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ENERGY TRANSFER IN MIXED MOLECULAR CRYSTALS OF AROMATIC HYDROCARBONS

By

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ABSTRACT

Energy transfer from solvent to solute in organic single crystals is studied experimentally. Naphthalene is used as a solvent and six other compounds as solutes. The solute concentration ranged from 10^{-7} to 10^{-4} mole/mole. Fluorescence currents were recorded by a photomultiplier, and readings were taken at two temperatures, 295°K and 130°K.

The results indicate that the efficiency of a particular impurity in capturing the excitation cannot be predicted on any simple basis. Also, it is found that this transfer efficiency is independent of wavelength of the exciting light in the region (2500 - 3000A°), and that it is temperature dependent.

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INTRODUCTION

The problem of energy transfer from solvent to solute has been the subject of many investigations. Interest in the problem grew continuously from studies of the anthracene - naphthacene system. Bowen (1938) and Ganguly (1943) observed that naphthacene, dissolved in small amounts in a solid solution of anthracene fluoresces brilliantly with its characteristic greenish-yellow color while the blue anthracene fluorescence is quenched. The phenomenon was studied in liquid solutions (Furst & Kallmann 1955) and in solid solutions (Bowen 1949, Lipsett & Dekker 1954).

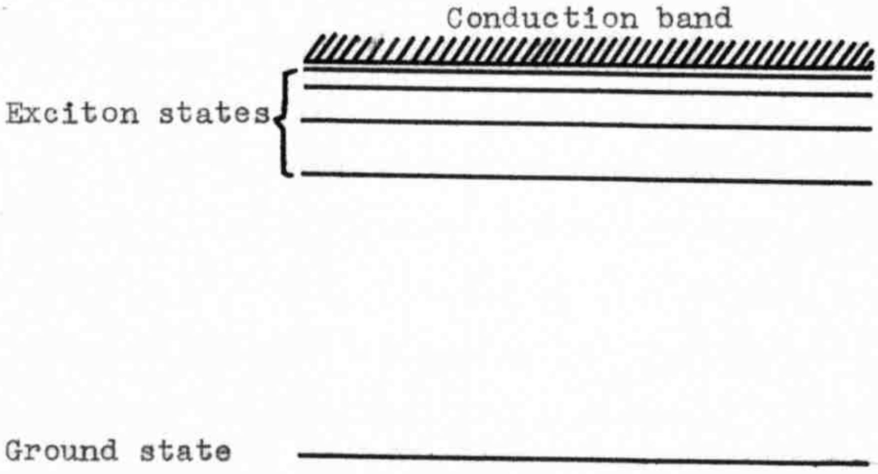
Though the knowledge of energy transfer in aromatic hydrocarbons has increased considerably through numerous experimental and theoretical investigations, it has not reached a state of maturity. Many aspects of the problem have to be studied more carefully. Few workers have studied the effect of temperature, wavelength of the exciting line, and crystal size on energy transfer from a host molecule to an impurity[13]. Also, little data is available concerning mean free paths of excitons, and their interaction with defects. More and more data would be worthwhile. This thesis is an effort in the field. It is mainly concerned with solid solutions of aromatic hydrocarbons. Naphthalene is used as a solvent (host crystal) and six other compounds as solutes (impurities). The fluorescence of naphthalene is partly quenched, and at the same time the impurity fluorescence is observed.

The difficulty in working with solid solutions is that at relatively high impurity concentrations ($> 10^{-5}$ mole/mole), one might not get a true solid solution. The excess crystallized undissolved impurity absorbs part of the excitation and part of the host crystal luminescence and thus makes it very difficult to pursue the study of energy transfer from the host crystal to the impurity[14]. The lowest impurity concentration used by Northrop and Simpson[6] was 10^{-5} mole/mole. Using naphthalene of high purity it was possible in this work to go down to 10^{-7} mole/mole. Low concentration of the impurity ensures that direct absorption of the radiation by the impurity is negligible and insignificant. This is in addition to the fact that the exciting lines are chosen in the region of strong absorption by naphthalene (2000-3100 Å). Irradiation in this region generates excitons in naphthalene crystals.

The high efficiency of transfer[2,5] and the use of thin crystals ($\sim 2\mu$) rule out the possibility of attributing the propagation of energy and its transfer to the photon cascade process. Also, the results of Northrop & Simpson[6] demonstrate that "the theory of sensitized fluorescence is inadequate to account for the final stage of transfer of excitation from solvent to impurity." The exciton mechanism remains the most probable process by which energy is transported through the lattice and ultimately transferred.

The exciton concept was first introduced by J. Frenkel[1] in 1931. It was the result of calculating the excited states of a non-conducting crystal lattice composed of atoms or molecules. The wavefunction of the whole crystal for a state in which one constituent is excited was found to describe an excitation wave propagating through the crystal with a wave vector $\vec{K}$. That is to say the excitation energy will not stay at the locality where it was absorbed, but will be handed over from one constituent to another. This transmission of the excitation energy is analogous to the spreading over the crystal of excitation waves, or excitons'. The mobile state of the excitation energy is called an exciton. This picture shows that the exciton mechanism is an interaction between the excited atom or molecule and all similar units[13]. It is not a single-step process in which interaction is between one excited "sensitizer" and a normal "activator", but is equivalent to stepwise propagation of excitation energy from one molecule to another.

In good insulators, excitons can be generated when the insulator is excited in its fundamental absorption band (first electronic transition). Often such excitation does not lead to conduction[7] (carriers are not freed). The non-conducting excited states are called exciton states. In weakly bound



Schematic energy diagram

solids (molecular crystals), the exciton states correspond closely to the lowest excited states of the constituent atoms or molecules in the free state. In strongly bound crystals (ionic crystals), they arise from the removal of an electron from an atom. The resulting positive hole may be filled by an electron from an adjacent constituent, and thus the hole roams about in the lattice. The removed electron, however, will not move freely in the lattice, but will be attracted to the positive hole by a coulomb force. The hole and the electron, bound together by a coulomb force, will, therefore, move as whole in the crystal. This picture of a hole and an electron coupled together in this way is the exciton picture of Wannier (1937) and Mott[3]. The exciton, according to this picture, can be treated as a hydrogen-like quasi-atom having a series of stationary states leading up to a series limit. Experiments with Cu_2O crystals[11,12] confirm this picture.

We can therefore see that different exciton models are used for different crystals. In molecular crystals the exciton is pictured as an excitation wave moving along the crystal (Frenkel exciton). In ionic crystals and semiconductors, the exciton, having a certain radius large compared with the lattice constant, is usually thought of as an electron and a hole moving as two quase-particles bound by coulomb forces forming a quasi-hydrogen atom. It should be noted that an exciton is electrically neutral. In its motion it transports energy, but does not transport charge.

Davydov[18] has shown that in molecular crystals two types of excitons may be produced upon the absorption of light. These are the free and the localized excitons. The free excitons coincide with those we have been describing. The excitation transfers from one molecule to another so quickly that displacement of molecules to new equilibrium positions does not have time to occur. The localized exciton is a slowly propagating excitation. The excitation transfers from one molecule to another so slowly that the molecules do have time to occupy new equilibrium positions. The localized exciton has a local deformation travelling with it. Free excitons have a higher probability of being captured, and are more important in the transfer process. The participation of localized excitons in the transfer of energy may be neglected[17].

The role of excitons in crystal luminescene is an important aspect of its complex nature. This role has been treated in detail in reference[15]. Since the production of excitons in molecular crystals is associated with the fundamental absorption, it was postulated that the observed crystal luminescence is due to transitions from exciton levels. This is called exciton-type luminescence. But the authors in the above reference[15], after a thorough analysis of experimental data, together with a theoretical treatment of luminescence, conclude (at least for low temperatures) that "no luminescence has been observed which exhibits the features and laws of exciton-type luminescence" and that the observed crystal luminescence" is actually caused by emission from structural defects and impurities". This conclusion, however, does not mean that exciton-type luminescence is absent, or that excitons do not participate in the luminescence mechanism. All it means is that exciton luminescence is strongly inhibited at low temperatures, and at higher temperatures its intensity may be expected to increase.* But at the same time non-radiative processes increase, and the result is a reduction of the overall brightness. And the role of excitons is the transfer of the absorbed energy from the host lattice to defects and impurities at which emission occurs.

The life of an exciton may thus be terminated by one of a number of possible events. It may decay with the emission of a quantum of fluorescence characteristic of the solvent, or it may decay non-radiatively, or it may be captured at an impurity center or at a defect. In the latter case, the capture may be followed by emission of the impurity fluorescence if the impurity itself is luminescent.

Exciton migration in crystal lattices has been inferred from many experiments.

i) It has been shown to account quantitatively for the observed quenching of the host crystal fluorescence[6].

ii) The work of Apker & Taft (1950) demonstrates how excitons interact with F-centers in alkali halides. To

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* In the case of naphthalene with a minor impurity content, Shpak and Sheka[19] succeeded in observing luminescence which may be called exciton luminescence.

explain their results they supposed that excitons, give up their energy to F-centers, ejecting the F-center electrons from the crystal.

iii) Sidman[8] has shown from absorption and fluorescence of anthracene, that excitons can be trapped at lattice imperfections.

iv) Agranovich & Kucherov & Faydish assumed a diffusion character for the exciton motion in anthracene crystal[9]. On the basis of this assumption they could explain adequately the observed dependence of the quantum yield of anthracene fluorescence and of the impurity (naphthacene) fluorescence on the impurity concentration and on the absorption coefficient of the exciting wavelength. The exciton diffusion displacement was estimated to be 1500Å.

v) Simpson[7] has demonstrated the actual migration of excitons from one locality to another, and has been able to measure the average displacement between the points of origin and decay of an exciton. He found a value of 1120°A.

vi) The work of Gross[11] and Nikitine[12] on Cu_2O crystals and other ionic crystals provide a strong evidence for the existence of excitons in these crystals.

EXPERIMENTAL

1. SAMPLES

A. Purity: The naphthalene used in this work was first purified by chemical processes and then zone-refined several times[16]. The impurity (probably anthracene) was reduced below one part in 10^7 parts of naphthalene. The purest naphthalene sample contained one impurity part in 10^8 naphthalene parts.*

B. Preparation: The samples are single crystals of naphthalene grown from solution as follows: about 2.8 mg of pure naphthalene are dissolved in 5cc normal hexane. The amount of impurity needed for a given impurity concentration is added to this solution. The solution is then poured gently on the surface of distilled water contained in a beaker. The beaker is covered with filter paper over which rests a heavy load to slow the evaporation rate (the faster the rate, the poorer the crystals). When all the solvent evaporates naphthalene crystallizes in the form of single crystals. Five to six hours were found necessary to get these crystals. The quality and the size of these crystals depend on many factors

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* This sample was specified to be of this purity by Dr. Zahlan.

among which are concentration, surface area, evaporation rate, and temperature variations. It was found that sometimes the obtained crystals have to be discarded because of their bad quality or of their small size. Handling crystals needs care and patience.

2. Apparatus and Procedure:

A sketch of the experimental setup is shown in Fig. 1.

