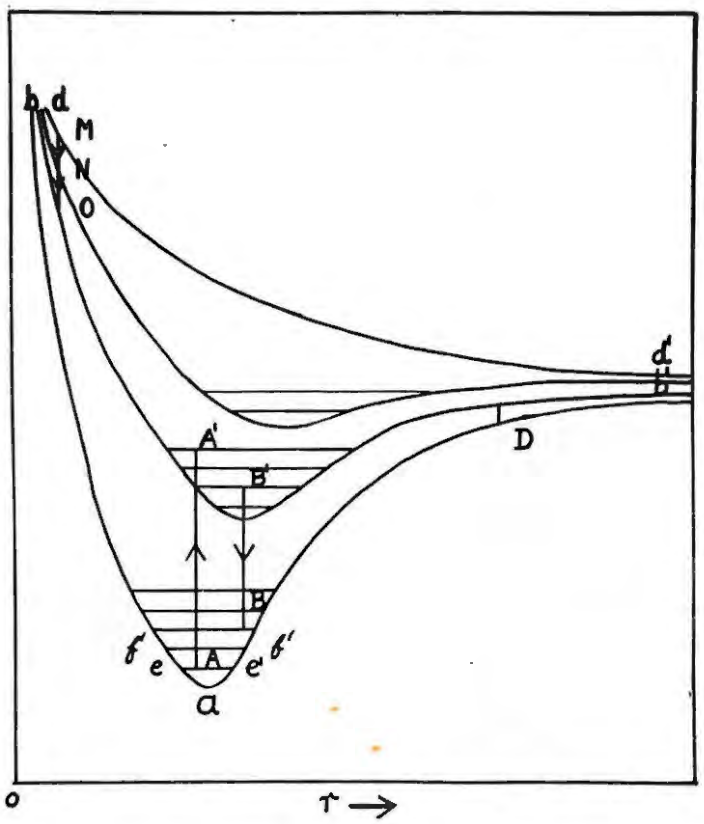


Figure I. MORSE DIAGRAM of a simple diatomic molecule. The Potential Energy 'V' plotted against the separation 'r' of the constituent atoms.

no longer remain bound and the atoms will separate.

The molecule also possesses energy by virtue of the vibration of its constituent atoms. Hence superimposed upon each of the electronic levels of the molecule will be the vibrational levels. The binding force of the atoms will determine the frequency ν with which they vibrate and the energy difference ΔE between these vibrational levels will be given by the quantum condition:

$$\Delta E = h\nu$$

The allowed configurations of the molecule are given by the constant energy lines ee', ff' etc., as shown in the figure. The atoms vibrate between the limits ee', ff' etc. with potential energy at any instant given by the position on the Morse curve, and with kinetic energy equal to the difference in energy between this position and the constant energy line ee', if it lies in the ee' vibrational level.

To determine in what state we are likely to find a particular molecule we must resort to Boltzmann statistics. (Garlick, 1949). The number of molecules n' in a particular energy level E is given by the equation:

$$n' = n_o e^{-\frac{E-E_o}{KT}}$$

where: E is the energy of level with population n'.

E_o is the energy of level with population n_o.

k is the Boltzmann constant.

T is the absolute temperature.

The first electronic level is a few electron volts above the ground state and the separations of the vibrational levels ~~is~~ are of the order of 0.08 eV for typical molecules. The product kT is of the order of 0.02 eV at room temperatures. By putting these values in the above equation we see that most of the molecules are in the lowest vibrational-levels of the ground state. In considering the absorption of light we can then limit ourselves to molecules in these low levels.

In the case of organic molecules composed of a large number of atoms, this Morse diagram must be replaced by one in many dimensions to allow for the interaction of all the particles. However, as most of the properties of fluorescence may be seen from the simpler model, we will use it to explain the basic ideas of emission, quenching and resonant transfer of energy in organic phosphors.

A (b) Fluorescence

Having obtained now a suitable model of the molecule let us consider what happens when it absorbs light and becomes excited. Later we will consider the more complicated process of excitation by ionising radiation.

From the above we see that the light will be absorbed by a molecule in one of the low vibrational levels of the ground state. Its energy will rise along the vertical line AA'. According to the Franck-Condon principle (Mott and Sneddon, 1948), the momentum and separation of the molecular constituents will not change appreciably during the time for this electronic transition. Thus on the diagram the line will be vertical and will meet one of the vibrational levels of the excited state at such a place that the momentum condition will be satisfied in this level. Owing to the different positions of equilibrium in each level, the molecule may be in both an excited electronic state and a high vibrational level. This "hot" molecule will dissipate its excess energy in one of three ways.

Firstly, if it is strongly coupled to its neighbours it will quickly reach thermal equilibrium with them by dissipating its excess vibrational energy before the optical transition to the ground state will have a chance to take place. This optical transition, which is the fluorescent emission of light, will then correspond to the return path BB'. From B it will lose further thermal energy until it again reaches equilibrium with its neighbours in the ground state.

The second possibility occurs if the molecule is not strongly coupled to its neighbours. In this case the optical transition may possibly occur before the molecule has reached thermal equilibrium. The molecule will then be able to make any transition between A'A and B'B. This is known as a resonant transition since ~~for~~ the processes of emission and absorption can occur at the same frequency and are thus thought of as being in resonance. This would result in a strong overlap of the emission and absorption bands.

The third case occurs if the molecule rises into such a high vibrational level that the constituent atoms move to D, where the ground and first excited states approach each other very closely. At D a non-radiative transition from the excited state to a high vibrational level of the ground state can occur, and all the energy is lost as heat to the lattice. If the probability of this process is q per unit time and the probability per unit time of the optical transition is p, then $\frac{q}{q+p}$ of the absorbed photons will be lost as heat. The quantum efficiency, which is defined as the ratio of emitted photons of flourescence to absorbed photons, will then be $1 - \frac{q}{p+q} = \frac{p}{p+q}$. A rise in temperature will increase the population of the higher vibrational levels of the ground state, and hence will increase the probability of a transition to an excessively high vibrational level in the electronically excited state. This will increase the probability of non-radiative dissipation of energy and thus decrease the quantum efficiency of the process.

In some molecules the position at which the constituent atoms are in equilibrium (in each of the excited states) may be approximately the same. In this case transitions from the ground state to a higher electronic state will take place between the ground state and only the low vibrational levels of the electronically excited state. The reason for this is that the momentum condition of the Franck-Condon Principle must be obeyed so that the absorption coefficient for radiation will be small except for transitions into the low vibrational levels. The factor q will be small and the quantum efficiency high. However, the emission and absorption bands will strongly overlap one another and the material will not be highly transparent to its fluorescent radiation.

A (c) Stokes' Law

It can be seen from the model that, in general, some heat will be dissipated to the neighbours in each of the emission processes. This loss of energy between the absorbed and emitted photon will cause the fluorescent light to be of longer wavelength than that of the absorbed light as is in agreement with the classical Stokes' Law (Pringsheim, 1949). This law states that the fluorescent light will be of longer wavelength than the absorbed light. Anti-Stokes' emission can be accounted for by the same model.

If a molecule, in a high vibrational level of the ground state, rises to a low vibrational level of the excited state and returns via B'B the difference in the vibrational energies will be converted into electronic energy which will give light of shorter wavelength than the absorbed light. This process has a smaller probability of occurrence than normal Stokes' emission.

If the higher electronic levels are excited in the molecule instead of the first level only (whether by light or ionising radiation) the energy is degenerated by dissipation of heat to the lattice, and the return path is generally believed to be down MNO into the first excited state. (Pringsheim, 1949). From here it may make the optical transition to the ground state with the same emission as that for the first electronic level directly excited. The spectrum of the emitted light will be of the same shape, regardless of the energy of excitation up to the ionisation level. Above ionisation or energy of dissociation we are no longer considering the same molecule so that the recombination spectrum might contain high energy components not found in the normal emission spectrum. It is supposed that the time for the return path via MNO is so short that the chance of a direct optical transition from any point along it is negligible, compared to the probability of the transition from the first excited state. This is based on the experimental evidence that the observed fluorescent spectrum is independent of the wavelength of the exciting light. This implies that the energy must have been thermally dissipated to the level of the first excited electronic state before an appreciable amount of light could have been emitted. An alternative explanation of this has been put forward recently by Birks (Birks 1952). However, this will be considered later in the light of some of the experimental results.

This simple model explains satisfactorily the fluorescent behaviour of the organic phosphors like anthracene, naphthalene and stilbene. These are all crystalline phosphors in which the molecules are rigid structures barely perturbed by environment and loosely coupled to one another in the lattice (Birks, 1953). Their behaviour should correspond closely to that of the second type considered above, in which the emission and absorption bands strongly overlap and the quantum efficiency is high.

Part I. Section B

(a) Energy Transfer Processes in Organic Phosphors

Bowen and others (Bowen et al, 1949; Ganguly, 1944) have shown that the molecule in a crystalline lattice, which emits light in the fluorescent process, is not necessarily the same molecule which originally absorbed

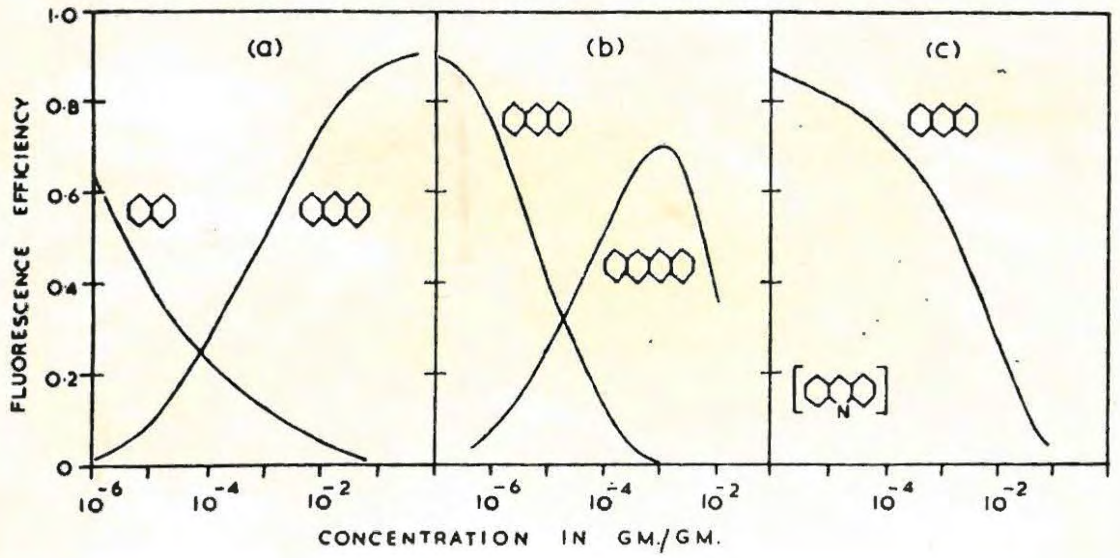


Figure 2. Photo-fluorescence of mixed organic Crystals.

the exciting light. This implies that the excitation energy is capable of moving about within the lattice of the phosphor. Several theories have been put forward in order to explain this energy exchange process. We will consider these in turn after reviewing some of the experimental evidence.

Bowen et al (1949) studied the energy transfer process by investigating the fluorescence of solid solutions of the phosphors containing a small known amount of impurity in the benzene ring series $C_{4n+2}H_{2n+4}$. Figure 2 shows the results they obtained with (a) anthracene in napthalene; (b) naphthacene in anthracene; and (c) acridine in anthracene. These results were obtained by measuring the relative intensities of the light transmitted by suitable filters selected so as to transmit either the fluorescence of the host or of the impurity. Three points should be noted in these results. Firstly, in the case of solutions of anthracene in napthalene (solid) it was arranged so that the exciting light was absorbed principally by the host. Thus it can be seen that even at concentrations as low as 10^{-5} gm/gm of impurity, an appreciable amount of the absorbed light energy is transmitted to the impurity. Secondly, in the naphthacene case we have a similar efficient transfer of energy, but where the concentration of the impurity exceeds 10^{-3} gm/gm the efficiency of the phosphor rapidly drops to a very low value. This is due to the impurity molecules being too close to one another in the anthracene lattice with a resultant quenching of the fluorescence. Thirdly, with acridine in anthracene, at the same low concentrations, it can be seen that the acridine captures the excitation energy, and, as it does not fluoresce itself, degrades it to heat without the emission of light.

At these very low concentrations of the impurity it is necessary to postulate some mechanism of transfer of energy which allows the energy to move through a large number of molecules. This enables the few impurity molecules which have a high capture cross-section for the energy to capture the excitation energy. At these impurity centres the energy is captured and emitted as fluorescence which is characteristic of the impurity (e.g. anthracene in napthalene) or, alternatively, it may be quenched, as in the case of acridine.

At the time when the experimental work to be described in this thesis was started (January 1952), four theories had been put forward in an effort to explain the transfer of energy in these organic phosphors. We will consider these in turn.

B (b) Theories of the Energy Transfer Processes

(I) Energy transfer by photon emission and reabsorption.

The first suggestion to account for the above results was that the host molecule absorbed the incident exciting energy, and emitted a fluorescent photon which was then re-absorbed by the impurity, and re-emitted as the characteristic fluorescence of the impurity. (Bowen 1949; Bowen & Lawley 1949). Evidence in favour of this process is provided by the fact that an efficient transfer of energy to the impurity takes place when the absorption bands of the impurity strongly overlap the emission bands of the host. However, Bowen discarded this theory on the grounds that:

(a) the fluorescent spectrum of the host suffers no change when it contains the impurity, whereas we should expect, from the above theory, that the structure of the absorption bands of the impurity would alter the observed spectrum of the host's emission.

(b) the intensity of the impurity's emission is greater in mixed crystals than in homogeneous mixed sols of the same composition. This indicates that the lattice plays an important part in the energy transfer process.

(c) when the crystals are dissolved in benzene, the transfer process disappears and the emission becomes solely due to the original host molecule. (Ref. Birks 1953).

Bowen et al considered that this was sufficient evidence against this theory to make it necessary to find some other mechanism for the transfer of the excitation energy. Franck and Livingston (1949) considered three other processes of energy transfer in organic materials. They are electron migration, exciton migration and sensitised fluorescence. Electron migration may be summarily dismissed, as Bowen used an energy of excitation which was below the ionisation level of the molecule so that the exchange of energy between nearby molecules cannot take place by the motion of the released electrons. Liebson (1952) observed further that even under excitation by gamma rays, the photo-conductivity is very small, so that even at these high energies of excitation this mode of exchange is relatively unimportant. We will consider the two other processes: exciton migration and sensitised fluorescence. However, as there appears to be some confusion in the literature over the question of sensitised fluorescence this will be considered in two parts: firstly, the intermediate host molecules between the excited host molecule and the impurity take part in the transfer of the excitation energy to the impurity; secondly, they do not take any part, and the energy is assumed to jump from the excited host directly to the impurity.

(II) Energy Transfer by Exciton Migration

The Exciton is defined by Frenkel (Mott and Sneddon 1948) as "an electron and a positive hole existing .....

.... in a series of states ..... in which they are bound in one another's field". Bowen uses this term in a different sense, just to label the position of the excitation energy at any moment.

As the electron is bound in the Coulomb field of the positive hole, the absorption bands of this will be similar to those of the hydrogen atom, with the levels broadened by heat motion. This, Franck and Livingston consider should be shown by an additional series of bands in the absorption spectrum of the solid crystal as compared to that of the solution or gas. In a typical organic phosphor like anthracene, in which a migration of energy takes place, the crystalline absorption spectrum is similar to that of its solution in alcohol and to its gas, except that the maxima suffer a slight shift to longer wavelength (Garlick, 1949). This appears to preclude this type of energy transfer.

(III) Energy Transfer by Sensitised Fluorescence.

The idea of sensitised fluorescence is taken directly from the process of the same name in gases (Arnot). For example, if mercury vapour and a small quantity of thallium vapour be excited by the resonance line of mercury, the mercury atoms will strongly absorb the light while the thallium will not. However, an excited mercury atom on colliding with a thallium atom can transfer its energy of excitation to it. The difference of energy of the excited states in the two atoms will be equalised by a change of the kinetic energy of the parting atoms. When this takes place the mercury emission will be quenched and the thallium spectrum will appear in its place. The probability of such an exchange taking place increases rapidly as the energy difference between the excited states of the two atoms is decreased. If this condition of resonance or near resonance is fulfilled, the transfer of energy can take place over large distances of the order of 50A in gases.

We might expect a similar process to occur in a crystalline lattice in which the absorption and emission bands of the constituents overlap. However, here we must draw a distinction between the process in gases and that in a solid lattice. In the case of a gas it is immaterial whether we consider that the excitation energy is capable of being transferred between similar molecules, or only between the host and the impurity, for the individual atoms are moving at random throughout the whole volume of the containing vessel. In a solid, though, the individual atoms are restricted to a fixed position in the lattice and it becomes very important whether transfer may take place between similar molecules or not.

(III) (a) Transfer between similar molecules.

In an organic phosphor the emission bands of the host are known to overlap both the absorption bands of the host and of the impurity, if an efficient transfer of energy to the impurity takes place. Also, the molecules lie very close to one another so we might reasonably expect a transfer of energy in the lattice to take place in the following way: at each vibration of the excited molecule, it would approach one of its neighbours very closely and a transfer of energy could take place. This next molecule would now become excited and could transfer the energy to any one of its neighbours in a like manner. As the period of vibration is very short compared to the time for the optical transition back to the ground state (10^{-12} secs compared with about 10^{-8} secs), the excitation energy (or Bowen's 'exciton') would pass through a great many molecules before being emitted as fluorescent light. If the excited molecule should come adjacent to one of the impurity molecules, the impurity would trap the excitation energy. The reason for this is that the energy levels of the impurity are slightly lower than those of the host, so that the impurity would act as a potential well. Wright (1953) has successfully used this theory to account for the results obtained by Bowen et al and for his own results on mixed crystals.

(III) (b) Transfer of energy to impurity only.

In gases it has been observed that energy may be transferred over distances of the order of 50A in this process of sensitised fluorescence. Some workers have interpreted the analogous case in the organic phosphors as an overlapping of the wavefunctions of the host and impurity molecules over distances of the same order. It is considered that the probabilities for the fluorescent emission of the host and the transfer of the energy to the impurity are about the same. The 30 odd molecules, which would lie in the path of the interaction, to account for the large capture cross-section of the impurity, are assumed to play no part in the transfer of the energy. (See Birks, 1953). This theory is open to the obvious criticism that physically it is very difficult to see how the wave-functions of the molecules could interact so strongly over large distances and yet leave the other host molecules completely unperturbed. It is even more difficult to see why the other host molecules should not accept this energy when they are much more in resonance with the excited molecule (being identical molecules) than the impurity. A possible way out of this impasse is for the transfer of the energy to take place by the actual emission and re-absorption of a photon.

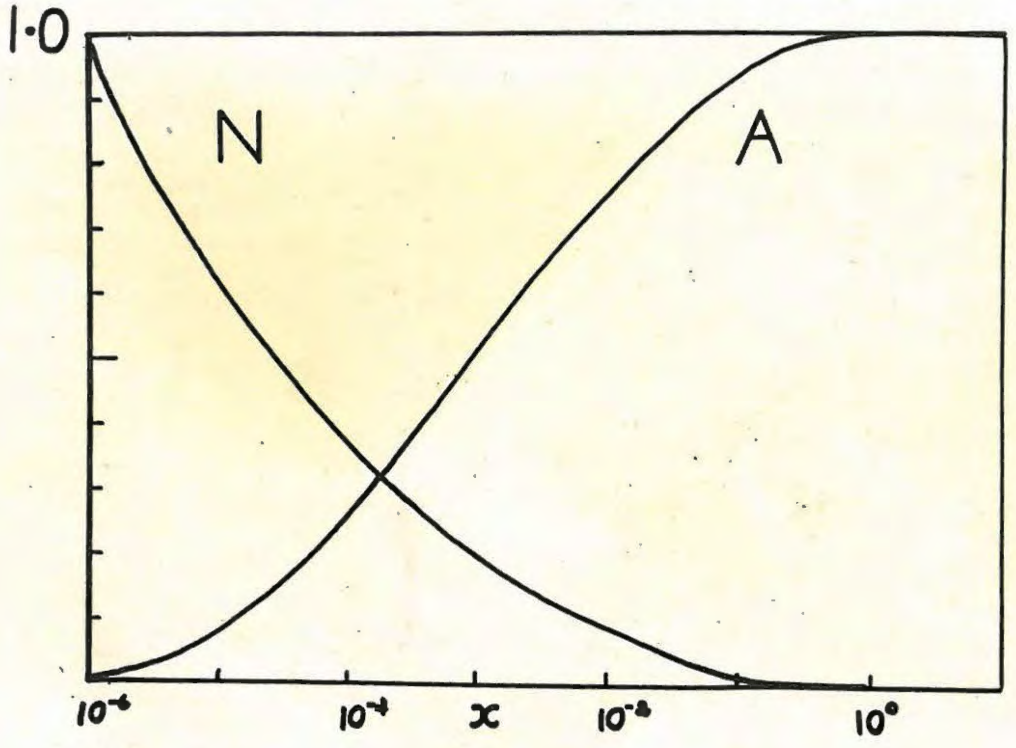


Figure 3. Relative Emission of Anthracene (A) to Naphthalene (N) in Mixed crystal of concentration x grams /gram of anthracene in naphthalene.

PART II. SPECTRAL MEASUREMENTS ON ORGANIC PHOSPHORS

Section A

Early Work

Bowen et al (1949) prepared specimens of mixed crystals of anthracene in a naphthalene lattice. They irradiated these with ultraviolet light and measured the intensities of the anthracene and naphthalene emission as a function of the concentration of the anthracene. Their results are shown in Figure 3, and could be expressed by the formulae: $A = \frac{Kx}{1+Kx}$, $N = \frac{1}{1+Kx}$,

where: x is the ratio of the number of molecules of anthracene to the number of molecules of naphthalene:

k is the relative probability of capture of the excitation energy by the anthracene to the probability of the capture of this energy by the naphthalene:

A is the anthracene intensity:

N is the naphthalene intensity.

The value of 'k' was 5×10^4. Bowen et al considered that this ruled out the possibility that the energy could be transferred entirely by the simple emission of the naphthalene's fluorescence and subsequent absorption by the anthracene. The relative absorption coefficients were nowhere large enough to allow such a large transfer probability. Bowen, therefore, postulated a theory of energy transfer by quantum mechanical

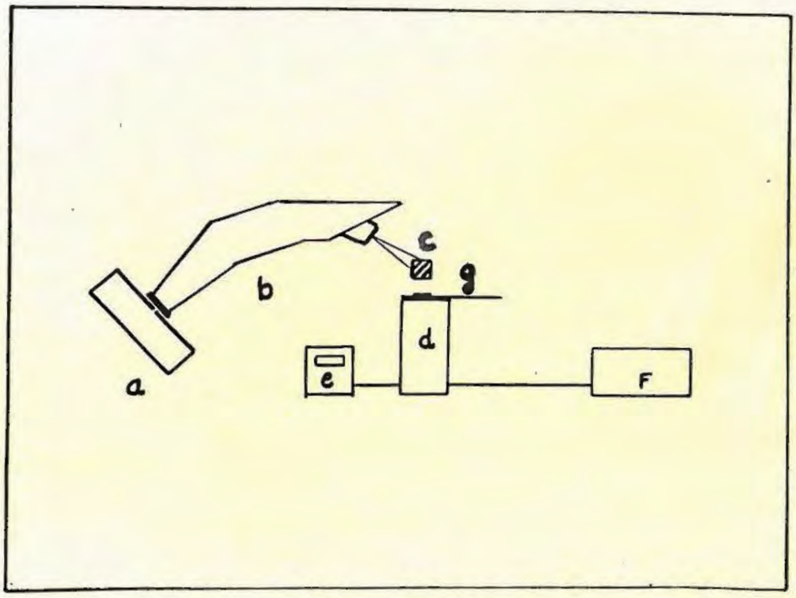


Figure 4. DIAGRAM of SIMPLE FLUORIMETER
(a) Mercury Arc Lamp.
(b) Quartz Monochromator.
(c) Fluorescent Crystal.
(d) Photomultiplier in Box.
(e) Galvanometer.
(f) 2Kv H.T. Power Supply
(g) Moveable Lid of Box with two filters.

resonance between adjacent molecules.

Birks (1950) had measured the same ratio by a scintillation technique. He measured the relative pulse height of the anthracene emission and the naphthalene emission using a photomultiplier and filters to detect and filter the light, and electrons from Indium 114 and alpha particles from Po$_{210}$ to excite the phosphors. His alpha particle and electron results agreed with one another and could be expressed by a similar relation to Bowen's results. However, the value of the parameter 'k' came out to be 43.

Birks' and Bowen's experiments were done under rather different experimental conditions, and it was felt if these measurements were repeated using the same crystals under ultra-violet and ionising radiation then the true difference between the values of 'k' by the two methods of determination could be found. Thus any theory of the energy transfer process would have to account for this difference in the capture parameter k in the two cases.

(a) (a) Preliminary Experimental Work

A simple fluorimeter was set up to measure the ratio of the anthracene emission to that of naphthalene in a series of mixed crystals of different concentrations. See Figure 4. The methods by which the crystals were grown are described in the Appendix. The fluorimeter

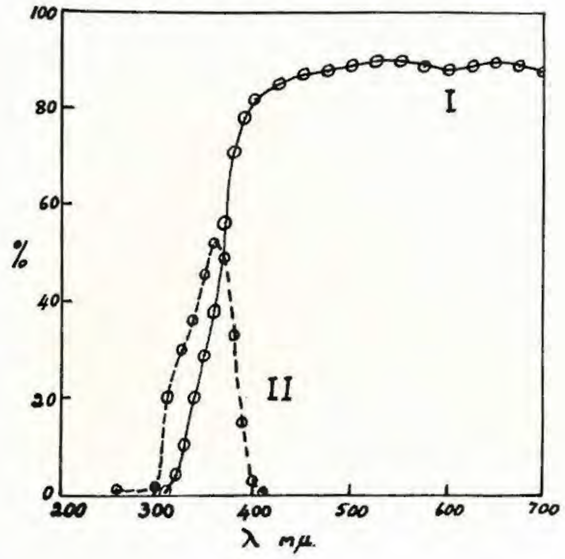


Figure 5. Characteristic Transmission Curves of filters used in measuring anthracene to naphthalene emission ratio.
(I) Filter to transmit anthracene emission.
(II) Filter to transmit naphthalene emission.

consisted of a type EMI 6262 photomultiplier in a brass container with a circular lid able to rotate and with three windows in it. Over one was a filter with the transmission characteristics shown in Figure 5(I). Over the second window was mounted a Wratten filter with the characteristics shown in 5(II). These transmission curves were measured on a Cenco-Sheard Spectrophotelometer. The third hole was left uncovered. The filters were chosen to differentiate as far as possible between the two components of the emission in the anthracene/naphthalene mixtures. The lid could be clipped into one of three positions, allowing the light to pass through either of the two filters or through the clear hole. The crystals under observation were mounted in front of this box and were excited by light from a low pressure mercury arc, from which the 254mu mercury line was selected by a quartz monochromator. This particular line was chosen for excitation since it lay outside the sensitive range of the photomultiplier. This made it possible to ignore any light from the surface of the crystals which might be scattered on to the photomultiplier. The phototube was operated by a high-voltage stabilised power-supply which is described in Appendix 2. The current from the collector anode was measured on a sensitive galvanometer. For low light intensities the current is proportional to the intensity of the light impinging on the photomultiplier. (Owen 1953).

(A) (b) Method of Measurement

The filter factors for the anthracene and naphthalene emission had first to be determined for the two filters. A crystal of pure anthracene was placed in position in front of the phototube, and the deflection for each of the three windows noted. The reduction factors for the two filters were thus found. This was repeated for naphthalene. If the factors for the first filter are F_1 and F_2, and for the second F_3 and F_4 for anthracene and naphthalene respectively, then the reading of the galvanometer for each of the three windows observing a mixed crystal might be expected to be:

$$\theta_1 = B(AF_1 + NF_2)$$
$$\theta_2 = B(AF_3 + NF_4) \qquad B = \text{constant.}$$
$$\theta_3 = B(A + N).$$

We have three equations from which to obtain B and the ratio A/N. This will give two values of this ratio which should be identical.

The experiment was carried out, but the values of A/N did not agree with one another. This can be explained if we assume that the filter factors for the emission of the anthracene and naphthalene light from the mixed crystal are different to those from the separate pure crystals. This implies that a variation

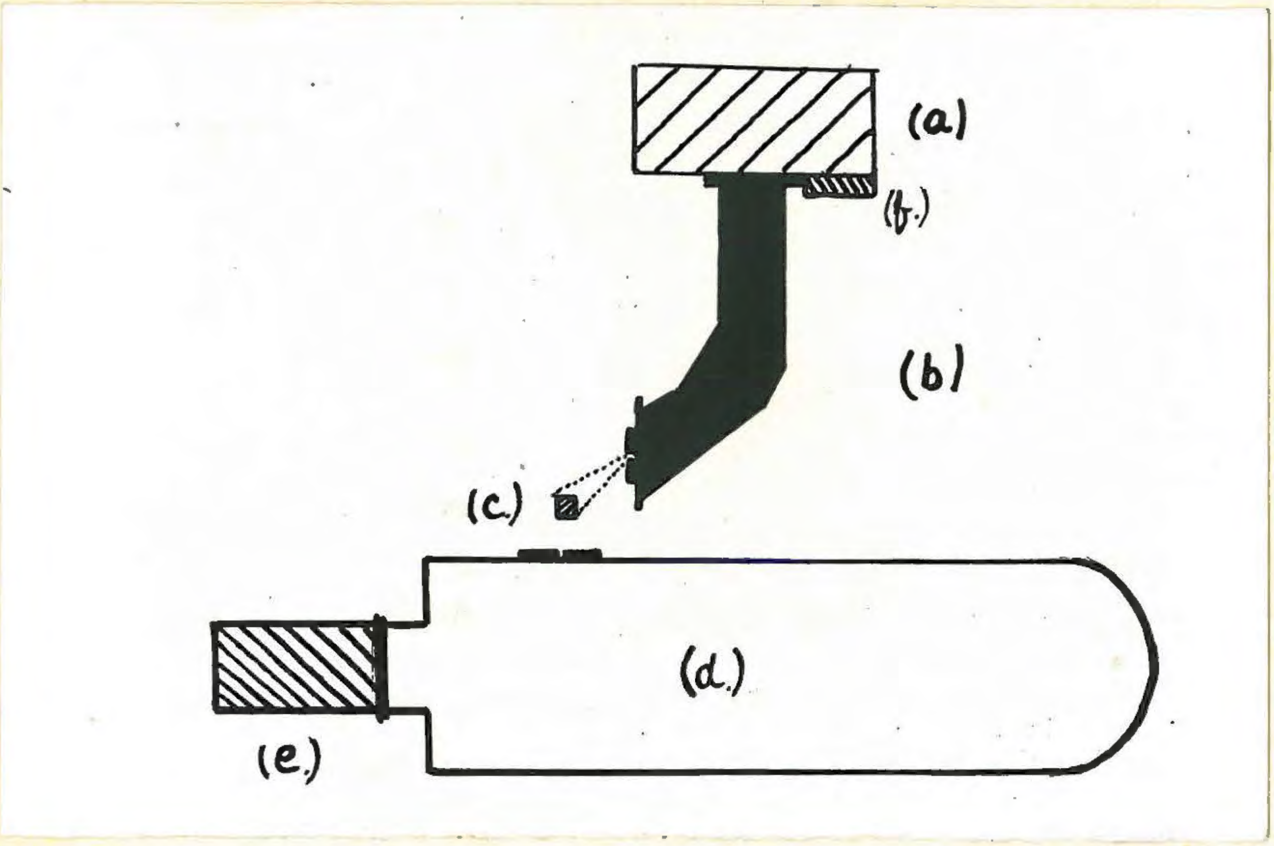


Figure 6. Apparatus for Fluorescence Spectra.

