

ON THE LUMINESCENCE OF SOME ORGANIC PHOSPHORS UNDER X-RAYS AND CATHODE RAYS.

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INTRODUCTION

The visible part of the luminescence spectra of anthracene, naphthalene, phenanthrene, triphenylmethane and diphenyl, under X-ray excitation were measured and reported earlier (Bose, 1945, 1948); the measurements have now been extended to the near ultraviolet region and in the present paper are reported the luminescence spectra of these samples under X-rays as well as cathode rays at room temperature (300°K.) and at liquid oxygen temperature. The long period decay exhibited by some of these compounds under cathode rays have been studied and their thermoluminescence curves measured.

The samples were purified by vacuum distillation and their luminescence spectra under ultraviolet excitation measured for the sake of comparison; as the same specimens have been used in all cases, the effect of impurity if any, is the same in different cases.

EXPERIMENTAL METHOD.

The experimental arrangement for X-ray excitation is essentially the same as that reported by Bose (1945, 1948); for low temperature work, the substance is rubbed in thin layer on the flattened surface of a tube containing liquid oxygen and it is enclosed in a larger tube which can be evacuated. The open end of the inner tube projected outside and is the inlet for liquid oxygen. The outer tube has two windows covered with aluminium foil and quartz plate respectively for introducing the X-ray beam and for the transmission of luminescence light (Chatterjee, 1950). X-rays from a copper target at 40 kV. with 10 m.a. were generally used for excitation.

In the case of cathode ray excitation, the cathode ray tube described by Bose and Sharma (1950) could be used for these samples also. The phosphors were excited by electrons of energy 2-5 kV. and even less where possible. Evaporation of the specimens is greatly reduced at low temperature and the stability of proper discharge condition can be realised by maintaining a high speed of vacuum. Even if the sample evaporates completely, fresh samples can be deposited on the cooled surface of the sample holder by sublimation of specimen introduced into the vacuum chamber. The whole system (cathode ray tube together with the suction line) should be thoroughly cleansed before working with separate phosphors. The measurements on decay and thermoluminescence of some of these organic compounds have been carried out with the help of photomultiplier tubes; the details of the experimental arrangements for recording the decay and glow curves have been described elsewhere by Bose and Sharma ('On the long period afterglow of alkali halides under cathode rays'—to be published shortly).

RESULTS AND DISCUSSIONS.

The luminescence spectra of these compounds consist of a number of bands which become quite sharp at liquid oxygen temperature. It has been found that the luminescence spectra under X-rays or cathode rays are not always the same as those exhibited under ultraviolet excitation; in general, a larger number of bands are emitted in the former case. The spectrum emitted under X-ray and cathode ray excitation is, however, identical in all the cases studied except for naphthalene. The phosphor specimens, of course, get spoilt by cathode ray irradiation for more than few minutes. Hence the luminescence spectra under cathode rays were taken with a comparatively wider slit. As a consequence, the closely spaced weaker components which could be measured from X-ray luminescence spectrum were, in some cases, lost due to overlapping in the case of cathode ray luminescence.

Under X-ray and cathode ray excitation most of these compounds show at liquid oxygen temperature a measurable afterglow which is most remarkable for triphenyl methane and can be seen even at room temperature in this case. Under cathode rays, the intensity as well as the persistence of afterglow is very prominent. The measurement of decay and glow curves have thus been carried out for some of these compounds under cathode ray excitation only. In recording the glow curves for these substances, it has been observed that as heating proceeds with consequent evaporation of the substance, the discharge tube is gradually filled up with its vapour, and sudden flashes of light are frequently emitted by the gaseous mass. This is evidently due to the fact that emission by collision processes occurs from the excited molecules which have passed into the gaseous state; this is perhaps one of the reasons why the glow peak which is a measure of the stored up energy of the phosphors, is so shallow in the case of organic phosphors. It has been verified that thermoluminescence exhibited by these compounds is no fortuitous effect. The sample after being excited at liquid oxygen temperature, may be quickly taken out of the discharge tube, and increased intensity of emission on simple touching or pouring warm water can be easily observed in a dark room.