The sample is a naphthalene crystal enclosed between two quartz disks, held tightly in a brass holder. The sample S is irradiated with five lines whose wavelengths are: 3020, 2970, 2890, 2810, 2650A^{o}. These lines were obtained from a Phillips mercury lamp (type 93110E) and a Leiss Prism double monochromater.

The glass filter G behind the sample was kept there to stop any radiation that might not have been absorbed. This glass filter transmits fractions of the naphthalene fluorescence, and the impurity fluorescence. The two glass filters, F,F are identical. The glass filter F is a corning glass filter No. 3-75. It stops all wavelengths shorter than 3700A^{o}. It passes a fraction of the impurity fluorescence, but stops all the naphthalene fluorescence.

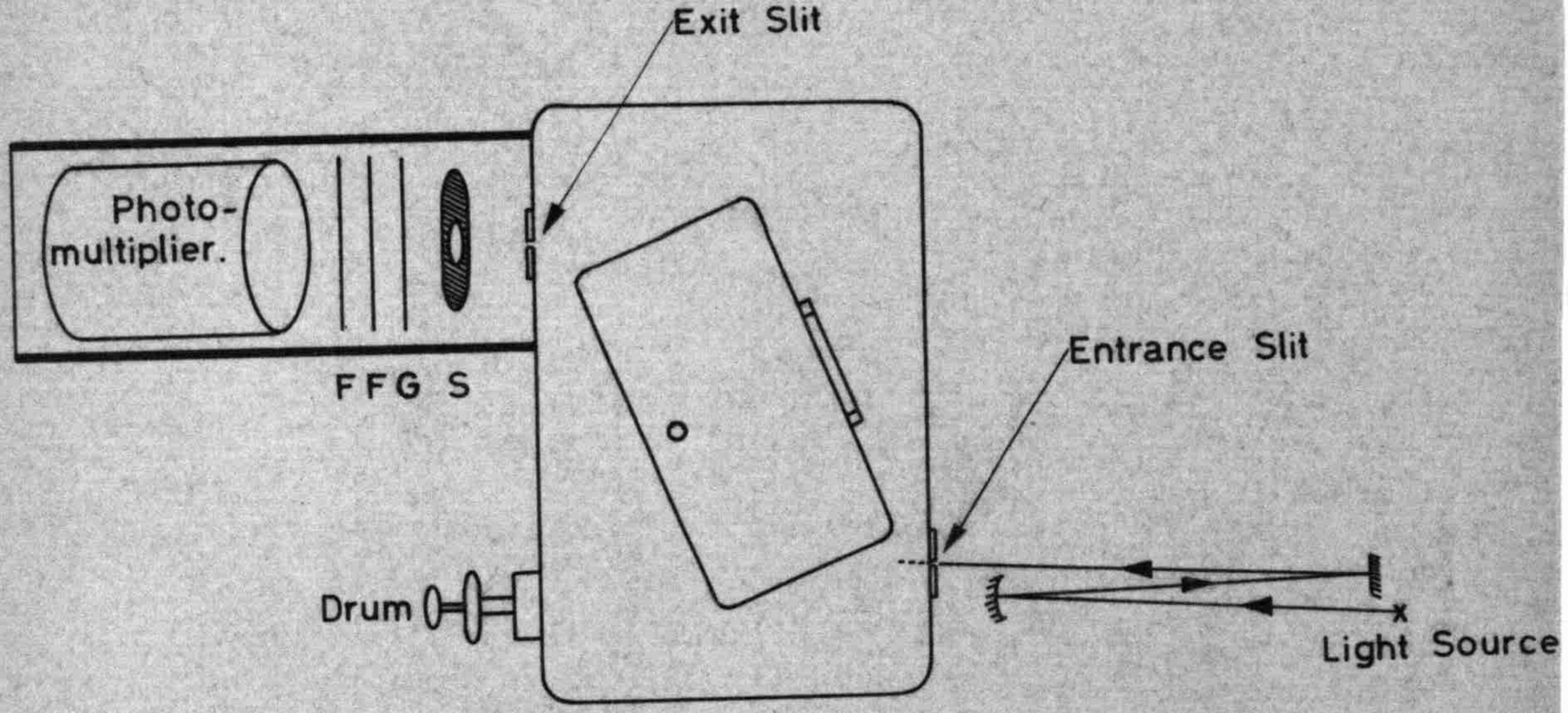

Fig. 1
Experimental Apparatus

The photomultiplier tube is an RCA tube No. 6342. It is sensitive in the visible region, but has a very low sensitivity in the UV region (region of exciting lines). The high voltage power supply of the photomultiplier is a Hamner one model N-401. The photocurrent was recorded by a Keithley Microvolt Ammeter Model 150AR.

In every experiment three observations were made:

i) The total fluorescence, i.e. naphthalene fluorescence plus the impurity fluorescence. This is represented by the total current obtained when both filters F,F are out.

ii) The impurity fluorescence alone with one filter F in. The naphthalene fluorescence is stopped and a fraction of the impurity fluorescence is recorded.

iii) The impurity fluorescence when both filters F,F are in. In this observation a fraction of the fraction in (ii) is observed and recorded. It will be explained later how (ii) and (iii) are combined to give the total impurity fluorescence.

The experiment was performed for four different impurity concentrations for each impurity, and at two different temperatures. The concentrations were 10^{-4}, 10^{-5}

10^{-6}, 10^{-7}, mole/mole. The two temperature were: 295°K (room temperature), and 130°K. The second temperature was obtained by cooking the sample with liquid air. The cooling apparatus is shown in Fig. 2. The temperature was measured with the aid of a Copper-Constantan thermocouple with one junction soldered very near to the sample, and the other junction kept in ice at 0°C. The thermocouple emf was measured with a Leeds & Northrup potentiometer type K-3, and the temperature read from the calibration curve of the thermocouple.

3. Correction Factors:

A. Glass Transmission: The glass filter G transmits 61.5% of the naphthalene fluorescence, while its transmission in the fluorescence region of the impurities is constant and has a value of 90%[16].

B. Photomultiplier relative sensitivity: The sensitivity of the RCA photomultiplier No. 6342 is not the same in the regions of fluorescence of naphthalene and that of the impurities. The relative sensitivity has therefore to be determined. This can be done by multiplying the fluorescence spectra of naphthalene and impurities by the sensitivity curve of the tube 6342, and taking the ratio of areas in each case. But the sensitivity curve of the tube 6342 is so peaked that it is difficult to use without making a large error. However,

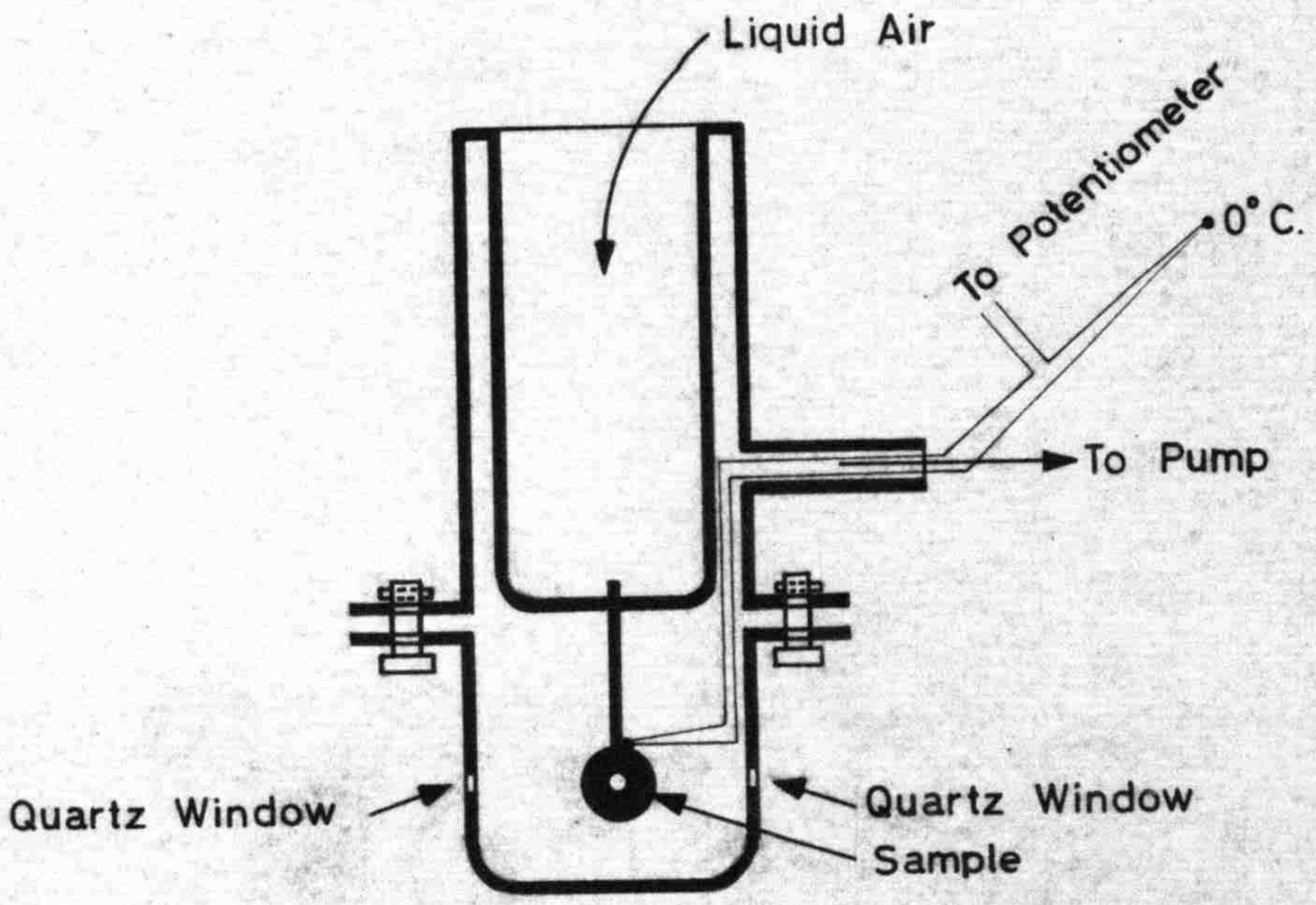
Liquid Air
To Potentiometer
0° C.
To Pump
Quartz Window
Quartz Window
Sample

Fig. 2

such a determination can easily be made with the help of a second tube that is almost equally sensitive in the different regions. The Dumont photomultiplier tube No. 7664 has this property.

Let us assume now that a naphthalene solution is placed in the position of the sample, and with both filters F,F removed two sets of readings are taken using both tubes in rapid succession. It can be assumed then that the number of quanta received by either tube is the same. The number of quanta received by a tube is proportional to the current recorded by that tube divided by its sensitivity. If we call the number of naphthalene fluorescence quanta N_n, the sensitivity of the tube 6342 S_n, the sensitivity of the tube 7664 S_n', and the two currents recorded by the two tubes I_n and I_n' respectively, then:

$$N_n = \frac{I_n}{S_n} = \frac{I_n'}{S_n'} \quad \ldots\ldots\ldots \qquad (1)$$

Similarly if an impurity solution is placed in the position of the sample, then:

$$N_i = \frac{I_i}{S_i} = \frac{I_i'}{S_i'} \qquad (2)$$

where the i subscript refers to "impurity."