(a) Mercury Lamp.

(b) Quartz Monochromator.

(c) Crystal specimen.

(d) Grating spectograph.

(e) Photomultiplier.

(f) Cooling fan.

in the spectra occurs in the mixed crystals. This spectral shift would have a major effect on the apparent value of the parameter 'k', so its investigation was considered of importance.

Section B

(A) (c) Measurement of Fluorescent Spectra

It was decided to measure the variation of the intensity of the fluorescent spectrum with wavelength for crystals of different sizes and of different concentrations of anthracene in naphthalene. It was necessary to determine the emission of the pure crystal of both the components i.e. anthracene and naphthalene:

Experimental Arrangement

Figure 6 shows diagrammatically the experimental arrangement. The crystals were excited by the mercury 254 mu line selected, as before, by a quartz monochromator. The crystals were mounted at the entrance slit of a grating spectrophotelometer which was adapted for these measurements by replacing the barrier-layer photocell (as radiation detector) by a photomultiplier EMI 6262 in order to obtain greater sensitivity. The integrated current was again measured on a sensitive galvanometer. The photomultiplier was operated from a stabilised 2KV Power supply.

For the measured spectra to have any absolute value for the determination of the parameter 'k', it is essential that:

(a) the spectrophotelometer be standardised for variation of transmission for different wavelengths;

(b) the variation of the response of the photomultiplier with wavelength be known;

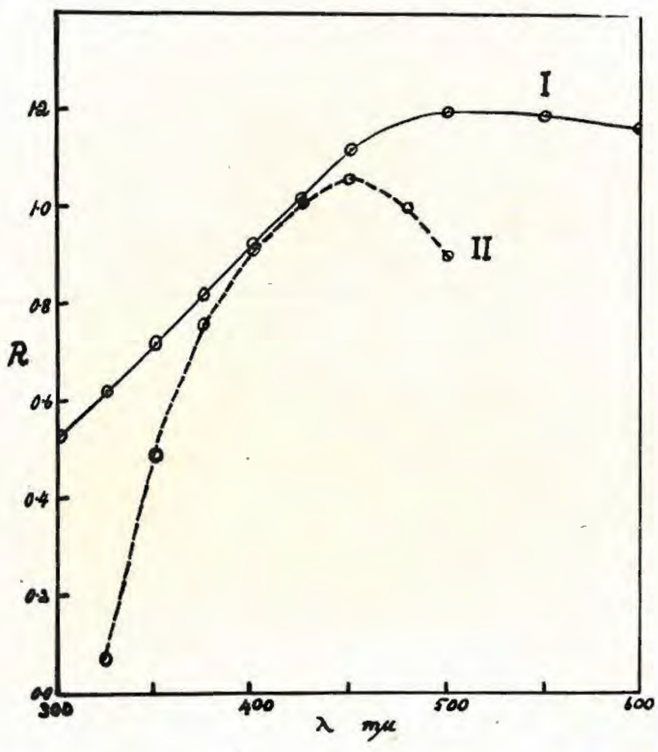


Figure 7. Curve I , variation of transmission of spectrophotelometer R, with wavelength.
Figure 8. Curve II , variation of Response of whole apparatus using the above curve and the Maker's sensitivity curve for the phototube.

(c) any effect due to stray light from the monochromator be eliminated.

(B) (b) Standardisation of the Spectrophotelometer

The Cenco-Sheard spectrophotelometer which was used for these measurements had been standardised for variation of transmission with wavelength by Dr. M.E. Szendrei who used a standard lamp of known colour temperature. The calibration curve is shown in figure 7. The variation of transmission with wavelength, but not the absolute transmission coefficient, was determined.

(B) (c) Photomultiplier Response

The absolute determination of the response of a photomultiplier to light of different wavelengths is an extremely long and difficult piece of work, so it was decided to use the approximate curve as supplied by the makers. The true curve is known to differ appreciably from the mean for individual tubes (Engstrom 1952); but as we were principally interested in that part of the spectrum where the response of the tube is determined chiefly by the transmission of the glass envelope, this could be reasonably expected to be more nearly the same for each tube. Figure 8 gives the variation of the response of the phototube and spectrometer. The spectra recorded here were corrected for this variation of response with wavelength. Subsequently,

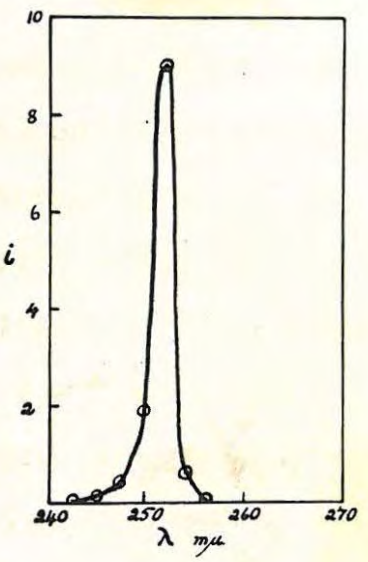


Figure 9. Curve to show the variation of the light output of the emitting crystal for different settings of the monochromator wavelength with a side input and output slit. Note that the stray light is negligible beyond 257 and 242 mu.

the spectral response curve of the photomultiplier was measured by Dr. M.E. Szendrei and found to agree well with the maker's curve.

(B) (d) Check for scattered light

In order to determine how much of the beam of 254 mμ radiation coming from the monochromator was light of longer wavelength (due to internal scattering in the instrument), the apparatus of the preliminary experiment was again used. The total current from the phototube was measured for different settings of the monochromator, the light from which excited the fluorescence of an anthracene crystal. Figure 9 gives the curve obtained. Any stray light can be expected to be appreciably constant for small variations of the setting of the monochromator. The figure shows that the stray light amounts to less than 2% of the total emission of fluorescent light from the crystal, and can be reasonably neglected where the fluorescence is strong, as in anthracene.

(B) (e) Instrument setting and adjustment of Arc Lamp

In order to obtain themaximum signal to noise ratio, i.e. the maximum ratio of 254 mμ radiation to stray light, the monochromator was adjusted to have a wide entrance slit and an exit slit just broad enough to allow the entire line-breadth to pass through. This widening of the exit slit further only increased the amount of stray light, without adding to the exciting radiation.

The most efficient use of the spectrophotelometer is made when the exit slit is made as wide as the decrease in resolution will allow. The reason for this is that if a fine exit slit is used, the stray light of the mercury lines will be comparable with the fluorescent light at these lines, whereas, by opening the slit further, more fluorescent light is admitted while the amount of mercury light from the narrowly defined lines remains constant. Then the fluorescent light can swamp the lines at the expense of resolution. (Harrison).

(B) (f) Mercury Lamp

The mercury lamp used was of the low pressure type run on direct current in an envelope of fused quartz. The power for this was obtained from the D.C. Mains. Once thermal equilibrium was reached, the intensity of the light was steady enough to do without any additional stabilisers. The initiation of the discharge was stabilised by a large inductance and resistance in series with the input-leads. At first it was found that the intensity of the lamp fell on heating and no increase of the potential across the lamp could make the intensity increase. As the intensity of the lamp was not sufficient to take readings on the poorer phosphor naphthalene, a cooling fan was fitted in order to cool the lamp and so allow it to operate at a higher current. By use of a miniature fan, the intensity was increased by a factor of four. The improvement was so good that it was thought worthwhile to consider the possibilities of water cooling the lamp.

A water-tight container was built with a sealed-in window of quartz arranged so that cool tap water could circulate round the lamp. The cooling circuit was very efficient and currents of up to 20 amps could be passed through the lamp thus causing an increase in intensity of ten-fold over that obtained by air cooling. However, the tap water was found to contain sufficient impurity with the result that while the visible emission was increased ten times (as measured on an exposure meter), in fact, the emission at the 254 mμ wavelength was reduced due to the strong absorption by impurities in the water. The air-cooled lamp was therefore used for the measurements.

(B) (g) Crystals

The anthracene used in the single crystal measurements was obtained from National Radiac Inc., while the anthracene, used for measurements on microcrystals, mixed crystals and some of the powder spectra, was obtained by Professor J.B. Birks from Professor J.W. Cook (Department of Organic Chemistry, Glasgow University). The naphthalene used in the mixed crystals was the purest available commercial naphthalene from Schering-Kaulbaum A.G. Berlin. It was not specially purified

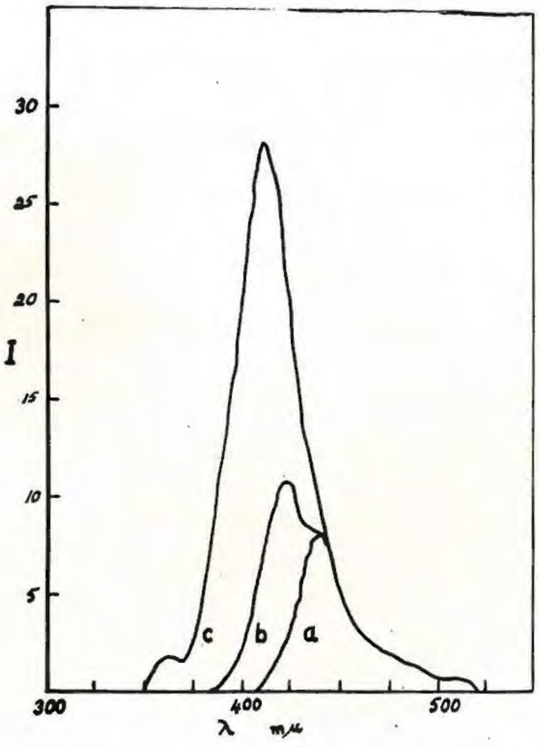


FIGURE 10. SPECTRA of ANTHRACENE of different sizes. (a) Transmission spectrum of Icm cube.

(b) Fine powder on quartz.

(c) Microcrystals on quarts.

Curves normalised at 445mu.

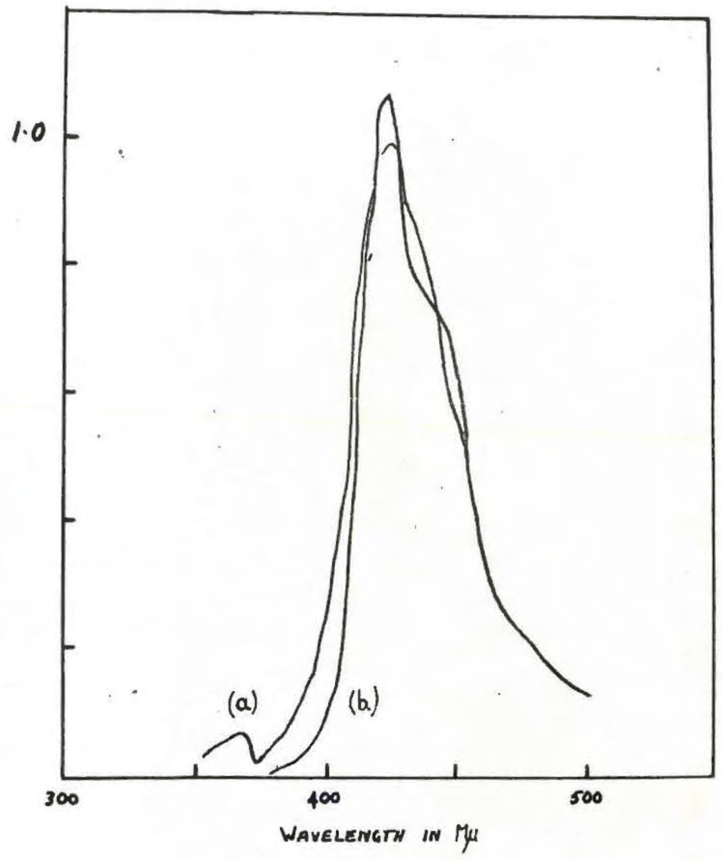


Figure II. (a) Anthracene-naphthalene mixed crystal spectrum.

(b) Powder spectrum of anthracene.

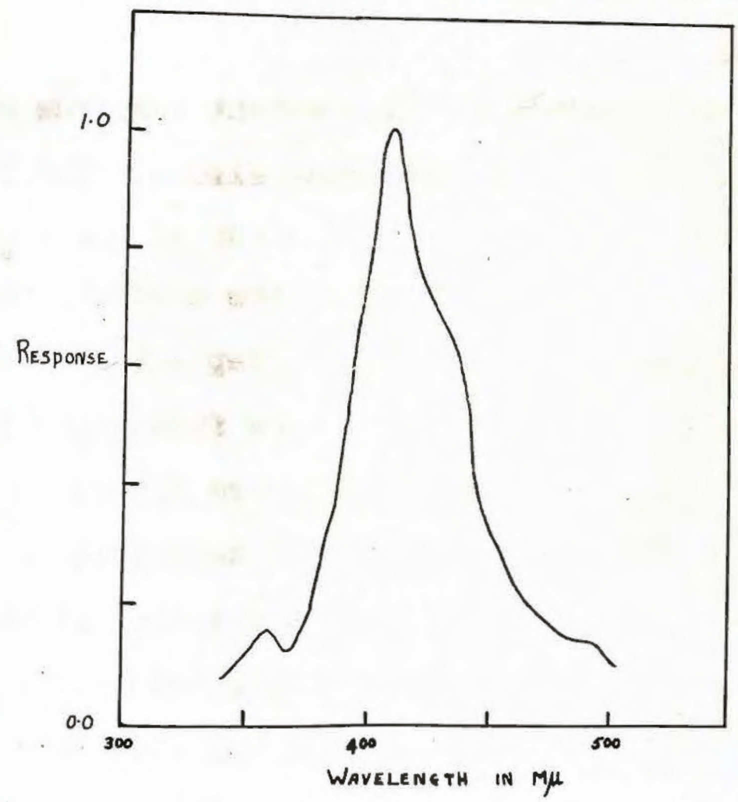


Figure I2. Anthracene-haphthalene crystal from 0.1% Melt.

before use and hence might be expected to contain minute traces of anthracene. (Bowen, 1952). The diphenyl-acetylene was obtained as a scintillation crystal from National Radiac Inc.

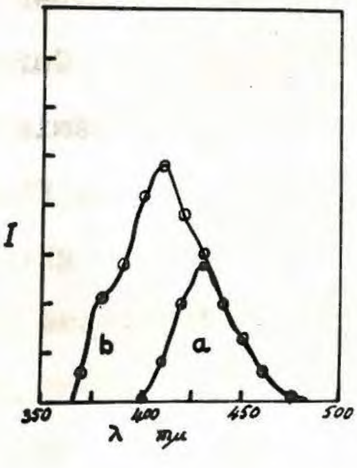
Section C. RESULTS

Anthracene

Figure 10 shows the fluorescent spectrum of anthracene crystals of different sizes. The lowest curve in the diagram is the spectrum of a 1 cm. cube viewed through the thickness of the crystal. Spectrum (b) is that of anthracene powder deposited on a quartz plate, while (c) is that of a very fine deposit of microcrystals. These crystals were formed by evaporating to dryness a weak solution of anthracene in xylene on a quartz plate. The intensity scales of the two crystals and the powder were normalised at a wavelength of 445 mµ. It can be seen that the spectra coincide at wavelengths longer than this. Preferential absorption of light of wavelengths less than 445 mµ occurs in the thicker crystals.

Anthracene Solid Solution

Figure II shows the spectra obtained from an anthracene/naphthalene mixed crystal grown from a melt of 1.0% concentration of anthracene to naphthalene, compared with the powder spectrum of Figure 10. These are strikingly similar.



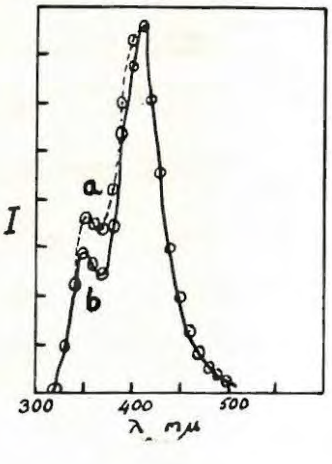


FIGURE I3. Anthracene in Naphthalene Mixed Crystal

Spectra. (a)3mm crystal from I.0%Melt.
(b)Fine powder from same crystal.

<u>Figure I4.</u> (a) 5mm crystal from 0.00I% Melt.
(b) Fine powder from same crystal.

In figure 12 are the results obtained for a crystal of 0.1% anthracene in naphthalene. The further shift towards the ultra-violet can be seen and the spectrum is similar to that of the microcrystals of pure anthracene. The small hump at the short wave end is due to the naphthalene component. In figure 13 are shown the spectra of (a) the fine powder and (b) the transmission spectrum of another crystal from the 1% anthracene in naphthalene melt. Figure 14 shows the spectrum of a crystal grown from a 0.001% anthracene in naphthalene melt. Curve (a) is of a 5 mm thick crystal viewed in transmission, while (b) shows the reflection spectrum of a fine powder rubbed from the same crystal on a ground glass plate. When this spectrum was taken it was noted that local differences in concentration of the crystal gave powder spectra of considerable variety. A typical spectrum is illustrated.

Naphthalene

Figure 15 shows the spectra obtained with naphthalene. The crystals were grown from the purest commercial naphthalene available, but probably contained minute quantities of anthracene or other impurities. This would account for the spectrum extending into the visible beyond 400 mμ, which, according to Bowen (1952) does not occur in the case of pure naphthalene. The first spectrum is that of a 4 mm thick crystal of naphthalene

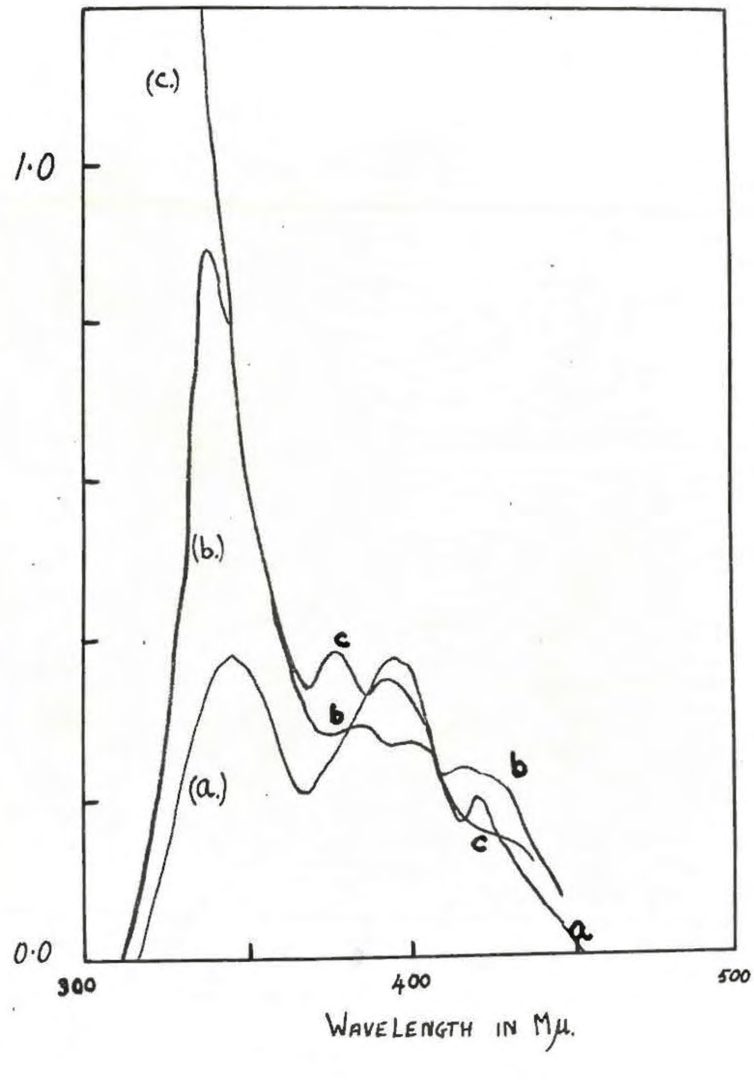


Figure 15. Naphthalene Fluorescence spectrum.

(a) Transmission spectrum of 4mm crystal.

(b) Reflection spectrum of 4mm crystal.

(c) Microcrystal spectrum.

[illegible] 360 mμ

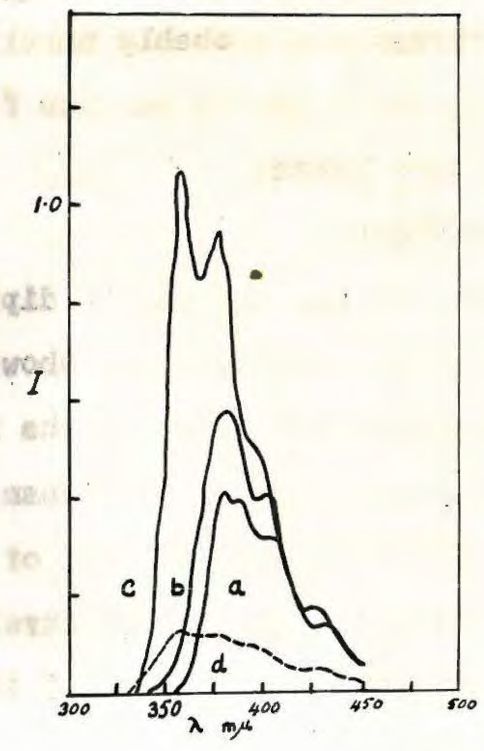


FIGURE I6. Spectra of Diphenyl-acetylene.

(a) Transmission spectrum of II mm thick crystal.
(b) Transmission spectrum of 3 mm thick crystal.
(c) Fine powder spectrum deposited on quarts.
(d) Noise curve.

viewed in transmission. (b) is the reflection spectrum of the same crystal. Again it can be seen that some of the light of short wavelength is preferentially re-absorbed within the thicker crystals. A fine powder deposited from a xylene solution on to quartz gave spectrum (c). The curves are probably unreliable at wavelengths below 330 mμ, where the correction factor for the instrument is very large.

Diphenyl-acetylene

In Figure 16 the spectra of diphenyl-acetylene excited by 254 mμ radiation are shown for different thicknesses of crystal. (a) is the fluorescence spectrum of a 1.1 cm. thick crystal in transmission. (b) is that of a 3 mm crystal and (c) is that of a fine powder deposited on quartz. Again a spectral shift to shorter wavelengths is seen as the size of the crystals is reduced.

Section D. DISCUSSION

It has been shown that in the case of pure anthracene and pure diphenyl-acetylene, the size of the specimens observed determines the shape of the emission spectrum. In both cases it is seen that the maxima of the curves shift towards the shorter wavelengths as the size of the specimens is reduced. This can be explained if the tail of the absorption spectrum continues through a considerable portion of the emission bands. If we take these two phosphors as typical examples of an organic phosphor, then we see that internal absorption of the emitted light plays an important part in determining the position and shape of the emission spectrum in crystals of the size used for scintillation counting ($\sim$ 1 cm. cube).

These results do not show whether the re-absorbed light is re-emitted, or lost as heat to the lattice. It is possible that the quantum efficiency for the emission process changes when the exciting wavelength lies within the normal emission region of the crystal. Here it may be so low that, effectively, all the re-absorbed light is lost as heat in a large crystal. Only if an appreciable amount of this re-absorbed light is re-emitted can we say that an appreciable amount of the energy-transfer process takes place by photon emission and re-absorption.

In the solid solutions of anthracene in naphthalene a similar shift towards the shorter wavelengths, as found for fine powders of the pure solid anthracene, took place when the concentration of the impurity in the lattice was reduced. The emission spectrum of a fine powder of anthracene was found to be very similar to that of a weak solid solution of anthracene in naphthalene. This clearly indicates that the principal cause of the shift in spectrum in solution is due to simple reduction in the self-absorption of the solute itself as the concentration is reduced. Koski (1951) has interpreted similar results of an experiment on weak solid solutions of anthracene in polystyrene as due to the different molecular environment in which the solute is situated. The shift that he observed was of the same order of magnitude as that found in naphthalene and may be partly due to this reduced self-absorption. Shifts have been observed in the absorption spectrum of some molecules which indicates that the environment does play some part.

In all spectra the size of the crystalline specimens had a major effect upon the observed spectrum, except in the case of the weakest solid solution of anthracene in naphthalene. In this case the spectrum of the 5 mm thick crystal was not appreciably different from that of the fine powder from the same crystal. Yet the efficiency of the transfer process of the excitation energy from the naphthalene lattice to the anthracene must have been about 100% as shown by the lack of any naphthalene emission. This strongly suggests that some agent, other than the simple emission by the host and subsequent absorption of the emitted light by the impurity, is responsible for the transport of energy at low impurity concentrations.

Phosphor Efficiency

The results on diphenyl-acetylene raise an interesting point. Dr. M.E. Szendrei (Birks & Szendrei, 1953) noted that the spectrum of anthracene did not suffer any appreciable change when the crystal size exceeded 1 mm. At the same time it can readily be seen from the spectra in Figure 16 that a very appreciable change occurs in the spectrum of diphenyl-acetylene even when the crystal is increased in size from 3 mm to 11 mm. If any of the light which is absorbed in traversing this extra 8 mm is not re-emitted, then the efficiency as a phosphor of the 11 mm crystal will be less than that of a smaller crystal, if the comparison be made with a crystal of anthracene of the same size as the specimen in eachcase. King (M.Sc. Thesis, Rhodes University 1952) noted a discrepancy in the values of the published efficiencies and suggested that such an absorption might account for it. Diphenyl-acetylene was particularly anomalous in the values which he listed and it was examined for this reason. We thus conclude that the efficiency of a phosphor is a function of the thickness and the shape of the 'tail' of the absorption.

Section E.

Conclusion

The results obtained from these spectra raised points of interest, in that they served to show the difficulty of obtaining a reliable value for the transfer parameter k. Ideally, if we could obtain a perfectly homogeneous mixed crystal of known concentration we could observe its emission spectrum, correct it for the variation of the sensitivity of the detecting apparatus for wavelength and then integrate the area under the curves for the anthracene and naphthalene components. The ratio of these would then give the ratio of the light emitted by the two components, and, knowing the concentration we could immediately find k. The difficulties in doing this are as follows.

It is inherently very difficult to grow homogeneous large crystals from a melt of a mixture of two materials. The crystals formed tend to become more pure, and, consequently, the concentration of the mother liquor will change as the crystallisation proceeds.

Anthracene/naphthalene crystals are a bad choice, for the naphthalene readily evaporates at room temperatures. In a mixed crystal we would, therefore, expect an increase in concentration of the anthracene towards the surface.

It would be necessary to measure the concentration of the anthracene in the mixed crystal after it had been used for the spectral measurements to ensure that the concentration had not been changed by either of the above causes.

Because of the relatively low intensity of the light source and the insensitivity of the detector, the spectral resolution obtainable was poor.

To obtain a reliable value of k, the emission of the anthracene and naphthalene should be comparable in intensity. At such concentrations the efficiency of the phosphor is very low and the light is spread over a wide interval of wavelengths, so that the signal strength at any one wavelength is low. It was found that the signal strength was only slightly above noise and no reliable spectra for extremely weak solutions of anthracene in naphthalene could be obtained with the apparatus.

At this time it was learned, too, that Wright had carried out accurate measurements on similar mixed crystals of anthracene in naphthalene using alpha particles and 254 mμ radiation. The concentrations of the crystals were determined after crystallisation from the melt by a fluorimeter technique. He observed a considerable purification of the melt during the crystallisation process. He obtained no significant difference between the parameter k for the two methods of excitation. (Ref. Wright, 1953). Furthermore, Birks' results agreed with Wright's, when they had been corrected for the purification during the crystallisation process.

The above difficulties and the work of Wright strongly suggested the desirability of a new approach to the study of the energy transfer process. It was felt that if a method could be found of measuring some other more distinctive characteristic than the emission spectrum of a molecule, then it might be possible to investigate the transfer mechanism as it occurs in pure crystals, and so avoid the difficulties of the mixed crystals. Furthermore, if this characteristic could also be measured under ionising radiation, it might be possible to understand that more complicated process. A property which is characteristic of the molecule and satisfies the second condition is the time for the decay of the intensity of the emitted light from an excited crystal. It was decided to investigate the possibility of measuring these decay times under excitation by ultra-violet light.

PART III. THE MEASUREMENT OF THE DECAY TIME OF FLUORESCENCE EMISSION FROM ORGANIC PHOSPHORS

Section A.