Naphthalene:

The luminescence spectrum of naphthalene under X-ray excitation consists of a number of diffuse bands extending throughout the visible region together with a group of closely spaced sharp bands in the region 330–450 $m\mu$. The ultraviolet group of bands is very intense and can be recorded very easily while the comparatively weaker emission in the visible region can be obtained only with long exposure. Under ultraviolet excitation naphthalene emits only the group of bands in 330–450 $m\mu$ region. At liquid oxygen temperature, the visible part of the emission is still more reduced in intensity and the u.v. band system is usually obtained by X-ray excitation; the band system shifts towards the shorter wavelength side and becomes sharper at low temperature. The ultraviolet band pattern is absent in the luminescence spectrum excited by cathode rays; because of the low temperature, the emission bands in the visible region attain linelike sharpness and are resolved into several components.

The ultraviolet bands of naphthalene excited by X-rays show an almost mirror image symmetry with the strong 260 $m\mu$ absorption of solid naphthalene terminating at 295 $m\mu$. Thus these two systems seem to belong to the same group of electronic transitions, ${}^1A_{1g} \leftrightarrow {}^1B_{2u}$. Seshan (1936) from his absorption data has assigned vibration frequencies of 260 $cm.^{-1}$ and 460 $cm.^{-1}$ for the ground and excited states of solid naphthalene respectively with 327 $m\mu$ ($= 30580 \text{ cm.}^{-1}$) as the longest wavelength limit of (260 $m\mu$) absorption bands of solid naphthalene. The mean vibration frequencies of 220 $cm.^{-1}$ and 470 $cm.^{-1}$ for the ground and excited state respectively are obtained from the ultraviolet fluorescence bands of naphthalene.

The emission bands in the visible region cannot be correlated with ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transition and seems to have a separate origin. There is nothing to indicate whether or not the higher excited states $B_{1u} \rightarrow A_{1g}$ or $B_{3g} \rightarrow A_{1g}$ (forbidden) are involved in the emission process. This also does not explain the low intensity of visible emission under X-rays or the absence of u.v. bands under cathode rays, although luminescence in both cases takes place through identical processes, i.e., through the intermediary of secondary electrons. It is possible that naphthalene is unstable under cathode rays and the unstable products or their recombination are responsible for these bands. In the case of cathode rays, electrons are absorbed within a thin layer and so the effect is greater. That similar results are not obtained with other phosphors studied so far is not quite clear.

TABLE I.
Luminescence spectrum of Naphthalene.

Under X-ray excitation.				Under cathode ray excitation.	
At 300°K.		At 90°K.		At 90°K.	
Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$	Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$	Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$
330.0	320	327.5	190	539.0	370
333.5	515	329.0	235	550.0	100
339.3	460	332.1	435	553.5	160
344.7	355	337.0	220	558.0	190
349.0	195	339.5	300	564.0	130
351.5	320	343.0	560	568.5	150
355.4	430	349.7	345	573.5	120
360.9	655	354.0	215	577.0	640
369.6	705	356.7	220	590.0	380
379.5	475	359.5	265	613.0	160
386.5	255	363.0		619.0	100
390.3	240			623.5	180
394.0	440			630.5	100
401.0	580			634.0	
410.5(?)	1965				
446.5					

Diphenyl:

The measurements of the luminescence spectra of diphenyl under X-rays and cathode rays are given in Table II. Besides these, diphenyl emits a number of

bands in the visible region which were measured by Bose (1948) with a glass spectrograph; these are comparatively weaker and have been omitted in the present measurement. Under the ultraviolet excitation of diphenyl, only four bands are obtained: 430, 409, 391 and 370 $m\mu$. The luminescence spectrum under X-rays and cathode rays is identical except that in the case of cathode ray excitation some of the weaker structures are lost due to overlapping because of greater slit width. The lowering of temperature has no marked effect on the positions of the band maxima, though greater accuracy in the measurement of the band positions can be attained due to the increased intensity and sharpness of the bands at liquid oxygen temperature. As the same samples have been used in different cases, it is to be surmised that additional emission bands of diphenyl under X-rays or cathode rays are due to some changes introduced in the crystal by this method of excitation.

TABLE II.
Luminescence spectrum of Diphenyl.