Combining (1) and (2) yields:

$$\frac{S_n}{S_i} = \frac{I_n}{I_i} \cdot \frac{I'_i}{I'_n} \cdot \frac{S'_n}{S'_i} \qquad (3)$$

To get $\frac{S_n}{S_i}$ we make use of the spectral response curve (S-13) for the tube 7664. The flourescence spectra of naphthalene and impurities[20,21] in solution are multiplied by (S-13). The ratio of the reduced area to the total area in every spectrum gives the relative sensitivity of the tube in this spectrum region. The ratios for naphthalene and anthracene[16] are 0.72 and 0.96 respectively so that $\left(\frac{S'_n}{S'_i} \right)_{anth} = \frac{0.72}{0.96}$.

The ratios for the other impurities are shown in Figs. 3, 4, 5 & 6. They are:

	S'_n/S'_i
Pyrene	$\frac{0.72}{0.93}$
Chrysene	$\frac{0.72}{0.92}$
Tetracene	$\frac{0.72}{0.75}$
Benzo(a)pyrene	$\frac{0.72}{0.97}$

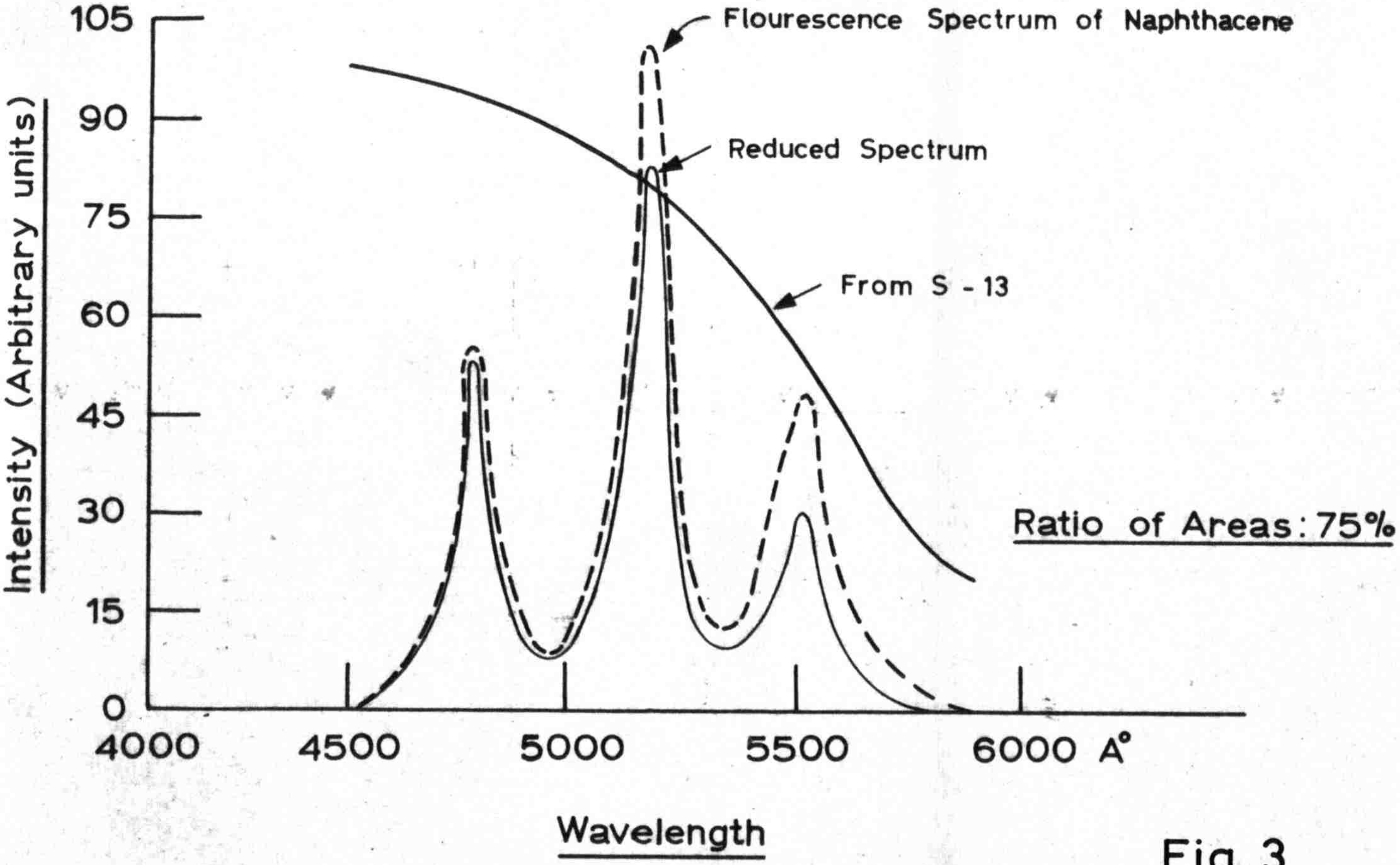
Flourescence Spectrum of Naphthacene
Reduced Spectrum
From S - 13
Ratio of Areas: 75%
105
90
75
60
45
30
15
0
Intensity (Arbitrary units)
4000
4500
5000
5500
6000 A°
Wavelength

Fig. 3

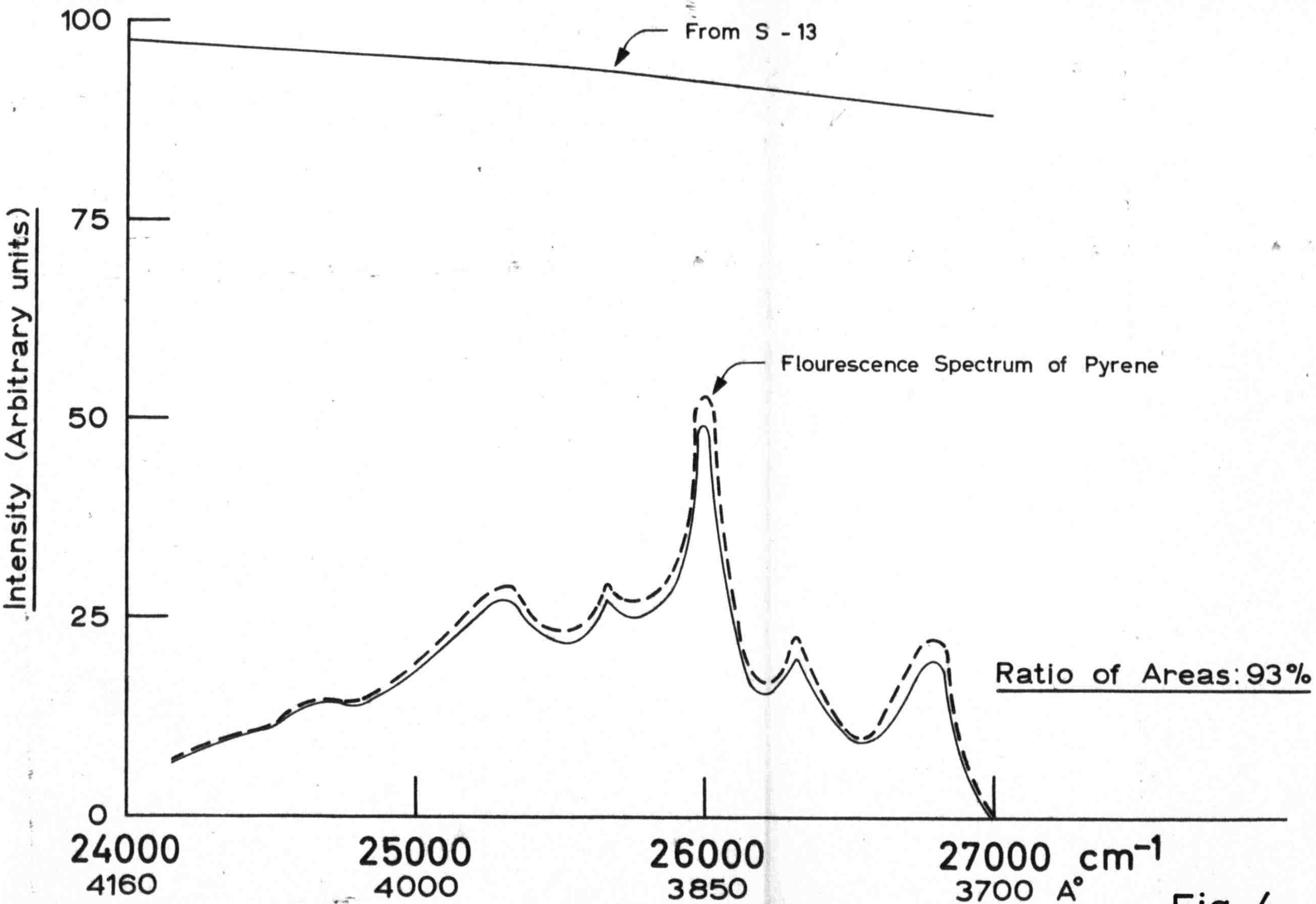
100
75
50
25
0
Intensity (Arbitrary units)
From S - 13
Flourescence Spectrum of Pyrene
Ratio of Areas: 93%
24000
4160
25000
4000
26000
3850
27000 cm⁻¹
3700 A°