Early Work

Before considering the results of earlier workers and their methods of approach, let us consider first what it is we are attempting to measure. If we take an isolated molecule which is in an excited state there will be a certain probability per unit time of its making the optical or a non-radiative transition back to the ground state. The reciprocal of this quantity will be of the dimensions of a time. It is this quantity which we wish to measure. This quantity known, the effect of the lattice, impurities and subsequent processes will be open to measurement.

If we take a large number of molecules the variation of the intensity of the emitted light as a function of time may be computed. If at a time $t = 0$ we have N_0 excited molecules, and the probability per unit time of an optical transition back to the ground state is p per second, and all other competing processes by which the molecule may de-excite is q per second, then the total number of molecules de-excited in a small interval of time dt will be:

$$-dN = -(dN_p + dN_q) = (p+q)N.dt \qquad (3)$$

The number of quanta emitted per second is the number of optical transitions taking place per unit time and hence the intensity of the emitted light will be proportional to $\frac{dN_t}{dt}$. The integrated equation (3) gives us the value of N at any time t.

$$N = N_0 e^{-(\rho+q)t} \tag{4}$$

The intensity at any time t will then be:

$$I = N_0 . \rho . e^{-(\rho+q)t} \tag{5}$$

or simply: $$I = I_0 e^{-\frac{t}{\tau}} \tag{6}$$

The decay time τ is defined by the value $\left(\frac{1}{\rho+q}\right)$ secs.

Using pulsed photomultipliers, and directly measuring the variation of the intensity of the emitted light from several organic phosphors bombarded by particles of ionising energies, Post (1952) has shown that the emitted light does, in fact, decay exponentially in accordance with equation (6).

During recent years a considerable interest has been taken in scintillation counters and phosphors capable of resolving ionising events separated by intervals of time of the order of 10^{-8} seconds and less. Numerous measurements have been made of the scintillation decay times of organic phosphors like anthracene, stilbene and similar compounds when bombarded by ionising particles and under gamma rays. (Sangster, 1952). These are of some technical interest, but as we know that the lattice suffers considerable damage (Birks, & Black, 1951) under particle bombardment and that the processes involved are extremely complex by which the energy of the incident particle is absorbed. These are not the most suitable measurements to use for the study of the energy transfer process. To simplify the problem as much as possible these measurements should be made under low energy ultraviolet light, i.e. at energies below the ionising energy of the molecule. An exhaustive search of the literature has revealed only three investigations of this type made during the last twenty-five years, each investigation based on the same general principle. The three investigations were made by Gaviola (1927), Tummerman (1941) in the U.S.S.R. and Liebson et al (1952), only the last named using a photomultiplier technique. The theory of the method is based on the work of Tummerman, but has not been published in English. For this reason the theory of the method developed by the author will be considered.

It will be shown that if a phosphor be excited by light which is modulated in intensity at an angular frequency ω of the form: $I = I_0 (1 + \alpha \sin^2 \omega t)$, the fluorescence emission will also be modulated in intensity, but will lag behind the exciting light in phase by an angle ϕ. This angle ϕ is given by the relation $\tan \phi = 2\omega\tau$, where τ is the decay time of the phosphor. Furthermore, the degree of modulation defined by: $\frac{S_{max} - S_{min}}{S_{max} + S_{min}}$ will be reduced by the factor Cos ϕ, where S_{max} is the maximum intensity of the fluorescence emission and S_{min} is the minimum intensity in the cycle.

The principle of the measurement of the decay time is to measure either the phase shift between the exciting and the fluorescent light, or the reduction in the degree of modulation.

Section B

Theory of the Method

Let us assume that the light is modulated according to the relation: $I = I_0\left[1 + \alpha \sin^2 \omega t\right]$, (7)
where I is the intensity at a time t, α is a constant, and ω is the angular frequency of the modulation. Then the intensity of the fluorescent light at any time t' may be obtained by summing the emission intensity due to light absorbed during the interval of time t to t + dt decayed by a factor $e^{-\frac{t'-t}{\tau}}$ over all values of t back to - infinity i.e.:

$$S_0 = I_0 \frac{Q}{\tau}\int_{-\infty}^{t'} e^{-\frac{t'-t}{\tau}}\left\{1 + \alpha \sin^2 \omega t\right\}.dt. \qquad (8)$$

where Q is the quantum efficiency of the phosphor, and I_0 is the same as in equation (7). This relation may be readily integrated by parts as follows:

$$S_0 = I_0 \frac{Q}{\tau}\int_{-\infty}^{t'} e^{-\frac{(t'-t)}{\tau}}\left\{1 + \frac{\alpha}{2}(1 - \cos 2\omega t)\right\}.dt.$$

$$= I_0 Q\left\{1 + \frac{\alpha}{2}\right\} - \frac{I_0 Q \alpha}{2\tau}\int_{-\infty}^{t'} e^{-\frac{t'-t}{\tau}}.\cos 2\omega t.\, dt.$$

Put the latter integral equal to A, then:

$$A = \int_{-\infty}^{t'} e^{-\frac{t'-t}{\tau}} . \operatorname{Cos} 2\omega t . dt.$$

$$= \tau \operatorname{Cos} 2\omega t' + 2\omega\tau \int_{-\infty}^{t'} e^{-\frac{t'-t}{\tau}} . \operatorname{Sin} 2\omega t . dt.$$

$$= \tau \operatorname{Cos} 2\omega t' + 2\omega\tau \left[\tau \operatorname{Sin} 2\omega t' - 2\omega\tau \int_{-\infty}^{t'} e^{-\frac{t'-t}{\tau}} . \operatorname{Cos} 2\omega t . dt \right].$$

$$A = \tau \operatorname{Cos} 2\omega t' + 2\omega\tau^2 \operatorname{Sin} 2\omega t' - 4\omega^2\tau^2 . A.$$

$$= \frac{\tau}{1+4\omega^2\tau^2} \left\{ \operatorname{Cos} 2\omega t' + 2\omega\tau \operatorname{Sin} 2\omega t' \right\}.$$

$$= \frac{\tau}{(\cancel{1+4\omega^2\tau^2})^{1/2}} \operatorname{Cos}\phi . \operatorname{Cos}(2\omega t' - \phi) \quad \text{Where } \tan\phi = 2\omega\tau.$$

$$\text{———} (9.)$$

$$S_0 = I_0 Q \left\{ 1 + \frac{\alpha}{2} \right\} - \frac{I_0 Q}{2} \alpha \operatorname{Cos}\phi . \operatorname{Cos}(2\omega t' - \phi)$$

$$= I_0 Q \left[1 + \frac{\alpha}{2} \left\{ 1 - \operatorname{Cos}\phi . \operatorname{Cos}(2\omega t' - \phi) \right\} \right].$$

$$\frac{S_{max} - S_{min}}{S_{max} + \underset{min}{S_{max}}} = \frac{1 + \frac{\alpha}{2}(1 + \operatorname{Cos}\phi) - \left\{ 1 + \frac{\alpha}{2}(1 - \operatorname{Cos}\phi) \right\}}{1 + \frac{\alpha}{2}(1 + \operatorname{Cos}\phi) + \left\{ 1 + \frac{\alpha}{2}(1 - \operatorname{Cos}\phi) \right\}}.$$

$$= \frac{\alpha \operatorname{Cos}\phi}{2 + \alpha}$$

The degree of modulation = $\frac{\alpha}{2+\alpha}$ Cos ϕ

The phase shift ϕ where tan ϕ = $2\omega\tau$.

The decay time of the phosphor may be measured from the phase shift ϕ by observing the change in the degree of modulation or the actual phase shift. The apparatus must be designed to:

(a) modulate light at a suitable frequency,

(b) detect the fluorescence emission, and

(c) measure the shift in phase or the degree of modulation.

The first requirement is to know the most suitable frequency for modulation of the ultraviolet exciting light. Liebson's measurements indicated that τ for anthracene and other associated compounds was of the order of 10^{-8} secs. Putting this value in relation (9) gives a value of about 7.5 Mc/sec for the frequency of modulation for $\phi = 45^{\circ}$. This value was chosen for the frequency of modulation.

Section C

APPARATUS

(a) Radio frequency Power Source

Radio frequency power was obtained from a single stage self-excited Hartley Oscillator dissipating 40 watts at 7.5 Mc/sec. This was built from parts of an old transmitter and the power for it was obtained from two laboratory power supplies, one providing 500 volts for the anode of the 807, and the other 300 volts for the screen, as well as the filament supply. A 70 ohm coaxial cable was connected and matched across the lowest two turns of the Tank Circuit and supplied power

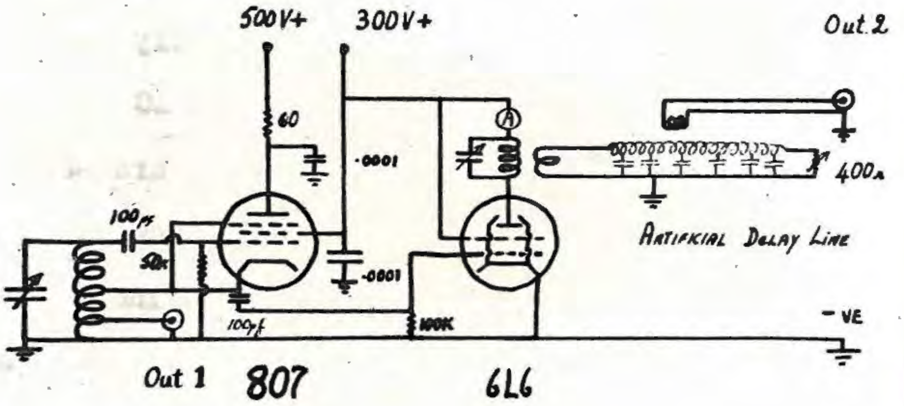
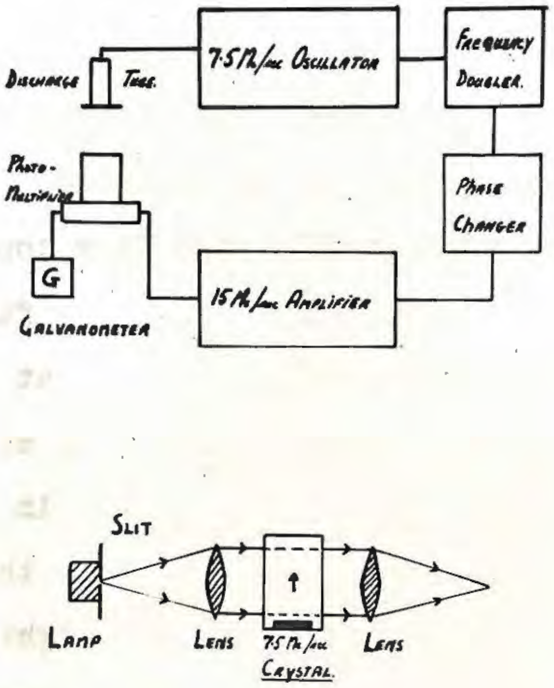


Figure 17. Power Oscillator Circuit Diagram.

either to the ultra-sonic generator or to the discharge tube resonant circuit, depending upon the method of light modulation used. A second lead provided excitation for the simple 6L6 frequency doubler, the output of which was inductively coupled to the phase shifter. The H.T. supply for this unit came from the screen power supply of the 807. The circuit is shown in figure 17.

(b) Phase Shifter

A phase shifter was required to give a signal of constant amplitude, but continuously variable in phase over 270° or more. RC or simple LC networks do not possess this property and hence a transmission line was used. An artificial delay line was built similar in principle to one described in Hund's book (1936), but designed to work at 15 Mc/sec. This consisted of ten 2μH coils wound on a 20 cm. long bakelite former in the form of a continuous winding, shunted to earth every 2μH by condensers of 50pf each. The line was terminated in its characteristic impedance of 400ohms pure resistance. Down the centre of the delay line a small pickup coil was mounted on a graduated screw shaft. It could be moved along the centre portion of the line. Flexible leads took this signal to a coaxial output plug. The line was fed by a matched inductive coupling on the tank circuit of the frequency doubler.



<u>Figure I8</u> (above) Second Phase detecting Method.

(Below) Optical System for ultrasonic cell.

(c) Modulated Light Sources

Much previous work has been done on the modulation of light for the determination of the velocity of light and for television. Consequently, several alternative methods are available. Gaviola in his classic experiments used biased Kerr cells. For work in the ultraviolet this method is not suitable. Almost all liquids which have a reasonably high Kerr constant have strong absorption in the ultraviolet. In fact, very few liquids can be found which transmit light at 254 mu at all. Besides this, polarisers are required which must also be transparent to the ultraviolet in this range. These were not available. Furthermore, this is a very inefficient way of modulating the light as only a small fraction of the incident light is available as modulated light.

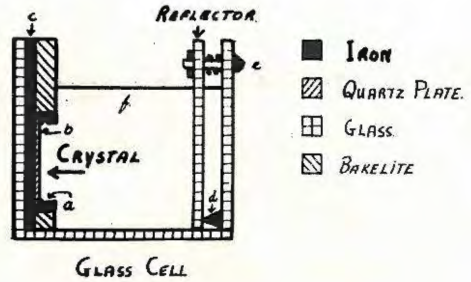
There are other more suitable methods of modulating the light: Bergmann (Ultrasonics, Bell & Son) describes how ultrasonic waves in liquids and solids may be used to modulate light, and Frey (1936) gives a method with a modulated discharge tube.

(c) (i) Ultrasonic Cell

Initially, the ultrasonic method was favoured. The idea is to generate a grid of parallel standing waves of sound at the modulating frequency in a liquid transversed by a parallel beam of light perpendicular to the sound waves. See figure 18. The varying density of the liquid at the nodes and antinodes causes some of the incident light to be diffracted out of the parallel beam. The grid of sound waves acts as a diffraction grating which is created and destroyed twice every cycle of the modulating frequency of the sound waves. The transmitted beam will be partially modulated at twice the frequency of the sound waves and the diffracted beam wholly so. By masking off the central beam and taking off only the diffracted light we should obtain 100% modulated light at twice the frequency of the sound waves. The advantage of this method is that the intensity of the exciting light may be readily increased by increasing the intensity of the source, and without having to use more R.F. power in the ultrasonic cell.

(c) (i) (a) Construction of ultrasonic cell

An ultrasonic cell was constructed as shown in figure 19. A 7.5 Mc/sec quartz crystal was silvered on both sides and mounted in a bakelite holder on a heavy steel plate. A phosphor bronze spring made connection to the front face of the crystal while the rear face lay pressed against the metal surface. When the crystal was excited by a varying potential of several hundred volts across it, in resonance with the crystal's frequency, the front surface vibrated



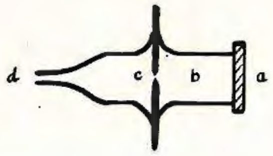


Figure I9. Construction of Ultrasonic Cell.

Figure 20. Discharge tube (a) quartz window.
(b) pyrex envelope.
(c) tungsten electrode
(d) evacuating pipe.

in and out like a piston, driving out sound waves across the liquid in the cell. The whole ensemble was contained in a square glass cell upon which were cemented quartz windows to allow the ultraviolet light to enter and leave the vessel. The cell contained distilled water.

(c) (i) (b) Preliminary Experiments

The cell was set up at right angles to the beam from a white lamp, slit and lens as shown in figure 18. The second lens focussed the parallel beam of light into a narrow image of the slit. On tuning of the oscillator through the resonant frequency of the crystal, the first and second order spectra became visible a few degrees on either side of the central line. To obtain a standing wave pattern a glass plate was used as a sonic reflector at the opposite end of the cell and adjusted to be accurately parallel to the oscillating crystal. This done up to 15 orders of the spectra could be seen on either side of the central image of the slit.

Care had to be exercised in adjusting the power fed to the crystal. The intensity of the light diffracted out of the central image is proportional to the power driving the crystal, so that as much power as possible should be used to get good intensity. However, as the power is increased the surface of the crystal heats up, and the water in contact with the surface is pushed across the light beam by the radiation pressure of the sound waves. When this happens the warm water shows up as streamers across the field of view and a good deal of stray light is scattered out of the beam which is of no use and is not modulated. The power had to be adjusted to obtain the optimum output without having streamers.

It having been ascertained that sound waves were being generated in the water, the field of view was examined by a low-powered microscope in parallel light. The standing wave pattern could be clearly seen extending from the crystal to the sonic reflector. It appeared as bright and dark bands of light accurately parallel to the crystal surface.

The diffracted light was next viewed with the tuned photomultiplier described in the next section. Briefly, this consisted of a photomultiplier coupled to a tuned 15Mc/sec amplifier, the output of which was displayed on the Y plates of an oscilloscope. The X-axis was swept by a 15 Mc/sec signal obtained from the frequency doubler coupled to the same oscillator which drove the ultrasonic generator. In general, the picture on the 'scope face should be an ellipse, the axes of which could be measured to obtain the relative phase relation of the X and Y signals.

A strong signal was observed at 15 Mc/sec, but the phase relation between the two was seen to fluctuate at great speed. A possible explanation of this is that the standing wave pattern may be considered as a very stable configuration which will only change between integral numbers of waves, while the oscillator may drift enough about the mean frequency in order to affect the measured phase displacement. Alternatively, it may be due to the system jumping between different modes of vibration, as happens in large electro-magnetic cavity resonators (as suggested by Professor Birks). Whatever the cause, no satisfactory method of eliminating this was found.

The difficulty could be overcome by using two tuned amplifiers and phototubes, one to view the exciting light and one to view the modulated fluorescent light. This would be probably the best way to do the experiment, but, as it entailed building a new amplifier and obtaining another phototube, a simpler method was tried using a directly modulated discharge tube.

(c) (ii) Discharge Tube

Frey (1936) had observed that the light from a simple discharge tube was still modulated in intensity when excited by an R.F. potential as high as 10^7 cycles/second. A preliminary check with a hydrogen lamp verified that the light output was modulated at 15 Mc/sec.

when excited by the field from the oscillator tank circuit. A quartz lamp containing hydrogen and yielding a continuous spectrum was next tried and this too gave a strong modulated signal. However, the discharge was spread throughout the tube making it rather difficult to excite the crystal, and the intensity was low.

At low pressure we should expect the decay of the intensity of light from an excited state in a gas to be exponential, just as in the case for a phosphor. The decay time is determined by the transition probability per unit time for the transition. In oxygen and nitrogen this decay time is of the order of 10^{-7} to 10^{-8} seconds. The effect of the decay time is similar to that for a phosphor considered previously. The degree of modulation of light from a volume of gas (which is excited by a modulated potential) will vary as Cos θ, where Tan $\phi = 2\omega\tau$, $\frac{\omega}{2\pi}$ is the modulating frequency and τ the decay time of the gas. If the decay time τ is very small compared to $\frac{1}{\omega}$ then the light will be effectively 100% modulated in intensity. If, however, $\tau \sim \frac{1}{\omega}$, then Cos ϕ will be considerably less than 1 and the modulated light will be superimposed on a continuous background.

If, however, the pressure of the gas be increased so that the excited molecules can make several collisions within their normal lifetime, the excitation may be quenched and the decay time shortened. If the emission is due principally to transitions from metastable states of the molecule, the high collision rate will knock the molecules from these states, and thus reduce ϕ and increase the degree of modulation of the source.

On the basis of this idea, a discharge tube was constructed to work at pressures of up to 15 cms. Hg of air. The tube consisted of two finely pointed tungsten electrodes one mm. apart in a pyrex envelope with a quartz window sealed to its end. (See figure 20). The fine points and small separation of the electrodes enabled the discharge to be maintained at higher pressures than are normally used in discharge tubes. Furthermore, the high field intensity localised the discharge to the electrode tips when the pressure was relatively high. The electrodes were connected to a resonant circuit driven by a coaxial cable from the 40 watt 7.5 Mc/sec oscillator. The discharge tube was connected to a vacuum pump and needle valve, and the pressure could be maintained at any value between 0.3 mm and atmospheric pressure.

Some difficulty was experienced in initiating the discharge. The normal sequence of operations was to evacuate to 0.3 mm pressure and then bring up a bright source of light close to the tube. The photo-electric emission from the electrodes released enough electrons into the r.f. field to start the discharge. The discharge immediately settled down and the pressure could then be raised to as high as 20 cms of mercury before the discharge was extinguished. At low pressures the discharge completely filled the tube but as the pressure was increased from about 1 cm Hg the size of the discharge decreased and formed into an intense blue sheath around the two electrodes. At higher pressures the sheath became more intense but thinner and crept towards the fine points. The discharge usually became unstable above about 18 cm Hg pressure.

(d) Detecting system

Two different detecting systems were used, the first for calibration of the apparatus, and the second for the actual measurements.

(d) (i) Oscilloscopic Display Method

For all the early work on investigating suitable light sources, an E.M.I. 6262 photomultiplier was used and later an E.M.I. 5060. The collector electrode was connected to a resonant circuit tuned to 15 Mc/sec., the output of which was fed via a cathode follower to a two-stage tuned amplifier. The output of this was taken to the Y plates of an oscilloscope adapted to take coaxial leads right up to the base pins of the tube. With an input signal of 5 milli-volts at 15 Mc/sec

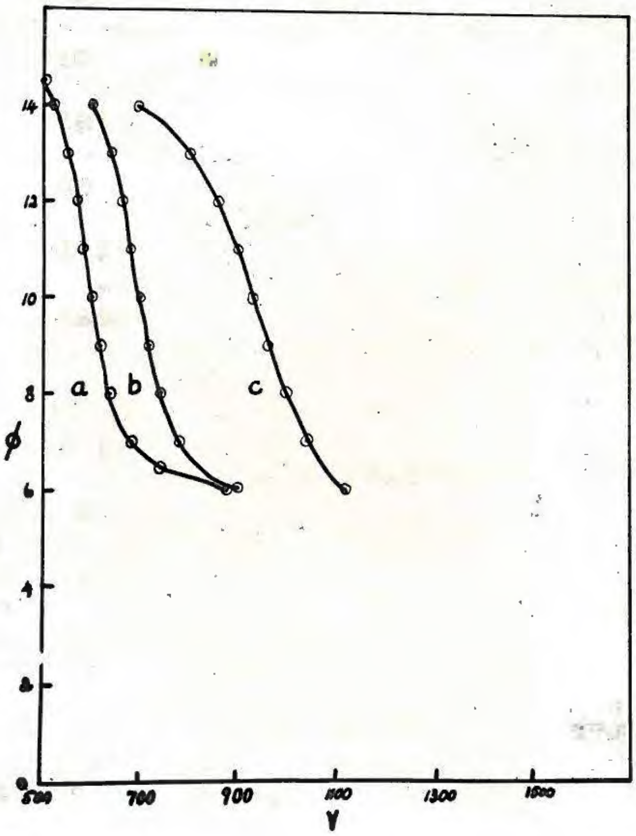


Figure 21. Plot of phase reading Ø vs voltage on phototube. (a) Light of high intensity.
(b) Lower intensity.
(c) Low intensity.

to the cathode follower, the amplifier gave a full screen deflection on the 'scope. The X plates were driven by the signal from the frequency doubler.

The artificial delay line was included in the frequency doubler lead so that the ellipse formed on the screen by the two sinusoidal 15 Mc/sec signals on the X and Y plates could be reduced to a straight line. Any variation in phase in either channel would show itself as a departure from the straight line into the ellipse. The magnitude of phase could be determined by the additional delay in the artificial delay-line channel necessary to obtain a linear trace on the screen.

Later, a phase distortion was observed in the amplifier which varied according to the intensity of the light on the photomultiplier when it was handling large signals and this method of detecting the phase difference between the two channels was abandoned in favour of the following method. (See figure 21). The reading of the phase shifter for a linear trace on the screen was plotted against the potential applied to the photomultiplier for light of three different intensities. (a) is the highest intensity and (c) the lowest. The intensity was changed by separating the lamp from the photomultiplier by a few centimeters. The variation in transit time for the electrons through the photomultiplier should account for the shift in phase as the voltage across the tube is changed. The three curves should coincide, and be independent of the intensity of the incident light. We can see that a considerable distortion occurs in the phase of the signal.

(d) (ii) Modulated photocathode detector

If the potential between the photocathode and the first dynode of a photomultiplier is varied, the gain of the tube as a whole will vary linearly with it for small potential changes (Zworykin). If now, the light, being detected, is itself modulated in intensity at the same frequency as this potential, then the output current will be a function of the phase difference between the light modulation and the cathode potential frequency.

If the cathode potential relative to the first dynode varies as Sin$(2\omega t + \alpha)$ when this is positive, the gain of the tube will be proportional to it, and when this term is negative, the gain of the tube will be zero. If the intensity of the exciting light varies as Sin$^2\omega t$, the average d.c. current over many cycles may be obtained by integrating:

$$i = i_0 \int_0^{t=\frac{\omega}{2\pi}} \mathrm{Sin}^2 \omega t . \mathrm{Sin}(2\omega t + \alpha)\, dt.$$

which becomes simply: $i = i_1 + i_0 \mathrm{Sin}\, \alpha.$

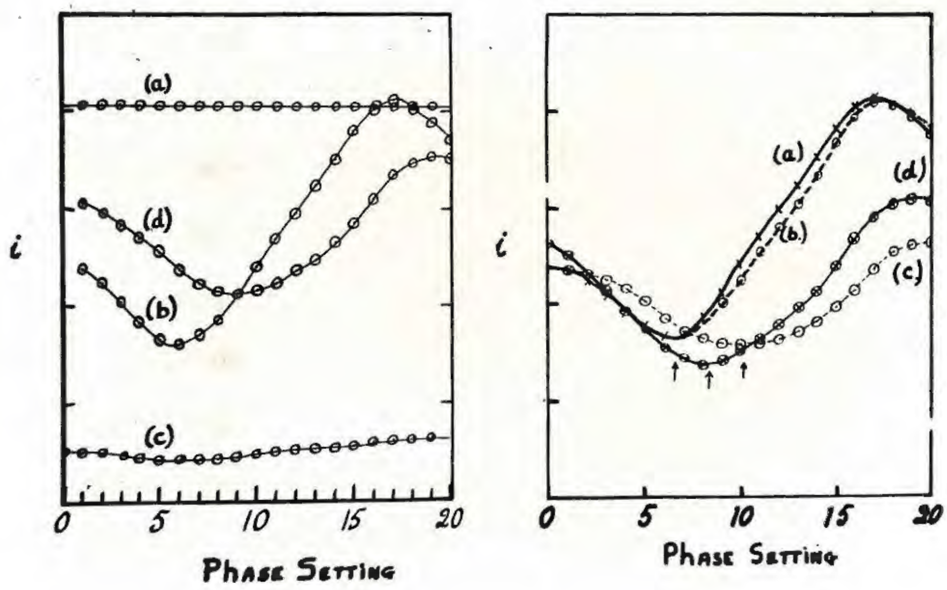


Figure 22. Current i vs Phase Setting Curves f

(a) Unmodulated light.
(b) Dischargetube's modulated light.
(c) Noise.
(d) Anthracene's fluorescence.

Figure 27.

(See Appendix). The effect of (a) harmonic terms in the modulated light and (b) non-linearity in the gain of the detector is considered in Appendix IV.

An R.C.A. 931A photomultiplier was used for these measurements. Across the dynode-cathode electrodes of the 931A photomultiplier a resonant circuit was connected, driven by a coaxial lead from the tuned amplifier described in the previous section. The input of the amplifier was fed by a signal of variable phase from the phase-changer. The phase-changer gave an output signal of about 50 volts which varied by about ten volts along the whole traverse of its pick-up coil. The signal was clipped by the first stage of the tuned amplifier and the clipped signal was fed on through the resonant circuits which restored the sinusoidal form of the signal. The output was fed to the photomultiplier resonant circuit. The voltage of the output signal of the amplifier was found to remain constant to better than one part in a thousand when the phase-changer was moved over its full traverse. The current from the collector anode of the 931A was measured by a 0 to 1.0 μamp Cambridge galvanometer. Figure 22 shows typical working curves obtained with this arrangement of the apparatus.

(a) is a curve obtained with the room light on and the discharge tube not illuminating the photocathode. Note that there is no variation of output with phase.

(b) shows the curve due to the modulated light from the discharge tube illuminating the photocathode.

(c) is a typical noise curve obtained by placing a Wood's glass filter between the lamp and the photocathode so as to cut out all but the ultraviolet component of the exciting light, followed by a Wratten 2A filter to cut out the ultraviolet. The small fraction of light transmitted by both filters gives this weakly modulated background signal.

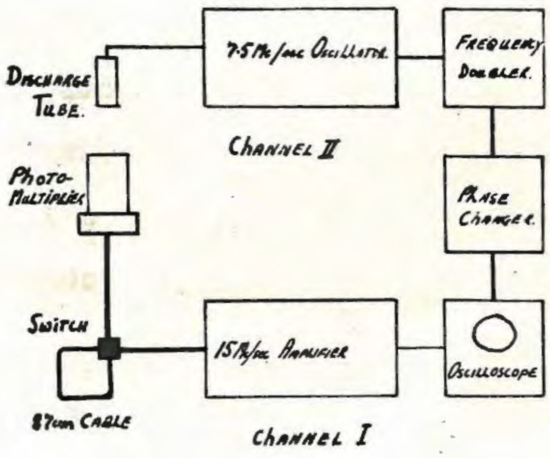
(d) is the signal obtained when an anthracene crystal is placed between the two filters. The fluorescent light of anthracene is passed by the 2A filter.

It should be noted that the signal vs phase curve is close to a sine curve with a small distortion due to the non-linearity of response of the phototube for variation of the photocathode potential, and to the light from the discharge tube not being exactly of the form $\sin^2 \omega t$. (See Appendix IV).

Section D.

Calibration of the Phase Changer

The oscilloscopic method of display was used to calibrate the phase changer against a known length of cable. The phototube was modulated by the light from the discharge tube. The signal from the phototube was fed via a length of cable to the tuned amplifier which



Diagrammatic Circuit for Calibration of Phase Changer.

drove the Y plates of the oscilloscope. This was Channel 1. The X plates of the oscilloscope were driven directly by the signal from the phase changer. This constituted Channel 2. Incorporated in channel 1 was a switch which could switch in or out an additional length of coaxial cable - a polythene-insulated cable of about 87 cms. The phase in this channel could be further altered by increasing the potential on the phototube and thus saturating the amplifier so that a phase change of about 90° would take place. A further change of phase could be introduced by slightly detuning the resonant circuits of the amplifier. By adjusting each of these in turn it was possible to obtain a line on the screen throughout the range of the phase changer.