Under X-ray excitation.				Under cathode ray excitation.	
At 300°K.		At 90°K.		At 90°K.	
Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$	Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$	Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$
353.0	240	351.0	240	353	320
356.0	300	354.0	150	357	390
359.8	120	355.0	160	362	740
360.0*	670	357.9	200	372	140
362.8*	230	360.5	250	374	970
370.8	430	363.8	420	388	330
380.1	770	369.4	120	393	1050
391.5*	180	371.0	210	410	1240
408.8	1304	374.0	490	432	1460
431.8	1330	381.0	360	461.5	
458.0	730	393.0	870		
474.0		407.0	390		
		414.4	970		
		431.8	1340		
		458.3			

Phenanthrene:

The luminescence spectra of phenanthrene are given in Table III. According to Pringsheim (1943), the blue emission of phenanthrene is due to the traces of anthracene contained in it. On comparison with the luminescence spectrum of

TABLE III.
Luminescence spectrum of Phenanthrene.

Under X-ray excitation at 300°K.		Under cathode ray excitation at 90°K.	
Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$	Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$
385.0	330	385.0	330
390.0	1190	390.0	580
409.0	1270	399.0	430
431.5	1390	406.0	530
459.0	1470	415.0	900
492.0		431.0	300
		456.5	

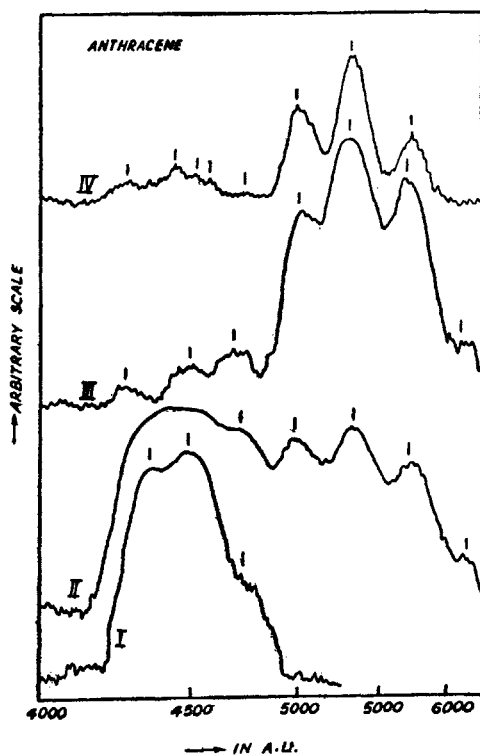


FIG. 1. Microphotometer records (reduced to half size) of various anthracene samples under X-rays. I—Pure. II—Anthracene containing slight traces of Naphthacene. III—Anthracene (Merck). IV—Ordinary anthracene (B.D.H.).

pure anthracene (Table V) it is surmised that the bands 492, 459, 431 are possibly due to anthracene of which the band 459 may be due to the overlapping of the bands 446 and 469 of pure anthracene. At low temperature, under cathode ray excitation the bands due to phenanthrene are resolved into further components.

Phenanthrene emits the same spectrum under X-rays, cathode rays or ultra-violet excitation. This shows that phenanthrene molecules are rather stable under X-rays or cathode rays. The presence of anthracene as impurity does not seem to interfere with the emission of phenanthrene and two systems emit quite independently.

Phenanthrene shows a long period afterglow; the decay of afterglow has been measured for cathode ray excitation at liquid oxygen temperature. The Intensity-time plots are shown in Figs. 2, 3. It is found that the semilog plot is nearly but not exactly a straight line. This non-exponential form of the decay can be due to the presence of two different emitting systems, anthracene and phenanthrene.

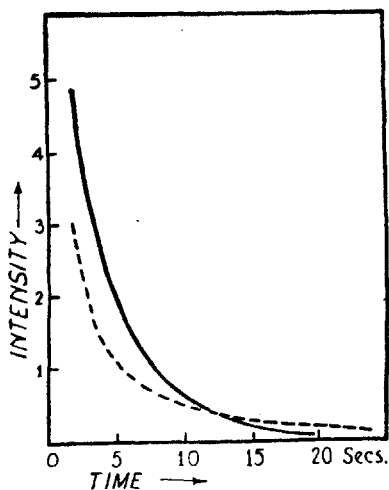


Fig. 2. The after-glow curves of Triphenylmethane (continuous) and Phenanthrene (dotted) with cathode rays excitation at liquid oxygen temperature.

