THE PHOTO-FLUORESCENCE PROPERTIES OF SOME ORGANIC MATERIALS

by

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THESIS PRESENTED FOR THE DEGREE OF DOCTOR
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This work was initiated under the supervision of Dr. J.B. Birks, whose inspired leadership was an ever-present encouragement. I wish to thank him for supplying stimulation during the inevitable periods of low morale, for his prompt and ready advice and criticism, and for his continued general help throughout the time this work was done.

It is to Dr. Birks that I am indebted for the suggestion of the problem investigated in Part I, and for his general guidance in the analysis of the results of both Part I and Part 2.

I wish to thank Dr. G.T. Wright for the suggestion and some discussion of the problem investigated in Part 2.

After the completion of the experimental work, Prof. J.A. Gledhill was appointed to the Chair of Physics, and immediately took an active interest in the analysis of the results of Part 2, and I must thank him for many informative lengthy discussions.

I have referred to Dr. M.E. Szendrei in the text, but I wish to thank him here for his calibration of the photomultiplier and spectrophotelometer used in Part I.

For invaluable assistance in the construction of the apparatus, my thanks are due to Mr. A. Ross-Scanlen, especially with regards to the attachment of the photomultiplier to the spectrophotelometer used in Part I.

For some early discussion on the chemical properties of the organic compounds used in this study, and advice on the selection of suitable solvents, I wish to thank my friends who were research students in the Department of Chemistry.

Finally, I wish to thank my parents for their active interest and continued support; Mrs. L.B. Jones for the meticulous care taken in the typing; Miss R.J.

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PREFACE

In this thesis I have given an account of the experimental work carried out by me at Rhodes University from the beginning of 1954 to the end of 1955, and the analysis of the results which was completed during the following two years, 1956 and 1957.

The dissertation is divided into two sections; Part I deals with the photo-fluorescence spectra of a large group of organic compounds, and Part 2 describes an investigation of the photo-fluorescence properties of and energy transfer in liquid organic solutions.

My entry into the research school was shepherded by Dr. J.B. Birks, who supervised the commencement of the work performed in Part I until his departure from the University in mid 1954. Because of the time taken in the lengthy process of assembling the apparatus, calibrating the instruments, and standardising on specimen thickness, etc., few results had been obtained when Dr. Birks departed; the work continued at a slowerpace partly due to my own inexperience in research methods and partly because I carried out most discussion of the results in correspondence with Dr. Birks. However, by early 1955, most of the experimental results had been obtained and early analysis showed the interesting results which are contained in a paper I read at the South African Association for the Advancement of Science Conference held in Grahamstown in July, 1955, and which are published in the South African Journal of Science.

It was at this stage that discussions with Dr. Wright led to the decision to leave further analysis of the spectral measurements until later, and to perform the experiments described in Part 2. During this period Dr. Wright left the University and I completed the experimental work and early analysis unsupervised until Prof. J. A. Gledhill was appointed to the Chair of Physics during the latter half of 1955.

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During 1956, while I was resident in England, I continued with the analysis of the results and was fortunate in being able to confer with Dr. Birks regularly, and with other workers conducting research into some of the many aspects of organic fluorescence. Such discussions were very valuable in producing a sound background which helped to guide me along the right track in the final analysis of the results.

The work was completed during 1957: the results of Part I are to be published in the "Proceedings of the Royal Society" during 1958, the results of Part 2 are published in the "Proceedings of the Physical Society".

DECLARATION:

I HEREBY CERTIFY THAT, UNLESS OTHERWISE SPECIFICALLY STATED IN THE TEXT, THE WHOLE OF THIS THESIS IS MY OWN ORIGINAL WORK. IT HAS NOT BEEN SUBMITTED FOR A DEGREE IN ANY OTHER UNIVERSITY.

A.J.W. Cameron.

PUBLICATIONS

1. "The Photon Cascade Process" by J.B. Birks and A.J.W. Cameron.
South African Annual Physics Conference, Pretoria. July, 1954.

2. "The Fluorescence Spectra of some Organic Crystals" by A.J.W. Cameron. South African Association for the Advancement of Science, Annual Conference, Grahamstown. July, 1955.

3. "The Fluorescence Spectra of some Organic Crystals" by J.B. Birks and A.J.W. Cameron.
South African Journal of Science. 53, 1, 16. August, 1956.

4. "Energy Transfer in Organic Systems. I. Photo-fluorescence of Terphenyl-Toluene Solutions". by J.B. Birks and A.J.W. Cameron.
Proceedings of the Physical Society. A72, 53-64. 1958.

5. "Crystal Fluorescence of Carcinogens and Related Organic Compounds". by J.B. Birks and A.J.W. Cameron.
To be published in the Proceedings of the Royal Society. 1958.
(submitted by Regius Prof. Mitchell, F.R.S. (Cambridge).

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SUMMARY.

The work reported in this thesis is divided into two distinct sections. Part I describes an experiment for the measurement of the crystalline photo-fluorescence spectra of aromatic hydrocarbons; Part 2 deals with an investigation into the photo-fluorescence of liquid organic solutions of para-terphenyl in toluene and the inter-molecular energy transfer occurring within such a system.

PART I:

An apparatus was designed for the measurement of the fluorescence spectra of crystalline specimens. It consisted of a concave grating spectrometer (Cenco-Sheard spectrophotelometer), whose transmission coefficient over the spectral range studied was known, attached to a photomultiplier tube of known spectral response whose output current was measured on a sensitive galvanometer. The overall spectral response of the spectrometer-photomultiplier combination was used to correct the observed fluorescence intensity of the spectra to the true relative intensity, I. The relative quantum intensity, Q, which is proportional to $I\lambda$ was obtained and plotted as a function of wavelength λ. Microcrystalline specimens were prepared by evaporating a certain volume of solution of known concentration onto a circular glass plate. The layers obtained gave an intense fluorescence uniformly distributed over the surface and were finely grained.

The three solvents used for the preparation of the solutions, cyclohexane, chloroform and acetone, were chosen primarily by solubility considerations but all three evaporated to leave finely-grained specimens.

Preliminary measurements on specimens of various thicknesses showed that a thickness of approximately 0.1μ was the most suitable to give sufficient intensity and the best spectral resolution. All specimens were thus made to this standard thickness which is sufficient to absorb over 90% of the incident radiation.

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Fluorescence was excited by a monochromatic radiation of 253.7 mμ wavelength incident on the front surface of the specimen, and the spectra were observed in transmission through the specimen itself and the glass backing plate. Glass plates were used because the quartz plates used previously by Birks and Wright (1954) were found to be feebly luminescent in the region λ = 360 mμ to 420 mμ .

In this way, the fluorescence spectra of a total of 41 organic compounds were measured.

For the anthracene spectrum, normalisation of the spectra prepared from different solvents on the maximum corresponding to the $1_0 \rightarrow 0_1$ vibrational transition, showed that the spectra coincided at longer wavelengths but that the intensity of the $1_0 \rightarrow 0_0$ transition varied over a wide range. A similar effect is exhibited by 1:2 benzanthracene though the corresponding intensity of the $1_0 \rightarrow 0_0$ transition is greater in all cases.

The reduction of intensity of band 0 is due to self-absorption of the fluorescence in this spectral region caused by the coincidence of the short wavelength end of the fluorescence spectrum and the long wavelength end of the absorption spectrum. Using the crystalline absorption measurements of Kortum & Finckh (1942) a method is evolved for correcting the intensity of band 0 to the value it would have if reabsorption were absent, and the true molecular fluorescence spectrum is obtained. This method is shown to apply equally to 1:2 benzanthracene and the mono-methyl and di-methyl derivatives of anthracene and 1:2 benzanthracene in which reabsorption occurs to a varying extent.

The maximum of the molecular fluorescence $1_0 \rightarrow 0_0$ transition does not coincide exactly with the corresponding absorption transition due to the existence of "trapped excitons" described by Sidman (1956).

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The spectra have been classified using anthracene, 1:2 benzanthracene and mono-methyl and di-methyl derivatives of both. A sequence of spectral types is observed ranging from Type A, where the vibrational structure is well-resolved (a. in the parent compounds), to Type F, which have a single broad diffuse band accompanied by a major bathochromic shift.

The spectra of all the other polycyclic hydrocarbons and other compounds exhibit Type A to F spectra.

In the analysis of the spectra three separate effects are distinguished :-

1. The "Solvent or Environment Effect" associated with the permittivity of the medium in which the fluorescent molecule is located. The result is a major bathochromic shift of the whole spectrum relative to that in light petroleum solution measured by Schoental & Scott (1949).
2. "The Molecular Substitution Effect " which causes the spectral shift realtive to the parent compound. This is particularly interesting in the series of compounds like 1:2 benzanthracene and its mono-methyl derivatives and the derivatives of 3:4 benzophenanthrene. The amount of shift, m_c, for the crystalline spectra is compared to that for solution measurements m_s, which show a similar effect.
3. "The Crystal Interaction Effect" due to intermolecular forces within the crystal, is responsible for the remaining differences between the spectra of crystals and solutions. The diffuseness and major bathochromic shifts of the spectra relative to the corresponding solution spectra are attributable to large molecular interactions within the crystal. This type of molecular interation has not been reported previously though an analysis of the results of Northrop & Simpson (1956), who measured the fluorescence spectra of solid

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solutions of anthanthrene in anthracene for various concentrations, shows its existence in other organic compounds.

The decay times of many of the compounds where the crystal interaction eff is strong are greatly increased compared to the parent compound.

29 of the compounds studied are carcinogens and a search was made for distinctive relations between the fluorescence spectra and the carcinogenic activit Some correlation is found between the degree of crystalline interaction and the carcinogenic potency, strong interaction leading to high potency. An approximate correlation between the shift of the spectra of the 1:2 benzanthracene derivatives relative to the parent compound and their carcinogenic potency is also suggested.

PART 2:

The experiments reported were designed to investigate solvent-solute energy transfer is liquid solutions of para-terphenyl in toluene excited by ultra-violet radiation. The solution under investigation was contained in a cylindrical glass vessel (to a depth of ~ 1 cm.) and was excited by illumination of the top surface with monochromatic radiation from a Beckman Model D.U. spectrophotometer.
The integrated intensity of fluorescence transmitted through the base of the container was detected using a photomultiplier tube, the observation being reported for excitation wavelengths between 2200 Å and 3300 Å, the region which includes both the toluene and the terphenyl first absorption bands.
he relative quantum intensity of the monochromator exit beam was determined over he spectral range studied (λ = 2200-3300 Å) and the observed fluorescence tensities are corrected to correspond to the same quantum flux of incident radiation.

Thus the fluorescence quantum intensities of normal and oxygen-free solutions of para-terphenyl in toluene have been measured as a function of concentration, c, excitation wavelength, λ, from 2200 Å to 3300 Å.

The absorption spectra of toluene and terphenyl have also been observed. The probability of solvent-solute transfer is found to be proportional to the solute concentration.

Three distinct regions are distinguished in the excitation spectra. The first where the toluene is transparent to the incident radiation which is absorbed directl by the terphenyl. At $\lambda \sim$ 2800 Å the toluene begins to absorb and the intensity of terphenyl fluorescence decreases rapidly as the toluene absorbs an increasing fraction of the incident radiation.

In the second and third regions corresponding to wavelengths below $\sim$2700 Å, the toluene absorption is high and the terphenyl fluorescence is mainly excited indirectly by energy transfer from excited toluene molecules.

Analysis of the excitation spectra leads to the derivation of an expression for the energy transfer coefficient, f, (this is the fraction of quanta initially absorbed by the solvent which are transferred to the solute) in terms of experimental parameters.

f is found to depend on wavelength, λ, and two characteristic values are found; f_1 in the second region (λ = 2500-2650 Å) and f_2 (which is greater than f_1) in the third spectral region (λ = 2200-2350 Å).

The observed wavelength dependence of f is in direct contradiction to an account of similar studies published by Cohen & Weinreb (1956). The two spectral regions giving rise to the values f_1 and f_2 correspond to excitation into the first and econd excited electronic singlet states of the toluene molecule, and the results ow that the energy transfer coefficient from toluene molecules excited initially

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into the second excited state, is higher than for molecules excited initially int the first excited state. It is shown that the process of solvent-solute energy transfer from the second excited state, which occurs in approximately 10^{-11} sec. competes efficiently with conversion to the first excited state of toluene.

Although no final conclusions are drawn about the energy transfer mechanism, the results are consistent with the radiative transfer process of photon emission and reabsorption rather than with any short-range non-radiative transfer process.

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PART 1.

THE CRYSTALLINE PHOTO-FLUORESCENCE SPECTRA OF SOME AROMATIC HYDROCARBONS

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PART 1.

THE CRYSTALLINE PHOTO-FLUORESCENCE SPECTRA OF SOME AROMATIC HYDROCARBONS

1. INTRODUCTION

This work deals with the photo-fluorescence properties of organic compounds and was carried out in order to determine more of the physical properties of these materials in the crystalline state. In order to interpret the data reported, an understanding of the process giving rise to fluorescence within a molecule is necessary. As a simple approximation, we will consider the theory of the luminescence of a simple diatomic molecule which has been derived from luminescence studies (BOWEN 1949).

1. 1. SIMPLE MOLECULAR MODEL:

The fluorescence of organic materials is an inherent molecular property and is brought about by the molecule changing from a higher to a lower energy state accompanied by the emission of light. The binding forces in organic crystals are relatively weak, compared with inorganic crystals, so that the molecules are loosely stacked and their energy levels are practically unperturbed by environment. If the potential energy of the configuration, V, is plotted against the interatomic separation, r, (FIG. 1) we obtain the familar Morse diagram which suitably represent the energy system of a diatomic molecule, where O and A are the constituent atoms. We can imagine atom O at rest with atom A vibrating about it so that curve aAa' represents the vibration amplitudes for atom A relative to atom O for all vibrationa energies of the molecule in the ground state. The molecule is in equilibrium when the atoms are at O and A, i.e. atom A is at the minimum of potential energy. A

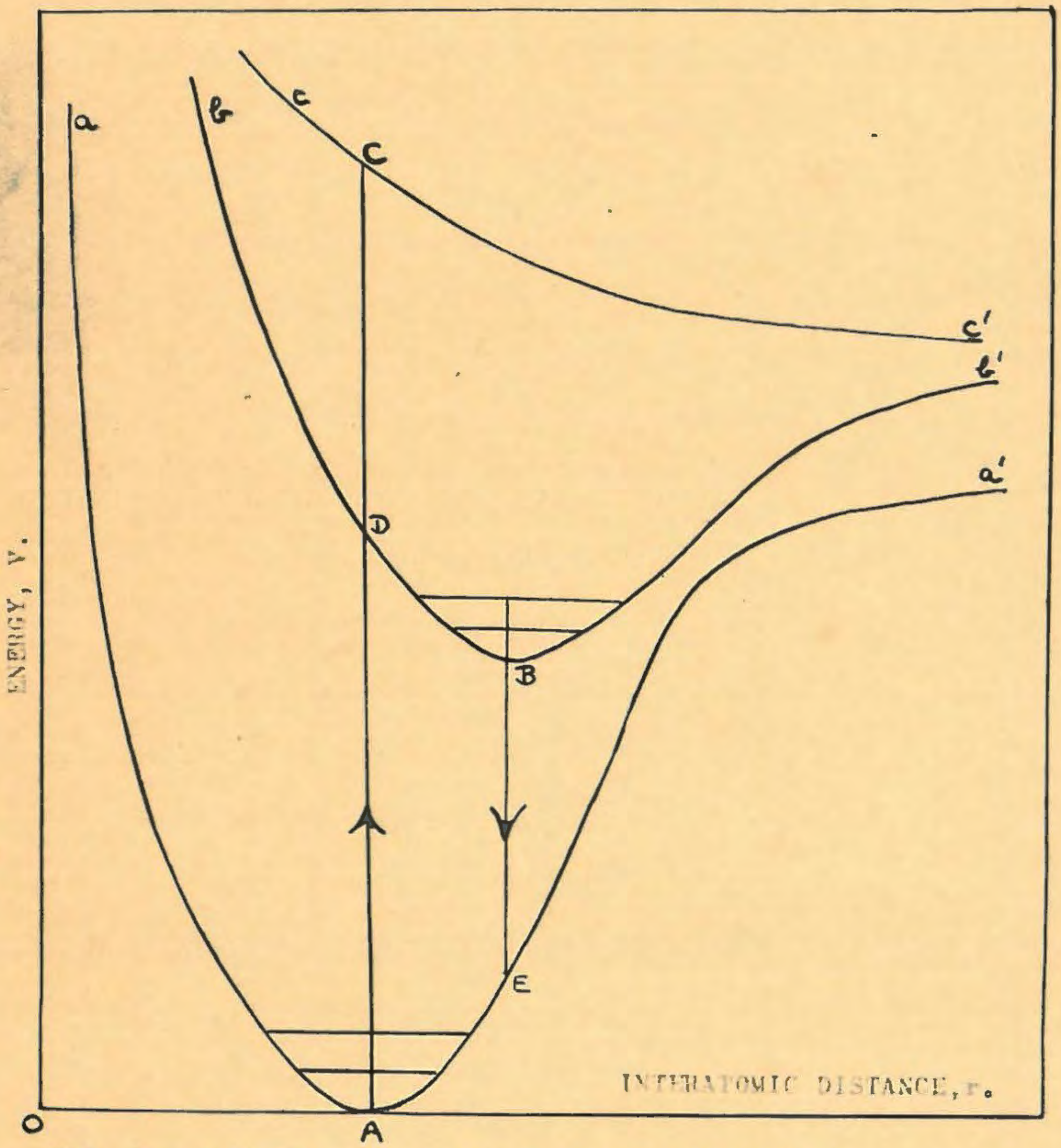

FIG. 1. Molecular potential energy configuration.

molecule in thermal equilibrium will possess only a few quanta of vibrational energy represented by the lower levels near A. The curve bBb' represents the vibrations of a molecule in an excited electronic state, and the lower vibrational levels near B represent the normal vibrational levels when the excited molecule is in thermal equilibrium. The minimum of potential energy, B, of this curve is displaced to the right of A showing that the position of equilibrium for this excited state is at a different nuclear separation from that of the ground state. This is because the molecule may have here a rotational energy causing a centrifugal broadening and the molecule will interact with its environment to an extent dependent on its electronic energy. Since these excited electrons are less "bonding", the molecule finds itself in a "compressed" condition immediately after an electronic transition to a lower state. Above bBb' there are other excited levels extending up to the curve cCc' which has no minimum. At this energy there are no stable vibrational levels, attraction is changed to repulsion, and the atoms separate causing dissociation of the molecule. In the case of organic molecules composed of a larger number of atoms, the number of vibrational sub-levels becomes so large and their spacing so close, that the discrete peaks of the spectra tend to coalesce into broad absorption bands or"band envelopes". This tendency is greatly enhanced in the liquid state and in solution where the vibrations are further damped by physical interaction between neighbouring molecules and by chemical solvation.

1. 2. FATE OF THE EXCITED MOLECULE - FLUORESCENCE:

The absorption of a photon by an unexcited molecule, which is in one of the lowe vibrational levels of the ground state, will cause a transition from the ground state aAa' to one of the excited states depending on the energy of the incident photon.

Such a transition will be represented by a vertical line on the diagram (e.g. AD) since, according to the FRANCK-CONDON principle, the electronic energy change is much more rapid than the atomic movements so that the momentum and separation of the molecular constituents will not change during the time for this electronic transition. Therefore, even though the energy absorbed by the molecule is greater than the dissociation energy, S, dissociation does not take place. However, the transition from A to C for a high energy photon causes the "photo-chemical dissociation" of the molecule into atoms as represented by Cc'. The electronic energy represented by the ordinate of C is converted into chemical energy given by the ordinate of c', the remainder going into translational energy of the atoms.

On the diagram the vertical line will meet one of the vibrational levels of the excited state bBb' at such a place that the momentum condition will be satisfied in this level. If D lies above b', dissociation will again occur, otherwise the molecule is in a high vibrational level of the excited state. It will dissipate its excess vibrational energy as heat rapidly (in $\sim 10^{-12}$ sec.) and fall to B. Most commonly, the excitation energy is given up as infra-red radiation or degraded into heat by stepwise loss of vibrational energy, partly spontaneous and partly assisted by thermal collisions. Alternatively, if it is strongly coupled to its neighbours, the molecule may return to the ground state along BE, a spontaneous electronic downward transition, by the emission of visible or ultra-violet fluorescence. The emitted light is generally of longer wavelength than the absorbed light because the excited molecule loses some vibrational energy before the downward electronic transition takes place, and also returns at first to a higher vibrational level of the ground state than that from which it started. This is in agreement with Stokes' Law (PRINGSHEIM 1949). If it is not so strongly coupled to its neighbours, the optical

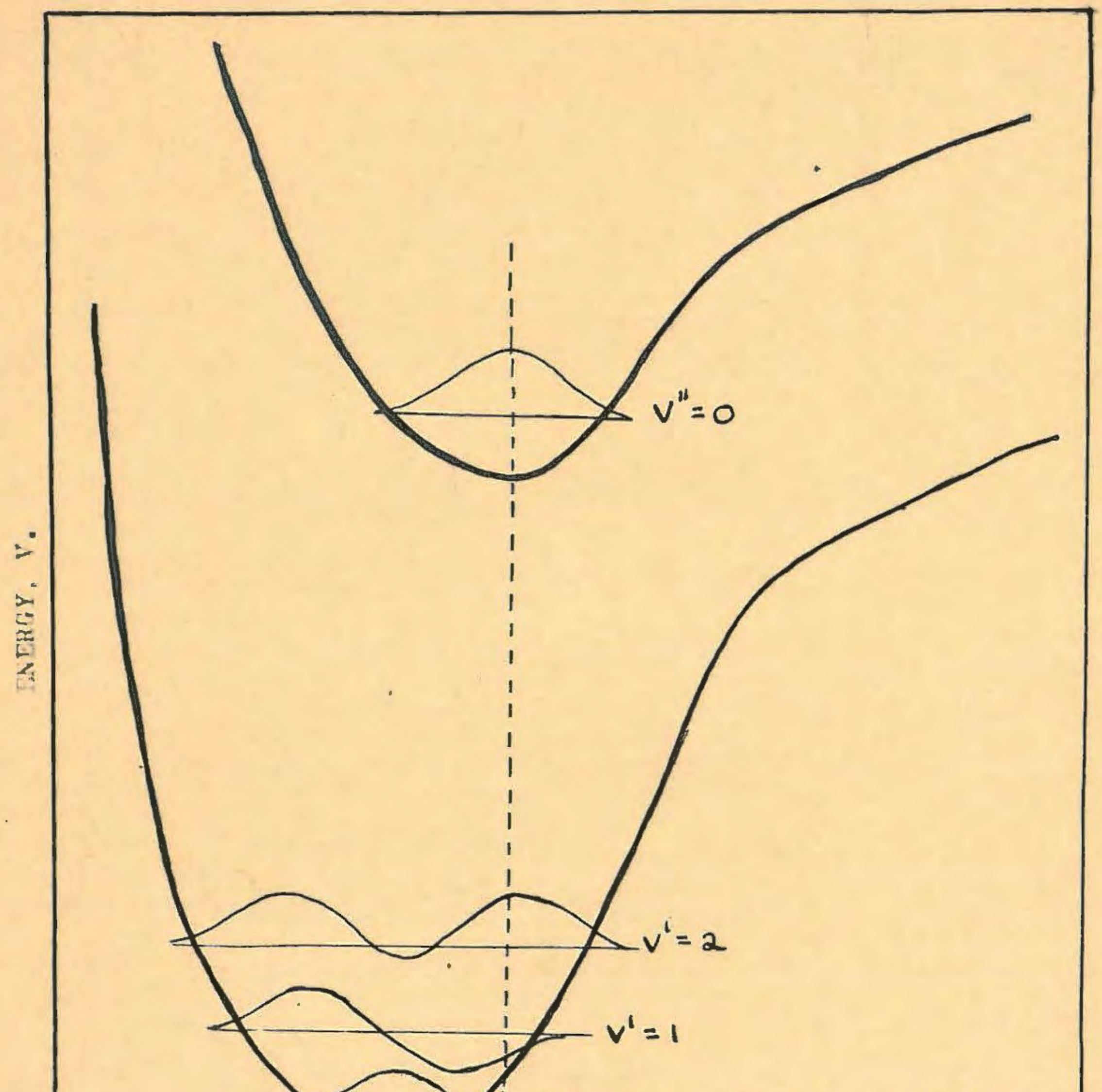

FIG. 2. Molecular potential energy configuration showing ψ-functions for vibrational levels.

transition may take place before the molecule has reached thermal equilibrium. The molecule can then make any transition between AD and BE. This is known as the "resonant" transition since the process of absorption and emission can take place at the same frequency. This would result in a strong overlap of absorption and emission spectra.

The manner in which the FRANCK-CONDON principle will affect the transition probabilities may be seen from FIG. 2. In this figure the curves for the probability density distribution of ψ functions for the various vibrational states are shown with their corresponding energy levels (ψ = wave function of molecule in vibrational level). The vibrational quantum number for the excited state is v'' and for the ground state v'. For the excited state, $v'' = 0$, the most probable value of the internuclear separation at the time of emission will be that for which ψ is at a maximum. Hence the most likely transition will be along the dashed line. For $v' = 0$ we note that $\psi(v')$ is small so the intensity of the transition is small. The transition to $v' = 1$ will be greater and to $v' = 2$ even greater. In this presentation it is seen that the probability depends upon the value of $\psi(v')$ on the dashed line. In the consideration of polyatomic molecules these general considerations hold true though a quantum description of the electronic state is very complicated.

Fluorescence is especially prevalent in complex organic molecules in which the nuclear framework is particularly rigid as in the polycyclic aromatic compounds, and when the region of excitation is shielded from collisional encounters. This effect can be enhanced by using a viscous or frozen solvent so that the excited molecules are embedded in a rigid glass; under such conditions the rate of thermal energy dissipation is much decreased and delayed fluorescence, phosphorescence, with life

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times up to the order of 10^{-2} seconds can be observed with compounds undergoing forbidden transitions (LEWIS & KASHA 1944 & 1945). The fluorescence mean life time, itself, is long ($\sim 10^{-8}$ sec.) compared with the period of molecular vibrations and, therefore, fluorescence occurs only in those molecules in which energy is not readily dissipated in other ways. In many molecules the curves aAa' and bBb' may come close to each other, at a point F say, (FIG. 1) and a molecule in the excited state vibrating along GF may make a non-radiative transition to a high vibrational level of the electronic ground state and all the energy is lost as heat to the lattice. A rise in temperature increases the probability of a non-radiative transfer and thus causes a decrease in the quantum efficiency of the process. Therefore, for an efficient fluorescence process the following conditions should be satisfied:-

(i) The potential energy curves of the ground and excited electronic states should be well separated.

(ii) No photo-chemical dissociation should occur on light absorption.

(iii) The probability of any transition from B other than to E of the ground state should be small.

The organic phosphors are mainly pure and substituted aromatic hydrocarbons, whose molecules contain conjugated double bonds. The benzene ring structure, with its six π-electrons shared between the carbon atoms to form molecular orbitals, occurs in all organic phosphors and forms the basis of the two well-known series, naphthalene, anthracene, etc., and diphenyl, terphenyl, etc.

The <u>absorption spectrum</u> corresponds to the electronic transition from the first few

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vibrational levels of the ground state up to bBb'.
The fluorescence spectrum consists of a system of regularly spaced bands corresponding to the spacing of the vibrational levels in the ground state; the absorption spectrum fine structure corresponds to the separation of the excited state vibrational levels. This produces the so-called "mirror image" relation between absorption and emission spectra.

Absorption bands also occur at shorter wavelengths due to transitions into the second and higher electronic states, but the fluorescence spectrum corresponds to transitions from the first excited electronic state only, and no transitions from higher states have yet been observed. An exception to this, is the recently observed fluorescence from the second excited electronic state of azulene, but this is a somewhat different molecule since there is no observable fluorescence from the first excited state (SIDMAN & McCLURE 1956). The possibility of fluorescence from the second excited state of toluene is discussed in Part 2.

Spectra of the same compound in the gaseous, liquid and solid states are usually different, much of the fine structure of the gaseous phase being lost and only regions of continuous spectral activity occur. This is due to greater molecular density in the condensed phases. Sometimes the absence of a band in the condensed phase corresponds to a band from the gaseous phase and vice versa. This is due to lattice vibrations within the crystal and loss of vibrational structure has been demonstrated in gaseous form by increasing the pressure. However, this spectrum is very different from the condensed phase.

It has been found experimentally that the fluorescent spectrum and the quantum efficiency (number of quanta emitted/number absorbed) of fluorescence is independent of the wavelength of the exciting light down to at least 2500 Å. Therefore,

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fluorescence can be produced with equal efficiency by excitation into the second or higher electronic states. For excitation into the higher states there are four possible modes of de-excitation, namely - fluorescence emission to the ground state, internal quenching to the ground state, fluorescence emission to the first excited state, and internal quenching to the first excited state. It is found (PRINGSHEIM 1949) that internal quenching to the first excited electronic state has a much greater probability than the other three processes. Neither of the two possible fluorescence emissions is observed while the emission that is observed has all the characteristics of emission from the first excited electronic state showing that direct internal quenching to the first excited state must occur. This quenching is very rapid ($\sim 10^{-11}$ sec.) compared to the life time of the detected emission ($\sim 10^{-8}$ sec.). An alternative theory (BIRKS 1953) suggests that excitation into the higher electronic states is followed by ultra-fast fluorescence ($\sim 10^{-11}$ - 10^{-12} sec.) to the ground state with 100% efficiency. The neighbouring molecules reabsorb the emission and the process recurs until excess vibrational energy is dissipated thermally and the molecule is in the first excited state where normal fluorescence occurs.

1. 3. SPECTRAL RELATIONSHIPS IN AROMATIC HYDROCARBONS - PREVIOUS WORK:

During 1951 a programme of research was initiated at Rhodes University on many of the fluorescence characteristics of the well-known efficient organic phosphors, e.g. anthracene, trans-stilbene, para-terphenyl and diphenylacetylene, which are of particular interest in scintillation counting. Among these characteristics are the scintillation and photo-fluorescence decay times and their dependence on temperature, the scintillation efficiency and its temperature dependence, the scintillation response

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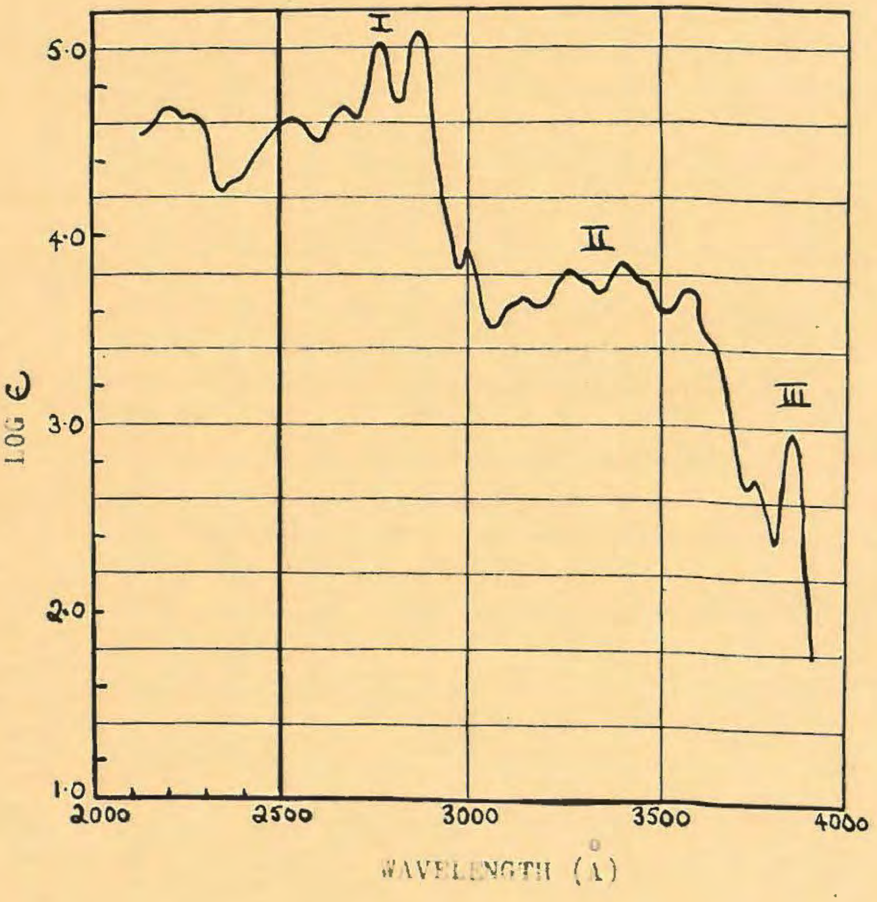
FIG. 3. Absorption of 1:2 benzanthracene showing group I, II & III bands.



to ionizing particles of different specific ionization and of different range, and the photo-fluorescence quantum efficiency. Many important results have already been obtained and BIRKS (1953, 1954) has developed a quantitative theory which agrees with these and other experimental data.

1. 3.1. ABSORPTION SPECTRA:

Absorption spectroscopy in the ultra-violet is a well established and important tool for the study of organic compounds in liquid solution. Prominent amongst those who have used this technique for the study of polycyclic aromatic compounds are MAYNEORD & ROE (1935), JONES (1947) and particularly CLAR (1952) who has reviewed in some detail the investigations into the spectral relationships of these compounds. The absorption spectra due to electronic transitions are considerably complicated by the superimposed vibrational fine structure and for this reason infra-red and Raman spectra are often employed by chemists for the analysis of compounds. Characteristic groups of bands are obtained for each chromophoric group of the molecule, and these spectra are more sensitive to small changes in the molecular structure, e.g. position of methyl substituent, than the corresponding electronic spectra. Most of the complex aromatic hydrocarbons give rise to absorption in three well defined regions of the ultra-violet and/or the visible regions.

The shortest wavelength region of absorption, group I bands, usually has $\log \epsilon_{max} \sim 4.5$ to 5.2 where ϵ_{max} is the maximum molar extinction coefficient; the next group, group II bands has $\log \epsilon_{max} \sim 3.6$ to 4.1, and the third group III bands, is a region of low intensity absorption with $\log \epsilon_{max} \sim 2.3$ to 3.2. FIG. 3 is the absorption of 1:2 benzanthracene and is a typical spectrum showing the three groups of bands.

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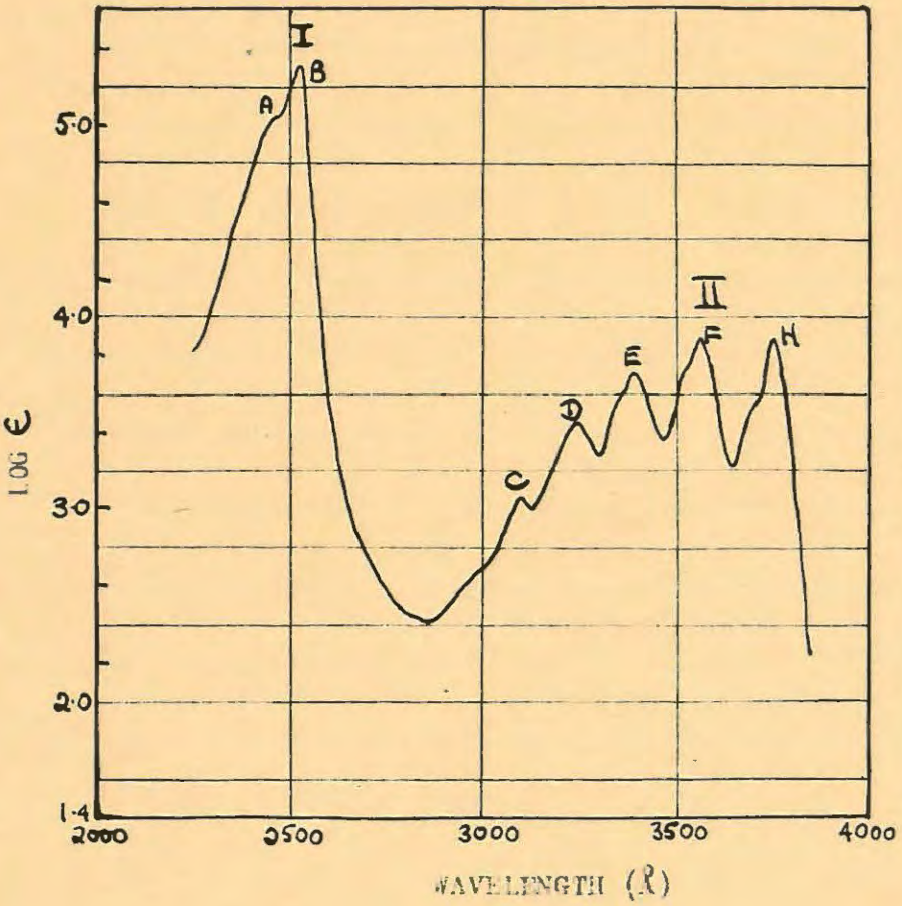
FIG. 4. Absorption of anthracene showing only group I & II bands.



The nomenclature of these bands is not fixed and they have been called the β, p and α bands by CLAR (1952) and ^1B_b, ^1L_a, ^1L_b, by KLEVENS & PLATT (1949).

CLAR found that not only do the polycyclic hydrocarbons give rise to regions of absorption closely related to those of benzene but that the shifts produced by linear or angular "anellation" follow certain definite and simple rules. In the polyacenes, for example, the series of linear homologues of benzene all the absorption bands are progressively displaced towards longer wavelengths as the number of rings increases. As the length of the molecule increases, the group II bands are shifted to a greater extent than the group III and group I bands, with the result that in anthracene and the higher polyacenes, the group III absorption is "swamped" under that of group II, and the absorption band of longest wavelength becomes the "p" band according to CLAR and the ^1L_a according to KLEVENS & PLATT. Similarly, three main groups of absorption may be discerned usually in the spectra of "angular" polycyclic compounds, but the shift of the group II bands with increasing number of benzene rings is much smaller than for linear annelation and the absorption spectrum of 1:2 benzanthracene shows the weak group III bands. FIG. 4 shows the absorption spectrum of anthracene in which only group I and II bands appear. Group I is represented by A and B and is due to excitation of the molecule into the second excited electronic state, that is the 0 → 2 electronic transition. Similarly the group II series at longer wavelength represented by C to H is the fundamental absorption of the molecule into its first singlet state, that is the 0 → 1 electronic transition. It is to this group that most attention is directed since the various maxima represent the vibrational sub-levelsof the first excited state and it is interesting to note that the frequency difference between the bands is practically constant and equal to 1400 cm.$^{-1}$ JONES (1947) associates these vibrational sub-levels with the carbon-hydrogen bending vibration of the molecule.

1. 3.2. FLUORESCENCE SPECTRA:

In fluorescence only the transition equivalent to the absorption band of longest wavelength is observed. To some extent, fluorescence is the reverse of absorption, for, while absorption corresponds to the excitation of π-electrons from the ground state to one of the vibrational levels of the excited state, fluorescence represents the return of the π-electrons from the lowest vibrational level of the excited state, to the ground state. BOWEN (1947) has stated that while the constant wavenumber spacing which is observed in the absorption spectrum corresponds to the vibrational sub-levels of the first excited state, the similar constant frequency spacings in the fluorescence spectrum correspond to the vibrational sub-levels of the ground state. Hence, the so-called "mirror-image" relationship (previously referred to in 1:2) between absorption and fluorescence spectra (PRINGSHEIM 1949) applies equally to the polycyclic aromatic hydrocarbons, and the same relationships noted in absorption are to be found in fluorescence spectra. That is to say (i) substitution generally shifts the fluorescence bands to longer wavelengths and (ii) angular or linear fusion of further benzene rings also shifts the position of the bands to longer wavelengths, the magnitude of the shift being greater for linear fusion. However, compared with ultra-violet absorption spectroscopy, relatively little use has been made of fluorescence spectroscopy, despite the success of the classic researches by which 3:4 benzpyrene, the potent carcinogen was identified and isolated from coal tar extracts by means of its fluorescence spectrum. KENNAWAY has described the fluorescence of this compound as "the single thread that led all through this labyrinth." However, in the last few years much research has been directed into the elucidation of the physical properties of the polycyclic aromatics, among the more important of which are:-

(i) Infra-red spectra (FUSON & JOSIEN 1956)

(ii) Phosphorescent spectra and singlet-triplet transitions (SZWARC 1955, McGLYNN, PADHYE & KASHA 1955).

(iii) Polarized absorption spectrum of anthracene (CRAIG et al 1955).

(iv) Fluorescent spectra at low temperatures (McCLURE 1954, SIDMAN & McCLURE 1956).

(v) Methyl affinities (LEVY & SZWARC 1954 COULSON 1955).

(vi) Theoretical treatments on the excited states of aromatic molecules based on the valence - bond and molecular orbital models (LONGUET-HIGGINS et al (1955) & MURREL (1955)).

The system usually used in these investigations was liquid solutions of the compounds, both for convenience and because approximations to the true molecular behaviour can be obtained by using dilute solutions. The important effect of molecular interaction in the solid state has received rather less attention, the first important work on the spectra of crystalline hydrocarbons being reported by KORTUM & FINCKH (1942) consisting of absorption and fluorescence spectra of anthracene in the vapour, liquid solution, and solid states. BOWEN & LAWLEY (1949) studied the effect of crystal size on fluorescence intensity and showed that the spectrum of the photo-fluorescence observed in transmission through an organic crystal is critically dependent on crystal thickness. Sometime after, BIRKS proposed his photon cascade process of emission and reabsorption of fluorescenc due to the overlap of emission and absorption spectra which was exhibited by LITTLE & BIRKS (1952). They measured the fluorescence transmission spectra of anthracene for

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various thicknesses ranging from a 1 cm. cube to a very thin flake where reabsorptio of the fluorescence is almost absent, and certainly small enough to allow resolution of the vibrational structure. These measurements confirmed those of KORTUM & FINCH and showed that due to the overlap of the absorption spectrum, there is a major difference between the molecular emission spectrum and the "technical"emission spectrum observed in transmission through a thick crystal. Approximately 80% of th fluorescence emission from the anthracene molecule is reabsorbed within the crystal. This self-absorption, followed by further emission and absorption processes, increas the molecular photo-fluorescence decay time from 6.3 mμ sec. to its technical value 24 ± 2 mμ sec. (HAMILTON 1958). BIRKS & WRIGHT (1954) used even thinner specimens of crystalline anthracene and obtained well resolved spectra approaching the true molecular emission.

1. 3.3. FLUORESCENCE AND CARCINOGENICITY:

This subject is dealt with in IV.4. but a brief introduction is necessary here before proceeding to IV because nearly all the more potent carcinogens are fluoresce and many of the compounds studied in the present work are carcinogenic. Much work has been done by A. & B. PULLMAN (1955) on the electronic structure of the aromatic hydrocarbons in relation to carcinogenicity. Their work shows that electronic structure plays an important role in carcinogenic potency, and it was thought that the present measurements on electronic spectra would throw further light on these important biophysical and biochemical properties. The most important work done previously on relationships between spectra and carcinogenicity is that of SCHOENTAL SCOTT (1949), who observed the fluorescence spectra of 78 polycyclic aromatic hydrocarbons in dilute solutions. A relationship between the position of the fluorescence bands and the "reactivity" of the molecule was reported (a similar relation was found by CLAR for absorption spectra), but since little information on the reactivity of polycyclic compounds is available this relationship is regarded as somewhat fortuitous. It was also stated that no direct relation between carcinogenicity and the position or intensity of the fluorescence spectrum could be detected. This work is important since it represents the first attempt to investigate the similarities and differences in the fluorescence spectra of closely related compounds, the interpretation of which may produce further data on the structure of the molecule.

1. 3.4. PRESENT WORK:

The spectral measurements described in the present work were obtained using an apparatus similar to but more refined than that used by BIRKS & WRIGHT (1954). The purpose of the investigation was :-

(a) To study crystalline spectra for a whole range of related fluorescent aromatic hydrocarbons, which has not previously been done for compounds more complex than anthracene. Comparisons have been made between the spectra of compounds belonging to a particular structural series, and some interesting discoveries are reported.

(b) To search for any crystalline interaction effects on the fluorescence spectra of the compounds. This is done by comparing the spectra of molecules bound in a crystalline lattice (present results) with the spectra of the free molecules of the same compounds in dilute liquid solution, obtained by SCHOENTAL & SCOTT (1949).

II. MEASUREMENT OF FLUORESCENCE SPECTRA AND DECAY TIMES.

II. 1. EXPERIMENTAL ARRANGEMENT:

The fluorescence spectra were excited with monochromatic radiation of wavelengt 253.7 mμ. It can be seen from the absorption spectra that the extinction coefficient of each of the compounds studied is so high at this wavelength that the exciting wavelength is completely absorbed in a very small thickness of the order of a wavelength. This is very convenient since it allows extremely thin layers of crystalline material to be used, without transmission of any incident radiation, thereby preserving similar fluorescence efficiencies for various thicknesses.

An intense steady source of radiation was obtained from a 7 watt Model 11A Hanovia quartz envelope mercury discharge tube, in which a large fraction of the radiation energy is of 253.7 mμ wavelength. The discharge tube was placed centrally in the entrance plane of a small quartz spectrograph from which the norma slit mechanism had been removed. The removal of the slit allowed more light into the spectrograph so that an exciting line of greater intensity could be obtained. An intense image of the 253.7 mμ line, completely resolved from the other mercury emission lines, was formed in the exit plane of the spectrograph. This radiation w then focussed onto the specimen under investigation. The fluorescence spectra were measured using a Cenco-Sheard grating "spectrophotelometer" to monochromate the fluorescence emission and an E.M.I. 6262 photomultiplier tube as a detector. The photomultiplier was operated from a stabilised power supply and had a gain of 10^7 at

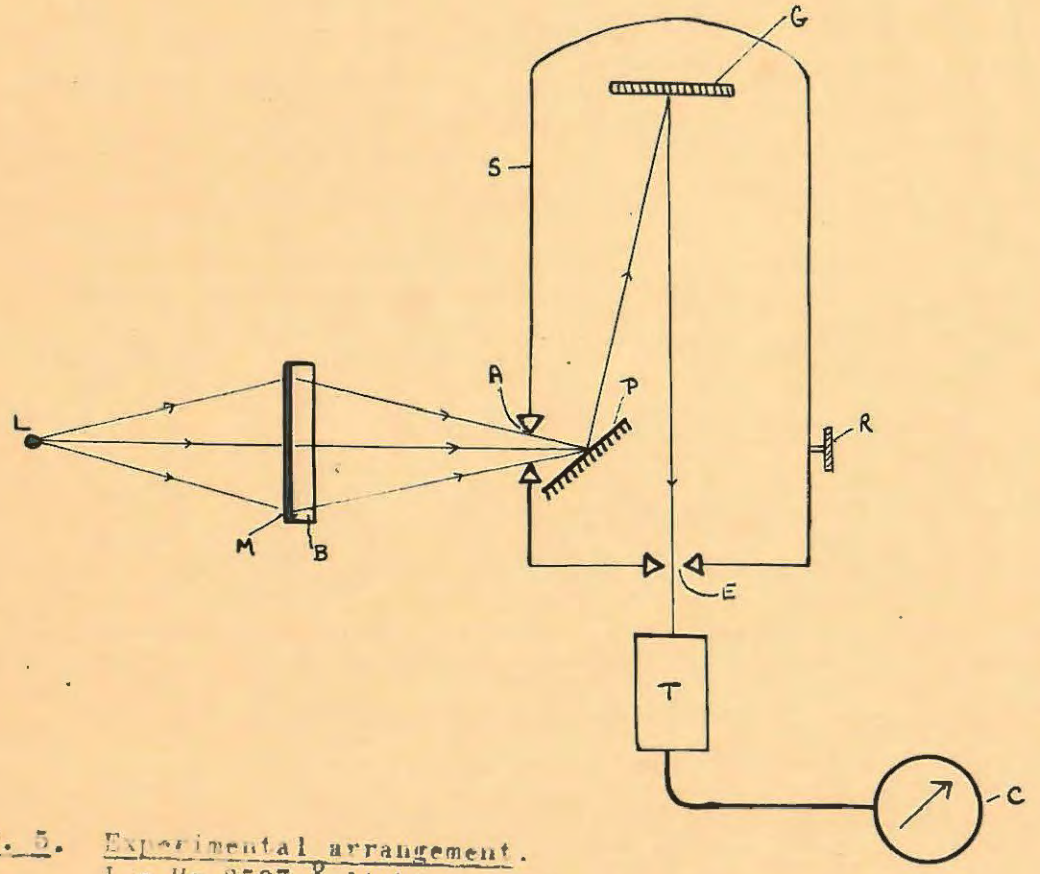


FIG. 5. Experimental arrangement.

L = Hg 2537 Å light source;
M = microcrystalline specimen;
B = glass backing plate;
A = spectrometer entrance slit;
S = spectrometer;
P = front aluminised plane mirror;
G = concave diffraction grating;
R = screw for rotating grating;
E = spectrometer exit slit;
T = photomultiplier tube;
C = sensitive galvanometer.

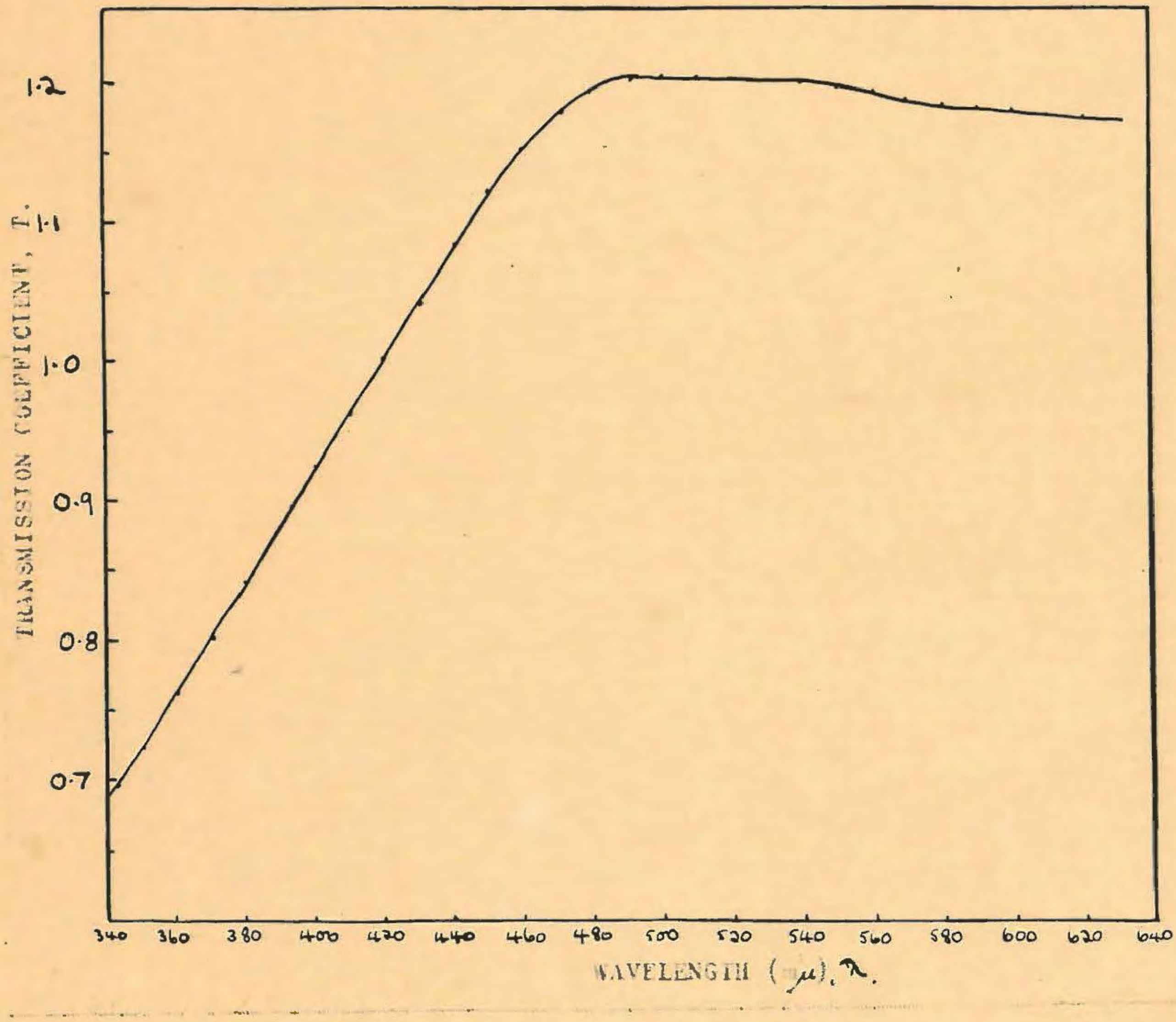
maximum allowable interstage voltage (200 V. per stage). It was coupled to a very sensitive galvanometer through a Universal shunt and the intensity of fluorescence was read off as a galvanometer deflection. Since the intensity of fluorescence over the spectral range considered varied over wide limits, it was necessary to use the Universal shunt in several different positions and, therefore, in order that the deflection should be directly proportional to the fluorescence intensity, the linearity of the galvanometer was checked for all shunt settings.

In order that the fluorescence spectra should represent the true relative emission over the whole spectral range measured, the variation of sensitivity of the photomultiplier with wavelength must be known. This calibration was carried out by Dr. M.E. Szendrei and is outlined briefly in a paper by BIRKS & SZENDREI (195 Large variations in the spectral response of photomultiplier tubes occur so that the manufacturer's calibration is not sufficiently accurate for this work. The experimental method and results are recorded below.

11. 1.1. TRANSMISSION COEFFICIENT OF SPECTROMETER:

In the Cenco-Sheard spectrophotelometer light from an entrance slit is reflected by an aluminised mirror on to a concave diffraction grating, which focuses a narrow wavelength band through the constant width exit slit. The light emerging falls on a barrier layer photocell, which has a linear current response which is proportional to the intensity and is measured on a galvanometer. The grating moves a modified Eagle mounting, so that the Rowland circle passes through the exit slit fo all positions of the grating. With such an arrangement the wavelength band $d\lambda$ emerg from the exit slit is independent of the wavelength λ, for a fixed slit width. The spectrometer is shown diagrammatically in FIG. 5. A narrow wavelength band was

FIG. 8. Transmission coefficient, T, of spectrometer vs. wavelength, λ.



selected by a monochromator (actually a Beckman Model D.U. spectrophotometer), and focussed on the entrance slit of the spectrometer, which was set for this wavelength. All the incident light passed through the entrance slit and, after dispersion, it did not exceed the exit slit width which was kept to its maximum. The intensities of the light before and after passing through the spectrometer were compared using the barrier photocell. The transmission coefficient, T, of the instrument at wavelength λ thus obtained is plotted in FIG. 6.

11. 1.2. RELATIVE SPECTRAL RESPONSE OF PHOTOMULTIPLIER:

The monochromatic light was replaced by a standard tungsten lamp of known colour temperature, and hence of known spectral energy distribution. The photomultiplier, which was connected to the sensitive linear galvanometer, was used to view the light from the exit slit of the spectrometer. The relative response, R, of the photomultiplier (in arbitrary units) can then be obtained as a function of the wavelength λ, since the galvanometer deflection is proportional to the product eTR, where e is the emissivity of the lamp at wavelength λ and $d\lambda$ is constant for the instrument. The variation of R with λ for the particular photomultiplier tube used is shown in FIG. 7, where the average curve for this type of tube is also shown for comparison. It will be noted that although the maxima of the curves coincide, considerable differences occur, particularly at longer wavelengths.
The combined correction curve for the overall spectral response of the spectrophotelometer and photomultiplier together is shown in FIG. 8.