(a) Calibration

The changer was calibrated by reducing the ellipse on the screen to a line. The 87 cms of cable in channel 1 was introduced to form an ellipse. The reading of the phase changer was noted and a further reading taken to determine how much delay had to be introduced in this channel 2 to again obtain a line on the screen. The cable was then switched out and a phase shift introduced (by either of the above methods) into channel 1 to reform the line. Then the procedure was repeated. This was continued through the range of the phase changer.

The electrical length of the cable was found by

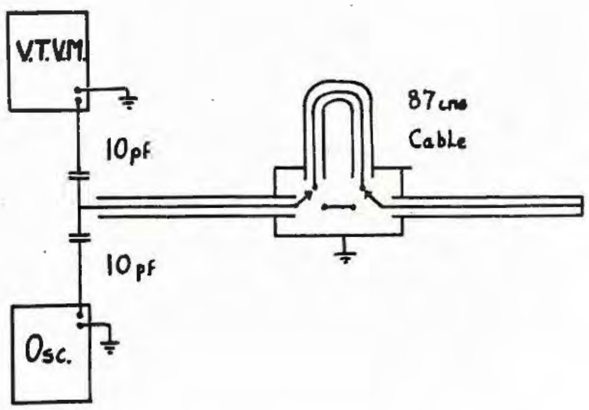


Figure 23. Circuit to measure electrica
Length of 87 cm Cable.

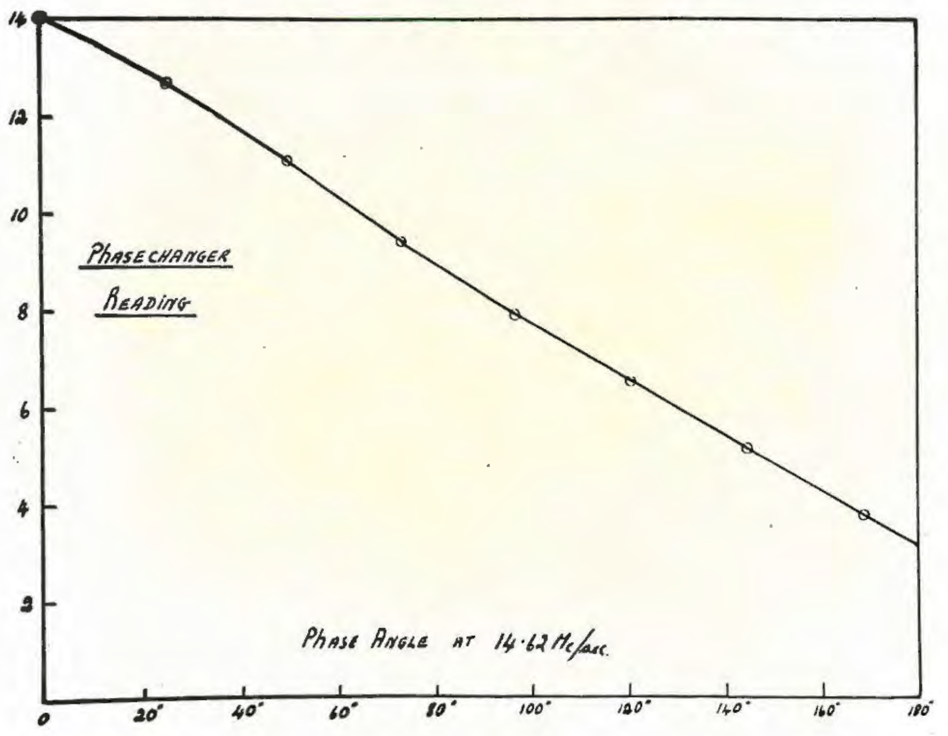


Figure 24. Phasechanger Reading vs Phase Angle Calibration Curve.

Measurement of Delay Time τ of Calibrating Cable.

Resonant Frequency		Cable Delay. τ
Cable Out ν_1	Cable In ν_2	$\tau = \frac{1}{4}\left(\frac{1}{\nu_2} - \frac{1}{\nu_1}\right)$
20.38 Mc/sec	14.78 Mc/sec	4.65 x 10^{-9} secs.
20.38	14.78	4.65
15.21	11.93	4.56
15.23	11.94	4.52
		Mean Delay 4.60 ± 0.02 x 10^{-9} seconds.

Table I.

measuring the resonant frequency of it when connected to an additional long cable, first with the cable switched out and then with it switched into the circuit. This is shown diagrammatically in figure 23. The measurements are shown in Table 1. The calibration curve is given in Figure 24. The calibration was checked subsequently by observing the phase shift from the maximum to the minimum position of the signal vs phase curve with the discharge tube exciting the photocathode. This was done using the second method of detecting the phase angle. This phase measurement came out to be $188 \pm 10^{\circ}$ which agrees with 180° within the experimental error.

(See Figure 22).

(b) Experimental Precautions

All adjustable controls on the oscillator and phase changer were sealed with wax before the calibration and were left unbroken throughout the experimental measurements.

The amplifier leads and phototube had to be carefully shielded in order to prevent direct pickup from the field about the discharge tube. All the "Pye" type of coaxial plugs had to be sandpapered to ensure good earth connection. All the units were separately earthed. The main oscillator and amplifier were housed in separate metal containing boxes. Care had also to be taken to terminate all interconnecting cables in their characteristic impedance in order to prevent reflections in the cable. This had to be done to the cable leading to the plates of the oscilloscope to prevent coupling between the X and Y plates.

Section E.

Investigation of discharge tube characteristics

(a) The variation of the degree of modulation with pressure

The unpertubed decay times of the excited state of oxygen and nitrogen molecules are of the order of 10^{-7} to 10^{-8} secs. (Frey, 1936). If, however, the pressure of the gas be increased the excitation of the molecules will be quenched by collision. The effect of this will be to reduce the decay time and reduce the intensity of the emitted light. In a collision the molecule will be able to make a non-radiative transition to the ground state. Thus it loses its excess energy by internal vibration or by a collision of the second kind i.e. loses all its excess energy as kinetic energy of the parting molecules. The frequency of collision will be proportional to the pressure of the gas, so the decay time of the excited state of the molecule should be

$\tau = \frac{\tau_0}{1+ap}$ where τ_0 is the unpertubed decay time.

'a' is a constant and p is the pressure of the gas.

If, then, we measure the degree of modulation of

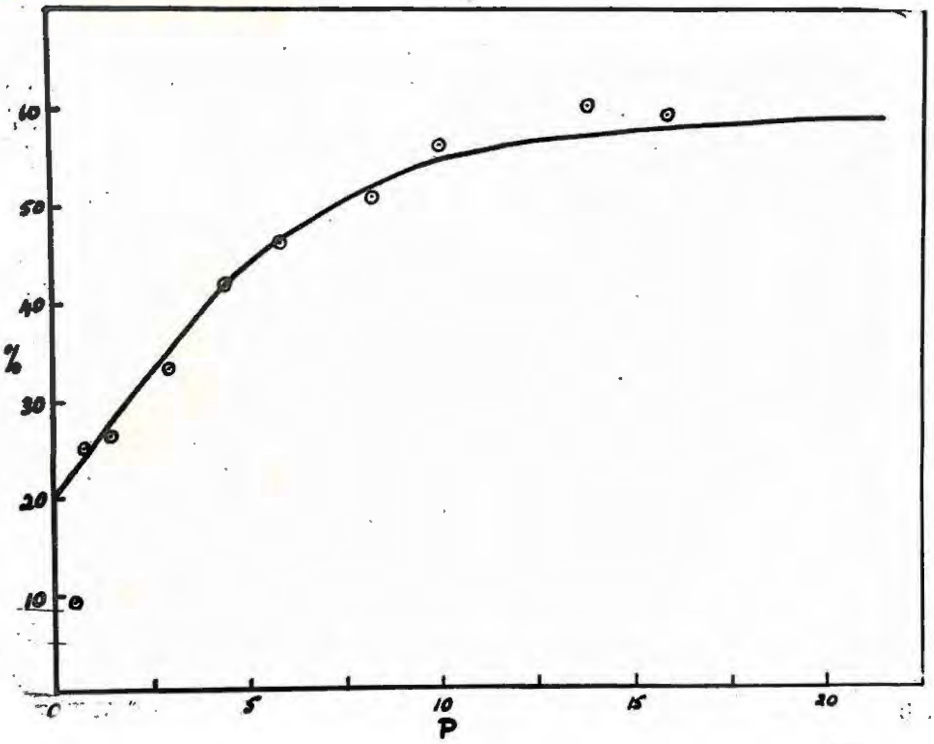


Figure 25. Percentage Modulation vs Pressure for discharge tube.

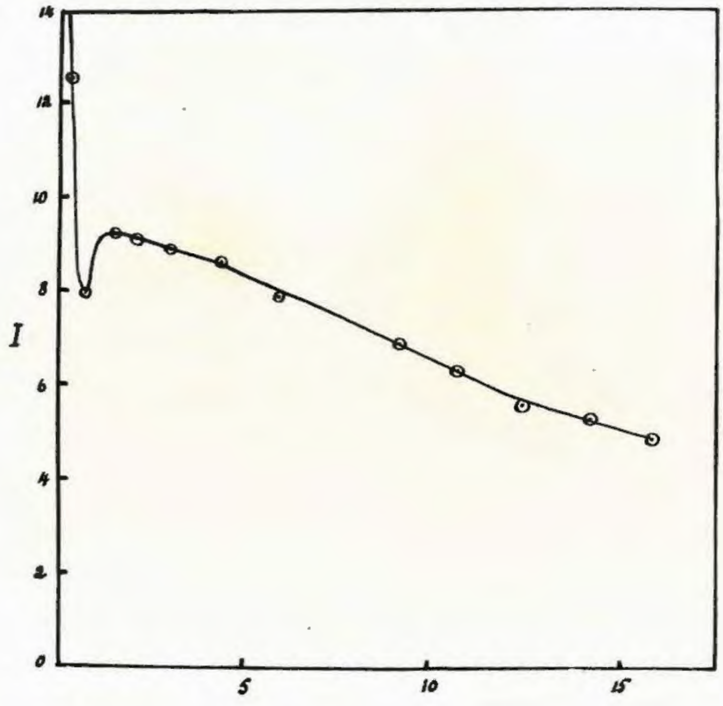


Figure 26. Intensity of modulated light from discharge tube plotted against gas pressure in cms of mercury.

the light from the discharge tube as a function of gas pressure it should be of the form $A \cos \phi$ where $\tan \phi = 2\omega\tau$ just as for a phosphor (Section B). The value of A was found not to be 1.0 as ~~it~~ would be expected ~~to be~~. This may be attributed to some light falling directly on the first dynode, so that the current does not fall to zero at the minimum in the cycle even for the highest pressures in the lamp.

The value of M, the measured degree of modulation, is plotted against pressure in Figure 25. A theoretical curve to get the best fit is drawn too. This is given for the values of $A = 0.65$; $\tau_0 = 3.26 \times 10^{-8}$ seconds for air; and $a = 0.35$ /cm Hg pressure.

In Figure 26 the variation of the intensity of the light from the tube is given. Quenching is seen to reduce the light output at high pressures. In both curves the points at low pressure are probably unreliable as here the discharge filled the whole volume of the tube, and the whole nature of the discharge changed.

This method of investigating the decay times of the excited states of gas molecules appears to offer great potentialities, particularly if narrow-band filters are used to separate the different optical transitions. Since, however, the work was subsidiary to the main investigation, measurements were restricted to those required to establish the optimum conditions of the operation of the modulated discharge tube.

Section F.

MEASUREMENT OF THE PHOTOFLUORESCENT DECAY TIME OF ORGANIC PHOSPHORS

(a) Method

For these measurements the discharge tube was mounted 2 cms above the photocathode of the 931A. In front of the quartz window of the discharge tube a Wood's glass filter was introduced to cut off all the visible light. In front of this was placed a copper gauze electrostatic shield which was earthed. This was necessary in order that the capacity of the resonant circuit of the discharge tube would remain unchanged on inserting the fluorescent specimen. Over the window giving access to the phototube compartment a Wratten 2A filter was placed. This filter stopped practically all the ultraviolet light transmitted by the Wood's glass filter from entering the phototube.

To measure the decay time of the specimen the following procedure was taken: the Wratten 2A filter was removed and a plot taken of the galvanometer reading against the reading of the phase changer. It was necessary to take up the backlash of the screw of the pickup coil of the phase-changer. The filter was next put into place and the potential across the phototube increased. The specimen was then put between the two filters. The galvanometer then gave something close to a full scale reading. A plot of the galvanometer vs phase changer reading was then taken. The crystal and filter were then removed and the first plot measured again to check that no shift of the phase had occurred in the amplifier or associated circuits. From the two curves obtained the displacement of their minima was obtained and read from the calibration graph (Figure 24) in degrees of phase. From the relation Tan $\phi = 2\omega\tau$ the decay time τ was found for each specimen. Several check experiments were made to verify that the shift in phase was due only to the decay time of the phosphor and not to any spurious cause.

(b) Check Experiments and Precautions

An important check was taken to see that the phase of the measured signal was independent of the potential applied across the phototube. It is reasonable to expect that it would be independent of the potential, as it is the potential of the photocathode itself which is modulated, and any transit-time effects would occur after the first dynode. However, the check was made by taking the plot of the exciting light falling directly on to the photocathode, and then taking another plot by interposing a sheet of paper which diffused the light and so reduced its intensity. The phototube potential was then increased until about the same current was flowing through the galvanometer as before. A second plot was then taken. The curves are seen to be essentially the same with their minima occurring at the same phase setting. See Figure 27 (a) and (b).

The phototube current was plotted against the setting of the phase-changer for light of different wavelengths selected by a series of Wratten filters. This allowed different parts of the spectrum of the lamp to fall on to the photocathode. There was no relative phase shift between these, which indicated that the decay time of the gas molecules was being determined principally by the high collision rate due to the high pressure of the gas. Hence, it does not matter at what wavelength the crystal absorbs the light.

The discharge tube was used at 5 cms Hg pressure at all times when readings were taken.

The apparatus was allowed to warm up for a period of an hour before any readings were taken. If this was not done it was found that the plot of the signal vs phase curve would change a few degrees in the time taken to take a plot of the crystal's curve. Furthermore, after this time the frequency of the oscillator settled down to the value originally measured. This frequency was measured by beating the radiated signal against the signal from a standard Marconi Signal Generator and listening to the beat on a receiver in the next room. The frequency of the oscillator was measured to be 7.31 Mc/sec. The accuracy of the decay time measurements was determined chiefly by the accuracy with which the minima of the phase plots could be found, which was of the order of 20%, and hence it was not necessary to know the frequency of the oscillator to a high degree of accuracy.

No change of the position of the phase minimum was observed when a wooden block was moved about between the photocathode and the electrostatic screen. This showed that the dielectric of the crystal was not responsible for a detuning of the resonant circuit of the discharge tube with a consequent phase change.

A considerable amount of difficultywas had in shielding the amplifier and leads from direct pickup of the radiated field from the leads to the discharge tube. This can be understood when it is realised that the photo-multiplier box had to be only 2 cms. from the discharge tube where the electric field rose to several hundred volts/mm. "Pye" plugs gave a lot of trouble until they were all sanded and worked into place. Separate earthed leads had to be taken from each of the units and the discharge tube was mounted on short leads close to its resonant circuit which was housed in a separate earthed metal box with a lid. The amplifier and main oscillator were in separate metal boxes and were kept at least ten feet from the phototube and discharge tube units, and connected to them by coaxial cables. In taking readings the operator kept well clear of the unshielded parts of the apparatus.

After the general trend of the curves had been established, only that portion of the curve close to the minima was plotted in each case. These were used to determine the decay times of the phosphors.

(c) RESULTS

Figure 27 indicates one of the earlier measurements on anthracene. (a) and (b) show the curve obtained for light of high and low intensity respectively. These show that the minima of the curves are unchanged on increasing the potential across the phototube. Curve (c) is that plotted for a 3 mm thick anthracene crystal wrapped in Al foil so that only the transmission spectrum of the specimen is observed by the photomultiplier. (d) is that obtained from a fine powder of anthracene. The powder was made by rubbing the crystal used in (c) on to a plate of ground glass. The phase shift for the two specimens, indicated by the displacements of their minima, should be noted. These phase shifts determined the decay times for the two specimens as 17 ± 5 millimicroseconds and 6.5 ± 1.0 millimicroseconds

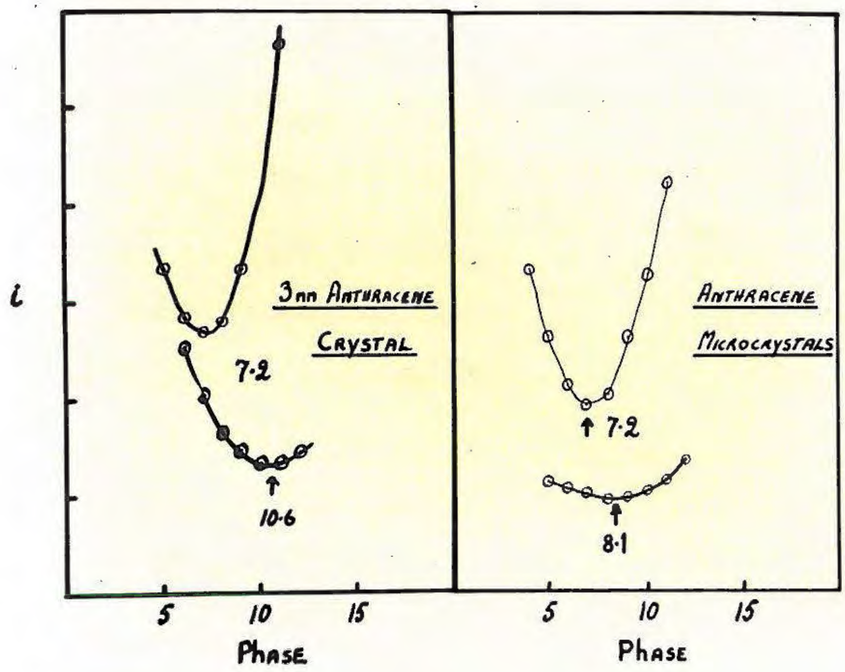


Figure 28. Intensity vs Phase plot.

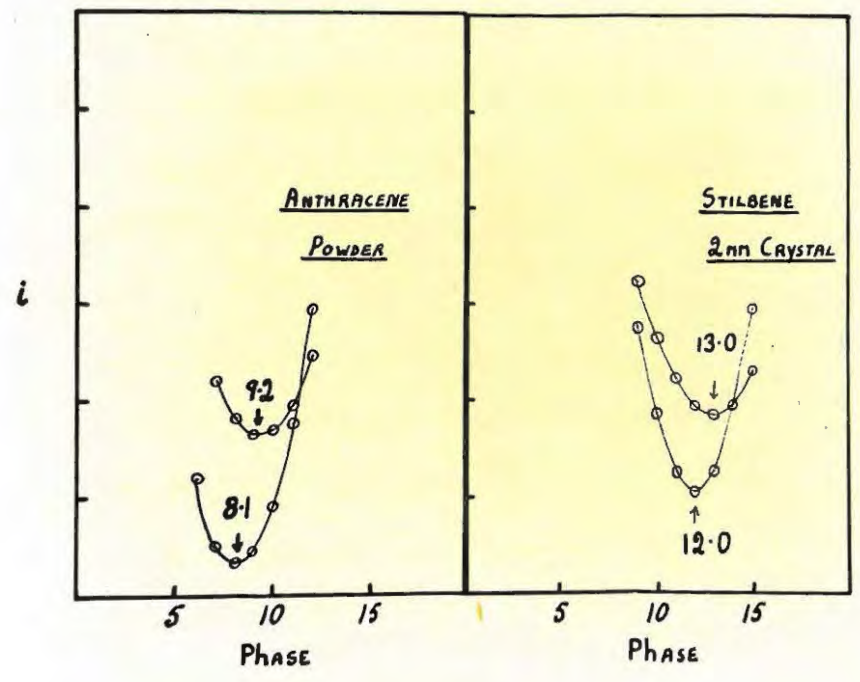

i
Anthracene
Powder
9·2
8·1
5
10
15
Phase
Stilbene
2mm Crystal
13·0
12·0
5
10
15
Phase

Figure 29.

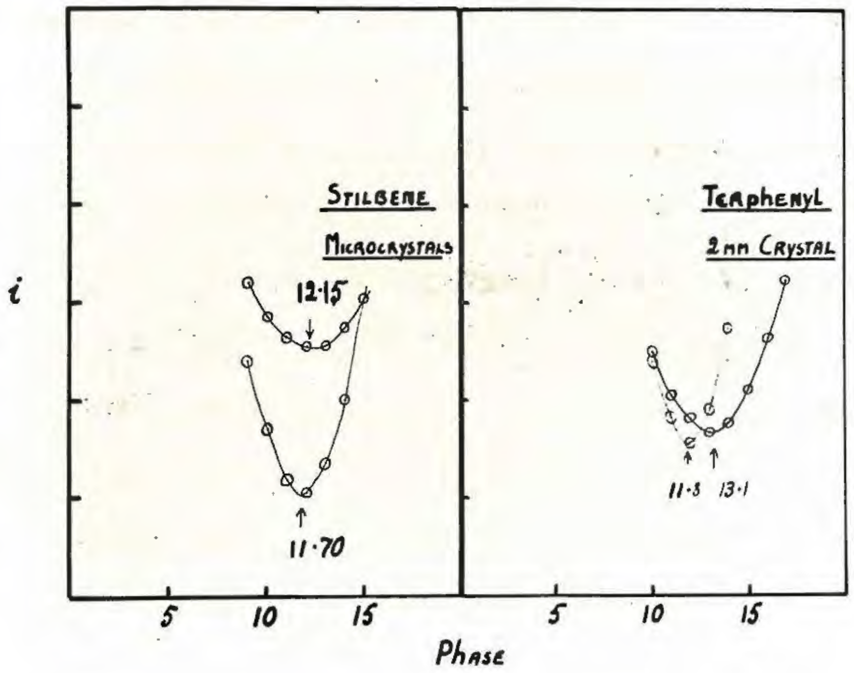

STILBENE
MICROCRYSTALS
12·15
11·70
TERPHENYL
2mm CRYSTAL
11·8
13·1
i
5
10
15
5
10
15
Phase

Figure 30.

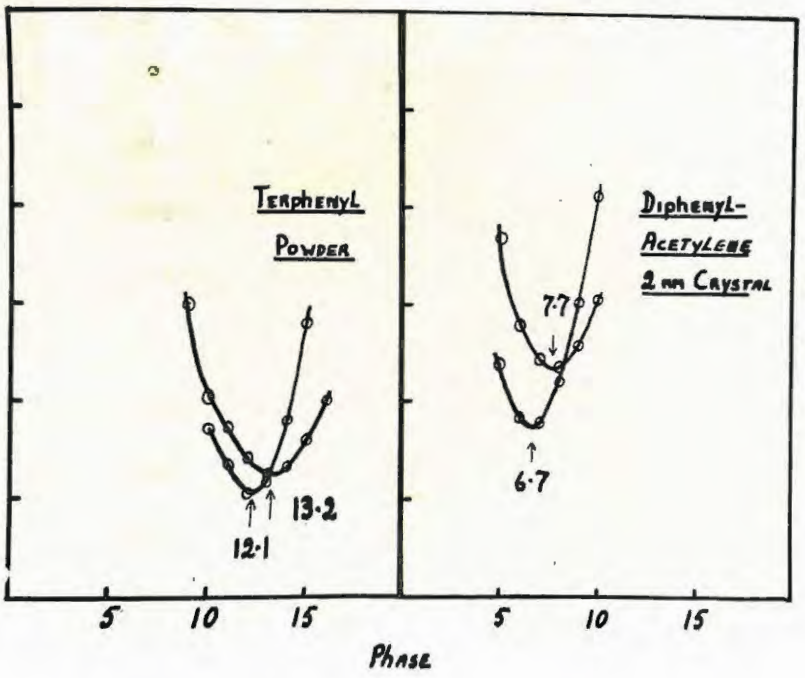

i
Terphenyl
Powder
12·1
13·2
Diphenyl-
Acetylene
2 mm Crystal
7·7
6·7
5
10
15
5
10
15
Phase

Figure 31.

on assumption that the fluorescence decayed exponentially.

With this arrangement it was found difficult to determine the minima with a high degree of accuracy owing to the small curvature at the minima. However, by an increase of the "Q" of the resonant circuit across the photocathode and first dynode of the 931A, a higher alternating potential was obtained to modulate the gain of the tube, and sharper minima were obtained for the following measurements:

Figure 28 shows the measurements of an anthracene crystal 3 mm thick, anthracene powder, and anthracene microcrystals prepared in the same way as for the spectral measurements.

Figure 29 are the measurements on stilbene 2 mm crystal, stilbene microcrystals, terphenyl 2 mm crystal and terphenyl powder, diphenyl-acetylene 2 mm crystal and naphthacene in anthracene. (Figures 29 - 32 inclusive).

The results obtained are summarised in Table II.

(d) Discussion of Results

The first and most obvious factor which these results bring to light is the very appreciable difference in the decay time between a fine powder and a crystal of the normal size used for scintillation counting. Figures 28 and 29 are conclusive evidence that the process of repeated emission and absorption of the absorbed

Table II.

Phosphor	ø	Decay-time
Anthracene 3mm crystal	53° ± 5°	14 ± 2 musecs.
Anthracene Powder	18° ± 3°	3.5 ± 0.5
Anthracene microcrystals	16 ± 3°	3.1 ± 0.5
Stilbene 2mm crystal	16 ± 3°	3.1 ± 0.5
Stilbene microcrystals	7 ± 2°	1.3 ± 0.4
Terphenyl 2mm crystal	20 ± 3°	3.9 ± 0.5
Terphenyl powder	18 ± 3°	3.5 ± 0.5
diphenyl-acetylene 2mm crystal	18 ± 3°	3.5 ± 0.5

energy plays an important part in the transfer of energy for crystals of this size. The spectral measurements in the previous part showed that a large portion of the absorbed light which was emitted as fluorescent light was re-absorbed in a large crystal. These measurements of the decay times show that this re-absorbed light is efficiently re-emitted and contributes much to the longer decay time of the large crystal as compared to that of a powder. To express this quantitatively we will consider the effect of size on the measured decay time of a crystal.

As we saw earlier, the number of optical transitions in a short time dt will be p.N.dt. If, however, the light is re-absorbed within the crystal with a probability $1-b$ then the net loss of excited molecules will be:

b

$$-dN = -(dN_r + dN_o) = -[q\,Ndt + p(1-b)\,Ndt]. \quad ?$$

$$= -[1 - \frac{pb}{q+p})(q+p)\,N\,dt.$$

$$= -(1 - Qb)\frac{1}{\tau}\cdot N.dt$$

where dN_o is the loss due to optical transitions, and dN_r is the loss due to non-radiative transitions. Then the intensity of the observed light will be dN_O/dt:

$$dN_O/dt = N \,.\, e^{-t(\frac{1-bQ}{\tau})}\,(I - b).p$$

We see that the decay time is still exponential in form but increased by the factor (I/ I - bQ), where

Q is the quantum efficiency for a fine crystal.

In this approximate analysis it is assumed that the light has the same probability of escaping from the crystal wherever it is emitted; and also that the quantum efficiency is constant over the whole emission range of the fluorescent light.

The value of 'b' may be calculated from the spectral measurements. If b' is the probability of escape of a photon of wavelength λ in the crystal, then the total probability of a photon escaping if it has an emission spectrum F( ) d , will be: $\frac{\int_0^\infty b' F(\lambda)\, d\lambda.}{\int_0^\infty F(\lambda)\, d\lambda.}$

This is immediately seen to be just the ratio of the area of the curve under the large crystal spectrum, divided by the area under the curve of the microcrystal spectrum, normalised where b' =1.0. (See Figure 10). The ratio of the two decay times, calculated from these two areas and Bowen's value of the quantum efficiency for anthracene of 0.9, is 3.3 for thick crystal to the micro-crystals of anthracene. The measured decay times are in the ratio of 4 ± 1:1. There is thus reasonable agreement between the two.

The other measurements show that the variation of decay time is not peculiar to anthracene. The others are typical phosphors all of which show this effect to a greater or lesser extent, so that we can generalise and say that all organic phosphors of this

Table III

Phosphor	Decay Time (Liebson et al)		Decay Time
	Gamma-ray	Ultra-violet	Measured.
Anthracene (size not stated)	30 musecs	I7 musecs	I4musecs
Stilbene	8	3.I	3.I
Terphenyl	6	II.0	3.9
Diphenyl-acetylene	4	2.5	3.5
½% Anthracene in Benzene	—	2.0	—
½% Terphenyl in Toluene	2.0	2.5	—

type have this property.

The second important result becomes apparent when we compare these results with those obtained by other workers using ionising particles for excitation. These ultraviolet values are all considerably less than the corresponding values for ionising radiations. Table III gives the results obtained here and the results obtained by others for the phosphors listed. These measurements are in good agreement with those obtained by Liebson et al who used ultraviolet excitation, in that they are all less than the decay time obtained for excitation by ionising radiation.