Fig. 4

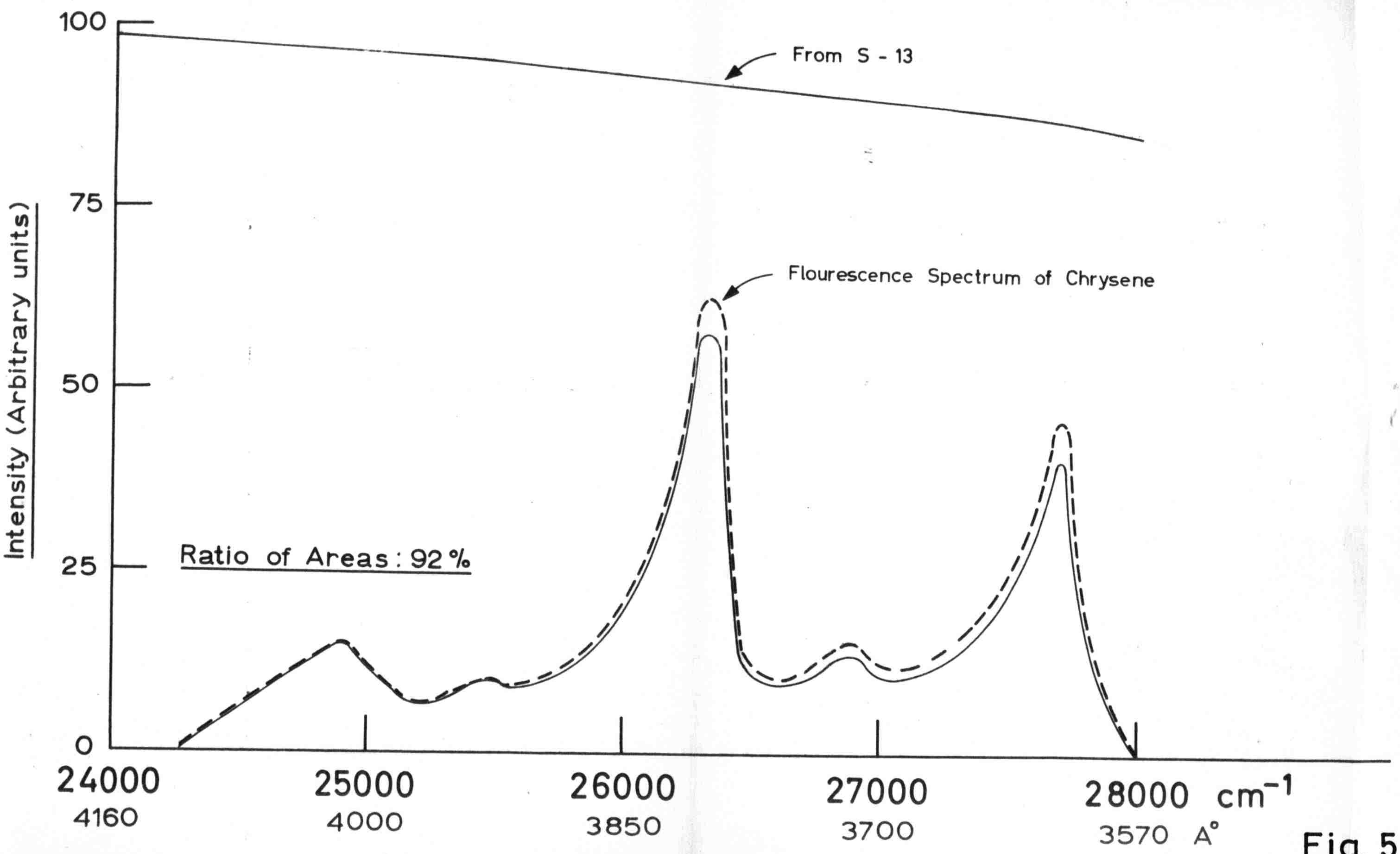
100
75
50
25
0
Intensity (Arbitrary units)
From S - 13
Flourescence Spectrum of Chrysene
Ratio of Areas : 92 %
24000
4160
25000
4000
26000
3850
27000
3700
28000 cm^{-1}
3570 A°

Fig. 5

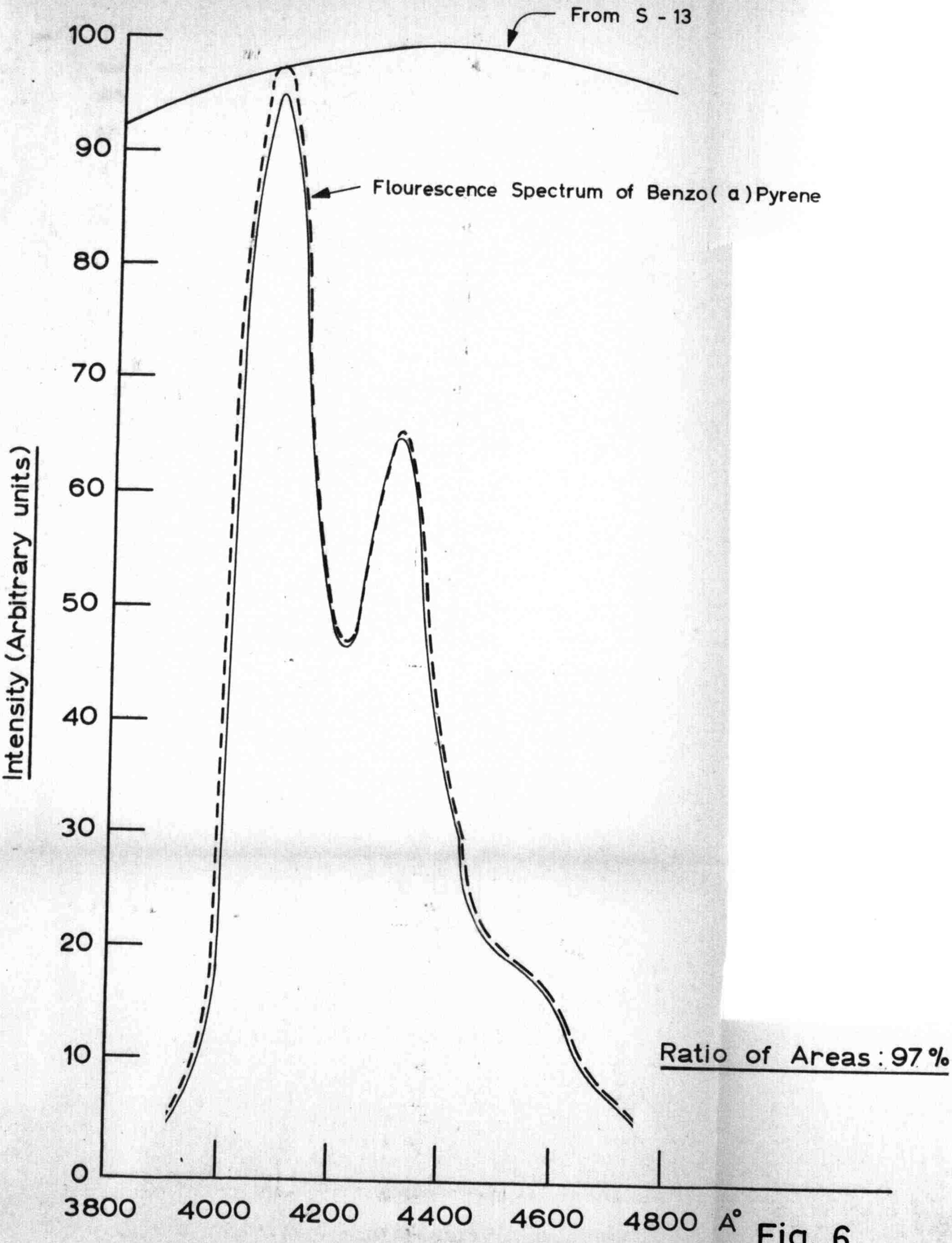
From S - 13
Flourescence Spectrum of Benzo(a)Pyrene
Ratio of Areas : 97 %
Intensity (Arbitrary units)
100
90
80
70
60
50
40
30
20
10
0
3800
4000
4200
4400
4600
4800
A°

Fig. 6

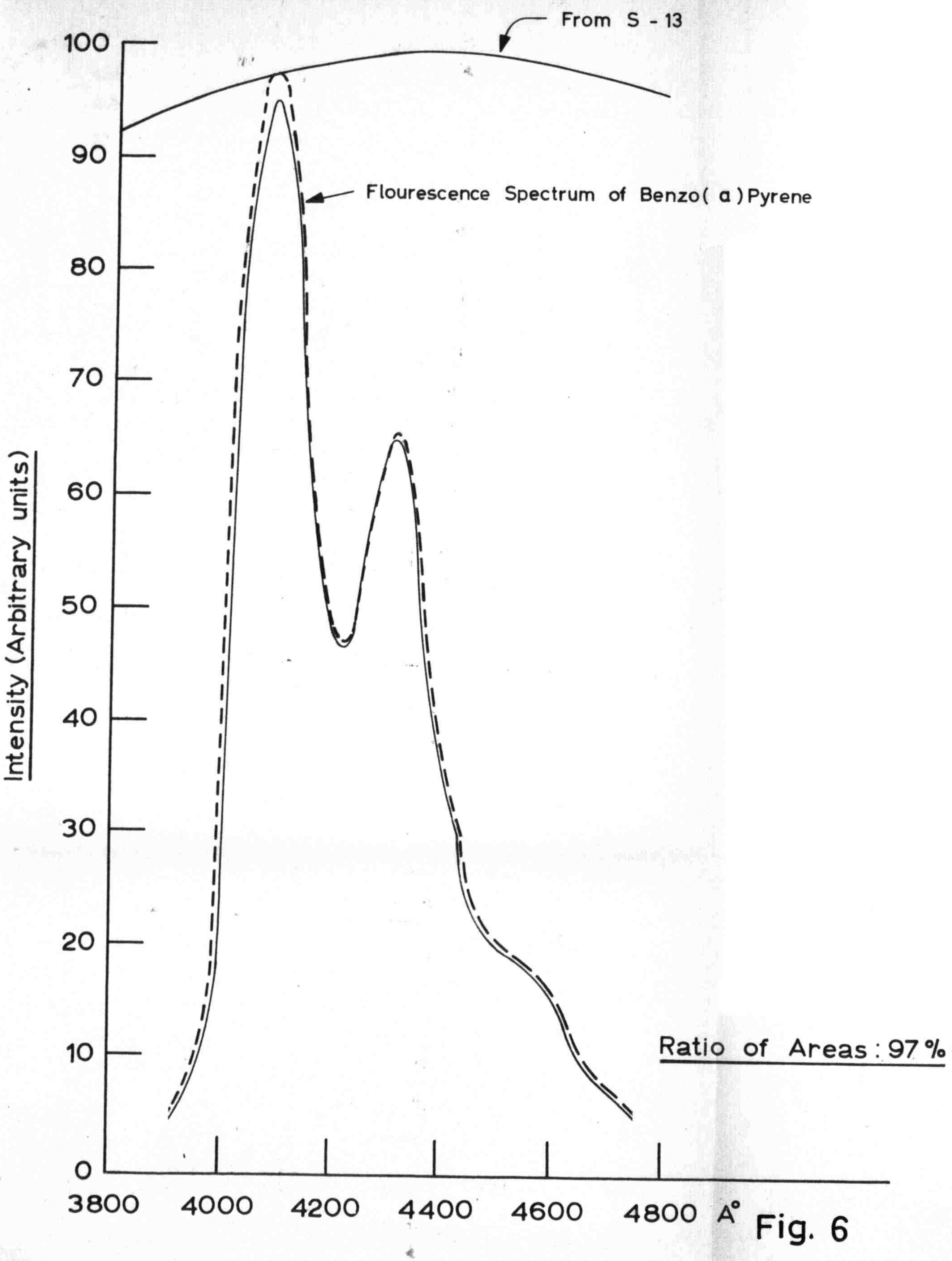
From S - 13
Flourescence Spectrum of Benzo(a)Pyrene
Intensity (Arbitrary units)
100
90
80
70
60
50
40
30
20
10
0
3800
4000
4200
4400
4600
4800
A°
Ratio of Areas : 97 %

Fig. 6

To find the corresponding $\frac{S_n}{S_i}$, solutions were prepared, and the experiment **performed.** Three exciting lines (2890, 2810, 2650A°) were used although one line suffices. Data and results as obtained from eq. (3) are shown in Table I.