11. 2. PREPARATION OF CRYSTAL SPECIMENS:

The earlier measurements of fluorescence spectra in the solid state (BIRKS &

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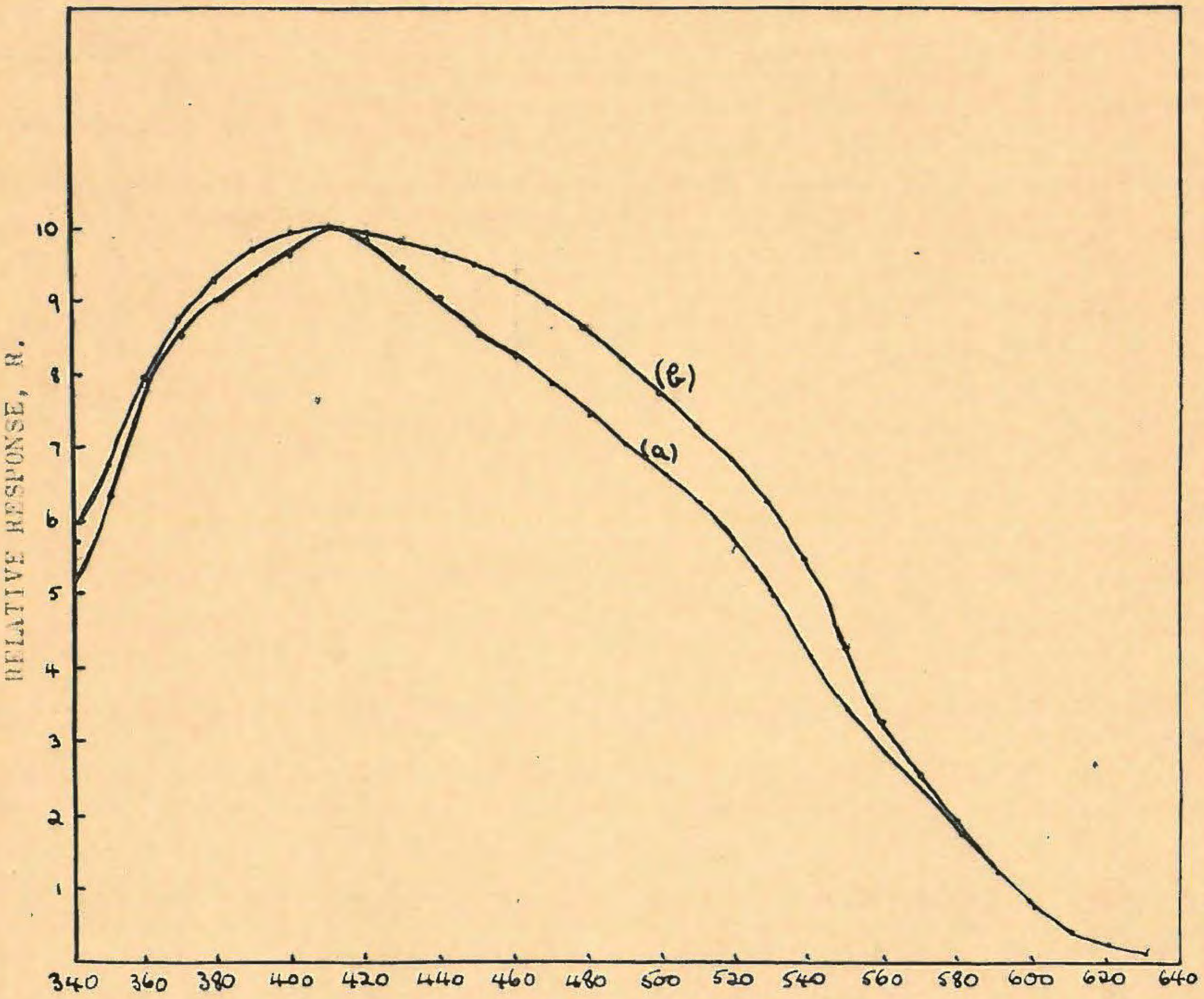
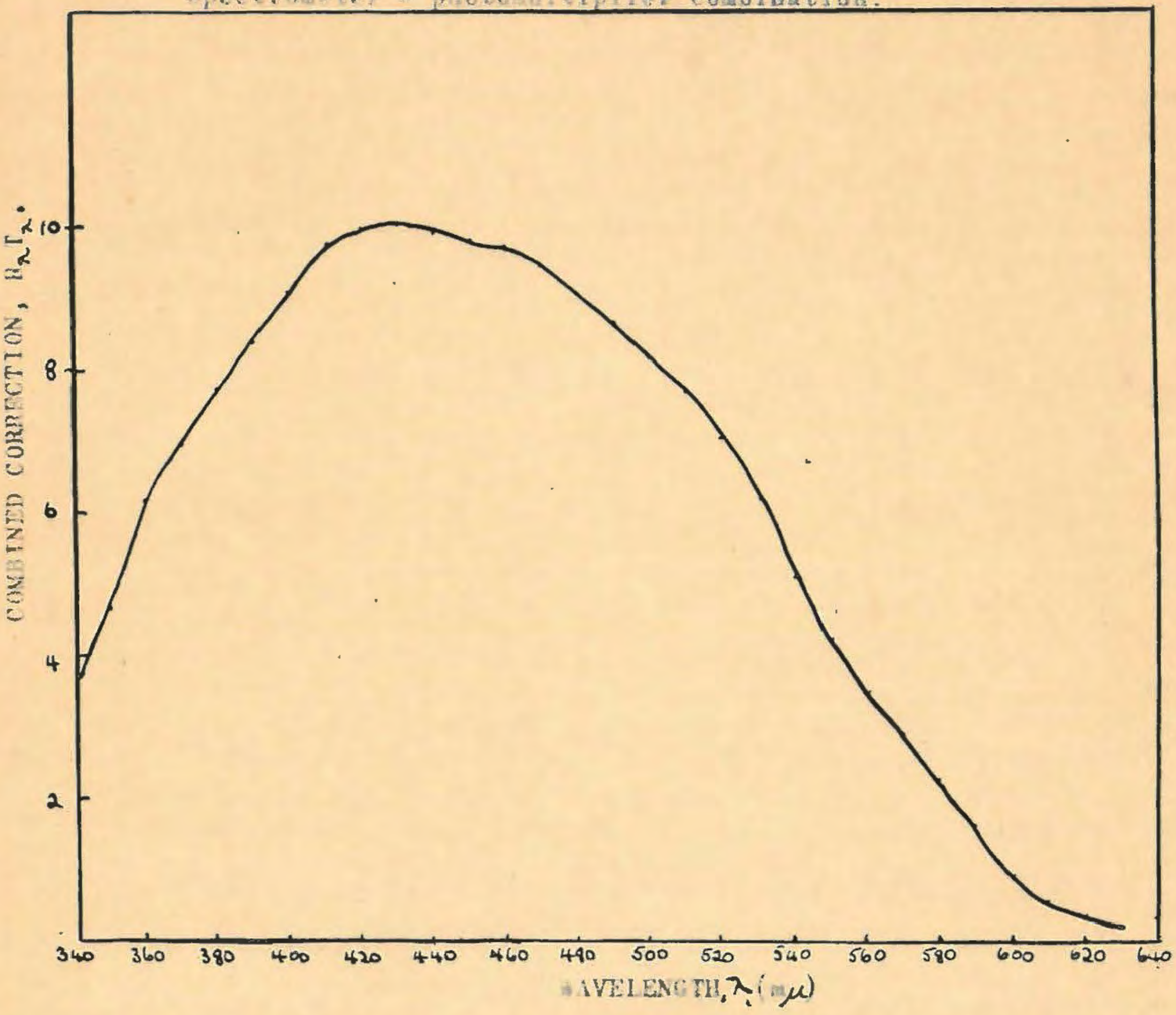
FIG. 7. Relative response, R, of photomultiplier vs. wavelength, λ. (a) Measured response; (b) Manufacturer's calibration.



LITTLE 1953) showed the importance of using extremely thin specimens to obtain resolution of the vibrational structure. These early measurements were made on very thin flakes, which, however, were very much thicker than the mean free path of a fluorescence photon produced near the surface. Later measurements by BIRKS & WRIGHT (1954) were made using specimens about 2μ thick which were formed by evaporation from xylene solution. These specimens gave spectra much nearer to the true molecular emission and all the vibrational maxima were resolved. Before the present measurements were commenced, the method of preparation of anthracene specimens used by BIRKS & WRIGHT was repeated using the same xylene. The xylene was not highly purified and was slightly coloured. The inclusion of impurities may, if they are fluorescent, influence the spectrum of the solute very strongly, but this effect is absent in their readings. However, microscopic examination of such specimens showed that they were non-uniform in thickness and this was thought to be partly due to the relatively poor volatility of xylene which allowed the solute to crystallize out preferentially around the first microcrystal. Warming the plates before evaporation did not improve the specimen as the xylene did not flow evenly over the heated surface. More volatile solvents were, therefore, tried in place of xylene, and of these the spectroscopically pure grade of chloroform, cyclohexane and acetone were found to be the most suitable. Microcrystalline layers evaporated from these solvents were finely grained, and gave an intense fluorescence, uniformly distributed over the surface. Since the fluorescence was fairly intense compared with specimens prepared from xylene solution, the obvious advantage presented itself of the possibility of using considerably thinner specimens whose emission was intense enough to be detected by the photomultiplier, thus allowing greater resolution of the vibrational structure. A series of spectra of anthracene

FIG. 8. Combined correction curve, $R_\lambda T_\lambda$, vs. wavelength λ for spectrometer - photomultiplier combination.



were measured for specimens of thicknesses ranging from 2μ to 0.01μ prepared from cyclohexane solutions. It was found that the intensity of the shortest wavelength peak is very sensitive to changes in specimen thickness, a decrease in intensity being exhibited for each successive increase in sample thickness, and in order to obtain as close an approximation to the true molecular emission as possible, the thickness of the layer should be reduced as much as possible. The limiting optimum condition applied to the reduction of thickness is supplied by the sensitivity of the apparatus. The thickness must be such that the fluorescence intensity emitted is sufficient to be detected by the photomultiplier after it has passed through the spectrophotelometer. The thickness chosen which satisfied these conditions was 0.1μ. For practically all the compounds studied, it is estimated, from solution absorption data (FRIEDEL & ORCHIN 1951), that over 90% of the incident radiation is absorbed in the specimen.
On the other hand, the specimens are almost completely transparent to their own fluorescence emission, except at the shortest wavelengths.

BIRKS & WRIGHT prepared their specimens on fused quartz plates but these were found to be feebly luminescent and the specimens used in the present studies were mounted on plane glass plates which were non-luminescent in the spectral region of interest. This is discussed further in III.2.1. The method of depositing the solution on the glass plates was as follows :-

A capillary tube of measured bore was used as the "dropper". A fixed mark was made along the tube which determined the height to which the solution was drawn into the capillary. The volume of liquid thus contained in the tube and which was finally deposited on the circular glass plate was, therefore, known. The surface area of the glass plate was calculated and hence for a given thickness of solute to cover this surface area, the required concentration of solution could be calculated. Since very small quantities of the compounds studied were available, it was found convenient to prepare 2 ml. of solution containing approximately 1.5×10^{-3} gm. of solute. This value, which was calculated for anthracene, depends on the density of the compound. However, the density of all the compounds studied is similar and far greater errors are introduced in the weighing, so that this mass of solute was weighed approximately for each compound. The solution was deposited on the glass plate in one drop which completely covered the area and was prevented from overflowing by surface tension. Uniform evaporation left a very fine polycrystalline surface of apparant uniform thickness, but the size of the individual microcrystals differed with the solvent. This was unavoidable in some cases as the solvents were chosen primarily by solubility considerations. Cyclohexane has been used wherever possible but it has sometimes been necessary to employ chloroform or acetone and all the compounds were soluble in at least one of these solvents. They are indicated in Tables by the letters (a) cyclohexane, (b) chloroform and (c) acetone.

II. 2.1. PURITY OF SAMPLES:

The degree of accuracy of fluorescence data depends on the sharpness of the bands. Not only is this a characteristic of some electronic transitions, but it is also associated with the state of "fluorescence purity" of the specimen. The criteria of purity for fluorescence spectrography are different from those for other purposes, as small traces of strongly fluorescent impurity may completely vitiate the fluorescence spectrum of the compound, and care must be taken to exclude even weakly fluorescent impurity. On the other hand, contamination with non-fluorescent materials

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is usually of little importance. The fact that compounds of similar structure exhibit fluorescence spectra of similar pattern furnishes a useful guide to the reliability of the spectra. Thus the persistence of the set of bands observed in the majority of the 1:2 benzanthracenes indicates that these bands are a characteristic feature of the spectra of hydrocarbons of this character. A further check was made on identical compounds derived from different sources. The compounds used in this investigation were donated by Professor Newman of Ohio State University, Prof. J.W. Cook and Dr. E. Clar of Glasgow University and Prof. E. Bergel of the Chester Beatty Research Institute, who assure their purity.

11. 3. PLOTTING THE FLUORESCENT SPECTRA:

The microcrystalline specimen 0.1μ thick was supported in the same horizontal plane as the entrance slit of the spectrometer. There are three alternative ways of observing the fluorescence emitted; these are :-

(a) In reflection from the front surface of the specimen. This was the method originally used to determine a suitable standard specimen thickness. The front surface of the specimen was illuminated with the exciting light and placed near to the entrance slit of the spectrograph so that the fluorescence emitted from the surface entered the instrument. Allowing the fluorescence to enter the spectrometer directly was found to be more efficient than focussing the fluorescence light on to the entrance slit with quartz lenses,

(b) In transmission through the specimen. The specimen was placed as close to the entrance slit of the spectrometer as possible and illuminated as shown in FIG.5. Precautions were taken to prevent stray light from the visible mercury lines from entering the spectrometer, the scattered 2537 Å radiation being unimportant since spectra were not observed below 3400 Å. This method was found to be so successful that the spectra for all the compounds were eventually plotted using this geometrical arrangement, with physical conditions, including temperature, kept constant.

(c) This method consisted of observing the fluorescence emitted through the edge of the glass plate on which the specimen was mounted, but the intensity of emission in this direction was found to be too low.

From now on, reference will be made to the measured "fluorescence spectra" and it is to be implicitly understood that these readings were taken in transmission through the specimen whose thickness was approximately 0.1 μ. The relative intensity of the fluorescence, I, is proportional to the output current from the photomultiplier which is detected on a galvanometer. From this deflection, the relative quantum intensity $I/h\nu \propto I\lambda$ where h = Planck's constant, ν, the frequency of the fluorescence and λ the wavelength, was obtained and plotted as a function of wavelength.

II. 4. MEASUREMENT OF PHOTO-FLUORESCENCE DECAY TIMES:

The molecular photo-fluorescence decay times of 32 of the compounds were measured by HAMILTON (1958) using the same microcrystalline specimens used for spectral

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easurements. An improved form of the apparatus developed by BIRKS & LITTLE (1953) as employed. An ultra-violet source, consisting of a high frequency discharge tube, modulated at a frequency, f (12-30 Mc/s.), was used for excitation of the photo-fluorescence of the specimen. Observations were made with a photomultiplier, whose sensitivity was also modulated at frequency, f, and whose output current was measured with a sensitive galvanometer. The degree of modulation of the source, m_s, was measured by varying the phase of the photomultiplier sensitivity relative to that of the source intensity, and this was compared with a similar measurement of the degree of modulation of the specimen fluorescence, m_f. The fluorescence decay time τ_0 is given by:

$$\tau_0 = \frac{\left[m_s^2 / (m_f^2 - 1)^{1/2} \right]}{2\pi f}$$

FIG. 21

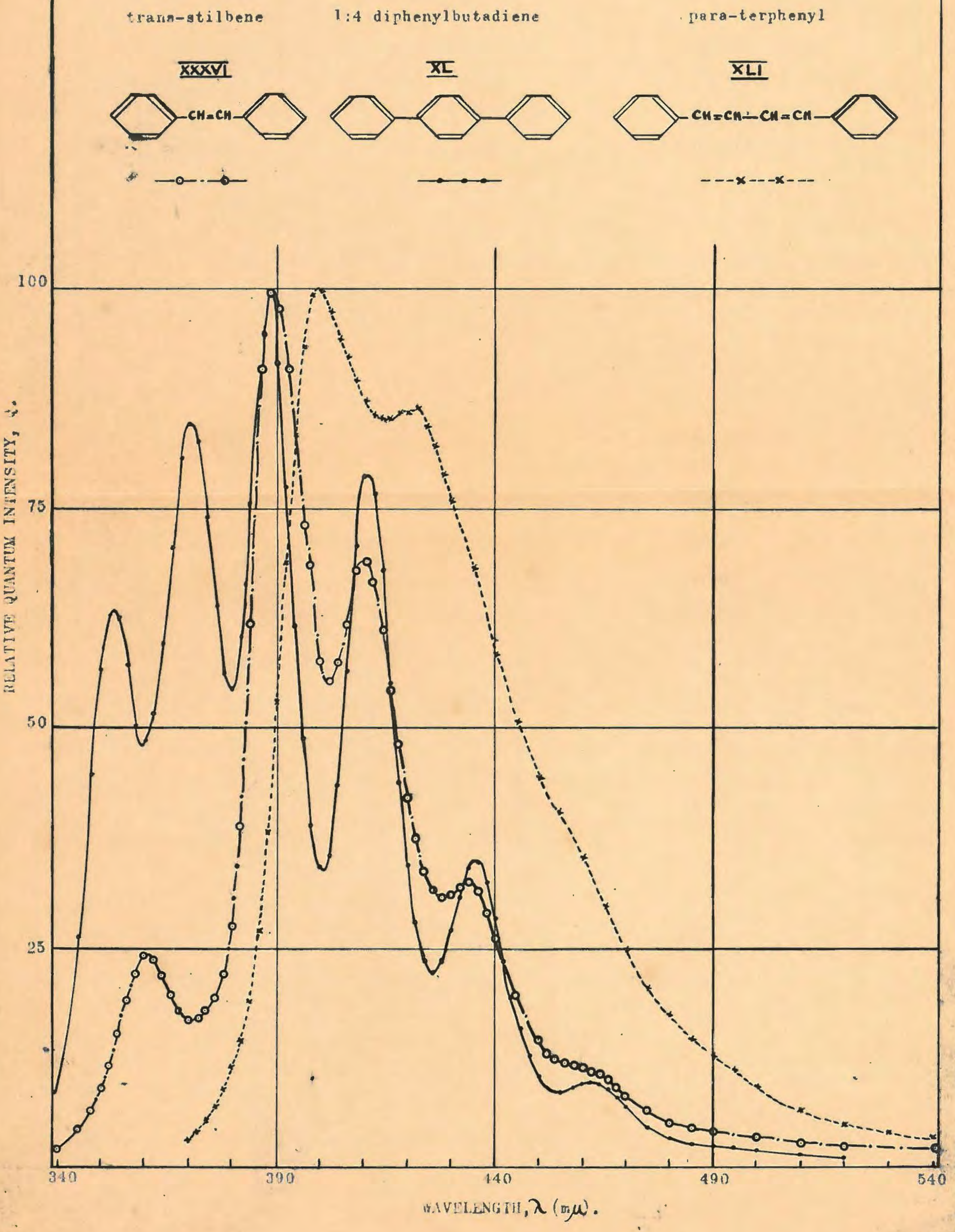

trans-stilbene
1:4 diphenylbutadiene
para-terphenyl
XXXVI
XL
XLI
CH=CH
CH=CH—CH=CH
100
75
50
25
340
390
440
490
540
RELATIVE QUANTUM INTENSITY, q.
WAVELENGTH, λ (mμ).

FIG. 20

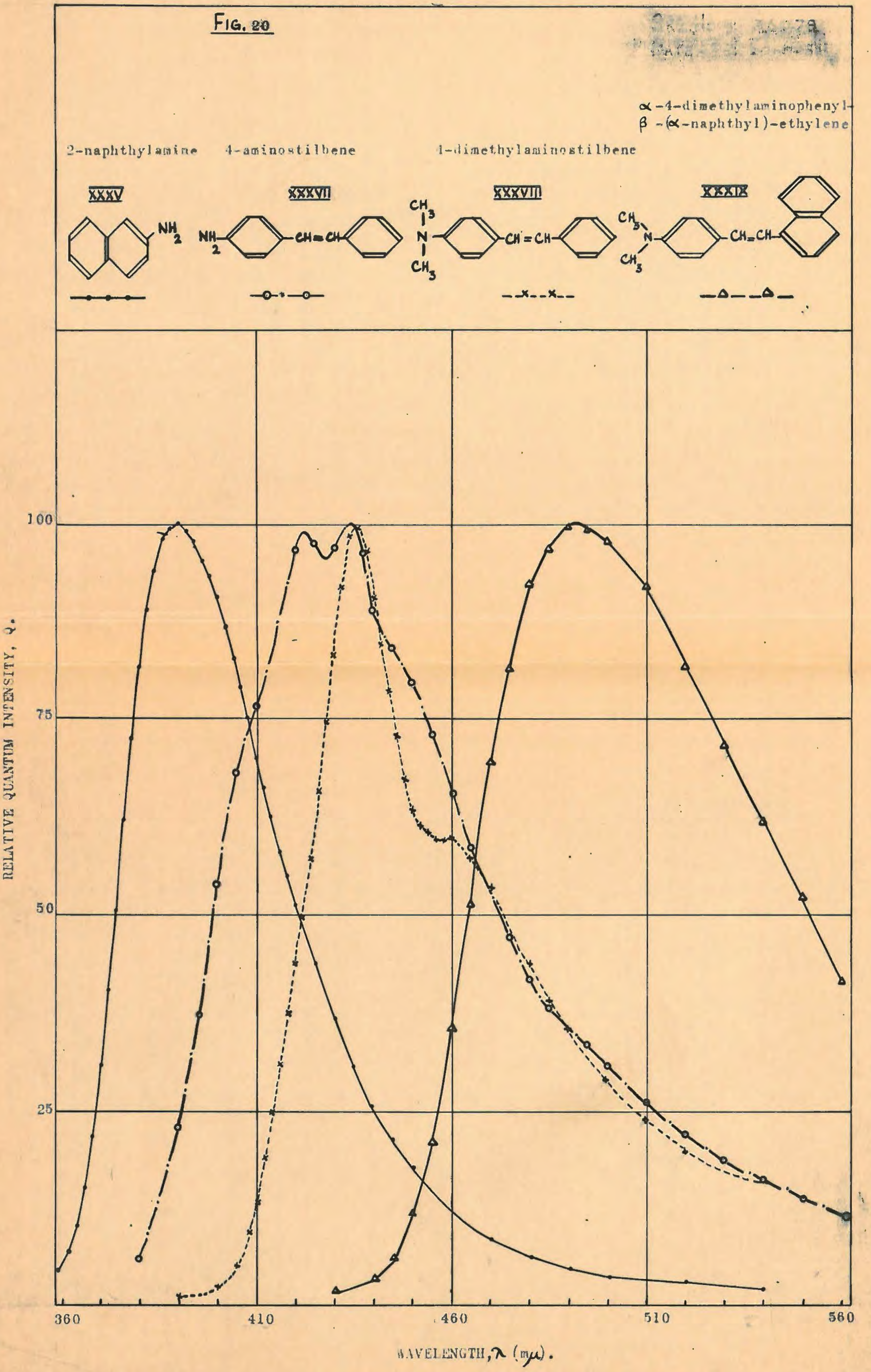

2-naphthylamine
4-aminostilbene
4-dimethylaminostilbene
α-4-dimethylaminophenyl-β-(α-naphthyl)-ethylene
XXXV
XXXVII
XXXVIII
XXXIX
NH2
CH=CH
CH3
N
RELATIVE QUANTUM INTENSITY, Q.
100
75
50
25
360
410
460
510
560
WAVELENGTH, λ (mμ).

FIG. 19.

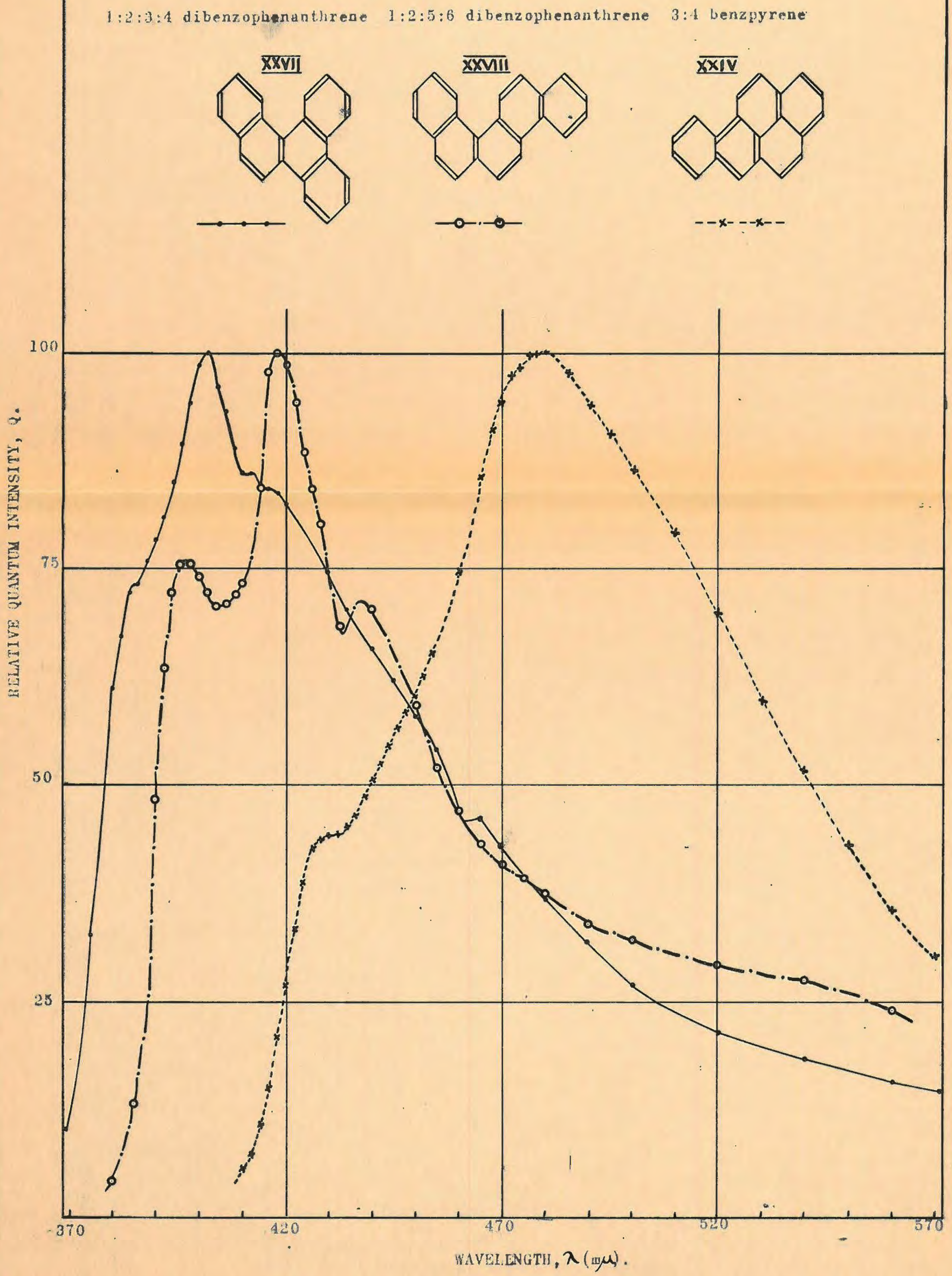

1:2:3:4 dibenzophenanthrene
1:2:5:6 dibenzophenanthrene
3:4 benzpyrene
XXVII
XXVIII
XXIV
100
75
50
25
RELATIVE QUANTUM INTENSITY, Q.
370
420
470
520
570
WAVELENGTH, λ (mμ).

FIG. 18

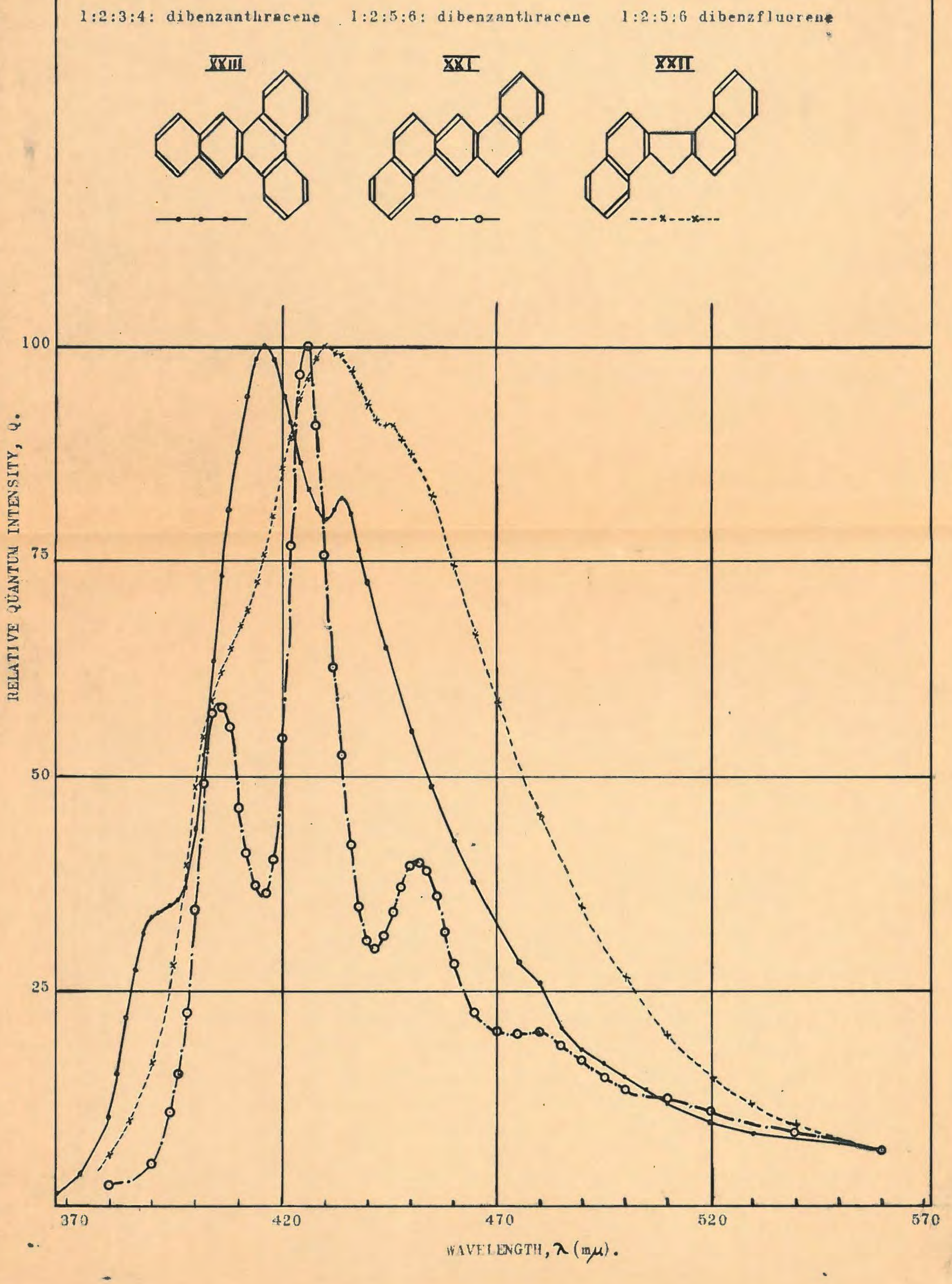

1:2:3:4: dibenzanthracene
1:2:5:6: dibenzanthracene
1:2:5:6 dibenzfluorene
XXIII
XXI
XXII
100
75
50
25
RELATIVE QUANTUM INTENSITY, Q.
370
420
470
520
570
WAVELENGTH, λ (mμ).

FIG. 17.

Derivatives of 3:4 benzophenanthrene

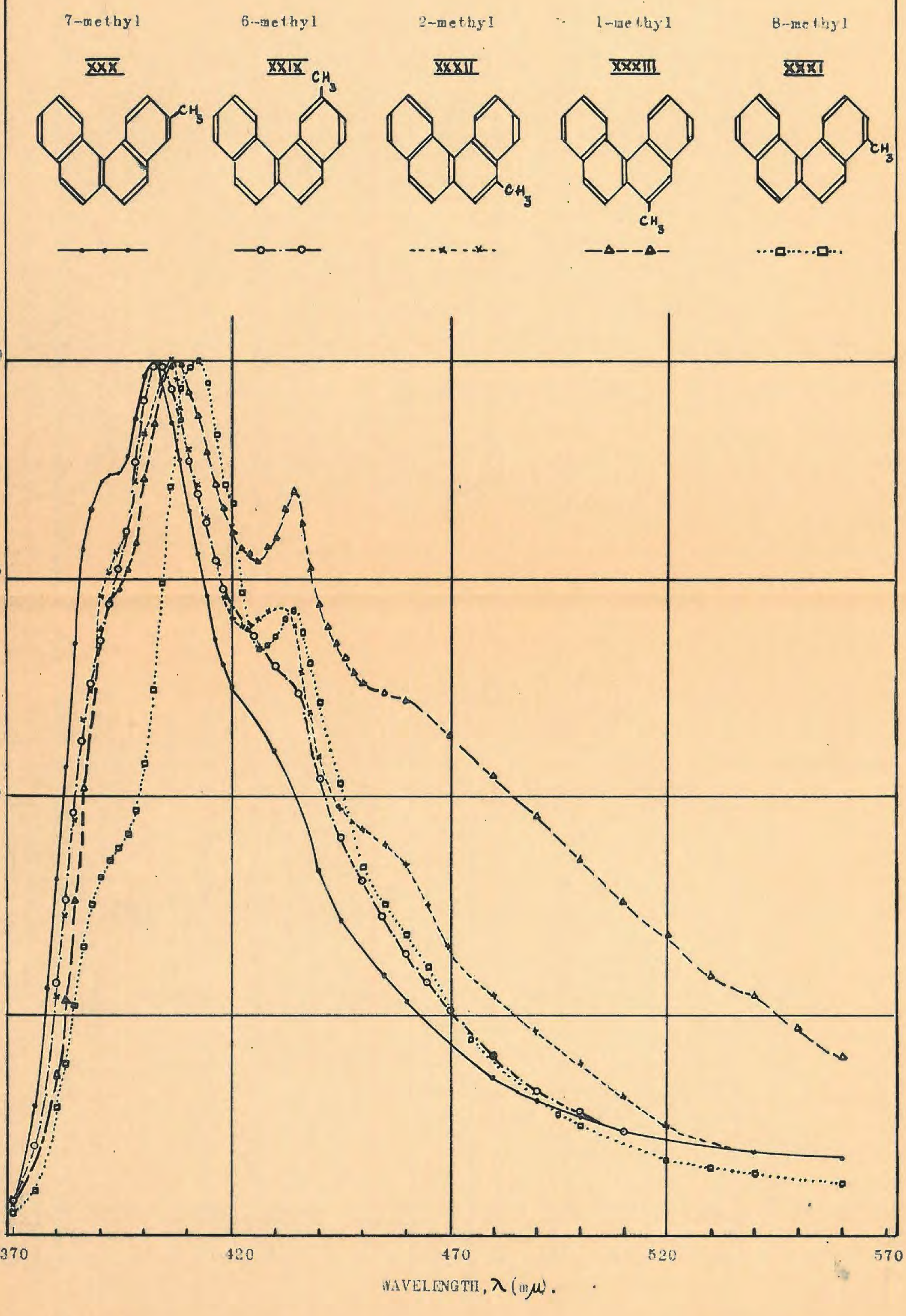


FIG. 16.

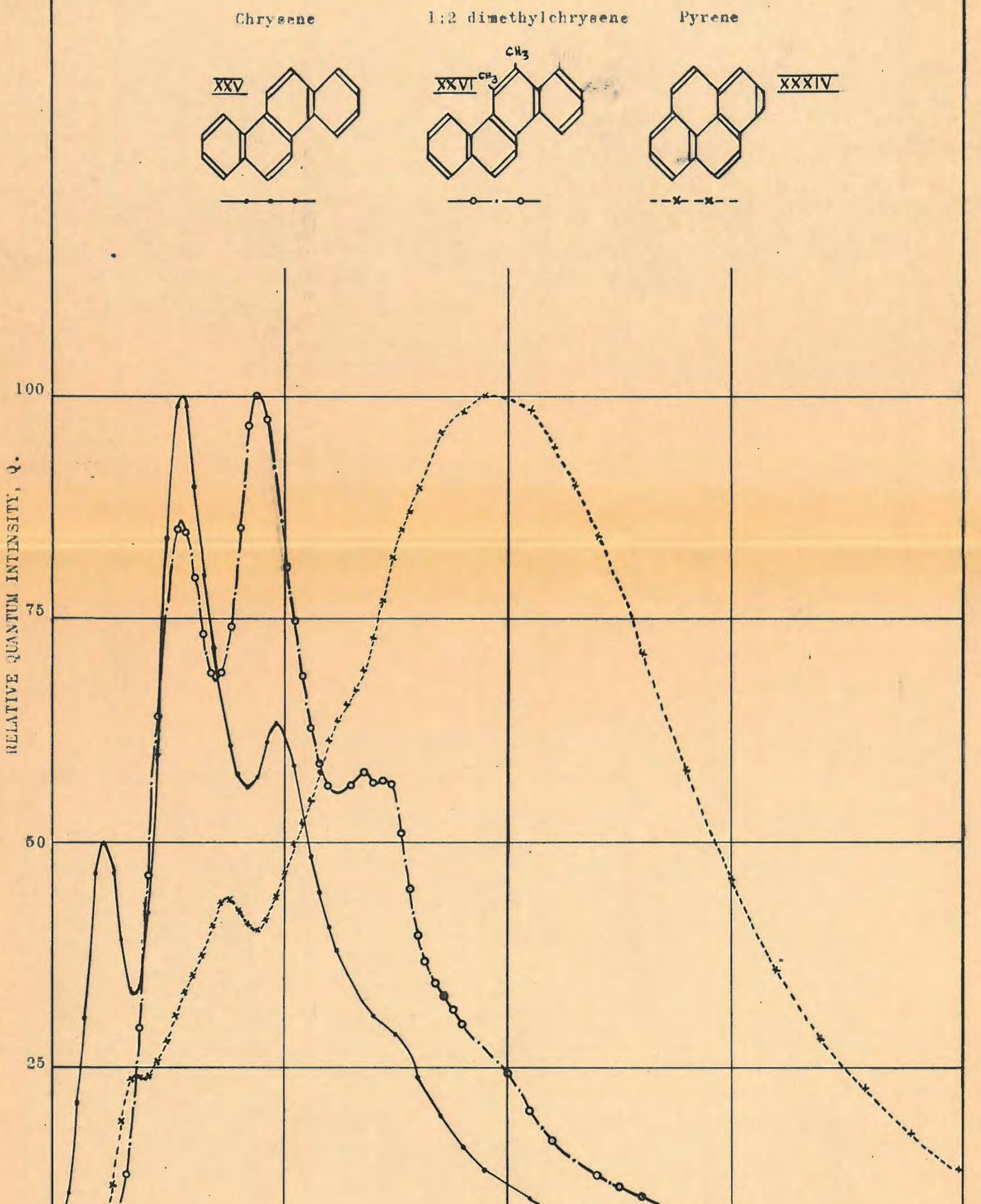

Chrysene
1:2 dimethylchrysene
Pyrene
XXV
XXVI
CH_3
CH_3
XXXIV
RELATIVE QUANTUM INTENSITY, ϕ.
100
75
50
25
360
410
460
510
560
WAVELENGTH, λ (mμ).

FIG. 15

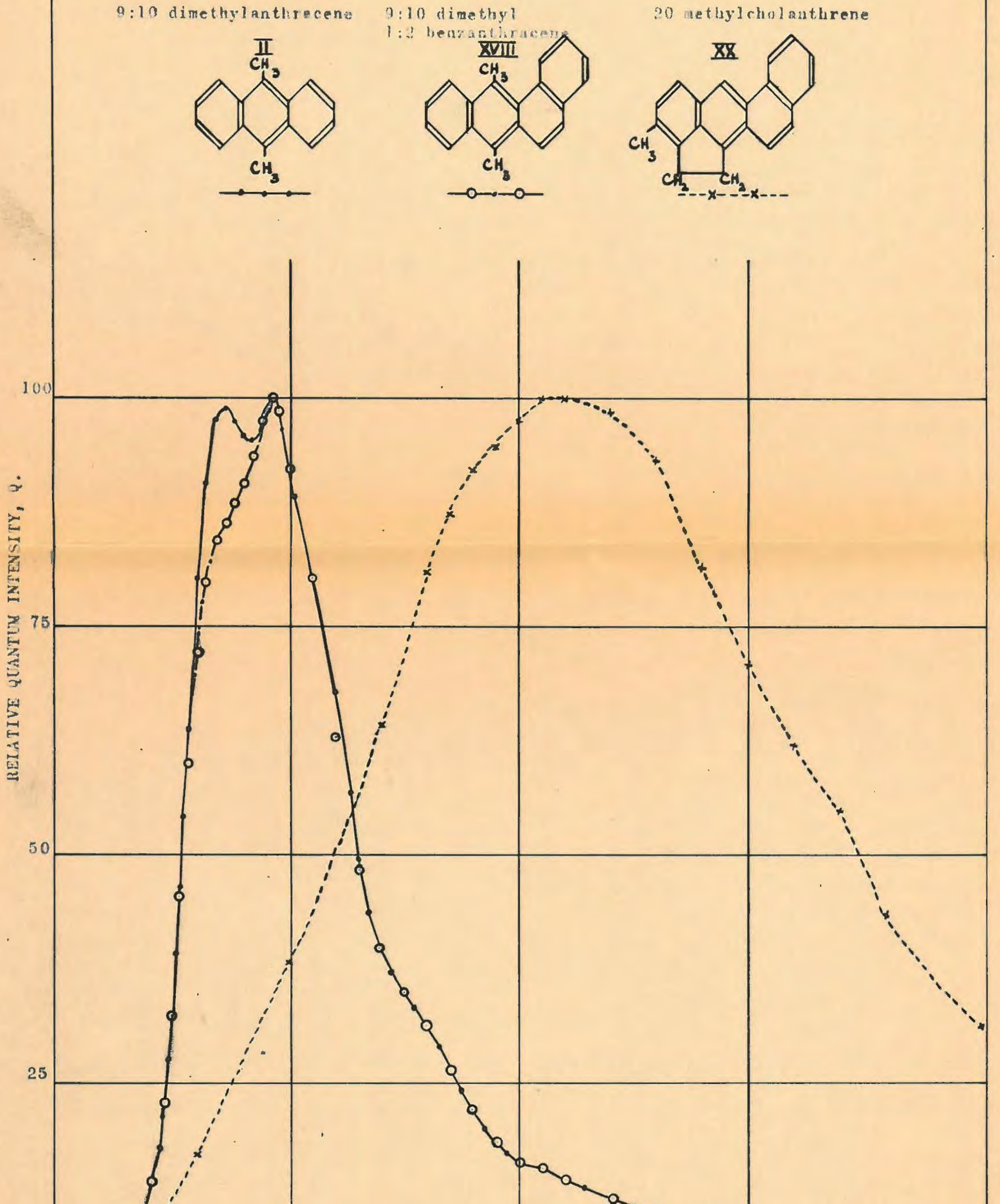

9:10 dimethylanthracene
II
9:10 dimethyl 1:2 benzanthracene
XVIII
20 methylcholanthrene
XX
CH_3
CH_2
RELATIVE QUANTUM INTENSITY, Q.
100
75
50
25
400
450
500
550
600
WAVELENGTH, λ (mμ).

FIG. 14

Derivatives of 1:2 benzanthracene

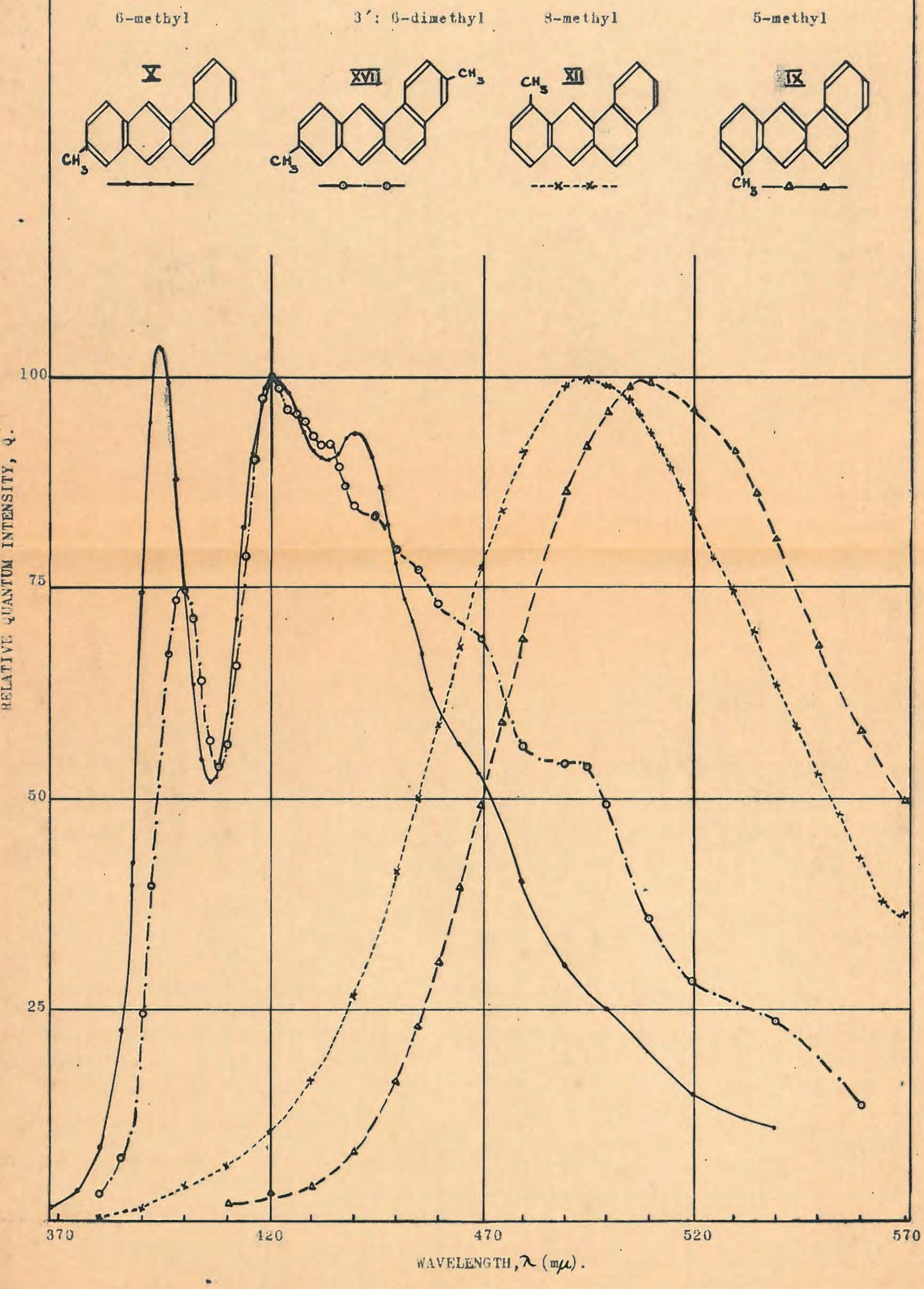


FIG.13

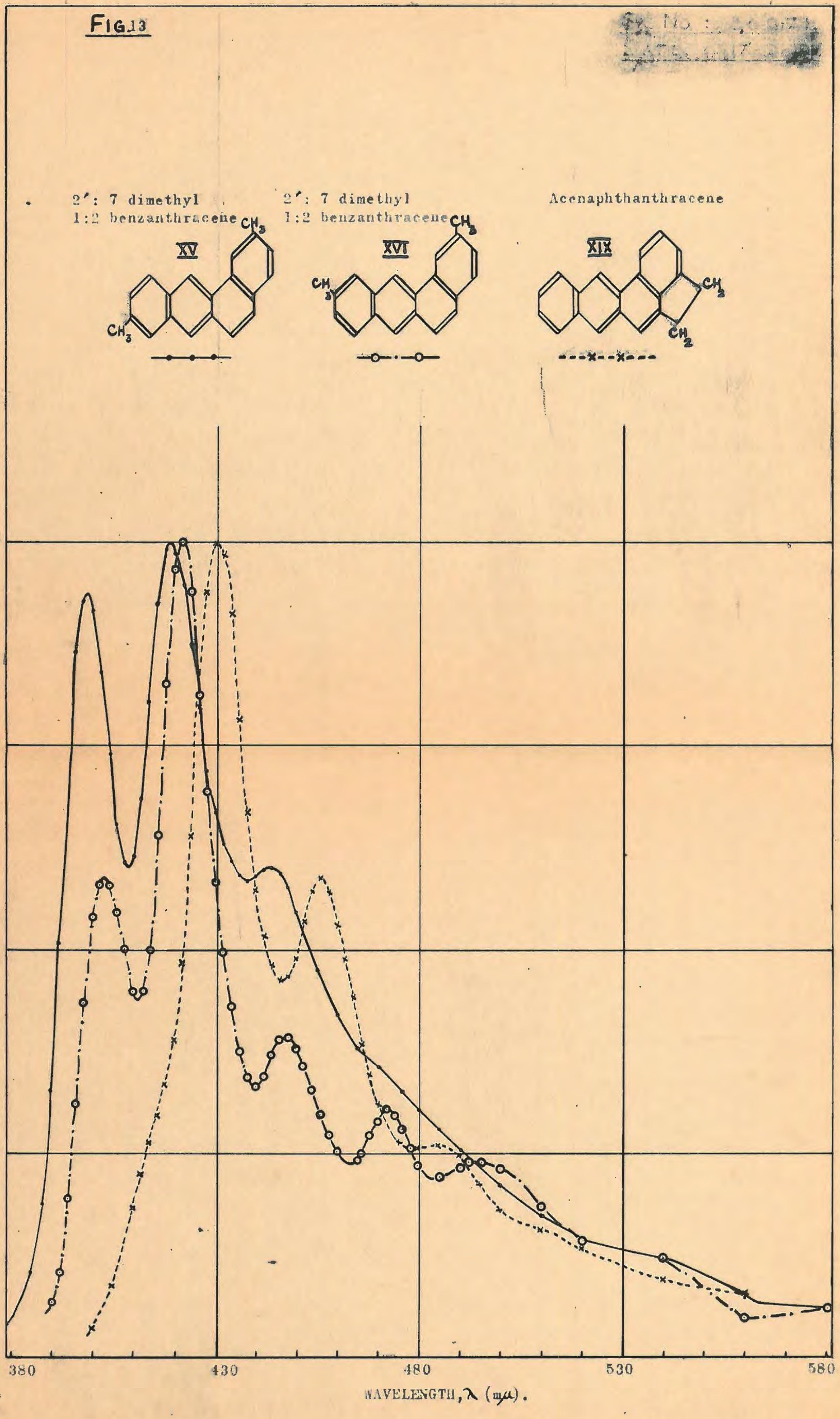

2': 7 dimethyl
1:2 benzanthracene
XV
CH3
CH3
2': 7 dimethyl
1:2 benzanthracene
XVI
CH3
CH3
Acenaphthanthracene
XIX
CH2
CH2
100
75
50
25
RELATIVE QUANTUM INTENSITY, q.
380
430
480
530
580
WAVELENGTH, λ (mμ).

FIG. 12

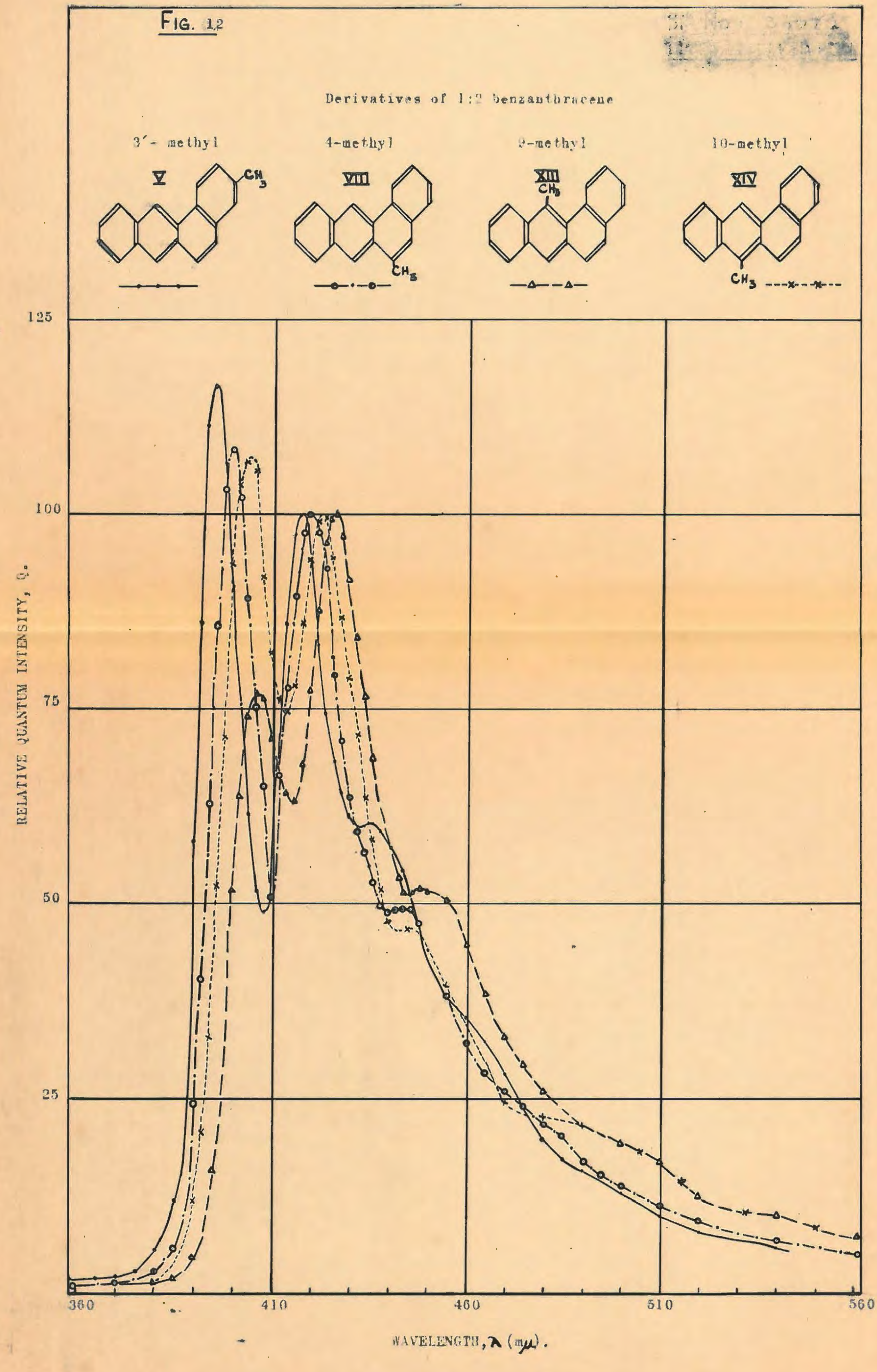

Derivatives of 1:2 benzanthracene
3′- methyl
V
CH3
4-methyl
VIII
CH3
9-methyl
XIII
CH3
10-methyl
XIV
CH3
125
100
75
50
25
RELATIVE QUANTUM INTENSITY, Q.
360
410
460
510
560
WAVELENGTH, λ (mμ).

FIG. 11

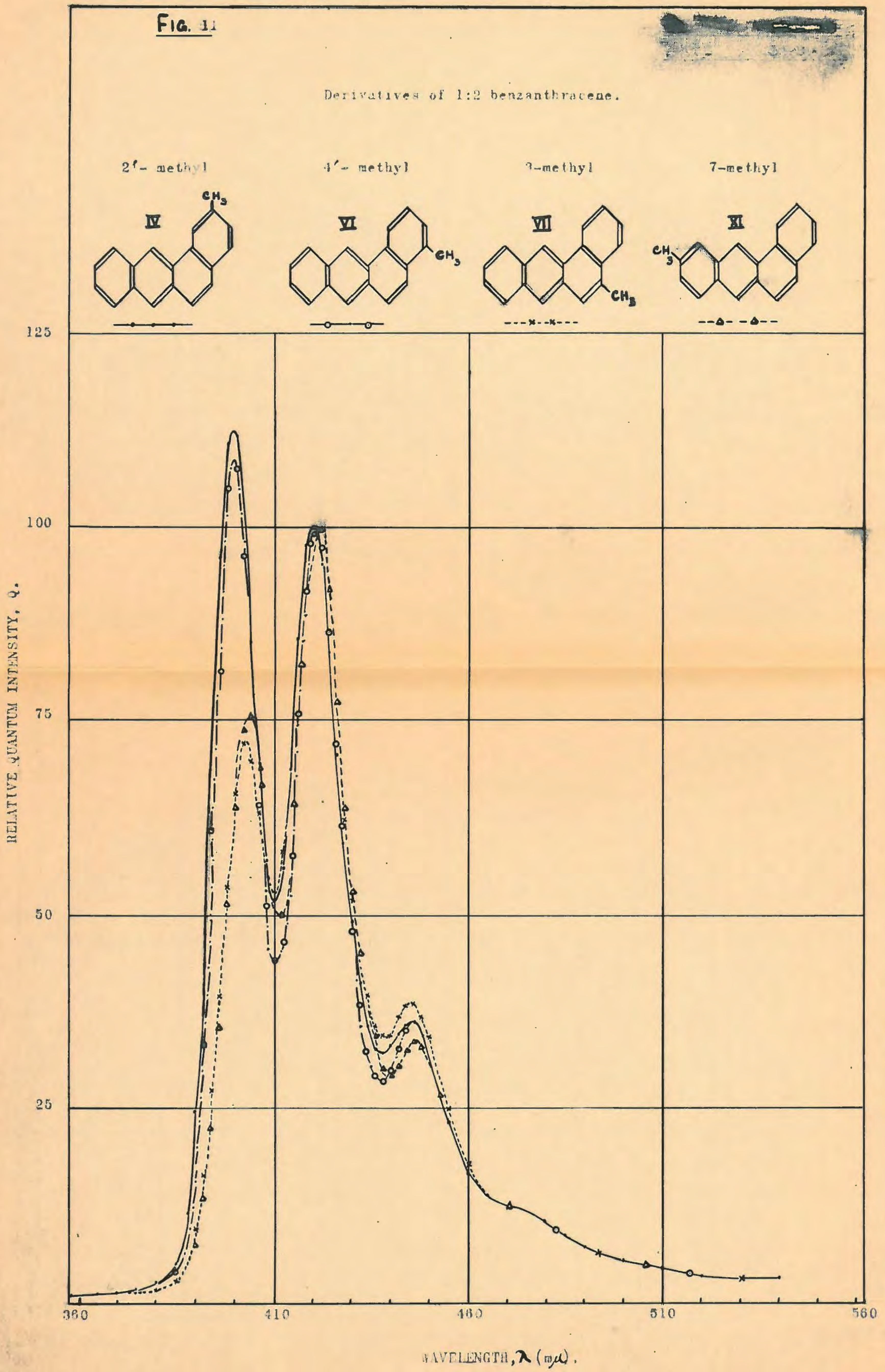

Derivatives of 1:2 benzanthracene.
2'- methyl
4'- methyl
3-methyl
7-methyl
IV
VI
VII
XI
CH3
125
100
75
50
25
360
410
460
510
560
RELATIVE QUANTUM INTENSITY, Q.
WAVELENGTH, λ (mμ).

Fig 10.