As the difference between the short decay time obtained for the small crystals could be readily explained by the assumption that the emitted light was emitted and re-absorbed a number of times before escaping, and, as this correlated several other results, Birks (1953) has proposed a theory on these lines to account for the photofluorescence and the ionising decay times. The gist of the theory is that the ionising particle ionises the molecule as it passes close to it. When the ionised molecule recaptures an electron it emits a photon in the far ultraviolet near its ionising energy. The absorption of photons in this part of the spectrum is very strong and the emitted photon is quickly re-absorbed in a nearby molecule, which, after

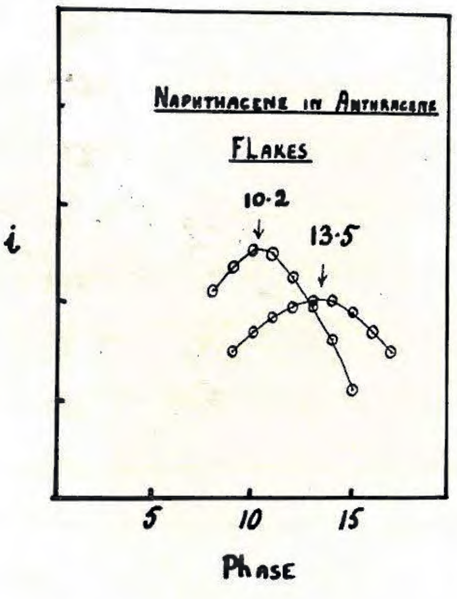


Figure 32.

its natural lifetime for this energy of excitation, de-excites with the emission of a photon. This process continues with the photon losing a little energy as heat in each of the molecules in which it resides until it is finally degraded, so that on emission it is able to escape entirely from the crystal in that portion of the spectrum to which the crystal is transparent. The sum of all the decay times due to these emission and absorption processes would account for the long decay time for ionising particle excitation, since here a larger number of transfers of energy would have to take place before the energy could be sufficiently degraded to be emitted as light in a crystal of normal size, than if the molecule were excited by low energy ultraviolet light. Wright (1953) has suggested that the longer decay time may be accounted for by the time taken for the ionised molecule to recapture its electron.

Figure 32 shows us that the decay time of a solid solution of naphthacene in anthracene has a decay time which is longer than that for pure anthracene, indicating that the energy transfer could be simply photon emission and re-absorption. It was not possible to excite the naphthacene without doing so via the anthracene lattice, so that a measure of the decay time of naphthacene alone could not be obtained. This would have shown whether the resultant decay time when excited via the anthracene was simply the sum of the anthracene and naphthacene decay times.

(e) Limitations of the Apparatus

The limitations of this "pilot" apparatus soon became apparent. Firstly, no filters were available to transmit light of shorter wavelength than the Wood's glass band near 350 mμ, so that it was not possible to excite naphthalene, or any of the anthracene-naphthalene mixed crystals via the naphthalene lattice. For this reason the mixed anthracene-naphthacene crystal was tried. Using the existing filters it was possible to excite the green fluorescence of naphthacene by absorption in the ultraviolet by the anthracene, followed by transfer to the naphthacene. However, the intensity of the lamp was not high enough to excite any measurable fluorescence in the naphthacene when using a blue filter to excite the naphthacene directly. Thus, in no case was it possible to measure the decay time of two components of a mixed crystal in both the mixed crystal and separately.

It had been hoped that the measurements could be checked by measuring the decay times of solutions used by Gaviola and Liebson, e.g. Rhodamine B in water. Here again the intensity of the lamp was too low to detect any appreciable fluorescence from a solution of Rhodamine B in water. Sodium Iodide could have provided a check, but the fluorescence of it could not be excited as the absorption bands of the lattice lie too far into the ultraviolet for the light from the Wood's glass filter to excite it.

Further, the intensity of the lamp was too low for the measurement of the decay times of solutions of anthracene in benzene. It was not possible either to do experiments on phosphors which have emission bands very close to the transmission band of the Wood's filter, since then the second filter was not able to transmit enough of the fluorescent light to be detected, without some of the exciting light also coming through.

Initially it had been hoped that it would be possible to select the exciting light with a quartz monochromator and to detect the fluorescent light with a spectrometer and photomultiplier. With this arrangement it would be possible to see the variation of the decay time with respect to the wavelength of excitation and of detection. The first would be able to give valuable information of the exchange mechanism and indicate whether it be due to sensitised fluorescence or to the emission and absorption of photons. The second would give information on the effect of thickness of the specimen on the decay time. Emitted light of long wavelength could be composed of components of single emission or of multi-emission processes, but that of the short-wavelength end of the spectrum could be composed only of single-emission processes. Therefore, a variation of decay time might be expected to occur across the emission spectrum. Unfortunately the intensity of the exciting light was too low to allow the use of any monochromators other than coarse filters with broad transmission characteristics, so this experiment could not be performed.

At this stage two lines of development lay open: either the apparatus could be refined and modified to enable the above experiments to be carried out, or the suggestions of Birks' theory could be followed up. This theory suggested that photons were emitted by these phosphors when excited by ionising radiation, which would lie in the ultraviolet at shorter wavelength than the normal emission band. However, they would be readily absorbed by the phosphor so that a search for such photons would have to be made using very thin crystals. As the possible existence of photons at these energies raised points of fundamental importance in the theory of fluorescence and the related fields of bio-physics (Birks - unpublished work) this line was selected for further research. A search was planned for photons of wavelength between 330 mμ and 185 mμ from anthracene when excited by ionising radiation.

Part IV.

THE INVESTIGATION OF THE SPECTRA OF SOME ORGANIC PHOSPHORS UNDER IONISING RADIATION

Section A

Early Work

Sangster (1952), Albrecht et al (1952), Pringsheim and others (1949) have measured the spectra of organic phosphors excited by Po-alpha particles, X-rays or ultraviolet light. Without exception the measurements show the emission spectra occurring purely in the visible or in the very near ultraviolet, with no difference between excitation by ionising radiation and ultraviolet excitation. The criticism of these results is that, firstly, the crystals used were usually quite thick and very much thicker than the estimated mean free path of photons of the expected energy near the ionising level ($\sim$ 7u). Secondly, the intensity of the emission was very low as radioactive sources or X-ray were used for ionising excitation, which meant that exposure times of 60 to 90 hours had to be taken. This meant that if any weak emission bands should lie to the ultraviolet side of the spectra, they would have a good chance of being missed. It was therefore decided to devise some method of exciting the crystals above the ionising energy and to use fine powders, so that the high energy photons would have the opportunity of escaping from the

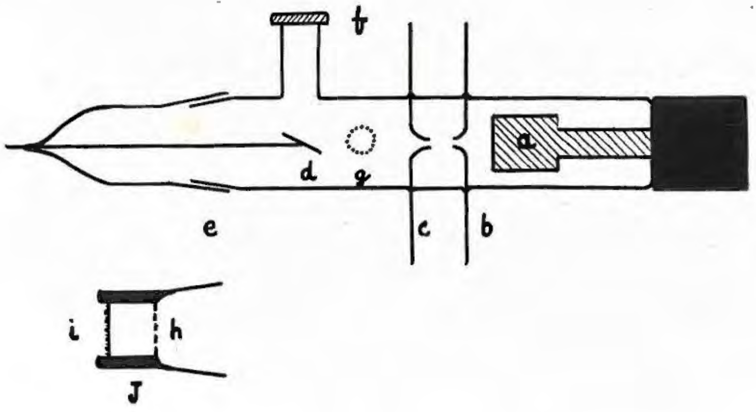


Figure 11. Vacuum Bombarding Chamber

(a) Electron gun.
(b) & (c) accelerating plates.
(d) Nickel anode.
(e) Ground glass seal.
(f) Fluorite window.
(g) evacuating tube.
(h) Electrostatic shield.
(i) Lenard window.
(j) Brass cone.

phosphor and being detected on the photographic plate.

Section B

Experimental Work

Preliminary experiments using a radioactive source for excitation showed that exposure times much in excess of 30 hours would be required for the sources and equipment available in order to obtain reasonable exposures.

A simpler method of excitation of anthracene appeared to be to place the specimen in a highly evacuated chamber and bombard it with electrons from an electron gun, accelerating the electrons through 1 to 2 kV. The vapour pressure of anthracene is comparable with that of mercury at the same temperature so that if the specimens were cooled to the temperature of dry ice, the anthracene vapour should give no trouble.

(B) (a) Vacuum Bombarding Chamber.

The vacuum of a small ex-army klystron was broken at the reflector anode, and a ground glass seal and an evacuating pipe were added beyond this point together with a viewing window of fluorite. See Figure 33. The other end of the ground glass seal held a glass fitting holding a nickel electrode to which the specimen was affixed with fine copper wire. The two copper plates of the resonant cavity were freed from the rest of the wave-guide and connected to different potential sources so as to act as focussing electrodes for the electron beam which passed through the hole in their centre and impinged upon the specimen which was held at about 500 volts with respect to cathode.

The seal was held with vacuum grease and the whole assembly evacuated with a backing pump and oil diffusion pump. This vacuum system and ionisation gauge had to be assembled and set up. The Phillips' ionisation gauge used was calibrated by the manufacturers, and, as it was unnecessary to know the pressure to a high accuracy, this calibration was used. Considerable trouble was had with the backing pump and drying tubes before a satisfactory high vacuum could be obtained. A mercury diffusion pump was used at first as there was a selection of ground glass fittings for this pump, but the need of liquid air at regular intervals made this inconvenient. Hence a fitting was made for the Metro-Vic. 03 oil pump which proved much more convenient once the backing pump could be arranged to reach the rather lower backing pressure necessary for the oil pump before it would take. With this arrangement pressures of 10^{-5} mm could be obtained after a few hours of pumping.

A 1 mm thick crystal of anthracene was put into the chamber on the anode and bombarded with an electron current of between 200 and 400 μ amps at 500 volts, concentrated into a spot focus on the crystal. Where the beam struck the specimen the fluorescence was brilliant blue, but after two or three seconds of bombardment changed to a pinkish glow. The intensity of the electron beam was so great that the surface of the crystal vapo~~u~~rised and sputtered anthracene all over the inside of the chamber. At first this rendered the electron beam visible, but as the pressure became too great the electron emission fell, and the tube flashed over.

Birks and Black (1949) have shown that the efficiency of anthracene is reduced after long periods of bombardment by high energy particles, and as the ionisation is more localised and more intense for slow particles we should expect electrons of 0.5 kV to do much damage for the amount of light they cause to be emitted. This was qualitatively found to be true.

The beam was swept over the surface of the crystal by using a magnetic field until the whole surface had been rendered only feebly fluorescent. Then the vacuum was broken and the surface of the damaged crystal was scraped. The system was re-evacuated and the whole process repeated. Still not enough light could be obtained from the crystal to obtain an adequate exposure using Kodak P1200 plates. This wasacumbersome and ineffective method of obtaining the full spectrum. Some improvement was necessary so that the spectrum

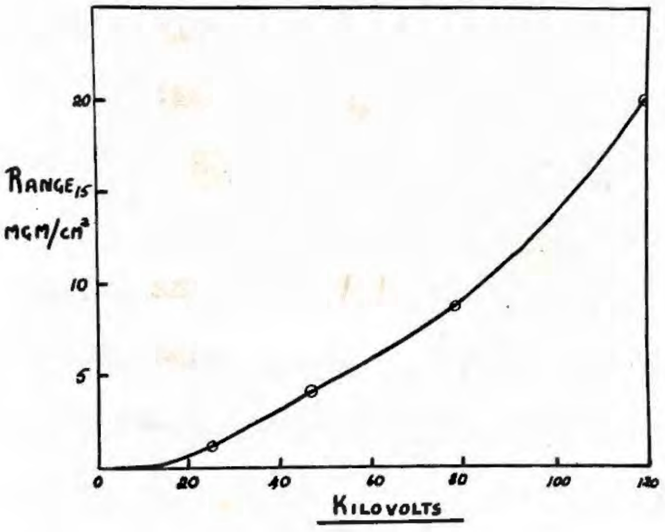


Figure 34. Range of electrons in aluminium plotted against electron energy.

could be obtained more quickly and without having to break the vacuum during the exposure. This was next attempted by applying 22 kV across the tube. An improvement did result but the vacuum was still contaminated with sputtered anthracene.

A more suitable method of exciting these crystals was devised so that the specimen could be held outside the vacuum.

(B) (b) Lenard Window Investigation

On account of the comparatively high vapour pressure of the phosphors used in this investigation, and the high rate at which these phosphors lose their fluorescent efficiency it was necessary to:

(a) bombard the specimen outside the vacuum;

(b) use electron energies much higher than 22 Kev.

Fortunately these two factors are not mutually exclusive but rather go hand in hand. The curve in Figure 34 shows the range of electrons in aluminium foil for different energies. (Hoag & Korff). If a foil of about 3 mgm/cm^2 is supported upon a grid of stronger gauze, such as that described in Cathode Ray Oscillography (MacGregor-Morris, 1936), it is capable of standing the pressure of the atmosphere.

Using aluminium foil from a discarded paper condenser of mass 1.96 mgm/cms backed by a coarse zinc gauze and waxed on to the end of a brass cone (turned to fit the ground glass joint at the end of the electron-gun) it was possible to maintain a high vacuum within the tube. (See Figure 33). The whole surface of the paper had to be waxed by flowing warm wax over it. This served to fill the tiny pinholes which puncture the foil. This, of course, increases the effective thickness of the foil.

A zinc grid was soldered on to the inner end of the brass fitting in order to act as an electrostatic shield and to allow the electrons to pass through the brass pipe and reach the Lenard window at the end without being drawn to the walls by the defocussing action of the cavity.

The filament of the electron gun of the klystron was heated by an accumulator, and the focussing electrodes were maintained at an adjustable potential between 0 and 500 volts with respect to the cathode which was earthed. The Lenard window and brass end pipe were connected to the H.T. of a large induction coil. The low end of the H.T. was returned to the cathode. The primary of the induction coil was driven by the D.C. Mains, using 40 volts at an average current of 3 amps interrupted by a motor driven mercury interrupter. This gave a spark between 7 and 10 cms in length between brass spheres 1 cm in diameter which indicated a potential of about 100 to 200 Kv.

At first the tube gave trouble by breaking down between the focussing electrodes and the brass anode. Sometimes these sparks punctured the glass, but the holes could be sealed with hot wax. This difficulty was partly overcome by painting a strip of Indian ink between the two electrodes, with a narrow band round the tube every centimeter. The resistance of the Indian ink served to act as a potential divider which distributed the potential along the glass and also served to focus the electron beam and prevent it diverging on to the walls of the tube. However, when the ink dried, a small amount of sparking took place between the granules of the dried ink.

After trying to use this apparatus for some time it was noted that the total emission from the cathode was only about 100 micro-amps as compared with several milli-amps as it was on first using the tube. It was thought that the oxide coating had been contaminated by the anthracene vapour which had been in the tube, and had so contaminated it as to render the emission very low. The cathode was re-activated by the following method described by Spangenberg (Vacuum Tubes, MacGraw-Hill, New York). First, the cathode was cleaned by dropping a weak solution of HCl on to it with a medicine dropper, by flushing with water, and next by cleaning with alcohol. Next, a 1:1 solution of $Sr(CO_3)$ and

$Ba(CO_3)$ in acetone was prepared and mixed with a little "Jewellex" cement and dropped on to the cathode. The cathode was then allowed to dry in air for some hours after which the tube was evacuated to the highest attainable vacuum, - 10^{-6} mm approximately. The filament was then heated to drive off the occluded gases and when the vacuum had again reached about the same value, the filament was re-heated to nearly white heat for 15 seconds. This served to liberate a small amount of Ba and Sr which dissolved in the cathode material. It was then drawn to the surface by the electrolytic action by maintaining the cathode at about 1000°C for 10 minutes with 500 volts applied to the accelerator plates. The current drawn from the plates increased steadily until a steady value of 2 ma was obtained. This was sufficient for all the work.

It was thought advisable to maintain the anode to which the Lenard window was fixed, at earth potential, so as to make the interchange of specimens and the setting up of the spectrograph less dangerous. While doing this a spark punctured the glass envelope of the tube close to the heated cathode and broke the vacuum. All attempts to seal the hole failed as the waxes and cements were unable to withstand the temperature without softening, and since with all this attention the hole developed into a crack the apparatus was set aside and a different one built.

(B) (c) Gaseous Electron Accelerator

A disused X-ray tube was opened where one of the side arms used for holding the target had been. Over this was placed a metal cap with 20, 1 mm holes in it. The cap was sealed on to the tube with hardwax to form a vacuum seal and the whole tube was fitted on to the top of the oil diffusion pump, through a needle valve fitting. Over the holes of the end cap was sealed a foil of aluminium which was waxed into place. The whole assembly was evacuated and a potential of about 120 Kv applied across the tube from the induction coil.

By applying a potential of the correct polarity so as to accelerate electrons towards the Lenard window, a small beam was observed outside the window by the blue emission of light in the air. However, the anode heated rapidly and softened the wax holding it in place. This difficulty was overcome by soldering a copper pipe round the end-plate and passing water through it. This cooling was effective in preventing the wax melting at the highest currents attainable, though care had to be taken to see that the vacuum was high enough before applying the high potential to the tube. If, on the other hand, the vacuum was poor a glow discharge would pass through the tube, and the heat from this would be too much for the cooling system, and so the wax would melt and break the vacuum.

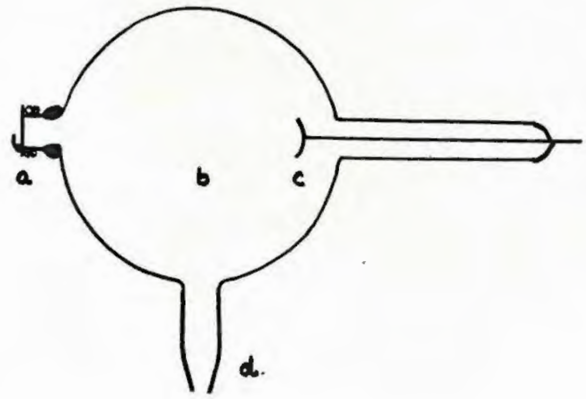


Figure 35. Gaseous Electron Accelerator.

(a) Water cooled end plate with perspex specimen holder.

(b) Glass bulb "ducoed" black.

(c) Concave Target.

(d) Evacuating pipe

Section C

Tests on the accelerator

Outside the window and in contact with it was placed a small holder constructed of perspex into which specimens to be irradiated could be placed. (See Figure 35). A nickel plate was placed in this holder and connected to the H.T. lead via a microammeter so as to measure the strength of the external beam from the tube. In this set-up of the apparatus, the anode of the tube was at earth potential and the target at about 120 Kv. The maximum beam current measured was 4.0 microamperes, but it was usually used at a beam current of only about 0.5 microamps. The effectiveness of this method of exciting the phosphors can be readily seen when compared with a radioactive source. The lower current corresponds to a source of about 200 curies directed on to the crystal, whereas sources usually used for this type of work are of the order of a few millicuries in strength.

RESULTS

Section D

The complete anthracene spectrum

A fine powder specimen of anthracene was rubbed on to a plate of fused quartz and placed in the specimen holder in the electron beam. The emitted light was photographed using a small quartz spectrograph and P1200 plates. The resultant spectrum is shown in Plate I.

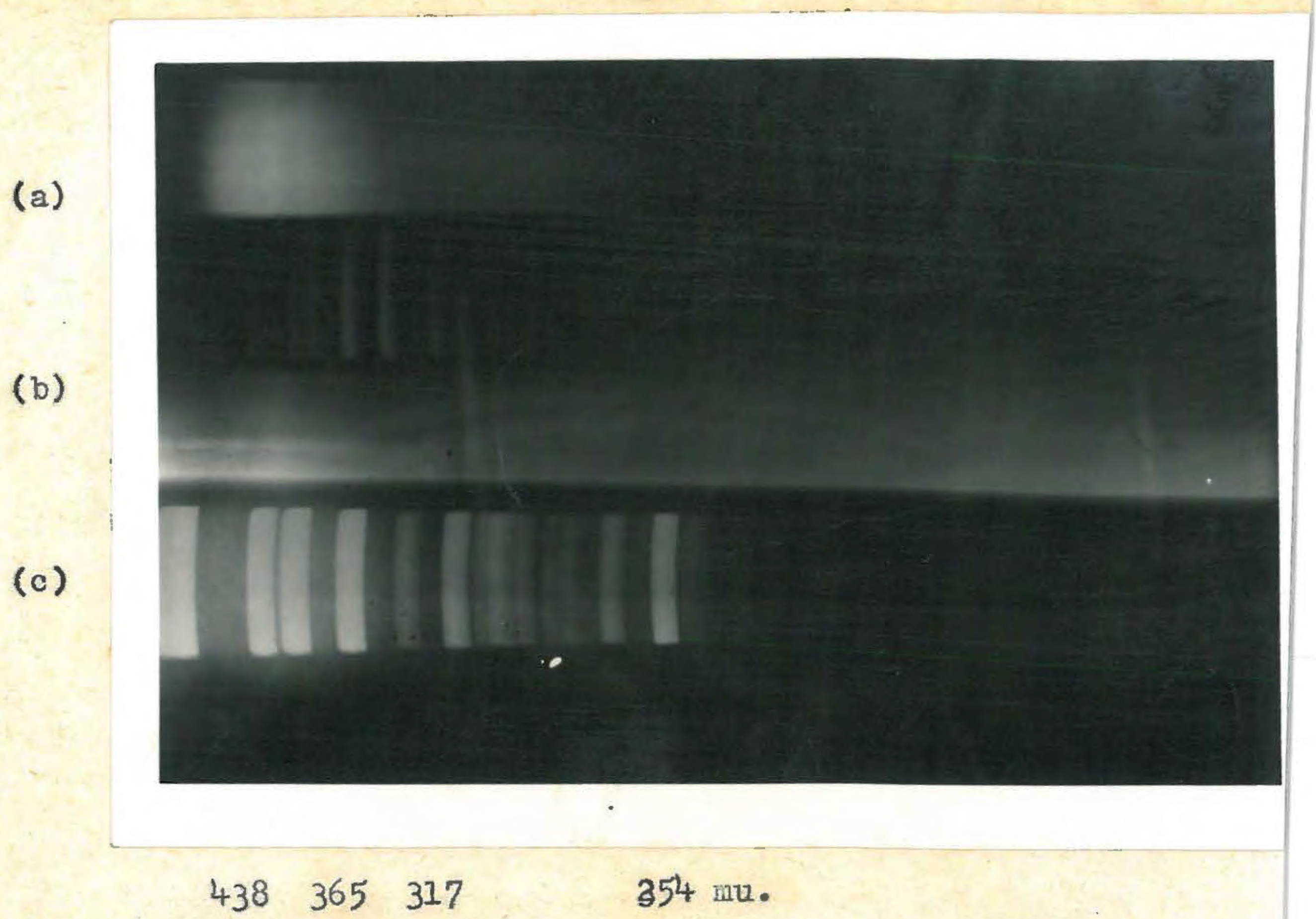


Plate I. (a) Anthracene microcrystals on quartz.

(b) Air emission.

(c) Mercury Calibration spectrum.

(a) shows the spectrum of anthracene microcrystals on quartz,

(b) the spectrum of air in front of the Lenard window with the anthracene and quartz removed, and

(c) mercury calibration spectrum.

At first sight this appeared to confirm completely the predicted spectrum according to the theory proposed by Birks. This theory predicted that anthracene would emit light in the region between its ionisation energy and its normal emission region, when it was excited by light above its ionisation energy or by ionising particles, if the observed specimen was sufficiently thin. The photographed spectrum was visible down to about 250 mμ, at which wavelength the plate became insensitive. A check experiment done on a clean piece of quartz, however, gave a similar spectrum. The quartz gave out a bright blue fluorescence. Plate II demonstrates this. The additional bands seen on the spectrum of anthracene on aluminium are due to the emission from the air immediately in front of the foil and into which the electrons from the beam penetrate.

The spectrum of quartz was investigated in a later section. It was found possible to support the anthracene microcrystals on aluminium foils and this is how spectrum (a) was obtained.

The method of depositing the anthracene on the

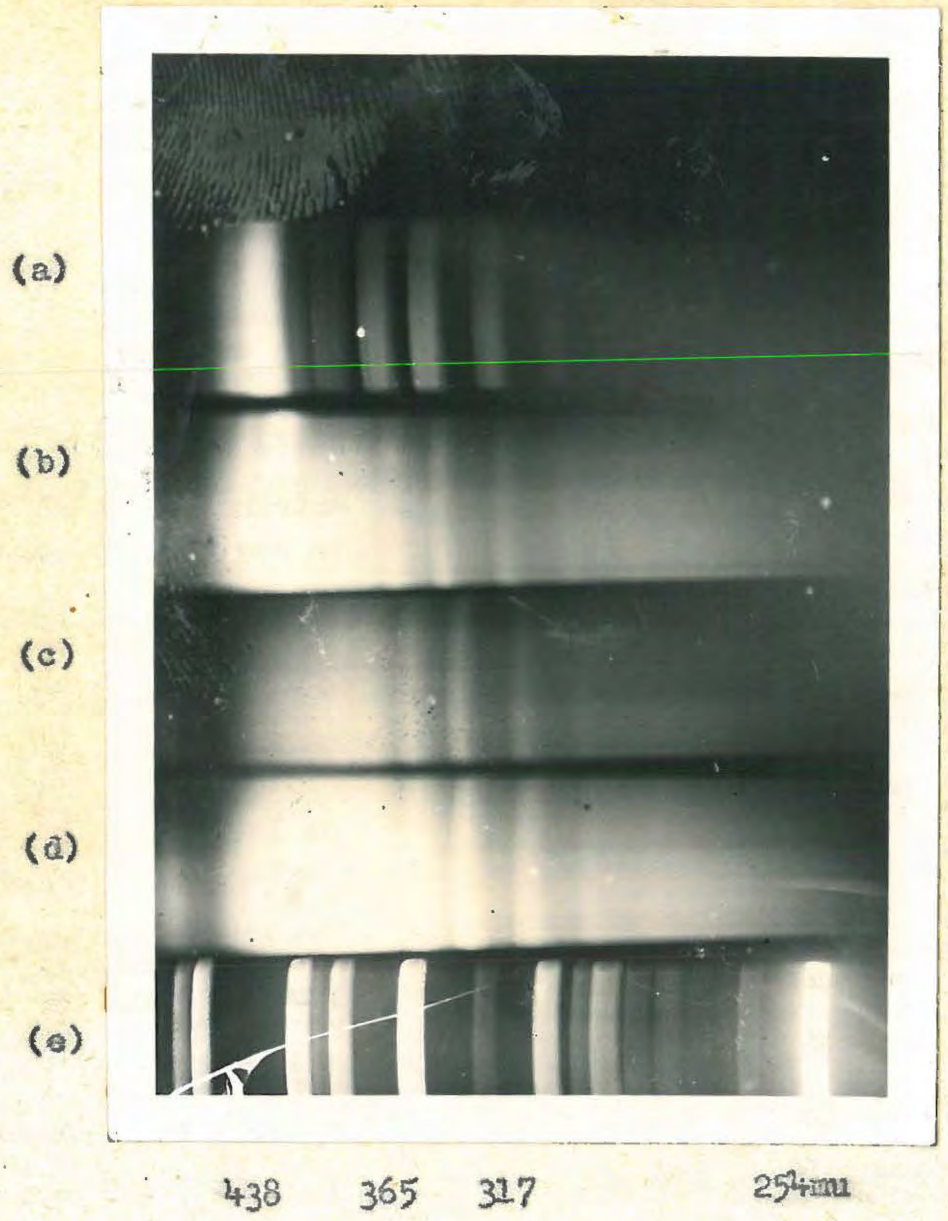


Plate II
(a) Anthracene on Aluminium foil backing.
(b) Anthracene on quartz.
(c) Quartz alone.
(d) Anthracene on quartz.
(e) Mercury calibration spectrum.

(Note emission from air in electron beam).

aluminium was as follows: a beaker containing anthracene was warmed and a cool piece of aluminium foil held above it in the vapour. The sublimed anthracene deposited itself in fine crystals and adhered to the metal surface. The foil used was thin enough to allow the electrons to penetrate through the foil and excite the anthracene which was directly opposite the entrance slit of the spectrograph.

In order to see whether any light was emitted by these fine crystals in the ultraviolet to which the plates were insensitive, they were sensitised by a technique given in Strong's book on Laboratory Practice (Blackie and Sons). This was done by making a dilute solution of liquid paraffin in acetone and dipping the unexposed plates into this. After drying, a thin layer of paraffin lay on the sensitive surface. Ultraviolet light falling on this layer causes it to fluoresce, and the plate under the fluorescing paraffin becomes exposed. Before development the plates were cleansed in a washbath of pure acetone, and then developed in the usual way.

As the light in the far ultraviolet emitted by the anthracene might be reasonably expected to be considerably less intense than that emitted in the normal emission bands, all the plates were severely over-exposed for the visible. After several attempts in which the whole

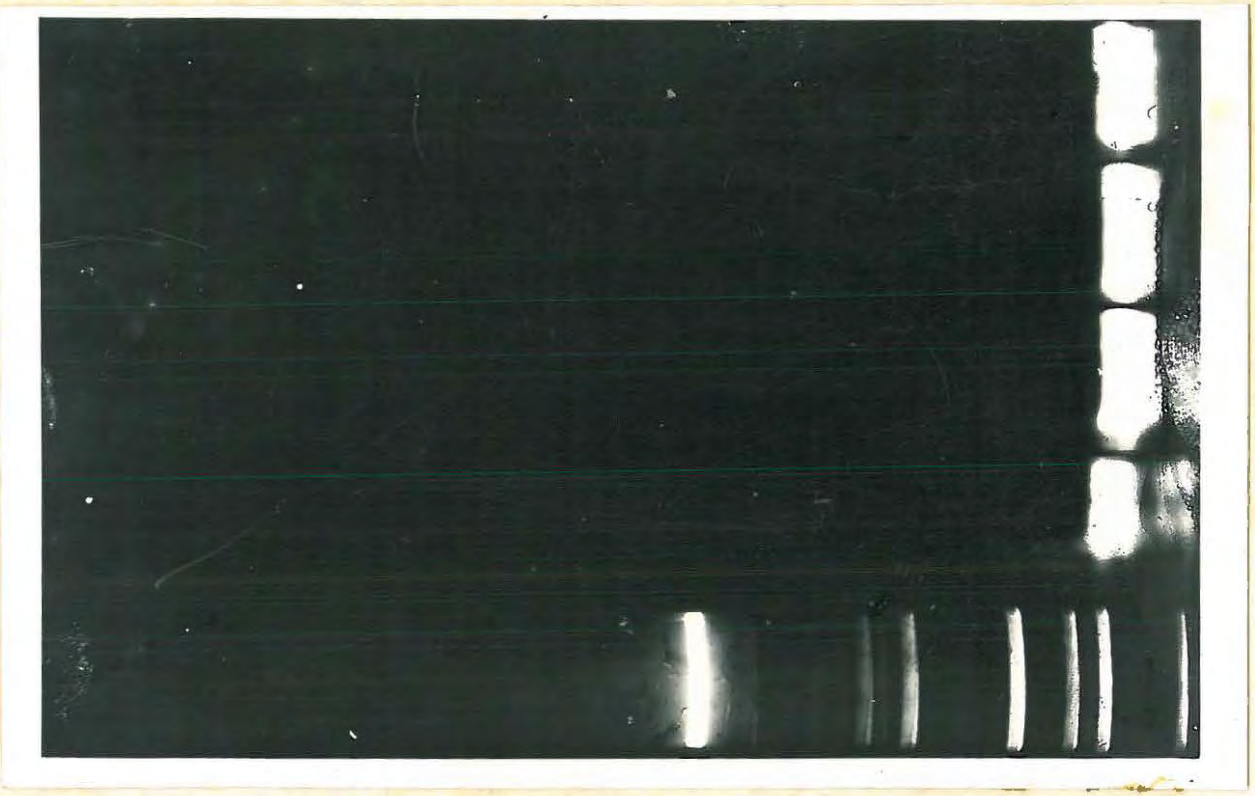


Plate III. Anthracene microcrystal spectrum on ultraviolet sensitised plates under ionising radiatio

Exposures from 30 minutes to 3 minutes.