Table I a

Impurity : Anthracene

Tube 6342		Tube 7664		S_n/S_i
$I_n \times 10^8$ amp	$I_i \times 10^8$ amp	$I'_n \times 10^8$ amp	$I'_i \times 10^8$ amp	
3.7	5.6	3.5	4.1	0.57
4.6	4.7	3.5	2.5	0.52
9.8	20.3	6.5	10.0	0.55
3.9	4.5	3.8	3.4	0.57
4.9	3.3	3.7	1.7	0.51
10.5	16.2	6.8	8.2	0.57
				ave. 0.54

Table I b

Impurity : Pyrene

Tube 6342		Tube 7664		S_n/S_i
I_nx10^8amp	I_ix10^8amp	I'_nx10^8amp	I'_ix10^8amp	
3.7	2.7	3.5	2.1	0.63
4.6	2.1	3.5	1.1	0.53
9.8	11.3	6.5	5.4	0.56
3.9	2.9	3.8	2.3	0.62
4.9	2.2	3.7	1.4	0.56
10.5	12.4	6.8	6.4	0.60
				ave. 0.58

Table I c

Impurity : Benzo (a) pyrene

Tube 6342		Tube 7664		S_n/S_i
$I_n \times 10^8$amp	$I_i \times 10^8$amp	$I'_n \times 10^8$amp	$I'_i \times 10^8$amp	
3.7	47.7	3.5	22.5	0.37
4.6	44.7	3.5	21.0	0.46
9.8	64.7	6.5	30.0	0.51
3.9	64.7	3.8	32.0	0.38
4.9	58.2	3.7	28.5	0.49
10.5	77.2	6.8	38.5	0.57
				ave. 0.47

Table I d

Impurity : Naphthacene

Tube 6342		Tube 7664		S_n/S_i
I_nx10^8amp	I_ix10^8amp	I'_nx10^8amp	I'_ix10^8amp	
3.7	31.0	3.5	15.0	0.50
4.6	116.	3.5	52.0	0.56
3.9	38.5	3.8	19.0	0.49
4.9	131	3.7	61.0	0.59
			ave.	0.53

Table I e

Impurity : Chrysene

Tube 6342		Tube 7664		S_n/S_i
I_nx10^8amp	I_ix10^8amp	I'_nx10^8amp	I'_ix10^8amp	
3.7	20.6	3.5	10.8	0.44
4.6	27.6	3.5	13.5	0.50
9.8	8.2	6.5	4.2	0.60
3.9	30.6	3.8	15.0	0.40
4.9	40.6	3.7	19.0	0.49
10.5	11.0	6.8	5.0	0.54
			ave.	0.50

As it is clear from Table I, the values of S_n/S_1 for different impurities are very near to each other. This is expected since the fluorescence spectra of all impurities are nearly in the same spectral region. Therefore, we can use one value for S_n/S_1 in our calculations without introducing a serious error. This value is the average value of S_n/S_1 over all impurities, i.e.

$$S_n/S_1 = \frac{0.54 + 0.58 + 0.47 + 0.53 + 0.50}{5} = 0.52$$

RESULTS

Most of our work is concerned with the study of energy transfer from solvent to solute, and how this transfer varies from impurity to another.

Grown single naphthalene crystals containing regulated concentration of impurities were examined. The glass filter G was kept in its place during all measurements. The corning glass filter F was inserted in whenever it was required to prevent the naphthalene fluorescence from reaching the photomultiplier.

When the sample is irradiated by the exciting light, the emission is composed of naphthalene fluorescence and impurity fluorescence.

Let the total current (recorded when both filters F,F are out) be called I_t, then :

$$I_t = \alpha_n \; I_n + \alpha_i \; I_i \qquad (4)$$

Where α_n - glass transmission of naphthalene fluorescence.

α_i - " " " impurity "

I_n - naphthalene current.

I_i - impurity " .

If now one filter F is inserted in, the naphthalene flourescence is stopped, and a fraction of the impurity flourescence is transmitted. If we call the current in this case, I_1, then:

$$I_1 = f \alpha_i I_i \qquad (5)$$

where f - corning glass filter transmission of impurity flourescence.

Let the second corning filter F be inserted. Then, if the recorded current now is called I_2, we have:

$$I_2 = f . f \alpha_i I_i = f^2 \alpha_i I_i \qquad (6)$$

Combining (5) and (6), we obtain:

$$\alpha_i I_i = I_1^2/I_2 \qquad (7)$$

If this result is inserted in (4), we get:

$$\alpha_n I_n = I_t - I_1^2/I_2 \qquad (8)$$

So that:

$$\frac{I_i}{I_n} = \frac{I_1^2/I_2}{I_t - I_1^2/I_2} \frac{\alpha_n}{\alpha_i} \qquad (9)$$

The fluorescence yield J (in quanta) is proportional to the current divided by the tube sensitivity. Therefore the naphthalene fluorescence is

$$J_n \sim \frac{I_n}{S_n}$$

and the impurity fluorescence is

$$J_i \sim \frac{I_i}{S_i}$$

so that

$$J_i/J_n = \frac{I_i}{I_n} \cdot \frac{S_n}{S_i}$$

substituting from (9), we get:

$$J_i/J_n = \frac{I_1^2/I_2}{I_t - I_1^2/I_2} \cdot \frac{\alpha_n}{\alpha_i} \cdot \frac{S_n}{S_i} \qquad (10)$$

I_t, I_1, I_2 are the three measured currents. α_n, α_i, S_n, S_i are constants whose values are:

$\alpha_n = 61.5\%$

$\alpha_i = 90\%$ (same for all impurities since glass has a constant transmission (90%) for all wavelengths longer than 3700A°).

$S_n/S_i = 0.52$.

Substituting the values of these constants in equation(10), we get:

$$J_i/J_n = 0.35 \frac{I_1^2/I_2}{I_t - I_1^2/I_2} \qquad (11)$$

In Table II, a complete set of the original data is given, together with J_i/J_n as calculated from equation (11). The results in each set of readings are arranged as obtained for the exciting lines : 3020, 2970, 2890, 2810, 2650A°.

Table II: A complete set of the original data arranged as obtained for the five exciting lines, 3020, 2970, 2890, 2810, 2650A° respectively.

Impurity : Anthracene

Conc. : 10^{-4} mole/mole

1st crystal

Temp. 295°K				Temp. 130°K			
x10^8amps				x10^8amps			
I_t	I_1	I_2	J_i/J_n	I_t	I_1	I_2	J_i/J_n
3650	1670	975	1.21	1490	710	410	1.57
1680	760	440	1.21	690	325	187	1.78
440	203	119	1.25	182	87.5	50.0	1.76
400	177	102	1.09	153	73.0	42.0	1.56
490	222	129	1.18	151	73.0	42.0	1.69

7-10 sets of readings like the above were recorded, and the average value of J_i/J_n for each exciting wavelength was found at both temperatures.

A similar data was obtained for more than one crystal at each impurity concentration. The results are:

Table II a

$(J_i/J_n)_{\text{Anth.}}$

Conc. = 10^{-4} mole/mole

295°K				130°K
First crystal	2nd	3rd	Average of 3 crystals	First crystal
1.26	1.15	1.17	1.19	1.54
1.16	1.12	1.09	1.12	1.82
1.27	1.14	1.20	1.20	1.68
1.17	1.06	1.10	1.11	1.56
1.28	1.26	1.09	1.21	1.56
			1.17 ave.	

Conc. = 10^{-5} mole/mole

0.79	0.91	-	0.85	1.08
0.83	0.80	-	0.82	1.29
0.87	0.82	-	0.84	1.14
0.82	0.86	-	0.84	1.05
0.86	0.78	-	0.82	1.18
			0.83 ave.	

Table II a - cont.

Conc. = 10^{-6} mole/mole

295°K				130°K
First crystal	2nd	3rd	Average of 3 crystals	First crystal
0.31				0.47
0.29				0.51
0.30				0.50
0.31				0.49
0.31				0.51
0.30 ave.				0.50 ave.

Conc. = 10^{-7} mole/mole

0.080	0.075	-	0.077	0.110
0.065	0.072	-	0.069	0.085
0.060	0.069	-	0.064	0.087
0.060	0.069	-	0.064	0.087
0.067	0.069	-	0.068	0.105
			0.068 ave.	0.095 ave.

Table II b

(J_i/J_n) Naphthacene

Conc. = 10^{-4} mole/mole

295°K				130°K			
First crystal	2nd	3rd	Average of 3 crystals	1st	2nd	3rd	Average of 3 crystals
7.84	8.15	6.13	7.37	-	∞	16.9	∞
6.82	6.05	6.80	6.56	-	∞	∞	∞
7.10	8.30	6.20	7.20	-	∞	∞	∞
8.19	6.65	5.90	6.91	-	27.7	∞	∞
6.58	7.42	5.25	6.42	-	39.2	∞	∞
			6.89 ave.				

Conc. = 10^{-5} mole/mole

4.00	3.22	3.67	3.63	-	5.85	6.23	6.04
2.40	2.80	2.68	2.63	-	4.48	4.55	4.51
2.85	3.10	2.90	2.95	-	5.88	4.72	5.30
2.07	2.63	2.95	2.55	-	5.70	4.85	5.27
3.10	3.10	3.92	3.37	-	8.20	5.70	6.95
			3.03 ave.				5.61 ave.

Table II b cont'd.

Conc. = 10^{-6} mole/mole

295°K				130°K			
First crystal	2nd	3rd	Average of 3 crystals	1st	2nd	3rd	Average of 3 crystals
1.64	1.55	1.53	1.57	5.67	3.96	3.78	4.47
1.28	1.43	1.23	1.31	3.57	4.76	3.40	3.91
1.33	1.49	1.40	1.41	3.60	5.25	3.92	4.26
1.19	1.33	1.37	1.30	3.33	4.80	3.78	3.97
1.44	1.47	1.45	1.35	4.06	5.50	4.20	4.59
			1.39				4.24

Conc. = 10^{-7} mole/mole

0.48	0.58	0.33	0.46	1.69	1.54	0.82	1.35
0.47	0.51	0.29	0.42	1.39	1.27	0.81	1.16
0.48	0.55	0.29	0.44	1.33	1.32	0.82	1.22
0.46	0.50	0.28	0.41	1.34	1.35	0.80	1.16
0.48	0.55	0.30	0.44	1.39	1.58	0.84	1.27

Table II c

(J_i/J_n) Chrysene

Conc. = 10^{-4} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Average	1st	2nd	3rd	4th	Average
1.30	1.73	1.91	1.52	1.61	1.44	2.44	2.68	2.33	2.22
1.32	—	1.44	1.40	1.39	1.84	2.23	2.14	2.84	2.26
1.21	2.30	1.49	2.06	1.76	1.62	2.98	2.11	2.19	2.22
1.14	1.87	1.71	1.84	1.64	1.36	3.20	1.97	2.43	2.24
1.10	1.91	1.82	1.88	1.68	1.37	3.30	2.70	2.10	2.37
				1.62					2.26

Conc. = 10^{-5} mole/mole

0.54	0.48	0.52	0.55	0.52	0.64	0.68	0.68	0.70	0.67
0.48	0.47	0.53	0.50	0.50	0.60	0.63	0.68	0.66	0.64
0.45	0.47	0.50	0.53	0.49	0.58	0.74	0.72	0.71	0.69
0.48	0.43	0.52	0.50	0.48	0.61	0.67	0.71	0.66	0.64
0.47	0.49	0.50	0.52	0.50	0.65	0.72	0.69	0.71	0.69
				0.50					0.67

Table II c con'd.