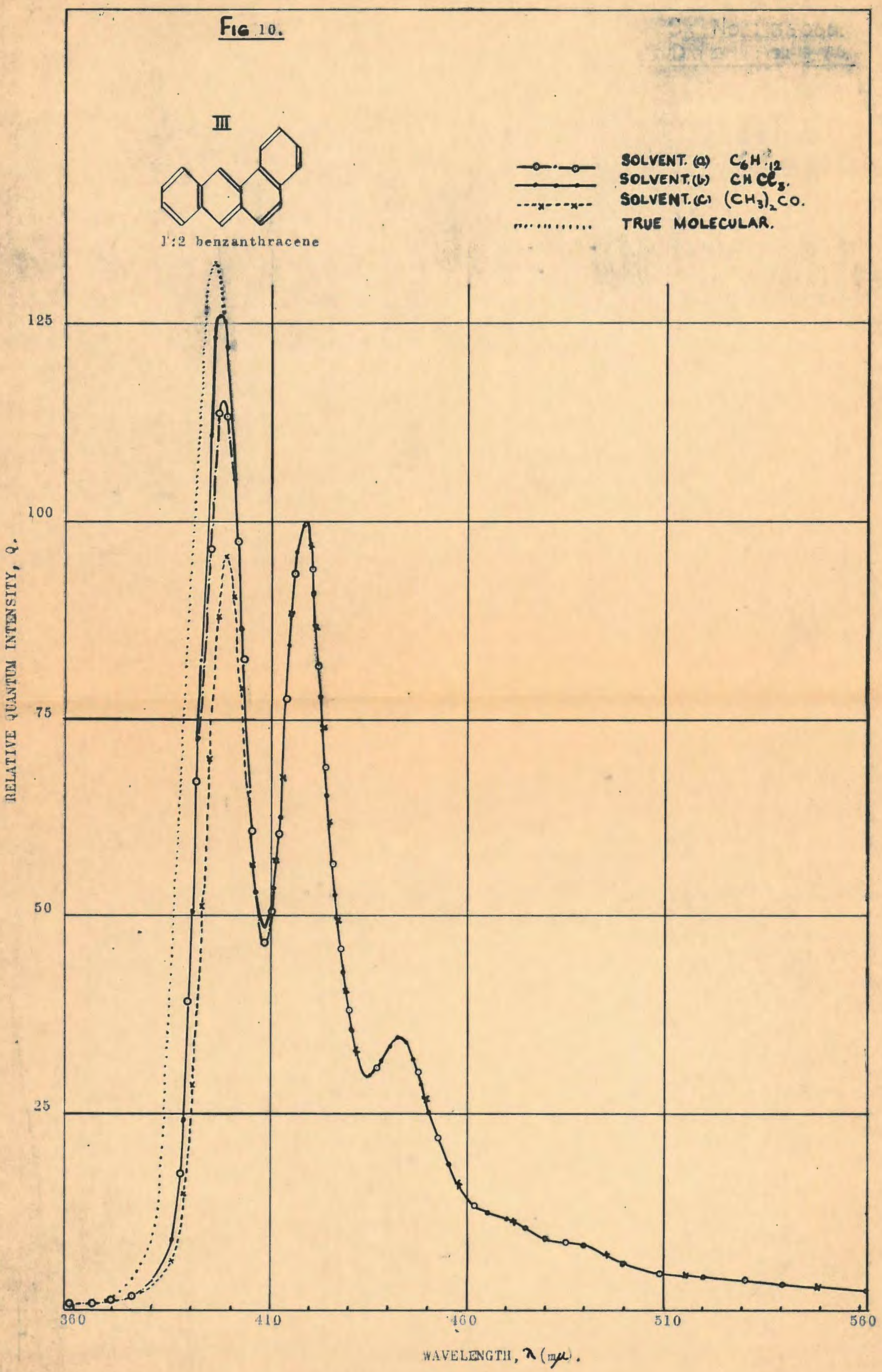
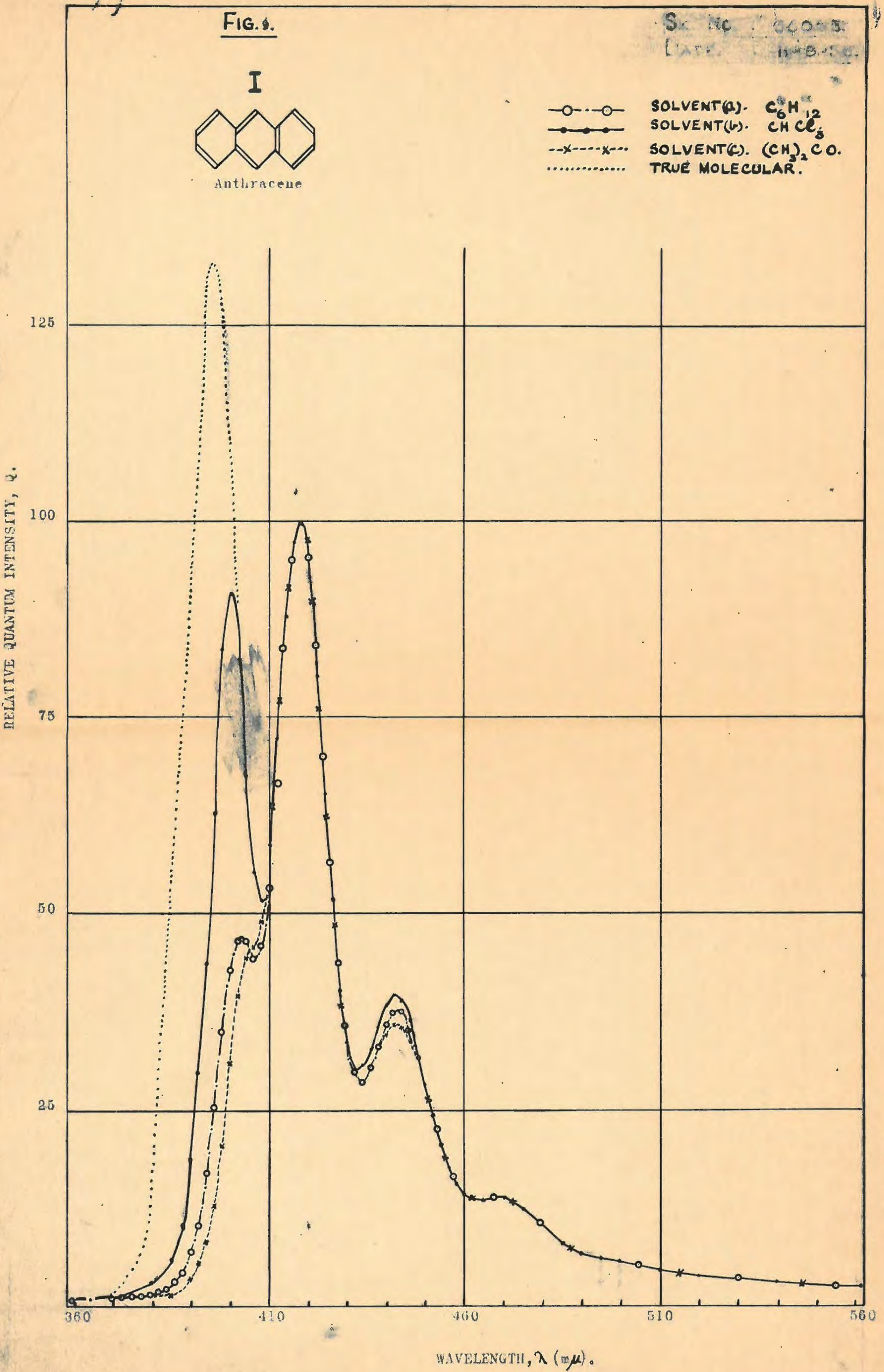

III
1:2 benzanthracene
SOLVENT. (a) C_6H_{12}
SOLVENT. (b) $CHCl_3$.
SOLVENT. (c) $(CH_3)_2CO$.
TRUE MOLECULAR.
125
100
75
50
25
360
410
460
510
560
RELATIVE QUANTUM INTENSITY, Q.
WAVELENGTH, λ (mμ).

FIG. 5.


I
Anthracene
SOLVENT(a). C_6H_{12}
SOLVENT(b). $CHCl_3$
SOLVENT(c). $(CH_3)_2CO$.
TRUE MOLECULAR.
RELATIVE QUANTUM INTENSITY, Q.
125
100
75
50
25
360
410
460
510
560
WAVELENGTH, λ (mμ).

III. ANALYSIS OF RESULTS

III. 1. INDEX TO COMPOUNDS:

The spectra of a total of 41 related conjugated aromatic hydrocarbon compounds have been measured and are shown in FIGS. 9-21. The relative quantum intensities have been normalised to a certain maximum intensity, either on the vibration maximum representing the 0 → 1 transition, i.e. peak 1, for those compounds for which the vibrational structure is well resolved, or on the maximum of the band envelope for the diffuse spectra where fine vibrational structure is lost. The advantage of such normalisation is shown in the clarity preserved, even though several spectra are reproduced on the same axes, and small differences between the spectra of similar compounds become apparent. No important information is lost by this normalisation since the actual measured relative fluorescence intensity is of no real value due to the variable factors in the production of the microcrystalline layer which affect the intensity of fluorescence escaping through the crystal.

The compounds are classified in Tables II + III according to molecular structure each with a Roman numeral by which it is designated in the text. Included in Tables II + III are columns indicating the solvent used in the preparation of the specimen from dilute solution, and the number of the corresponding figure. The compounds are fairly easily classified on the basis of similarity of molecules and fall into broad general groups. The most important group, as far as the present measurements are concerned, because they represent a continuous series of allied compounds, includes anthracene, 1:2 benzanthracene and the mono-methyl and di-methyl derivatives of each, and some related compounds. Other distinct molecular groups are the chrysene and phenanthrene type, and the 3:4 benzophenanthrene derivatives. Another group includes molecules like trans-stilbene, para-terphenyl and other phenyl derivatives.

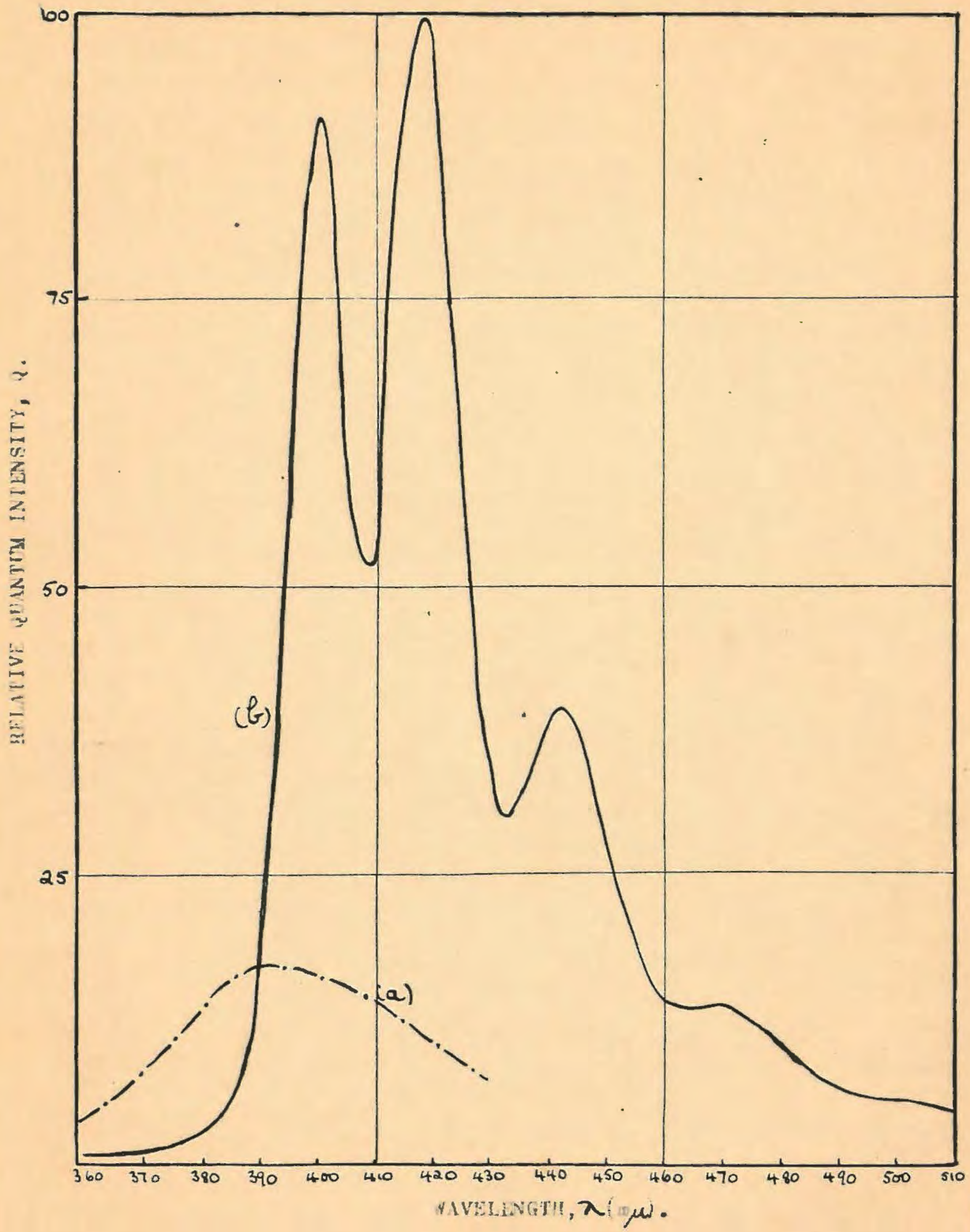
Using the anthracene, 1:2 benzanthracene group of similar compounds, change in the spectral distribution of fluorescence is studied as a function of molecular substitution. The two types of molecular substitution are - (a) benzenoid substitution in the 1:2 position of anthracene followed by (b) the various mono-methyl and di-methyl substitutions of the 1:2 benzanthracene chromophore. The anthracene and 1:2 benzanthracene spectra have been used as reference throughout this work and have, therefore, been studied in detail initially.

III. 2. THE ANTHRACENE SPECTRUM:

III. 2.1. VIBRATIONAL ANALYSIS:

Microcrystalline specimens of this compound were prepared from solutions in each of the three solvents, chloroform, cyclohexane and acetone, the fluorescence spectrum from each sample being drawn on FIG. 9. By referring to the abundant absorption data available, the correct transitions corresponding to the vibrational maxima may easily be assigned. These are, in order of increasing wavelength, due to he $1_o \rightarrow 0_o$, $1_o \rightarrow 0_1$, $1_o \rightarrow 0_2$, $1_o \rightarrow 0_3$ electronic transitions of the molecule. 1 and 0 efer to the first excited singlet state and the ground state respectively, and the ubscripts refer to the principal vibrational levels within the electronic states. r convenience, in the subsequent discussion, only the final subscript will be used identify the transitions so that the $1_o \rightarrow 0_o$ transition becomes $0 \rightarrow 0$, the $1_o \rightarrow 0_1$ comes $0 \rightarrow 1$ and so on. The vibrational maxima of the spectra corresponding to ese transitions will be referred to simply as the 0,1,2, etc. bands respectively.

FIG. 22 Fluorescence of quartz (a) and anthracene (b).



ir relative quantum intensities and wavenumbers will be referred to as Q_0, Q_1, , ..., and ν'_0, ν'_1, ν'_2 for peaks 0,1,2 respectively. The spectra of FIG. 9 re normalised to a relative quantum intensity, Q_1 = 100, peak 1 occurring at 17.5 mμ. Each showed the same vibrational maxima though there are variations in he relative intensities according to the solvents used for preparing the dilute solutions.

BIRKS & WRIGHT (1954), using specimens 2μ thick prepared from xylene solution evaporated on to a quartz disk, reported the appearance of a low intensity vibrational peak at 380 mμ. This peak was not observed in the present measurements, and in order to resolve the anomaly of its existence, their method of preparation was repeated and the peak at 380 mμ was detected only when the microcrystalline sample was prepared on a quartz backing. The fluorescence of the fused quartz plates was found to have its maximum at ~ 390 mμ which accounted for this spurious peak, and the quartz emission is plotted in FIG. 22 on the same intensity scale as the anthracene fluorescence.

A 2μ specimen is sufficiently thick to absorb all the incident 253.7 mμ radiation, and the assumption that the quartz fluorescence was excited through minute holes in the microcrystalline layer is supported by its inconsistent appearance.

BIRKS & WRIGHT suggested this "peak" corresponded to the 1 → 0 transition on the assumption that the molecules, at the moment of fluorescence, were not in thermal quilibrium; this is hardly likely since the excess vibrational energy is usually dissipated long before fluorescence occurs. This recognition was supported by the nfortunate coincidence that its wavenumber spacing from the 0 peak is approximately he same as the spacing of the other bands from each other.

nce the fluorescence spectra detected in the present investigation lie at longer

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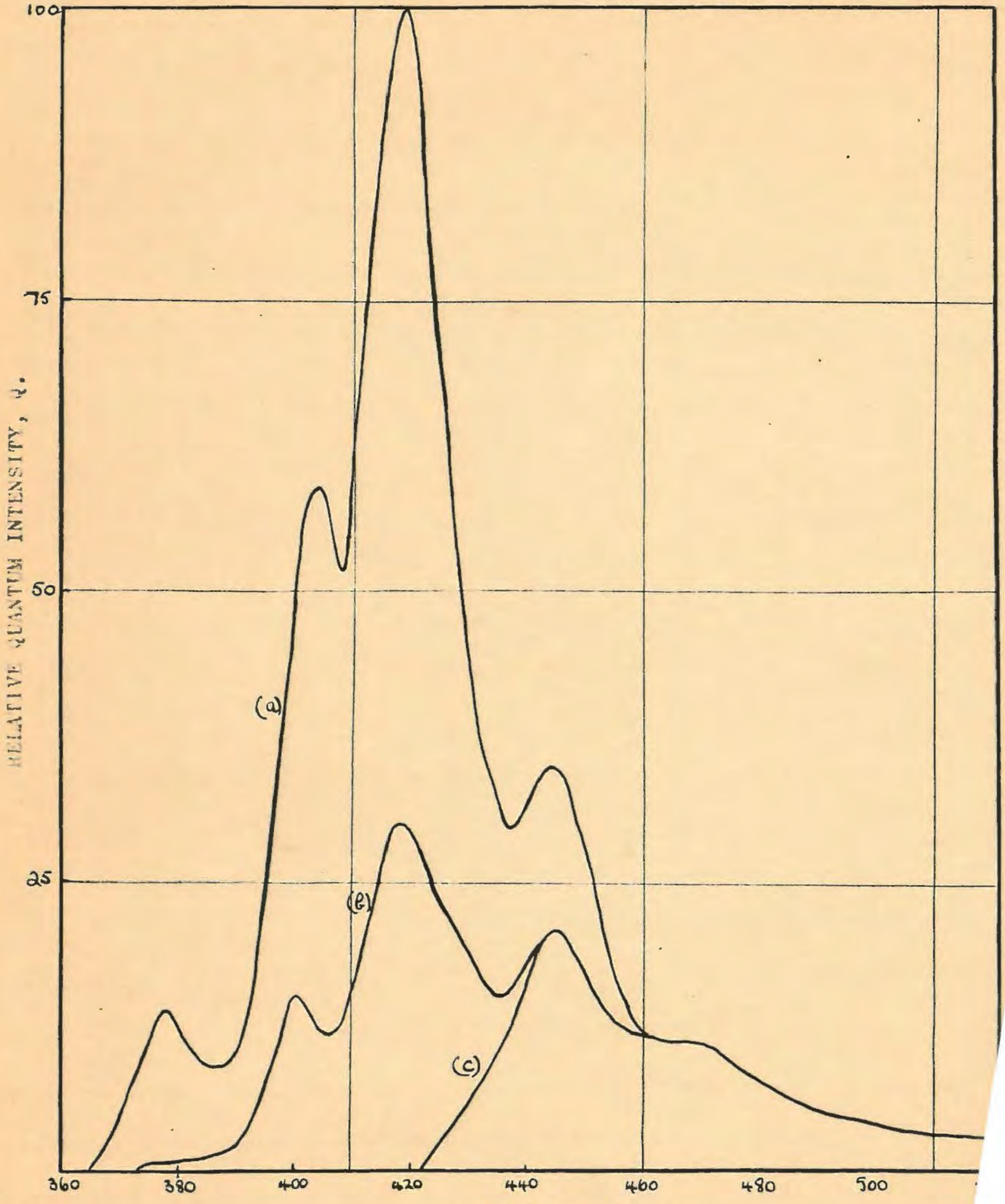
FIG. 23. Fluorescence of anthracene (a) Microcrystals
(b) Reflection)
(c) Transmission) 1 cm. crystal.



wavelengths than 3000 Å, non-fluorescent glass backing plates, which are transparent in this region, were used.

III. 2.2. SELF-ABSORPTION OF FLUORESCENCE:

The effect of self-reabsorption of fluorescence was shown by LITTLE (1954) who compared the emission spectra for fine powders, thin crystals, and several millimetres thick crystals. The same effect is clearly shown by BIRKS & WRIGHT (1954) who reported the fluorescence measured in reflection from a microcrystalline layer and from a thick crystal, in this case a 1 cm. cube, and also the spectrum of the fluorescence transmitted through the 1 cm. thick crystal. The differences in these spectra suggested that for the thicker specimens increased reabsorption of the fluorescence photons passing through the specimen effectively filtered out the fluorescence in certain spectral regions whose relative intensity was, therefore, reduced. The effect is exhibited clearly by FIG. 23, in which the following three spectra are plotted:

(a) fluorescence of microcrystal observed in transmission through specimen.

(b) fluorescence of 1 cm. cube observed in transmission through specimen.

(c) fluorescence of 1 cm. cube observed in reflection from front excited face.

(a) approximates to the true molecular emission of the molecule where reabsorption is absent and the effect of reabsorption is seen by comparing this with spectrum (b). In the latter, only those fluorescence photons to which the crystal is transparent escape and it is clear that reabsorption in the short wavelength region is pronounced

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and the fluorescence intensity thus reduced. At longer wavelengths reabsorption decreases until it is entirely absent as shown by the coincidence (in both spectra) of peak 3 and their longdr wavelength tails. The reflection spectrum (c) from the thick crystal represents an intermediary stage where fluorescence is emitted from a relatively thin layer of molecules out of the initially excited surface so that the fluorescence passes through only a small thickness of the crystal before being emitted, and is thus not completely filtered. It has been found that anthracene exhibits reabsorption strongly and some compounds like 1:2 benzanthracene are similar but there are other extremes like para-terphenyl where reabsorption is completely absent. In this case the emission spectrum from a 1 cm. cube is identical to that from a microcrystal, which is, therefore, the true molecular emission of the molecule. FIG. 9 shows the microcrystalline spectra of anthracene for specimens prepared using three different solvents. Their similarity for wavelengths greater than 410 mμ indicates that in this region self-absorption of the fluorescence emission is negligible, and the true molecular emission is observed. There are differences in intensity of the observed spectra, however, for wavelengths shorter than 410 mμ, which are attributed to variations in the amount of self-absorption by the microcrystals. It was observed that in going from chloroform, through cyclohexane, to acetone, the size of the individual microcrystals in the specimen increased which suggested that the amount of reabsorption should vary accordingly, and this order is reflected in the observed spectra.

The effect of crystal size on the relative intensities of the various maxima in the fluorescence spectrum of anthracene has previously been reported by BOWEN & LAWLEY (1949) for rather larger crystallites, who showed that internal trapping of the fluorescence emission within the microcrystals increases the effective light path

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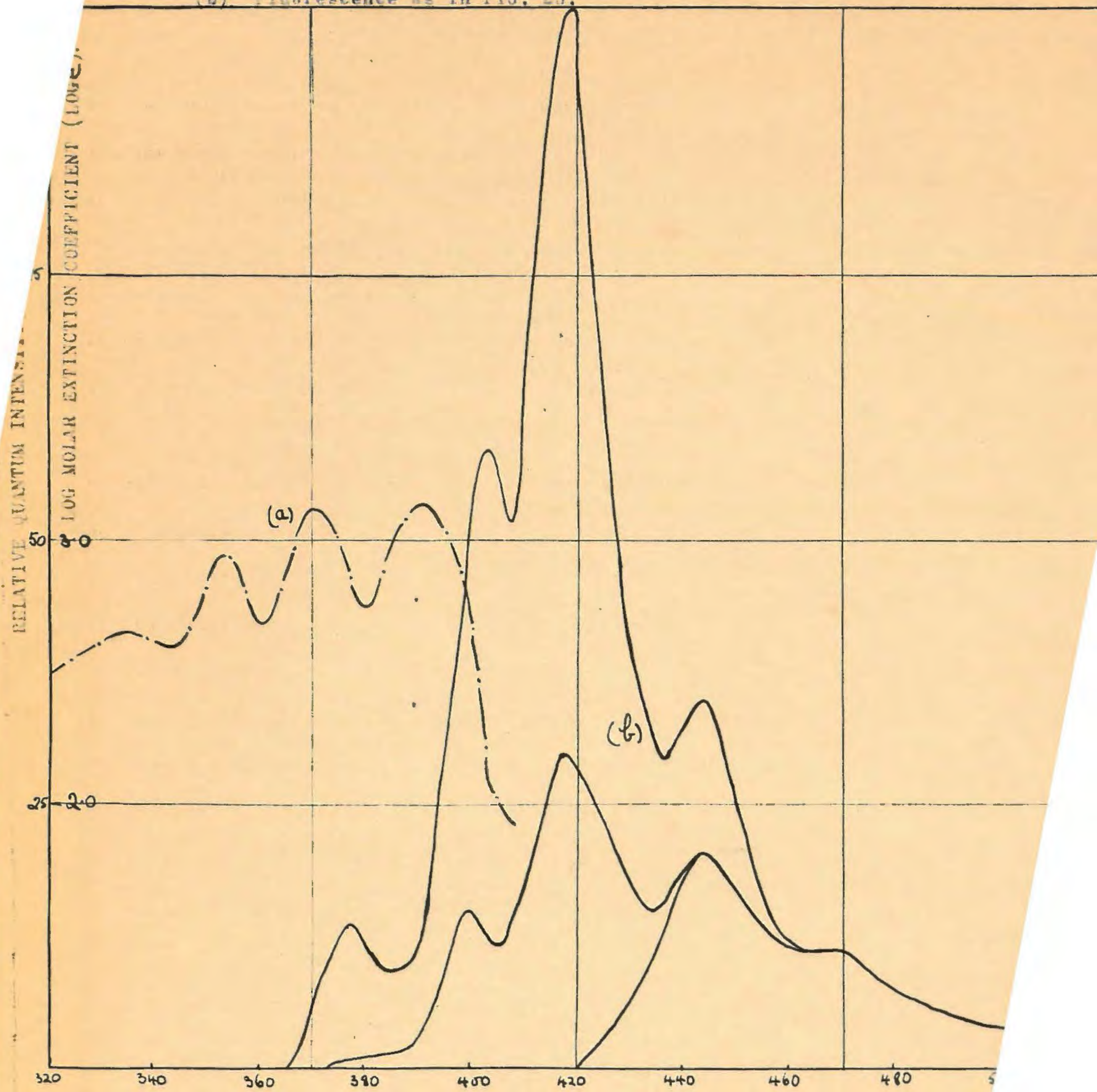
. 24. Absorption and fluorescence of anthracene.
(a) Absorption of microcrystal (KORTUM & FINCKH 1942)
(b) Fluorescence as in FIG. 23.



beyond the nominal thickness.

III. 2.2.1. Absorption Overlap:

The self-reabsorption of fluorescence in a crystal is obviously due to some degree of coincidence of the absorption and fluorescence spectra of the compound. The extent of this spectral overlap, as it is called, of the long wavelength end of the absorption spectrum and the short wavelength end of the fluorescence determines the amount of reabsorption and hence the shape of the technical spectrum. It varies considerably with the compound from extremes like para-terphenyl where there is no spectral overlap to anthracene where the region of spectral coincidence is large.

A detailed investigation into the reabsorption of anthracene fluorescence due to spectral overlap is possible using the absorption spectra data of KORTUM & FINCKH (1942), who used very thin specimens in the crystalline state similar to the specimens used in the present studies. The effect of reabsorption with increasing path length of fluorescence photons on the observed spectra has been shown in FIG. 23, and FIG. 24 shows the same fluorescence spectra with the addition of the absorption spectrum of anthracene in the crystalline state. The addition of the absorption spectrum clearly shows the extent of overlap of the spectra, the absorption spectrum extending under the short wavelength end of the fluorescence spectrum such that the intensity of the technical emission is greatly reduced, the vibrational peaks 0 and 1 being completely reabsorbed.

More recently PESTEIL & BARBARON (1954) have observed absorption bands in solid anthracene extending up to a wavelength of 420 mμ.

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III. 2.2.2. Wavelength of Molecular 0 → 0 Transition:

The existence of an overlap of the absorption and fluorescence spectra of anthracene has thus been demonstrated, and its effect on the fluorescence spectra shown.

In the extreme case, for a 1 cm. thick crystal, the two shortest wavelength peaks, termed 0 and 1, are completely filtered out by reabsorption, whereas for the microcrystalline spectra, FIG. 9, only peak 0 is appreciably affected, the reduction in fluorescence intensity of this peak varying with small differences in specimen thickness. Experiment has shown that even for the very thin microcrystalline samples where reabsorption over the greater part of the spectrum is absent, the fluorescence intensity of peak 0 is extremely sensitive to small changes in specimen thickness and the reason for this is explained inFIG. 24. The maximum of the longest wavelength absorption peak overlapping the fluorescence spectrum occurs at 25600 cm.$^{-1}$ while the fluorescence peak 0 occurs at 25000, 24800, 24720 cm.$^{-1}$ for the three spectra in FIG. 9. It is clear that the amount of reabsorption in this region determines the wavelength of the maximum of the fluorescence vibrational peak 0 in such a way that as reabsorption increases and the intensity of the peak is reduced, so its maximum moves towards longer wavelengths and hence the wavenumber spacing from peak 1 decreases. The successive wavenumber spacing between the other peaks is 1370 cm.$^{-1}$ which is equivalent to the energy difference between successive vibrational levels in the ground state and since this spacing is constant for the higher levels, it is to be expected that a similar energy difference will separate the two lowest levels. Hence the wavenumber spacing between peak 0 and peak 1 is expected to be 1370 cm.$^{-1}$ for true molecular emission, and, therefore, the wavenumber

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of the maximum of band 0 will be 25320 cm.^{-1} (wavelength λ = 395.0 $m\mu$).

FIG. 9 shows that the intensity of band 0 increases rapidly with increase in spacing from peak 1, the greatest separation measured being 1050 cm.^{-1}; hence it is to be expected that the molecular band 0 will have considerably greater intensity than any of those resolved for the microcrystalline samples. In order to determine the true molecular fluorescence spectrum by correcting band 0 for reabsorption, the following data are required: (i) Position of maximum of band 0, (ii) True shape of molecular band 0 and (iii) The intensity of molecular band 0. The first of these requirements has been obtained in this section and the following sections will be devoted to determining (ii) and (iii).

III. 2.2.3. True Shape of Molecular 0 → 0 Peak:

In the microcrystalline spectra of anthracene, FIGS. 9 and 23, where reabsorption only affects peak 0, the shape of successive peaks 1 and 2 are similar though of different intensities. Since their wavenumber spacing is the same as that between peak 1 and the true molecular band 0, it is expected that in the absence of reabsorption band 0 will be similar in shape to band 1 though its intensity will be different. The shape of the true molecular band 0 and hence its half width at half maximum intensity are, therefore, determined by analogy with the adjacent band 1 Band 1 is actually a Gaussian curve and this allows a check to be made to substantiate the method used for plotting the true shape of band 0. A Gaussian curve was plotted for band 0 (having the required maximum intensity) and this was found to coincide with the curve plotted by analogy with band 1.

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III. 2.2.4. True Molecular Intensity of 0 -> 0 Transition:

The determination of the molecular fluorescence intensity of band 0, i.e. wh reabsorption is completely absent, will be discussed with reference to FIGS. 25 & FIG. 25 shows the relative quantum intensity, Q_0, of band 0 plotted as a function the separation of its maximum, δ_o, from the maximum of band 1 (see (i) below). Transmission curves are plotted on the same horizontal scale (see (ii) below). FIG. 27 is a graph of technical intensity, Q_t, of the band 0 (for various thicknesses of specimen) versus the technical 0 -> 1 wavenumber spacing δ_o, obtained fr experimental readings.

(i) Assumption of true molecular intensity:

FIG. 9 shows that the technical intensity of band 0 for the three spectra increases rapidly with an accompanying relatively small change in wavenumber spacing from band 1 and by simple extrapolation an approximate value of the molecular intensity at the true spacing of 1370 $cm.^{-1}$ can be deduced. This intensity value is approximately 130, i.e. 1.3 times the intensity of peak 1. Confirmation that this is the correct order of magnitude is obtained from FIG. 10 where for 1:2 benzanthracene the maximum wavenumber spacing is 1350 $cm.^{-1}$ and the intensity of band 0 for this value is 126. The approximate true molecular fluorescence band 0 may now be plotted using the data obtained (position of maximum, shape of curve and intensity of maximum); it is similar to the dotted curve in FIG. 9, and the heavy continuous curve of FIG. 25, where half of band 1 is also drawn. It will be shown in

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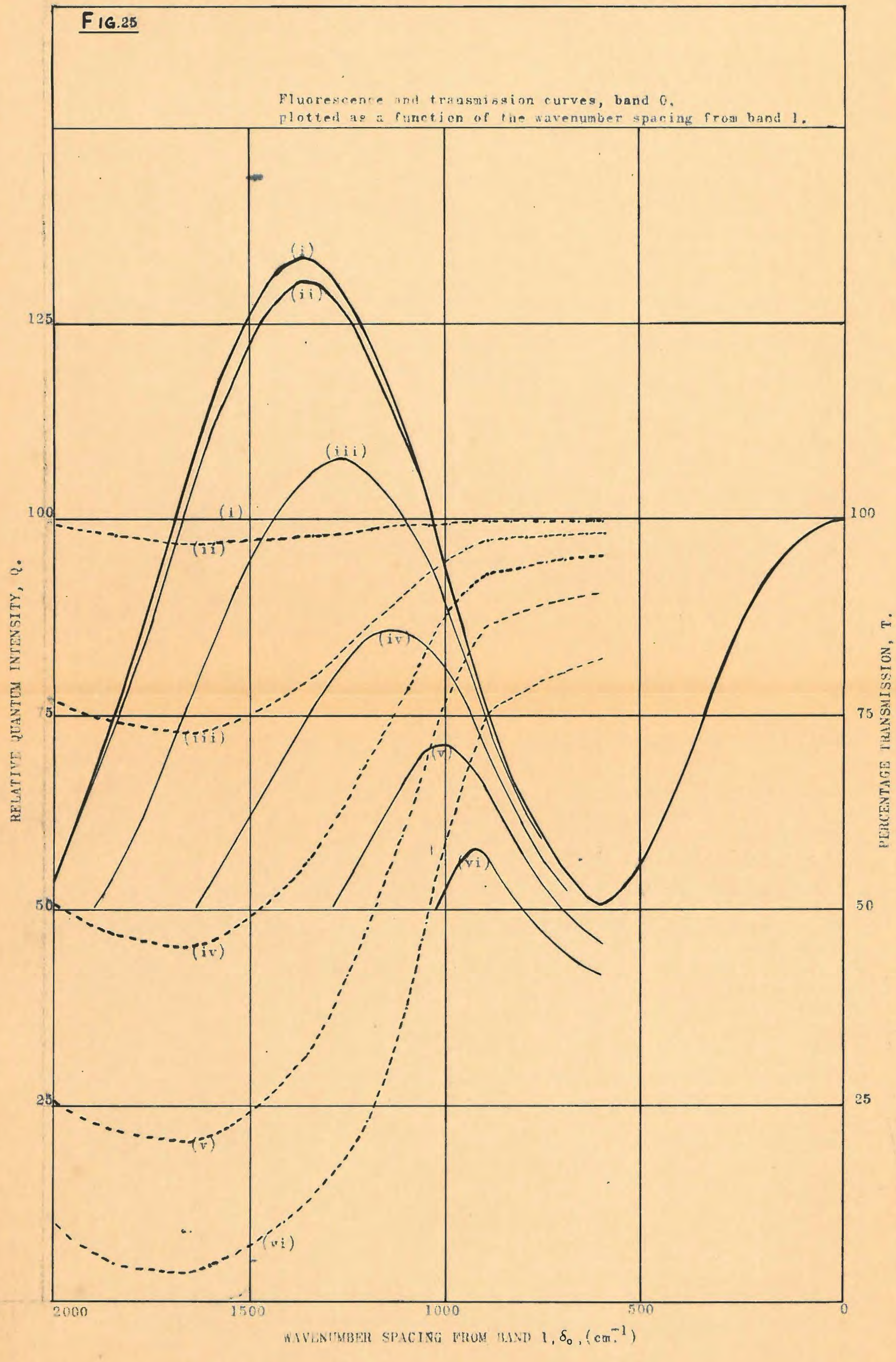
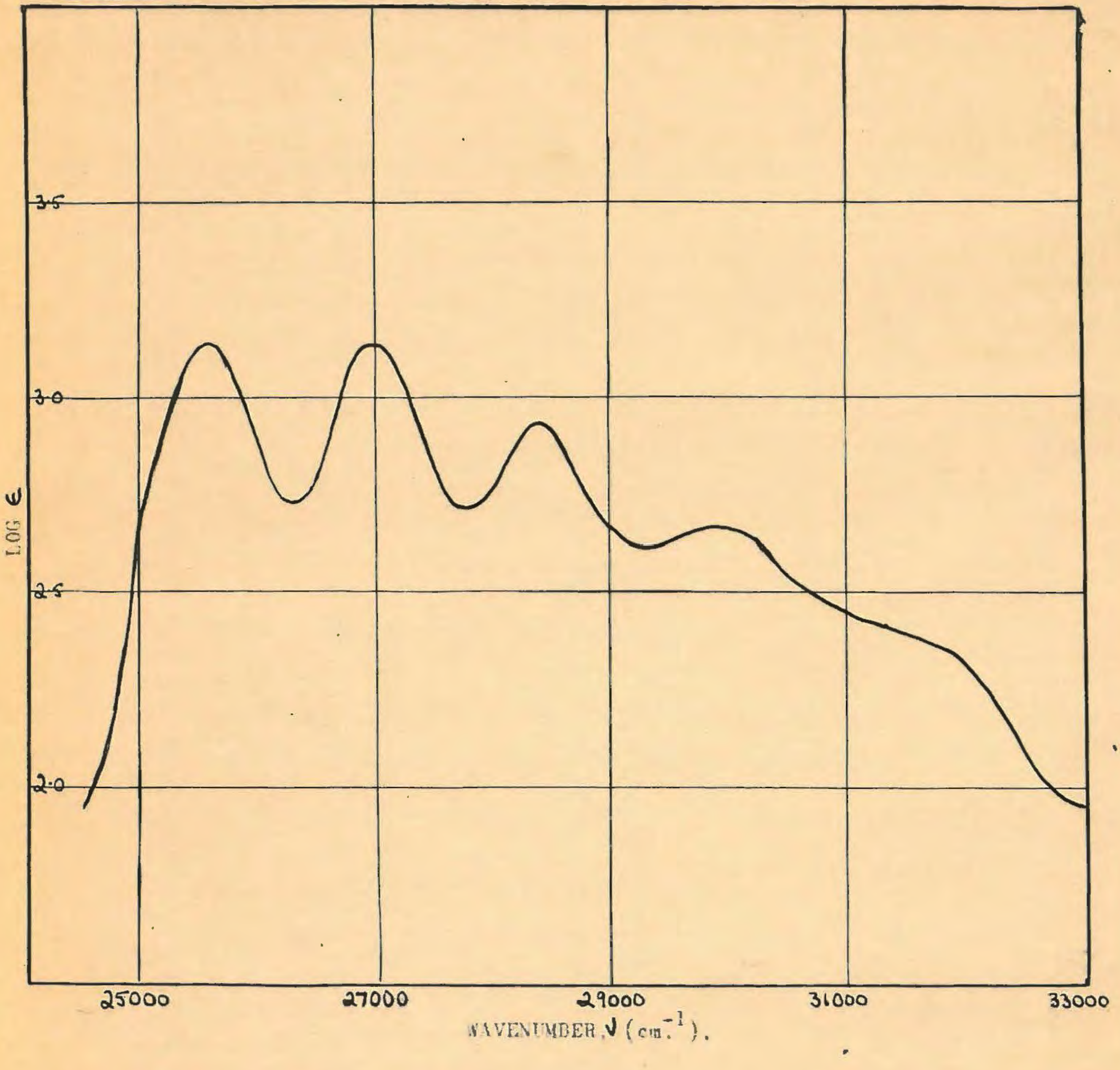
FIG.25



Fluorescence and transmission curves, band 0, plotted as a function of the wavenumber spacing from band 1.

FIG. 26. Absorption of anthracene (KORTUM & FINCKH 1942).



the following paragraphs that the actual intensity is not exactly 130, as can be seen from FIGS. 9 & 25, but these curves may be referred to generally in the present discussion, because the true molecular intensity which they show was obtained using the approximate value of 130, followed by normalisation to experimental readings.

(ii) Computation of Transmission Curves:

Drawn also on FIG. 25 are transmission curves for anthracene of various effective specimen thicknessess; these are the dotted curves of percentage transmission versus wavenumber for thicknesses ranging from 10^{-5} to 10^{-3} cm. They are derived from the data of KORTUM & FINCKH (1942) who measured the molecular absorption spectrum of crystalline anthracene shown in FIG.26. In this figure logϵ is plotted against wavenumber ν' and ϵ is the molar extinction coefficient defined by $\epsilon = \frac{A.M.}{b.c.}$ where A = absorbance, M = molecular weight of compound, b = path length of transmitted light and c = concentration (when applied to solutions). On FIG. 25, the percentage transmission is plotted against the wavenumber spacing of the absorption 0 → 0 transition and the fluorescence 0 → 1 transition in order that the curves may be drawn on the same horizontal scale as the fluorescence curve. The set of transmission curves for various thicknesses are derived from the relation $\log_e t = -2.3 \frac{\epsilon x}{M}$; therefore

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$\log_{10} t \propto \in x$ where t is the percentage transmission and x is the thickness of the specimen, and the range of thicknesses for which they are drawn is sufficient to demonstrate the rapid increase in absorption from very little in the thinnest to over 90% in the thickest at the maximum.

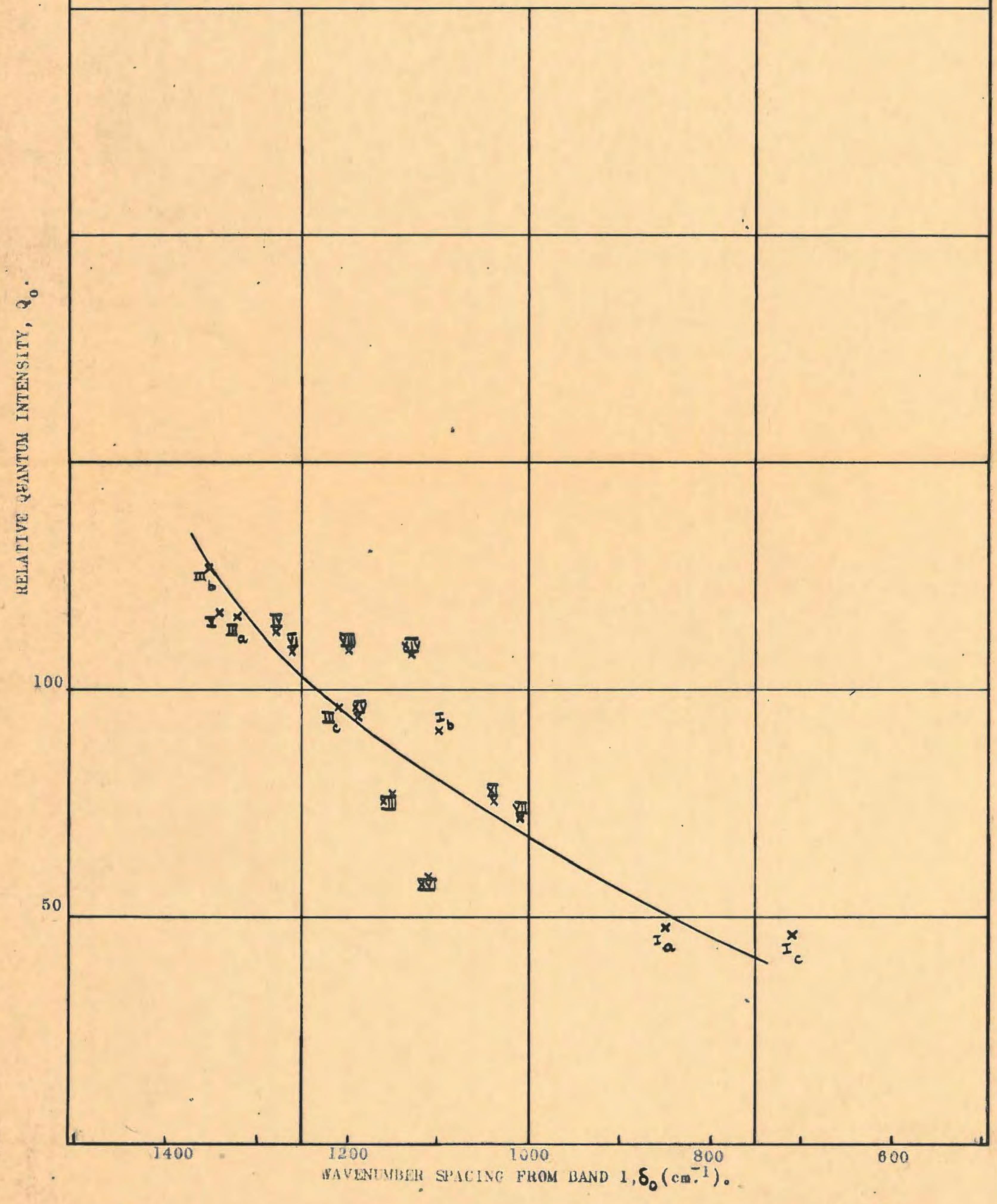
Another important point demonstrated by FIG. 25 is the non-coincidence of the maxima of the absorption and fluorescence 0 → 0 transitions, which is discussed fully in III.6.

(iii) Calculation of Technical Spectra:

FIG. 25 shows quantitatively how increasing thicknesses in the range 10^{-5} to 10^{-3} cm. increases reabsorption thus producing different technical spectra. The series of technical fluorescence 0 bands were obtained by multiplying the molecular fluorescence spectrum by each of the transmission spectra in turn, and they may be compared with the observed spectra of specimens prepared from different solvents. The theoretical treatment exhibits all the effects of reabsorption which have been observed in experiment, namely - (a) a decrease in the intensity of the fluorescence emission becoming more pronounced with increased specimen thickness and (b) an accompanying shift of the maximum of band 0 towards longer wavelengths thus reducing the separation from band 1. This apparent shifting of the maximum of band 0 is due to the position of the overlapping absorption band whose maximum

FIG. 27

Relative quantum intensity of band 0 plotted as a function of the wavenumber separation from band 1 for anthracene, 1:2 benzanthracene and their mono-methyl and dimethyl derivatives.



does not coincide with the maximum of the corresponding fluorescence transition, and reabsorption is greatest on the short wavelength edge of the fluorescence band 0.

A curve drawn through the maxima of the various technical 0 bands for different thicknesses gives a graph of technical intensity, Q_t, versus the technical 0 -> 1 wavenumber spacing, δ_o. The curve will terminate at a wavenumber spacing of 1370 $cm.^{-1}$, the spacing of successive vibrational levels in the ground state, and its intensity at this point will be that of the molecular fluorescence emission.

An approximate value of 130 relative to 100 for peak 1 has been chosen for the molecular intensity in this case, but by normalising the curve to the experimental observations of the intensity of the technical fluorescence 0 bands for anthracene (FIG. 9), the true molecular fluorescence intensity of the 0 -> 0 transition is obtained.

FIG. 27 shows the curve of Q_t vs. δ_o normalised to the three readings obtained from the anthracene spectra prepared from the three solvents which gives points I_a, I_b and I_c on the diagram. The other points on this diagram derived from experimental readings of other compounds will be referred to later.

(iv) <u>True Molecular Fluorescence Intensity</u>:

The normalisation of the Q_t vs. δ_o curve to the experimental results allows the true molecular fluorescence intensity of the compound to be read off at a separation δ_o from band 1 of

1370 $cm.^{-1}$. The value of Q_0 thus obtained is 133, relative to $Q_1 = 100$.

It can be seen that the original approximation of Q_0 does not affect the final result obtained since it is used in conjunction with the transmission curves to find only the shape of the Q_t vs. ε_0 curve which is then normalised to the experimental readings.

The fluorescence curve of FIG. 25 is corrected to the true molecular intensity of 133 and the various technical bands calculated using the transmission curves for various thicknesses have the true shape, spacing and intensity for their respective specimen thicknesses.

In FIG. 9 the dotted curve is the true molecular emission band 0.

III. 3, THE 1:2 BENZANTHRACENE SPECTRUM:

Microcrystalline specimens were prepared for this compound in a similar way to that described for anthracene, the same three solvents, chloroform, cyclohexane and acetone being used. The spectra are normalised to a relative quantum intensit $Q_1 = 100$ of band 1, which occurs at 418 $m\mu$. The spectra, plotted in FIG. 10, sho a close resemblance to the anthracene spectra in FIG. 9 especially towards longer wavelengths, though for each of the solvents the intensity of band 0 is considerabl greater than its anthraceneequivalent. As for anthracene, the size of the microcrystals for 1:2 benzanthracene increases in going from chloroform, through cycloh to acetone, though the greater relative intensity of band 0 suggests that the amou reabsorption is less due to a smaller overlap of the absorption spectrum than in the case of anthracene. At wavelengths greater than 410 mμ the spectra of anthracene and 1:2 benzanthracene are very similar, the spacing between successive bands, $\Delta\nu'$, being 1370 $cm.^{-1}$ in both cases, so that the method used for finding the true molecular intensity of band 0 for anthracene may be applied equally to 1:2 benzanthracene.

Although no direct measurements on the absorption of crystalline 1:2 benzanthracene are available, it is reasonable to assume that the position and shape of the $0 \rightarrow 0$ absorption band is similar to that of anthracene in view of similarities of (a) solution absorption spectra and (b) solid emission spectra of the two compounds. The magnitude of the molar extinction coefficient of the $0 \rightarrow 0$ absorption band measured in solution by FRIEDEL & ORCHIN (1951) is a factor of 10 less than for anthracene and it is expected that the crystalline self-absorption of fluorescence will be correspondingly reduced. This agrees with the present experimental observations.

The three technical 0 bands in FIG. 10 have been used to supply additional experimental points to FIG. 27, their maxima being represented by points III_a, III_b III_c on the curve of intensity versus wavenumber spacing from band I. It is clear that they are consistent with the reabsorption theory suggested for anthracene and are in accordance, within the experimental error, with the value of the relative quantum intensity of molecular band 0, $Q_0 = 133$ at a wavenumber spacing from band I 1370 $cm.^{-1}$

III. 4. SELF-REABSORPTION IN DERIVATIVES OF ANTHRACENE AND 1:2 BENZANTHRACENE:

As evidence of the generality of this reabsorption effect on band 0 due to variable degrees of overlap of fluorescence and absorption spectra, the maxima of the observed 0 bands for the other anthracene and 1:2 benzanthracene derivatives are plotted on FIG. 27 and they are shown to be in very good agreement with the proposed effect. It is seen, therefore, that for all these compounds there is some degree of overlap of absorption and fluorescence spectra, which, for the microcrystalline specimens used, is only appreciable for the 0 → 0 transition. Hence, a similar correction for self-absorption requires to be applied to the intensity and position of band 0 for these compounds. The technical intensity and wavelength of this band 0 depends only on the extent of spectral coincidence and the thickness of the specimen and for all the compounds the molecular emission, where reabsorption is absent, produces a band 0 with a separation from band 1, δ_o, of 1370 cm.$^{-1}$ and an intensity Q_o = 133 relative to Q_1 = 100.

III. 5. EFFECT OF MOLECULAR ENVIRONMENT ON ANTHRACENE SPECTRUM:

Many measurements have been made on the absorption and fluorescence spectra of anthracene in different states, e.g. SESHAN (1936) who measured absorption in the crystalline state, the previously quoted results of KORTUM & FINCKH (1942) who measured absorption in the vapour state, in liquid solution and in the crystalline state, and BIRKS & WRIGHT (1954) who investigated the absorption and fluorescence properties of a dilute solid solution of anthracene in naphthalene. Results like these together with the present microcrystalline measurements are recorded in Tabl

TABLE I

ANTHRACENE

State	Absorption $\times 10^{-2}$ cm^{-1}		Fluorescence $\times 10^{-2}$ c	
Vapour(1)	275	15	274	13.5
Dioxane solution(1)	265	14.3	262	13.5
Naphthalene solution(2)	260.5	14.5	259.5	14
Crystal(1) (3)	256	14.5	253	13.7

References:		
	(1)	Kortum & Finckh (1942).
	(2)	Birks & Wright (1954),
	(3)	Present work.

--oOo--

where ν'_0 is the wavenumber of band 0, and $\Delta\nu'$ the wavenumber separation of successive vibrational bands. It will be seen from this Table that as for absorption, so a general bathochromic shift of the molecular fluorescence spectrum is observed in going from the vapour state, through liquid and solid solutions, to the crystalline phase and the shift is approximately the same as in absorption. This "solvent effect" producing a shift to longer wavelengths is due to the molecular environment and the shift increases as the molecules become more rigidly bound and hence held in closer proximity to each other until eventually they are bound in a rigid lattice in the crystalline state. This suggests that bathochromic shift is dependent on molecular interaction (see III.8 for confirmatio
Table I shows that the wavelength of the absorption 0 → 0 transition, band 0, is n
identical with that of the reverse fluorescence transition, though the shift in going from one state to the next is the same for both transitions. In the same wa
the wavenumber separation of successive bands $\Delta\nu'_0$ varied very little with the physical state but the separation for absorption is always greater than for the corresponding fluorescence.

It is very interesting that apart from this environmental bathochromic shift, the molecular fluorescence spectrum is virtually unchanged in the crystalline phase. The relative intensities Q_0, Q_1, Q_2 of successive vibrational bands decrease in a similar way to those observed in liquid solutions (KORTUM & FINCKH 1942).

III, 6. NON-COINCIDENCE OF THE $1_0 \rightarrow 0_0$ TRANSITION IN FLUORESCENCE AND ABSORPTION:

(i) Existence of energy gap:

SCHOENTAL & SCOTT (1949) observed that the shortest fluorescence band of a large number of compounds in solution does not coincide exactly with the corresponding longest wavelength absorption band of the compound in solution.. This observation is supported by the results of HAUSSER, KUHN & KUHN (1935) who investigated the relation between fluorescence and absorption spectra of a series of diphenylpolyenes and found the deviation of coincident bands to increase with the number of double bonds. No such regularity was observed by SCHOENTAL & SCOTT but the deviation, about 300 cm.$^{-1}$ was considered greater than the limits of experimental error and any differences to be attributed to the use of different solvents for the two types of spectra.

A similar wavenumber separation of the two bands is reported by BIRKS & WRIGHT (1954) for crystalline anthracene when their results are compared with the crystalline absorption measurements of KORTUM & FINCKH (1942). The determination of the true molecular spectrum from the present measurements gives a wavenumber separation of 280 cm.$^{-1}$ of the two bands.

More recently other authors, e.g. SIDMAN (1956) have confirmed the existence of this energy gap.

The problem which is at once presented is why the fluorescence transition from the lowest vibrational level of the first excited singlet state to the lowest vibrational level of the ground state of the molecule should be at lower energy than the reverse absorption transition which involves the same quantity of energy.

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It is impossible for the excited molecule to lose any energy in a non-radiative process because it is already in the lowest quantised level of the first excited state, it is equally impossible for the emission process to be terminated in a higher vibrational level of the ground state since the actual detected deviation is considerably less than the energy spacing between successive vibrational levels of the molecule.

(ii) WRIGHT's results:

WRIGHT (1955) suggested that this energy gap did not really exist. He measured the fluorescence excitation spectra of 1 cm. anthracene crystals by detecting the transmitted fluorescence, and the curve obtained is similar in shape to the absorption spectrum of the crystal, the minima corresponding to the absorption maxima. Observations were reported indicating that the band 0 occurs at 25200 $cm.^{-1}$ which is at a longer wavelength than previously reported by SESHAN (1936) and KORTUM & FINCKH (1942), and is almost identical with the wavenumber of 25300 $cm.^{-1}$ of the molecular fluorescence band 0 found from the present measurements. WRIGHT, therefore, concludes that $1_0 \rightarrow 0_0$ absorption and fluorescence transitions coincide and suggests that the anomaly found by other workers is due to their use of thin crystalline films for direct transmission measurements instead of large single crystals which gave spectra more indicative of the true crystal absorption.

The results of WRIGHT are inconsistent with those of KORTUM &

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FINCKH (1942) which are considered reliable and also with the latest measurements of SIDMAN (1956), who has explained the existence of the energy gap on a trapped exciton theory. The effect is, therefore, considered genuine and SIDMAN's theory is given in the next section.

(iii) SIDMAN's results:

SIDMAN (1956) reported the polarized absorption and fluorescence spectra of crystalline anthracene at low temperatures (4°K) and found spectral evidence for "trapped excitons" which may be used to explain the energy difference between the $1_o \rightarrow 0_o$ transition in absorption and fluorescence. At 4°K the spectra are much better resolved than at room temperature and it is clear that the origin of the strong absorption at 25400 $cm.^{-1}$ does not coincide with the origin of the fluorescence which lies principally below 24975 $cm.^{-1}$ It is possible to account for this gap on the basis of the trapped exciton theory of FRENKEL (1936) & DAVYDOV (1948). According to FRENKEL's original theory of the free exciton, absorption of light by a molecular crystal can lead to an excited electronic state in which the excitation may move through the crystal in a manner similar to the motion of a particle. FRENKEL also considered the case in which the crystal lattice may become distorted in the vicinity of the exciton and the local deformation produced by the exciton can lead to its trapping at the site of the lattice distortion if the energy of the trapped exciton is less than the energy of the free exciton. FRENKEL predicted that trapped excitons should be able to exist in most molecular crystals though no experimental verification has been proposed. SIDMAN measured the polarized spectrum of anthracene in two directions at right angles in the same plane in the crystal and detected in the one case a set of absorption bands at 25400 cm.$^{-1}$ which were assigned to the transition from the ground state to the free exciton band, and in the other case an additional group of bands at slightly longer wavelengths which were due to transitions to the trapped exciton levels of the molecular crystal. Fluorescence from the free exciton bands was totally absent indicating that radiationless conversion to the trapped levels is very rapid, the trapped levels quenching the fluorescence from the free exciton levels in the same way as an impurity molecule. The trapped exciton levels at $\nu \sim$ 24930 cm.$^{-1}$ and 24910 cm.$^{-1}$ are particularly effective in trapping the excitation and emitting the fluorescence which will, of course, be at longer wavelengths than emission from the originally excited free exciton band. Thus, this theory accounts for the fact that the origin of fluorescence is several hundred cm.$^{-1}$ below the origin of absorption, and, as has been previously stated, has been verified by other workers.

In the light of these results and interpretations it is considered that the results obtained in the present work confirm SIDMAN's suggestions and show that the gap which is still present, even if the position of origin of the absorption as detected by WRIGHT is used, is too large to be due to any spurious effects.

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Studies by McCLURE & SCHNEPP (1955) for crystalline naphthalene and phenanthrene show a similar energy gap between the absorption and fluorescence spectra.

III. 7. THE SPECTRA OF OTHER COMPOUNDS:

III. 7.1. DERIVATIVES OF ANTHRACENE AND 1:2 BENZANTHRACENE:

The interest of this set of compounds is in the study of (a) the effect on the anthracene spectrum of the annelation of a benzene ring to anthracene in the 1:2 position, and (b) the spectral changes of the 1:2 benzanthracene chromophore for methyl substitution in the twelve possible positions.

The compounds studies were :-

9:10 dimethyl-anthracene (II); eleven of the twelve mono-methyl derivatives of 1:2 benzanthracene (IV to XIV), the omission being 1′methyl which was unobtainable; four dimethyl derivatives of 1:2 benzanthracene, namely - 2′: 6-, 2′: 7-, 3′: 6-, and 9:10 dimethyl 1:2 benzanthracene (XV to XVIII); acenaphthanthracene (XIX); and 20-methylcholanthrene (XX).

The observed microcrystalline fluorescence spectra are normalised on band 1 to $Q_1 = 100$ or, in cases where band 1 is not readily identified or the vibrational structure is not resolved, to $Q = 100$ at the maximum intensity.

The spectra are drawn on FIGS. 11 to 15.

III. 7.2. OTHER POLYCYCLIC HYDROCARBONS AND DERIVATIVES:

The other 4-ring hydrocarbons and derivatives whose spectra have been studied were:-

Chrysene (XXV) and its 1:2 dimethyl derivative (XXVI); five of the six mono-methyl derivatives of 3:4 benzophenanthrene (XXIX to XXXIII), the 5-methyl compound being

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omitted because it was unobtainable; and pyrene (XXXIV).
The spectra are plotted in FIGS. 16 & 17.

Three of the 5-ring hydrocarbons studied namely - 1:2:5:6 dibenzanthracene (XXI), 1:2:3:4 dibenzanthracene (XXIII) and 3:4 benzpyrene (XXIV) are derivatives of 1:2 benzanthracene (III). The related heterocyclic compound (1:2:5:6 dibenzfluorene (XXII) was also included and is of special interest because it contains a pentagonal ring. The other two 5-ring compounds studied, 1:2:3;4 dibenzophenanthrene (XXVII) and 1:2:5:6 dibenzophenanthrene (XXVIII) are derivatives of chrysene or 3:4 benzophenanthrene. The spectra are plotted in FIGS. 18 & 19.

III. 7.3. OTHER COMPOUNDS:

These are the compounds which do not fall into the general category of "condensed aromatic hydrocarbons".
2-naphthylamine (XXXV) was chosen, because of its availability in a very pure state, as representative of the 2-amine carcinogens. The polyene group studied consisted of trans-stilbebe (XXXVI) and three of its carcinogenic 4-amino derivatives namely - 4-aminostilbene (XXXVII), 4-dimethyl-aminostilbene (XXXVIII) and α-4-dimethylaminophenyl-β-(α-naphthyl)-ethylene (XXXIX).
Two related compounds, 1:4 diphenylbutadiene (XLI) and para-terphenyl (XL), which like anthracene and trans-stilbene are of interest for scintillation counting, were also included.
The spectra are plotted in FIGS. 20 & 21.