Mercury calibration spectrum.

plate became fogged, through the paraffin being incompletely removed by the wash bath, Plate III resulted. No trace of light can be found anywhere, but in the normal emission bands round 400 mμ. This plate shows clearly that if any light is emitted in the region considered, i.e. from 185 mμ to the normal emission bands of anthracene at about 400 mμ, the intensity is very much less than that in the visible. The crystals were certainly smaller than the mean free path of the expected photons, and furthermore, the electrons were of such an energy as to just penetrate the anthracene and enter the air beyond.

This result suggests that the energy of excitation is degraded internally by the molecule to the level of the first excited state, and not by the actual emission and re-absorption of photons.

Section D.

(b) Ionisation spectra of other Phosphors

By use of this method of exciting phosphors above the ionisation level, the spectra of other organic phosphors were photographed using the quartz spectrograph. These are shown in Plates IV to VI.

Section E.

Discussion of Spectra

We see that the ionisation spectra are effectively the same as those obtained when the phosphors are excited

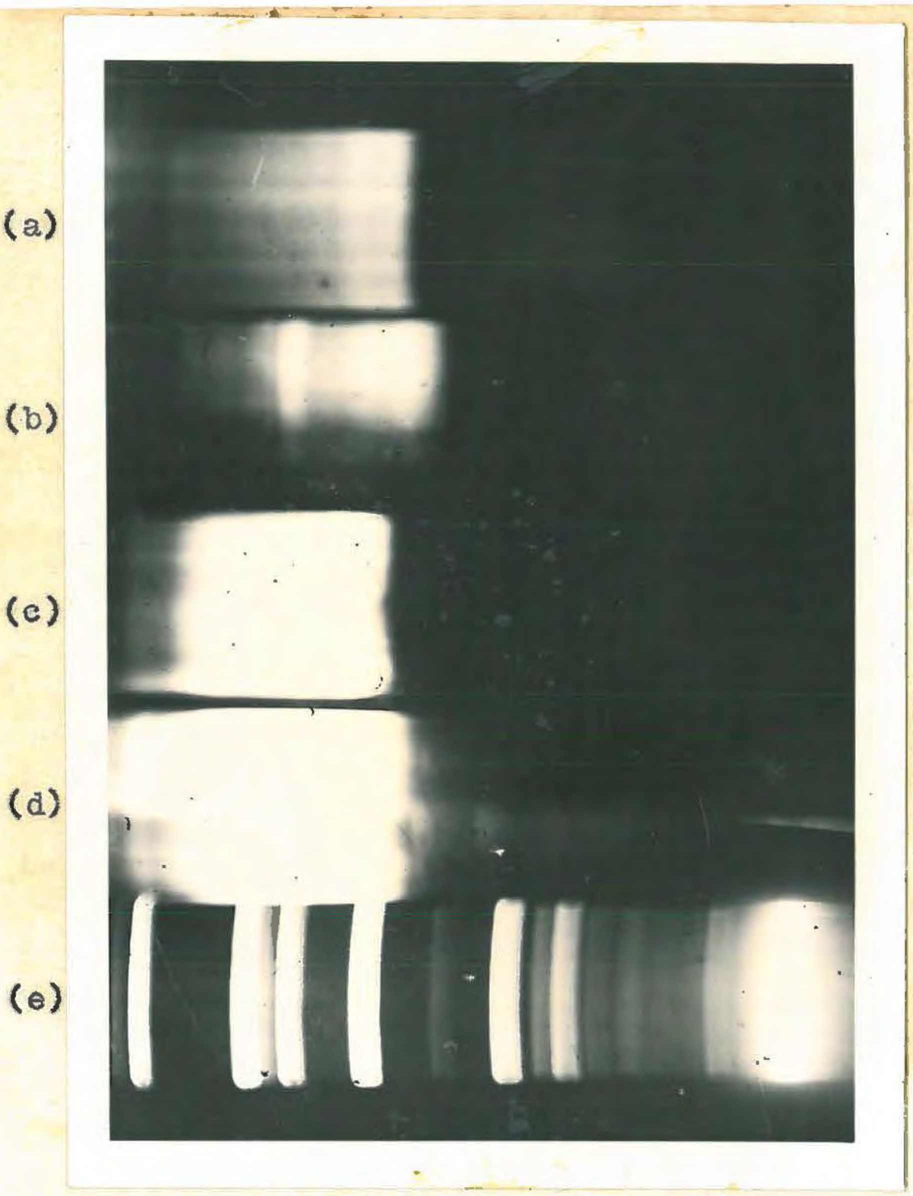


Plate IV. Specimen Changes under bombardment.

(a)	Naphthalene 2mm crystal	
(b)	Naphthalene powder	Turns pale yellow.
(c)	Terphenyl 3mm crystal	
(d)	Terphenyl powder.	Turns yellow.
(e)	Mercury calibration.	

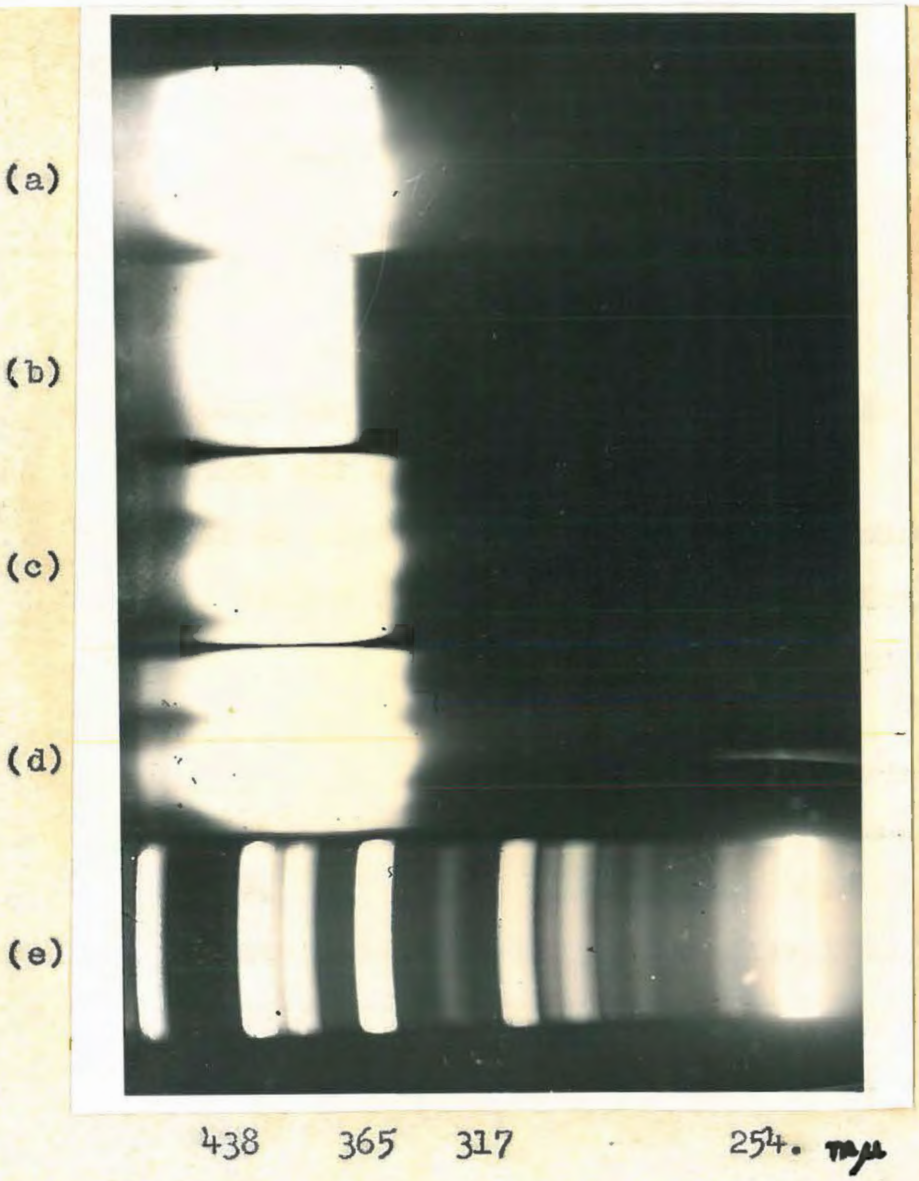


Plate V.

Specimen.	Changes under bombardmen
(a) Diphenyl-acetylene powder	Turns Yellow.
(b) Diphenyl-acetylene crystal 3mm	
(c) Terphenyl crystal 3mm	
(d) Terphenyl powder	Turns very pale yellow-g
(e) Mercury calibration spectrum.	

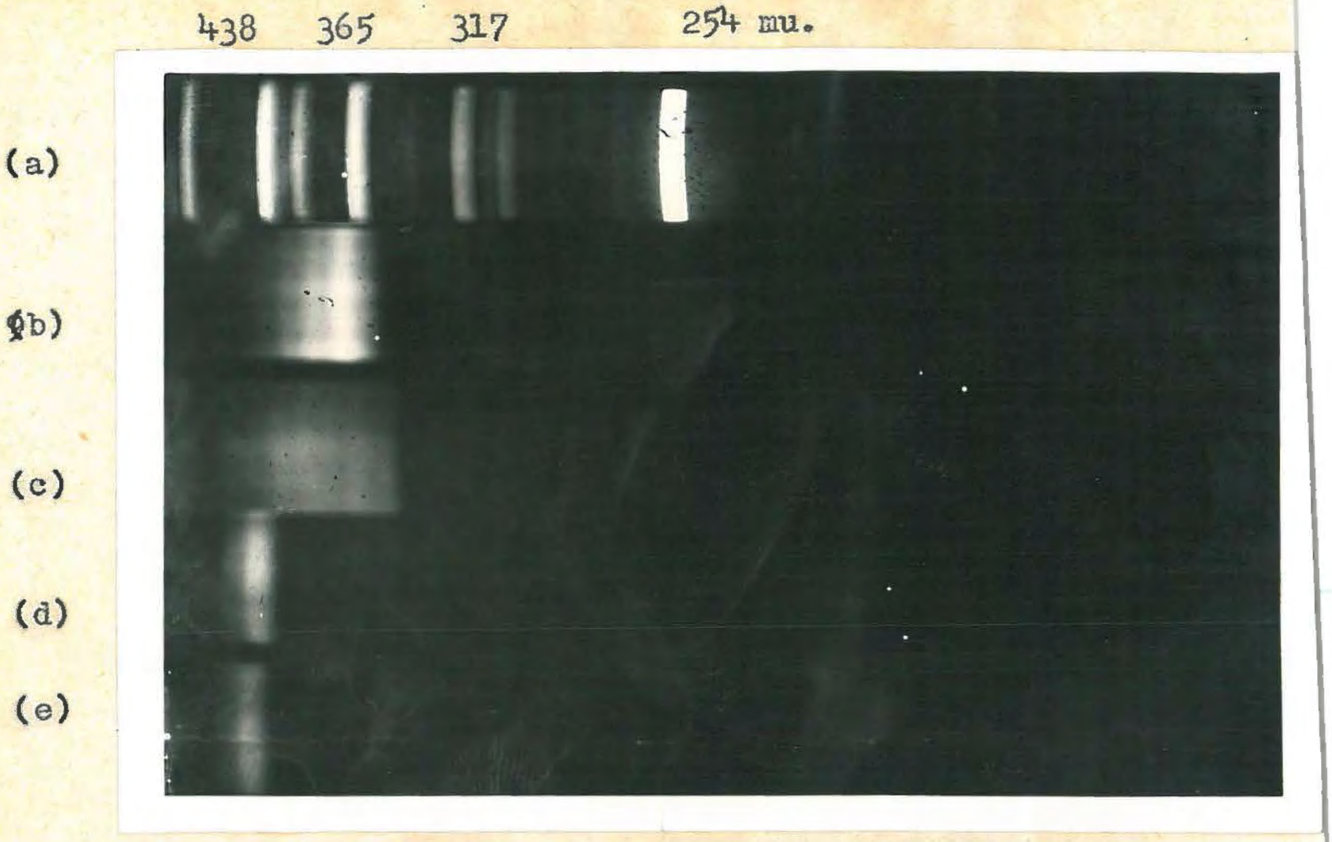


Plate VI. Ultraviolet Sensitised Plate.

(a) Mercury Calibration.

(b) Terphenyl on Aluminium.

(c) Naphthalene on Al.

(d) Anthracene on Al.

(e) Anthracene on Al.

by ultraviolet light. No additional components appear in the spectrum in the region between the visible and the limit set by the transmission of the quartz in the spectrograph, which is at about 185 mμ.

The difference of the spectra between the powder and the large crystal specimens is again illustrated. Owing to the poor dispersion of the quartz spectrograph in the visible and near ultraviolet portions of the spectrum, however, the spectra are crowded together in one corner of the plate so that the effect does not show up so well as it did using the grating spectrograph and phototube as in Part III.

It was again observed that after a period of bombardment in the intense electron beam, the specimens all lost their fluorescence, and after the intensity of emission fell they became discoloured, as shown in the remarks column under Plates IV and VI. This shows that either the crystal is becoming oxidised in the beam or some violent damage is being done in the lattice.

It had been shown in the discussion in Section A of Part I that the excited molecule is usually left very hot immediately after becoming excited into one of the electronic levels. If the time taken for this molecule to return to thermal equilibrium with its neighbours could be calculated from its thermal properties, and the time compared with the lifetime of the electronic state, a reasonable guess could be made whether this damage was due to oxidation or to dissociation of the atoms of the molecule and consequent damage to the regularity of the lattice. I am indebted to Dr. G.T. Wright for suggesting the use of the thermal conductivity as a method of determining the time the molecule would take to reach thermal equilibrium.

PART V.

Theoretical Investigation for the Time for an Excited Molecule to reach Thermal Equilibrium with its Neighbours.

Initially we can consider that all the heat energy is concentrated in the one molecule which is excited. The problem is then to see how long this molecule takes to dissipate enough of this heat to allow its temperature to become comparable with its neighbours'. A broad interpretation is here used for the word temperature: it is considered that a single molecule can have a unique temperature. The temperature of the molecule is taken to be the mean vibrational energy of the molecule divided by the Boltzmann constant k. i.e. E/k = T.

The temperature at any point a distance 'r' from the origin of the heat source at any time t may be got from the thermal conductivity κ and specific heat S in the following way.

The quantity of heat crossing the surface of a sphere of radius r in a time dt is -dQ.

Then -dQ/dt = $+ 4\pi r^2 \kappa \frac{dT}{dr}$ — (1)

The heat used to raise the temperature of the spherical shell at r is:

$$\frac{\partial}{\partial r}\left(\frac{\partial Q}{\partial t}\right) = -4\pi r^2 \rho . S . \frac{dT}{dt} \qquad \text{—— (2)}$$

ρ = density.

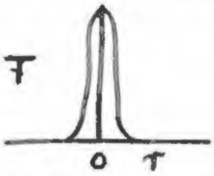
and we get the equation that there is no loss of heat:

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right) = \lambda r^2 \left(\frac{\partial T}{\partial t}\right), \text{ where } \lambda = \frac{\rho S}{\kappa} \qquad (3)$$

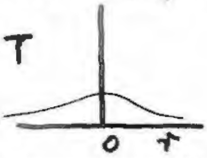
This can be easily shown to have the solution:

$$T = \frac{A}{t^{3/2}} e^{-\frac{hr^2}{t}} \text{, where } A \text{ is a constant.} \qquad (4)$$

which behaves like: when t is small. - a δ-function.



and like this, when t is large:



If we average the temperature over a volume dV then we can normalise the equation and get:

$$T = T_0 \left(\frac{h}{\pi t}\right)^{3/2} e^{-\frac{hr^2}{t}} . \Delta V \qquad \text{——} \quad (5)$$

ΔV is taken to be the size of the molecule and is then $4/3\pi r_0^3$, where r_0 is the radius of the molecule. T_0 is the mean temperature over the molecule at the time t = 0. At large t, the heat is spread out over many molecules and $e^{-\frac{hr^2}{t}}$ will be practically constant and equal to 1.0 over small variations of r near the origin. The average temperature of the molecule will then be:

$$T = T_0 \left(\frac{h}{\pi t}\right)^{3/2} \left[\frac{4}{3}\pi r_0^3\right] \qquad \text{——} \quad (6)$$

For anthracene the ionisation level lies at about

8 eV and the first excited electronic level at about 3 eV, so that even if the molecule took up the whole of this energy difference as vibrational energy, the highest vibrational level of the electronically excited first level would be less than 5 eV above the vibrational ground state. At room temperatures the average energy of each mode of vibration of the molecule is of the order of 0.02 eV. The time for the molecule to reach thermal equilibrium with its neighbours must be of the order of 't' in the equation:

$$\left(\frac{T}{T_0}\right) = \left(\frac{hr^2}{\pi t}\right)^{3/2} \cdot \frac{4\pi}{3} \qquad (7)$$

where $\frac{kT}{kT_0} = \frac{0.02\,eV}{5.0\,eV} \sim \frac{1}{250} = \frac{T}{T_0}$

From tables we see that $\rho = 1.25$, $r_0 = 7 \times 10^{-8}$ cms, 8 = 0.3 cals/gram/°C. at 50°C and $k = 10^{-3}$ cals/sec/°C/cm/cm^2.

By substituting these figures in equation (7) a time of 5.9×10^{-11} seconds is given for the time to reach thermal equilibrium in anthracene.

This estimate of the time should only be considered as correct to an order of magnitude since several criticisms can be levelled at the naive approach to this estimate. Firstly, it is highly unlikely that one can consider the microscopic properties of a material can be extrapolated to regions of the order of the molecule in size. Secondly, the thermal conductivity will certainly rise in magnitude when the amplitude of vibration of the molecule is large, as it will be in the early stages of the cooling process. This will have the effect of causing the temperature of the excited molecule to fall very much faster at first, and then to settle down to the rate as here predicted. The overall effect of this will be to shorten the time necessary to reach thermal equilibrium. Thirdly, the axes of the crystal have been ignored and an average taken over all directions for the thermal constants. Fourthly, it is highly unlikely that the molecule would rise to a vibrational energy as high as 5 eV above the first excited state, without rising into one of the higher electronic levels; so this again sets the estimate as an upper limit to the time necessary to reach thermal equilibrium in the lattice.

(B) Discussion

We have arrived at a value of less than 5.9×10^{-11} secs. for the time that the anthracene molecule takes to reach thermal equilibrium in thelattice. Also we see from Part III that the half life of the first electronic state of the molecule is 3.5×10^{-9} seconds. We are thus justified in saying that the excited molecule does reach thermal equilibrium with its neighbours before it has an appreciable chance of emitting its fluorescent photon.

It was observed that all the phosphors exposed to bombardment by electrons were rendered less efficient as the result of either oxidation or other damage to the molecule or crystal lattice. In anthracene it was noticed that the damage took place even when the bombardment took place in vacuum, indicating that the damage was probably not due to oxidation. This is not conclusive as it is possible for some oxygen to be occluded on the surface, or as small bubbles in the crystal. Furthermore, the molecule remains hot for such a short time (as compared to the collision rate of oxygen molecules on the surface of a phosphor exposed to the radiation in air at normal pressures. Time between collisions of an oxygen molecule with an anthracene molecule at N.T.P. 4×10^{-10} seconds) that we can rule out the possibility of the anthracene being oxidised when it is hot.

The damage seems likely to be caused by:

(a) the lattice being severely distorted near the path of the ionising particle, due to:

(b) the possible production of complex ions at the high energy of excitation,

(c) the dissociation of the molecules into groups of atoms causing:

(d) vacancies and interstitial atoms in the lattice.

PART VI.

Experiments with Electron Beam

Section A

The first photographs of anthracene on quartz excited by the external beam of electrons showed that the fused quartz, upon which the anthracene crystals were mounted, emitted an intense blue light. Furthermore, it was noticed that, when looking at the plate, more light seemed to be emitted at an angle of 90° towards the direction of the incident electron beam. This type of anisotropy in the distribution of light would be explicable if the source of the light was bremstrahling from the decelerated electrons. Dieners (1953) has shown that when a low-energy electron of only a few kV enters a material it knocks on a very great number of other electrons. These electrons will move predominantly in the forward direction. Consequently, on losing speed they will have to be decelerated along the axis of the motion of the incident electron. This will cause the light from the decelerated electrons to be emitted with a maximum of intensity in a plane at 90° to the incident direction and polarised with the electric vector along this direction. The intensity of the light emitted in this type of process is proportional to the inverse of the radius of curvature of the electron's path and proportional to the 4th power of the energy.

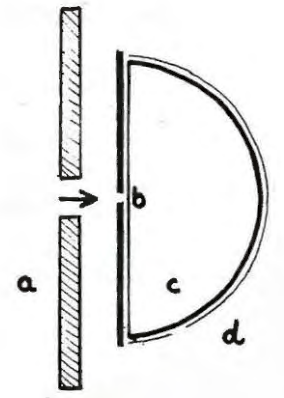


Figure 36. D-shaped Glass block.

(a) Heavy lead screen.

(b) Narrow slit in aluminium shield.

(c) Glass block.

(d) Aluminium guide to hold film.

These relations have been verified qualitatively by observations on the light emission from the electrons in the Berkeley synchrotron (Annual Review of Nuclear Physics, Vol. 1 1953).

To investigate this further a D-shaped glass block was placed with the centre of the D in the electron beam and so shielded that only a narrow flat beam could enter the glass. The maximum of the light, in this case, seemed to lie towards the green, but again a slight anisotropy appeared in the distribution of the light as seen by the eye. A strip of photographic paper was stuck round the glass block as shown in figure 36. This showed a greater darkening of the paper at 90° to the electron beam. However, as this part of the paper was nearest the glass bulb of the x-ray tube, it was thought that the darkening might be due to X-rays. The glass block was then carefully shielded with a lead screen and another exposure taken. This time very little change could be seen in the density of the paper over the range 0° to 90°. It was concluded that if an anisotropy did exist in the angular distribution of the light, the amount of light involved in this anisotropy was smaller than that which arose from the fluorescence of the glass in the range covered by the photographic paper.

Using a sheet of polaroid, no preferred direction of polarisation of the emitted light at 90° could be found. As several people agreed that an anisotropy did appear in the angular distribution of the emitted light the answer may be physiological owing to its low intensity.

Section B

Investigation of the light emission from thin metal foils under electron bombardment

Norman et al.(1953) and Richards and Cole (1951) had bombarded thin films of metal with Po_{210} α-particles and had observed photon emission in the near ultraviolet region of the spectrum. Richards had observed the light with a photomultiplier and Norman had been able to photograph the spectra. The spectra obtained by Norman et al.were the same for all the metals used by him. Also his published spectra agreed with that obtained here for fused quartz. As his specimens had all been mounted on quartz, it seemed possible that he had erroneously attributed the quartz spectrum to the metals. Richards had also mounted his metal foils on quartz and noted that the scintillations from the metal foils appeared to stop when the range of the bombarding particles was insufficient to penetrate the quartz. As these results could be easily checked with the beam of electrons with the existing apparatus, several metals were bombarded in turn, and their emission spectra

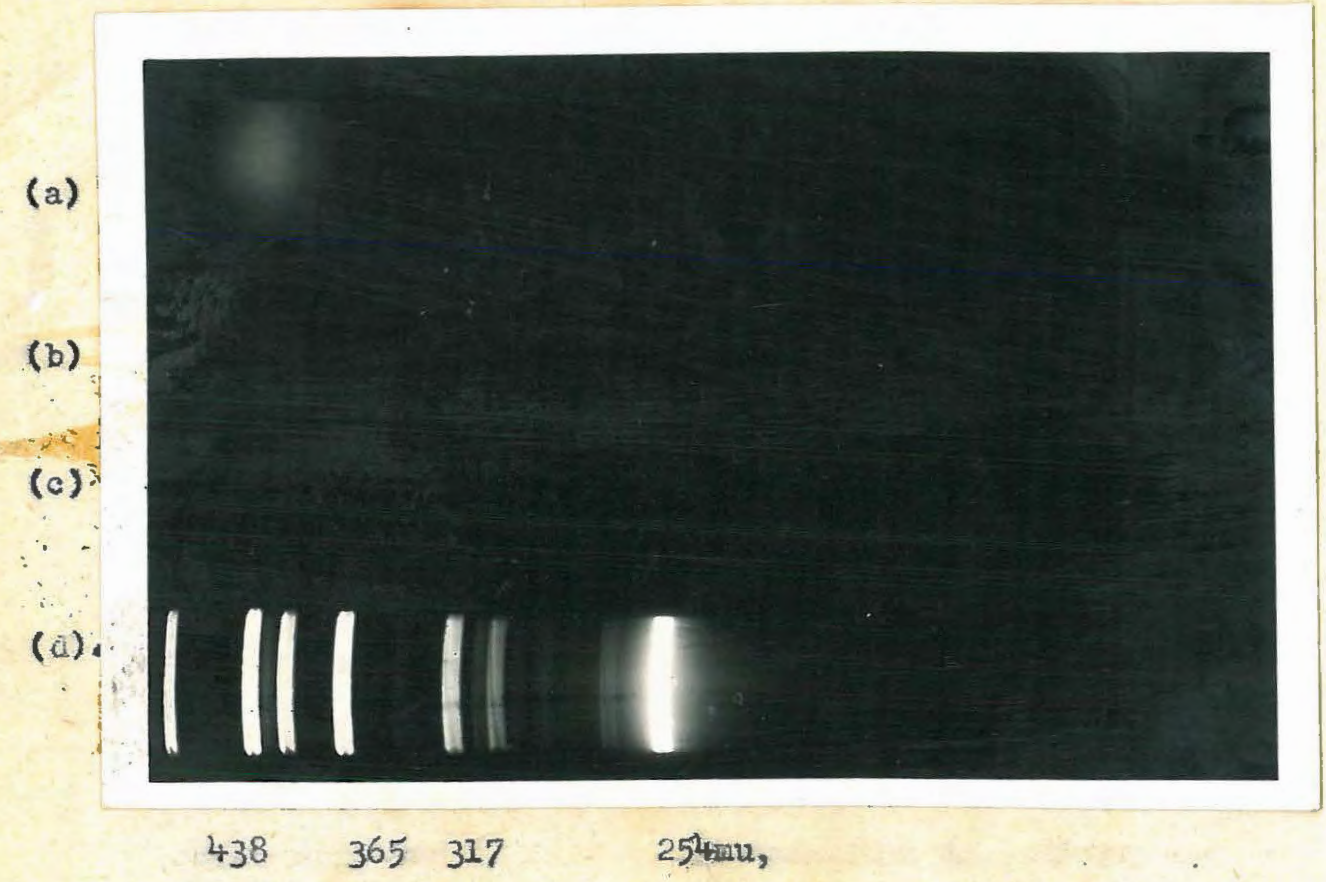


Plate VII. (a) Quarts 10 minutes exposure.

(b) Aluminium foil 1 hour exposure.

(c) Cellophane paper ½ hour exposure.

(d) Mercury calibration spectrum.

(a)

(b)

(c)

(d)

(e)

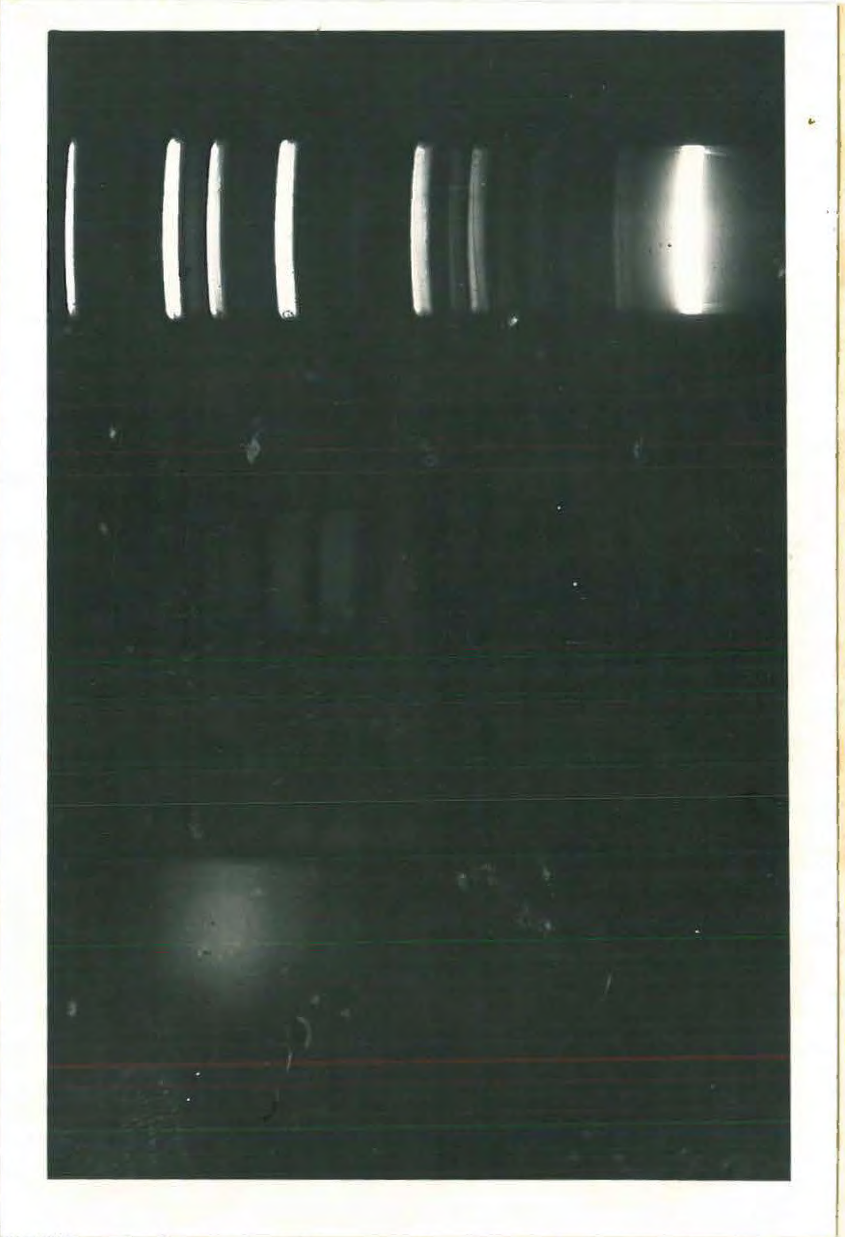


Plate VIII. (a) Mercury calibration spectrum.