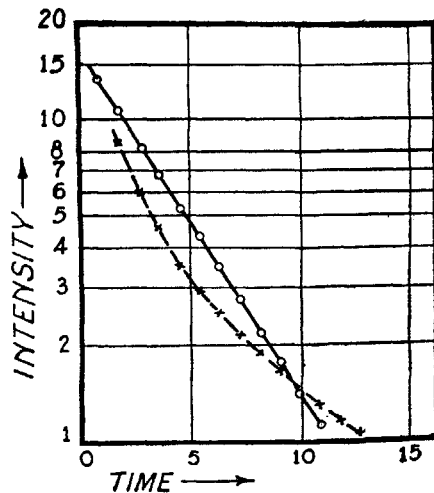


Fig. 3. After-glow curves of Triphenylmethane and Phenanthrene (dotted) plotted on semilog graph paper.

The glow curve of phenanthrene has also been measured; the glow curve (Fig. 4) consists of more than one shallow and extended peaks overlapping with each other, so that the trap depths could not be calculated. The presence of a weak peak observed in the case of anthracene is also suspected in the glow curve.

Triphenylmethane:

A continuous absorption spectrum ranging from 700–230 $m\mu$ is reported for triphenylmethane (Seshan, 1936). When excited by ultraviolet rays an almost continuous emission (500–406 approx.) is obtained; weak maxima which nearly agree with the band maxima of the X-ray luminescence spectrum in this region (471, 464, 447, 427 $m\mu$) can be suspected. The luminescence spectra of triphenylmethane under X-ray and cathode ray excitation is given in Table IV. In these cases, the emission consists of a number of discrete bands extending throughout the whole of the visible region. At liquid oxygen temperature, the bands are very

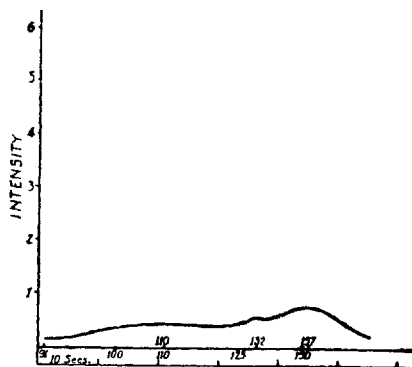


FIG. 4. Thermoluminescence record of Phenanthrene starting at liquid oxygen temperature with cathode rays excitation.

TABLE IV.

Luminescence spectrum of Triphenylmethane.

Under X-ray excitation at 300°K.		Under cathode ray excitation at 90°K.	
Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$	Wavelength in $m\mu$	$\Delta\nu$ in $cm.^{-1}$
426.5		427.0	
	1050	450.0	1200
446.5		459.0	430
	870	517.0	2450
464.5		538.0	750
		550.0	410
		558.0	260
		564.0	190
		577.0	400
		590.0	480
		631.0	1100

sharp and split up into several components. X-ray luminescence spectrum taken at room temperature, thus consists of diffuse bands which do not agree well with those obtained under cathode rays at liquid oxygen temperature.

Triphenylmethane has a perceptible afterglow under X-rays even at room temperature. At liquid oxygen temperature, under cathode rays, the afterglow increases greatly in intensity and persistence. The long period decay curve is shown in Figs. 2, 3. The semilog plot is a straight line; thus the decay is

exponential. No perceptible difference in the decay curve is obtained for different spectral region.

The glow curve of triphenylmethane under cathode ray excitation has been measured and is shown in Fig. 5; the glow peak with glow temperature at 215°K. is prominent while another peak at about 149°K. is also suspected. Triphenylmethane thus has got at least two meta-stable states.

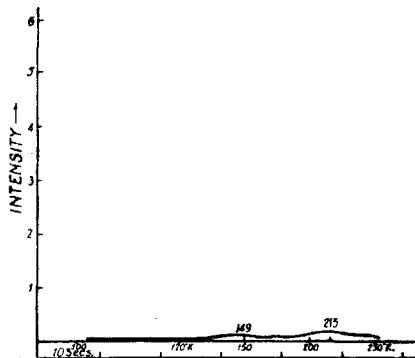


FIG. 5. Themoluminescence record of Triphenylmethane starting at liquid oxygen temperature with cathode rays excitation.