III. 8. CLASSIFICATION OF SPECTRA:

III. 8.1. DERIVATIVES OF ANTHRACENE AND 1:2 BENZANTHRACENE:

The important fluorescence studies of SCHOENTAL & SCOTT (1949) on polycyclic aromatic hydrocarbons in solution show that the spectra of these compounds in solution are similar to those of the parent compound, apart from bathochromic shifts due to the substituents. They are simple, consisting of three to four vibrational bands of diminishing intensity, equally spaced at ~1400 $cm.^{-1}$; no data on their relative quantum intensities are available. This spectral similarity between parent and derivatives is not unexpected since FRIEDEL & ORCHIN (1951) have shown that the absorption spectra of the compounds in solution are also similar to those of the parent compound.

The crystalline fluorescence spectra, om the other hand, are not all similar to those of the parent compound, and they may be classified into a sequence of types, dependent on the degree of difference from the spectrum of the parent compound:

(i) Spectral Types:

The classification into six types designated by letters A to F is as follows :

Type A spectra; represented by 2′, 4′, 3- and 7- methyl 1:2 benzanthracene (FIG. 11), are very similar to the spectrum of the parent, 1:2 benzanthracene (FIG. 10) apart from slight bathochromic shifts. The spacings and relative quantum intensities of the 1,2 and 3 bands are almost unchanged. The observed position and intensity of the 0 band in each of the compounds are influenced by self-absorption as in anthracene and 1:2 benzanthracene. These observations are plotted in FIG. 27 (see III.4) and they are found to be consistent with similar values of Q_0 ~133.

Type B spectra; are represented by 3′, 4-, 9- and 10- methyl 1:2 benzanthracene (FIG. 12), 2′: 6- and 2′: 7- dimethyl 1:2 benzanthracene, and acenaphthanthracene (FIG. 13)

Although the same vibrational structure as for 1:2 benzanthracene is resolved, they differ from the parent compound in that the relative intensity beyond band 1 does not decrease so rapidly with increasing wavelength, and several of the spectra show relatively large bathochromic shifts. The spacing of the resolved maxima remains at $\Delta\nu' \sim 1370$ cm.$^{-1}$ The 0 band is affected by self-absorption, and the observed values of Q_t and δ_0, plotted in FIG. 27, are again consistent with $Q_0 \sim 133$ (see III. In acenaphthanthracene the 0 band is not resolved, and it appears only as an inflextion at $\lambda \sim 410$ mμ. The spectrum of the 2′: 7 dimethyl derivative is of interest, since six vibrational maxima are resolved. This is discussed further in III.8.1.(ii).

<u>Type C spectra</u>; are represented by 6-methyl and 3′: 6 dimethyl 1:2 benzanthracene (FIG.14). The band 0 is clearly resolved, but the 1 band coalesces with the intensified 2 band, and the spectrum at longer wavelengths is diffuse. In the 6-methyl compound, the spacing between the 0 and 1 bands is abnormally large (~ 1600 cm.$^{-1}$) (see (ii) below).

<u>Type D spectra</u>; only exhibited by 3:4 benzpyrene and described in IV.3.1.

<u>Type E spectra</u>; are shown by 5-methyl and 8-methyl 1:2 benzanthracene (FIG. 14) and by 20-methylcholanthrene (FIG. 15). The spectrum consists of a single broad band, with its intensity maximum shifted considerably to longer wavelengths. No trace of the vibrational structure of crystalline 1:2 benzanthracene is shown, though the fluorescence spectra of the compounds in solution exhibit well-resolved vibrationa structure similar to the parent compounds.

<u>Type F spectra</u>; are represented by 9:10 dimethyl anthracene and 9:10 dimethyl 1:2 benzanthracene (FIG. 15). There is a remarkable similarity between the spectra of these two compounds. As in Type E, there is considerable loss of vibrational

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structure. The 0 and 1 bands coalesce to form a single band of approximately double the width of a normal vibrational band, with a large bathochromic shift.

(ii) Detailed Structure:

Having classified each of the observed fluorescence spectra into one of six spectral types, it is convenient to make some general comments on the more important features of fine structure of some of the compounds.

Type A spectra; Solution absorption spectra (FRIEDEL & ORCHIN) for the compounds whose spectra are of this type show a shift to longer wavelengths compared to that of 1:2 benzanthracene. Assuming the crystalline absorption spectra behave similarly, it is to be expected that the intensity of the 0 band in the fluorescence of these compounds will be decreased relative to the parent compound because of greater reabsorption. This is in agreement with the experimental results. The close similarity between the four spectra and the 1:2 benzanthracene spectrum suggests that methyl substitution in the 2'-, 4'-, 3- and 7- positions of 1:2 benzanthracene do not appreciably affect the physical properties of this molecule.

Type B spectra; For the four mono-methyl derivatives of 1:2 benzanthracene which fall into this category, the bathochromic shift increases in the order 3'-, 4-, 10-, 9- methyl, and is accompanied by an intensity reduction in the same order, which agrees with the expected extent of absorption overlap estimated from solution measurements. The general bathochromic shift of spectra is due to variations in energy difference between the first excited state and the ground state of each molecul The extent of the shift varies with the position of substitution and runs parallel to the shift of the longest absorption band; it varies in the same order as the intensity of the 0 band. The measurements of SCHOENTAL & SCOTT (1949) did not reveal this relation because reabsorption is almost negligible in dilute solutions. For solution measurements SCHOENTAL & SCOTT (1949) reported a connection between the extent of bathochromic shift of the spectrum of a substituted molecule, and the position of methyl substitution. 10-, 9- and 3- methyl are the most reactive positions of the unsubstituted 1:2 benzanthracene molecule but no such correlation is observed for the crystalline spectra.

For 2′: 6- and 2′: 7- dimethyl 1:2 benzanthracene and acenaphthanthracene, there is a rapid reduction in the intensity of band 0 accompanied by the corresponding bathochromic shift; for the acenaphthanthracene band 0 is completely absent, though at longer wavelengths it is very similar to 2′: 6- dimethyl 1:2 benzanthracene. 2′: 7- dimethyl 1:2 benzanthracene is somewhat different as its spectrum shows a total of six well-resolved vibrational maxima corresponding to the 0 -> 0, 0 -> 1, 0 -> 2, 0 -> 3, 0 -> 4, and 0 -> 5 transitions, whose wavenumber separation is ~1370 cm.$^{-1}$ A possible explanation for the occurrence of these additional vibrational maxima is that 2′: 7- dimethyl 1:2 benzanthracene does not possess the subsidiary vibrational levels in the ground state which SCHOENTAL & SCOTT (1949) have shown exist for other compounds, producing a set of subsidiary maxima superimposed on the principal maxima of the fluorescence spectrum. These secondary maxima are not often resolved in the crystalline spectra, though their presence may prevent the resolution of the lower energy vibrational transitions Their non-existence in the 2′: 7 dimethyl 1:2 benzanthracene molecule permits the resolution of the longer wavelength principal transitions.

Type C spectra; Due to the poor resolution of the subsidiary bands which occur on the long wavelength edge of the spectra and the resulting diffuse nature of the spectra, they cannot be used for quantitative analysis. They do show, however, the general broadening of the spectrum with the accompanying increase in intensity of the long wavelength edge. It has not been possible to explain the abnormally large spacing of bands 0 and 1, ~ 1000 cm.$^{-1}$, for the 6-methyl isomer (a similar value is to be expected for the 3′: 6-dimethyl isomer if reabsorption were absent) and no connection between this high value and the intensity increase at long wavelengths has been found.

<u>Type E spectra</u>; the bathochromic shifts for the compounds in this category are greater than for any of the other compounds; the maxima occur at 20200 cm.$^{-1}$ for 8-methyl 1:2 benzanthracene and at 19600 cm.$^{-1}$ for 5-methyl 1:2 benzanthracene and 20-methylcholanthrene, whereas band 1 for 1:2 benzanthracene occurs at 23900 cm.$^{-}$ Their diffuseness is interesting because their absorption spectra (FRIEDEL & ORCHIN 1951) and their fluorescence spectra (SCHOENTAL & SCOTT 1949) in liquid solution are very similar to the spectrum of the parent compound. It is concluded that the differences in the crystalline fluorescence spectra are directly attributable to large molecular interactions within the crystal (see IV. 3).

<u>Type F spectra</u>; There is general similarity to Type E spectra, though the bathochromic shift, ~ 1500 cm.$^{-1}$, relative to the parent compound is smaller (~ 3700 cm.$^{-1}$ for Type E).

III. 8.2. <u>OTHER POLYCYCLIC HYDROCARBONS AND DERIVATIVES</u>:

The spectra of these compounds may be classified into Types A to F, similar to the derivatives of anthracene and 1:2 benzanthracene (III.8.1). The chrysene spectrum (FIG. 16) is similar to the Type B spectra of the 1:2 benzanthracene derivatives, but it originates at shorter wavelengths, band 1 appearing at 385 mμ (compare λ = 420 mμ for Type B spectra). The observed band 0 is shifted and reduced in intensity, probably due to self-absorption. The spectrum of 1:2 dimethyl chrysene (FIG. 16) is similar, but with a fairly large substitutional bathochromic shift.

The 1- , 2-, 6-, 7- and 8- methyl derivatives of 3:4 benzophenanthrene have related spectra (FIG. 17), originating at slightly shorter wavelengths than the 1:2 benzanthracene derivatives. The spectra are rather diffuse and little vibrational structure is resolved. The maximum intensity in each case appears to correspond to band 1, while band 0 is observed only as an inflexion at $\lambda \sim 390$ mμ due to self-absorption. The spectrum of the 1-methyl compound has a long tail, reminiscent of the Type C spectrum of 6-methyl 1:2 benzanthracene (FIG. 14), and is probably due to molecular interaction (see IV.3). Pyrene, the most compact of the 4-ringed polycyclic hydrocarbons, is a symmetrical molecule and exhibits the tendency for the more compact symmetrical molecules to have diffuse spectra. Its spectrum (FIG. 16), a broad diffuse band similar to Type E, has two weak maxima, corresponding to bands 0 and 1, resolved near the origin. The maximum of the diffuse band occurs at 455 mμ, and there is, therefore, less bathochromic shift than for the Type E spectra whose maxima occur at $\sim$ 510 mμ. The spectrum in dilute solution has a banded structure (SCHOENTAL & SCOTT 1949), showing that the crystalline spectrum is due to molecular interaction, which is pronounced for compact symmetrical molecules. The crystalline spectrum represents a transition between Type C and Type E, and is called Type D, the definition of which will be given later in IV.3.1., with reference to the spectra observed in strong solid solutions of anthracene (NORTHROP & SIMPSON 1956).

The broad rather featureless spectrum of 3:4 benzpyrene (FIG. 19) is closely related to that of pyrene (FIG. 16) with a bathochromic shift. The solution spectru

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(SCHOENTAL & SCOTT 1949) has a banded spectrum, and the crystal spectrum, which is clearly Type D, is greatly influenced by molecular interaction.

The spectrum of 1:2:5:6 dibenzanthracene (FIG. 18) is similar to that of the other 1:2 benzanthracene derivatives with a Type B spectrum. In 1:2:5:6 dibenzfluorene (FIG. 18) the vibrational structure is lacking, possibly due to the division of the π-electron system by the five-membered ring in the centre of the molecule, though the fluorene spectrum observed by SANGSTER & IRVINE (1956) shows clearly resolved vibrational levels.

The vibrational bands are broadened, though partially resolved, in the spectrum of 1:2:3:4 dibenzanthracene (FIG. 18). The inflexion at $\lambda \sim 392$ mμ probably corresponds to band 0.

1:2:3:4 dibenzophenanthrene is structurally related to the mono-methyl derivatives of 3:4 benzophenanthrene (FIG. 17), and their spectra show similar features, band 1 being resolved and band 0 appearing only as an inflexion. 1:2:5:6 dibenzophenanthrene may be considered as a derivative of either chrysene or 3:4 benzophenanthren and its spectrum (FIG. 19) is a hybrid of these two compounds, with a slight bathochromic shift. The vibrational structure, corresponding to the 0, 1 and 2 bands is coarser and broader than in chrysene (FIG. 16) while the form of the spectru resembles some of the mono-methyl 3:4 benzophenanthrenes (FIG. 17).

III. 8.3. <u>OTHER COMPOUNDS</u>:

The spectrum of 2-naphthylamine (FIG. 20) consists of a single smooth peak, and the vibrational structure of the parent hydrocarbon naphthalene, which is similar to anthracene (FIG. 9) though at shorter wavelengths, is completely lacking. The fluorescence and absorption solution spectra are similar. The addition of the

TABLE II.

DERIVATIVES OF ANTHRACENE AND 1:2 BENZANTHRACENE

No.	Compound	Solvent	Figure.	Type	ν'_0	ν'_1	ν'_2	ν'_{max}	S	m_c	m_s	Carcinogenicity	Decay time (mμsec).
I	Anthracene	abc	9	A	253	239.5	226	–	12	-0.5	-5.5	–	6.3
II	9:10 dimethylanthracene	a	15	F	(229)	(224)	–	224	–	(15)	–	+	6.1
III	1:2 benzanthracene	abc	10	A	252.5	239	226	–	7	0(Ref)	0(Ref)	Slight	11.6
IV	2' methyl 1:2 benzanthracene	a	11	A	251.5	238	224.5	–	–	1	–	–	11.1
V	3' methyl 1:2 benzanthracene	a	12	B	252.5	239	–	–	–	0	–	–	10.1
VI	4' methyl 1:2 benzanthracene	a	11	A	251.5	238	224.5	–	–	1	–	–	13.7
VII	3-methyl 1:2 benzanthracene	a	11	A	251.5	238	224.5	–	5	1	3	+	15.3
VIII	4-methyl 1:2 benzanthracene	a	12	B	251.5	238	224.5	–	7	1	1	+	10.1
IX	5-methyl 1:2 benzanthracene	a	14	E	–	–	–	196	(62.5)	(56.5)	1	++	125
X	6-methyl 1:2 benzanthracene	a	14	C	253.5	237.5	227	–	4	-1	2	+	12.9
XI	7-methyl 1:2 benzanthracene	a	11	A	251	237.5	224	–	6.5	1.5	2	+	8.8
XII	8-methyl 1:2 benzanthracene	a	14	E	–	–	–	202	(55)	(50.5)	2.5	+	99.1
XIII	9-methyl 1:2 benzanthracene	a	12	B	248	234.5	222	–	6	4.5	5.5	++	10.1
XIV	10-methyl 1:2 benzanthracene	a	12	B	250	236.5	–	–	6	2.5	3.5	+++	–
XV	2':6 dimethyl 1:2 benzanthracene	b	13	B	252.5	239	225	–	5	0	2	–	15.2
XVI	2':7 dimethyl 1:2 benzanthracene	b	13	B	250.5	237	223.5	–	5	2	4	–	13.1
XVII	3':6 dimethyl 1:2 benzanthracene	b	14	C	250.5	238	–	–	7.5	1	1.5	–	11.5
XVIII	9:10 dimethyl 1:2 benzanthracene	b	15	F	–	(224)	–	224	(25)	(15)	12.5	++++	5.2
XIX	Acenaphthanthracene	b	13	B-	–	232	219	–	–	7	–	+	8.2
XX	20 methylcholanthrene	a	15	E	–	–	–	196	–	(56.5)	–	++++	–
XXI	1:2:5:6 dibenzanthracene	c	18	B	248.5	235	221.5	–	6.5	4	5.5	++	14.7
XXII	1:2:5:6 dibenzfluorene	a	18	–	246	232.5	–	–	–	6.5	–	+	6.6
XXIII	1:2:3:4 dibenzanthracene	c	18	–	254	240	230	–	–	-1	–	–	7.9
XXIV	3:4 benzpyrene	a	19	D	232	–	–	208.5	16	20.5	11.5	++++	8.6

2-amino group causes a major bathochromic shift relative to the naphthalene spectrum, bringing the spectrum into a similar region to the primary carcinogens (see IV.4); it is probable that the 2-amino group is responsible for the loss of fine structure observed for the parent compound.
The spectrum of trans-stilbene (FIG. 21) consists of four sharp vibrational bands, with an inflexion at the long wavelength end representing the fifth. The first of these bands, at ~ 360 mμ, can be clearly identified as the 0 band, thus removing the uncertainty in earlier measurements of ascribing the correct vibrational transitions to the resolved peaks of the spectra from thick stilbene crystals (BIRKS & WRIGHT 1954, SANGSTER & IRVINE 1956). Due to the self-reabsorption of the short wavelength fluorescence (about 40% for thick specimens) this band 0 was not resolved in the measurements of SANGSTER & IRVINE (1956).

In contrast, the spectra of the three 4-amino derivatives (FIG. 20) are relatively featureless. As with 2-naphthylamine, the amino group causes a pronounced bathochromic shift, relative to the parent hydrocarbon, which increases with molecular weight. In the absence of solution spectral data, substitutional and molecular interaction effects cannot be distinguished. The spectrum of 1:4 diphenylbutadiene (FIG. 21) which is the next member of the diphenylpolyene series after stilbene, differs markedly from that of the latter compound. The vibrational structure observed in solution absorption measurements (HAUSSER, KUHN & KUHN 1935) is not resolved due to broadening of the bands. However, the intensity decreases with increasing wavelength in a similar manner to the stilbene spectrum, indicating that crystal interaction effects are relatively weak.

The para-terphenyl spectrum (FIG. 21) has a well-defined vibrational structure with six clear maxima. The 0 and 1 bands which are obscured in the thick crystal

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TABLE III.

OTHER COMPOUNDS

No.	Compound	Solvent	Figure	ν'_0	ν'_1	ν'_2	ν'_{max}	S	Carcinogenicity	Decay Time (mμ sec).
XXV	Chrysene	c	16	272	258.5	245	-	4.5	-	17.6
XXVI	1:2 dimethylchrysene	a	16	261	247.5	234	-	-	++	-
XXVII	1:2:3:4 dibenzophenanthrene	a	19	-	(249)	-	-	-	+	-
XXVIII	1:2:5:6 dibenzophenanthrene	b	19	252	239	228	-	-	+	-
XXIX	6-methyl 3:4 benzophenanthrene	c	17	-	248	-	-	-	+	17.7
XXX	7-methyl 3:4 benzophenanthrene	c	17	-	249	-	-	-	+	18.3
XXXI	8-methyl 3:4 benzophenanthrene	c	17	256	242.5	230	-	-	+	19.9
XXXII	2-methyl 3:4 benzophenanthrene	c	17	-	246.5	232.5	-	-	+++	20.9
XXXIII	1-methyl 3:4 benzophenanthrene	c	17	-	245.5	230.5	-	-	++	20.6
XXXIV	Pyrene	c	16	265.5	252	-	219	3	-	46.5
XXXV	2-naphthylamine	a	20	-	-	-	256.5	—	Yes	-
XXXVI	<u>trans</u>-stilbene	c	21	277	257.5	244	257.5	-	-	3.9
XXXVII	4-aminostilbene	b	20	-	(237.5)	-	230.5	-	Yes	-
XXXVIII	4-dimethylaminostilbene	b	20	-	(229.5)	(217.5)	229.5	-	Yes	-
XXXIX	α-4-dimethylaminophenyl-β-(α-naphthyl)-ethylene	c	20	-	-	-	203	-	Yes	-
XL	1:4 diphenylbutadiene	c	21	251	237.5	-	251	-	-	5.4
XLI	<u>para</u>-terphenyl	c	21	283.5	270	257	257	-	-	5.5

spectra (BIRKS & WRIGHT 1954, SANGSTER & IRVINE 1956) can be readily identified. However, reabsorption is completely absent for this material and the microcrystal and technical spectra are identical.

III. 9. SUMMARY OF PROPERTIES:

The properties of the compounds are summarised in Tables II and III as follows Number and name of compound; solvent used in preparation of specimens; figure reference of spectrum, spectrum Type; the wavenumbers, ν'_0, ν'_1, ν'_2, of the 0, 1 and 2 bands respectively; ν'_{max}, the wavenumber of the intensity maximum in cases where no vibrational structure is resolved; "s", the wavenumber shift of the crystal spectrum relative to that in light petroleum solution (SCHOENTAL & SCOTT 1949); m_c and m_s, the wavenumber shifts relative to the 1:2 benzanthracene spectrum in the crystal phase and in light petroleum solution respectively; the carcinogenicity rating (PULLMAN & PULLMAN 1955, HARTWELL 1951); and the molecular photo-fluorescence decay times (HAMILTON 1958). All wavenumbers are expressed in units of 10^2 $cm.^{-1}$, and doubtful identifications are either omitted or enclosed in brackets.

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IV. DISCUSSION

In III, Analysis of Results, several interesting effects have been distinguished, notable amongst which are :-

(a) The self-absorption of fluorescence due to overlap of absorption and fluorescence spectra, and the calculation of a suitable correction, the application of which produces the true molecular fluorescence spectrum (III.2, III.3 and III.4).

(b) The classification of the observed crystalline spectra into Types A to F, and the comparison with solution spectral measurements. In analysing the different types of spectra three separate effects may be distinguished:-

(i) The "solvent" or Environment Effect; associated with the permittivity of the medium in which the fluorescent molecule is located.

(ii) The Molecular Substitution Effect; which causes the spectral shift, relative to the parent compound.

(iii) The Crystal Interaction Effect; due to intermolecular forces within the crystal.

(a) has been extensively described in III, but the three effects reporte in (b) will now be discussed fully.

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IV. 1. THE "SOLVENT" OR ENVIRONMENT EFFECT:

This is distinguished by comparing the observed crystalline fluorescence spectra with the solution spectra of SCHOENTAL & SCOTT (1949); it causes a bathochromic shift of the whole spectrum relative to that in solution (see Table I). The values of "s", the wavenumber shift relative to the spectrum in light petroleum solution, are listed in Table II. The positions of either band 1 or band 0 (corrected for self-absorption as in III.2) are taken as reference points. It has not been possible to predict the magnitude of the bathochromic shift due to changing the molecular environment. The values of "s" are similar and of the order of 600 cm.$^{-1}$ for all the compounds except anthracene and those with major crystalline interaction (IV.3) having D, E and F spectra. The value for anthracene, 1200 cm.$^{-1}$, is only a slight anomaly since reference to Table I shows that for crystalline anthracene, s = 900 cm.$^{-1}$ and 550 cm.$^{-1}$ relative to the fluorescence spectra in dioxane and naphthalene solutions respectively. "s" may be increased to 1200 cm.$^{-1}$ relative to solution in light petroleum.

IV. 2. THE MOLECULAR SUBSTITUTION EFFECT:

The effects of substituents on the spectra of aromatic compounds are not unique to crystalline fluorescence spectra; they are observed in absorption (CLAR 1952, JONES 1943, 1945) and in the fluorescence of solutions (SCHOENTAL & SCOTT 1949). Methyl substitution of 1:2 benzanthracene causes a shift of the whole spectrum relative to the parent compound; and a similar effect is obtained for other substituted compounds.

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The values of m_c and m_s, the shifts relative to the parent compound for crystalline and solution measurements, are listed in Table II.
In addition to these bathochromic shifts, some of the other differences between the spectra of the compounds and their parents, e.g. loss of fine structure, may also be substitution effects.

IV. 3. THE CRYSTAL INTERACTION EFFECT:

This effect is responsible for the remaining differences between the spectra of crystals and solutions, and is strikingly exhibited by the Type E spectra of 5-methyl and 8-methyl 1:2 benzanthracene. Their solution spectra are similar to that of 1:2 benzanthracene, with only a small substitution shift, m_s. The diffuseness and major bathochromic shift of the crystal spectra are attributable to large molecular interactions within the crystal. The spectra of several other compounds exhibit this loss of vibrational structure accompanied by a large bathochromic shift, and this general effect, due to molecular interactions in the crystalline state, which has not previously been reported, will be discussed in detail with reference to the results of NORTHROP & SIMPSON (1956).

IV. 3.1. RESULTS OF NORTHROP & SIMPSON:

Little work has been done on the fluorescence of microcrystalline layers of organic compounds, but the measurements of NORTHROP & SIMPSON (1956) on the fluorescence spectra of microcrystalline solid solutions of anthanthrene in anthracene throw an interesting light on the molecular interaction effects. They produced crystalline layers 5μ thick, by vacuum sublimation onto glass plates, and observed the emission spectra by a photographic method. Although this is susceptibl

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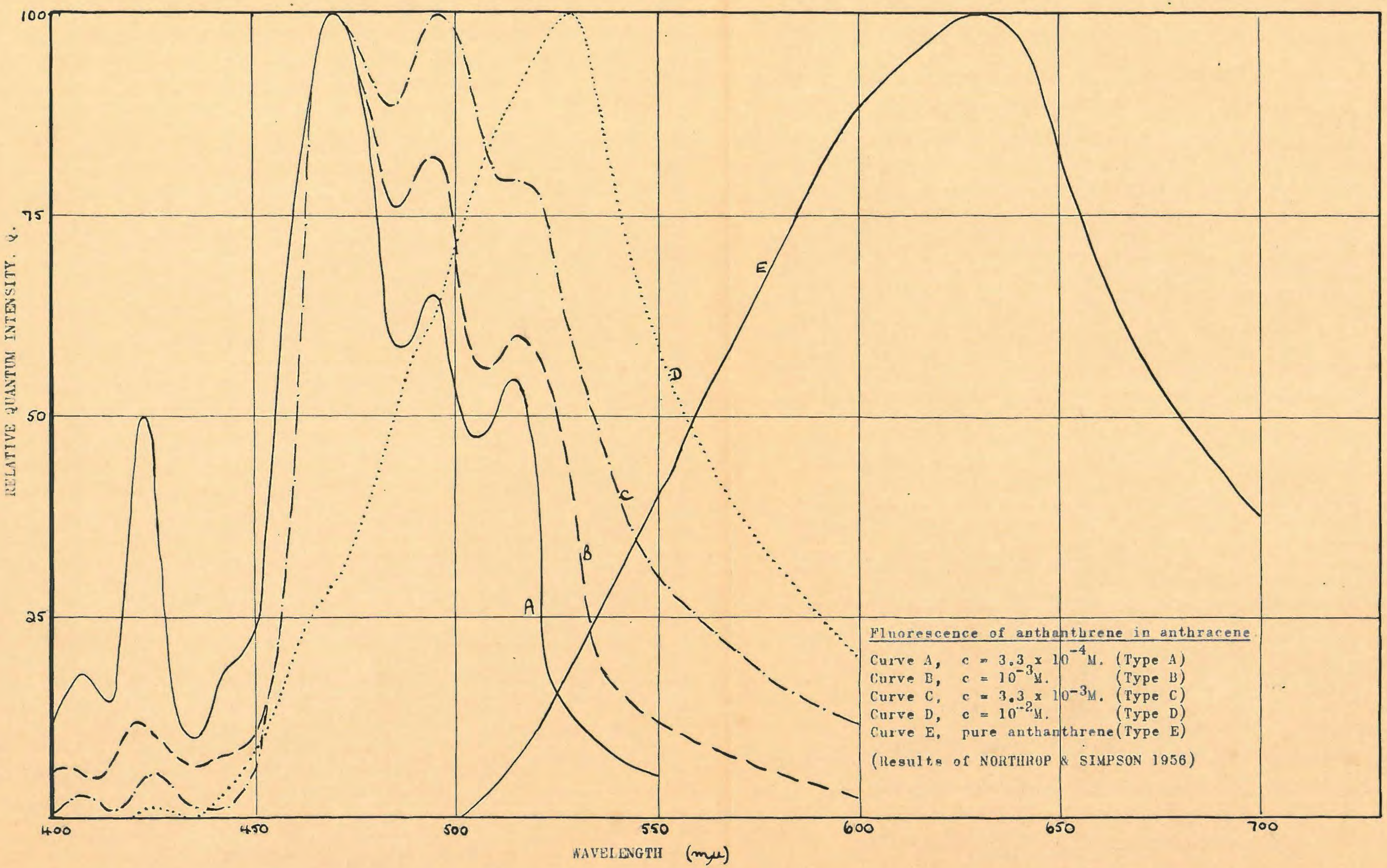
FIG. 28.


100
75
50
25
RELATIVE QUANTUM INTENSITY. Q.
400
450
500
550
600
650
700
WAVELENGTH (mμ)
A
B
C
D
E
Fluorescence of anthanthrene in anthracene
Curve A, c = 3.3 x 10^{-4}M. (Type A)
Curve B, c = 10^{-3}M. (Type B)
Curve C, c = 3.3 x 10^{-3}M. (Type C)
Curve D, c = 10^{-2}M. (Type D)
Curve E, pure anthanthrene (Type E)
(Results of NORTHROP & SIMPSON 1956)

to larger errors than the photomultiplier technique used for the present measurement the results, e.g. for anthracene, are in good agreement with the present results. Spectra were observed for anthanthrene concentrations ranging from 10^{-5}M to 10^{-3}M and for pure anthanthrene, whose fluorescence lies at longer wavelengths than the anthracene emission, and whose absorption spectrum overlaps the anthracene emission. The conditions required for energy transfer from the solvent to the impurity molecules are, therefore, satisfied (see Part 2.1.3.(i)), and for low impurity concentrations of 10^{-5}M to 3.3×10^{-4}M the characteristic anthanthrene fluorescence gradually appears, accompanied by a reduction in the intensity of anthracene fluorescence.

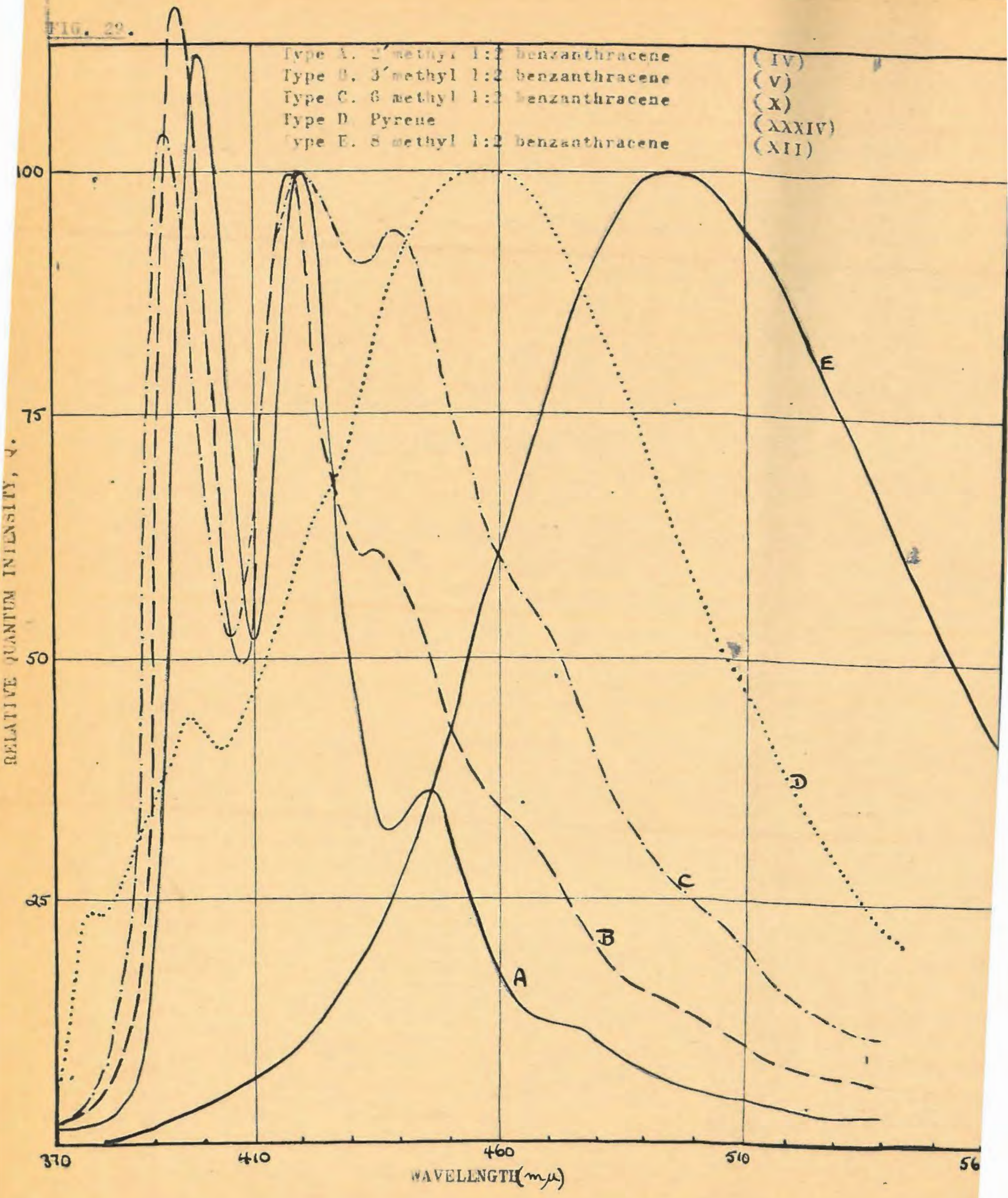
FIG. 28 shows the progression of spectra obtained by NORTHROP & SIMPSON for increasing concentration of anthanthrene. As the anthanthrene concentration, c, is increased, the fluorescence spectrum changes from one similar to our Type A, through intermediate stages, to one similar to Type E. For the purpose of comparison, a similar progression for the present results has been plotted in FIG.29, by selecting one spectrum typical of each Type. The spectra of the following compounds are shown:- 2'- methyl 1:2 benzanthracene (IV) (Type A); 3'- methyl 1:2 benzanthracene (V) (Type B); 6-methyl 1:2 benzanthracene (X) (Type C); pyrene (XXXIV) (Type D); 8-methyl 1:2 benzanthracene (XII) (Type E).

FIG. 28 shows that at concentrations of $c = 3.3 \times 10^{-4}$M, the 0, 1 and 2 bands of anthanthrene at λ = 467, 490 and 507 mμ are resolved, and the intensity falls away with increasing wavelength (Type A).

The anthracene spectrum appears at shorter wavelengths but with low intensity.

At $c = 10^{-3}$M, the three bands are still resolved but the intensity at longer wavelengths is increased showing a tendency towards a broader spectrum with consequen

FIG. 22.


Type A. 2'methyl 1:2 benzanthracene (IV)
Type B. 3'methyl 1:2 benzanthracene (V)
Type C. 6 methyl 1:2 benzanthracene (X)
Type D. Pyrene (XXXIV)
Type E. 8 methyl 1:2 benzanthracene (XII)
100
75
50
25
RELATIVE QUANTUM INTENSITY, Q.
370
410
460
510
56
WAVELENGTH (mμ)
A
B
C
D
E

less resolution of the longer wavelength bands. This is similar to the Type B spectrum (see FIG. 29).

At $c = 3.3 \times 10^{-3}$M the 0 band is still resolved but the 1 band is increased to a similar intensity and coalesces with higher bands to form a diffuse continuum extending to $\lambda \sim 600$ mμ (Type C).

At $c \approx 10^{-2}$M the spectrum is a broad band with a maximum at $\lambda = 510$ mμ (the positi of the original band 2) with inflexions at shorter wavelengths corresponding to bands 0 and 1. This spectrum may be classified as Type D, and was not described in III.8. However, 3:4 benzpyrene, which is a derivative of anthracene and 1:2 benzanthracene, has a Type D spectrum. The only other representative of this Type in the present measurements is pyrene (XXXIV) whose spectrum is drawn in FIG.2 As the concentration is increased further, this diffuse spectrum shifts towards longer wavelengths, and the spectrum of pure anthanthrene is a broad band, with a maximum at $\lambda \sim 620$ mμ, similar to a Type E spectrum.

It appears from this comparison that the sequence of spectral types A,B,C,D, and E corresponds to an increase in molecular interaction by several orders of magnitud from negligible interaction in Type A to very strong interaction in Type E, as the distances between the anthanthrene molecules decrease with increasing concentration.

NORTHROP & SIMPSON (1956) have proposed as a generalisation that the fluorescence spectrum of an organic compound in the pure solid phase is shifted to longer wavelengths, equivalent to a decrease in energy of 0.3 to 0.4 eV (2500 to 3300 cm.$^{-1}$) relative to its spectrum in solid solution. This is only valid for compounds with strong crystalline molecular interaction, such as anthanthrene, characterised by Type E spectra. The values of "s" in Table II show that for these compounds the energy decrease is only $\sim$ 0.07 eV in going from liquid solution to the pure crystal

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and the anthracene data in Table I indicate that "s" is even less, relative to solid solutions.

In view of the theoretical significance that NORTHROP & SIMPSON attach to this point, the clear distinction between compounds like anthracene and 1:2 benzanthracene with negligible crystal interaction, and those like 5-methyl 1:2 benzanthracene and anthanthrene with major crystal interaction, must be emphasised.

Whether the Type F spectra of the 9:10 dimethyl derivatives are due to molecular interaction or molecular substitution effects, cannot be resolved without fuller data on the fluorescence spectra in solution. Only a single diffuse peak is recorded by SCHOENTAL & SCOTT (1949) in the solution spectrum of 9:10 dimethyl 1:2 benzanthracene.

IV. 3.2. PHOTO-FLUORESCENCE DECAY TIMES:

The method of measuring the decay times of the microcrystalline samples is described in II.4. The measurements were carried out by Mr. T.D.S. Hamilton (HAMILTON 1958), and the values are listed in Tables II and III.

The decay times of 1:2 benzanthracene and the majority of its mono- methyl derivatives are between 8 and 16 mμ sec. The two exceptions are 5-methyl and 8-methyl 1:2 benzanthracene whose decay times are 125 mμ sec. and 99 mμ sec. respectively. Their Type E spectra are similar in shape to those of ionic crystals such as the alkali halides, and their molecular energy levels appear to have merged into broad crystal energy bands; their decay times have values similar to those of the alkali halides. The increased decay times may be due directly to crystal interaction effects, or to the increased probability of transitions between the singlet and metastable triplet states, due to the reduction of the energy gap.

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Increase in decay time with increase in spectral diffuseness due to crystal interaction is by no means a general rule as can be seen, for example, by 20-methylcholanthrene which has a Type E spectrum but the short decay time of 2.8 $m\mu$ sec. However, it does seem that compounds showing well resolved vibrational structure in their spectra have relatively low decay times; compare para-terphenyl ($\tau = 5.3$ $m\mu$ sec.), trans-stilbene ($\tau = 3.9$ $m\mu$ sec.), the mono-methyl 1:2 benzanthracenes ($\tau \sim 10$ $m\mu$ sec.). The crystal structure, the absorption spectra, the semi-conductivity, the photo-conductivity and other related properties of these compounds merit further study to elucidate the phenomena of long decay times in compounds such as 5-methyl and 8-methyl 1:2 benzanthracene

IV. 4, CARCINOGENICITY:

Of the 41 compounds listed in Tables II and III, 29 are known carcinogens belonging to one of the following six groups into which the known chemical carcinogens are divided:-

(i) Aromatic polycyclic hydrocarbons, their derivatives, and related compounds.

(ii) Amino derivatives of aromatic hydrocarbons.

(iii) Derivatives of 4-aminostilbene.

(iv) Derivatives of azobenzene.

(v) Certain aliphatic and heterocyclic compounds (e.g. urethane, nitrogen mustards).

(vi) Miscellaneous inorganic salts of arsenic, zinc, nickel, etc.

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The compounds listed in Table II belong to group (i) and are classified as "primary" carcinogens since they have the highest potency. Compounds in the other five groups are generally less potent and are called "secondary" carcinogens. Examples of this group are included in Table III. Fluorescence appears to be a common property of all the primary carcinogens and some of the secondary carcinogens, and since the electronic structure determines the physical property of fluorescence, it is of interest to search for distinctive relations between the fluorescence spectra and the carcinogenic activity of the compounds.

It has been found that carcinogens form relatively stable complexes with proteins. which retain fluorescence properties similar to those of pure carcinogens PULLMAN & PULLMAN (1955) proposed the formation of the protein-carcinogen complex is associated with a high electron density in a certain region (designated the "K" region) of the carcinogen molecule. It might be expected that those molecules which form strong protein complexes will also tend to show strong crystalline interaction effects, and the spectral data in Table II show a fair degree of correlation along these lines. Thus, all six compounds with Type D, E or F spectr (strong interaction) are carcinogens, and three of these are of the highest potency. Of the six compounds with Type A spectra (negligible interaction) four have negligible or slight carcinogenicity, and the other two are only weak carcinogens. Of the ten compounds with Type B or C spectra (intermediate interaction) six are carcinogens, and four are non-carcinogens. Certain exceptions to this simple rule relating crystal interaction effects and carcinogenicity occur and may possibly be due to differences between the molecular interaction with like molecules, and that with proteins. However, the present results are insufficient for a further study of this subject, and it is likely that other factors influence carcinogenic activity

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There is an approximate correlation between the values of m_c for the 1:2 benzanthracene derivatives listed in Table II and their carcinogenic potency. Thus $m_c \ll 100$ cm.$^{-1}$ for all non-carcinogens (except 2': 7 dimethyl 1:2 benzanthracene for which $m_c = 200$ cm.$^{-1}$). For eleven out of the fifteen carcinogens, $m_c \gg 250$ cm.$^{-1}$, and it is only less for those compounds showing weak activity.

The other compounds studied (Table III) do not contain the 1:2 benzanthracene nucleus and the correlation between m_c and carcinogenicity has not been extended to them. A similar correlation might be expected relative to chrysene or 3:4 benzophenanthrene but insufficient compounds in these groups have been studied to attach significance to such an analysis of the present data.

V. CONCLUSION

The photo-fluorescence spectra of a related group of organic compounds have been measured. The purpose of the investigation was:-

(a) to study the crystalline spectra for such a large group of compounds; no similar measurements have been made for compounds more complex than anthracene.

(b) to search for any crystalline interaction effects on the fluorescence spectra due to the molecules being rigidly bound in a crystal lattice. Dilute solution spectral measurements, which approximate to the true molecular emission, are used for comparison.

A photomultiplier technique giving good spectral resolution was used, and the sensitivity of the apparatus was such that very thin microcrystalline layers emitted fluorescence of sufficient intensity for all the vibrational structure (where present) to be resolved.

Of the 41 compounds studied, anthracene is the simplest molecule, and the spectra of this compound was studied in detail initially in III.2 Due to coincidence of the absorption and fluorescence spectra in the wavelength region of the fluorescence $1_o \rightarrow 0_o$ transition, the intensity of the corresponding fluorescence vibrational band 0 is reduced by an amount dependent on the specimen thickness. This thickness was such that the vibrational peaks at longer wavelengths are not affected by self-absorption. By using the fluorescence spectra obtained from specimens prepared using different solvents and the absorption spectra of KORTUM &

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FINCKH (1942), a method was evolved in III.2.2. for the calculation of the true molecular intensity of band 0, i.e., the intensity it would have if reabsorption were completely absent. This method of correcting the observed technical spectra is found to apply equally to all the derivatives of anthracene, 1:2 benzanthracene and all its derivatives which have been studied in this work.

The method can, therefore, be generally applied to all crystalline fluorescer spectra where reabsorption occurs in the region of the $1_0 \rightarrow 0_0$ transition. The spectra of the other 40 compounds vary in appearance from those similar to anthracene, showing well resolved vibrational structure, to very diffuse spectra where the vibrational bands have coalesced leaving a broad featureless band. Loss of vibrational structure is usually accompanied by a bathochromic shift of the whol spectrum. The spectra are classified into six types, A to F, in III.8. Some of the compounds belong to a well-defined sequence, e.g. 1:2 benzanthracene and its mono-methyl and dimethyl derivatives; 3:4 benzophenanthrene and its mono-methyl derivatives, and these groups are particularly useful in the study of the effect of substitution on the parent chromophore. Molecular substitution effects have been observed previously in absorption and in the fluorescence of solutions, and the pres results show a similar bathochromic shift of the whole spectrum relative to the spectrum of the parent compound (IV.2). Comparison of the crystalline spectra with the corresponding solution measurements c SCHOENTAL & SCOTT (1949) show the effect of changing the environment of the fluorescent molecule, from liquid petroleum solution in which it is free to move at random, to a rigidly bound lattice of similar molecules. The general effect is a bathochromic shift of the crystalline spectra relative to solution spectra (IV.1).

The most important effect, however, observed from the present measurements is

Crystal Interaction Effect (IV.3) which occurs between similar molecules bound in a crystal lattice. Some compounds, e.g. 5-methyl and 8-methyl 1:2 benzanthracene possess solution fluorescence spectra similar to the parent compound, showing well resolved vibrational structure. However, in the solid state, their spectra are broad bands possessing no vibrational structure and are shifted to longer wavelengths. Their decay times are greatly increased compared to the parent compound. This effect is found to occur to a varying degree in many of the compounds whose spectra are reported, and it is this effect which provides for the classification of the spectra. This type of molecular interaction effect has not been explicitly reported previously, though an analysis of the results of NORTHROP & SIMPSON shows its existence in other organic compounds.

Carcinogenicity is a property of 20 of the compounds and in IV.4 some remarks are made on the possibility of a connection between crystal interaction and carcinogenicity. An approximate correlation between the shift of the spectra of the 1:2 benzanthracene derivatives relative to the parent compound and their carcinogenic potency is suggested.

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PART 2.

PHOTO-FLUORESCENCE OF AND INTER-MOLECULAR ENERGY TRANSFER IN LIQUID ORGANIC SOLUTIONS OF PARA-TERPHENYL IN TOLUENE.

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PART 2.

PHOTO-FLUORESCENCE OF AND INTER-MOLECULAR ENERGY TRANSFER IN LIQUID ORGANIC SOLUTIONS OF PARA-TERPHENYL IN TOLUENE.

I. 1. INTRODUCTION:

I. 1.1. THE FLUORESCENCE PROCESS:

In the General Introduction of Part 1. of this work, Sections I.11 and I.12 were devoted to the explanation of the process which gives rise to fluorescence within a molecule. A simple diatomic molecule was used as a model but, although this presents an oversimplified picture of the fluorescence process, it is a sound basis on which to study photo-luminescence and provides the necessary background for the study of the mechanism of energy transport between molecules. The molecular fluorescence of organic compounds is identical in the vapour, solution and solid states excluding any perturbations due to environment, concentration or temperature, but in condensed systems the additional process of "resonance transfer" of the excitation energy from one molecule to another within the system is observed. Because of this transfer the luminescence process generally involves several molecules rather than just a single molecule as we ideally supposed before in Part 1. Section I.

FIG. 1 is a simplified molecular energy level system comprised of singlet π-electronic levels and vibrational levels. It is similar to FIG. 1 in Part 1., but is slightly more detailed and is included for easy reference to the reader. The various processes which can occur are adequately depicted and described on the diagram where the electronic levels are denoted 0, 1, 2 etc., and the vibrational levels are indicated as discrete sub-levels (suffixes 0, 1, 2 etc.). It is perhaps of interest to note that the energy level systems of molecules are amenable to calculation as, for example, DEWAR & LONGUET-HIGGINS (1954) & POPLE (1955) have recently shown for anthracene.

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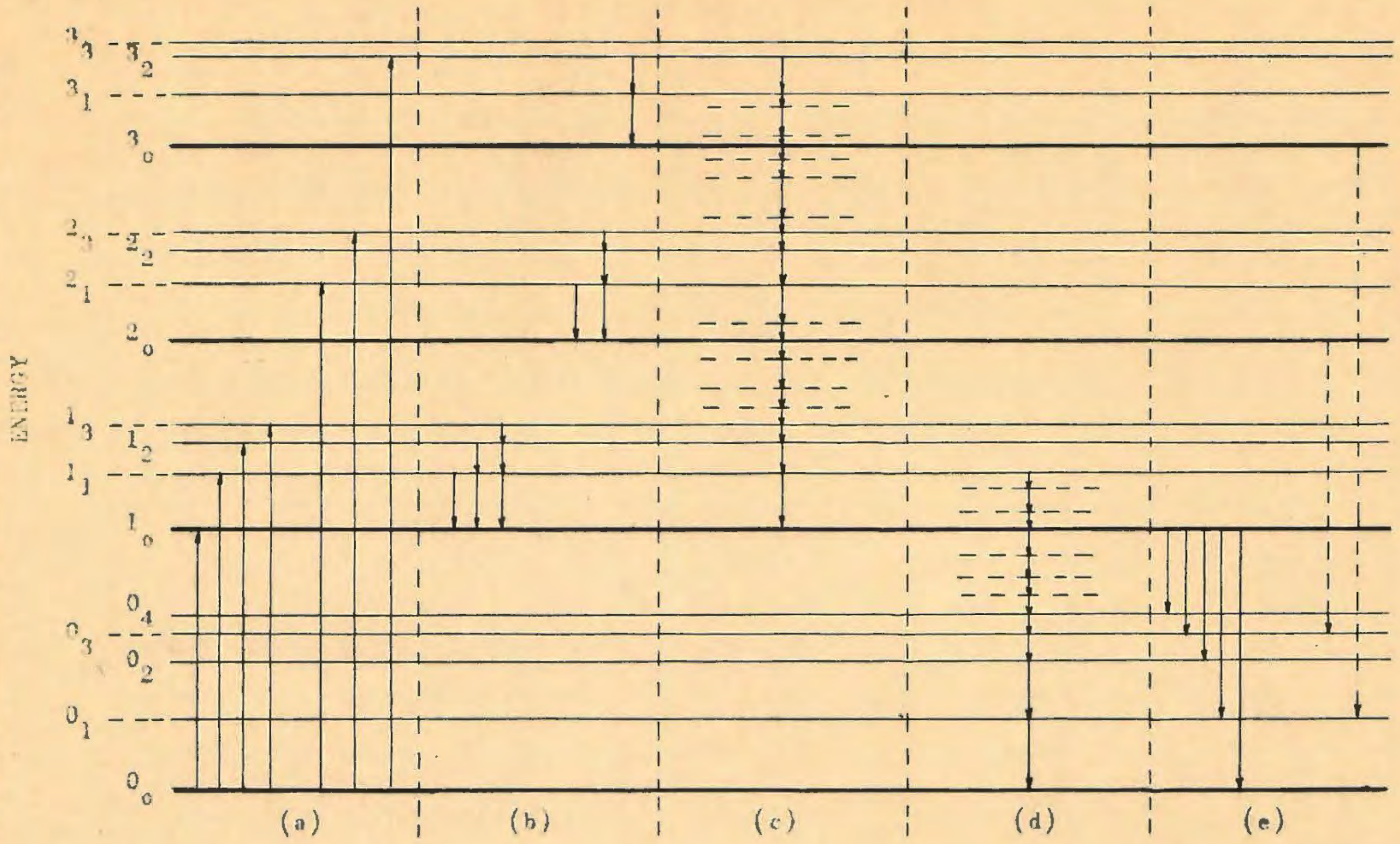
FIG.1. Energy levels in an organic molecule and luminescence processes.
(a) Excitation. (b) Internal Degradation. (c) & (d) Internal Conversion.
(e) Fluorescence.



Experimental evidence indicates that energy transfer between molecules usually occurs after stage (c) (of FIG. 1) of the molecular luminescence process, that is from the 1_0 level (i.e. the lowest vibrational level of the first excited electronic state) of the initially excited molecule. Hence one important and obvious condition for transfer between two molecules is that the 1_0 excitation energy of the donor be equal to, or greater than, that of the acceptor molecule. Bearing this in mind, it is readily seen how transfer affects the luminescence characteristics of various systems. A system of identical components, such as a pure organic crystal scintillator, is one in which transfer may occur according to the above condition. However, provided the component molecules retain their individuality, the characteristics of such a system are in no way affected by the energy transfer process. The energy levels of all the molecules are identical as also are their $1 \rightarrow 0$ emission and $1 \rightarrow 0$ internal quenching probabilities.

It is in two-component systems like mixed crystals, liquid solutions and plastic solutions that energy transfer achieves a significant purpose (BOWEN et al 1949, KALLMANN & FURST, 1950). These contain in small concentration an efficient impurity, or solute, molecule which possesses a 1_0 level of lower energy than that of the host or solvent molecules. When solvent molecules are excited, transfer amongst themselves eventually brings some of their excitation energy within reach of a solute molecule. Then when solute excitation results from solvent-to-solute energy transfer, the solute molecules rapidly drop to their 1_0 levels by internal conversion (FIG. 1(c)), so that excitation energy is effectively "trapped" in the solute because it cannot return to a solvent molecule. From the point of view of the solvent, trapping represents a special kind of quenching. However, if the solvent itself is a less suitable emitter than the solute, by reason, for example, of its lower quantum efficiency (as in liquid and plastic solutions) or the shorter wavelength of its emission, this type of quenching

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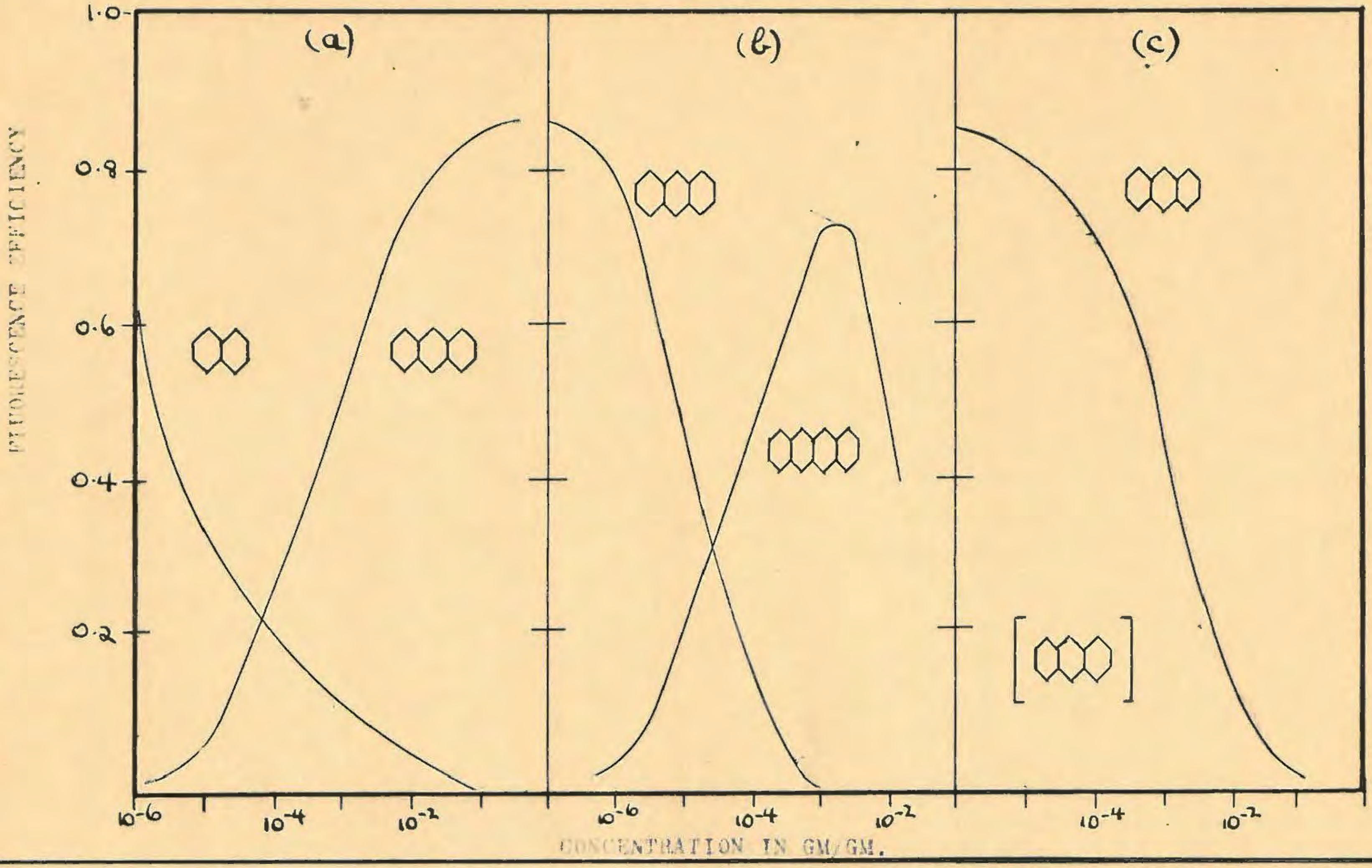
FIG. 2. Photo-fluorescence of mixed organic crystals (BOWEN et al 1949)
(a) Anthracene in Naphthalene.
(b) Naphthacene in Anthracene.
(c) Acridine in Anthracene.



is desirable for scintillation purposes. At solute concentrations sufficient to ensure trapping of all or most of the solvent excitation energy, the luminescence characteristics of the two component system depend entirely on the transfer process and the characteristics of the solute; the emission spectrum is that of the solute and the quantum efficiency and mean life time are determined by those of the solute and the efficiency of the transfer process.

BOWEN et al (1949) investigated the transfer process in solid solutions of phosphors, containing a small amount of impurity, in the benzene ring series $C_{4n+2}H_{2n+4}$, where 'n' is the number of benzene rings fused in a straight line. Usually the solute impurity was the next member of the series, whose fluorescence spectrum lay at longer wavelengths than the host material, showing that its 1_0 level occurred at lower energy than that of the host. As explained previously, the excitation energy of the solvent molecules, which is transferred amongst themselves, eventually reaches a solute molecule and is effectively trapped there due to internal conversion to the 1_0 level.

The mixed crystal systems used were (a) anthracene in naphthalene, (b) naphthacene in anthracene and (c) acridine in anthracene, and the results obtained are shown graphically in FIG. 2. These spectra were obtained from measurements of the relative intensities of light emission using filters selected to transmit either the fluorescence of the host or of the impurity.

The photo-fluorescence of the mixed crystal specimens has two components characteristic of the solvent and the solute molecules respectively, but the solvent fluorescence is suppressed and replaced by that of the solute even at concentrations of $\sim 10^{-5}$ gm/gm (FIG. 2(a)). FIG. 2(b) exhibits the existence of a similar transfer of energy but when the solute concentration exceeds 10^{-3} gm/gm the efficiency of the

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phosphor drops due to "self-quenching" by the abundant naphthacene molecules. A comparable effect is shown in (c), transfer to the anthracene occuring at the same order of concentration. Acridine has negligible fluorescence itself in the solid state and quenches the energy transferred from the anthracene without radiating.

Energy transport of this type in mixed systems where the fluorescence emission is characteristic of the included molecule and not the initially excited host, is now a well observed fact and various theories have been postulated to determine the mechanism by which energy moves through a large number of similar molecules to be eventually captured by an impurity molecule (which presents a high capture cross-section for the energy).

For their experiment with such low concentrations, BOWEN et al described the energy transport mechanism as "exciton migration", the term "exciton" is used merely to indicate the excitation energy transferred from molecule to molecule to distinguish it from the process of radiation transfer by photon emission and reabsorption. The term "energy transfer" is usually interpreted to include both radiative transfer, or absorption and re-emission, and non-radiative transfer. Since the first experiments on this subject, there have been many attempts to define the mechanism by which molecular energy is transferred from molecule to molecule; the two distinct mechanisms are non-radiative and radiative transfer, but various authors have expounded their own particular theories on the exact nature of the non-radiative process. It is, therefore, important at this stage to define and explain the various theories of the energy transfer process which have been considered by other workers based on their experimental results.