(b) Gold foil. I hour exposure.

(c) Cellophane paper. ½ hour exposure.

(d) Tin foil. 1 hour exposure.

(e) Quartz plate. 10 minute exposure.

photographed.

Plate VII shows the spectra obtained from quartz, Al foil, cellophane paper and the calibration spectrum of Hg from a discharge tube.

Plate VIII is that of quartz, tin foil, thick cellophane, gold foil and the calibration spectrum.

In the above the spectra for the metals were obtained using an exposure of one hour in each case, and that for the quartz was under 10 minutes for the same conditions of beam strength.

No detectable light could be found from the metal foils under the bombardment by the electrons. In the case of cellophane the light emitted by the air between the specimen and the Lenard window is recorded with characteristic emission bands near 350 mμ.

Conclusion

One is forced to conclude that the light detected by Norman et al and Richards came from the quartz support, and that metal foils do not emit an appreciable amount of light when bombarded by ionising radiation.

PART VII

Measurements of the Decay Times of Organic Phosphors under Ionising Radiation

It was realised at this stage that a considerable amount of useful information could be obtained about the energy transfer process and the part played by the molecular structure in determining fluorescence characteristics, if a systematic examination of a large number of different phosphors were made of the spectra and decay time under u.v. and ionising particle excitation. The magnitude of the task was thought to be beyond the capacity of one worker, so the part assigned to the writer was the investigation of a method of measuring decay times under ionising radiation, which would be suitable for a rapid survey of a large number of phosphors.

Section A

Early Work

Measurements on the decay times of the fluorescence of phosphors under excitation by ionising radiation are based on a scintillation counting technique. The excited phosphor is observed by a photomultiplier which converts the light flash into a current pulse. The difficulty of measuring decay times of organic phosphors lies in the fact that the pulses rise in the order of 10^{-9} secs. An amplifier of approximately 1000 Mc/sec band-width would be required to amplify faithfully a pulse with a rise-time of this order. Amplifiers with such characteristics are not readily available owing to the obvious difficulties of stray capacities, inductive leads and electron transit times in the valves when working at these prohibitive frequencies. In order to overcome these difficulties several methods have been used to avoid the use of wide-band amplifiers. The earliest work was done by directly coupling the collector anode of the photomultiplier to the deflector plates of a fast oscilloscope, and photographing the resultant trace when the phototube was viewing an excited phosphor. (Collins, 1948). By taking a large number of photographs and averaging the rate at which the charge collected on the deflector plate, a measure was obtained of the decay time of the phosphor. The deflections obtained were less than a millimetre in height so that the accuracy attainable was not high. R.F. Post (1952) improved on this method by increasing the gain of the phototube. By applying a pulse of up to 5 Kv to a 931A photomultiplier (which normally works at 1.25 Kv) for a few microseconds at a low repetition rate he was able to get a gain of 10^9 directly from the photomultiplier. This was sufficient to give pulses of up to 70 volts for stilbene, and noise pulses

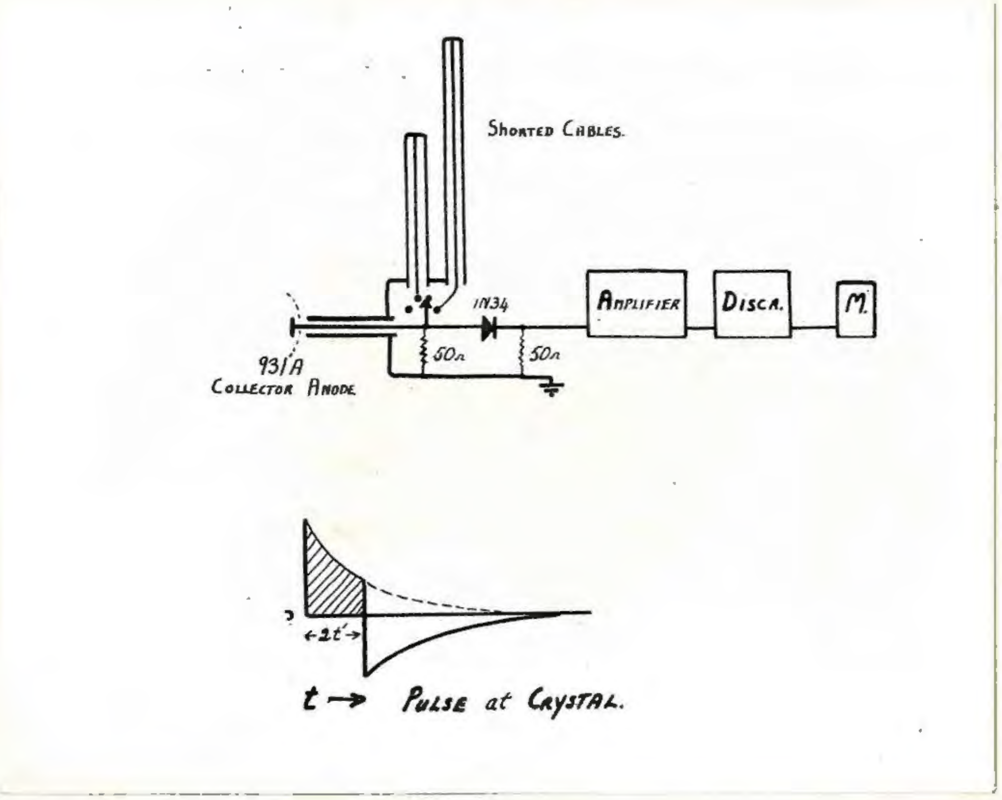


Figure 37. Apparatus for measurement of Scintillation Decay-times.

of up to 70 volts for stilbene, and noise pulses of 15 volts. The 931A is an electrostatically focussed photomultiplier so that the spread in transit time is small. Furthermore, the extremely high fields in the tube reduced the spread in the transit time to the order of 5×10^{-10} seconds. By photographing a large number of pulses he was able to show that the decay in intensity was exponential with respect to time and that the rise time was determined by the rise time of the photomultiplier pulse and associated circuits. Though elegant this method of measuring decay times is not suitable for a rapid survey of a lot of different phosphors. Liebson has devised a more simple method. (Liebson, 1952).

Post had shown that the pulse from the collector anode of the photomultiplier may be expressed by $\frac{dq}{dt} = i_0 e^{-\frac{t}{\tau}}$ where q is the charge on the collector, t the time, and τ the decay time of the phosphor. The rise time is effectively vertical at t = 0. Liebson fed this pulse down a 50 ohm coaxial cable to a crystal diode. At the diode another cable, of variable length and shorted at its end was connected. The integrated pulse from the diode was fed to an amplifier, and the pulse height measured with a discriminator and scaler. (See figure 37). The pulse, on arrival at the crystal diode, would feed through to charge up the capacity of the leads to the amplifier until that portion of the pulse which had gone down the shorted cable had returned. The reflection at the shorted end would invert the pulse and it would now interfere destructively with the pulse at the diode and no more current would contribute to the charge entering the amplifier. The shorted cable would become effective in reducing the size of the phosphor's pulse when its length was such that the time for the reflected pulse to return to the diode was of the order of the decay time of the phosphor.

We will consider this process further. The incoming pulse from the photomultiplier viewing the phosphor will be of the form, $e^{-\frac{t}{\tau}}$, and zero for negative t. The out-of-phase reflection will arrive back to cut this pulse, when t = 2t', where t' is the electrical delay introduced by the cable of the shorted line. The factor of two appears owing to the fact that the pulse must go to the end of the cable and come back again. The reflected pulse will interfere destructively with the original pulse as shown in Figure 37.

The charge which will collect on the grid of the first valve in the amplifier will be proportional to the integral of the current which can flow through the crystal diode. The crystal diode is a non-linear rectifier and the current flowing across it is given by:

$$i = \kappa V^{n} \qquad \text{(i)}$$

where n is assumed to be a constant. V is the potential applied across the diode, and k is a constant. Then the total charge collected is:

$$\int_0^\infty i\,dt. \tag{ii}$$

where i is $\sim e^{-\frac{tN}{\tau}}$. Then the pulse height, as measured by the amplifier with a long integrating time, is given by integrating this from t = 0 up to the time set by the clipping time of the shorted line.

$$P_{t_0} = A\int_0^{t_0} e^{-\frac{nt}{\tau}}.\,dt. \tag{iii}$$

This gives:

$$P_{t_0} = P_0\left\{1 - e^{-\frac{nt_0}{\tau}}\right\} \tag{iv}$$

We see then that by plotting the pulse height against the length of the shorted line we obtain a straight line parallel to the x-axis for long lines. When the pulse begins to interfere with itself, the pulse height falls. When the pulse height falls to (I - I/e) then the decay time τ becomes equal to 'n' times 2ce, the length of the shorted line.

This method appears to be ideally suited to the rapid measurement of the decay times of a large number of phosphors. It would only be necessary to plot the pulse height of the pulses from the phosphor against a series of different lengths of cable, and then read off the value of $\frac{\tau}{n}$, and knowing n, to find the decay time τ.

Section B

Experimental Arrangement

A 931A photomultiplier was selected as the most suitable photomultiplier to use for the measurements. It has electrostatically focussed dynodes for focussing the electrons in the multiplication processes, which enables the electrons to pass through the tube with a very small spread in transit time. This phototube was mounted in a brass container which, in turn, was mounted on a copper chassis with the electrodes connected so as to have the collector anode at earth potential and the photocathode at the high negative potential. The collector anode was connected to a 60 ohm T7324 cable which was matched at this point to a 60 ohm resistance to earth. The cable led to a six position switch and a Type IN34 crystal diode. The anode of the diode was connected to another matched 60 ohm cable which conveyed the pulse to the input of the amplifier. Cables of different lengths were led from each of the six positions of the switch. These cables had their outer sheaths earthed and they were securely shorted at the end farthest from the switch. A series of different lengths of shorted line could thus be connected in turn across the output of the photomultiplier. The output of the amplifier went via a discriminator to a counting rate meter.

As the pulse from the photomultiplier is fed across a 60 ohm load and is further attenuated by passing through the crystal diode and into another 60 ohm load, the major problem in this experiment was obtaining an amplifier which could give a gain of about 10^6 without any appreciable noise. It was found impossible to use two standard amplifiers in series without getting an excessive amount of noise even at such modest gains of 10^5. The amplifier which had been built in the laboratory on the design of the Model 100 M.I.T. is credited with being able to give a gain of about 10^6 when used in conjunction with its pre-amplifier. A pre-amplifier for this was built and the original amplifier modified to cut down hum and shorten the pulse length by adding a differentiating circuit between the two rings-of-three. With ten megohms as the input impedance to the pre-amplifier and at a maximum gain setting, the noise level was less than one volt in height. This was considered satisfactory.

The pulse from the crystal diode circuit was fed into this stage by a 10 pf condenser. To speed up the time taken for measurements, the output of the amplifier was fed to a standard scaler with discriminator, and the pulse taken off at the first stage beyond the discriminator and fed to the counting rate meter of a radiation monitor.

The phosphor to be examined was tied to the glass face of the photomultiplier with aluminium foil and taped into position. For gamma ray measurements the phosphor was bombarded with Co.60 gamma rays from a strong source close to the photomultiplier assembly. For the measurements, using alpha-particles, a small window was cut in the aluminium foil backing and a Po210 source of alphas used to bombard the crystal beyond.

In order to obtain pulses of sufficient height it was necessary to over-run the photomultiplier at between 1500 and 1200 volts. It was found that immediately after applying this high potential to the tube, the noise counts went up to a very high counting rate, but after a few minutes at this potential the noise pulses returned to only a very little above the original value.

Section C

Method of Taking Measurements

In taking a measurement on a phosphor, the shorting switch was set at the longest available shorted line, which was about six metres in length and corresponded to a clipping time of 6.21×10^{-8} seconds. This is effectively an infinite line for pulses of the length used, which were of the order of less than about 2×10^{-8}

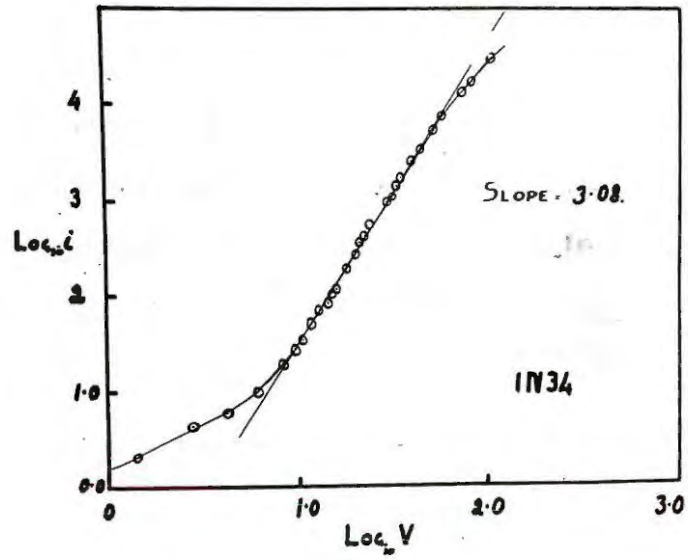


Figure 38. Log-log plot of current in microamperes against potential in 1/100ths of volts applied across crystal diode Type IN34.

seconds.

A plot was then taken of the counting rate against the discriminator bias level P for the pulses from the amplifier, with the phosphor under bombardment by the gamma rays or alpha particles. This done the counting rate was next plotted for different bias settings of the discriminator for varying lengths of shorted cable and for a particular bias setting, P_o, on the counting - rate vs cable length curve. The length of cable which gave this counting rate was read off. The mean of this length for each of the bias curves on the second graph was taken for each specimen, and the result converted into time by using the maker's value of the velocity coefficient. This time is equal to $\frac{\tau}{n}$, where n is the crystal constant, and τ the required decay time of the phosphor (equation iv).

At first it was thought that the value of n would be easily obtained by doing a simple experiment with a potentiometer and measuring the current through the diode for different potentials applied across the diode. The result obtained is shown in Figure 38. Above about 0.1 volts the diode shows a linear relation of the log-log plot with a slope of very nearly 3. This indicates a cube law variation and $n = 3$. However, using this value of n in the measurements on anthracene gave a result widely different to the accepted value for the decay time. Liebson had found a value of 0.9 for his value of n, so it was suspected that the high frequency response of the diode was very different to its d.c. characteristics.

Liebson had been able to measure the value of nø by using pulses from a pulse generator which gave pulses of the same size and length as those obtainable from the photomultiplier. We were not in possession of even a simple pulse generator so some other method had to be devised whereby the actual pulses from the photomultiplier could be utilised to measure the value of 'n'.

A determination of n should be possible from the following considerations. Without the crystal diode in the circuit and with the pulses applied directly to the input of the amplifier, let the pulse height be a function f(V) of the voltage across the phototube. f(V) is just the gain of the photomultiplier for different values of the potential. Now, with the diode in place, the non-linearity of its response should then yield another function of V such that this would be related to the first function f(V) in the following way. The new function $F(V) = A.\ (f(V))^n$. By plotting the pulse height against voltage across the photomultiplier for the two cases, the logarithm of their pulse heights with the crystal diode in the circuit could be plotted against the logarithm of the pulse height with the diode removed. The slope of this curve would then

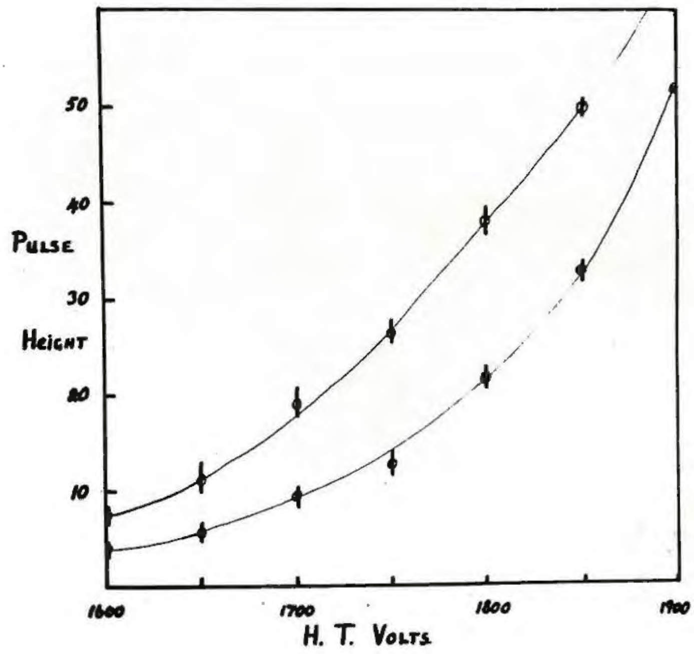


Figure 39 (a) Plot of Pulse Height against H.T.Volts on photomultiplier, using Stilbene excited by gamma-rays. Upper curve with crystal diode in circuit. Lower curve no crystal diode.

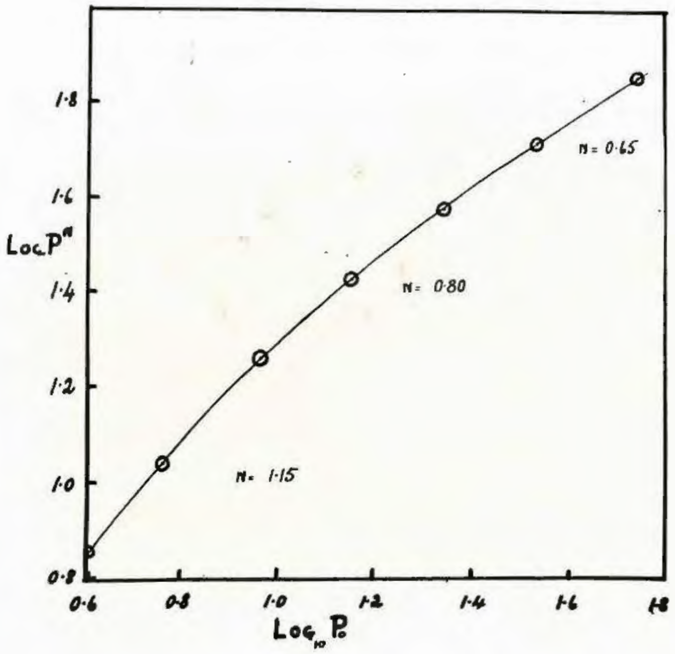


__Figure 39.__ Plot of Log of Pulse height with crystal diode in circuit against Log of Pulse height with no diode, for different values of H.T. Potential.

give the value of 'n'. This is done in Figure 39.

This clearly shows that 'n' is not a constant for the crystal diode but decreases for large pulse heights at the diode input to a value well below that obtained for anthracene pulses by Liebson. In order to use this method of measuring decay times it is important then to measure the value of n for each of the phosphors because the height of the pulse at the input of the crystal is dependent on both the efficiency of the phosphor and the decay time as well as the gain setting of the photomultiplier and the optical coupling to the photocathode of the phosphor.

Section D

Preliminary Experiments

In getting the apparatus to work a very interesting effect was observed. The amplifier was at this time connected so that it counted only positive pulses at the input to the pre-amplifier. With the gain at maximum, and a high potential applied to the phototube, counts were recorded on the counting-rate meter when anthracene was used as the phosphor and bombarded with gamma rays. The usual discriminator integral-bias-curve was plotted and the counting rate vs cable length plotted to find the effective decay time of the pulses recorded. The value obtained was 4×10^{-9} seconds. This clearly could not have been the decay time of the anthracene pulses which are nearly ten times longer than

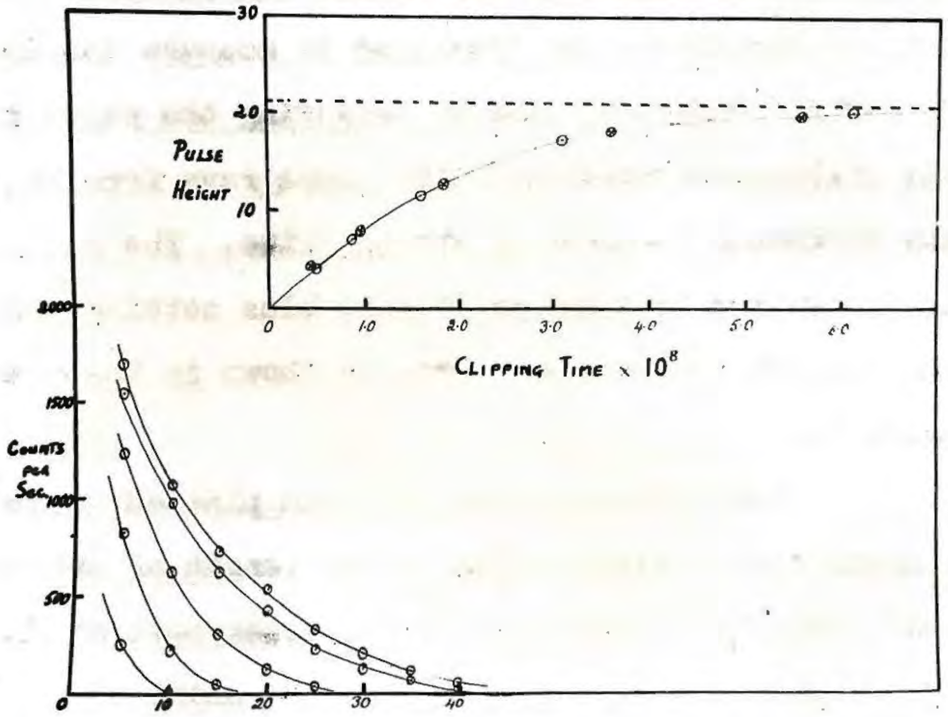


Figure 40. Anthracene under gamma-ray bombardment discriminator curves for different lenghts of shorted li
Upper curve shows pulse height plotted against clipping
of cables. Continuous curve is theoretical curve.
Circles with dots are experimental points and circles with crosses are theoretical points.

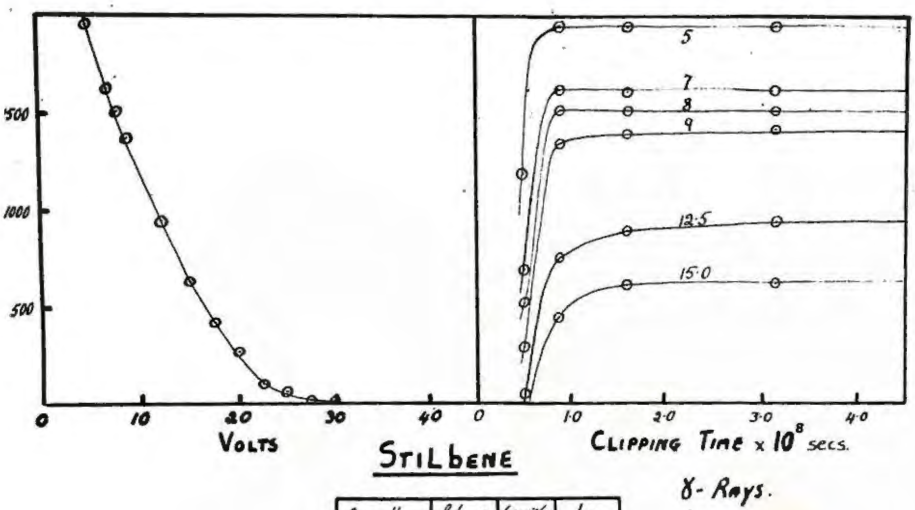
this. A reasonable explanation seems to be as follows: the crystal could only see pulses which were positive, so that, in effect, if a negative pulse comes along it sees it upside down - the rising edge now being a falling edge and the falling edge being the rising edge. The circuit then behaves in the normal way and measures the decay time of the falling edge. The value obtained should then be the rise time of the original pulse at the photomultiplier anode. This value is in approximate agreement with the value obtained by Liebson at these potentials on a type 931A., which he used to correct his measured decay times.

Section D (b)

Check of Theory of Method

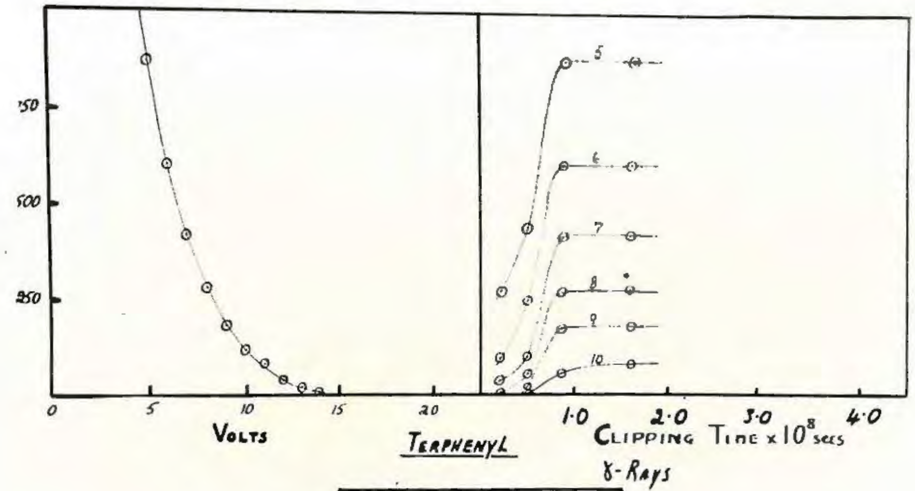
A preliminary experiment was performed to verify that the simple theory developed to measure the decay time was valid. This was done by measuring the pulse height from anthracene bombarded with gamma rays from Co_{60} for five different lengths of shorted line. The pulse height was determined by finding at what bias setting the counting rate was 500 per second. This is shown in the lower part of Figure 40.

This pulse height was then plotted against the clipping time corresponding to the length of shorted cable used. This is illustrated in the upper part of Figure 40. From these points the length of cable,



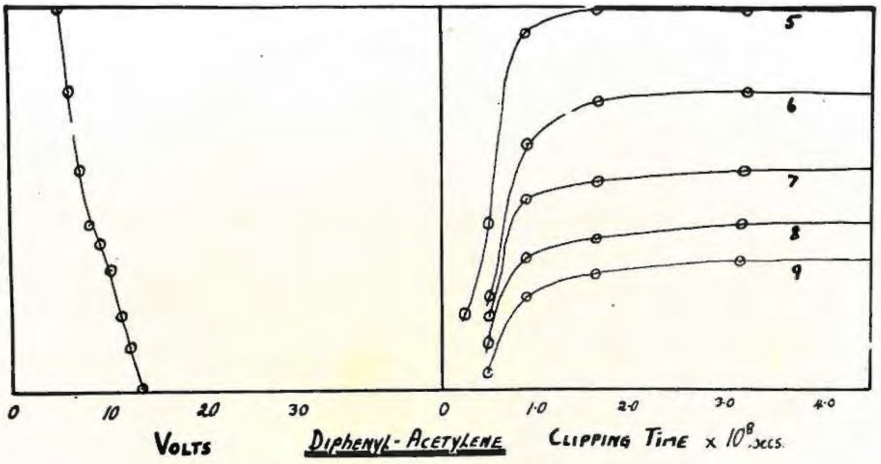
Pulse Height	P_0/0·632	Counts/sec	L_c
5	7·92	1550	0·55
7	11·1	1100	0·56
8	12·6	930	0·55
9	14·2	740	0·60
12·5	19·8	270	0·55
15·0	23·6	–	0·55

Figure 41. Stilbene counting rate against discriminator setting and against clipping-time.



Pulse Height	[illegible]	[illegible]	[illegible]
5	7·92	285	0.35
6	9·49	150	0.36
7	[illegible]	72	0.40
8	12·6	26	0.36
9	14·2	10	0.40

Figure 42. Plot of Counting rate against discriminator setting and clipping time for Terphenyl crystal.



Pulse Hight	E/E·632	Counts/sec	[illegible]
5	7·92	466	0·50
6	9·49	320	0·53
7	11·1	190	0·50
8	12·6	110	0·50
9	14·2	35	0·46

Figure 43. Plot of counting-rate vs discriminator setting and clipping time for Diphenyl-crystal.

which would give a clipping time such that the pulse height would be reduced by the factor (I - I/e) i.e. 0.632, was read off. This came to a clipping time of 18.5 millimicroseconds. By use of this value for τ/n in equation (iv), and normalising at a pulse height of 21.0 volts, for t = infinity, the solid curve was obtained.

This is seen to agree very well with the experimental points which are those shown by a circle and a dot in the middle. The only point which appears to be slightly off the theoretical curve is the one at the shortest time interval, where the length of the shorted line is comparable with the rise time of the photomultiplier's pulse. As these measurements agreed well with the theory, the simpler method of taking the measurements as described in Section C, was used in all the subsequent measurements of the decay times.

Section E

RESULTS

Figures 41, 42 and 43 are the results obtained for stilbene, terphenyl and diphenyl-acetylene respectively. In column 4 in each case is recorded the critical length Lc of cable giving a clipping-time in units of 10^{-8}seconds, such that the pulse height is reduced by the factor 0.632. The phosphors were bombarded by gamma-rays in each case.