Conc. = 10^{-6} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Ave.	1st	2nd	3rd	4th	Average
0.14	0.11	0.11	0.09	0.11	0.22	0.21	0.21	0.16	0.20
0.13	0.11	0.11	0.10	0.11	0.23	0.21	0.18	0.16	0.19
0.13	0.11	0.10	0.10	0.11	0.23	0.21	0.18	0.15	0.19
0.14	0.11	0.10	0.10	0.11	0.21	0.22	0.18	0.15	0.19
0.13	0.10	0.10	0.10	0.11	0.22	0.22	0.18	0.15	0.19
				0.11					0.19

Conc. = 10^{-7} mole/mole

	0.059	0.063		0.061			0.10	0.13	0.11
	0.052	0.060		0.056			0.11	0.13	0.12
	0.049	0.056		0.052			0.11	0.12	0.12
	0.049	0.056		0.053			0.11	0.12	0.11
	0.049	0.053		0.057			0.11	0.12	0.12
				0.055					0.12

Table II d

(I_1/I_n) Benzo (a) pyrene

Conc. = 10^{-4} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Ave.	1st	2nd	3rd	4th	Ave.
0.27	0.18	0.14	0.15	0.19	0.46	0.28	0.21	0.24	0.30
0.27	0.18	0.15	0.14	0.18	0.47	0.29	0.24	0.24	0.31
0.28	0.17	0.15	0.14	0.18	0.51	0.33	0.25	0.26	0.34
0.27	0.18	0.15	0.14	0.19	0.49	0.31	0.24	0.27	0.33
0.25	0.17	0.15	0.14	0.18	0.48	0.28	0.23	0.26	0.31
				0.18					0.32

Conc. = 10^{-5} mole/mole

0.063	0.060	0.049	0.056	0.057	0.10	0.12	0.09	0.10	0.10
0.070	0.060	0.053	0.077	0.065	0.13	0.13	0.14	0.13	0.13
0.070	0.056	0.049	0.074	0.062	0.12	0.13	0.14	0.13	0.13
0.070	0.056	0.049	0.077	0.063	0.13	0.13	0.15	0.14	0.14
0.063	0.056	0.046	0.060	0.056	0.12	0.12	0.11	0.12	0.12
				0.061					0.12

Table II d cont'd.

Conc. = 10^{-6} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Ave.	1st	2nd	3rd	4th	Ave.
0.045	0.039	0.039	0.053	0.044	0.084	0.056	0.077	0.100	0.079
0.045	0.031	0.039	0.049	0.041	0.10	0.056	0.090	0.100	0.086
0.042	0.031	0.035	0.049	0.039	0.10	0.053	0.088	0.100	0.085
0.042	0.031	0.039	0.049	0.040	0.10	0.056	0.088	0.100	0.083
0.040	0.031	0.035	0.049	0.039	0.095	0.053	0.084	0.100	0.083
				0.041					0.084

Conc. = 10^{-7} mole/mole

0.035	0.046	0.028		0.036	0.070	0.077	0.063		0.070
0.039	0.046	0.028		0.038	0.090	0.080	0.074		0.081
0.038	0.046	0.028		0.037	0.084	0.077	0.070		0.077
0.038	0.042	0.028		0.036	0.090	0.080	0.073		0.081
0.035	0.042	0.028		0.035	0.080	0.077	0.070		0.076
				0.036					0.077

Table II e

(J_i/J_n) Pyrene

Conc. = 10^{-4} mole/mole

295°K				130°K			
First crystal	2nd	3rd	Average	1st	2nd	3rd	Average
0.039	0.049	0.053	0.047	0.060	0.074		0.067
0.032	0.056	0.053	0.047	0.074	0.095		0.084
0.035	0.053	0.049	0.046	0.070	0.091		0.080
0.039	0.056	0.053	0.049	0.070	0.095		0.082
0.046	0.049	0.046	0.047	0.062	0.088		0.075
			0.047				0.077

Conc. = 10^{-5} mole/mole

0.035	0.028	0.046	0.036	0.056	0.039	0.080	0.058
0.035	0.032	0.042	0.036	0.067	0.046	0.091	0.068
0.035	0.025	0.039	0.033	0.066	0.046	0.095	0.069
0.032	0.025	0.039	0.032	0.066	0.046	0.095	0.069
0.032	0.025	0.039	0.032	0.063	0.046	0.095	0.068
			0.034				0.066

Table II e cont'd

Conc. = 10^{-6} mole/mole

295°K						130°K			
First crystal	2nd	3rd	4th	5th	6th	1st	2nd	3rd	4th
0.024	0.042	1.23	0.032			0.077	0.09		0.060
0.025	0.042	1.34	0.032			0.098	0.12		0.074
0.024	0.039	1.52	0.028			0.100	0.12		0.074
0.025	0.039	1.90	0.028			0.100	0.12		0.073
0.025	0.039	1.40	0.028			0.088	0.11		0.070

Conc. = 10^{-7} mole/mole

0.039	0.13	2.45	0.23	0.23	0.18		0.23		0.56
0.049	0.14	2.62	0.25	0.23	0.16		0.24		0.58
0.049	0.13	2.71	0.23	0.23	0.16		0.23		0.58
0.049	0.13	2.84	0.24	0.25	0.15		0.22		0.56
0.039	0.13	2.73	0.24	0.24	0.16		0.23		0.59

Table II f

(J_i/J_n) Coronene

Conc. = 10^{-4} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Ave.	1st	2nd	3rd	4th	Ave.
0.039	0.049	0.049	0.042	0.045	0.084		0.084	0.074	0.081
0.039	0.046	0.046	0.042	0.043	0.095		0.098	0.095	0.096
0.039	0.042	0.042	0.042	0.041	0.098		0.088	0.091	0.092
0.039	0.042	0.042	0.042	0.041	0.098		0.091	0.091	0.093
0.039	0.046	0.042	0.042	0.043	0.091		0.088	0.084	0.088
				0.043					0.090

Conc. = 10^{-5} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Ave.	1st	2nd	3rd	4th	Ave.
0.039	0.046			0.042	0.063	0.11			0.086
0.032	0.049			0.040	0.066	0.13			0.098
0.032	0.049			0.041	0.067	0.12			0.094
0.032	0.046			0.039	0.063	0.12			0.091
0.032	0.046			0.039	0.067	0.12			0.093
				0.040					0.092

Conc. = 10^{-6} mole/mole

295°K					130°K				
1st cry.	2nd	3rd	4th	Ave.	1st	2nd	3rd	4th	Ave.
0.059	0.25	0.034			0.11	0.60	0.10		
0.056	0.25	0.029			0.12	0.71	0.12		
0.053	0.25	0.028			0.12	0.69	0.11		
0.053	0.26	0.028			0.12	0.70	0.12		
0.053	0.25	0.028			0.11	0.69	0.12		

DISCUSSION

Numerous investigations have shown that the luminescence of molecular crystals is connected with the defects in the crystal lattice which may be formed by minor impurities or structural disturbances[15]. The introduction of impurity molecules in the crystal will result in the distortion of the crystal lattice. Impurity molecules will cause local deformations in their vicinity, and a loss in the regularity of the lattice, thus disturbing the perfection of the lattice. This distortion might be due to the fact that the impurity molecule is different in size from the host molecule. Consequently different impurity molecules are expected to distort the lattice to different degrees; moreover the distortions must increase with increasing the impurity concentration. And at high concentrations of the impurity, its molecules might not be uniformly distributed, but clustered in groups thus leading to a change in the emission spectrum of the impurity due to the direct interaction of its clustered molecules.

A. Size Effect

Below is a table[4] of the crystal data for the aromatic hydrocarbons used.

	unit cell dimensions				No. of molecules per cell	size per molecule (A^3)
Compound	a α	b β	c γ	(A°)		
Naphthalene	8.24	6.00	8.66		2	180
	90°	122.9°	90°			
Anthracene	8.56	6.04	11.16		2	237
	90°	124.7°	90°			
Naphthacene (Tetracene)	7.98	6.14	13.57		2	305
	98.0°	112.4°	92.5°			
Pyrene	13.60	9.24	8.37		4	260
	90°	100.2°	90°			
Chrysene	8.34	6.18	25.0		4	290
	90°	115.8°	90°			
Coronene	16.10	4.70	10.15		2	360
	90°	110.8°	90°			
Benzo(a)pyrene	7.59	7.69	22.38		4	320

Fig. 7 is a plot of J_i/J_n VS size/molecule. It shows that there exists no obvious simple relation between the fluorescence yield of the impurity and the size of its molecule. J_i/J_n is highest for tetracene although the size of its molecule is not the largest. The size of the anthracene molecule is least, while $(J_i/J_n)_{anth.}$ is higher than for some other impurities with bigger molecules. Our results, therefore, illustrate the fact that other factors have to be taken into consideration. It is plausible that the larger the molecule the larger is the deformation caused and the larger is its cross-section for capturing an exciton. But this is true only when the impurity molecule enters the naphthalene lattice, i.e. when it forms a solid solution. Impurity molecules which occupy substitutional sites in the host lattice are said to be forming a solid solution, and are referred to as guest molecules. Therefore the solid solubility of the impurity in crystalline naphthalene in the sense that it enters or fits in a certain manner in the naphthalene lattice should be an important factor in the process. The details of why certain pairs of molecules form substitutional solid solutions while others do not are not yet known[23]. Impurities, that do not dissolve in crystalline naphthalene, form their own microcrystals; and if an impurity fluorescence is observed it is due to direct absorption by the impurity not