Non-radiative transfer has several manifestations which need clarification with regard to both the mechanism and the interactions between molecules which lead to their existence. This will be followed with a description of the radiative transfer process.

I. 1.2. NON-RADIATIVE ENERGY TRANSFER:

For our purposes it is convenient to describe the degree of interaction of two fluorescent molecules in terms of their π-electron "clouds", or in reality their respective π-electron wave functions. We may define the interaction as "negligible" when the "clouds" are widely separated and strong when the π-electron wave functions overlap by an arbitrary appreciable amount. There may be an intermediate region of "weak" interaction when overlap is negligible, due to the VAN DER WAALS' or polarization forces between molecules.

When two molecules possessing similar electronic levels interact strongly they reach a state where their individual π-electron systems can no longer be resolved. The latter must instead be considered as a single system whose levels are similar but somewhat broader than those of its components. An arrangement of a large number of strongly interacting identical molecules similarly becomes characterised by a banded energy level system instead of a number of identical but discrete molecular systems.

In these strongly interacting arrangements the π-electrons of component molecules are non-localised and consequently electronic excitation energy is also non-localised over all the molecules. The term "inter-molecular" energy transfer thus loses its meaning since only the system as a whole but not its individual molecules contain excitation energy. Energy transfer between different positions of the system has a meaning, however, and here molecules serve to define different positions.

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The following modes of non-radiative transfer may be distinguished:-

I. 1.2.1. Electron Migration:

This is the first of the two possible modes of transfer in the above system and can only occur when the excitation energy is sufficient to raise an electron from the highest broadened level, or filled band, of the system to its lowest empty band. The excited electron and its "positive hole" it leaves behind in the filled band, being non-localised and independent of one another, may move freely in their respective bands. The "electron migration" resulting constitutes a transfer of both excitation energy and charge. The removal of an electron from the molecule in the filled band constitutes ionization of the molecule which can only be produced by ionizing radiations and is, therefore, not relevant to the present photo-fluorescence studies where lower energy radiation only has been used. This mechanism of energy transfer need not, therefore, be considered further.

I. 1.2.2. Exciton Transfer:

The second mode of transfer in a strongly interacting system can occur when the excitation energy is insufficient to excite an electron to an empty band and arises because it is possible for the excited electron and its positive hole to exist in a series of states in which they are bound together in one another's field. FRENKEL (1931) has termed an electron and positive hole bound together in this way an "exciton" and has described how the non-localised nature of the exciton leads to energy transfer in a system of strongly interacting atoms. "Exciton transfer" is to be distinguished from "electron migration" by the fact that only excitation energy, not charge, is transferred.

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BOWEN et al (1949), as previously stated, used the term "exciton" in a different sense, merely to label the position of the excitation energy at any moment, thereby distinguishing it from radiative photon transfer. The "exciton" is envisaged to migrate through the lattice until it is eventually captured by a molecule which radiates the energy as fluorescence or quenches it. In a mixed crystal or a solution the exciton energy corresponds to the first electronic excitation level of the solvent. The solute molecule has a lower excitation energy since its first absorption band lies at longer wavelengths, and hence if the exciton is transferred to it the solute molecule is raised into a high vibrational level of the first excited state and excess vibrational energy is lost as heat to the lattice. The energy is thus effectively trapped and fluorescence, characteristic of the solute, subsequently occurs.

From the results of BOWEN et al (FIG. 2) three factors emerge which contribute to the high efficiency of the energy exchange process:

(i) The absorption spectrum of the solute (corresponding to transitions from the first excited state) almost coincides with the solvent fluorescence spectrum so that a state of "resonance" is established.

(ii) The fluorescence of the solvent and the absorption of the solute in the same spectral region are both plane polarized in the same direction relative to the molecular axis.

(iii) The added solute molecules fit into the lattice of the solvent, parallel to the solvent molecules.

I. 1.2.3. Sensitized Fluorescence:

In outlining exciton transfer and electron migration a system of molecules in

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permanent strong interaction was considered. What might be considered a variation of this system is that where localised groups of two or more molecules interact strongly but only for intermittent periods, during collisions for example. We would, from our previous considerations, expect intermittent exciton and electron transfer to occur in this system. Transfer phenomena of the former type were in fact observed and studied (CARIO & FRANCK, 1923, KALLMANN & LONDON, 1929) in monatomic gases where strong interactions between molecules are intermittent, but where transfer can take place over large distances of the order of 50 Å if the condition of resonance is fulfilled. These observations were made prior to FRENKEL's exciton hypothesis and the transfer mechanism was described as "sensitized fluorescence". By analogy, intermittent energy transfer in molecular systems has also been called sensitized fluorescence.

FRANCK & LIVINGSTON (1949) reject exciton migration as a likely mechanism of energy transfer in organic crystals since strong molecular coupling within the lattice is necessary for transfer between similar adjacent molecules.

The absorption spectrum of crystalline anthracene showed no evidence of an additional series of bands indicating stronger inter-molecular coupling than for solution and vapour. Recent results, however, have shown such an "exciton" band structure in the crystalline state. In addition, FRANCK & LIVINGSTON stated that the spectral distribution of the fluorescence indicates that every molecule stays in the excited state long enough to adjust its vibrational energy to the surrounding temperature. Each molecule must remain, therefore, in the excited state much longer than the vibrational period, a condition which excludes exciton migration. Therefore, a similar process of energy exchange to that in gases might be expected to occur in a crystalline lattice in which the absorption and emission bands of the constituents

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overlap. However, there is an important distinction between this process in gases and in the solid state. For the gas it is immaterial whether the excitation energy can be transferred to similar molecules or only the impurity, for the individual atoms are moving at random and eventually an impurity molecule will approach the excited host molecule. In a solid the individual atoms are restricted to a fixed position so that transfer between similar molecules becomes important. On the sensitized fluorescence theory, the solvent molecules between the excited molecule and the impurity play no part in the exchange process.

In gases it has been observed that energy may be transferred over distances ~50 Å; therefore, transfer over ~30 molecular distances (the figure obtained from the concentration (FIG. 2) at which host and impurity fluorescence is equally probable) in the solid from the excited solvent to the solute molecule, is considered to have equal probability with fluorescence emission of the excited solvent molecule.

LITTLE & BIRKS (1952) and BIRKS & LITTLE (1953) have, however, shown from spectral measurements that the electronic energy configuration of both the solvent and the solute molecules are virtually unperturbed by their neighbours. It is not clear, therefore, how the molecular wave functions could overlap sufficiently at ~30 molecular distances for transfer to occur and yet leave the intervening molecules unperturbed. It is difficult to see why the unexcited host molecules can not receive this energy when they are much more in resonance with the excited host than the impurity.

We have seen that intermittent exciton transfer in molecular systems can be called "sensitized fluorescence"; at the same time intermittent electron migration can be called a type of transfer by "ionization".

The important distinction between exciton transfer and sensitized fluorescence on the one hand, and electron migration and ionization on the other, is that in the latter processes excitation energy is intermittently localised on individual molecules (between transfers) whereas in the former it is permanently non-localised.

I. 1.2.4. Dipole-Dipole Transfer:

FORSTER (1948, 1949, 1951) described this form of energy transfer which arises from "weak" VAN DER WAALS' forces between molecules. To picture this interaction we must recall that the π-electrons of a fluorescent molecule are not stationary in their "clouds" but correspond to rapidly alternating electric waves. There are as a result rapidly varying dipoles in the electrical structure of the molecule (although its time average dipole moment may be zero) and these can induce in neighbouring molecules other dipoles in phase and in interaction with themselves. It occurs in this way that the "dipole of transition" of an excited molecule can induce a similar dipole and transition in a neighbouring unexcited molecule, thus producing energy transfer. A principal feature of FORSTER's analysis of the dipole-dipole transfer is that the transfer probability varies, like the energy of the VAN DER WAALS' interaction, as the inverse sixth power of the distance between the molecules.

I. 1.3. RADIATIVE TRANSFER.
PHOTON EMISSION AND REABSORPTION:

BIRKS (1953) finds the non-radiative hypothesis of inter-molecular energy transfer inadequate to explain experimental observations and proposes the radiative process of photon emission and reabsorption as the dominant transfer mechanism. It is proposed that due to the close directional energy and polarization alignment of the excited solvent and solute molecules (factors (i), (ii) and (iii) in I. 1.2.2.), the absorption coefficient of the impurity molecule is sufficiently enhanced over its value

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measured in dilute solution for photon emission and reabsorption to take place. The theory is immune from the criticisms levelled at the sensitized fluorescence hypothesis because it allows for transfer to adjacent similar molecules, the process recurring until the energy is eventually trapped at an impurity molecule. Equations have been derived on the photon theory which are in general agreement with available experimental results (see BOWEN et al (1949) and WRIGHT 1953) and the theory gives a physical interpretation of the processes of resonance energy transfer, self-quenching and concentration quenching (BIRKS 1954). BOWEN & LAWLEY (1949) and BOWEN (1951) offered various objections to this theory but BIRKS (1953) has given suitable explanations to meet these.

I. 2. RELATIONSHIP BETWEEN MODES OF ENERGY TRANSFER:

At this stage it is appropriate to point out that several workers consider the various modes of non-radiative transfer and radiative transfer each to be a limiting condition of one general transfer process. This has been explained mathematically in reviews by HELLER & MARCUS (1951) and DEXTER (1953). There still exists, however, considerable disagreement amongst experimental workers in the interpretation of results. Some consider one of the non-radiative mechanisms to be dominant and the radiative mechanism only "trivial", while others attempt to show that the photon emission and reabsorption process is alone responsible for the transfer. (BIRKS (1953) and (1954) shows that the photon cascade theory provides a quantitative description of the fluorescence properties of organic phosphors, which is in excellent agreement with experiments and provides strong evidence of the validity of the photon theory of energy transfer. Several other workers since, e.g. COHEN & WEINREB (1956), NORTHROP & SIMPSON (1956) have interpreted their experimental results in terms of a non-radiative transferprocess.

The possibility that each mechanism is a limiting condition of a general transfer process is discussed by BROOKS (1956) in a review of organic scintillators. He draws the analogy of energy transfer between molecules and transfer of radio frequency energy between antennae. This analogy is firmly established firstly by the resemblance of the "conducting" π-electron clouds of fluorescent molecules to antennae and secondly by the fact that the states of electronic excitation of the molecule can be described as electronic waves in such antennae; these waves could be obtained by subtracting the π-electron waves of the molecule in its ground state from those of the excited state. The only way energy can migrate between two widely spaced antennae (negligible interaction) is by electromagnetic waves, i.e. radiative transfer. The probability, or rate, of transfer varies, like the energy of the wave, inversely as the square of the distances, R, between the antennae. At smaller spacings the radio frequency current in one antenna can induce a current in the other ("weak" interaction) producing "inductive transfer", which is analogous to dipole-dipole transfer. At smaller distances of separation, inductive transfer is considered to overshadow radiative transfer because its efficiency varies as R^{-6}.

When two antennae are placed in very close proximity their mutual inductive coupling is so enhanced and further supplemented by capacitive coupling that they become the primary and secondary of a transformer where energy may be transferred from one to the other with an efficiency approaching 100%. However, the analogy with molecules is obscured in this region of "strong" interaction because of the diffuse nature of the π-electron cloud compared to the discrete boundaries of typical metallic antennae. The π-electron cloud could be more easily simulated if we used antennae constructed from perfect conductor along its axis to perfect insulator of unit

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dielectric constant at its surface. Thus the merging of the two antennae surfaces into a common new medium would become the analogy of π-electron cloud overlap in the strong interaction. This would lead to highly efficient transfer analogous to exciton transfer.

This simple analogy helps to clarify some of the factors governing intermolecular energy transfer. The resonance condition for transfer of molecular energy, i.e. the energy of the donor must be greater than or equal to that of the acceptor, has its analogous condition of equivalent resonant frequencies of antennae. Also, in the same way as radio frequency radiation from its equivalent flat antenna, emission from an excited molecule is polarized and has a polar diagram (showing probable direction of emission) with a maximum perpendicular to its plane. Thus the efficiency of radiative transfer between two molecules is sensitive to their mutual orientations reaching a maximum when their planes are parallel and their axes (which are perpendicular to their planes) are aligned.

It is also readily seen that the various modes of non-radiative transfer depend on the mutual orientation of the molecules in exactly the same way. Therefore, the basic conditions governing energy transfer between molecules apply equally to all the proposed modes of migration, whether they be radiative or non-radiative. This leads to the assumption that there is a continuous transition between different modes of transfer, which makes it difficult to attribute any experimentally observed transfer effect to a particular mode.

The elucidation of this problem in various solid, plastic and liquid fluorescent systems has been the subject of much experimental work. Many workers have attempted to assign one particular mode of transfer to explain their experimental results, though often it has not been possible to go further than to decide whether the transfer mechanism is radiative or non-radiative.

Some of the published work of various workers is disucssed in I.3. Their discussions and conclusions in the allotting of a particular transfer mechanism are given and in some cases criticised by the author.

I. 3. PREVIOUS WORK:

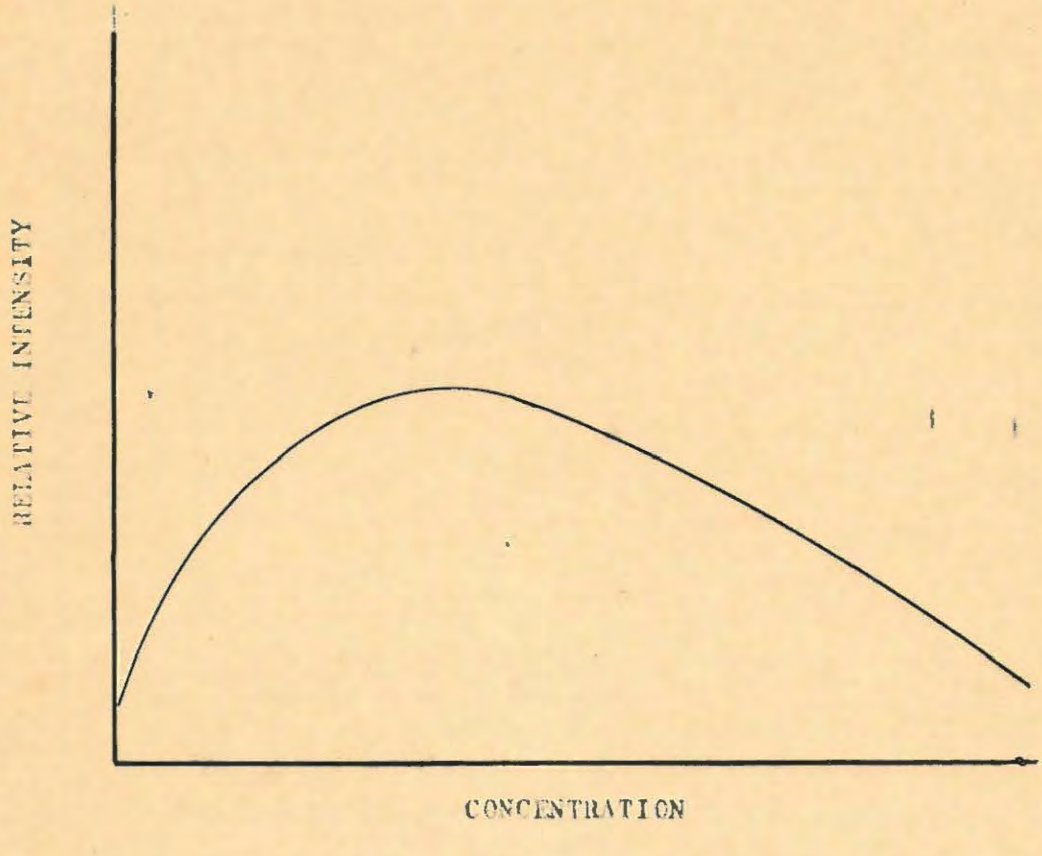
Energy transfer processes have been identified in scintillators and in similar systems by studying characteristics such as quantum efficiency, emission life time, spectra, polarization of emission and the dependence of these characteristics on one another and on the composition, size, temperature, etc., of the scintillator.

In the present work a study has been made of solvent-solute energy transfer in liquid organic solutions, and the subsequent discussion will be limited to such systems.

The high fluorescence efficiency of certain organic liquid solutions, when excited by ionizing radiations, was observed initially by AGENO, CHIOZZOTO & QUERZOLI (1949, 1950), KALLMANN (1950) and REYNOLDS, HARRISON & SALVANI (1950). The last named observed that solutions of para-terphenyl in toluene, xylene, benzene and similar aromatic solvents have a high scintillation efficiency, equivalent at optimum concentration to almost 50% that of a single anthracene crystal.

Following on the initial work of KALLMANN (1950), KALLMANN & FURST (1950, 1951a) continued investigations on solutions, prepared from a number of organic solutes in various solvents, excited by ionizing radiations. It is now realised that the use of ionizing radiations, instead of ultra-violet radiation of selected wavelength, complicates the elucidation of the energy transfer mechanism, because inter-molecular

FIG. 3. Relative Fluorescence Intensity vs. Concentration for liquid solutions (diagrammatic).



energy transfer occurs from the lower excited states of the molecule, and therefore, internal conversion of the excitation energy must occur first. However, since the spectrum of the fluorescence emission is independent of the manner of excitation, these results provide relevant background to the present experiments. For the solutions, the Relative Intensity of the Fluorescence Emission was measured as a function of concentration of the solute (or impurity) and curves similar to FIG. 3 were obtained. The spectral position of the fluorescence precluded the possibility that it was emitted by the solvent, yet its intensity was greater than could be accounted for by direct absorption of the incident energy by the solute. Thus a transfer of energy from the initially excited solvent molecules to the solute was demonstrated, the probability of transporting to and trapping of the excitation by the fluorescent molecule being proportional to the concentration of the fluorescent molecule. All solutions showed the general characteristics of FIG. 3. A sharp rise in intensity is observed with small concentrations, then a slower or almost constant intensity over a large range of concentrations, and finally a slow decrease in intensity. During the first part of the curve, the transport of excitation energy to the fluorescent molecules is most effective and little self-quenching occurs. In the middle section, self-quenching of the excited molecules competes with the increasing transport of energy from the solvent until in the last section both self-quenching of the fluorescent molecules and saturation in the transport of energy are effective with the resultant decrease in Intensity.

The term "self-quenching" is used to describe the overall decrease in emission probability of a fluorescent solution which occurs in strong solutions ($>10^{-3}$ mole/litre) due to interaction between an excited solute molecule and an identical unexcited molecule. It is not necessary for us to investigate the probable mechanism which give rise to the self-quenching effect; it is sufficient to note that its occurrence is due to the close proximity of fluorescent solute molecules and that it only commences at concentrations 100 times higher than those necessary for weakening of radiation by internal quenching (loss of vibrational energy within the molecule without radiation) and by reabsorption.

KALLMANN & FURST (1950) attempted a quantitative theoretical analysis of their results in order to determine whether the energy transfer mechanism they had exhibited was radiative or non-radiative. Their non-radiative mechanism was envisaged as a collisional transfer between excited solvent "double-molecules" and fluorescent molecules. Solvent "double-molecules" are formed by the combination of one excited and one unexcited solvent molecule forming a system which does not radiate but retains the excitation energy. This energy may then be transferred to a fluorescent solute molecule by collision.

The actual intensity of fluorescence emission from the solvent was small which, on the radiative theory, infers that the quenching time of solvent molecules is also small. Therefore, transfer to solute molecules must occur in a shorter time than the quenching time and KALLMANN & FURST (1950) stated that molecular interaction energies of the order of 1 Volt were necessary to account for the strong output.

On the non-radiative theory, however, because the excited solvent "double-molecule" does not radiate, a much longer quenching time can be assumed and, therefore, smaller interaction energies are necessary for transfer.

A non-radiative mechanism is thus indicated though the authors state that the evidence is inconclusive.

REID (1952) reported the conditions necessary for an efficient transfer of energy from one molecule to another, which are summarised in FIG. 4, and at this stage it is

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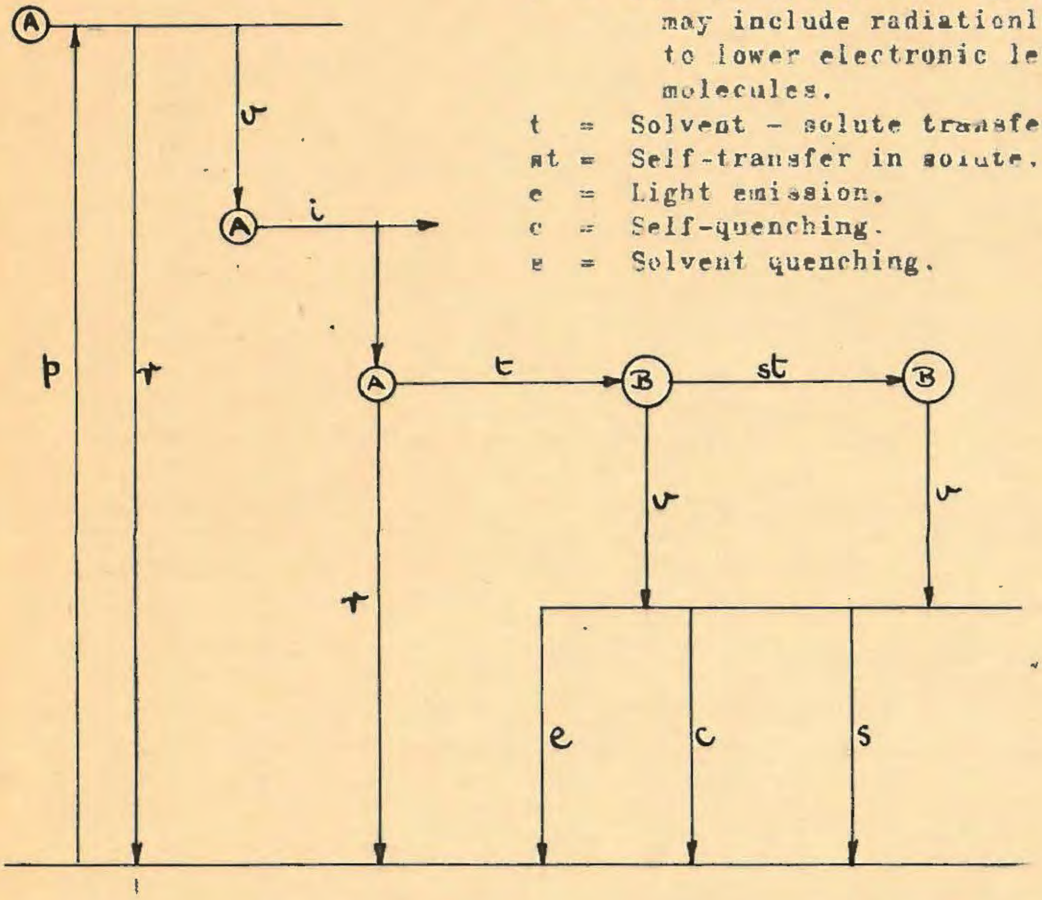
FIG. 4. Intermolecular energy transfer and associated processes.

A = Solvent molecule energy levels.
B = Solute molecule energy levels.
p = Primary excitation of solvent.
r = Non-radiative solvent quenching.
v = Loss of vibrational energy (which may include radiationless crossover to lower electronic levels of some molecules.
t = Solvent - solute transfer process.
st = Self-transfer in solute.
e = Light emission.
c = Self-quenching.
s = Solvent quenching.



convenient to review them.

For an efficient scintillation process, "e", the requirements are:-

1. High efficiency of solvent-solvent transfer of electronic energy (i) relative to radiationless quenching by the solvent so that energy transport from the body of the solvent to a solvent molecule adjacent to a solute molecule can occur.
2. High probability of transfer from solvent-solute (t) but low efficiency of reverse process.
3. High probability of emission from excited solute molecule (e) relative to self-quenching (c) or solvent quenching (s).

Solvent-Solvent Transfer:

Efficient transfer between identical molecules will occur only if transfer is rapid compared with the rate of loss of vibrational energy in the excited electronic state, otherwise the remaining energy is insufficient to excite another molecule. Good solvents should, therefore, be those with high polarizability (good electric coupling with adjacent molecules) but with few branches or long side chains which would facilitate dissipation of vibrational energy. The usual solvents, e.g. toluene, xylene, etc. are polarizable aromatic compounds. Any substituents present are of the electron donating kind which further increase the π-electron density of the aromatic ring and thus the polarizability.

Solvent-Solute Transfer:

High efficiency at the solvent-solute step is dependent on good electronic coupling between the two kinds of molecules but retransfer back to the solvent must be prevented by rapid loss of vibrational energy by the solute. This can be best attained if the molecule is of the "flapping"kind with low vibrational frequencies.

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Para-terphenyl is one of this type. For such molecules both retransfer to the solvent and "self-transfer" to other dissolved molecules is minimised.

Emission of Radiation:

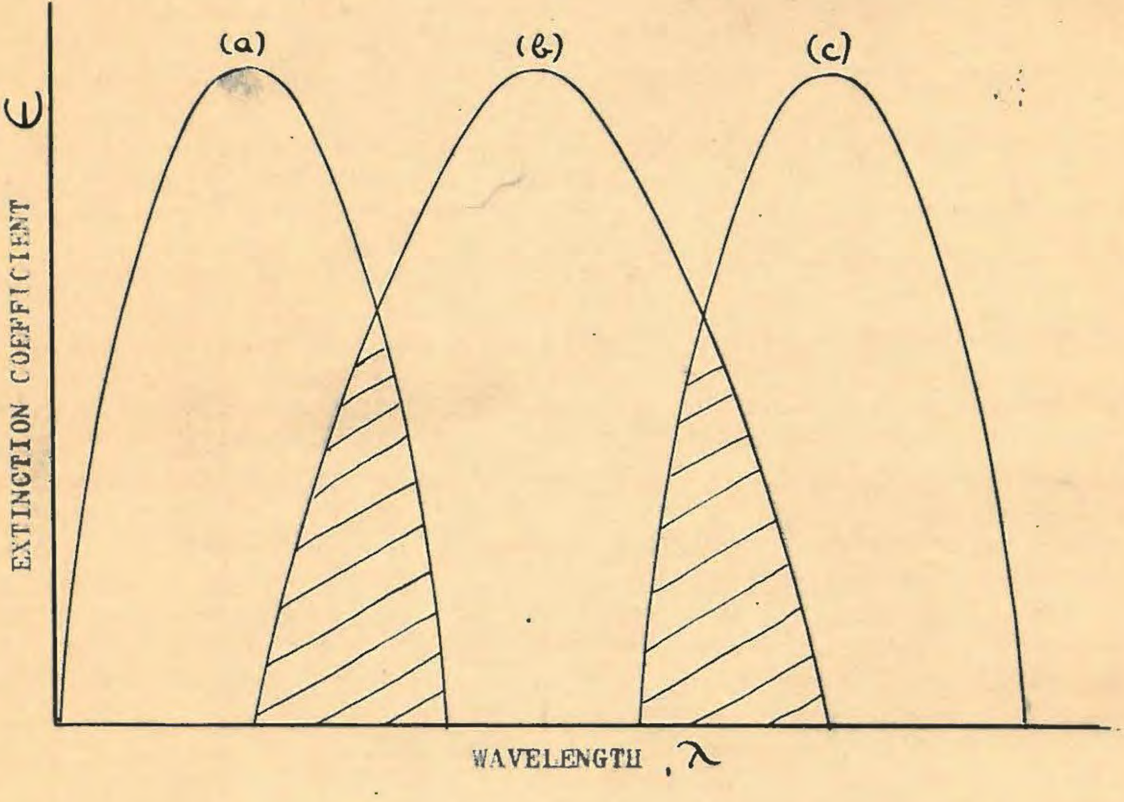
Self-transfer results in a decreased emission probability per unit time and consequently increases the chance of energy loss by competing radiationless processes. Therefore, emission is better for a solute where loss of upper state vibrational energy is rapid.

Molecules which show self-transfer fall into a class of inefficient scintillators whereas those showing no self-transfer are efficient. Anthracene is an example of the former type and terphenyl the latter.

KALLMANN & FURST (1951a) attempted to localise the excitation energy, to assist in the elucidation of the transfer mechanism, by dissolving an additional solute in the fluorescent solution. Additional solutes were chosen to give comparatively no light emission of their own so that they do not mask the main fluorescence, but small amounts influence the shape of the light emission curve (Intensity vs. Concentration). The type of system investigated was fluoranthene in xylene, with o-diphenyl-benzene as the additional solute, excited by ionizing radiations. The use of ionizing radiations to excite the system complicates the analysis of the experimental results and for this reason we shall not dwell on the interpretation of the result of this experiment. It is sufficient to state that KALLMANN & FURST found evidence in favour of a non-radiative transfer mechanism on the following grounds:-

The absorption band of o-diphenyl-benzene lies at wavelengths between the absorption bands of xylene and the fluorescent solute, fluoranthene. The additional solute then acts as a second solvent. The positions of the respective

FIG. 5. Diagrammatic sketch showing relative wavelength position of absorption bands of:
(a) Xylene.
(b) o-diphenyl-benzene.
(c) Fluoranthrene.
(magnitude of extinction coefficients not relative).



absorption bands are shown diagrammatically in FIG. 5 (the values of ϵ are not relative).

On the radiative theory of photon transfer, the excitation energy of the solvent is radiated and absorbed by the o-diphenyl-benzene which in turn radiates to the fluorescent solute. KALLMANN & FURST (1951a) have shown, however, that o-diphenyl-benzene quenches any absorbed radiation, hence they expected that adding this substance to the solution of fluoranthene in xylene should reduce the fluorescence intensity of the latter greatly. Experiment showed that only a slight decrease in fluorescence intensity occurred, hence it was proposed that the transfer mechanism is non-radiative.

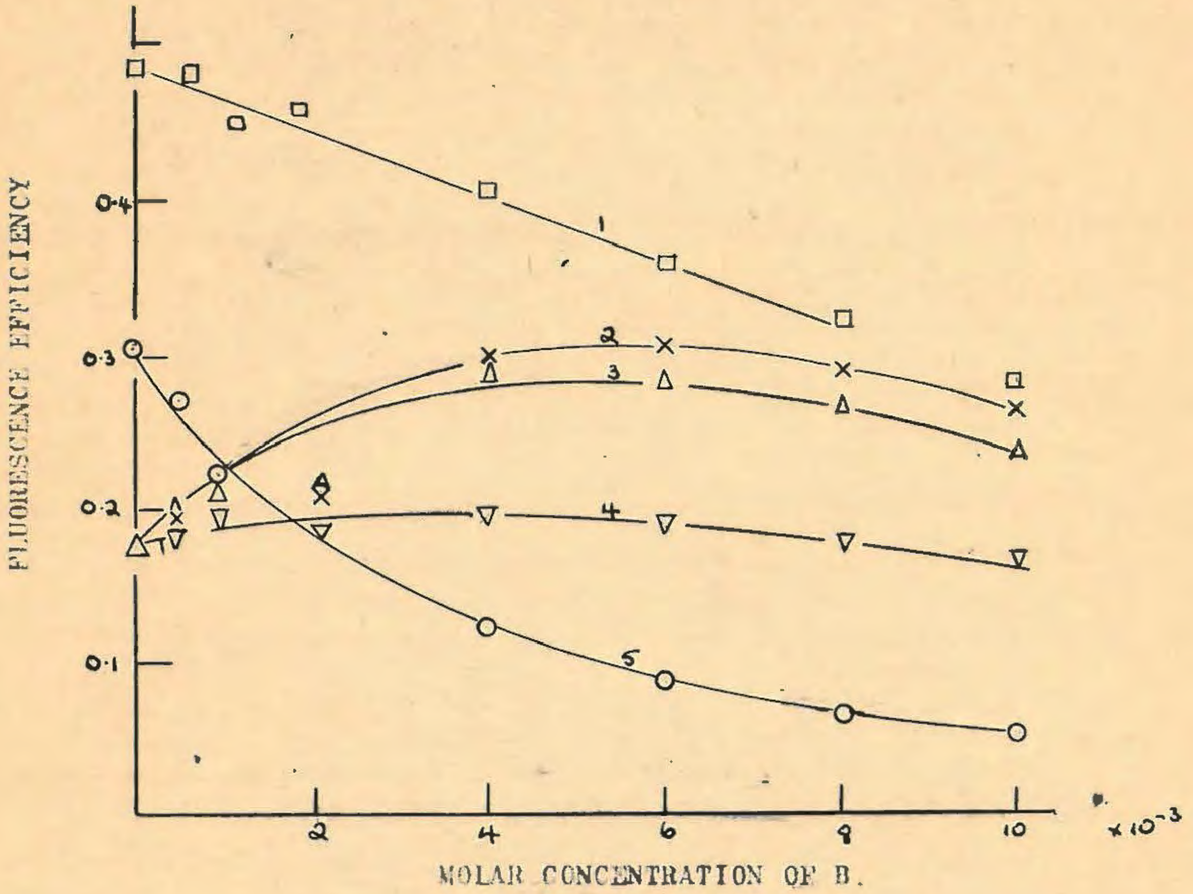
BOWEN & BROCKLEHURST (1953) simplified the investigation of the energy transfer mechanism by exciting liquid solutions with ultra-violet light instead of ionizing radiations. Thus it was possible to excite only one constituent of the solution by an appropriate choice of wavelength. Like KALLMANN & FURST (1951a) they used pairs of aromatic hydrocarbons dissolved in a solvent, the one solute absorbing the incident radiation and the second, whose energy levels are somewhat lower, receiving the electronic energy by direct transfer. The system used was 9-phenyl anthracene, hereafter referred to as A, which absorbs the incident light, with 9:10 dichloro-anthracene, hereafter referred to as B, as the additional solute, dissolved in benzene.

BOWEN & BROCKLEHURST measured the total fluorescence intensity of the mixed solutions over a range of concentrations of B and by comparison with the individual spectra it was possible to estimate the efficiencies of emission of each constituent. on the basis of the total light absorbed.

FIG. 6 shows the curves obtained when Fluorescence Efficiency is plotted as a function of concentration of B.

Curve (1) is the combined fluorescence efficiency which falls off with concentration because of quenching.

FIG. 6. Fluorescence of mixed solutions in benzene of 9-phenyl anthracene and 9:10-dichloro anthracene in 1:1 molar ratio. (BOWEN & BROCKLEHURST 1953).



Curve (5) is the emission of the absorbing substance A.

Curve (3) is the emission of the second substance B.

At higher concentrations the fluorescence of A is replaced by that of B.

Curve (2) is the calculated expected fluorescence of B if the primary electronic energy absorbed by A from the incident beam is immediately transferred to B, i.e. non-radiative transfer.

Curve (4) is that expected if the transfer process is the simple reabsorption by B of the emission of A., i.e. radiative transfer.

Since the calculated Curve (2) approximately coincides with the experimental Curve (3), whereas Curve (4) shows a smaller fluorescence efficiency than that actually found, it is concluded that the transfer process is purely non-radiative.

The molar concentrations used in this experiment were $\sim 10^{-2}$ to 10^{-3}, similar to those found by FORSTER for dye solutions, so that the transfer occurs over a distance of ~ 50 Å. These experiments differ from the previous ones, in that energy transfer between two different solutes, rather than between solvent and solute, was studied.

FURST & KALLMANN (1954) recognised the advantage of using light excitation and excited a system of anthracene in xylene with naphthalene as the additional solvent excited by Hg 3130 Å.

The detected fluorescence of the solvent, xylene, is very weak and the addition of as much as 70 gm/litre of naphthalene produces only a relatively small increase in intensity of light output; the emission occurs at wavelengths shorter than 3500 Å. The xylene is practically transparent to the exciting wavelength (3130 Å) whereas the solutes naphthalene and anthracene show considerable absorption, the extinction coefficient of anthracene being approximately 5 times greater than naphthalene to this wavelength (FRIEDEL & ORCHIN 1951).

The addition of naphthalene to the anthracene solutions reduces the intensity of emitted light by about 50%, the emission remaining characteristic of anthracene though nearly all the incident radiation is absorbed by naphthalene. Thus a transfer of energy from naphthalene to anthracene is demonstrated and KALLMANN & FURST consider that the mechanism cannot be the radiative process of photon emission and reabsorption for the following reasons:-

Because of the internal quenching of the anthracene molecule in solution its quantum efficiency is approximately 20%. Hence, if anthracene absorbed the naphthalene emission and then radiated, it is to be expected that the intensity of its fluorescence will be five times smaller than the original naphthalene fluorescence.

FURST & KALLMANN consider that since an increase in fluorescence intensity was observed when the anthracene was added, therefore the energy transport mechanism cannot be radiative.

As in the experiments of BOWEN & BROCKLEHURST, energy transfer between two different solutes is considered, rather than the more fundamental problem of solvent-solute transfer. The results are not considered conclusive since the authors do not allow for:-

(a) The reduced sensitivity (about 20%) of the photomultiplier detector for the naphthalene fluorescence, compared with that for the anthracene fluorescence.

(b) The self-absorption of the naphthalene fluorescence, which reduces the observed technical efficiency of the pure naphthalene solutions to a fraction of its true molecular

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fluorescence efficiency. The latter is the relevant parameter in considering radiative transfer to the anthracene.

COHEN & WEINREB (1954) showed the existence of energy transfer in solutions of para-terphenyl in xylene or toluene excited by Hg 254 $m\mu$ radiation which is almost totally absorbed by the solvent. Before this experiment, AGENO et al (1952) found evidence for fluorescence emission occurring over a region a few millimetres from a P_o^{210} α-particle source immersed in a solution of para-terphenyl in xylene, and suggested that energy transfer takes place by a long range secondary radiation emitted by the solvent and absorbed by the solute. They continued by showing that exchange of energy can take place from a solvent to a solution separated by a glass plate. COHEN & WEINREB (1954) however, show that by using a quartz cell of various thicknesses, there is no appreciable radiative transfer over distances greater than 0.1 mm. These results of COHEN & WEINREB (1954) suggested the more detailed study of solvent-solute energy transfer in binary liquid solutions, under ultra-violet excitation, undertaken in the present investigation. The use of ultra-violet excitation and binary solutions avoids many of the complications introduced in the earlier measurements using ionizing radiation and multi-component systems.

The present experiment was designed to elucidate the mechanism of energy transfer in a liquid organic solution of para-terphenyl in toluene. The ingredients were chosen because of their suitability for energy transfer as indicated in Section I.3, page 17.

The fluorescence quantum intensity of this binary solution has been measured as a function of concentration and of excitation wavelength from 2200 Å to 3300 Å. The use of low energy exciting light eliminates the additional complicatory effects of

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primary ionization. The absorption spectra of the two components, and other data relevant to a quantitative analysis of energy transfer, have also been measured.

Since the completion of the experimental work in November, 1955, an account of similar studies by COHEN & WEINREB (1956) has been published. The present results, analysis, and conclusions differ from theirs in several important respects.

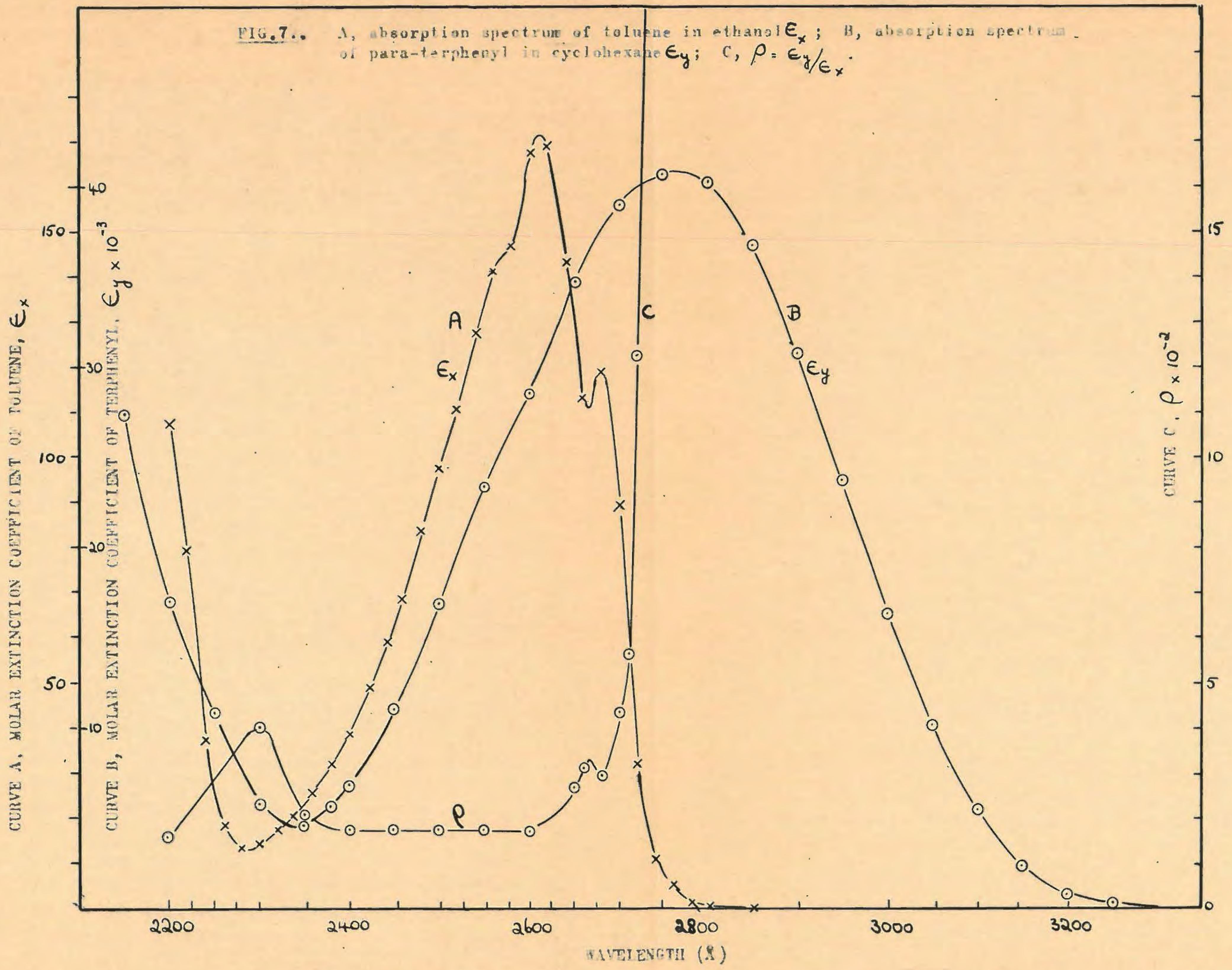

FIG.7.. A, absorption spectrum of toluene in ethanol ϵ_x ; B, absorption spectrum of para-terphenyl in cyclohexane ϵ_y; C, $\rho = \epsilon_y/\epsilon_x$.

II. EXPERIMENTAL

II. 1. ABSORPTION SPECTRA:

High purity toluene and "scintillation" grade para-terphenyl supplied by the Larco Instrument Company were used. The absorption spectrum of toluene in ethanol is shown in FIG. 7(a) while FIG. 7(b) shows that of para-terphenyl in cyclohexane solution, the measurements being made with a Beckman Model D.U. spectrophotometer. The absorption spectrum of para-terphenyl in toluene was measured down to 2950 Å at which wavelength the toluene starts to absorb, and a similar spectrum to that of cyclohexane solution was observed. This shows that the variation of molar extinction coefficient with wavelength is the same in both solvents.

The observed spectra are similar to those reported by FRIEDEL & ORCHIN (1951).

The ratio, ρ , of the molar extinction coefficients ϵ_y and ϵ_x of terphenyl and toluene respectively, is plotted in FIG. 7(c).

II. 2. FLUORESCENCE OF SOLUTIONS:

The experimental arrangement is shown diagrammatically in FIG. 8. The solution under investigation was contained in a cylindrical vessel, the depth of the solution ($\sim$1 cm.) being the same for all specimens. The fluorescence was excited by illumination of the top surface with monochromatic radiation from a Beckman Model D.U. spectrophotometer, the horizontal exit beam M being deflected vertically downwards by a quartz prism Q. The vessel was placed on a Chance OY 10 glass filter F, adjacent to the photo-cathode window of a Du Mont 6291 photomultiplier P mounted vertically. The filter transmits the terphenyl emission efficiently, but it is opaque to shorter

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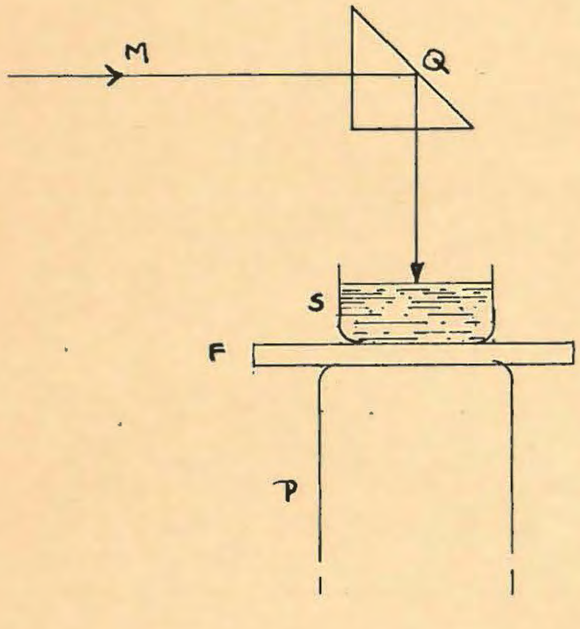
FIG. 8.. Experimental arrangement. M, exit beam from monochromator; Q, quartz prism; S, solution specimen in glass vessel; F, OY 10 glass filter; P, photomultiplier.



wavelength radiation; it thus serves to prevent scattered incident radiation from reaching the photo-cathode. A careful check showed that neither the filter nor the glass vessel were luminescent, an important precaution since fused silica and some glasses luminesce in the near ultra-violet and visible regions. Optical contact between the surfaces was improved by thin films of glycerine.

The experimental method consisted of illuminating the top surface of each solution specimen and measuring the integrated intensity of the fluorescence transmitted through the base. This observation was repeated for excitation wavelengths between 2200 Å and 3300 Å, the region which includes both the toluene and the terphenyl first absorption bands. The fluorescence intensity at each wavelength was normalised to the same quantum flux of incident radiation as described in II.3. Thus the fluorescence excitation spectra of several solutions of different concentrations were determined. Each set of solutions was prepared by diluting aliquots from a parent solution; the concentrations being such that even for the weakest solution all wavelengths of the incident monochromatic radiation were almost completely absorbed.

Since the integrated fluorescence emission always lies within the same spectral region and has the same band width it is unnecessary to know the spectral response of the photomultiplier.

II. 3. CALIBRATION OF INCIDENT RADIATION:

In order to normalise the observed fluorescence intensities to correspond to the same quantum flux of incident radiation, the relative quantum intensity of the monochromator exit beam was determined by two independent methods:

(i) Using the Beckman Spectrophotometer Phototube.

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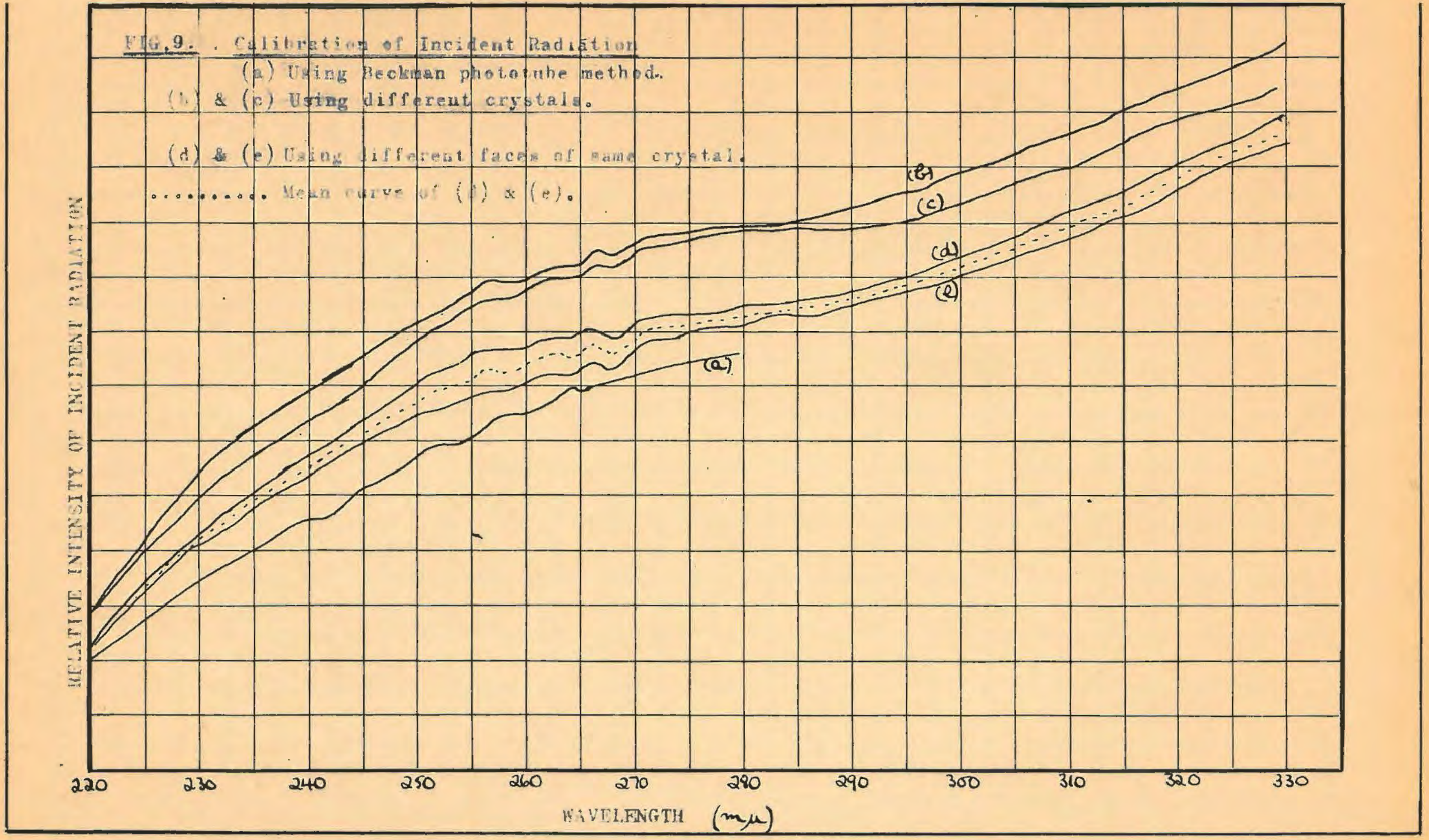

FIG. 9. . Calibration of Incident Radiation

(a) Using Beckman phototube method.

(b) & (c) Using different crystals.

(d) & (e) Using different faces of same crystal.

.... Mean curve of (d) & (e).

The response of the ultra-violet sensitive phototube supplied with the Beckman spectrophotometer had previously been measured by standardising it against a Hilger Linear Vacuum Thermopile Model F.T.16 fitted with a fluorite window (WRIGHT 1955). The intensity of the incident radiation was measured relative to the maximum at 3500 Å, the longest wavelength used in the experiment for exciting the fluorescence of the solutions. The percentage transmission reading of the Beckman spectrophotometer was set at 100% for $\lambda = 3500$ Å and the readings taken for shorter wavelengths. The calibration curve obtained by this method is shown in FIG. 9(a). Small errors may be introduced by this method because the calibration of the phototube is not easily determined at the shorter wavelengths due to the reduction in sensitivity of the thermopile.

(ii) Using Para-terphenyl Crystal as a Converter.

Previous measurements by WRIGHT (1955) have shown that the technical photo-fluorescence quantum efficiency of a terphenyl crystal is constant and independent of wavelength down to 2537 Å and that this uniform response can be assumed to extend down to at least 2200 Å. Hence the intensity of the integrated fluorescence from a crystal is directly proportional to the quantum intensity of the incident beam. For this calibration the solution specimen was replaced by a 1 cm. cube para-terphenyl crystal which converted the incident radiation into a region to which the photomultiplier was sensitive. FIG.9(b) and (c) are curves obtained using two different crystals and curves (d) and (e) were obtained using two different faces of the same crystal.

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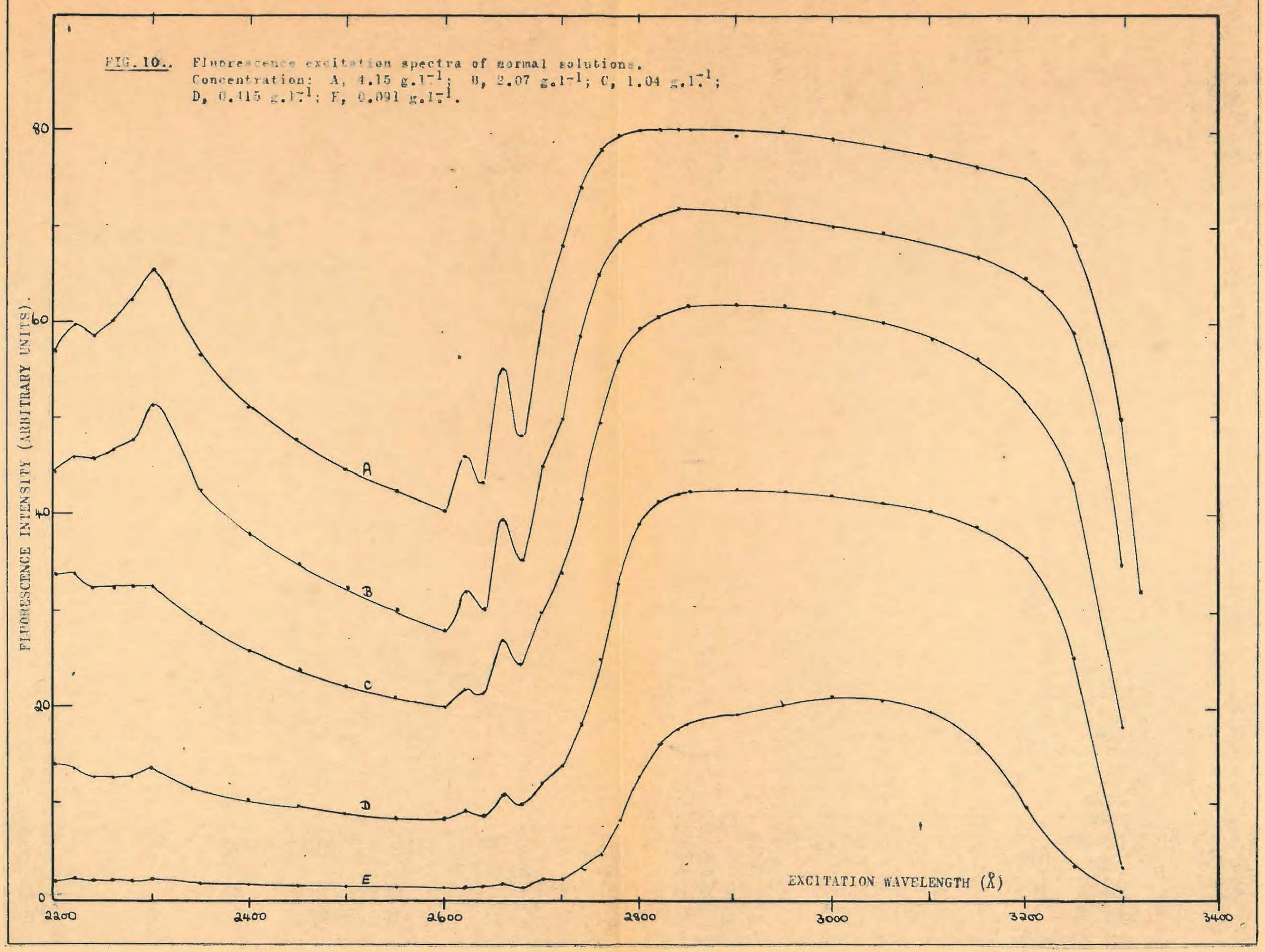

FIG. 10.. Fluorescence excitation spectra of normal solutions.
Concentration: A, 4.15 g.l^{-1}; B, 2.07 g.l^{-1}; C, 1.04 g.l^{-1};
D, 0.415 g.l^{-1}; E, 0.091 g.l^{-1}.

The dotted curve is the mean of the latter two and was used to calibrate the incident radiation. It can be seen that very good agreement is obtained between the two independent calibrations.

II. 4, FLUORESCENCE EXCITATION SPECTRA:

Fluorescence excitation spectra, normalised to a constant flux of incident quanta, were measured from 3300 Å to 2200 Å, for a range of solutions of different concentrations.

FIG. 10 shows the results for five solutions, in normal toluene, of concentration from 4.15 gm/litre to 0.09 gm/litre. These solutions contained dissolved oxygen, which is known to act as a quenching agent, in equilibrium concentration at normal atmospheric pressure. FIG. 11 shows the results for two solutions of concentrations 1.08 gm/litre and 0.054 gm/litre, from which the oxygen had been removed by bubbling nitrogen through the toluene during distillation.

The scales of relative quantum intensity are arbitrary and they are not necessarily the same for different solutions. This is particularly so for the different sets because there was an interval of several days between each set of readings during which time the apparatus was switched off. During this period the equilibrium conditions, e.g. photomultiplier voltage, intensity of incident beam, etc., may have changed slightly.

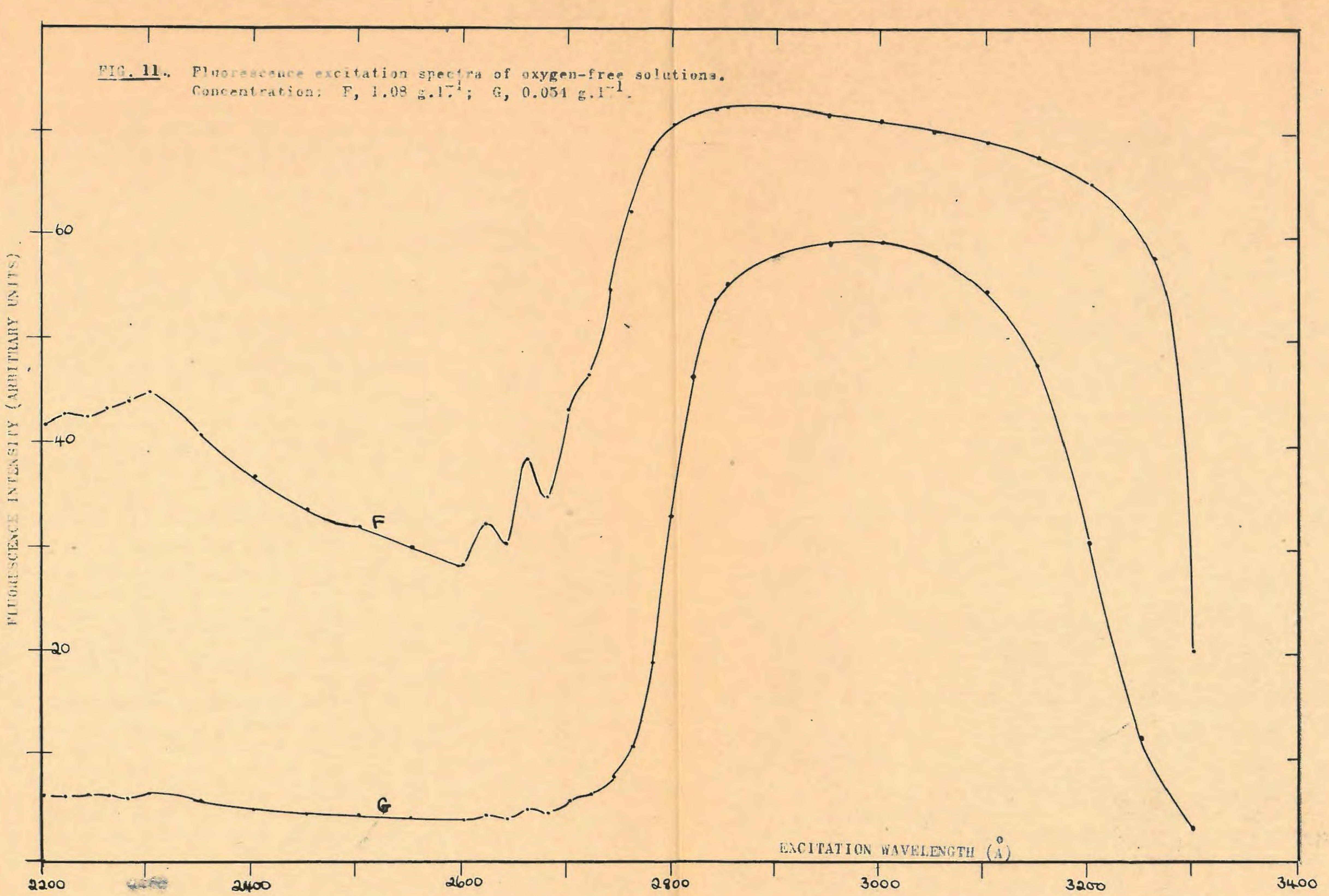

FIG. 11. Fluorescence excitation spectra of oxygen-free solutions. Concentration: F, 1.08 g.l^{-1}; G, 0.054 g.l^{-1}.