The results obtained for all the measurements are

Table IV.

Phosphor	Excitation	Decay Time in IO^{-9} sec
Anthracene 3mm	γ - rays	26 ± 3
Anthracene 3mm	α-particles	I5.I ± 2
Anthracene fine powder	α-particles	II.3 ± 2
Stilbene 3mm	γ-rays	6.8 ± I.0
Stilbene 3mm	α-particles	5.0 ± I.0
Terphenyl 3mm	γ- rays	5.7 ± I.0
Diphenyl-acetylene	γ- rays	7.0 ± I.0

Table IV.

summarised in Table IV.

Section F

Discussion of Results

These results bring to light several points of interest. Firstly, we should look again at the preliminary experiment carried out on anthracene, where the experimental technique was checked. The curve plotted, assuming the decay of the emitted light to be exponential, agreed very well with the experimentally determined points. This then confirms our initial assumption and we may be reasonably sure that in anthracene no other exponential decay lies within the region from about 4×10^{-9} seconds to about 6×10^{-8} seconds, apart from the measured decay. Outside this range the experiment gives no information.

Secondly, it should be noted that the decay times measured under α-particle and γ-ray excitation are different in both anthracene and stilbene. In both cases the alpha-particle decay time is the shorter. Under alpha particle bombardment it is known that the ionisation in the path of the particle is very intense so that it may cause the density of the excited molecules to be so great that they interact with one another and quench their fluorescence and so decrease the observed decay time. This has been observed by Bittman et al (1952).

Thirdly, a fine powder of anthracene was bombarded with alpha-particles and the decay time of fluorescence measured. It was found to be considerably smaller than that found for the 3 mm thick crystal indicating that photon emission and re-absorption did play a fairly large part in determining the decay time of the large phosphor. It was not possible to use microcrystals for this experiment as an appreciable thickness is required in which to stop the alpha-particles, so as to obtain a pulse at the photomultiplier collector sufficiently large to be detected after passing the low impedance loads on the crystal. However, it was judged from the results obtained under ultra-violet excitation that the molecular decay time for anthracene under alpha-radiation appeared to be about 10 mμsecs, compared with 3.5 mμseconds under ultra-violet excitation.

It was noticed that if the crystal was poorly tied to the optical system of the photomultiplier, then the apparent decay time appeared to be considerably less than that for the crystal correctly fixed in place. If only a few photoelectrons were emitted, owing to poor light collection efficiency, the pulse at the collector anode would be indistinguishable from a group of noise pulses, and a measurement of the decay time would only give information on the spread in the transit time through the tube. Thus, unless we have enough photoelectrons so that the individual pulses overlap and smooth out the collector pulse, the measured decay time will be less than the true value. Hence all the above results are probably slightly lower than the true decay times.

It should be noted further that the above decay times have not been corrected for the effect of the finite spread in the transit time in the photomultiplier. This will amount to about -2 to -4×10^{-9} seconds.

Section G

Conclusion

We have come to the conclusion that this method is suitable for measuring the decay times of organic phosphors when a rapid, approximate survey is required of a large number of specimens. However, the following precautions should be followed:

(a) the value for n should be determined for each specimen, instead of relying on the value obtained by comparing the pulse height of the specimen with that of stilbene with a standard amplifier set-up, and deducing the pulse height at the crystal diode from the apparent decay time $\frac{\tau}{n}$, as was done in these measurements.

(b) the phosphor must be excited by high energy pulses to obtain enough photoelectrons from the photocathode.

(c) good light collection geometry is essential.

From the above it would appear that for accurate measurements it would be preferable to use either a pulsed x-ray beam, or, alternately, a system similar to that for ultraviolet described in Section B of Part III, but using modulated x-rays.

PART VIII.

Conclusion

In summing up the results obtained here, two of the latest developments of the theory of the transfer of energy in organic phosphors will be considered and then the author's own ideas on the subject will be put to the fore.

Birks (1953) has put forward a theory to account for the transfer mechanism. This is a development of the transfer process taking place by photon emission and re-absorption. He suggests that a "primary" photon is emitted by the phosphor molecule when it is excited by an ionising particle. This primary photon is expected to lie in the far ultraviolet, close to the molecular ionisation level. At this energy, the mean free path of the photon in the organic specimen will be about 7 μ. He suggests three possible ways in which this primary photon may be emitted:

(i) by ion recombination after dissociation.

(ii) by any allowed transition from a highly excited electronic level to the ground state.

(iii) by excitation of the continuous x-ray spectrum and the characteristic x-rays of carbon by the ionising particle.

On assumption that primary photons are emitted, this theory is capable of explaining some of the properties of organic phosphors under both ionising and ultraviolet excitation.

Taylor et al (1951) and Birks and King (1952) had shown that the specific fluorescence dS/dr, (where dS is the fluorescence emission from a length dr of track), was not related linearly to the energy loss dE/dr for short range alpha-particles nor for very slow electrons. Birks and King found the effect could be quantitatively accounted for by assuming that photons were escaping from the surface of the crystal when the particle penetrated less than about 7µ into the crystal. Aluminium reflectors did not appreciably affect the dS/dr vs dE/dr curve. This indicated that the photons were probably of such high energy that they were only poorly reflected by the aluminium.

If primary photons were produced initially by ion recombination, followed by a large number of high energy transitions from the highly excited electronic states to the ground state, followed by absorption and subsequent emission, this theory would also be able to account for the difference between the decay times of ultraviolet excited phosphors and phosphors excited by ionising radiation. In the case of particle excitation, a large number of emission and absorption processes would take place before the energy could be sufficiently degraded to be emitted in the normal emission bands as fluorescence light. On the other hand, if the phosphor was excited by ultraviolet light of energy, well below the ionisation level, then the light would have less energy to lose before reaching that portion of the spectrum to which the crystal would be transparent, and consequently the decay time would be smaller.

Furthermore, in anthracene it is found that about 67 eV of energy has to be dissipated by the ionising particle for each photon of 3 eV energy which is emitted, whereas it is known that an energy of about 30 eV is required to produce an ion pair in gaseous organic compounds similar to anthracene. This indicates that the quantum efficiency must be about 30/67 in transferring energy from the ionisation level to the first excited state, while in the ultraviolet, Bowen has found that the quantum efficiency is independent of wavelength over a large range and equal to 0.9. The difference can be accounted for if a large number of emission processes take place. If this number is "n", then the effective quantum efficiency would be 0.9^n. The value of n, determined from decay time measurements makes the result agree well with the experimentally derived one.

Ageno et al have shown that in stilbene crystals excited by alpha-particles the excitation energy is transferred over distances of the order of a few millimetres. This suggests that the energy is transferred by primary photons. However, the writer considers that this is simply the photon emission and absorption process observed in any thick organic-phosphor specimens and not due to photons of high energy.

Further evidence for primary photons was given by Richards and Cole (1951), Dee and Richards (1951) and Birks and King (1952), by their observation of materials which were not normally fluorescent under ionising radiation. However, these have been recently shown to be an incorrect interpretation of the experimental results, so we will not consider them further.

This theory appears to be able to account quantitatively for most of the properties of scintillation phosphors and in this way it is very useful and suggests the line which research should follow in this field. It strongly suggests that the spectra and decay times of phosphors in the vacuum ultraviolet should be investigated more fully. This is a relatively uncharted part of the spectrum, and absorption and fluorescence measurements here will open up a field entirely new to the chemist and the biophysicist. It is suggested that the light emission from the accelerated electron beam in the Berkeley and other synchrotrons might be usefully employed to provide a light source in this region. The intensity is large enough, and the spectrum extends down to below 50A, and is, of course, generated in vacuum and is a continuous spectrum - in fact one ideal for absorption measurements.

A criticism of this theory lies in the fact that these photons have never been observed. The spectrum of anthracene itself was investigated in the text in Part IV. No emission of light of any appreciable intensity was found in the region from 185 mμ up to the normal emission bands. This does not preclude the possibility of the primary photons having energy greater than that corresponding to a wavelength of 185 mμ. However, as the energy has to be transported to the visible part of the spectrum from the ionising region, some other process, other than that of photon emission and absorption, is suggested whereby the energy is degraded and not emitted until the energy corresponds to that of the first excited electronic state. Wright has made an effort to account for all the above properties of fluorescent materials by an entirely different theory. This theory is a quantitative development of the theory of sensitised fluorescence which was described in Part I of this Thesis.

Wright (1953) considers the behaviour of pure crystals with regard to excitation by ionising particles, and mixed crystals with regard to their fractional emission of fluorescence light with respect to concentration, and the variation of the decay time with concentration.

In the path of the ionising particle, Wright considers that the particle loses energy to the molecules and they dissipate this energy in three ways:

(i) by bimolecular quenching.

(ii) by monomolecular quenching.

(iii) by fluorescence emission.

The monomolecular quenching is considered to be important when the ionisation is low as in the case of fast electrons. However, when the intensity of ionisation becomes intense, as for example, along an alpha-particle track or at the end of an electron track the ions are produced so close to one another that they may interact with one another. The Coulomb field from the ions may interact strongly with neighbouring molecules and allow them to return non-radiatively to their ground states. The highly excited molecules may interact with one another forming complex molecules (such as di-anthracene in the case of anthracene). These quenching centres cause a reduction in the specific fluorescence at the end of the track of an electron, and further, cause the relative response of the phosphor to alpha-particles to be less than to electrons of the same energy. Using experimentally determined values in the equations obtained by the above considerations, Wright obtained excellent agreement for the variation of dS/dr with dE/dr, and also successfully accounted for the difference between the response to alpha-particles and electrons, without adding any adjustable, arbitrary constants.

Wright has developed this theory further in considering a fourth process which may occur in both a mixed and a pure crystal (but which cannot be readily studied in a pure crystal). This is the transfer of the excitation energy to a neighbouring molecule. He considers that the excited molecule transfers its energy only to one of its immediate neighbours. He considers that the expanded electron orbits of the excited molecule will have a strong chance of interacting directly with the immediate neighbours, and further that these molecules will strongly shield the more distant molecules from the excited molecule.

He equates the frequency of transfer of the excitation energy from molecule to molecule to the frequency of vibration of the molecules in the lattice. For anthracene this is of the order of 10^{12}/second, so that in the normal lifetime of the molecule (of the order of 10^{-8} secs.) the energy may pass through 10^{4} molecules. This enables the excitation energy to be readily trapped by even a very low concentration of impurity. Using a more sophisticated analysis and obtaining the full mathematical equations he was able to plot the fractional emission of the components in a mixed crystal as a function of the concentration of the impurity, and compare them with the experimental values obtained by careful measurements. He obtained reasonably good agreement.

A criticism of this theory might be that equating the vibrational frequency of the molecules to the frequency of the energy transfer is not entirely justified, and furthermore, the measurements in Part III show that the decay time of the anthracene molecule is considerably smaller than the value obtained for a large crystal (the so called technical decay time), as used by Wright. However, these are not serious criticisms, as the order of magnitude is certainly right and until more experimental evidence is forthcoming on the interaction of highly excited molecules in a lattice, it would be dangerous to dispute that the energy could not be transferred considerably more often than once in each vibration of the widely expanded excited molecule.

At first sight these two theories appear to be entirely different in all respects. However, it is felt that a true interpretation of all the experimental facts could be found by going back a little and studying further the process of sensitised fluorescence. In this process the energy is transferred by the method outlined by Wright, but the probability of the transfer taking place is determined by the optical properties of the molecule, just as it occurs in gases. This brings in the reasoning employed by Birks. The fact that the photons were not observed in the case of anthracene lends strength to this argument that the two processes are bound together by this link. In biophysics and in many of the processes of radiation chemistry, the understanding of what happens is greatly simplified if we assume that the energy can be transferred from one molecule to another, or from one radicle to another, if the energy lies only in a narrow band (Birks, unpublished work). This is explicable if the photons exist in a narrow band in the high energy regions of the spectra, but also if the transfer occurs by way of virtual photons. These photons would never actually see the light of day, but could carry energy between two adjacent molecules if the emitting and absorbing centres were in resonance with one another i.e. their emission and absorption bands would overlap one another. Thus the probability of the process would be determined by the optical absorption coefficients, while the transfer mechanism would take place by sensitised fluorescence.

The above line of reasoning is so analogous to the wave and particle aspects of radiation that it suggests that a thorough wavemechanical treatment of the problem would clear up all the difficulties. However, this might obscure the physical ideas of the theories, and for this reason it would be as well to rely on the two theories as they stand, in order to suggest suitable lines for further development. As yet not nearly enough experimental work has been done in these fields to allow us to argue which is the right and which is the wrong theory. It is much more important to see what experiments are worth doing.

It has been suggested earlier that much of value would be obtained if we were to measure the decay times of crystals at different wavelengths of excitation. This is probably one of the most valuable methods of obtaining data on the transfer process.

Another experiment, which the writer considers might help to clarify the position, is to measure the decay time of isolated molecules, as, for example, molecules in a molecular beam. Then we would be able to find out the effect of the lattice on the molecule. This arrangement might also be used to see how the internal vibration of the molecule affects the decay time and the quantum efficiency, by varying the temperature of the oven feeding the molecular beam. The obvious advantage of the molecular beam over the use of the gas itself is that the density of the molecules in the beam corresponds to the conditions in the comparatively high pressure oven, while the collision rate corresponds to that in the high vacuum enclosure.

Furthermore, it would be useful to study the emission spectrum of the molecule by this method, both as regards polarisation of the fluorescence light with respect to the polarisation of the exciting light, and as regards the spectrum of the fluorescence light in the vacuum ultraviolet.

The writer considers that the use of the ionising particles to study the energy transfer mechanism tends much too much to complicate the issue. It is felt that much more could be learned if some of the above experiments were carried out so that we could understand first the behaviour of the molecule itself and then attempt to see how it behaves when localised in the lattice.

One might fittingly conclude with the words of Cecil John Rhodes, which so aptly describe the present state of solid state physics,

"So little done, so much to do".

Appendix I

Crystal Growing Technique

In the early part of this work mixed crystals of anthracene in naphthalene were required. Naphthalene was the basic lattice and anthracene was introduced as an impurity of known concentration.

Crystals may be conveniently grown in a number of different ways which may be divided up into two distinct sections: growth from the melt, and growth from a cooling saturated solution. For mixed crystals the melt is the most convenient way of obtaining crystals with a constant ratio of the constituents. In all the different techniques of growing crystals from the melt three important points must be borne in mind:

(a) the crystal growth must be allowed to develop from only one crystal nucleus. This ensures that initially only one crystal will grow, and a polycrystalline mass will not be able to develop.

(b) the melt must be allowed to cool very slowly so that the crystal will only form on the nucleus crystal and not on the walls of the vessel and upon any other speck of impurity which might be present. The seed crystal should be the coolest part of the melt.

(c) after the crystal has reached the required size it must be allowed to anneal very slowly until it reaches room temperature. This is a precaution against thermal

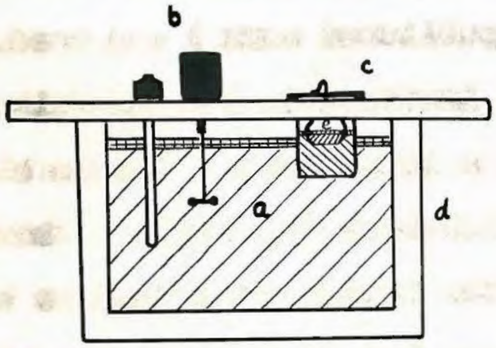


Figure 44. Thermostatic Tank.

(a) Large volume water bath.

(b) Stirring motor, heater and thermostatic control.

(c) Beaker containing melt.

(d) Earthenware tank.

(e) Brass stirrup holding crystal.

fracture to which most large crystals are prone.

Several different techniques were tried for growing these crystals and these will be described in turn.

Thermostatic Bath Technique

Initially, a technique developed by Black of Glasgow (unpublished work) was used. A beaker containing the melt was immersed in a water-filled thermostatic tank held at a temperature a little above the melting point of naphthalene (79.2 °C). When all the naphthalene had melted, the beaker was raised so that the surface of the naphthalene lay about a quarter of an inch above the surface of the water in the thermostat. The slightly cooler air above the surface of the water gives rise to a thermal gradient across the surface of the molten naphthalene. When the temperature is correctly adjusted a thin film of solid naphthalene forms on the surface. This is prevented from falling back into the liquid by hanging a stirrup of brass wire just below the naphthalene surface. The surface skin adheres to this and gradually the crystal grows downwards into the melt. (See figure 44). The wire stirrup may be now either slowly lifted from the beaker to allow the growth to continue, or, alternately, the thermostat control can be adjusted to bring the temperature down in steps of 0.1 °C. every few hours. By this method crystals an inch thick and three inches in diameter were grown of pure naphthalene.

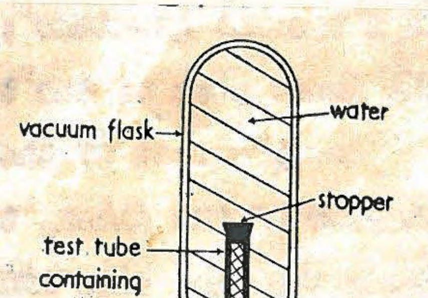
When the melt was almost exhausted the whole crystal was lifted from the beaker and transferred to a large wide-mouthed thermos flask, which had previously been heated with warm water. This allowed the crystal to cool slowly away from the melt, and anneal to the temperature of the room. After several hours the crystal was removed and cleaned up in preparation for use.

Basically this seems to be a perfectly fool-proof method, but in practice, quite a considerable amount of trouble was had in maintaining the thermostat at a temperature which was constant to better than 0.1°C. The water level had to be maintained constant so that the thermostat control element would be held always at the same depth below the surface of the water. This difficulty was solved by covering the water with paraffin wax which melted and prevented the water from evaporating during the growth of the crystal. Some difficulty was had with the stirring motor due to the high temperature environment in which it had to be run which caused the bearings to seize.

This technique yielded some good naphthalene crystals and mixed crystals, but the method seemed to be unnecessarily laborious, so a simpler method was devised.

Vacuum Flask Technique

A vacuum flask was filled with boiling water, and into the stopper in the neck a test-tube containing the melt was inserted. When this melted, the test-tube was



Vaccum flask scintillation crystal growing bath

Figure 45.

stoppered and all the air carefully removed. The whole assembly was then inverted and allowed to stand for several hours. Across the neck of the vacuum flask, between the cool outside air and the hot water of the interior, there was a thermal gradient so that the naphthalene in the lower part of the tube was crystallised first. As the rest of the water slowly cooled in the interior of the flask, the cool region spread inwards along the test tube and the crystal solidified along the 79.2 °C isotherm as it spread inwards. When the crystal was full grown and all the melt exhausted the temperature fell slowly and annealed the crystal to room temperature. It only remained to open the flask and gently crack the test tube off the crystal. The reason for inverting the flask is that the naphthalene on solidifying is heavier than its mother liquor and would tend to fall to the bottom of the containing vessel and hence several nuclei would form if the bottom were not made the coolest part of the tube. (See diagram 45).

This technique was tried out and gave several single crystals 5 cms in length and 5 to 8 mm in thickness. It was not possible to grow a single rod of pure crystal in a test tube. This was probably due to the crystal growing from several smaller crystals at the cooler end of the tube. A test tube with a constricted neck gave slightly improved results, but never a single crystal per test tube. This technique has been published in the "Journal of Scientific Instruments" (Vol. 30, p 253, July 1953).

The above techniques are only suitable for growing crystals which have a melting point between about 30 °C and the boiling point of water. When other phosphors are required rather higher temperatures are needed. Pure anthracene, for example, melts at 216 °C. In order to grow crystals of this type a thermal oven technique was tried.

The oven was constructed on the following lines. A coil of heating wire was wound round a porcelain pipe one inch in diameter and one metre long. Six inches from the top of the tube the wire was closely wound and further down the tube the windings were spaced farther and farther apart. Down the pipe a thermocouple could be moved to read the temperature at any point. The temperature was plotted along the length of the tube and showed a high temperature region at the top with a gradual decrease down to room temperature at the bottom.

A string support attached to the "hundreds" shaft of a wattmeter lowered the test tube, containing the melt, at about an inch an hour through the pipe. The test tube had a flat bottom with a capillary tube extending a few centimetres below the centre of the base and sealed off at its bottom. As the test tube passed the warm section of the pipe the phosphor melted and as it moved further down the tube, that part of the melt which was in the constricted tube crystallised and formed a seed crystal from which the rest of the crystal grew. The temperature of the crystal was allowed to fall slowly as the specimen proceeded to the cooler parts of the tube.

This is an ideal experimental arrangement for growing any type of crystal. However, it was not easy to get this oven to work properly.

By attaching a thermocouple to the test tube carrying the melt it was possible to read the temperature of the melt at all times during its passage down the heated pipe. In use it was found that the current to the heaters of the oven had to be controlled to extremely fine limits in order to keep the temperature constant in any one part of the oven. Furthermore, care had to be taken to see that the specimen was never overheated so as to cause oxidation.

No successful results were obtained with this set-up as, at the time, we had no means by which the temperature could be accurately controlled in the oven, and the mains fluctuations and variations in the temperature in the room caused the temperature to drift through several degrees in the hour. Thus the cooling of the specimen never took place in the manner sought. As we were not desperately in need of crystals other than anthracene in naphthalene, no more time was spent in trying to stabilise the temperature of the oven and it was abandoned until the need arose.

Working of Crystal Surfaces

Anthracene-naphthalene mixed crystals are very soft and may be readily cleaved with the aid of a razor-blade. Similarly, they may be shaved to any required shape with a blade. They may be polished by rubbing gently the surface of the crystal on a piece of filter paper. No abrasive is necessary, but care must be taken so as not to heat locally the rubbing surface, and so crack the crystal. After a few hours, however well the surface has been polished, the shine will go from the surface owing to the evaporation of the surface layers in an uneven manner.

Appendix II

High Voltage Stabilised Power Supply

A high voltage stabilised power supply was built to provide a stabilised voltage for the photomultiplier. The power supply was built out of the parts of an older unstabilised supply. The high voltage was obtained from a 10 KV transformer from which the 2.5 KV tapping was used. This was rectified through a half wave rectifier and filtered through a choke input filter. The output current was drawn through a pentode which was stabilised with a CV 71 Neon stabiliser. The output varied by less than 1% for a 20% variation in Mains voltage. The output was not stabilised against change of current so that a change of load from 0.3 mA to 0.4 mA caused a change of 150 volts in 1200 volts. However, as the photomultiplier current changed by microamperes only, this did not matter. The power supply could not give a larger current that 0.4 mA stabilised.

Appendix III

In Part III, Section (d) (ii)

$$i = i_0\int_0^{\frac{2\pi}{\omega}} \sin^2\omega t . \sin(2\omega t+\alpha)\, dt.$$ is required.

$$= \frac{i_0}{2}\int_0^{\frac{2\pi}{\omega}} \left[1-\cos 2\omega t\right] \sin(2\omega t+\alpha)\, dt.$$

$$= \frac{i_0}{2}\int_0^{\frac{2\pi}{\omega}} \sin(2\omega t+\alpha)dt - \frac{i_0}{4}\int_0^{\frac{2\pi}{\omega}} \sin(4\omega t+\alpha)dt - \frac{i_0}{4}\int_0^{\frac{2\pi}{\omega}} \sin\alpha\, dt.$$

$$= -\frac{i_0}{4}\cdot\frac{2\pi}{\omega}\sin\alpha.$$

$$= -I_0 \sin\alpha.$$

In the more general case we may have light which is incompletely modulated i.e. instead of $\sin^2\omega t$ we may have $1 + K \sin^2 t$. In this case it is seen from the above that the result will be:

$$i = I_A - I_B \sin\alpha.$$

Appendix IV

The effect of Harmonic Terms in the Modulated light and the effect of non-linearity in the detector

Suppose the gain of the photomultiplier is not a linear function of the potential between the photo-cathode and the first dynode. Then, if this potential is modulated sinusoidally the gain will not vary sinusoidally with it. The non-linearity will distort the sinusoidal component and introduce harmonic terms with the modulating frequency as the fundamental. We can take this into account by expressing the gains at any time t by the function:

$B\sum_{n=0}^{\infty}{}' b_n \cos n\omega t,$ where B and b_n are constants and n any +ve integer. 'ω' is the angular frequency of the fundamental.

The intensity of the light falling upon the photo-cathode may not vary sinusoidally with time. We can express its time dependence by the general function:

$I = A\sum_{m=0}^{\infty}{}' a_m \sin(m\omega t + \alpha_m)$ where A, a_m and α_m are constants, and m is any +ve integer.

The current at the collector of the photomultiplier will be proportional both to the intensity of the light and to the gain of the detector. The instantaneous current at time t will be proportional to:

$$AB\sum_{m}{}'\sum_{n}{}' a_m b_n \sin(m\omega t + \alpha_m)\cos n\omega t.$$

The average d.c. current will be proportional to the product integrated over a period of the fundamental. i.e.

$$AB\int_0^{\frac{2\pi}{\omega}} \sum_N{}' \sum_m{}' a_m b_N \sin(m\omega T + \alpha_m) \cos N\omega T.\, dt.$$

$$= \frac{AB}{2}\int_0^{\frac{2\pi}{\omega}} \sum_N{}' \sum_m{}' a_m b_N \{\sin (m+N)\omega T + \alpha_m\} dt + \frac{AB}{2}\int_0^{\frac{2\pi}{\omega}} \sum_N{}' \sum_m{}' a_m b_N \{\sin(m-N)\omega T + \alpha_m$$

$$= 0 \text{ unless } m = n \text{ or } m = n = 0.$$

$$= \frac{AB}{2} \cdot \frac{2\pi}{\omega} a_0 b_0 \sin\alpha_0 + \frac{AB}{2} \sum_m{}' a_m b_m \sin\alpha_m.$$

$$\approx 1 + K \sum_{m}{}' a_m b_m \sin\alpha_m.$$

The effect of introducing the phosphor is to introduce a phase shift ϕ_m between the Fourier components of the exciting modulated light and the corresponding components of the fluorescence. The shift in phase will be different for each value of m. This shift is given by the relation $\phi_m = \tan^{-1}(m\omega\tau)$. Thus the effect of harmonic terms and a non-linearity in the detector is to introduce an error in the measured decay time. The magnitude of this error may be found by knowing the values of the harmonic terms a_M and b_M.

Curve (b) in Figure 22 shows that this error is small. This curve behaves essentially as $1 + K \sin\alpha$ with no terms of appreciable magnitude of the form $K_n \sin n\alpha$ with $n > 1$. This shows that the harmonic terms were considerably smaller than the fundamental in these measurements.

BIBLIOGRAPHY

Ageno M., Cortellesa, G.	1952, Nuovo Cimento 9, 196.
Arnot, F.L.	"Collision Processes in Gases" Methuen Monographs.
Albrecht, H.O & Mandeville, C.E.	1952, Rev. Sci. Instr. 22, 855.
Bergmann, L.	"Ultrasonics", G. Bell & Sons, Ltd. London.
Birks, J.B.	"Scintillation Counters" Pergamon Press, London, 1953.
Birks, J.B.	1950, Proc. Phys. Soc. A63,1044.
Birks, J.B. & Black, F.A.	1951, Proc. Phys. Soc. A64, 511.
Birks, J.B. & King, J.W.	1953, Proc. Phys. Soc., B66, 81.
Birks, J.B. & Szendrei, M.E.	1953, Phys. Rev., Vol. 91, No.1.
Bittmann, L, Furst, M. & Kallmann, H.	1952, Phys. Rev., 87, 83.
Bowen, E.J.	1949, "Chemical Aspects of Light", Oxford.
Bowen, E.J.	1952, Nucleonics, Vol. 10, No. 7, 14.
Bowen, E.J. & Lawley, P.D.	1949, Nature, 164, 572.
Collins, G.B.	1948, Phys. Rev. 74, 1543.
Dee, P.I. & Richards, E.	1951, Nature, 168, 736.
Dieners, G.J.	1953, Annual Review of Nuclear Physics, Vol. 2, 85.
Engstrom, R.W., Stoudenheimer, R.G. & Glover, A.N.	1952, Nucleonics, 10, 58.
Frank, J. & Livingston, R.	1949, Rev. Mod. Phys., 21, 505.
Frey, H.	1936, Phys. Rev., 49, 305.

Ganguly, S.C. 1944, Nature, 153, 652.

Garlick, G.F.J. 1949, "Luminescent Materials", Oxford.

Gaviola, E. 1927, Z. Physik 42, 862.

Harrison, G.R. Lord, R.C. & Loofbourow, J.R. "Practical Spectroscopy", Blackie & Sons.

Hoag, A. 1938, "Electron & Nuclear Physics" London.

Hund., A. "Phenomena in High Frequency Systems", McGraw-Hill.

King, J.W. 1952, M.Sc. Thesis, Rhodes University.

Koski, W.S. 1951, Phys. Rev. 82, 230.

Liebson, S.H. 1952, Nucleonics, 10, 41.

MacGregor-Morris 1936, "Cathode Ray Oscillography", London.

Mott, N.F. & Sneddon, I.N. 1948, "Wave Mechanics and its Applications", Oxford.

Norman, A. Greenfield, M.A. & Kratz, P.M. 1953, Nature, 171, 487.

Owen, R.B. 1951, J. Sci. Instr. 28, 221.

Post, R.F. 1952, Nucleonics, 10, 46.

Pringsheim, P. 1949, "Fluorescence and Phosphorescence", Interscience Publishers, New York.

Richards, E., & Cole, J.F.I. 1951, Nature, 167, 286.

Sangster, R.C. 1952, M.I.T. Technical Report 55.

Spangenberg, K.R. "Vacuum Tubes".

Strong, J. "Modern Physical Laboratory Practice", Blackie & Sons, London.

Taylor, C.J., Jentschke, W.K. Remby, M.E. Eby, F.S. & Kruger, P.G.	1951, Phys. Rev. 84, 1034.
Tummermann, L.A.	1941, J. Phys. (U.S.S.R.) 4, 151.
Wright, G.T.	1953, Phys. Rev. 91, 1282, Sept. 1953.
Wright, G.T.	1953, Proc. Phys. Soc. A66,777.
Zworykin, V.K. & Ramberg, E.G.	"Photoelectricity", John Wiley & Sons.