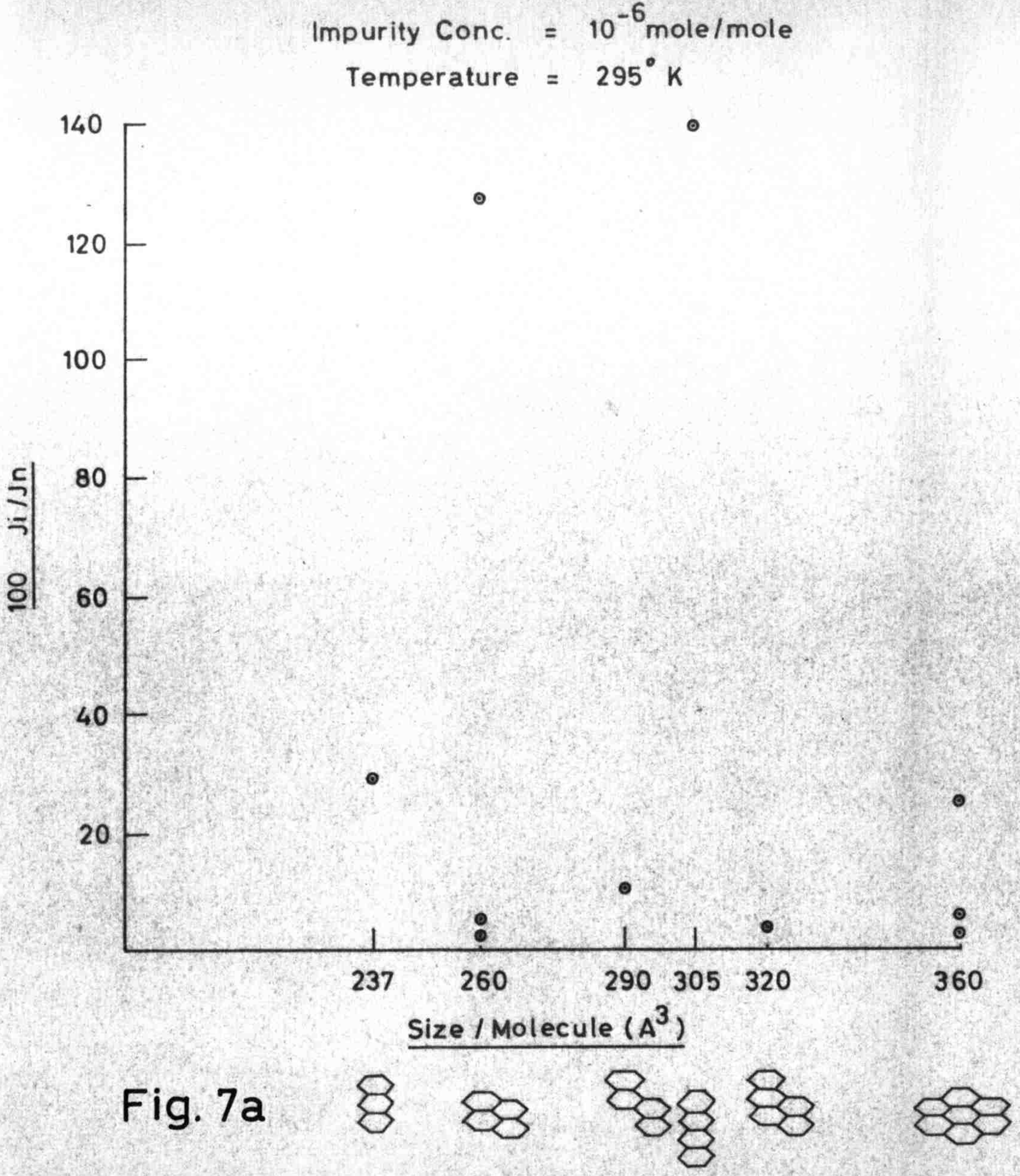
Impurity Conc. = 10^{-6} mole/mole
Temperature = 295° K
140
120
100
80
60
40
20
100 Ji / Jn
237
260
290
305
320
360
Size / Molecule (A^3)

Fig. 7a

to energy transfer from host to guest and therefore must be very weak. On the other hand, impurities that do dissolve are either difficultly soluble (low distribution coefficient) or easily soluble (high distribution coefficient). Difficultly soluble impurities and easily soluble ones both occupy substitutional sites in the host lattice. The fundamental difference between them is that the former ones do not fit properly in the lattice sites and lead to greater departure from ideality. Therefore the difficultly soluble impurities are expected to cause more serious local deformations, and the probability of trapping the excitation energy is increased accordingly[24].

Our results seem to support these inferences. Pyrene and Coronene (both of the condensed type hydrocarbons) show very weak fluorescence at high concentrations. At concentrations of 10^{-4} and 10^{-5} Pyrene in Naphthalene, $J_i/J_n = 0.04$. A similar result was obtained for Coronene. Remembering that $J_i/J_n = 0.03$ for naphthalene with no added impurity[16], we can conclude that the emission of Pyrene and that of Coronene are absent at high concentrations. At low concentrations, however, different results are obtained. The fluorescence yield of the impurity from naphthalene crystals containing 10^{-6} and 10^{-7} mole/mole Pyrene varies enormously. The values of J_i/J_n for different crystals with the same impurity concentration are widely different. The values range from 0.04 to 2.70.

Crystals with $J_i/J_n = 0.04$ have no appreciable impurity fluorescence; and when the front surface of the crystal is observed visually while it is being excited, no emission can be seen. Crystals with $J_i/J_n = 2.70$ show an intense green fluorescence when observed visually, crystals with $J_i/J_n = 1.30$ an intense green fluorescence, crystals with $J_i/J_n = 0.25$ a weak green emission, and crystals with $J_i/J_n = 0.13$ a bluish voilet fluorescence.

Naphthalene crystals containing 10^{-6} mole/mole Coronene showed similar effects. Those with $J_i/J_n = 0.05$ or 0.03 exhibit no emission when observed visually, while those with $J_i/J_n = 0.25$ show a weak green color filling their surfaces.

In view of the fact that, for impurities soluble at all concentrations such as anthracene, the higher the impurity concentration the higher is J_i/J_n, the above results may be explained as follows: At high concentrations (10^{-5} mole/mole and greater) Pyrene and Coronene do not enter the naphthalene lattice, i.e. do not dissolve in naphthalene, or no solid solution is formed, and the question of energy transfer does not arise. This tendency of the above two hydrocarbons not to dissolve in naphthalene and form their own microcrystals might have an explanation in the condensed nature of their molecules.

At low concentrations (10^{-6} mole/mole and smaller) Pyrene dissolves in most of the naphthalene crystals. And when it dissolves it enters the crystal either in the form of a monomer or in the form of a dimer, the second form being more probable. The monomer emission is in the blue (3700 - 4200A°) and the dimer emission is in the green (broad band around 4760° A)[10]. Coronene at a concentration of 10^{-6} dissolves in some crystals, and when it does its weak green emission is observed.

The other four impurities do not show the effects shown by Pyrene and Coronene. They display the concentration dependence of J_i/J_n established by other workers for the naphthalene-anthracene system[16], and for the anthracene - naphthacene[9] system. The ratio J_i/J_n increases with increasing the impurity concentration. This indicates that these impurities enter the naphthalene lattice and form solid solutions with naphthalene at all the impurity concentrations studied. The variation of J_i/J_n from one impurity to another for a given impurity concentration must therefore be connected with physical properties of the impurities such as their molecular sizes, the orientation of their molecules in the naphthalene lattice, or the affinity of their molecules to cluster together. Unfortunately the distribution coefficients of the impurities in naphthalene are not known. But it is known[24] that difficultly soluble impurities have a higher probability of trapping the excitation energy due to the more serious deformation they cause. Our data therefore can be used to compare the deformations in the naphthalene lattice produced by introducing different impurities. Such a comparison is only possible at low impurity concentration, since at high concentrations some impurities (Pyrene & Coronene) do not form solid solutions and therefore comparison looses its meaning.

At low concentrations (10^{-6} and 10^{-7}), naphthacene has the highest value of J_i/J_n, although $(J_i/J_n)_{\text{pyrene}}$ for one crystal is higher than $(J_i/J_n)_{\text{naphthacene}}$, a fact that illustrates the complex nature of the deformations that are very difficult to predict on any simple basis.

Thus, naphthacene is expected to cause more serious defects in the naphthalene lattice than other impurities, and must therefore be least soluble. Anthracene comes next, and so on. An experimental test of these conclusions seems to be interesting. Such a test lies in the measurement of the distribution coefficients of these impurities in naphthalene.

B. Wavelength Dependence

Fig. 8 is a plot of J_i/J_n VS. Wavelength of the exciting light for grown naphthalene crystals with two impurity concentrations. Except for the first line with the longest wavelength (3020A°) in the cases of anthracene and tetracene, the variation in J_i/J_n is not large for a given impurity concentration. It is not more than 10%. It is however, difficult to make a precise estimate of the errors involved because of the many corrections that have to be made, and of some uncontrolable complications such as non-uniformity in the distribution of the impurity, structural defects, and surface effects. It is thought therefore that this variation falls within the limits of experimental error, and that the transfer efficiency is independent of wavelength of the exciting light below 3000A°. This result agrees with the result obtained by Cohen and Weinreb[22].

The value of J_i/J_n for the line 3020A° is higher than for other lines by an amount not falling within the limits of experimental error when anthracene and tetracene are used as impurities. This result might be explained on the basis of the prediction of Agranovich and Faiydish[9]. They have shown that the ratio J_i/J_n increases as the absorption coefficient of the exciting light decreases. It is known that the absorption

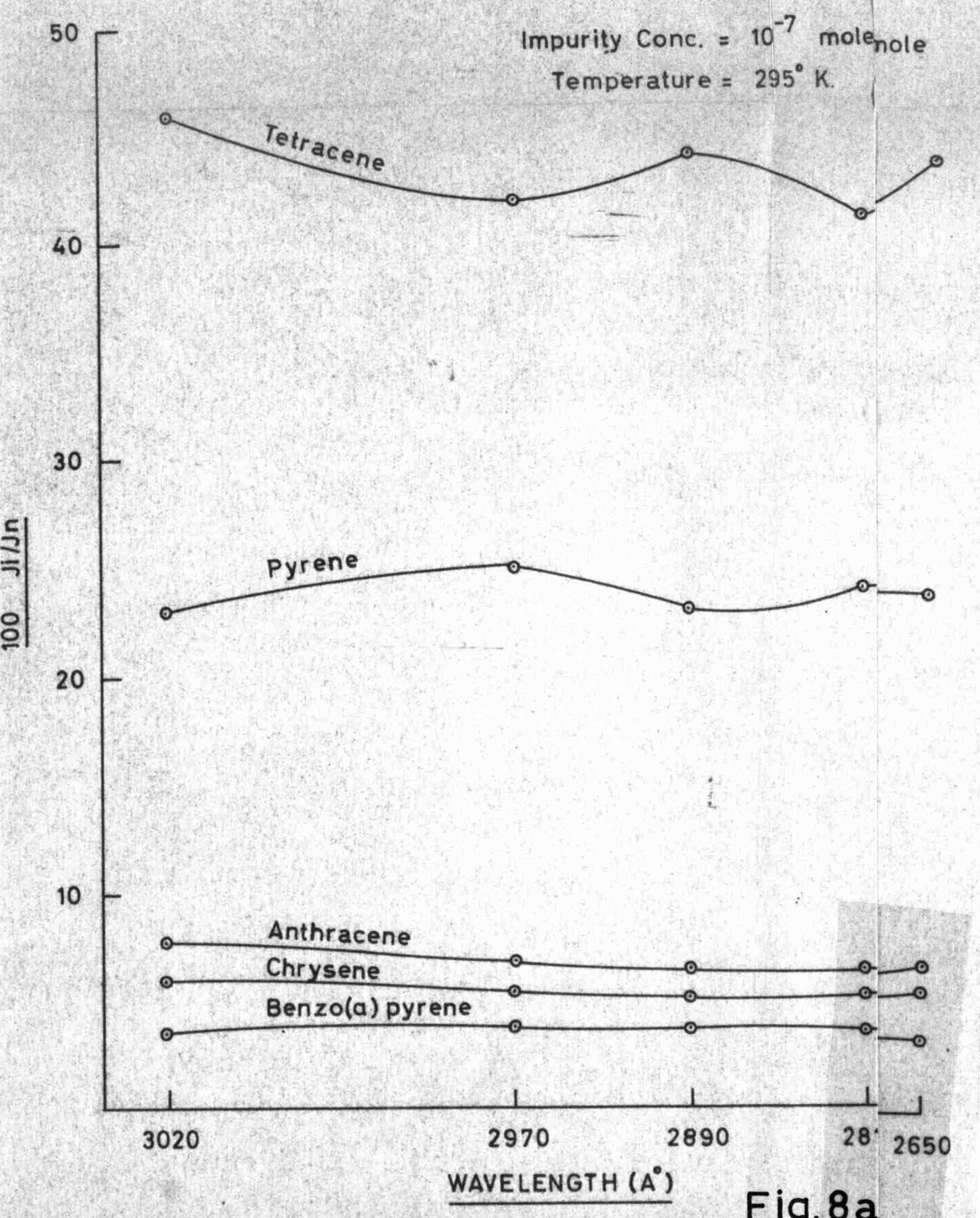
Impurity Conc. = 10^{-7} mole/mole
Temperature = 295° K.
50
40
30
20
10
100 Ji/Jn
Tetracene
Pyrene
Anthracene
Chrysene
Benzo(a) pyrene
3020
2970
2890
28
2650
WAVELENGTH (A°)