III. ANALYSIS OF RESULTS.

III. 1. QUALITATIVE DESCRIPTION:

Three distinct regions may be distinguished in the excitation spectra. At the long wavelength edge ($\lambda \sim 3200$ Å to 3300 Å) where the terphenyl begins to absorb the incident radiation, there is a sharp rise in the fluorescence intensity. In the first region (0) from 2800 to 3300 Å, the toluene is practically transparent, and the terphenyl fluorescence is excited directly by absorption of the incident radiation. At $\lambda \sim 2800$ Å the toluene begins to absorb and the intensity of terphenyl fluorescence decreases rapidly as the toluene absorbs an increasing fraction of incident radiation. Thus, the region of direct excitation of terphenyl is bounded at $\lambda \sim 3300$ Å by the terphenyl absorption edge, and at $\lambda \sim 2800$ Å by the onset of the toluene absorption.

In the second and third regions (I and II) corresponding to wavelengths below ~2700 Å, the toluene absorption is high, and practically all the incident radiation is absorbed by the solvent. In these regions the terphenyl fluorescence is mainly excited indirectly by energy transfer from excited toluene molecules.

The fluorescence intensity shows variations, associated with changes in ϵ_x and ϵ_y with wavelength, and these are allowed for in the subsequent analysis. However, it may be noted at this stage, that the fluorescence intensity, which depends on the energy transfer efficiency, is higher at the shorter wavelengths (2200-2350 Å), designated region II, than at the longer wavelengths (2500-2650 Å) designated region I.

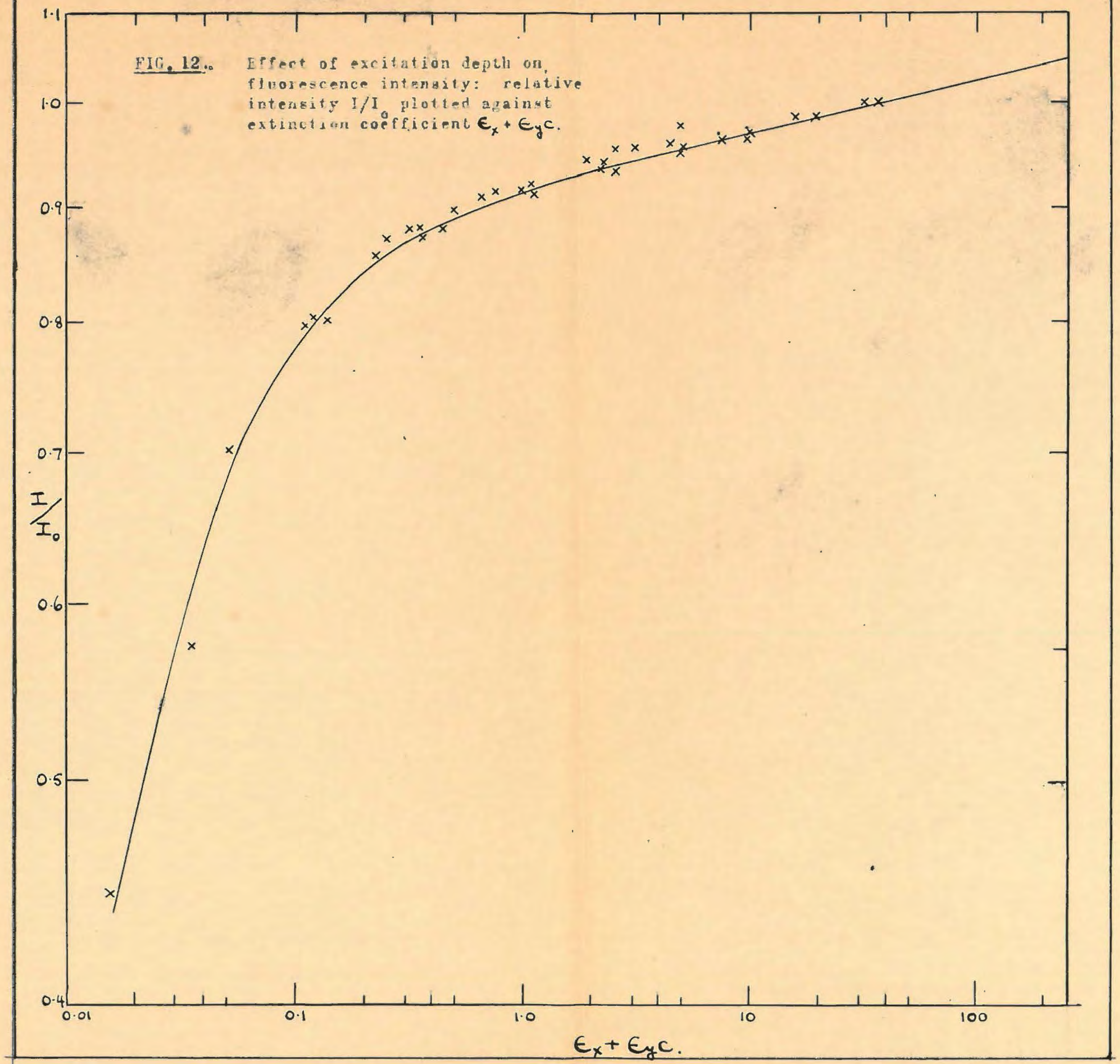

FIG. 12. Effect of excitation depth on fluorescence intensity: relative intensity I/I_0 plotted against extinction coefficient $\epsilon_x + \epsilon_y c$.

III. 2. CORRECTION FOR EXCITATION DEPTH:

Before a quantitative analysis of the results can be undertaken, a correction must be made for the variation with wavelength and concentration of the depth of penetration of the incident radiation. This effect was reported by WRIGHT (1955), who studied the fluorescence excitation spectra of organic crystals. These show major variations with excitation wavelength of the transmitted fluorescence intensity, associated with variations in the absorption coefficient.

The effect is clearly seen in the present measurements (FIGS. 10 & 11) for wavelengths from 3000 Å to 3300 Å. In this spectral region the toluene is transparent, all the terphenyl fluorescence is directly excited, and the fluorescence quantum efficiency of terphenyl is constant. Nevertheless the observed fluorescence intensity decreases with increasing wavelength, due to the decrease in ϵ_y, and the consequent increase in the depth of penetration of the incident radiation.

The observed fluorescence intensity, I, has been expressed in terms of I_o, the observed fluorescence intensity at a wavelength of 3000 Å, and I/I_o has been normalised to correspond to the strongest solution (4.15 gm/litre). In FIG. 12, I/I_o for all the solutions from 3000 Å to 3300 Å is plotted on a logarithmic scale against the molar extinction coefficient $(\epsilon_x + \epsilon_y c)$ where c is the concentration of solute molecules per solvent molecule. In this spectral region $\epsilon_x = 0$. The calculations required for the production of FIG. 12 are given in Table I.

Within the experimental error, the values of I/I_o for the different solutions lie on a single smooth curve. For values of $\epsilon_x + \epsilon_y c$ from 1 to 36 the curve is linear, and it is reasonable to extrapolate it linearly to higher values of $\epsilon_x + \epsilon_y c$.

FIG. 12 thus shows the change in the observed fluorescence intensity, I, from the

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DEPTH CORRECTION FACTOR

TABLE I.

CALCULATIONS AND READINGS FOR FIGURE 14.

CONCENTRATION. C. Mols/Mol	WAVELENGTH λ	OBSERVED FLUORESCENCE * INTENSITY. I.	$\epsilon_y.C$	LOG $\epsilon_y.C$	CORRECTION FACTOR I/Io	LOG $I/_{Io}$
19.1×10^{-4} (solution a) (4.15 gm/litre)	3000	2.0	30.9	1.49	1	0
	3050	1.97	19.1	1.28	0.985	$\bar{1}.993$
	3100	1.94	10.1	1.00	0.97	$\bar{1}.987$
	3150	1.92	4.4	0.64	0.96	$\bar{1}.982$
	3200	1.88	1.34	0.127	0.94	$\bar{1}.973$
9.58×10^{-4} (solution b) (2.07 gm/litre)	3000	2.96	15.4	1.188	1	0
	3050	2.92	9.55	0.98	0.985	$\bar{1}.993$
	3100	2.86	5.05	0.703	0.965	$\bar{1}.985$
	3150	2.82	2.2	0.34	0.95	$\bar{1}.978$
	3200	2.72	6.67	$\bar{1}.83$	0.92	$\bar{1}.964$
4.78×10^{-4} (solution c). (1.04 gm/litre)	3000	1.55	7.77	0.89	1	0
	3050	1.52	4.8	0.68	0.98	$\bar{1}.99$
	3100	1.48	2.54	0.405	0.955	$\bar{1}.98$
	3150	1.42	1.10	0.04	0.915	$\bar{1}.96$
	3200	1.30	0.336	$\bar{1}.526$	0.84	$\bar{1}.924$
1.91×10^{-4} (solution d). (0.415 gm/litre)	3000	1.52	3.1	0.49	1	0
	3050	1.49	1.91	0.28	0.98	$\bar{1}.99$
	3100	1.45	1.01	0.004	0.955	$\bar{1}.98$
	3150	1.40	0.44	$\bar{1}.64$	0.92	$\bar{1}.964$
	3200	1.27	0.134	$\bar{1}.127$	0.835	$\bar{1}.922$
0.418×10^{-4} (solution e). (0.0906 gm/litre)	3000	2.67	0.68	$\bar{1}.83$	1	0
	3050	2.63	0.42	$\bar{1}.62$	0.985	$\bar{1}.9912$
	3100	2.51	0.22	$\bar{1}.34$	0.94	$\bar{1}.973$
	3150	2.07	0.097	$\bar{2}.99$	0.775	$\bar{1}.89$
	3200	1.22	0.029	$\bar{2}.46$	0.46	$\bar{1}.663$
4.98×10^{-4} (solution f). (oxygen-free solution) (1.08 gm/litre)	3000	3.53	8.1	0.909	1	0
	3050	3.49	5.0	0.7	0.99	$\bar{1}.996$
	3100	3.42	2.65	0.42	0.97	$\bar{1}.987$
	3150	3.39	1.15	0.061	0.96	$\bar{1}.982$
	3200	3.23	0.35	$\bar{1}.54$	0.915	$\bar{1}.961$
0.232×10^{-4} (solution g). (oxygen-free solution) (0.054 gm/litre)	3000	2.96	0.37	$\bar{1}.57$	1	0
	3050	2.9	0.23	$\bar{1}.36$	0.98	$\bar{1}.991$
	3100	2.72	0.12	$\bar{1}.08$	0.92	$\bar{1}.964$
	3150	2.4	0.053	$\bar{2}.72$	0.81	$\bar{1}.909$
	3200	1.52	0.016	2.20	0.513	$\bar{1}.71$

* Observed values of fluorescence intensity are arbitrary. See II.4, Fluorescence Excitation Spectra.

value I_o, that it would have if the molar extinction coefficient $(\epsilon_x + \epsilon_y c)$ were 36, i.e. if the radiation were absorbed at the same depth as in the strongest solution at $\lambda = 3000$ Å.

FIG. 12 has, therefore, been used to correct the observed fluorescence excitation spectra (FIGS. 10 & 11) by normalising them to the standard excitation depth, corresponding to I_o. This has been done by dividing the observed fluorescence intensity I (FIGS. 10 & 11) by the value of $I/_{Io}$ from FIG. 12 corresponding to the value of $(\epsilon_x + \epsilon_y c)$ for the particular solution and excitation wavelength.

The analysis of the results of this experiment is confined to the wavelength range from 2650 Å to 2200 Å, in which region the value of $(\epsilon_x + \epsilon_y c)$ varies from 12.4 to 214 (see Table II) for all solutions. The correction factors corresponding to these values of $(\epsilon_x + \epsilon_y c)$ lie between 0.98 and 1.05. Observations at wavelengths between 2650 Å and 2800 Å are omitted from the subsequent analysis because of experimental uncertainties in the determination of the exact position of the toluene absorption edge, since the absorption spectrum (FIG. 7(a)) measured for an ethanol solution does not correspond exactly to that for pure toluene. Near this absorption edge, a slight shift to longer wavelengths would produce a marked increase in the value of ϵ_x, while a similar shift will probably have only a small effect on ϵ_x at wavelengths greater than 2650 Å.

The corrected fluorescence spectra are similar in form to FIGS. 10 & 11, except for uniform plateaux from $\lambda \sim 2900$ Å to 3300 Å, and are not, therefore, reproduced.

III. 3. ENERGY TRANSFER COEFFICIENT:

We must now proceed to analyse the corrected excitation spectra in order to

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derive an expression giving the fraction of quanta initially absorbed by the solvent which are transferred to the solute.

From absorption law equations, for toluene

$$I = I_0 e^{-\mu x d}$$

where I = intensity of transmitted radiation,

I_0 = intensity of incident radiation

μx = molecular absorption coefficient of toluene

d = thickness of specimen.

Similarly for terphenyl,

$$I = I_0 e^{-\mu y d}$$

the suffixes x and y referring to toluene and terphenyl respectively.

It can be shown that the total quantity of incident light absorbed by both the toluene and the terphenyl

$$= I_0 \left(1 - e^{-\Sigma \mu d}\right)$$

Therefore, the ratio, Fraction of light absorbed by terphenyl/Fraction absorbed by toluene

$$= \frac{\mu y}{\mu x}$$

$$= \frac{\epsilon_x [X]}{\epsilon_y [Y]}$$

where ϵ_x and ϵ_y are the molar extinction coefficients of toluene and terphenyl respectively and $[X]$ and $[Y]$ are the molecular concentrations of the solvent and solute molecules X and Y. Square brackets will be used throughout to denote molecular concentrations.

For incident photons of wavelength λ, let the fraction absorbed directly by the

λ	I_{obs}	ϵ_x	$\epsilon_y c$	$\epsilon_x + \epsilon_y c$	log $\epsilon_x + \epsilon_y c$	log Cor.Fac.(1)	Cor. Fac.(1)	n_f(2)	$\frac{n_f}{n_{fo}}$(3)	ρc	$1-\frac{n_f}{n_{fo}}$	$\rho c\left(1-\frac{n_f}{n_{fo}}\right)$	f(4)
Solution (g), $c = 2.32 \times 10^{-5}$													
2650	14.0	129.0	0.8	129.8	2.11	0.014	1.03	13.6	0.064	0.006	0.936	0.006	0.058
2600	11.5	158.5	0.6	159.1	2.20	0.016	1.04	11.0	0.052	0.004	0.948	0.004	0.048
2550	13.0	132.0	0.5	132.5	2.12	0.014	1.03	12.6	0.059	0.004	0.941	0.004	0.055
2500	14.0	95.5	0.4	96.0	1.98	0.01	1.02	13.7	0.065	0.004	0.935	0.004	0.061
2450	14.5	64.6	0.3	65.0	1.81	0.007	1.02	14.2	0.067	0.004	0.933	0.004	0.063
2400	16.0	38.0	0.2	38.2	1.58	0.001	1.0	16.0	0.075	0.004	0.925	0.004	0.071
2350	18.5	21.4	0.1	21.5	1.33	$\bar{1}$.995	0.99	18.7	0.088	0.005	0.912	0.005	0.083
2300	21.0	12.6	0.1	12.7	1.10	$\bar{1}$.99	0.98	21.5	0.101	0.012	0.889	0.011	0.090
2250	20.0	26.3	0.3	26.6	1.42	$\bar{1}$.998	1.0	20.0	0.094	0.009	0.906	0.008	0.086
2200	20.0	107.2	0.4	107.6	2.03	0.012	1.03	19.4	0.091	0.004	0.909	0.004	0.087
3000	187.0	$= 1.6 \times 10^4$	0.37	0.37	$\bar{1}$.57	$\bar{1}$.945	0.88	213.0					

(1) Cor.Fac. = Correction Factor obtained from Table I.

(2) $n_f = \frac{I_{obs}}{\text{Cor.Fac.}}$

(3) $n_{fo} = \frac{(I_{obs})_{3000}}{(\text{Cor.Fac.})_{3000}}$

(4) $f = \frac{n_f}{n_{fo}} - \rho c\left(1 - \frac{n_f}{n_{fo}}\right)$

λ	ρ
2650	2.5×10^2
2600	1.7×10^2
2550	1.7×10^2
2500	1.7×10^2
2450	1.7×10^2
2400	1.9×10^2
2350	2.1×10^2
2300	5.1×10^2
2250	4.0×10^2
2200	1.6×10^2
3000	1.6×10^4

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λ	I_{obs}	ϵ_x	$\epsilon_{y.}c$	$\epsilon_x+\epsilon_y c$	log $\epsilon_x+\epsilon_y c$	log Cor.Fac.(1)	Cor. Fac.(1)	n_f (2)	$\frac{n_f}{n_{fo}}$ (3)	ρ_c	$1-\frac{n_f}{n_{fo}}$	$\rho_c(1-\frac{n_f}{n_{fo}})$	f (4)
Solution (d), c = 1.91×10^{-4}													
2650	23.5	129.0	6.3	135.3	2.13	0.014	1.03	22.8	0.224	0.048	0.776	0.037	0.187
2600	20.0	158.5	5.2	163.7	2.21	0.016	1.04	19.2	0.189	0.032	0.811	0.026	0.163
2550	19.5	132.0	4.2	136.2	2.13	0.014	1.03	18.9	0.186	0.032	0.814	0.026	0.160
2500	21.0	95.5	3.2	98.7	1.99	0.011	1.03	20.4	0.20	0.032	0.80	0.026	0.174
2450	22.5	64.6	2.1	66.7	1.82	0.007	1.02	22.0	0.216	0.032	0.784	0.025	0.181
2400	24.0	38.0	1.3	39.3	1.59	0.001	1.00	24.0	0.236	0.036	0.764	0.027	0.209
2350	27.0	21.4	0.85	22.25	1.35	$\bar{1}.995$	0.99	27.2	0.267	0.04	0.733	0.029	0.238
2300	31.0	12.6	1.1	13.7	1.14	$\bar{1}.991$	0.98	31.6	0.31	0.098	0.69	0.068	0.242
2250	29.5	26.3	2.1	28.4	1.45	$\bar{1}.998$	1.0	29.5	0.29	0.076	0.71	0.054	0.236
2200	32.0	107.2	3.2	110.4	2.04	0.012	1.03	31.1	0.305	0.03	0.695	0.021	0.284
3000	96.5	= $1.6\text{x}10^4$	3.05	3.05	0.48	$\bar{1}.976$	0.946	102.0					
Solution (e), c = 0.418×10^{-4}													
2650	11.0	129.0	1.4	130.4	2.12	0.012	1.03	10.7	0.057	0.010	0.943	0.009	0.048
2600	9.0	158.5	1.1	159.6	2.22	0.016	1.04	8.7	0.047	0.007	0.953	0.007	0.040
2550	10.0	132.0	0.9	132.9	2.32	0.012	1.03	9.7	0.052	0.007	0.948	0.007	0.045
2500	10.5	95.5	0.7	96.2	1.98	0.008	1.02	10.3	0.055	0.007	0.945	0.007	0.048
2450	11.0	64.6	0.5	65.1	1.81	0.008	1.02	10.8	0.058	0.007	0.942	0.007	0.051
2400	12.2	38.0	0.3	38.3	1.58	0	1.0	12.2	0.065	0.008	0.935	0.007	0.058
2350	14.0	21.4	0.2	21.6	1.33	$\bar{1}.995$	0.99	14.1	0.076	0.009	0.924	0.008	0.068
2300	16.8	12.6	0.25	12.85	1.11	$\bar{1}.992$	0.98	17.2	0.082	0.021	0.918	0.019	0.063
2250	15.5	26.3	0.5	26.8	1.43	0	1.0	15.5	0.074	0.017	0.926	0.016	0.058
2200	14.0	107.2	0.7	107.9	2.03	0.012	1.03	13.6	0.065	0.007	0.936	0.007	0.058
3000	168.5	= $1.6\text{x}10^4$	0.67	0.67	$\bar{1}.83$	$\bar{1}.956$	0.904	186.5					
Solution (f), c = 4.98×10^{-4}													
2650	9.2	129.0	16.6	145.6	2.16	0.015	1.04	8.8	0.48	0.125	0.52	0.065	0.415
2600	7.0	158.5	13.8	172.3	2.23	0.016	1.04	6.7	0.366	0.085	0.634	0.054	0.312
2550	7.5	132.0	11.0	143.0	2.15	0.014	1.03	7.3	0.40	0.085	0.60	0.051	0.349
2500	8.0	95.5	8.5	104.0	2.02	0.012	1.03	7.8	0.425	0.085	0.575	0.049	0.376
2450	8.35	64.6	5.6	70.2	1.85	0.008	1.02	8.2	0.447	0.085	0.553	0.047	0.40
2400	9.15	38.0	3.5	41.5	1.62	0.002	1.01	9.05	0.494	0.095	0.506	0.048	0.446
2350	10.1	21.4	2.2	23.6	1.37	$\bar{1}.996$	0.99	10.2	0.557	0.105	0.443	0.047	0.51
2300	11.2	12.6	3.8	15.4	1.19	$\bar{1}.989$	0.975	11.5	0.627	0.255	0.373	0.095	0.542
2250	10.6	26.3	6.9	33.2	1.52	0	1.0	10.6	0.58	0.2	0.42	0.084	0.496
2200	10.25	107.2	10.7	117.9	2.07	0.013	1.03	9.95	0.543	0.08	0.457	0.037	0.506
3000	17.7	= $1.6\text{x}10^4$	8.1	8.1	0.909	$\bar{1}.985$	0.966	18.3					

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CALCULATION OF TRANSFER COEFFICIENT, f.

TABLE II.

λ	I_{obs}	ϵ_x	$\epsilon_y c$	$\epsilon_x + \epsilon_y c$	log $\epsilon_x + \epsilon_y c$	log Cor.Fac.(1)	Cor. Fac.(1)	n_f (2)	$\frac{n_f}{n_{fo}}$ (3)	ρc	$1-\frac{n_f}{n_{fo}}$	$\rho c(1-\frac{n_f}{n_{fo}})$	f (4)
Solution (a), c = 19.1×10^{-4}													
2650	7.0	129.0	66.2	195.2	2.29	0.018	1.04	6.73	0.673	0.48	0.327	0.157	0.516
2600	5.1	158.5	55.1	213.6	2.33	0.019	1.05	4.86	0.586	0.325	0.514	0.167	0.319
2550	5.35	132.0	43.8	175.8	2.25	0.017	1.04	5.14	0.514	0.325	0.486	0.158	0.356
2500	5.7	95.5	34.0	129.5	2.11	0.014	1.03	5.53	0.553	0.325	0.447	0.145	0.408
2450	6.0	64.6	21.4	86.0	1.93	0.01	1.02	5.9	0.59	0.325	0.41	0.133	0.457
2400	5.6	38.0	13.5	51.5	1.71	0.004	1.01	5.55	0.555	0.363	0.445	0.162	0.493
2350	7.2	21.5	8.5	29.9	1.48	0	1.0	7.2	0.72	0.4	0.28	0.112	0.608
2300	8.25	12.6	11.5	24.1	1.38	$\bar{1}.996$	0.99	8.33	0.833	0.975	0.167	0.163	0.670
2250	7.6	26.3	20.9	47.2	1.67	0.003	1.01	7.52	0.752	0.765	0.248	0.19	0.562
2200	7.2	107.2	32.4	139.6	2.15	0.014	1.03	7.0	0.70	0.306	0.30	0.092	0.618
3000	10.0	= 1.6×10^4	30.6	30.6	1.49	0	1.0	10.0					
Solution (b), c = 9.58×10^{-4}													
2650	7.0	129.0	32.0	161.0	2.21	0.016	1.04	6.7	0.446	0.24	0.554	0.133	0.313
2600	5.9	158.5	26.0	184.5	2.27	0.017	1.04	5.7	0.38	0.16	0.62	0.1	0.28
2550	6.3	132.0	21.0	153.0	2.18	0.015	1.04	6.1	0.406	0.16	0.594	0.095	0.311
2500	6.9	95.5	16.0	111.5	2.06	0.012	1.03	6.7	0.446	0.16	0.554	0.089	0.357
2450	7.2	64.6	11.0	75.6	1.88	0.004	1.01	7.1	0.473	0.16	0.527	0.084	0.389
2400	8.0	38.0	6.8	44.8	1.65	0.002	1.00	8.0	0.533	0.18	0.467	0.084	0.449
2350	8.95	21.4	4.3	25.7	1.41	$\bar{1}.997$	1.00	8.95	0.597	0.20	0.403	0.080	0.517
2300	10.8	12.6	5.8	18.4	1.26	$\bar{1}.994$	0.984	11.0	0.735	0.49	0.265	0.13	0.605
2250	9.5	26.3	10.5	36.8	1.56	0	1.00	9.5	0.633	0.38	0.367	0.14	0.493
2200	9.2	107.2	16.0	123.2	2.09	0.013	1.03	8.9	0.592	0.15	0.408	0.061	0.531
3000	14.75	= 1.6×10^4	15.3	15.3	1.19	$\bar{1}.992$	0.982	15.0					
Solution (c), c = 4.78×10^{-4}													
2650	38.0	129.0	16.0	145.0	2.16	0.015	1.04	36.5	0.359	0.12	0.641	0.077	0.282
2600	32.0	158.5	13.0	171.5	2.23	0.016	1.04	30.8	0.303	0.081	0.697	0.056	0.247
2550	34.0	132.0	10.5	142.5	2.15	0.017	1.04	32.8	0.323	0.081	0.677	0.055	0.268
2500	36.0	95.5	8.1	103.6	2.01	0.011	1.03	35.0	0.344	0.081	0.656	0.053	0.291
2450	38.5	64.6	5.4	70.0	1.85	0.008	1.02	37.8	0.372	0.081	0.628	0.051	0.321
2400	42.0	38.0	3.4	41.4	1.62	0.002	1.01	41.5	0.408	0.091	0.592	0.054	0.354
2350	46.0	21.4	2.1	23.5	1.37	$\bar{1}.996$	0.99	46.5	0.458	0.1	0.542	0.054	0.404
2300	52.5	12.6	2.9	15.5	1.19	$\bar{1}.992$	0.98	53.5	0.526	0.24	0.474	0.114	0.412
2250	52.5	26.3	5.3	31.6	1.50	0	1.0	52.5	0.516	0.19	0.484	0.092	0.424
2200	54.0	107.2	8.1	113.3	2.05	0.012	1.03	52.5	0.516	0.077	0.484	0.037	0.479
3000	98.0	= 1.6×10^4	7.65	7.65	0.88	$\bar{1}.985$	0.966	101.7					

solvent and solute molecules be n_x and n_y respectively.

Then $$\frac{n_y}{n_x} = \frac{\epsilon_y[Y]}{\epsilon_x[X]} = \rho c \qquad \text{———————} \qquad (1)$$

where $\rho = \frac{\epsilon_y}{\epsilon_x}$ (the ratio of the molecular extinction coefficients) and c is the concentration of solute molecules per solvent molecule. The value of ρ varies with wavelength λ and

$$n_x = \frac{1}{1+\rho c}, \qquad n_y = \frac{\rho c}{1+\rho c} \qquad \text{———————} \qquad (2)$$

The quantum efficiency, q_{f_y}, of the observed solute fluorescence, which is defined as the ratio of the number of photons emitted to the total number absorbed, is

$$q_{f_y} = \frac{n_f}{n_y + f n_x} \qquad \text{———————} \qquad (3)$$

where n_f is the number of photons emitted and f is the energy transfer coefficient, i.e. the fraction of quanta, initially absorbed by the solvent which are transferred to the solute.

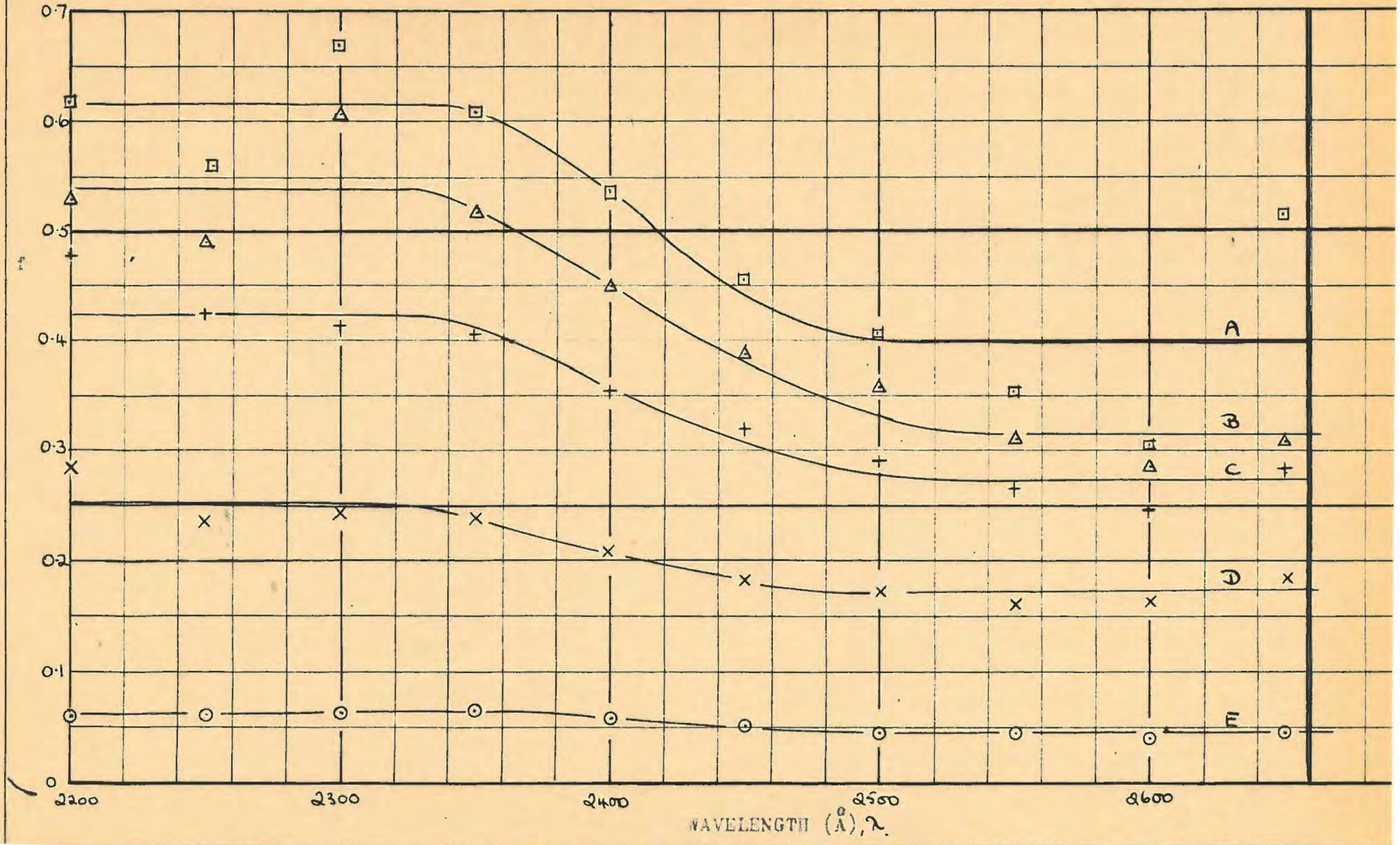
q_{f_y} is characteristic of the solute in the particular solvent used at a given value of c. It is independent of λ within the first absorption band of the solute (down to 2350 Å in the present case) and by analogy with other organic fluorescent compounds (PRINGSHEIM 1949, FUCHLOCHER & GLASER 1954, WRIGHT 1955), it may be expected to remain constant down to at least 2200 Å.

In the spectral region designated 0, where the solvent is transparent and the incident radiation is thus absorbed only by the solute, $n_x = 0$, $n_y = 1$ and, therefore

$$q_{f_y} = n_{f_0} \qquad \text{———————} \qquad (4)$$

where the suffix 0 refers to this spectral region.

FIG.13.. Energy transfer coefficient, f, plotted against wavelength λ.. Normal solutions. Concentration: A, 4.15 g.l.$^{-1}$; B, 2.07 g.l.$^{-1}$; C, 1.04 g.l.$^{-1}$; D, 0.415 g.l.$^{-1}$, E, 0.091 g.l.$^{-1}$.



An expression for f in terms of experimental parameters is obtained from equations (2), (3) and (4), namely -

$$f = \frac{nf}{nf_0}(1 + \rho_c) - \rho_c \qquad (5)$$

The ratio $\frac{nf}{nf_0}$ is obtained directly from the corrected fluorescence excitation spectra. It is the ratio of the relative quantum intensity in regions I and II at any particular wavelength to that in region I where the solvent is transparent and the relative quantum intensity is constant. ρ is obtained from FIG. 7(c).

The values of f, derived from (5), are plotted against λ in FIGS. 13 & 14. FIG. 13 consists of five curves for the normal solutions a, b, c, d and e, while FIG. 14 shows the two curves obtained from the oxygen-free solutions f and g. For each solution it is found that f has two characteristic values producing the two horizontal sections of each curve: The first value, f_1, which is constant within experimental error, occurs at wavelengths between 2500 Å and 2650 Å, designated region I. The second value, f_2, is similarly constant but higher and occurs in region II at wavelengths between 2200 Å to 2350 Å. Between the two spectral regions I and II, f has a value intermediate between f_1 and f_2.

It is thus shown that the value of f depends on λ, the wavelength of the exciting radiation and this interesting point will be discussed in Section IV.2.

The readings required for the calculation of f for each solution at various values of λ are given in Table II. In this Table I_{obs} is the observed value of Relative Fluorescence Intensity at each wavelength normalised to the value of $I_{obs} = 10$ at $\lambda = 3000$ Å for the solution of highest concentration ($c = 19.1 \times 10^{-4}$ mols/mol). The values of ϵ_x and ϵ_y are obtained from FIG. 7(a) and (b) and the calculated values of log $(\epsilon_x + \epsilon_y c)$ are used to read off from FIG. 12 the

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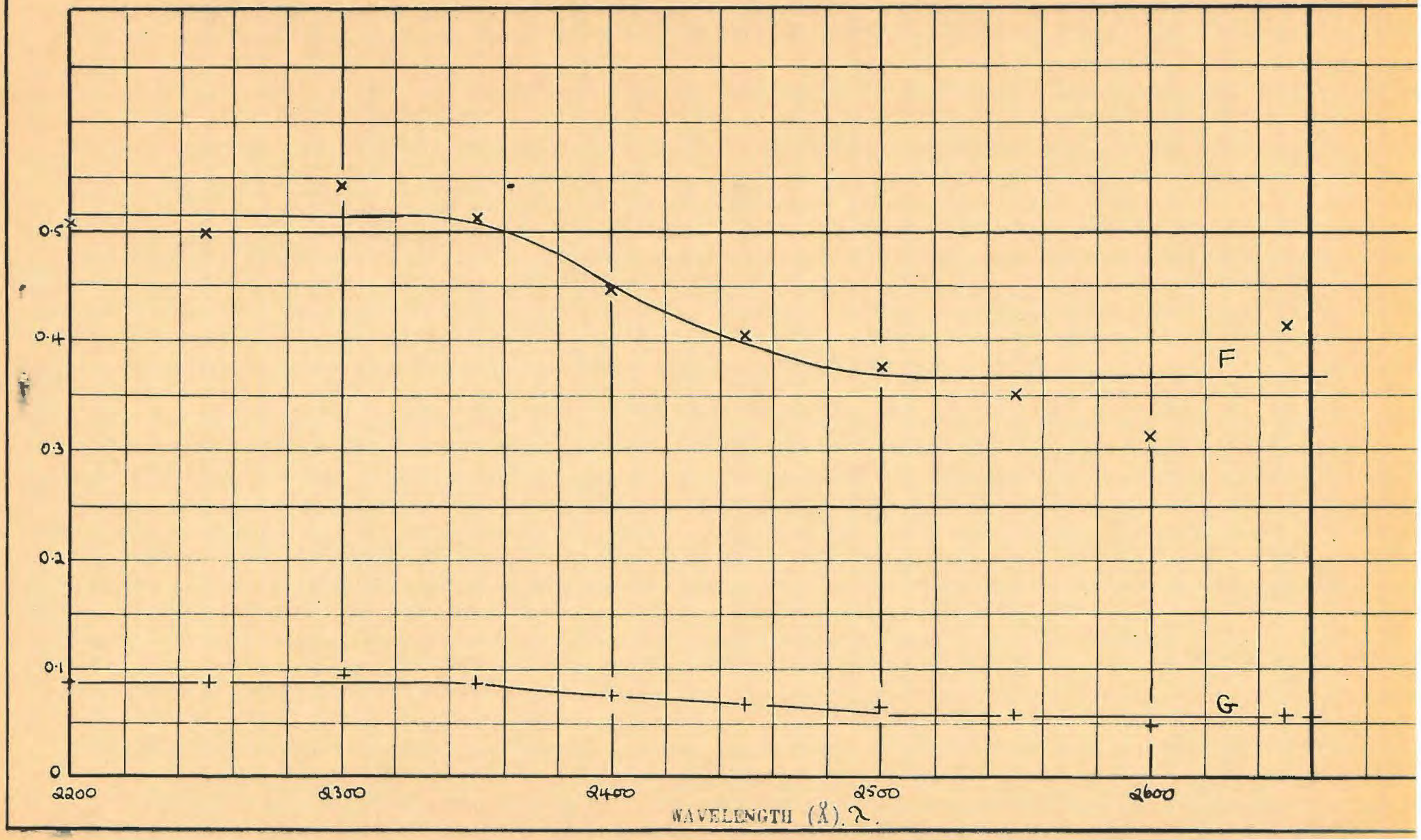
FIG. 14. Energy transfer coefficient, f, plotted against wavelength λ for oxygen-free solutions. Concentration: F, 1.08 g.l.$^{-1}$; G, 0.054 g.l.$^{-1}$.



Correction Factor to be applied to the detected fluorescence intensity at each wavelength. The corrected values of n_f and n_{f_0} are then obtained from the following relations:-

$$n_f = \frac{(I_{obs})_\lambda}{(\text{Correction Factor})_\lambda}, \qquad \text{at each wavelength } \lambda.$$

$$n_{f_0} = \frac{(I_{obs})_{3000\,\text{Å}}}{(\text{Correction Factor})_{3000\,\text{Å}}}, \qquad \text{at } \lambda = 3000\ \text{Å}$$

The transfer coefficient f is then obtained from equation (5) as follows:

$$f = \frac{n_f}{n_{f_0}} - \rho_c\left(1 - \frac{n_f}{n_{f_0}}\right)$$

The mean values of f_1 and f_2, are plotted as a function of concentration, c, in FIG. 15. There are four curves representing values of f_1 for normal solutions plotted against c, f_2 for normal solutions plotted against c, and the equivalent two curves for the two oxygen-free solutions.

III. 4. CONSIDERATION OF ASSUMPTIONS:

The two assumptions made in the calibration of the incident radiation (II.3) and the analysis of the results should be noted, since if they were invalid, the results at $\lambda < 2537$ Å might not be reliable.

They are as follows:-

(i) The molecular fluorescence quantum efficiency, q_{f_y} of terphenyl in solution is constant down to $\lambda = 2200$ Å (III.3)

(ii) The technical fluorescence quantum efficiency of the 1 cm. cube terphenyl crystal is constant down to $\lambda = 2200$ Å (II.3)

Since crystalline terphenyl is transparent to its own fluorescence emission

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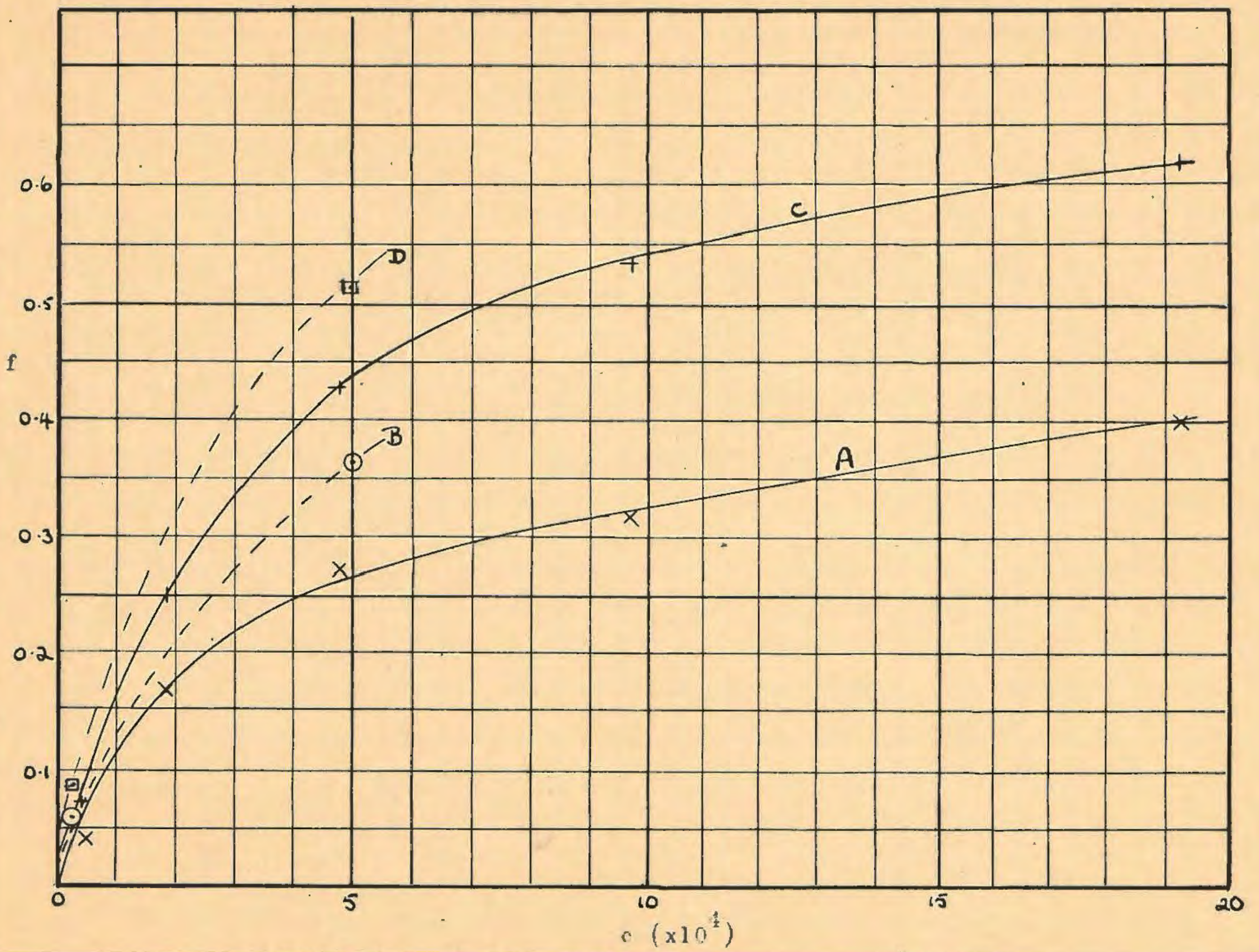
FIG. 15. . Energy transfer coefficient, f, plotted against concentration, c. A, normal solutions, λ = 2500-2650 Å; B, oxygen-free solutions. λ = 2500-2650 Å; C, normal solutions, λ = 2200-2350 Å; D, oxygen-free solutions. λ = 2200-2350 Å.



(BIRKS & WRIGHT 1954), its technical and molecular fluorescence efficiencies are identical. Hence (i) and (ii) are equivalent assumptions for terphenyl molecules in solution and in the crystalline state.
These assumptions are consistent with all the experimental data on organic fluorescent materials, excited by non-ionizing radiation (see PRINGSHEIM 1949 & WRIGHT 1955) and there is no reason to doubt their validity.

COHEN & WEINREB (1956) also make assumption (i), and a similar assumption to (ii) for the aqueous solution of fluorescein used for calibration of the incident radiation.

The choice of terphenyl both as solute and for calibration of the incident radiation flux means that, even if (i) and (ii) are not valid, provided the ratio of the molecular fluorescence efficiencies of terphenyl in solution and in the crystal is constant down to $\lambda = 2200$ Å, the values of f calculated from the observations will be unchanged.

III. 5. THE ENERGY TRANSFER PROCESS:

On the photon transfer theory, and some of the alternative non-radiative mechanisms proposed, the probability of solvent-solute transfer is proportional to the concentration, c. The various processes, occurring within the solvent-solute system for an incident unit flux of photons ($h\nu$) are shown in Table III.

The asterisks refer to excited molecules. k and q are molecular absorption coefficients and quantum efficiencies respectively. Suffixes x and y refer to the solvent X and solute Y respectively; f, i and e refer to fluorescence, internal quenching and external quenching respectively; and 1 and 2 refer to the fluorescence emission of X and Y respectively. $\bar{k}_{x_1}$, $\bar{k}_{y_1}$, represent the values of molecular absorption coefficients averaged over the emission spectrum of X, that is,

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TABLE III.

RADIATIVE TRANSFER

	Process	Rate	Description
(i)	$X + h\nu \rightarrow X^*$	$n_x = -k_x[X]$	Absorption of incident radiation by solvent.
(ii)	$Y + h\nu \rightarrow Y^*$	$n_y = -k_y[Y]$	Absorption of incident radiation by solute.
(iii)	$X^* \rightarrow X + h\nu_1$	$q_{fx}[X^*]$	Fluorescence of solvent.
(iv)	$X^* \rightarrow X$ + heat	$q_{ix}[X^*]$	Internal quenching of so
(v)	$X^* + X \rightarrow X+X$+heat	$q_{exx}[X^*]X$	External self-quenching solvent.
(vi)	$X^* + Y \rightarrow X+Y$+heat	$q_{eyx}[X^*]Y$	External quenching of so by solute.
(vii)	$X + h\nu_1 \rightarrow X^*$	$-\overline{k_{x1}}\ q_{fx}[X^*][X]$	Absorption of solvent em by solvent.
(viii)	$Y + h\nu_1 \rightarrow Y^*$	$-\overline{k_{y1}}\ q_{fx}[X^*][Y]$	Absorption of solvent e by solute.
(ix)	$Y^* \rightarrow Y + h\nu_2$	$q_{fy}[Y^*]$	Fluorescence of solute.
(x)	$Y^* \rightarrow Y$ + heat	$q_{iy}[Y^*]$	Internal quenching of s
(xi)	$Y^* + X \rightarrow Y + X$	$q_{exy}[Y^*][X]$	External quenching of by solvent.
(xii)	$Y^* + Y \rightarrow Y+Y$+heat	$q_{eyy}[Y^*][Y]$	External self-quenchin solute.

--oOo--

they represent the fraction of solvent fluorescence which is reabsorbed by both the solvent, X, and the solute, Y. The excitation, i.e. absorption, processes (i, ii, vii, viii) are distinguished from de-excitation, i.e. emission or quenching, processes (iii to vi, and ix to xii) by a negative sign. Since the complete system is practically opaque to the emission of X, and transparent to the emission of Y, processes corresponding to the escape of the former, or the reabsorption of the latter, are omitted.

A similar analysis is applicable to non-radiative processes in which the transfer probability is proportional to the concentration. In such cases the energy $h\nu$, representing the fluorescence photon, would be taken to refer to a "virtual photon" or exciton, and $k_{x1} q_{fx}$ $k_{y1} q_{fx}$ to the quantum efficiencies of solvent-solvent and solvent-solute inter-molecular energy transfer. Such an analysis is not, however, applicable to non-radiative transfer processes in which the energy transfer rate is not linearly proportional to the concentration.

From Table III, an expression for the intensity of the solute fluorescence n_f, may be evaluated as follows:-

$$
\begin{aligned}
n_f &= q_{fy}[Y^*] && \text{———— (Process ix)} \\
&= q_{fy}\{-k_y[Y] - \overline{k}_{y1} q_{fx}[X^*][Y]\} && \text{——— (Processes ii \& vi} \\
&= -q_{fy}[Y]\{k_y + \overline{k}_{y1} q_{fx}(-k_x[X] - \\
&\qquad \overline{k}_{x1} q_{fx}[X][X^*])\} && \text{—— (Processes i \& vii} \\
&= -q_{fy}[Y]\{k_y - \overline{k}_{y1} q_{fx} k_x[X](1 - \overline{k}_{x1} q_{fx}[X] \\
&\qquad + \overline{k}_{x1}^2 q_{fx}^2 [X]^2 - \ldots\ldots)\} \\
&= q_{fy}\{n_y - \overline{k}_{y1} q_{fx}[Y] n_x (1 - \overline{k}_{x1} q_{fx}[X] \\
&= \qquad + \overline{k}_{x1}^2 q_{fx}^2 [X]^2 - \ldots)\} \\
&= q_{fy}\left\{n_y - \frac{n_x q_{fx} \overline{k}_{y1}[Y]}{1 + q_{fx}\overline{k}_{x1}[X]}\right\} && \text{———————— (6}
\end{aligned}
$$

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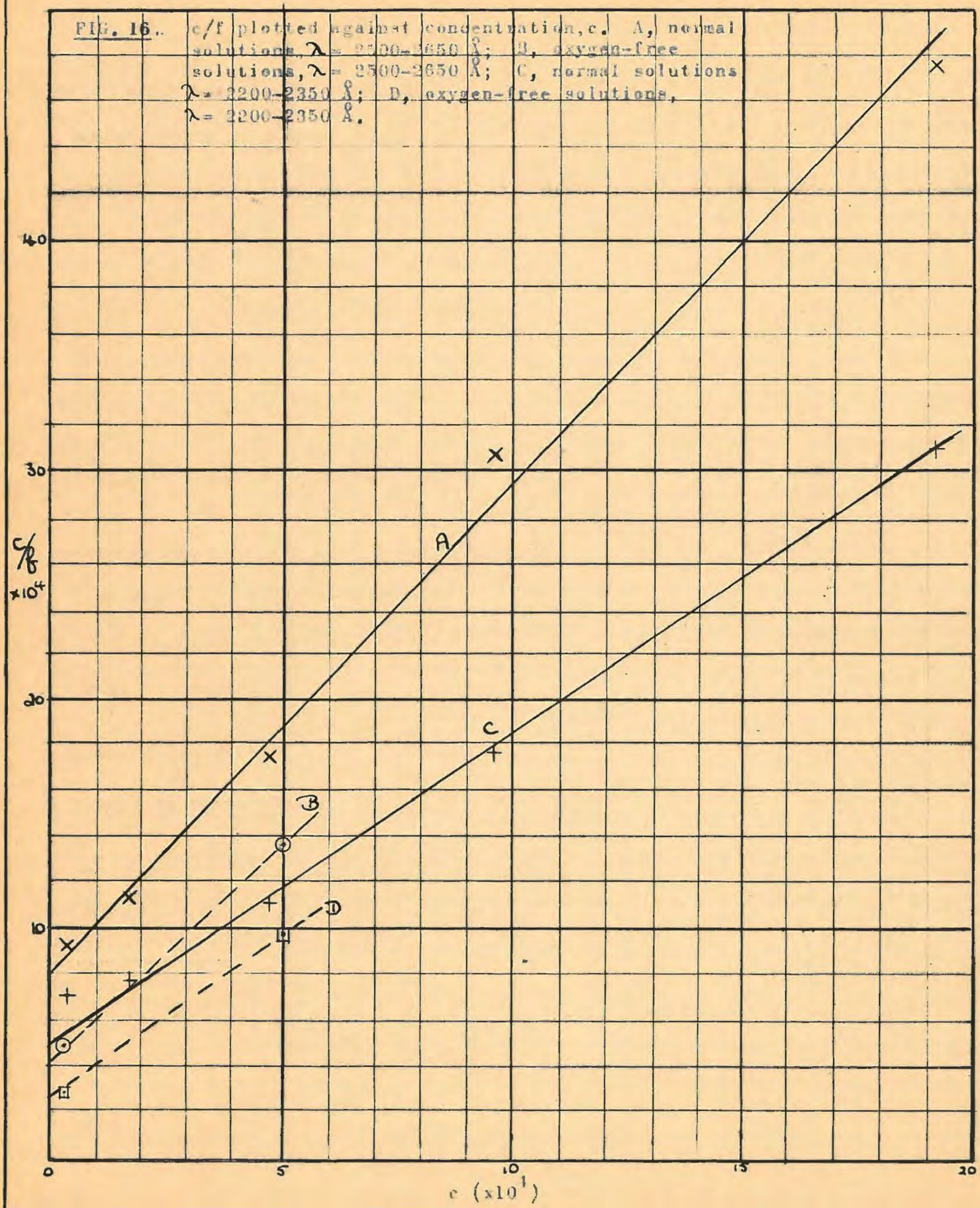


FIG. 16. c/f plotted against concentration, c. A, normal solutions, λ = 2500-2650 Å; B, oxygen-free solutions, λ = 2500-2650 Å; C, normal solutions λ = 2200-2350 Å; D, oxygen-free solutions, λ = 2200-2350 Å.

The first component of this equation, $q_{f_y} n_y$, is the emission excited directly by the incident radiation. The second component, $q_{f_y} n_x f$, is the emission excited indirectly by energy transfer from the solvent.

From equations (3) and (6)

$$f = -\frac{q_{fx}\overline{k_{y_1}}[Y]}{1 + q_{fx}\overline{k_{x_1}}[X]}$$

$$= \frac{q_{fx}\overline{k_{y_1}}\,C}{k_x + k_y C - q_{fx} k_{x_1}}$$

$$\doteqdot \frac{q_{fx}\overline{\epsilon_{y_1}}\,C}{\epsilon_x + \epsilon_y C - q_{fx}\overline{\epsilon_{x_1}}} \qquad \text{———————— (7)}$$

where $\overline{\epsilon_{x_1}}, \overline{\epsilon_{y_1}}$ represent molar extinction coefficients averaged over the emission spectrum of the solvent X. Their ratio, $\overline{\epsilon_{y_1}}/\overline{\epsilon_{x_1}}$, will be denoted by $\overline{\rho_1}$. Due to external quenching, q_{f_x} and q_{f_y} decrease with increase in concentration.

$$q_{f_x} = 1 - q_{ix} - q_{exx}[X] - q_{eyx}[Y] \qquad \text{(Processes iii to vi)}$$

$$= 1 - q_{ix} - q_{exx} - q_{eyx}C \qquad (\text{for } C \ll 1) \qquad \text{——————— (}$$

$$q_{f_y} = 1 - q_{iy} - q_{exy}[X] - q_{eyy}[Y] \qquad \text{(Processes ix to xii)}$$

$$= 1 - q_{iy} - q_{exy} - q_{eyy}C \qquad (\text{for } C \ll 1) \qquad \text{——————— (}$$

By simplifying our equation (7) we obtain -

$$f = \frac{c}{Ac + B} \qquad \text{——————— (7}$$

In FIG. 16 the experimental values of $\frac{c}{f_1}$ and $\frac{c}{f_2}$, shown in Table IV, are plott against c for both the normal solutions and the oxygen-free solutions. Linear relations in agreement with equations (7a) are obtained for each of the four curve from which the values of the constants A and B in this expression may be determine

Since $\frac{c}{f} = Ac + B$

A is the slope and B the intercept of the curves.

TABLE IV

SOLUTION	CONCENTRATION C MOL/MOL	$^{c}/_{f_1}$	$^{c}/_{f}$
a	19.1×10^{-4}	47.6×10^{-4}	31.1 x 1
b	9.58 "	30.7 "	17.8
c	4.78 "	17.6 "	11.1
d	1.91 "	11.2 "	7.65
e	0.418 "	9.3 "	6.75
f (oxygen-free)	4.98 "	13.7 "	9.7
g (oxygen-free)	2.32×10^{-5}	4.2 "	2.67

For the normal solutions the following values are obtained:-

In Spectral Region I (2500 Å - 2650 Å) $A_I = 2.1$

$B_I = 8 \times 10^{-4}$

and in Spectral Region II (2200 Å - 2350 Å) $A_{II} = 1.4$

$B_{II} = 5 \times 10^{-4}$

For the oxygen-free solutions, the corresponding values are:-

$A_I = 2.1$

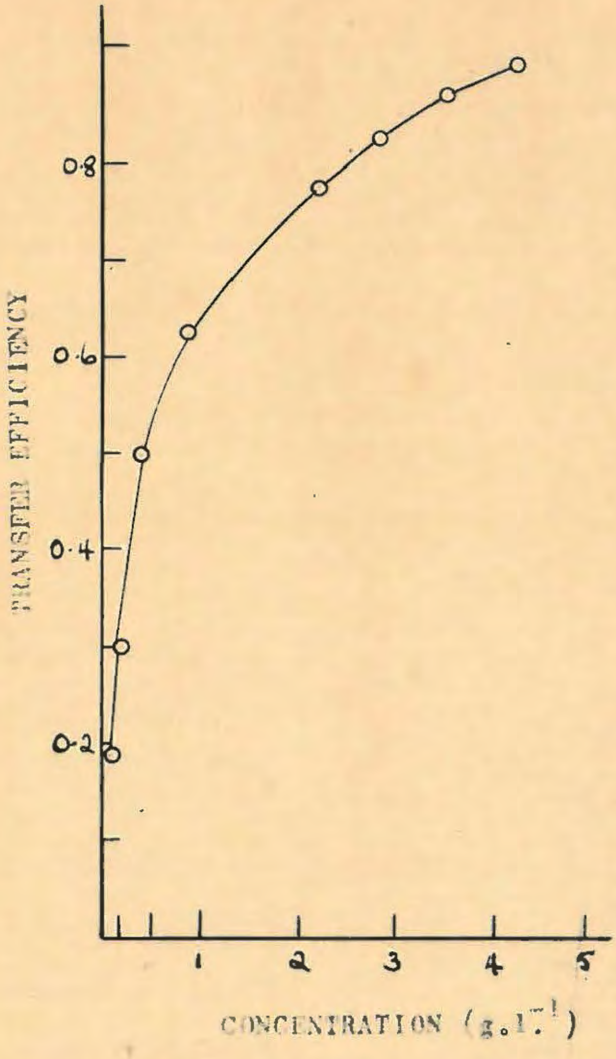
$B_I = 4 \times 10^{-4}$

and $A_{II} = 1.4$

$B_{II} = 2.5 \times 10^{-4}$

where suffixes I and II refer to the corresponding spectral regions.