Fig. 8a

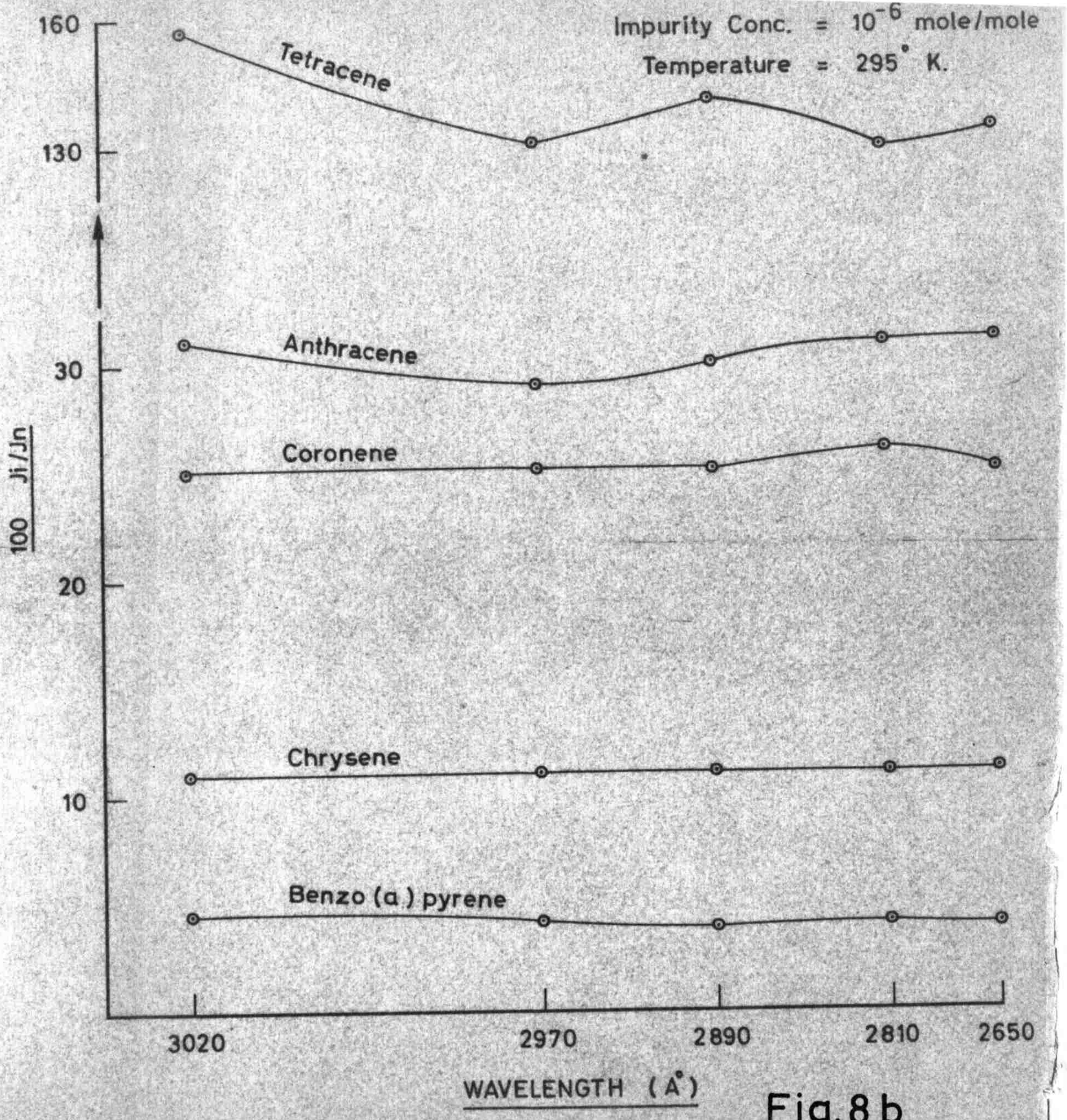
Impurity Conc. = 10^{-6} mole/mole
Temperature = 295° K.
160
130
30
20
10
100 Ji/Jn
Tetracene
Anthracene
Coronene
Chrysene
Benzo (a.) pyrene
3020
2970
2890
2810
2650
WAVELENGTH (Å)

Fig. 8 b

coefficient for naphthalene decreases with increasing wavelength in the region 3200 - 2600A^{o}. The value of the coefficient for the line 3020A^{o} is approximately half its value for the other lines whose coefficients have values that are not far from each other. This perhaps, may be the reason of why the effect is more easily observable with the 3020A^{o} line.

C. Temperature Dependence

Our data is not complete enough to enable us to give a detailed picture of the temperature effect on the transfer efficiency. J_i/J_n is measured at only two temperatures, 130°K and 295°K. Measurement of J_i/J_n over a wide range of temperatures is necessary before a thorough interpretation can be made.

With the present data, however, it is possible to compare the transfer efficiency at the two temperatures. The data shows that the value of J_i/J_n at 130°K is considerably higher than its value at 295°K for all impurities at all concentrations. This increase in J_i/J_n (at the low temperature) is more pronounced for some impurities than for others. For example the increase is about 40% when anthracene is used as an impurity, and greater than 100% when naphthacene is used. In all cases this increase was due to a relative increase in the impurity current, a fact that leads to the conclusion that J_i is greater at the low temperature. In other words the transfer efficiency is higher at the low temperature.

This increase in the transfer efficiency at the low temperature might perhaps be explained as follows. As previously mentioned, there are several competitive processes for the annihilation of excitons:

An exciton may decay giving up a photon (exciton luminescence).

<u>or</u> it may decay non-radiatively

<u>or</u> it may be captured by an impurity center where emission occurs.

The first process is greatly inhibited at low temperature.[15] The allowed optical transitions are those in which the exciton wavevector $\vec{k}$ is equal to the light wavevector $\vec{q}$ (momentum conservation). But since $\vec{q}$ is very small for visible and UV light the point $\vec{k} = \vec{q}$ is very close to $\vec{k} = 0$. Theoretical analysis shows that the lowest exciton band possesses a complicated structure and that the bottom of the band is located at $\vec{k} \neq 0$. The excited state possesses excitons with different values of $\vec{k}$, but the majority of excitons will be close to the bottom of the lowest exciton band since kT is small at low temperatures. The concentration of excitons with $\vec{k} = 0$ is then small so that luminescence without phonon participation is considerably attenuated.

Non-radiative transitions are those in which the absorbed energy is transformed into heat. This transformation may take place in different ways[18]: the excitation energy may be converted to lattice vibration energy with the aid of the interaction forces between molecules, or it may be converted to vibrational energy of the atoms making up the molecules and this vibrational energy of atoms in a molecule to vibrational energy of molecules in a lattice. The probabilities of these processes are expected to decrease when kT is small, since the displacements of molecules from the equilibrium positions are small.

Therefore it seems plausible that the probability of capturing excitons by impurity centers increases at low temperatures, thus producing an increase in the impurity emission.

REFERENCES

1) Frenkel, J., Phy. Rev., 37, 1276 (1931).

2) Bowen, E.J., Mikiewicz, E. & Smith, F., Proc. Phy. Soc., A62,26 (1949).

3) Mott & Gurney, Electronic Processes in Ionic Crystals, Clarendon Press, Oxford (1940).

4) Robertson, Organic Crystals and Molecules, Cornell University Press, Ithaca, New York (1953).

5) Lipsett and Dekker, Nature, 173, 736 (1954).

6) Northrop, D. & Simpson O., Proc. Roy. Soc. (London), A234, 136 (1956).

7) Simpson, O., Proc. Roy. Soc., A238, 402 (1957).

8) Sidman, Phy. Rev., 102, 96 (1956).

9) Agranovich, Kucherov, Faidish, Ukran. Fiz. Zhur., Vol. 2, 61-7 (1957).

10) Ferguson, J., J. Chem. Phy., 28, 765 (1958).

11) Gross, E., AN U.S.S.R., 28, No. 10, 11-19 (1958).

12) Nikitine, S., Phil. Mag., S. 8, Vol. 4, 1 (1959).

13) Ganguly, S. and Chaudhury, N., Rev. Mod. Phy., 31, 990-1017 (1959).

14) Rousset, A., Lochet, R., Lacueille, R. and Meyer, Y. C.R. Acad. Sci. (Paris), Vol. 248, 2045-8 (1959).

15) Broude, V.L., Prikhot'ko, A.,Rashba, E., Soviet Phy. Uspekhi, 67, 38-49 (1959).

16) Kazzaz, Thesis, American University of Beirut (Jan. 1961).

17) Agranovich, Faidish, Optica i Spect., 1, 983-7 (1956).

18) Davydov, Theory of Molecular Excitons, Translated by M. Kasha and M. Oppenheimer, McGraw-Hill, (1962).

19) Shpak and Sheka, Bull. Acad. Sci. (USSR) Phy. Ser., 24, 559-61 (1960).

20) Schoental & Scott, J. Chem. Soc. (1949), Page 1683.

21) Moodie & Reid, J. Chem. Phys. 20, 1511 (1952).

22) Cohen and Weinreb, Proc. Phy. Soc., 75, 623-5 (1960).

23) Hochstrasser, Rev. Mod. Phy., 34, 531-50 (1962).

24) Naboikin, Y., Dobrokhotova, V., and Uglanova, V., Optics & Spect., 12, 364 (1962).

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