FIG.17. Variation of energy transfer efficiency in solutions of p-terphenyl in toluene with concentration of p-terphenyl.



IV. DISCUSSION

IV. 1. COMPARISON WITH OTHER EXPERIMENTAL RESULTS:

After the completion of the experimental work reported here, an account of similar studies on liquid organic solutions excited by ultra-violet radiation was published by COHEN & WEINREB (1956). Their experimental procedure was similar to that of the present work, yet the interpretation of their results differs in certain important respects.

It is of interest, therefore, to compare the present results with those of COHEN & WEINREB in order to make a comprehensive study of the energy transfer process.

In their experiments COHEN & WEINREB (1956) used, amongst others, solutions of para-terphenyl in toluene and measured the efficiency of transfer of energy from solvent molecules to solute molecules as a function of various variables such as exciting wavelength, concentration and presence of quenching agents. No reference is made to the oxygen content of their solutions, which are presumably air-saturated.

(i) The concentration dependence of energy transfer:

Most of the measurements of COHEN & WEINREB were made using 2537 Å and 3130 Å radiation for excitation; these wavelengths lie within the spectral regions designated I and 0 respectively in the present work, so that their values of f, the transfer efficiency between excited solvent and unexcited solute molecules, correspon to the values of f_1 in the present work.

FIG. 17 is reproduced from COHEN & WEINREB (1956) and shows the similarity betwe

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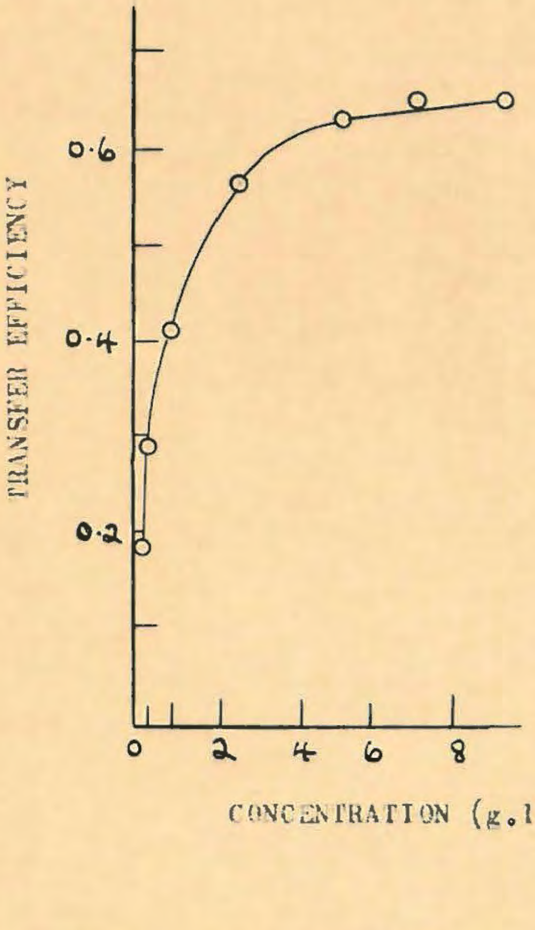
FIG. 18. Variation of energy transfer efficiency in solution of anthracene in anisole with concentration of anthracene.



their curve of Transfer Efficiency vs. Concentration and the curve obtained from the present work (FIG. 15). These authors observed a linear relationship between $\frac{c}{f_1}$ and c, as is given by equation (7a), although in the derivation of their empirical equation for the value of f_1 (compare (7a)), external quenching of the solvent fluorescence by solute molecules, process v of Table III, was equated to zero. Hence they found (FIG. 17) that f_1 tended towards a limiting value of unity, as c increased, rather than to the limits, given by $\frac{1}{A_I}$ and $\frac{1}{A_{II}}$, of $f_1 = 0.48$ and $f_2 = 0.7$ obtained from the present measurements.

It may be noted that although COHEN & WEINREB assumed that there was no quenching of solvent fluorescence by solute molecules in their theoretical analysis, their measurements on solutions of anthracene in anisole are not consistent with the predictions of this hypothesis. This is shown in FIG. 18 where the transfer efficiency, f_1, tends towards a lower limiting value of ~ 0.8. However, their result like the present ones, show clearly that the probability of solvent-solute energy transfer is proportional to the solute concentration, c. Earlier attempts by KALLMAN & FURST (1950) to demonstrate this relation in the case of gamma-ray excitation were complicated by the concentration dependence of quenching of solute fluorescence and more complicated equations with a greater number of parameters have to be introduced.

(ii) Influence of quenching agents on energy transfer:

COHEN & WEINREB investigated the influence of carbon tetrachloride as a quenching agent, on the solvent fluorescence. The carbon tetrachloride is transparent to the incident radiation but competes with the terphenyl molecules for the absorption of the toluene fluorescence, and in addition decreases the toluene fluorescence by collisiona quenching of the solvent molecules. The results showed that the addition of carbon tetrachloride to a 3 gm/litre to 5 gm/litre solution of terphenyl in toluene quenches the energy transfer by about 30%. While there appears to be no reason to question these relative efficiency values, the absolute values are subject to the same degree of uncertainty as the others discussed in IV.1.(i). These studies using a second solvent have not been repeated in the present work.

(iii) <u>Dependence of transfer efficiency on exciting wavelength</u>:

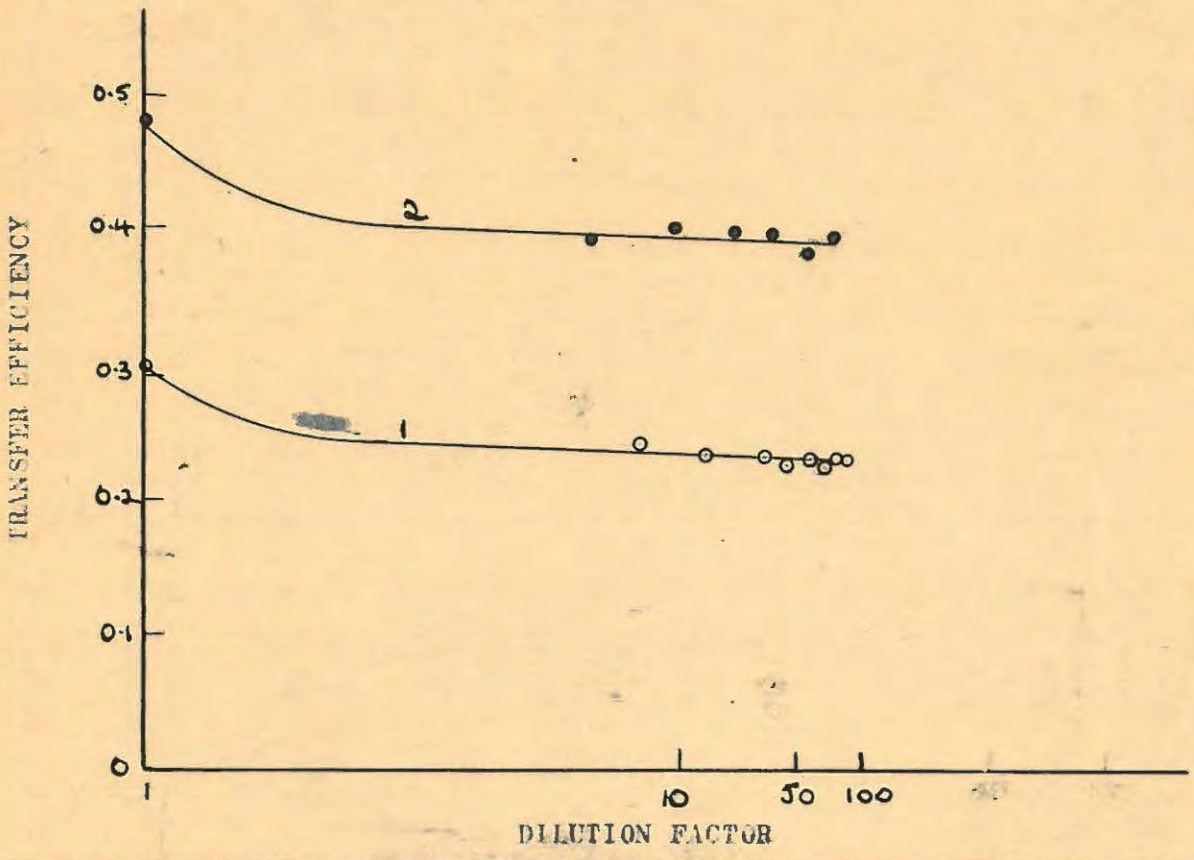
It is here that the results of COHEN & WEINREB are in distinct contrast to the present work. In III.3. and FIGS. 13 & 14 of the present work, it is shown clearly that the transfer coefficient, f, varies with the wavelength, λ, of the exciting light, whereas COHEN & WEINREB report that the energy transfer coefficient is independent of λ for wavelengths from 2200 Å to 2700 Å. In this spectral range, the absorption spectrum of toluene shows two bands (FRIEDEL & ORCHIN 1951) and for exciting wavelengths shorter than 2300 Å one therefore expects the second electronic state to be excited. The constancy of their calculated values of f suggested that the transfer always takes place from the first excited state, even though the second state may be initially excited.

FIG. 15 of the present work is in direct contradiction to this suggestion, since there are two distinct values of f, viz: f_1 and f_2, the latter occurring at wavelengt <2350 Å, which suggests that the transfer from the second excited state of toluene i greater than from the first. This wavelength dependence of f is discussed more full in IV.2.

(iv) <u>Effect on transfer efficiency of dilution of transferring solvent</u>:

An experiment to study the effect of dilution on the transferring solvent by a second inert solvent was designed to investigate the possibility, suggested by KALLMA & FURST (1950), that the solvent molecular excitation energy is propogated through th solvent by a quantum mechanical exchange interaction between neighbouring solvent

FIG. 19. Variation of ϵ in solutions of p-terphenyl in toluene-cyclohexane with dilution factor. Concentration of p-terphenyl: 1, 0.25 $g.l^{-1}$; 2, 0.5 $g.l^{-1}$.



molecules until an excited solvent molecule finally transfers its energy to a neighbouring solute molecule.

The intrinsic transfer efficiency was measured as a function of the degree of dilution of the transferring solvent while the solute concentration was kept constant. The function of the second solvent is only to separate the molecules of the absorbing solvent. The type of curve obtained for solutions of para-terphenyl in toluene diluted with cyclohexane is shown in FIG. 19. After a small initial decrease in the transfer efficiency corresponding to relatively low dilution factors, the transfer efficiency remains remarkably constant even at the very highest dilutions. In order to interpret this curve properly, COHEN & WEINREB investigated the influence of dilution on the natural fluorescence of the absorbing solvent which they found increased considerably with dilution, because of the decrease in the extent of self-quenching.

The possibility of photon emission and reabsorption being the dominant mechanism by which molecular energy is transferred was investigated by comparing the solute fluorescence intensity (isolated from the solvent fluorescence and primary radiation) obtained from "thin" and "thick" layers of solutions, where the primary exciting radiation is completely absorbed by the absorbing solvent; the terms "thick" and "thin" imply distances large or small compared with the mean free paths of the natural fluorescent radiation of the absorbing solvent. The existence of an appreciable radiative transfer from the solvent to the solute would give rise to an increased solute fluorescence when a "thick" layer is used, since only in this case is a large fraction of the solvent fluorescence completely absorbed by the solute. It is stated that in the case of toluene, the amount of radiative transfer was not greater than 2% of the total transfer, even at high dilution and at the lowest concentrations used in the dilution experiments. FIG. 19 led COHEN & WEINREB to the conclusion that in the process of energy transfer from an excited solvent molecule to a solute molecule, other molecules play no part. The results were interpreted on the theory of a long range dipole-dipole interaction similar to that proposed by FÖRSTER (1949) for dye solutions, though this theory in its quantitative form does not apply to the organic systems used in this work.

(v) The influence of transfer on the natural fluorescence of the solvent:

The assumption that the process of natural solvent fluorescence competes with the process of transfer of energy to the solute was investigated by COHEN & WEINREB (1956) for various solutions of anthracene (usually in toluene). They measured the intensity of fluorescence of the pure solvent and of "thick" and "thin" layers of solution. The thick layer fluorescence arises almost completely from the solvent-solute transfer, whereas the thin layer fluorescence includes both the solvent and solute fluorescence; the difference between the "thick" and "thin" layer fluorescence gives the solvent fluorescence in the presence of solute molecules and is compared with the pure solvent fluorescence intensity. It was found that no quenching of the solvent fluorescence occurred as a consequence of the addition of solute molecules which seems to show that the assumption of competing processes stated above is not true. This conclusion is supported by FIG. 19, in which the transfer efficience remains constant even though the fluorescence efficiency of the solvent increases with increasing dilution.

Radiative transfer and several non-radiative processes, e.g. sensitized fluorescence are, therefore, eliminated as possible energy transfer mechanisms in these liquid systems.

COHEN & WEINREB suggest that the natural fluorescence of toluene is small because

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of self-quenching, yet the solvent molecules which finally transfer energy to terphenyl can exist for times of the order of 10^{-9} sec. This, they suggest, is further evidence that solvent fluorescence and energy transfer take place from different molecular states.

(vi) Discussion of COHEN & WEINREB's results:

The experiments reported in IV.1.(iii) dealing with the quenching effect of carbon tetrachloride on the transfer process show, according to COHEN & WEINREB, that a relatively long time, of the order of 10^{-9} sec., must elapse before solvent-solute transfer occurs. The fluorescence decay time is of the order of only 3 x 10^{-9} sec., hence during 10^{-9} sec. the excited molecule will make numerous collisions and will diffuse until it approaches a solute molecule.

In spite of this general picture of diffusion of the excited solvent molecules for a considerable time, followed by transfer, the authors do not assume that the solvent-solute transfer takes place in a close collision occurring directly between the two molecules, because this would lead to greater scintillation decay times than those observed (HARRISON 1952). Instead they attempt to interpret their results on the theory of dipole-dipole interaction proposed by FORSTER (1949) for dye solutions but as previously stated in I.3.(ii), they do not obtain quantitative agreement with this theory.

As stated in IV.1.(iii), the present results which show a wavelength dependence of the energy transfer coefficient are in direct contrast to those of COHEN & WEINREB (1956). This difference may partly arise from the correction for excitation depth (III.2) because while the latter refer to a correction for geometrical and self-absorption effects being applied, no details of the correction, which is stated to be generally small, are given.

In the present measurements, covering a similar range of concentrations, the values of $(\epsilon_x + \epsilon_y c)$ at 2537 Å and 3130 Å (the wavelengths used by these authors) range from 170 down to 0.06, corresponding to values of $I/_{Io}$ from 1.04 down to 0.7.

IV. 2. DEPENDENCE OF ENERGY TRANSFER ON EXCITING WAVELENGTH:

The most interesting result discovered from the present measurements is that the energy transfer probability depends on the wavelength of excitation. The two spectral regions I (λ = 2500-2650 Å) and II (λ = 2200-2350 Å) correspond to excitation into the first and second excited electronic singlet states of the toluene molecule. FIGS. 13 & 14 show that the energy transfer coefficient, from toluene molecules excited initially into the second excited state, is higher than from molecules excited initially into the first excited state.

The fluorescence life times of the first and second excited states are of the order of 10^{-9} sec. and 10^{-11} sec. respectively. In IV.1.(vi) the results of the experiments performed by COHEN & WEINREB (1956) to investigate the quenching effect of carbon tetrachloride (IV.1.(ii)), are discussed, and it is shown that energy transfer from the first excited state occurs in the order of 10^{-9} sec. The efficient energy transfer from the second excited state shows that in this case transfer must occur in about 10^{-11} sec. or less. The very short life time of the second excited state excludes any possibility that the energy transfer from this state is collisional in nature, since the average time required by an excited solvent molecule to diffuse into the proximity of a solute molecule is in excess of 10^{-11} sec.

Because of the short life time of the second excited state the external quenching will be relatively small. The chief process competing with solvent-solute energy transfer from this state will be conversion into the first excited state of the solvent

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molecule, either by internal conversion or by solvent-solvent energy transfer. This conversion process is known to be highly efficient and rapid (PRINGSHEIM 1949). Nevertheless, the results show that the solvent-solute transfer can compete efficiently with such inter-state conversion.

IV. 3. THE PHOTON TRANSFER THEORY:

The results of the present work have been discussed so far without specific reference to any particular mode of energy transfer.

The energy transfer from the second excited state of the solvent is consistent with the suggestion of BIRKS (1954) that fluorescence emission occurs from the second and higher electronic excited states of a fluorescent molecule. The results show, therefore, that the concept, previously accepted (PRINGSHEIM 1949) that all the excitation energy of such higher electronic states is internally converted into that of the lowest excited state, is invalid. In pure solvents, the internal conversion plus solvent-solvent transfer, gives 100% inter-state conversion efficiency so that only emission from the lowest state is observed, but in solutions, the solvent-solute transfer is an efficient competitor for the excitation energy and solvent emission from the higher states is probable.

The time required for energy transfer is of the order of 10^{-11} and 10^{-9} sec. respectively for the second and first excited states, which is about the same as for fluorescence emission from these two states. Photon emission and reabsorption is, therefore, a likely mechanism of energy transfer.

Between spectral regions I and II, where all the excited solvent molecules are initially in the first and second excited states respectively, there is a transition region extending from 2350-2500 Å. In this transition region, solvent molecules

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co-exist initially in either of the two excited states. This region is also that where fluorescence from the second excited state would be expected to occur.

In I.3. pages 22 & 23 and IV.1.(v) the results of COHEN & WEINREB (1956) are discussed, in which they show that the solvent-solute transfer efficiency in region I is unchanged if the solvent is diluted by a factor of 1000 with an "inert" liquid. They have thus demonstrated that solvent-solvent "collisional" energy transfer is negligible.

It would also appear that any short range non-radiative solvent-solute transfer processes, which depend on thermal diffusion to bring the excited solvent molecule and the solute molecule into reasonable proximity, are similarly excluded by these observations since their efficiency would be reduced by an increase in the diffusion time due to dilution. Fluorescence of the solvent, leading to photon transfer, appears to be the one possible long range mechanism. The dilutant, cyclohexane, being transparent, does not decrease the efficiency of photon transfer. The fluorescence spectrum of the emission from the first excited state of toluene, observed in dilute alcoholic solution, has vibrational maxima at λ = 2622, 2646, 2676, 2740, 2808 and 2886 Å (PRINGSHEIM 1949). There is thus a major overlap of the fluorescence and absorption spectra, and in pure toluene the mean free path of the emitted photons will be only a few microns. The relatively low technical fluorescence efficiency, q_t, observed with thicker toluene specimens by KALLMANN & FURST (1951b) will be considerably less than the molecular fluorescence efficiency, q_o, due to this high self-absorption. Since $q_t = (q_o)^n$, where $\frac{1}{n}$ is the probability of photon escape without absorption (BIRKS 1954), by taking values of $q_t \sim 0.015$ (KALLMANN & FURST 1951b), $n \sim 6$ (estimated from the absorption and emission spectra) we obtain a rough estimate of $q_o \sim 0.5$. The experimental data thus appear consistent

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with the photon cascade and transfer theory, but not with the alternative mechanisms proposed.

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V. CONCLUSION

The experiment was performed to investigate the energy transfer mechanism by which energy is transferred from the initially excited solvent molecules to the solute molecules in solutions of para-terphenyl in toluene under ultra-violet radiation.

It is found that:-

(i) The probability of solvent-solute transfer is proportional to the solute concentration.

(ii) The efficiency of energy transfer depends on the excitation wavelength, the energy transfer being more efficient from solvent molecules in the second excited state than from the first excited state.

Although no final conclusions can be drawn about the energy transfer mechanism, the results appear to be consistent with the radiative transfer process than with any short range non-radiative transfer process.

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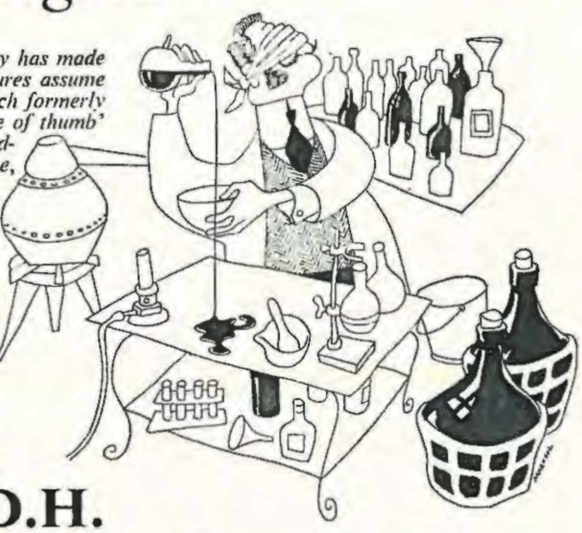

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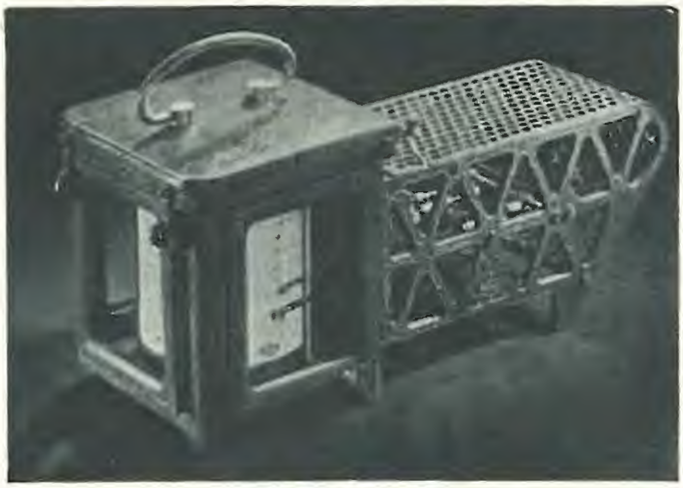

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The Association's Library

For the information of members we publish in this number an up-to-date list of the serial publications received currently in the Library of the South African Association for the Advancement of Science. These include the proceedings and transactions of learned and scientific societies and other national associations for the advancement of science, and the published results of investigations carried out by scientific expeditions, geological and archaeological surveys, observatories, museums, botanical gardens, research laboratories, etc., in all parts of the world, most of which are received in exchange for this Journal.

The Association's Library, though a separate unit, is administered as part of the Library of the University of the Witwatersrand, and the two supplement and reinforce each other. The resources of both libraries are made available free of charge to members of the Association, the University and its associated institutions, and through the University and the inter-library loan system to research workers in every part of the country.

For a full account of the history and constitution of the Association's Library readers are referred to an article by the Librarian, Mr I. Isaacson, which was printed in the September, 1955, issue of this Journal.

Shrinking Glaciers

Scientists are interested in finding out more about the world's great glaciers because they are long-range recorders of climatic change. Hidden in the layers of ice far below the surface there are physical phenomena that can throw invaluable light upon the climatic conditions under which glaciers in the past have grown and then diminished in size.

Observations of glaciers made in the past have shown that most glaciers in the temperate zones have been shrinking during the last century. In places the rate of recession since the 1920's has been very much more rapid than in previous decades.

While the cause is generally believed to be a gradual warming up of the world's climate, the problem is complex and more information is needed. The presence of a few advancing glaciers, as in Alaska, remains unexplained. Other glaciers have been observed which advance and recede in a way which is not believed to be primarily the result of the warmer climate or other meteorological conditions.

During the International Geophysical Year an effort will be made to find answers to some of these questions. (Usis).

Honour for Dr Jeffreys

Dr M. D. W. Jeffreys, Lecturer in Anthropology at the University of the Witwatersrand, has been elected a Fellow of the American Association for the Advancement of Science.

NEW HORIZONS FOR SCIENCE AND INDUSTRY*

S. M. Naude

One reads so much in the daily press about automation and nuclear energy and its possible effects on the survival of our present way of living, and even of the human race itself, that on this occasion when scientists from all over Southern Africa are gathered together, it is perhaps opportune for the scientist to express an opinion on these subjects. A timely word about the probable effects on science and industry, and the adjustment of our methods of training the scientist and engineer of the future to meet the demands of this brave new world, may also not be out of place.

I. AUTOMATION

Newspapers and journals have recently published several articles expressing the fear that the world is entering upon a second industrial revolution. In these articles, comparisons were made with the first industrial revolution which took place in Britain from 1770 to 1825. The steam engine invented by James Watt in 1769 played a great rôle in this revolution, but various other inventions also contributed to the unrest of the workers, such as new labour saving devices in the textile industry. The result was that thousands of handicraftsmen were forced out of the factories and deprived of the means of earning their livelihood. This led to the formation in 1811 of organized bands of English rioters called Luddites. These bands were formed with the purpose of destroying machinery in the factories, but in the end they had to give in. The factory owners succeeded in installing labour-saving machinery and through low-priced quantity production were able to expand their markets throughout the world.

Recently a similar situation arose at Coventry in Britain when fears of automation brought out 11,000 workers on strike at the Standard motor factory, because 3,000 redundant workers were dismissed when a £4,500,000 automation plant was being installed. The factory manager argued that instead of 250 tractors per day about 600 could be produced by the new plant with 3,000 workers less. The fact was again stressed that Britain must make use of the most efficient production equipment in order to maintain her competitive position in the world's markets.

Throughout its history the world has been faced by similar situations. From earliest times man has applied his ingenuity to improve his productive means: his skills, his tools, his machines. In South Africa we have beautiful collections of tools from the Stone Age and many papers of this Society have dealt with them. Even Aristotle dreamed of the day when "every tool, when summoned, or even of its own accord, could do the work that befits it". To-day it almost seems as if Aristotle's dream is becoming a reality for not only has automation opened up vast possibilities but at the same time nuclear energy has appeared upon the scene to enhance these possibilities.

First of all we should be quite clear that it would be suicidal for us in South Africa to try to ban these "demons", automation and nuclear energy, or to try to destroy them. In recent history we know of an instance where an attempt was made to put back the clock of industrial development when Gandhi tried to get his people to go back to the hand loom when he preached that everybody should be self-sufficient. We all know that such a policy can only lead to the retarding of the progress of a nation. In the long run it will not be able to compete with the rest of the world which makes use of all the industrial and scientific advances.

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* Presidential Address to the S.A. Association for the Advancement of Science, Nelspruit, July, 1956.

Automation connotes the employment of machinery or equipment to perform operations that would otherwise have to be done by human beings. The first completely mechanized factory, a continuous process flour mill, was built by Oliver Evans in Delaware in 1785. Evans made use of powered conveyors, and, untouched by human hand, the grain went into the mill and came out as flour. In 1801 Joseph Jacquard exhibited his automatic loom, controlled by paper cards. This loom had a memory in the form of punched paper cards on which the pattern to be woven was registered. This invention of Jacquard's made it possible to weave complicated patterns automatically without the help of the workman. It is still employed to-day in the most modern machinery and is even used in electronic computing machines to store the instructions which are fed into the machines.

What is new about modern automation and what is really responsible for the great interest it has aroused at present, is the advent of electronic methods of control and computation. A further factor which has contributed immensely to the advent of automation on a large scale is the use to which automation was put during World War II. In 1941 the largest electronic equipment, such as television sets, contained about 30 vacuum tubes and one of the reasons why television did not develop faster was that many people were afraid of its technical complexity. By comparison the electronic gear which goes into a typical automation system contains hundreds and sometimes even thousands of vacuum tubes or their equivalents. Military necessity caused this change, for it forced us to devise and employ very complex equipment. Thus direction finding equipment was developed by the research workers in Britain in 1944 to track the V_1 projectiles from the moment they were launched on their course to London. The anti-aircraft guns were automatically directed onto them and very soon 90% of them were shot down over open country before reaching their destination.

A second basic aspect of the new automation is that this complex equipment is rarely a goal in itself, like a radiogram or motor car, but usually appears as a component that is integrated into a complex system involving men, methods, procedures and machines which is basically non-technical. Hence automation equipment is nothing more than a tool. Like a tool it must therefore be designed specifically for the enhancement of the efficiency of business and industrial operations which in themselves are often not at all technical.

Not long ago, for instance, a motor's engine block was milled at one machine, removed by a worker and put on a conveyor, removed by another worker and bored at the next machine, and so on as the engine moved down the line. To-day, complex handling devices automatically remove the parts from the milling machine, turn and position them as necessary and hold them in place for the next machine's operation. Thus an engine block goes through 530 distinct operations in a continuous, automatic process in less than 15 minutes.

But there is more to automation than a process of continuous production, viz. the element of control. Automation seeks to make the production system as self-regulating as possible. What would happen to our continuous process if a single machine started to turn out parts which were too large or too small on account of tool wear? We could station workers at each machine to measure the parts and adjust the machines, but then we should lose all the advantages of the continuous process. We must therefore install a machine or device which will do the inspection and adjustments which the human operator could do without interrupting the flow. Behind these self-regulating devices lies a simple principle called "feedback". It is the same principle as that employed by James Watt's flyball governor to maintain his steam engine at constant speed. Thus in a machine which manufactures sheet metal, use is made of a device which continuously measures the thickness of the sheet. If the sheet is too thin, this device sends a signal to the motor driving the sheet mill to retard the speed at which the sheet goes through the mill, so that the sheet becomes thicker again. What is more, these devices are so sensitive that the thickness of the sheet can be controlled to be absolutely constant within a very small fraction of an inch!

Feedback control is now also introduced through the medium of the electronic computer, into offices and factories. All that is needed is to organize all parts of the process — production, pricing, advertising, sales, design and so on — in such a way that the control centres have continuous and accurate information concerning the operation of every part. This is where automatic high speed information processing machines come in. These great computers have most strongly aroused the curiosity of the public. They are used daily to find answers to questions in the design and testing of aircraft, guided missiles and warships. Use of a computer enabled the DC-7B airliner to fly six months sooner than would have been possible if conventional methods had been used to make all the necessary calculations.

The question is sometimes asked whether automation will bring large-scale unemployment. We often read of the future "workerless factory, a great hive of humming machines controlled by an electronic computer". This "workerless factory" is just as much of a myth as the perpetual motion machine. There will be some automatic factories, but they will not be without workers. An example of such a factory is the atomic processing plant at Oak Ridge. Although the entire operation is controlled there by a few girls at a central control panel, hundreds of skilled workmen are required to replace defective equipment which is sent to the manufacturer for repair.

Automation also will not make a robot out of the ordinary worker, as is often stated. It will certainly replace the routine repetitive jobs, but will set man free to use his intuition and brain for more creative jobs. This should improve the job satisfaction of the workers.

We come, therefore, to the conclusion that automation is the natural development of a long process of improving the ideas which the intuition of the human being has conceived and applied to improve his environment and raise his standards of living. To thwart the application of automation would be suicidal. It has already made possible the control and application of nuclear energy to the benefit of humanity. It has created problems such as the increase of the knowledge required by the workman, but these problems have to be faced. By solving these problems the human being can only be uplifted and not degraded. Automation does, however, raise the problem that the unqualified workman will have to make way for the highly trained and skilled, and this is an aspect to which I should like to pay more attention later.

II. NUCLEAR ENERGY

The development of nuclear energy is certainly one of the greatest factors affecting our present and future life. The economic possibilities of its application have been dealt with by several writers but several problems still await solution.

After the discovery of radio-activity by Becquerel in 1896 this new branch of science developed very rapidly, especially in the able hands of Lord Rutherford. In due course it became clear that the nucleus of the atom contained vast quantities of energy, but even Rutherford stated categorically in 1937 that he did not expect that it would ever be possible to control the release of this energy, or apply it as an industrial source of power.

Then suddenly Hahn and Strassmann in 1939 discovered that if neutrons are shot into uranium, it splits up into two atoms whose combined atomic weights are less than that of the parent atom. At the same time it releases additional neutrons which could split further uranium atoms. Here therefore we had the possibility of a chain reaction. Furthermore the fact that the total atomic weight or mass had decreased, indicated that energy was released according to the Einstein equation:

Energy (released) = mass (disappeared) x square of the velocity of light.

According to this formula one pound of uranium (if completely split up into lighter elements) produces as much energy as 3,000 tons of coal of 250,000 gallons of petrol! The truth of these facts was dramatically demonstrated to the world when the first atomic bombs exploded over Hiroshima and Nagasaki in August 1945 and brought the war against Japan to a sudden end. These bombs were small compared with the most recent hydrogen or fusion bombs which have an explosive power equivalent to 1,000 atomic bombs of the type dropped on Hiroshima or 1,000,000 of the most powerful high-explosive bombs used during the second World War.

Nuclear energy was discovered just in time to save several industrialized countries like Great Britain and Germany from strangulation owing to the shortage of the coal on which their industries were established. After the war Britain immediately took steps to apply nuclear energy for peaceful uses such as the production of electricity. In this process the heat liberated when uranium atoms split up will be used to produce steam which will drive turbines. These will drive electric generators which will send their electric current into the electric grid of Britain. It is expected that the electricity produced in this way will cost about as much as electricity produced from coal in Great Britain at present. Several groups of firms in Britain are at present competing to reduce the cost of electricity produced from nuclear energy and they feel confident that the price can be reduced by about one quarter to less than half a penny per unit. If this proves to be possible, electricity produced from nuclear energy will be cheaper than that produced from coal in Britain.

During a recent visit to the atomic energy research establishments in Britain and during discussions with industrial firms doing research in this field, it became clear to me that the fundamental physical problems in connection with the production of nuclear energy from fission had practically all been solved, but scientists were now faced by quite formidable problems in the fields of applied physics, mechanical engineering, metallurgy and chemistry. It was very refreshing, however, to find the prevalent attitude of the scientist to be that no problem was too difficult to be solved.

New types of reactors are actively being studied in Britain and the U.S.A. by physicists and engineers. It is already clear that the reactors now under construction at Calder Hall will very soon be surpassed by new types called homogeneous reactors. This whole field of research offers a most fascinating field of adventure to the young scientist. It is hence no wonder that almost every young physicist today wants to study nuclear physics. The physicists are also working on a new idea: the harnessing of nuclear power liberated by the fusion of the light elements such as lithium and hydrogen to form heavier elements. This is the type of energy which is released in the hydrogen bomb which is 1,000 times more powerful than the plutonium bomb.

In the field of mechanical engineering there was the problem of how to construct uranium fuel elements which must be protected against corrosion, by some element such as aluminium which has a low absorption for neutrons, in such a way that the heat produced by the fission process could be passed to the cooling liquid or gas most efficiently. I saw various designs of these fuel elements which at that time were being tried out in experimental reactors.

One of the metallurgical problems which is being investigated in all countries interested in nuclear energy, is to find a metal or alloy with a higher melting point than aluminium for encasing the uranium, but which at the same time has a low absorption cross section for neutrons. The ultimate aim is to run these reactors at temperatures of 1,000°F or higher, for it is well-known that the efficiency of the water-steam cycle in the production of electricity by means of steam turbines, is greater at these higher temperatures.

The reason for the search for casings of the uranium with a low neutron absorption is the importance of neutron economy in the reactor process. Uranium consists of 0.7% U^{235}, which fissions when struck by slow neutrons. The rest mainly consists of U^{238}. Plutonium is produced when a neutron is captured by U^{238}. For every U^{235} atom which is fissioned, 2.56 neutrons are released. One neutron is required to keep up the chain reaction, 0.9 neutrons are used up in producing plutonium from U^{238}, and 0.61 neutrons are lost in different ways. Thus only 0.05 neutrons are left to keep up the activity of the reactor or to produce radio-isotopes. According to an experiment first carried out in Chicago in 1942 this chain reaction starts when the total mass of natural uranium exceeds a certain critical value provided sufficient moderating material like graphite is interspersed to slow down the neutrons.

Zirconium is such a metal with a melting point of 3,400°F. Although far from the ideal casing metal, it is much better in this respect than aluminium. This led to an immediate search for zirconium minerals all over the world. Once a mineral is found, methods of ore dressing and the recovery of the metal in a pure form must be studied. Zirconium occurs in nature mixed with hafnium, which has very similar properties to zirconium and hence it is difficult to separate it chemically. It is, however, important to purify the zirconium completely from traces of hafnium, for hafnium has a high absorption cross section for neutrons. Previously this was considered to be almost impossible. Methods have, however, been developed and to-day zirconium without a trace of hafnium can be produced.

The metallurgy of metals like uranium, thorium, gallium, beryllium and zirconium have been studied in great detail. Uranium has different crystalline forms at different temperatures and its volume increases when it is taken through successive cycles of an increase and decrease of its temperature. This is an important disadvantage of uranium used in reactors, for it must be encased in aluminium to prevent corrosion and the escape of poisonous and radio-active gases produced in the fission process, and this property of uranium has the inevitable result that the aluminium cases do not last long. For this reason thorium which has only one crystalline form at different temperatures and which is transformed into fissionable U^{233} by neutron bombardment, is actively being studied as a new fuel element.

Besides a careful study of the new elements like uranium, zirconium and beryllium which have suddenly become so important in this new atomic age which we are entering, the chemical properties of the new elements like plutonium created in the reactor needed a careful study. Plutonium is very toxic and must be handled with the greatest care. In fact, the operator is usually protected by a frogman's suit and communicates with the outside world by a telephone built into the hood. Other elements like ruthenium and technetium produced in the fission process in the reactor need a careful study to determine the best ways for chemical separation. Certain elements again which are produced in the reactor give off very penetrative radiations. Their chemistry must be studied from behind a screen of lead blocks and manipulations of the chemical flasks and beakers must be carried out with artificial "tackle" simulating the arms of a human being. All this work is carried out in a fume cupboard with a constant current of air being sucked into the chamber and blown out of a high chimney to dissipate all dangerous gases.

In industry new techniques of producing perfect gastight welds of the great steel spheres containing the reactors have become essential. Thus welding in an argon atmosphere has become quite a common procedure at the new nuclear energy reactors of the Calder Hall power station. Artisans were trained on the spot in these new techniques.

At the research establishment, electronic computers were used to solve all the complicated differential equations which describe the processes taking place in the reactors.

In fact, one almost became bewildered by the way in which all the sciences were being mustered for a mass onslaught on these problems. Everything took place according to a fixed master plan which gave final dates for the design, construction and completion of the various tasks required to produce a nuclear reactor. One got the impression that the methods of the field marshal in planning a major wartime operation had been introduced into the scientific field, and the results as seen at Windscale, where the reactors are housed in buildings almost as high as Escom House in Johannesburg, were definitely awe-inspiring. A remarkable observation was that all the constructional operations of these new ventures of the atomic age were in the hands of comparatively young scientists and engineers. I commented upon this fact and the reply of one of the brains behind these tremendous projects was that older men had been tried but that they simply could not stand the tremendous strain of these modern developments.

When uranium fissions into two parts in the reactor, a whole series of elements ranging in atomic weight from 71 to 161 is produced. These elements are all radio-active and a careful study is being made of ways of using this radio-activity for industrial purposes. Thus it has been found that food and medicines can be sterilized by exposing them to these radiations. It has also been discovered that the chemical properties of certain plastic materials can be completely changed by these radiations. In the U.S.A., these radiations have also been used to kill insects in wood and sterilize their eggs. Grain and maize are also passed through tubes where they are exposed to these rays before they are stored in elevators or shipped overseas. In this way, all beetles are killed and their eggs sterilized.

In the reactor a whole series of artificial radio-active elements called radio-isotopes can be produced. Thus radiocarbon is produced by irradiating nitrogen, radiophosphorus in a similar way from sulphur and radio-iodine from tellurium. Radiophosphorus, e.g., behaves chemically like phosphorus but emits characteristic radiations by which it can be traced, in its whole course from the root of a plant to the farthest corner of the leaf or to the fruit, by means of sensitive instruments called Geiger-Müller counters or scintillation counters. The discovery of radio-isotopes has quite legitimately been considered to have the greatest possibilities as a scientific tool since the invention of the microscope. A prominent member of the American Atomic Energy Commission stated that, in his opinion, the human race would benefit as much from the many applications of radio-isotopes as from the eventual use of uranium and other fissionable materials to produce electricity. It is stated that the American motor industry already benefits from the application of radio-isotopes to an amount exceeding £300,000,000 per annum.

It will be out of place here to discuss all the applications of radio-isotopes which are already known. It will be enough to indicate that it is used in medicine to reduce human suffering, in industry to study various problems such as the wearing of the cylinders of internal combustion engines and the efficiency of lubricants, in chemistry to study the actual course of atoms in reactions (something which could never before be accomplished). Radiocobalt is used to replace the more expensive radium in radiotherapy, and is also used by the agriculturalist to produce new varieties of plants. Thus a new variety of wheat which has a shorter stalk and is thus less prone to fall over in rain and wind storms, and ripens earlier, has already been produced in England. It has also been found that we do not yet know the first principles of the way in which superphosphate assists maize and tobacco plants in their growth, and that we may be overfertilizing at wrong stages in the growth of the plant. In short, radio-isotopes have opened up a new line of approach in almost every field of science. All that is required is that the scientist should become acquainted with the simple way in which they can be employed, and he must be willing to apply them. Unfortunately many of our universities have not realized these vast possibilities, and through failing to train one or more of their staff members in this field, are not in a position to offer courses to their students in the applications of this new tool.

III. OPLEIDING

(Aangesien dit 'n tweetalige vereniging is wil ek die slotgedeelte van my toespraak in Afrikaans tot u rig.)

Ons het hierbo kennis gemaak met twee nuwe ontwikkelings, outomatisme en kernenergie, wat ons nuwe vergesigte laat sien het beide vir die wetenskap en die industrie. By albei hierdie nuwighede het ons daarop gelet dat die opgeleide natuurwetenskaplike en tegnoloog 'n geweldige rol speel. In die geval van kernenergie was die strenge vereistes selfs sodanig dat die ouer man van 'n 50 of 60 jaar nie die geweldige pas kon meemaak nie.

Volgens die Amerikaanse Kommissie-verslag oor outomatisme is die ontstellendste feit die tekort aan tegnici om die leiding in hierdie eeu te kan behou. Volgens 'n berig in die New York Times van 1 April 1956 word in die V.S.A. groot kommer uitgespreek oor die feit dat te min studente opgelei word as natuurwetenskaplikes en ingenieurs. In 1954 is 9164 meestersgrade in die wetenskap en 23,000 baccalaureusgrade in ingenieurswese in die V.S.A. toegeken. In Rusland daarenteen het die aantal graduandi in ingenieurswese alleen van 30,000 in 1952 na 63,000 in 1955 toegeneem. Hulle verwag dat daar in

Rusland in die volgende dekade 1,200,000 studente sal gradueer in ingenieurswese en fisiese wetenskappe teen 900,000 in die V.S.A. Volgens die leier van 'n Britse wetenskaplike sending na Rusland my onlangs persoonlik meegedeel het, is die gehalte van die opleiding in Rusland goed en in die geval van ingenieurswese beter as die B.Sc.-standaard in Suid-Afrika.

Die Weste staan hier voor 'n ontstellende feit. Ons staan aan die begin van 'n tegnologiese eeu. Die wêreld is verdeeld in twee kampe: die Weste en die Ooste. Die Ooste besef dat daar geen kragtiger wapen in hierdie tydperk is as opleiding op die gebied van die wetenskap en tegnologie nie. In hulle diktatorstaat is dit baie makliker om 'n beleid te volg wat doelgerig afstuur op die bevordering van die opleiding van steeds groter getalle op dié gebied.

Ons verneem dat in Rusland die beste wetenskaplike kragte aangemoedig word om onderwysers van wetenskap op skool te word. Hulle ontvang hoër salarisse en word kosteloos voorsien van vakansiehuise aan die kus of een of ander binnelandse see in die somer. Hierdie onderwysers besiel die kinders op skool en die bestes word aangemoedig om na die Universiteite te gaan waar hulle vry opleiding ontvang. Die wat goed slaag, het 'n briljante loopbaan. As hy uitblink, word hy lid van die Wetenskaplike Akademie in Moskou en hy ontvang 'n salaris wat drie keer so hoog is as die van sy minder gelukkige broer wat self egter ook nie sleg betaal word nie. Laasgenoemde kry 'n woonstel in Moskou, 'n huis op die land en 'n motor met 'n bestuurder. Die wetenskaplike word dus die aristokraat van die kommunistiese staat.

Onlangs het ek 'n bekende medikus wat agter die ystergordyn 'n wetenskaplike besoek afgelê het, gevra wie volgens sy indruk die besbetaalde wetenskaplike agter die ystergordyn is: die medikus of die natuurwetenskaplike. Sy onomwonde antwoord was laasgenoemde. Hieruit blyk duidelik dat die Russe deur 'n stelselmatige beleid van geldelike bevoordeling van die wetenskaplike daarvoor gesorg het dat die room van die jeug in daardie rigting getrek is met die gevolg dat hulle vandag reeds meer wetenskaplikes oplei as die V.S.A. Aan die ander kant word 'n bestuurder van 'n vragmotor in die V.S.A. meer betaal as die meeste professore van natuurwetenskappe of selfs die Doktor in Filosofie wat navorsingswerk doen.

Die V.S.A. is tans bewus van die Russiese strategie en oorweeg tans die hoër besoldiging van hulle onderwysers. Hulle het ook probeer om 'n stelsel wat jare reeds bestaan uit te brei. Gedurende die afgelope 30 jaar bied die meeste Amerikaanse Universiteite reeds 'n sogenaamde Somerkollege aan, veral vir onderwysers wat dan verlof van hulle skole kry vir die maande midde Junie tot die einde van Augustus. Deur vier agtereenvolgende Somerkwartale by te woon kan so 'n onderwyser een jaar krediet kry vir sy studie en moontlik 'n verdere graad behaal. In die V.S.A. word onderwysers nou met beurse aangemoedig om meer gebruik te maak van hierdie metode om hulle kennis van die moderne wetenskap aan te vul en aan hulle leerlinge oor te dra. Hulle is daardeur ook in staat om hulle leerlinge te besiel om in die natuurwetenskaplike vakke te spesialiseer.

Beskou ons die toestand in Suid-Afrika dan vind ons dat volgens 'n analise wat gesamentlik deur die Departement van Onderwys, Kuns en Wetenskap en die S.A. Akademie vir Kuns en Wetenskap gemaak is, daar 'n tekort van 6,000 ingenieurs teen 1960 verwag word. Die toestand is nie bekend wat natuurwetenskaplikes betref nie, maar almal wat met die werwing van sulke kragte te doen het, weet dat ons voor 'n ernstige tekort staan. Die vraag is nou wat ons te doen staan.

In die eerste plek meen ek moet die owerhede by die opstelling van leerplanne vir matrikulasie daarvan kennis neem dat die fisiese vakke soos matesis, fisika en skeikunde in hierdie tegnologiese eeu waarvoor ons staan 'n steeds groter rol gaan speel. Geen kind wat 'n natuurlike aanleg in die rigting het, behoort die geleentheid ontsê te word om daarmee kennis te maak nie. Trouens Suid-Afrika sal elke moontlike werkkrag in die rigting nodig hê. Die skole moet dus almal ingerig word om 'n kursus in skeikunde-natuurkunde te doseer. Elke kind moet tot by standaard 8 kennis maak met die fundamentele beginsels van dié vak en rekenkunde. Onlangs op 20 Oktober 1955 het 'n verslag in Pretoria verskyn van 'n Oorsese Sending in verband met Gedifferensiëerde Middelbare Onderwys in Transvaal. 'n Mens sou graag sien dat daar by die uitvoering van die aanbevelings van die verslag ook spesiaal aandag gewy sal word aan die noodsaaklikheid dat die kind met aanleg vir die fisiese vakke na standaard 8 geleentheid gegee sal word om 'n meer intensiewe opleiding te geniet in die fisiese wetenskappe, net soos in Duitsland en Holland. Die kind wat meer aanleg het vir die biologiese vakke of tale moet op dieselfde manier kan spesialiseer in sy eie rigting.

In die tweede plek moet onderwysers van natuurwetenskaplike vakke, indien nodig. 'n ekstra vergoeding ontvang om te verhoed dat al die bestes verkies om in navorsingsinrigtings of industrieë werk te soek. Die onderwysers moet die kinders besiel en aanmoedig om in dié rigting verder te studeer aan die universiteite.

Suid-Afrikaanse universiteite moet ook meer somervakansie-kursusse aanbied vir onderwysers om hulle kennis van die nuutste ontwikkelinge van die wetenskap op te fris. Onderwysers moet ook studieverlof ontvang en beurse om vir ekstra uitgawes te vergoed sodat hulle van tyd tot tyd vir een jaar kan teruggaan na die universiteite om hulle verder in die wetenskappe te bekwaam.

Net soos in die geval van landbou moet spesiale studiebeurse vir studente in die natuurwetenskappe en ingenieurswese aan die universiteite beskikbaar gestel word. Studente moet aangemoedig word om indien enigsins moontlik die meesters- of doktorsgraad te behaal.

Stappe moet geneem word om te sorg dat die natuurwetenskaplike en ingenieur op die selfde basis as die mediese professor of navorser vergoed word vir sy dienste. As vroeëre dosent aan die Universiteit van Kaapstad kan ek getuig dat die student in die natuurwetenskappe niks vir die kollega in die medisyne hoef agteruit te staan nie. Vir dié rede moet hy op gelyke voet besoldig word. Dit sal ook meebring dat meer studente net soos in Rusland aangemoedig sal word om in hierdie rigting te studeer.

Die industrieë wat genoodsaak sal wees om outomatisme toe te pas as hulle op die wêreldmark wil meeding, moet sorg dat hulle arbeiders opgelei word in die nuwe tegnieke. Die industrieë moet ook self kursusse invoer om hulle vakleerlinge op te lei op die gebied van outomatisme en natuurwetenskappe. Dit is die geheim van die groot sukses van die naoorlogse Duitse industrie.

IV. SLOT

Die volgende 50 jaar bied 'n geweldige uitdaging aan vir die wêreld en ook vir Suid-Afrika op die gebied van die natuurwetenskap en tegnologie. Dit wil voorkom asof Rusland dit reeds vir die afgelope 10 of 20 jaar besef het en dat hulle stelselmatig en doelbewus met hulle regeringstelsel daarvoor voorberei het. Toe ek verlede jaar die "Atome vir Vrede" konferensie in Genève as 'n Suid-Afrikaanse afgevaardigde bygewoon het, was ek verbaas oor die besonder deeglike werk wat deur die jong Russiese fisici gedoen is. Hulle het daar ontpop as heeltemal die gelykes van die Britse of Amerikaanse atoomdeskundiges. Ek het self leidende Amerikaanse fisici hulle verbasing hoor uitspreek oor hierdie feit. Vandag wen die Russe reeds die agting van lande soos Sjiena, Indië en Egipte met hulle vordering op die gebied van kernenergie. Sjiena is reeds besig om Rusland se voorbeeld te volg met die opleiding van wetenskaplikes.

Dit was die toepassing van die wetenskap wat die Weste gedurende die afgelope 150 jaar die voorsprong oor die Ooste verskaf het. Gaan ons toelaat dat die Ooste ons verbystreef op wetenskaplike gebied of gaan ons ons omgord en die stryd aanbind saam met die groot lande van die Weste?

Die oplossing is baie duidelik. Ons het die materiaal in Suid-Afrika. Etlike buitelandse professore het al aan my geskryf dat die Suid-Afrikaanse student niks hoef agteruit te staan vir sy Europese of Amerikaanse kollega nie. Dit is ook die mening van 'n paar buitelandse dosente aan Suid-Afrikaanse universiteite. Ons moet egter planne beraam om die talent te ontdek en te ontwikkel. In hierdie opsig kan die organisasies soos die Suid-Afrikaanse Genootskap vir die Bevordering van Wetenskap ook behulpsaam wees. My wens is dat die idees wat hierbo uitgespreek is, daartoe sal bydra dat die regte stappe betyds in Suid-Afrika geneem word.

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  Proceedings.
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NATAL museum, Pietermaritzburg.
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OPORTO, Portugal. Universidade. *Faculdade de ciências.*
  Anais.
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  Annual report of scientific works.
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QUEEN Victoria Museum and Art Gallery, Launceston.
  Annual report.
  Records.
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  s.B: medical and veterinary.
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REVUE internationale des industries agricoles. (Commission internationale des industries agricoles) Paris; Geneva; etc.
RHODESIA scientific association, Bulawayo.
  Proceedings and transactions.
RHODESIA, Southern. *Geological survey.*
  Bulletin.
  National museum
    Occasional papers.
RICERCA scientifica; (Consiglio nazionale delle ricerche) Rome.
ROMANISTISCHES Jahrbuch. (Hamburg. Universität. *Romanistisches Seminar*) Hamburg.
ROYAL aeronautical society, London.
  Journal.
ROYAL anthropological institute, London.
  Journal.

- ROYAL astronomical society of Canada, Toronto.
  - Journal.
  - Observers' handbook.
- ROYAL astronomical society of London.
  - Monthly notices.
  - Monthly notices. Geophysical supplement.
  - Occasional notes.
- ROYAL Canadian institute, Toronto.
  - Proceedings.
  - Transactions.
- ROYAL Dublin society.
  - Economic proceedings.
  - Scientific proceedings.
- ROYAL institution of Great Britain, London.
  - Weekly evening meeting.
- ROYAL philosophical society of Glasgow.
  - Proceedings.
- ROYAL society of arts, London.
  - Journal.
- ROYAL society of Canada, Ottawa.
  - Proceedings.
  - Transactions. Sections I-V.
- ROYAL society of New Zealand, Wellington.
  - Transactions and proceedings.
- ROYAL society of New South Wales, Sydney.
  - Journal and Proceedings.
  - Monographs.
- ROYAL society of South Africa, Cape Town.
  - Transactions.
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  - Annual report.
- SOUTH African institute of electrical engineers, Johannesburg.
  - Transactions.
- SOUTH African institution of civil engineers, Johannesburg.
  - Transactions.
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    - Circular.
- UNITED empire. (Royal empire society) London.
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        - Yearbook of agriculture.
    - *Geological survey.*
        - Bulletin.
        - Circular.
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        - Water supply papers.
    - *National museum.*
        - Bulletin.
        - Proceedings.
        - Report.
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Vintage Wine Made in Laboratory

Twelve of the thirteen substances which contribute chiefly to the taste, aroma, body and all the other characteristics of wine can be made in the laboratory, according to chemists of the University of California. The thirteenth substance is exclusively a grape product. It is the tannin formed from the seeds and stems of grapes, imparting a dry quality to wines. Among the substances the scientists found in wine are ethyl alcohol, the sugars dextrose and laevulose, glycerine, which gives wine its "body", fruit acids and cream of tartar. Sulphur dioxide preserves the wine, and ethyl acetate and acetaldehyde are the substances that give wine its aroma or bouquet. The scientists are now trying to determine whether they can synthesize a particular vintage by mixing the chemicals in the proper way.

◆

No Metal Adequate for Space Travel

The best materials found on earth will disintegrate after prolonged exposure to space conditions, and even the most promising alloys are inadequate, according to researchers in the United States. The scientists make this allegation after testing nearly thirty metals in a "space chamber" imitating conditions to be found 400,000 feet and more above the earth. In this chamber samples of metals and other materials are bombarded with invisible electrically-charged particles that move as fast as 20,000 miles an hour. The purpose of the work is to find out what metals will withstand the prolonged attack by atoms and molecules that are found above the earth. It is hoped that the space chamber will enable scientists to design high altitude vehicles. The work may also be important for the construction of the artificial earth satellite to be launched by the United States.

FLUORESCENT SPECTRA OF SOME ORGANIC CRYSTALS

J. B. Birks[*] and A. J. W. Cameron[*]

ABSTRACT

Observations have been made of the microcrystalline fluorescence spectra of anthracene, 1:2 benzanthracene and eleven of its twelve mono-methyl derivatives. The spectra were excited by 253.7 *mu* radiation and the relative quantum intensities observed with a calibrated spectrophotometer and photomultiplier. Analysis of the results shows spectral shifts due to environment and to methyl substitution. An unusual effect in the 5-methyl and 8-methyl compounds is reported.

INTRODUCTION

Absorption spectroscopy in the ultra-violet is a well-established and important tool for the study of aromatic organic compounds[1]. Fluorescence spectroscopy of these compounds has received much less attention, despite the success of the classic researches by which 3:4 benzpyrene, the potent carcinogen, was identified and isolated from coal-tar extracts by means of its fluorescence spectrum[2]. In view of the biological importance and chemical interest of many such compounds, it is surprising that often the only data available on their fluorescence emission describes it vaguely as "blue", "blue-green", "green", etc., and as "intense" or "weak". Schoental and Scott[3] have observed photographically the fluorescence spectra of a number of polycyclic hydrocarbons in solution. More recently detailed studies have been made of the crystalline fluorescence spectra of the simpler compounds such as benzene, naphthalene and anthracene by e.g. Craig and Hobbins[4], Pesteil[5] and others, following Kortum and Finckh[6].

The technique introduced by Birks and Little[7] and extended by Birks and Wright[8] is particularly suitable for quantitative studies of crystalline fluorescence spectra. The use of microcrystalline layers enables the complete molecular emission spectrum to be observed, while the use of a calibrated photo-multiplier for detection enables the relative quantum intensity to be determined.

Anthracene, 1:2 benzanthracene and the methyl derivatives of 1:2 benzanthracene were chosen for study by this technique for various reasons. Data on the fluorescence spectra of these molecules in liquid solution are available[3], so that the effects of molecular crystalline environment can be obtained by comparison. The effect of methyl substitution in the 12 alternative positions in 1:2 benzanthracene is of interest for comparison with the predictions of molecular orbital and valence-bond theories.

Moreover, certain of these compounds are carcinogens, and further light might be thrown on this important biochemical or biophysical property.

EXPERIMENTAL METHOD

The fluorescence spectra were excited by monochromatic radiation of wavelength 253.7 m*u*. An intense steady source was obtained by using a 7-watt Model 11 Hanovia mercury discharge tube, in which a large proportion of the energy radiated is of 253.7 m*u* wavelength. In this spectral region the extinction coefficient of the crystals is so high that all the incident radiation is absorbed in a few wavelengths thickness.

The thin discharge tube was placed in the entrance plane of a quartz spectograph whose entrance slit mechanism had been removed, and an intense image of the 253.7 m*u* line, resolved from the other mercury lines, was formed in the exit plane of the spectograph. This radiation was focussed on the specimen.

The fluorescence spectra were observed using a Cenco grating spectrophotometer and an E.M.I.6262 photomultiplier tube, operating from a stabilised power unit and coupled to a sensitive galvanometer. The grating mounting employed is such that the spectrophotometer has a constant wavelength bandwidth, and its variation of transmission coefficient with wavelength had been measured. The relative spectral response of the photomultiplier had also been determined[9].

The photomultiplier output current was therefore corrected for the overall response of the spectrophotometer and the photo-

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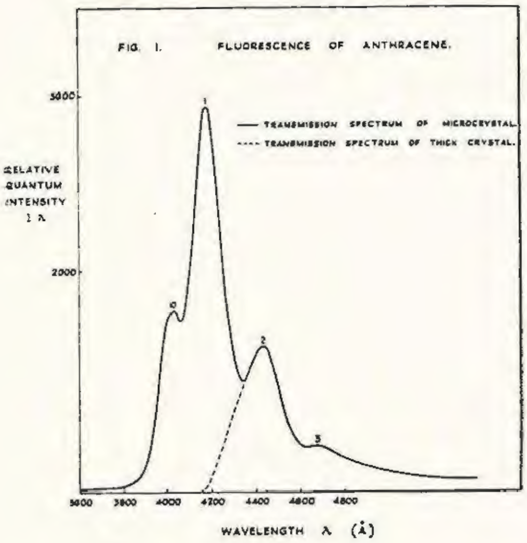

FIG. 1. FLUORESCENCE OF ANTHRACENE.

multiplier to give readings proportional to the intensity, I, of the fluorescence.

RESULTS AND DISCUSSION

Anthracene

Figure 1 shows the fluorescence spectra of anthracene specimens with quantum intensity, Iλ, which is proportional to *I/hν*, plotted against wavelength, λ.

(a) from a microcrystalline layer, in which the reabsorption is negligible; and

(b) from a 1 cm. thick crystal cube which partially reabsorbs its own emission. Both spectra were measured in transmission through the specimens.

The microcrystalline specimens were prepared by evaporation from dilute solution onto a glass plate. Their thickness was chosen as 0.1*u* approximately to give optimum resolution of the spectral vibrational structure. Reabsorption is negligible and the spectrum observed approximates to the true *molecular* fluorescence emission.

For the thick crystal, about 80% of the fluorescence emission is reabsorbed within the crystal[10]. Molecules too distant from the surface to be excited directly by the incident radiation absorb some of the fluorescence emission, and in turn emit fluorescence radiation. This photon cascade process [11] proceeds through the body of the crystal, which effectively filters out the portion of the spectrum to which the crystal is not transparent. The thick crystal spectrum is called the *technical* fluorescence spectrum. The effect of reabsorption of fluorescence in anthracene is pronounced because of the considerable overlap of the absorption and emission spectra.

The microcrystalline spectrum corresponds to the complete set of transitions from the first excited singlet electronic state of the molecule to the ground state. The maxima are due to the ground-state vibrational structure, and correspond to the following energy transitions, in decreasing magniture (Figure 2).

(0) 1_0—0_0, (1) 1_0—0_1, (2) 1_0—0_2,
(3) 1_0—0_3.

The amplitude of the peaks corresponds to the relative probability of the transition to the particular vibrational state.

1:2 *Benzanthracene and Mono-Methyl*

Derivatives.

Measurements have been made of the microcrystalline fluorescence spectra of 1:2 benzanthracene and eleven of its twelve monomethyl derivatives, namely, 2′-, 3′-, 4′-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 10- methyl, using speci-

FIG. 2. ENERGY LEVEL DIAGRAM.

mens 0.1*u* thick. Each of the compounds has a similar high molar extinction coefficient for the exciting radiation (253.7m*u*), so that over 90% of the incident radiation is absorbed in this thickness. The specimens are practically completely transparent to their own fluorescence emission. In order to compare tho relative intensities of the fluorescence from different compounds, the same standard conditions of preparation, excitation and observation were observed throughout. Figure 3 shows the molecular fluorescence spectrum of 1 : 2 benzanthracene. It will be noted that the vibrational structure is similar to that of anthracene, and there is little difficulty in assigning the principal maxima observed to the corresponding vibrational transitions. The general form of the spectra of the monomethyl derivatives is similar to that shown in Figure 3, with the exception of the 5-methyl and 8-methyl derivatives, whose spectra are diffuse. The spectrum of 5-methyl 1 : 2 benzanthracene is shown in Figure 4.

The detailed results and analysis are being published elsewhere[12] but the principal effects observed are as follows.

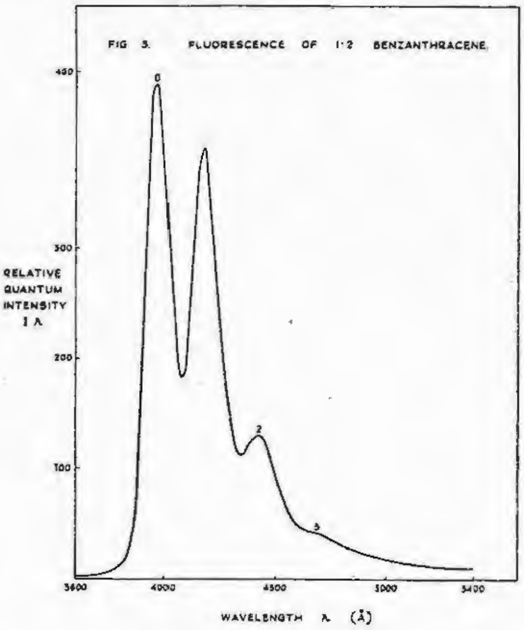
FIG 3. FLUORESCENCE OF 1·2 BENZANTHRACENE.

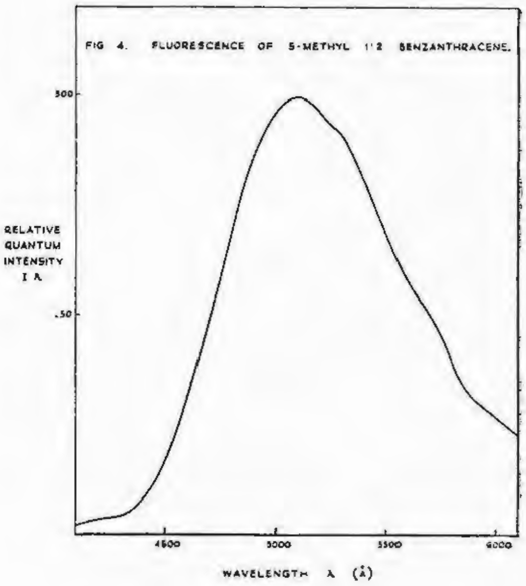
FIG 4. FLUORESCENCE OF 5-METHYL 1·2 BENZANTHRACENE.

(a) In the free molecule (i.e. in solution) the wave-number interval $\triangle v' \simeq 1400$ cm^{-1} between *all* the vibrational bands is similar in *all* the compounds (Schoental and Scott 1949).

In the crystalline molecule, $\triangle v'$ between bands 1 and 2, and 2 and 3 (Fig. 2), and higher bands. has a similar value $\simeq 1370$ cm^{-1} for *all* the compounds except the 5-methyl and 8-methyl, where there is no vibrational structure. Hence the interval between the 1st, 2nd, 3rd vibrational levels of the ground state is not generally perturbed by the crystal environment. The quantum intensities of these bands decrease monotonically.

(b) The complete crystalline spectra are shifted to longer wavelengths relative to those of the free molecules. This is due to the " solvent " effect, attributable to the different permittivity of the environment.

(c) The $\triangle v'$ interval between bands 0 and 1 in the crystalline molecule is in general less than 1370 cm^{-1}, the lowest value being 900 cm^{-1} for anthracene (Figure 1). This effect is attributable to the overlap of the absorption edge and is accompanied by a reduction in the intensity of the 0 band. The magnitude differs for the different compounds.

(d) In the case of the 5-methyl (Fig. 4) and 8-methyl compounds, there is a major shift of the *whole* spectrum and there is no resolved molecular structure. This is probably an extreme case of an "exciton" shift[13], and it merits further detailed study. It has since been observed in other compounds, and it is usually accompanied by an abnormally long fluorescence decay time.

(e) Methyl substitution in different positions in the 1:2 benzanthracene molecule produces a spectral shift (band 1 is taken as reference) towards longer wavelengths relative to the parent compound. The magnitude of this shift varies from 50 cm^{-1} for 2′-methyl to 420 cm^{-1} for 9-methyl. Similar shifts are observed for the free molecules (Schoental and Scott 1949). The shifts observed in the 5-methyl and 8-methyl molecular crystals are $\simeq$ 4000 cm^{-1} however, compared with only $\simeq$ 200 cm^{-1} for the free molecules.

The spectra thus reveal the existence of several interesting molecular and crystalline effects, some of which have not been previously reported or recognised.

ACKNOWLEDGMENTS

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DEPARTMENT OF PHYSICS,
RHODES UNIVERSITY, GRAHAMSTOWN.

Fourth Alex. L. du Toit Memorial Lecture

Orders for copies of this lecture may now be placed and are available to members of $S^2 A^3$ at the nominal charge of 4s. per copy. Postal orders should be made payable to the Geological Society of South Africa and should be sent to the Joint Secretaries, $S^2 A^3$, Box 6894, Johannesburg.

Iboga: A Plant that Prevents Fatigue

The stimulant properties of the iboga plant have long been known to various Central African peoples. The Pygmies chew iboga leaves and stalks before certain tribal ceremonies during which they must remain awake for several days, drumming on their tom-toms. Other tribes use the plant for initiation ceremonies, when adolescent boys are left alone to roam the forests for five days, living solely on the iboga plant. Hunters of certain tribes also consume iboga before undertaking particularly long and dangerous treks through the forest. French chemists, who have been carrying out research on the plant over the past ten years, have now succeeded in extracting alkaloids from which they can manufacture a stimulant with very little toxic effect. (Unesco).

The World of Science

THE TELL-TALE TREE

Lucien Néret

Three thousand-year-old giant sequoias from the forests of California are today enabling scientists to delve back deep into the past and establish an accurate chronology of life in prehistoric times.

The method, evolved in the United States but as yet little known in Europe, was foreshadowed at the beginning of the 19th century by the English chronologist Henry Fynes Clinton. Known as "dendrochronology" from the Greek "dendron" — tree, and "chronolgy" — the science of time and dates, it is based on the study of the different layers of wood which form the trunk of a tree.

The process of tree growth has been known for centuries. Almost all children are taught in school that each year a new ring forms around the core of the tree. By counting the number of rings it is easy to calculate the age of the tree. But for hundreds of years nobody suspected that any other information could be gained from the study of these rings. It was known that the lighter coloured, better developed part of the ring forms in the spring, while the wood cells that grow in the autumn are harder, more compact and darker in colour. When spring comes around again — after the winter halt in natural growth — the cells are once more pale in colour and better developed.

Several scientists including Ernst Antevs and Andrew Douglass of the University of Arizona, believed, however, that this alternation of different layers of wood could be interpreted to reveal other data than the mere age of trees. They noted variations in the thickness of the layers which appeared to correspond to variations in climate over the years. Their theory seemed to be borne out by the fact that when different trees growing in the same area were studied, every species revealed the same type of layer for each successive year.

This led the American scientists to devise a means of identification for each type of layer. Douglass gave them code numbers according to the species of the tree, the position of the layer on the cross-section of the trunk and other characteristics, while Antevs used a graduated chart to describe the different rings.

Both these methods of identification now enable scientists to draw up a complete "climatic biography" of the life of a tree. By examining a 70-year-old pine, it is possible to follow all the atmospheric variations which occurred, for instance, between 1886 and 1956. And a three thousand-year-old Californian equoia offers an almost unlimited field for research.

The trees of any one region present common growth characteristics. By "deciphering" the data contained in the layers of a wooden beam discovered in an ancient Inca dwelling and comparing it with trees of the same region, it is relatively simple to obtain information on the age of the beam and the period when it was made. It has thus been possible to date a piece of timber hewn in 1473 and a wooden prop supporting the roof of a house in Mexico which was still a shrub in 1344. Other specimens examined have been traced back to the year 11 A.D., and the record thus established covers fifteen centuries of American Indian prehistory. Step by step the archaeologists are able to work back over hundreds and even thousands of years.

Climate by Tree Rings.

This method of dating is extraordinarily accurate. Douglass has worked out a scietntific system of cross-checking which only leaves room for an extremely small margin of error — never more than one year or the time it takes for a ring of wood to form in a tree. This is much more precise than the method based on the radioactivity of Carbon 14 where the margin of error is as much as 200 years for an object dating back to the beginning of the Christian era. However, the Carbon 14 method offers the distinct advantage of covering a much longer period of prehistory than dendrochronology.

Apart from its value to historical and prehistorical research, dendrochronology is an extremely useful adjunct in other fields of study. Research undertaken in the United States has revealed that there is a distinct relationship between the speed at which the layers of wood form during a given period and all the other climatic phenomena of the same period. Professor Douglass has demonstrated the close correlation between the growth rate of tree rings and the solar cycle, for irregularities in the seasons coincide with the phenomenon of sunspots. Accordingly, it has now been proved that the length of the solar cycle has varied in past centuries. Specimens of wood examined in Arizona show that in the 17th century this cycle extended only over ten years where as today it covers eleven years.

Dendrochronology is a new science but it offers immense possibilities for historians, meteorologists and geographers. It will enable them to unravel many mysteries of the past, and provide further data on the climatic changes which have taken place during the centuries. It also holds the promise of a better knowledge of Nature which mankind is ever seeking to master. (Unesco).

Camera Lens

A new camera for taking amateur moving pictures has a revolutionary new device which automatically adjusts the lens opening for the correct exposure under the prevailing light conditions. The light control mechanism operates on the same principle as the human eye, contracting in strong light and opening for weak light. The camera can follow the actions of people moving from areas of deep shade into strong, bright sunlight and back again to deep shade without any adjustment for the changing light by the operator. The mechanism that changes the size of the lens opening is activated by an electric eye or photo-electric cell. Impulses from this cell operate a small motor which operates on electrical power provided by six tiny mercury cell batteries. A warning flag in the camera's view finder tells the photographer when the light is too weak for good pictures. (Usis).

METALS

Metal Industry Handbook and Directory, 1956. *London, Louis Cassier & Co. Ltd. 472 pp. Numerous tables. Price* 15/-.

This well known publication, now in its 44th year, is an ideal reference work for the buying, selling and use of non-ferrous metals and alloys. It is divided into sections covering the general properties of metals and alloys, general data and tables, electroplating, polishing and finishing, and a directory for buyers. In this form, information is easy to find although a vast amount of detail is present. Trade names, many of which are very similar, can be a source of great confusion, and a welcome new inclusion is the list of proprietary alloys together with their manufacturers, compositions, properties and uses.

This compact but exhaustive handbook is well worth its reasonable price.

R. B. G. Yeo.

MINERALOGY

Handbuch der Mikroskopie in der Technik. Band IV Teil I. Mikroskopie der Gesteine edited by Dr Hugo Freund Wetzlar. Pp. xxiii + 873; Umshau Verlag, Frankfurt am Main 1955. DM 98 net.

This volume forms part of the series being published on the application of the microscope to technology.

Prof. H. v. Phillipsborn of Bonn deals with the historical background of the petrological microscope from the seventeenth century to the present day.

Prof. W. Tröger of the Technischen Hochschule, Darmstadt, describes the optical properties of the important rock-forming minerals. These are given in considerable detail with excellent drawings, photomicrographs and a large number of graphs. Over a hundred minerals are described including all the characteristic minerals found in igneous, sedimentary and metamorphic rocks. The section on the felspars alone covers forty pages and that on the pyroxene group twenty pages.

The section devoted to the petrography of rocks, by Prof. D. Hoenes of the Technische Hochschule, Karlsruhe, describes measurements under the microscope, such as grain size, geometric proportion of minerals, shape of grains, orientation of grains (petrofabrics) etc. Considerable detail, mineralogical and textural, is given for all the three major groups of rocks. Interesting paragraphs on the behaviour of the different rock types subjected to exposure and weathering in buildings etc., are given.

Prof. C. W. Correns, Gottingen University, and Dr H. Pillar of Zeiss-Winkel have contributed the section on the microscopic examination of clay minerals. Methods of preparation, variation in properties, staining techniques, etc., are discussed. Detailed optical properties are given.

A final section contributed by Dr S. Matthes, deals with the optical properties of asbestos.

The volume covers a large field in petrography in considerable detail, and is liberally illustrated. Probably beyond the means of the average student, the book is of value to libraries in scientific institutions and universities, and particularly technical departments of industries concerned with rocks and minerals.

E.M.

AGRICULTURE

MANAGING THE FARM BUSINESS, by R. R. BENEKE (1st edition). *New York, John Wiley and Sons, Inc.* 1955. vi + 451 *pp.* 158 *figures,* 80 *tables. Price* $3.96.

Though written for American students of farm economics, excellent use can be made of this book in South African faculties of agriculture in courses on farm organization and management for undergraduate students. Although every one of the 21 chapters is an excellent contribution, as far as South African readers are concerned special attention can profitably be given to the chapter on soil conservation measures in which a large number of economic factors are dealt with. The book is exceedingly well written and each chapter contains a fairly complete and appropriate list of references.

F. R. TOMLINSON.

MATHEMATICS

ADVANCED CALCULUS. An Introduction to Classical Analysis by LOUIS BRAND. *New York, John Wiley and Son. London, Chapman and Hall Ltd.* xii + 574 *pp.* 1955. *Price* $8.50.

This is one of the most comprehensive and satisfactory books of its kind available.

Starting from a discussion of groups and fields the author leads the student naturally to the real and complex number systems. Especially good are the sections on "sequences', "vectors" and "the definite integral". It is refreshing to find a clear presentation of such topics as "cluster points", "bounded sets", "nested intervals", etc. The author early touches on the fascinating subject of transfinite numbers, gives the Cantor-Dedekind Axiom and interests the reader by posing the famous "continuum" problem.

For some years past, of course, vectors have been increasingly used in treatises on advanced calculus, and the author follows the now accepted practice of devoting a chapter to this topic delving, however, rather more deeply than is usual. It is, perhaps, a pity that only the Riemann Integral is discussed. The more so as the author introduces the concept of "a set of zero measure" and could have led easily to mention of the Lebesgue Integral. this, however, is a small matter when contrasted with the general excellence of the work.

There is a chapter on Functions of a Complex Variable and examples of the evaluation real integrals by the "contour" method. The book closes with a discussion of orthogonal sets of functions, leading naturally to Fourier Series. Four appendices deal with a couple of theorems on "cluster points", and introduce, briefly, "difference equations", "the difference calculus" and "dimensional checks".

M. G. CLARKE.

◆

ASTRONOMY

METEOR ASTRONOMY, by A. C. B. LOVELL. *Oxford: Clarendon Press,* 1954. xiv + 444 *pp.,* 187 *figus. Price* 60/-.

This monumental volume, intended to be the first of two parts of a comprehensive textbook, is the first of its kind to appear since C. P. Olivier's well known text which is now already thirty years old. During the intervening generation the whole field of meteor astronomy has been enlarged and in a great measure fundamentally revised, mainly as the result of the photographic work at Harvard and of the application of short-wave radio techniques. The time is thus more than ripe for a work such as this, and one can think of no one more competent than Lovell, himself one of the leaders of the new developments in radio-astronomy, to have written it.

After a discussion of the observational techniques, both those of ordinary astronomy and of the radio-echo method, and a brief excursion into the equations of meteoric motion, Lovell proceeds to discuss in great detail and with great insight the results of the application of these techniques. The results are grouped under the main heads: number and mass distribution of sporadic and of shower meteors, the velocities of sporadic meteors, the major meteor showers, and the cosmological relationships of meteors. The necessary theory is given at all times, and the book fills with great distinction what has for long been a noticeable gap in astronomical literature. It will certainly become the standard text for meteor astronomers, and one looks forward with eager anticipation to the promised second volume, on meteor physics.

A.E.H.B.

◆

THE HISTORY OF ASTRONOMY, by GIORGIO ABETTI (translated from the Italian by Betty Burr Abetti). *London: Sidgwick and Jackson,* 1954. xv + 328 *pp.* 34 *plates. Price* 25/-.

Among the sciences, that which exhibits the most clearly marked unity is astronomy, which may explain why there are more readable histories of that science than of any other. Professor Abetti has added another valuable work to the list of semi-popular books on the history of the development of man's understanding of the starry heavens, which will certainly prove of interest and value to every student of astronomy. Even the interested layman will find

in this book an eminently readable story, stretching from the early beginnings of the science among the Babylonians to the major contributions of our own times. The author has added to the value of the work by paying attention, not merely to the problems and their solution, but also to the men who contributed to the development of the science, thus adding a touch of humanity to an already fascinating narrative.

A.E.H.B.

BIRDS

Check List of Birds of the S.W. Cape, 1955. *Published by the Cape Bird Club.* 59 *pp.* 1 *Map.*

This list gives a picture of present knowledge of bird distribution in the South West Cape. Based essentially on sight records and published literature, it contains the names of 320 species, all of which have been observed in the area since 1930. The distribution of the birds by district is indicated, and an appendix is included of extinct and doubtful species, old records and escapes.

J.L.

THE HEAVENS IN SEPTEMBER*

SUN

Equinox on the 23rd at 3.36 a.m.

MOON

New Moon on the 4th at 8.57 p.m.
First Quarter on the 12th at 2.13 a.m.
Full Moon on the 20th at 5.19 a.m.
Last Quarter on the 27th at 1.25 p.m.
Perigee on the 3rd at 6 a.m.
Apogee on the 15th at 7 a.m.

PLANETS

Mercury evening star, stationary on the 13th, inferior conjunction on the 26th, morning star after that date, one degree north of the Moon on the 6th at 7 p.m.

Venus morning star, one degree north of the Moon on the 1st at 2 p.m., 9 degrees south of Pollux on the 2nd.

Mars in Aquarius, nearest to the Earth (35 million miles) on the 7th, opposition on the 10/11th at midnight, 11 degrees south of the Moon on the 19th at 4 p.m.

Jupiter in Leo, conjunction on the 4th, 6 degrees north of the Moon on the 5th at 1 a.m.

Saturn in Libra, 2 degrees north of the Moon on the 10th at 9 a.m.

Bulletiin.

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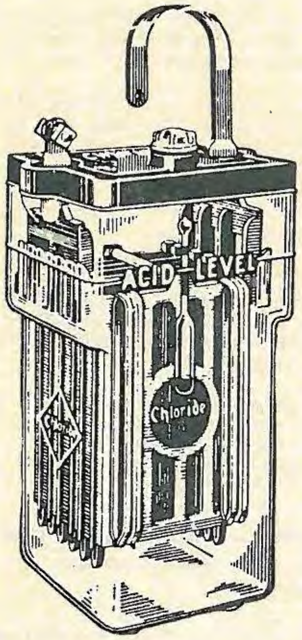
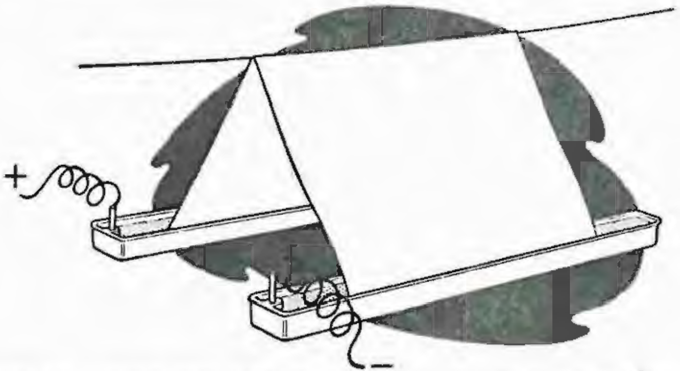
*Data supplied by Union Observatory, Johannesburg, August, 1956.



PROGRESS IN

CHROMATOGRAPHY 2



SEPARATION OF LARGE MOLECULES BY ELECTROPHORESIS

Since most large molecules and colloidal particles carry a charge, electrophoresis is obviously a convenient method of separation. However, the disadvantage is that, when the potential gradient is merely applied across a buffered solution of the material to be separated, re-mixing may occur owing to convection currents, and complete resolution of the fractions is not possible.

Such difficulties have been overcome by using filter paper to provide a capillary mesh to hold the solution. Each end of a filter paper sheet soaked in buffer dips into a trough containing an electrode and a quantity of the buffer solution. When a solution of the test material is applied to the centre of a strip, its components will migrate towards one or other of the electrodes. Their direction and rate of travel (hence their position on the strip) will furnish a clue to their identity. Re-mixing cannot occur, and the fractions are available for both qualitative and quantitative examination.

ELECTROPHORETIC ANALYSIS OF SERUM PROTEINS IN CHRONIC RHEUMATIC DISEASES

The analysis of serum protein for purposes of diagnosis has been greatly advanced by paper electrophoresis. Kunkel and Tiselius *(J. Gen. Physiol.,* **35**: 89. 1951-2) have described a procedure which is 'extremely simple and surprisingly accurate', but lay great stress upon the importance of using the right filter paper. The reason for this is that, though human albumin migrates towards the anode, there is an electro-osmotic flow of buffer solutions towards the cathode. It has been found that Whatman 3MM. paper is satisfactory in reducing this flow to the desired minimum. The physician's diagnosis is confirmed by an increase of gamma globulin and some decrease in albumin, both of which are revealed by simple inspection. The paper strip method brings electrophoretic analysis well within the scope of normal clinical laboratory routine, and compares very favourably with previous techniques on cost, time, and accuracy.

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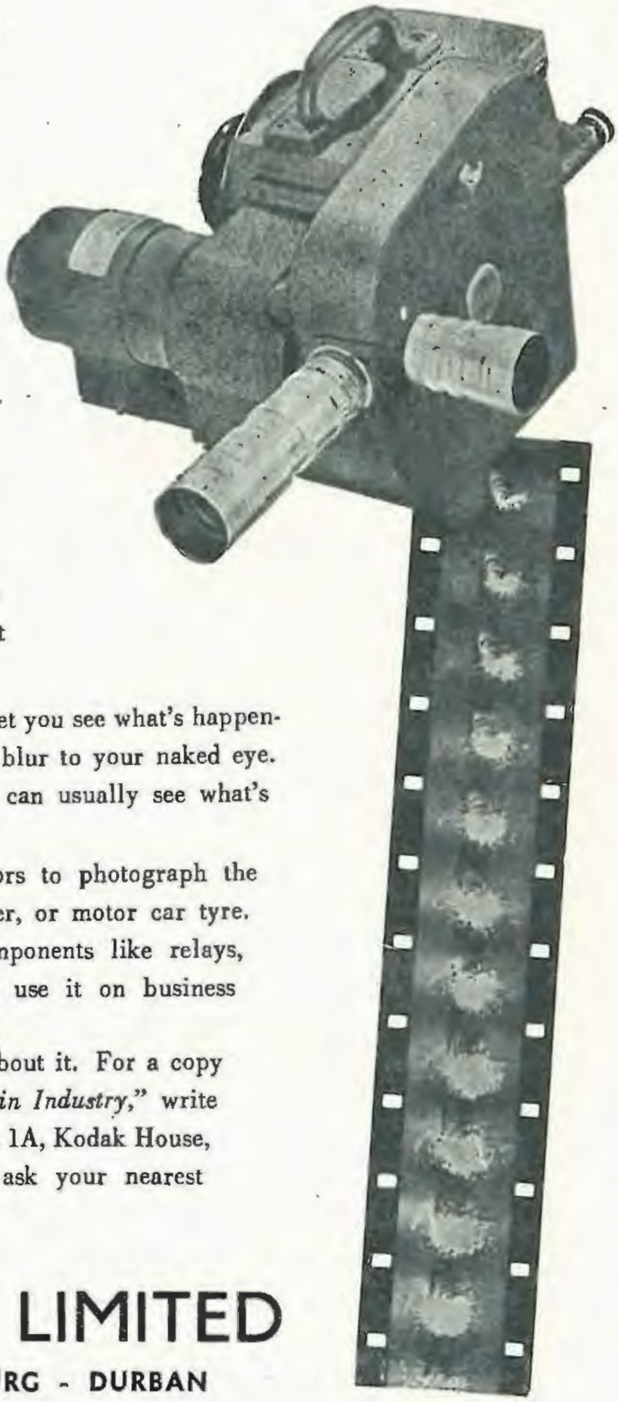

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Energy Transfer in Organic Systems
I: Photofluorescence of Terphenyl-toluene Solutions

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MS. received 9th January 1958, and in final form 5th March 1958

Abstract. The fluorescence quantum intensities of normal and oxygen-free solutions of *para*-terphenyl in toluene have been measured as a function of concentration c and of excitation wavelength λ from 2200 Å to 3300 Å. The absorption spectra of toluene and terphenyl have been observed. The energy transfer coefficient f from excited toluene molecules to terphenyl molecules has thus been obtained.

f is found to depend on λ. For a given c, $f=f_1$ in region 1 ($\lambda=2500$–2650 Å), $f=f_2>f_1$ in region 2 ($\lambda=2200$–2350 Å), and $f_2>f>f_1$ for intermediate λ. Regions 1 and 2 correspond to the first and second excited electronic singlet states of toluene. The solvent–solute energy transfer from the second excited state, which occurs in approximately 10^{-11} sec, competes efficiently with conversion to the 1st excited state of toluene.

§ 1. INTRODUCTION

THE high fluorescence efficiency of certain organic liquid solutions, when excited by ionizing radiations, was observed initially by Ageno, Chiozzoto and Querzoli (1949, 1950), Kallmann (1950), and Reynolds, Harrison, and Salvani (1950). Such solutions are now extensively used for scintillation counting, particularly where a large detection volume and a rapid response time are required.

Kallmann and Furst (1950, 1951) observed that, although the fluorescence is characteristic of the solute, its intensity greatly exceeds that from direct excitation of the solute molecules by the incident ionizing radiation. A transfer of electronic energy from solvent molecules, initially excited, to solute molecules was thus demonstrated. The energy transfer process for a wide range of liquid solutions has been studied by Furst and Kallmann (1952, 1954 a), Reynolds (1952) and others.

The mechanism of the inter-molecular energy transfer in liquids and in related fluorescent organic systems has been a matter of some discussion, and several alternative processes have been proposed. Birks (1953, 1954) has formulated a photon theory of energy transfer. Other observers (e.g. Cohen and Weinreb 1954, 1956, Furst and Kallmann 1952, 1954 a, b, Kallmann and Furst 1950, 1951, Reid 1952, Reynolds 1952, Schmillen 1953, Terenin 1954) consider that such a radiative transfer process is inadequate to account for the magnitude of the

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† Now at the Physical Laboratories, University of Manchester.

energy transfer observed. They propose that the intermolecular energy transfer is primarily non-radiative (Förster 1948, 1949, 1951).

Several non-radiative transfer mechanisms, some of which are equivalent, have been suggested. These include exciton migration, dipole–dipole interaction, quantum-mechanical resonance, or inductive transfer, sensitized fluorescence, collisional transfer and the formation of excited ' double molecules ', or of solvent–solute molecular complexes. While some of these processes are plausible on theoretical grounds, others that have been borrowed by analogy from different physical systems, such as ionic crystals and monatomic gases, are not necessarily applicable to liquid organic solutions.

The use of ionizing radiation for stimulation of the fluorescence complicates the interpretation of the experimental data. The manner of conversion of the primary molecular ionization and excitation energy into lower excited states of the molecules is not yet fully understood. Birks (1953, 1954) has proposed a possible mechanism: a cascade of successive fluorescence and re-absorption transitions from and to higher electronic states, degenerating through vibrational energy dissipation into lower electronic states. The fluorescence from the lowest excited singlet state of the solute ultimately escapes without re-absorption and is observed externally. While many data are consistent with this theory, prior to the present work it lacked any direct verification.

It was therefore considered desirable to study the solvent–solute energy transfer, without the additional effects of primary ionization. Cohen and Weinreb (1954) have shown that such energy transfer occurs in organic liquid solutions, when excited by non-ionizing ultra-violet radiation. Furst and Kallmann (1954 b) have also extended their earlier scintillation studies of various solutions to ultra-violet excitation. However, the latter's use of multi-component solutions complicates the analysis of their results.

In the present work, the fluorescence quantum intensity of a binary solution, *para*-terphenyl in toluene†, has been measured as a function of concentration and of excitation wavelength from 2200 Å to 3300 Å. The absorption spectra of the two components, and other data relevant to a quantitative analysis of the energy transfer, have also been measured.

Since the completion of the experimental work in November 1955, an account of similar studies by Cohen and Weinreb (1956) has been published. Our results, analysis, and conclusions differ from theirs in several important respects.

§ 2. Experimental

2.1. *Absorption Spectra*

High-purity toluene and 'scintillation grade' *para*-terphenyl were used. The absorption spectra of toluene in ethanol (figure 1, curve A) and of terphenyl in cyclohexane (figure 1, curve B) were measured with a Beckman Model D U spectrophotometer. The absorption spectrum of terphenyl in toluene was measured down to 2950 Å, at which wavelength the toluene starts to absorb, and a similar spectrum to that of the cyclohexane solution was observed. The observed spectra are similar to those reported by Friedel and Orchin (1951).

† This solution was chosen because its high scintillation efficiency indicates efficient solvent–solute energy transfer.

The ratio ρ, of the molar extinction coefficients ϵ_y and ϵ_x of terphenyl and toluene respectively, is plotted in figure 1, curve C.

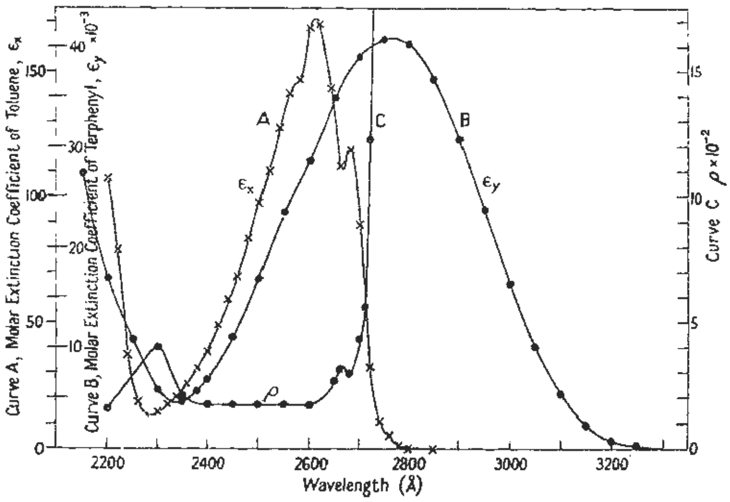

Figure 1. A, absorption spectrum of toluene in ethanol ϵ_x; B, absorption spectrum of *para*-terphenyl in cyclohexane ϵ_y; C, $\rho = \epsilon_y/\epsilon_x$.

2.2. *Fluorescence of Solutions*

The experimental arrangement is shown diagrammatically in figure 2. The solution S was contained in a cylindrical glass vessel, the depth of the solution (1 cm) being the same for all specimens. The fluorescence was excited by illumination with monochromatic radiation from a Beckman Model D U spectrophotometer, the horizontal exit beam M being deflected vertically downwards by a quartz prism Q. The vessel was placed on a Chance OY 10 glass filter F, adjacent to the photo-cathode window of a Du Mont 6291 photomultiplier P mounted vertically.

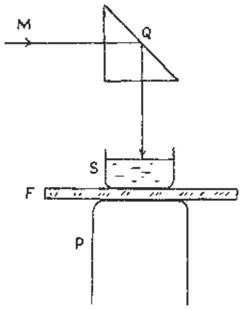

Figure 2. Experimental arrangement. M, exit beam from monochromator; Q, quartz prism; S, solution specimen in glass vessel; F, OY 10 glass filter; P, photomultiplier.

The filter transmits the terphenyl emission efficiently, but it is opaque to shorter wavelength radiation: it thus serves to prevent scattered incident radiation from reaching the photo-cathode. A careful check showed that neither the filter nor the glass vessel were luminescent, an important precaution since fused silica and some glasses luminesce in the near ultra-violet and visible regions. Optical contact between the surfaces was improved by thin films of glycerine.

The experiments consisted of illuminating the top surface of each solution specimen, and measuring the integrated intensity of the fluorescence transmitted through the base. This observation was repeated for excitation wavelengths from 2200 Å to 3300 Å. The fluorescence intensity at each wavelength was normalized to the same quantum flux of incident radiation, as described in § 2.3. Thus the fluorescence excitation spectra of several solutions of different concentrations were determined.

2.3. *Calibration of Incident Radiation*

The relative quantum intensity of the incident radiation at different wavelengths was determined by a method, similar to that described by Wright (1955). The solution specimen S was replaced by a 1 cm cube *para*-terphenyl crystal, thus converting the incident radiation into terphenyl fluorescence radiation to which the photomultiplier is sensitive. Wright (1955) has shown that the technical photofluorescence quantum efficiency of such a terphenyl crystal is constant, and independent of wavelength, down to 2537 Å, and that this uniform response can be assumed to extend down to at least 2200 Å.

The intensity of the integrated fluorescence from the terphenyl crystal was thus taken as directly proportional to the quantum intensity of the incident beam. This calibration was checked down to 2537 Å using the ultra-violet-sensitive phototube, supplied with the spectrophotometer, as detector. The photo-tube response had been previously measured against a Hilger Model F.T. 16 linear vacuum thermopile, fitted with a fluorite window (Wright 1955). Excellent agreement was obtained between the two independent calibrations.

2.4. *Fluorescence Excitation Spectra*

Fluorescence excitation spectra, normalized to a constant flux of incident quanta, were measured from 3300 Å to 2200 Å, for a range of solutions of different concentrations. Figure 3 shows the results for 5 solutions, in normal toluene, of

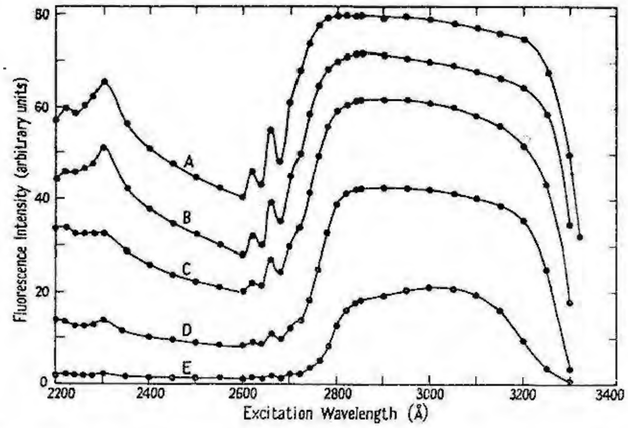

Figure 3. Fluorescence excitation spectra of normal solutions. Concentration: A, 4·15 g l.$^{-1}$; B, 2·07 g l.$^{-1}$; C, 1·04 g l.$^{-1}$; D, 0·415 g l.$^{-1}$; E, 0·091 g l.$^{-1}$.

concentration from 4·15 g l.$^{-1}$ to 0·09 g l.$^{-1}$. These solutions contained dissolved oxygen, which is known to act as a quenching agent, in equilibrium concentration at normal atmospheric pressure. Figure 4 shows the results for two solutions, from which the oxygen had been removed by bubbling nitrogen through the toluene during distillation.

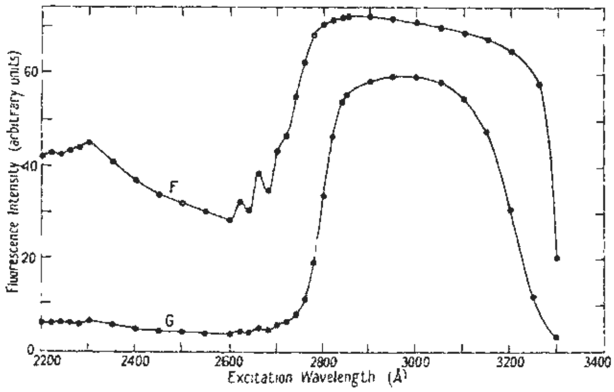

Figure 4. Fluorescence excitation spectra of oxygen-free solutions. Concentration: F, 1·08 g l.$^{-1}$; G, 0·054 g l.$^{-1}$.

§ 3. Analysis of Results

3.1. *Qualitative Description*

Three distinct regions may be distinguished in the excitation spectra. In the first region (O) from 2800–3300 Å, the toluene is practically transparent, and the terphenyl fluorescence is excited directly by absorption of the incident radiation. This region of direct excitation is bounded at $\lambda \sim 3300$ Å by the terphenyl absorption edge, and at $\lambda \sim 2800$ Å by the onset of the toluene absorption.

In the second and third regions (1 and 2), corresponding to wavelengths below about 2700 Å, the toluene absorption is high, and practically all the incident radiation is absorbed by the solvent. In these regions, the terphenyl fluorescence is mainly excited indirectly by energy transfer from excited toluene molecules.

The fluorescence intensity shows variations, associated with changes in ϵ_X and ϵ_Y with wavelength, and these are allowed for in the subsequent analysis. However it may be noted at this stage, that the fluorescence intensity, which depends on the energy transfer efficiency, is higher at the shorter wavelengths (2200–2350 Å) designated region 2, than at the longer wavelengths (2500–2650 Å), designated region 1.

3.2. *Correction for Excitation Depth*

Before undertaking a quantitative analysis of the results, a correction was made for the variation with wavelength and concentration of the depth of penetration of the incident radiation. This effect was reported by Wright (1955), who studied the fluorescence excitation spectra of organic crystals. These show major variations with excitation wavelength of the transmitted fluorescence intensity, associated with variations in the absorption coefficient.

The effect is clearly seen in the present measurements (figures 3 and 4) for wavelengths from 3000 Å to 3300 Å. In this spectral region the toluene is transparent, all the terphenyl fluorescence is directly excited, and the fluorescence quantum efficiency of terphenyl is constant. Nevertheless, the observed fluorescence intensity decreases with increasing wavelength, due to the decrease in ϵ_Y, and the consequent increase in the depth of penetration of the incident radiation.

The observed fluorescence intensity I has been expressed in terms of I_0, the observed fluorescence intensity at a wavelength of 3000 Å, and I/I_0 has been normalized to correspond to the strongest solution (4·15 g l.$^{-1}$) In figure 5, I/I_0 for all the solutions from 3000 Å to 3300 Å is plotted on a logarithmic scale against the molar extinction coefficient $(\epsilon_X + \epsilon_Y c)$, where c is the concentration of solute molecules per solvent molecule. In this spectral region $\epsilon_X = 0$.

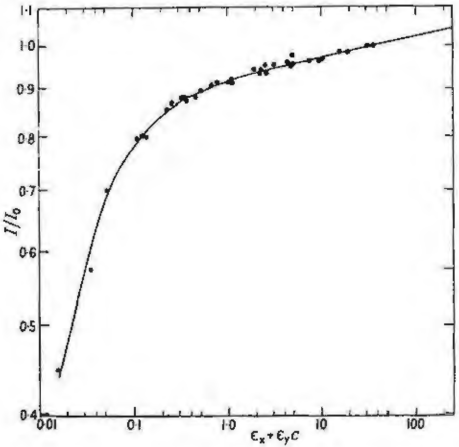

Figure 5. Effect of excitation depth on fluorescence intensity: relative intensity I/I_0 plotted against extinction coefficient $\epsilon_X + \epsilon_Y c$.

Within the experimental error, the values of I/I_0 for the different solutions lie on a single smooth curve. For values of $\epsilon_X + \epsilon_Y c$ from 1 to 36 the curve is linear, and it is reasonable to extrapolate it linearly to higher values of $\epsilon_X + \epsilon_Y c$.

Figure 5 thus shows the change in the observed fluorescence intensity I from the value I_0 that it would have if the molar extinction coefficient $\epsilon_X + \epsilon_Y c$ were 36, i.e. if the radiation were absorbed at the same depth as in the strongest solution at $\lambda = 3000$ Å. Figure 5 has therefore been used to correct the observed fluorescence excitation spectra (figures 3 and 4) by normalizing them to the standard excitation depth, corresponding to I_0. This has been done by dividing the observed fluorescence intensity I (figures 3 and 4) by the value of I/I_0 from figure 5, corresponding to the value of $\epsilon_X + \epsilon_Y c$, for the particular solution and excitation wavelength.

In the wavelength range 2650–2200 Å, which is analysed below, $\epsilon_X + \epsilon_Y c$ varies from 12·4 to 214 over all the solutions, corresponding to correction factors from 0·98 to 1·05. Observations at $\lambda = 2650$–2800 Å are omitted from the subsequent analysis, because of experimental uncertainties in the exact position of the toluene absorption edge, since the absorption spectrum (figure 1, curve A) measured for an ethanol solution, does not correspond exactly to that for pure toluene.

The corrected fluorescence excitation spectra are similar in form to figures 3 and 4, except for uniform plateaux from $\lambda \sim 2900$ Å to 3300 Å.

3.3. *Energy Transfer Coefficient*

We shall now proceed to analyse the corrected excitation spectra, to determine the fraction of quanta transferred from solvent to solute molecules.

For incident photons of wavelength λ, let the fraction absorbed initially by the solvent and solute molecules be n_x and n_y respectively.

$$n_x = \frac{1}{1+\rho c}$$

$$n_y = \frac{\rho c}{1+\rho c} \qquad \ldots\ldots (1)$$

where $\rho = \epsilon_y / \epsilon_x$.

The quantum efficiency q_{fy} of the observed solute fluorescence is

$$q_{fy} = \frac{n_f}{n_y + f n_x} \qquad \ldots\ldots (2)$$

where n_f is the number of photons emitted per incident quantum absorbed, and f is the energy transfer coefficient, i.e. the fraction of quanta, initially absorbed by the solvent, which are transferred to the solute. q_{fy} is characteristic of the solute in the particular solvent at a given value of c. It is independent of λ within the 1st absorption band of the solute (down to 2350 Å in the present case) and, by analogy with other organic fluorescent compounds (Pringsheim 1949, Fuchslocher and Glaser 1954, Wright 1955), it may be expected to remain constant down to at least 2200 Å.

In the spectral region 0, where the solvent is transparent, $n_x = 0$, $n_y = 1$, and

$$q_{fy} = n_{f0} \qquad \ldots\ldots (3)$$

where suffix 0 refers to this spectral region.

An expression for f in terms of experimental parameters is obtained from (1), (2) and (3), namely

$$f = \frac{n_f}{n_{f0}} (1 + \rho c) - \rho c. \qquad \ldots\ldots (4)$$

The ratio n_f / n_{f0} is obtained directly from the corrected fluorescence excitation spectra: ρ is obtained from figure 1, curve C.

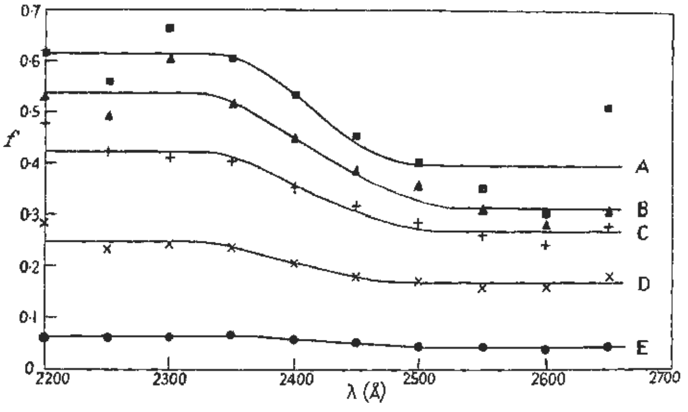

Figure 6. Energy transfer coefficient f plotted against wavelength λ. Normal solutions. Concentration: A, 4·15 g l.$^{-1}$; B, 2·07 g l.$^{-1}$; C, 1·04 g l.$^{-1}$; D, 0·415 g l.$^{-1}$; E, 0·091 g l.$^{-1}$.

The values of f, derived from (4), are plotted against λ in figures 6 and 7. For each solution, it is found that f has two characteristic values: f_1, which is constant within the experimental error, for $\lambda = 2500$–2650 Å (region 1); and f_2, which is similarly constant, but higher, for $\lambda = 2200$–2350 Å (region 2). Between these two spectral regions, f has a value intermediate between f_1 and f_2.

The mean values of f_1 and f_2 are plotted as a function of c in figure 8.

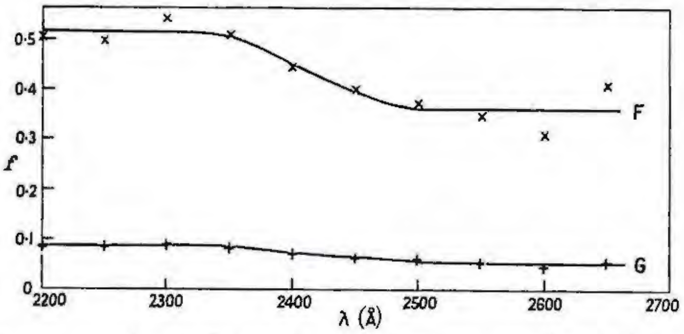

Figure 7. Energy transfer coefficient f plotted against wavelength λ for oxygen-free solutions. Concentration: F, 1·08 g l.$^{-1}$; G, 0·054 g l.$^{-1}$.

3.4. *Energy Transfer and Quenching*

On the photon transfer theory, and some of the alternative non-radiative mechanisms proposed, the probability of solvent–solute transfer is proportional to the concentration c. On an elementary analysis, the probabilities of the various processes competing for the solvent excitation energy may be enumerated as follows: (i) solvent–solute transfer, kc; (ii) quenching by solute, lc; (iii) self-quenching by solvent, s; and (iv) quenching by oxygen, m.

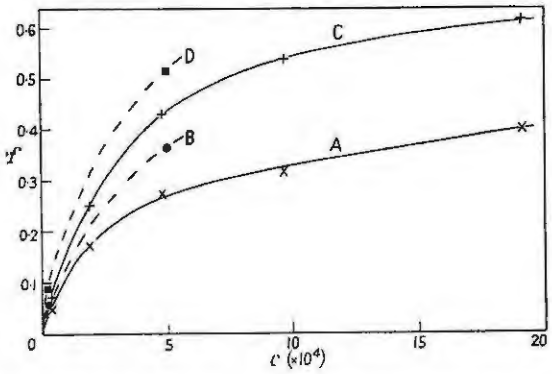

Figure 8. Energy transfer coefficient f plotted against concentration c. A, normal solutions, $\lambda = 2500$–2650 Å; B, oxygen-free solutions $\lambda = 2500$–2650 Å; C, normal solutions $\lambda = 2200$–2350 Å; D, oxygen-free solutions $\lambda = 2200$–2350 Å.

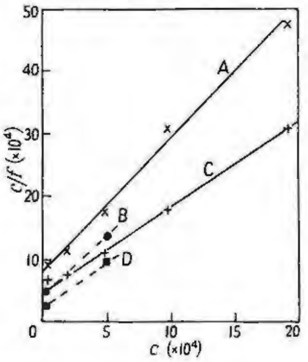

Figure 9. c/f plotted against concentration c. A, normal solutions $\lambda = 2500$–2650 Å; B, oxygen-free solutions $\lambda = 2500$–2650 Å; C, normal solutions $\lambda = 2200$–2350 Å; D, oxygen-free solutions $\lambda = 2200$–2350 Å.

Hence we obtain,

$$f=\frac{kc}{(k+l)c+s+m} \qquad \ldots\ldots(5)$$

$$=\frac{c}{Ac+B} \qquad \ldots\ldots(5a)$$

In figure 9 the experimental values of c/f_1 and c/f_2 are plotted against c for the normal and oxygen-free solutions. Linear relations in agreement with (5*a*) are obtained. From the gradients and intercepts, for the normal solutions $A_1=2{\cdot}1$, $B_1=8\times10^{-4}$; $A_2=1{\cdot}4$, $B_2=5\times10^{-4}$; and for the oxygen-free solutions $A_1=2{\cdot}1$, $B_1=4\times10^{-4}$; $A_2=1{\cdot}4$, $B_2=2{\cdot}5\times10^{-4}$, where suffixes 1 and 2 refer to the spectral regions 1 and 2.

It is tempting to evaluate the relative values of k, l, s and m from these data, as has been done by other observers. However, it will be shown by Birks (to be published) that (5) is over-simplified, since the effect of solvent absorption and re-emission (' photon regeneration ', Birks 1953, 1954) has not been allowed for. A fuller theoretical analysis, which leads to a relation similar to (5*a*), is given by Birks (to be published) and A and B are there related to the molecular quantum efficiency of the solvent and the relative solute/solvent absorption coefficient ρ.

§ 4. Discussion

4.1. *Comparison with other Experimental Results*

These results differ in certain important respects from those of Cohen and Weinreb (1956) on similar solutions.

These authors do not refer to the oxygen content of their solutions, which presumably were air-saturated. They reported that the energy transfer coefficient f was independent of λ for wavelengths from 2200–2700 Å. This is in distinct contrast to the present results.

Most of the measurements of Cohen and Weinreb were made using 2537 Å and 3130 Å radiation for excitation, corresponding to our spectral regions 1 and 0. They observed a linear relation between c/f_1 and c as given by (5), but with the parameter $l=0$. Thus they found that f_1 tended towards a limiting value of 1·0, as c increased, rather than to the limits, given by $1/A_1$ and $1/A_2$ of $f_1=0{\cdot}48$ and $f_2=0{\cdot}7$ obtained from the present measurements. It may be noted that Cohen and Weinreb assumed $l=0$ in their theoretical analysis, and also that their own measurements on anthracene in anisole, reproduced in figure 2(*b*) of their paper, are not consistent with this hypothesis. Their results, like the present ones, do however show clearly that the probability of solvent–solute transfer is proportional to c.

The other studies of Cohen and Weinreb on the influence of carbon tetrachloride as a quenching agent, and of the dilution of the transferring solvent with cyclohexane, have not been repeated. While there appears to be no reason to question their relative transfer efficiency values, the absolute values are subject to the same degree of uncertainty as the others discussed above.

The difference between the present results and those of Cohen and Weinreb may partly arise from the correction for excitation depth (§ 3.2). While the latter refer to a correction for geometrical and self-absorption effects being applied no details of the correction, which is stated to be generally small, are given.

In the present measurements, covering a similar range of concentrations, the values of $\epsilon_x + \epsilon_y c$ at 2537 Å and 3130 Å (the wavelengths used by these authors) range from 170 down to 0·06, corresponding to values of I/I_0 from 1·04 down to 0·7.

4.2. *Consideration of Assumptions*

Two assumptions made in the analysis and calibration should be noted, since if they were invalid, the results at $\lambda < 2537$ Å might not be reliable. (i) The molecular fluorescence quantum efficiency q_{fy} of terphenyl in solution is constant down to $\lambda = 2200$ Å (§ 3.3.) (ii) The technical fluorescence quantum efficiency of the 1 cm cube terphenyl crystal is constant down to $\lambda = 2200$ Å (§ 2.3). Since crystalline terphenyl is transparent to its own fluorescence emission (Birks and Wright 1954), its technical and molecular fluorescence efficiencies are identical. Hence (i) and (ii) are equivalent assumptions for terphenyl molecules in solution and in the crystalline state.

These assumptions are consistent with all the experimental data on organic fluorescent materials, excited by non-ionizing radiation (Pringsheim 1949, Wright 1955) and there is no reason to doubt their validity. Cohen and Weinreb (1956) also make assumption (i), and a similar assumption to (ii) for the aqueous solution of fluorescein used for calibration.

The choice of terphenyl both as solute and for calibration of the incident radiation flux means that, even if (i) and (ii) are not valid, provided the ratio of the molecular fluorescence efficiencies of terphenyl in solution and in the crystal is constant down to $\lambda = 2200$ Å, the values of f calculated from the observations will be unchanged.

4.3. *Dependence on Wavelength*

The most interesting result is that the energy transfer probability depends on the wavelength of excitation.

The two spectral regions 1 (2500–2650 Å) and 2 (2200–2350 Å) correspond to excitation into the first and second excited electronic singlet states of the toluene molecule. It is found that the energy transfer coefficient from toluene molecules excited initially into the second excited state, is higher than from molecules excited initially into the first excited state.

The lifetimes of the first and second excited states, estimated from the absorption strengths of the electronic transitions, are of the order of 10^{-9} sec and 10^{-11} sec respectively. Cohen and Weinreb (1956) have estimated, by measurements of the effect of carbon tetrachloride on quenching, that energy transfer from the first excited state occurs in the order of 10^{-9} sec. The efficient energy transfer from the second excited state shows that in this case transfer must occur in about 10^{-11} sec or less. The very short lifetime of the second excited state reduces the probability that the energy transfer from this state is collisional in nature, since the average time required by an excited solvent molecule to diffuse into the proximity of a solute molecule is in excess of 10^{-11} sec.

Because of the short lifetime of the second excited state the external quenching will be relatively small. The chief process competing with solvent-solute energy transfer from this state will be conversion into the first excited state of the solvent molecule, either by internal conversion or by solvent–solvent energy transfer. This conversion process is known to be highly efficient and rapid

(Pringsheim 1949). Nevertheless, the results show that the solvent–solute transfer can compete efficiently with such inter-state conversion.

4.4. *Photon Transfer Theory*

The results have been discussed so far without specific reference to any particular mode of energy transfer.

Birks (1954) has suggested fluorescence emission from the second and higher electronic excited states of a fluorescent molecule. The results show that the concept, previously accepted (Pringsheim 1949), that all the excitation energy of such higher electronic states is internally converted into that of the lowest excited state, is invalid. In pure solvents two components, internal conversion and solvent–solvent transfer, combine to give 100% inter-state conversion efficiency; in solutions, solvent–solute transfer is an efficient competitor against solvent–solvent transfer for the excitation energy. The time required for energy transfer is of the order of 10^{-11} and 10^{-9} sec respectively for the second and first excited states. This is about the same as for fluorescence emission from these two states.

Between region 1 and region 2, where all the excited solvent molecules are initially in the first and second excited states respectively, there is a transition region extending from 2350–2500 Å. In this transition region, solvent molecules co-exist initially in either of the two excited states. This region is also that where fluorescence from the second excited state might be expected to occur.

Further information on the energy transfer process is given by the experiments of Cohen and Weinreb (1956), who have shown that the solvent–solute transfer efficiency in region 1 is practically unchanged if the solvent is diluted by a factor of 1000 with an ‘ inert ’ liquid, such as cyclohexane. They have thus demonstrated that solvent-solvent ‘ collisional ’ energy transfer is negligible. It would also appear that any short-range non-radiative solvent–solute transfer processes, which depend on thermal diffusion to bring the excited solvent molecule and the solute molecule into reasonable proximity, are similarly excluded by these observations, since their efficiency would be reduced by an increase in the diffusion time due to dilution. Fluorescence of the solvent, leading to photon transfer, appears the one possible long-range mechanism. The dilutant, cyclohexane, being transparent does not decrease the efficiency of photon transfer.

The fluorescence spectrum of the emission from the first excited state of toluene, observed in dilute alcoholic solution, has vibrational maxima at $\lambda = 2622$, 2646, 2676, 2740, 2808 and 2886 Å (Pringsheim 1949). There is thus a major overlap of the fluorescence and absorption spectrum, and in pure toluene the mean free path of the emitted photons will be only a few microns. The relatively low technical fluorescence efficiency q_t observed with thicker toluene specimens by Kallmann and Furst (1951 b) will be considerably less than the molecular fluorescence efficiency q_0, due to this high self-absorption. Since $q_t = (q_0)^n$, where $1/n$ is the probability of photon escape without absorption (Birks 1954), by taking values of $q_t \sim 0{\cdot}015$ (Kallmann and Furst 1951 b), $n \sim 6$ (estimated from the absorption and emission spectra†) we obtain a rough estimate of $q_0 \sim 0{\cdot}5$. This is in reasonable agreement with the value obtained by a fuller analysis of the results (Birks, to be published).

It is hoped to obtain more direct data on the molecular emission from the first and second excited states (the latter will be even more difficult to observe

† $n = 4$–5 for pure anthracene (Birks 1954).

since it is completely overlapped by the absorption spectrum) by observations on thin films.

The theory of the scintillation and fluorescence processes in solutions will be developed in more detail by Birks, when experimental data on other liquid and plastic solutions will be considered.

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