Anthracene:

In the present investigation, anthracene, pure, and with different percentages of naphthacene, have been worked with. The measurements are given in Table V.

The luminescence spectrum in all cases is the same under X-rays, cathode rays and u.v. excitation. In anthracene containing 0.2% of naphthacene, bands due to anthracene are very weak and can be obtained only after long exposure. When naphthacene concentration is reduced ($\sim 10^{-5}$), the emissions due to anthracene and naphthacene are of equal intensity. Shifts in the band positions in different cases, of course, take place, and at liquid oxygen temperature under cathode rays the emission bands are considerably sharpened and number of bands is increased.

The mechanism for the transfer of energy from anthracene to naphthacene molecules has been a matter of controversy (Bowen, E. J., and others, 1938, 1944, 1947, 1949 and Ganguly, S. C., 1944 and 1945). Bowen made elaborate measurements on the luminescence of anthracene-naphthacene system and has come to the conclusion that some type of resonance or exciton transfer of electronic energy takes place in this system.

Under X-rays at room temperature the emission spectrum of pure anthracene consists of 492, 469, 446, 431; of these, 446 $m\mu$ is very strong and 431 does not seem to be a single band. For anthracene containing naphthacene this band system is greatly reduced in intensity, but the most intense band 446 $m\mu$ is affected to a greater extent than any other. According to Ganguly, the absorption spectra of the crystal (containing naphthacene) shows a continuous band shorter than 405 $m\mu$, due to anthracene, and absorption bands at 435, 460 and 491 $m\mu$ which are associated with naphthacene. The relatively greater quenching for the shorter wavelength emission bands of anthracene cannot be explained by the process of self absorption unless stronger absorption bands in the corresponding regions are assumed (or continuous absorption).

A very small quantity of purified anthracene could be procured, and so the luminescence spectrum of pure anthracene under cathode rays was not taken (in



(a)



(b)



(c)



(d)



(e)



(f)



(g)



(h)



(i)

Fluorescence spectra of some organic substances. (a) Anthracene pure under X-rays; (b) Anthracene containing traces of Naphthacene under X-rays. (c) Anthracene (Merck) containing greater amount of Naphthacene under X-rays, (d) Triphenylmethane under X-rays, (e) Naphthalene under X-rays at liquid oxygen temperature, (f) Diphenyl under cathode rays at liquid oxygen temperature, (g) Phenanthrene under cathode rays at -184°C ., (h) Naphthalene under cathode rays, (i) Triphenylmethane under cathode rays at liquid oxygen temperature.

(h) and (i) have been photographed with glass spectrograph while (a) to (g) with a quartz spectrograph.

discharge tube the sample is lost by evaporation). At liquid oxygen temperature, as is observed in the luminescence spectra under cathode rays, the emission due to anthracene in anthracene-naphthacene system gains in relative intensity. This seems to indicate that energy transfer is dependent on temperature.

TABLE V.

(1) *Pure anthracene under X-rays at 300°K.*

Wavelength in A.U.	Wave numbers cm. -1	$\Delta\nu$ cm. -1	Remarks.
4310	23200	780	The measurements published earlier (Bose, 1947) were made on anthracene containing 0.2% of naphthacene; as a matter of fact, the pure anthracene bands are not at all present there.
4460	22420	1120	
4695	21300	990	
4925(?)	20310		

(2) *Anthracene with about .005% of naphthacene.*

Under X-rays at 300°K. in A.U.	Under cathode rays at 90°K. in A.U.	Remarks.
6520	?	Both anthracene and naphthacene bands are present in almost equal intensity. At low temperature the relative intensities of anthracene bands are increased.
5760	?	
5365	5360	
5010	5240	
4730	5040	
?	4810	
?	4710	
..	4450	
..	4250	
..	4210	

(3) *Anthracene with 0.2% of naphthacene.*

Under X-rays at 300°K. in A.U.	Under cathode rays at 90°K. in A.U.	Remarks.
6320	?	Anthracene bands are very poor in intensity; at low temperature the relative intensity of the anthracene emission is increased.
5755	?	
5360	5370	
5055	5010	
4725	4710	
4485	4559	
4270	4435	
..	4230	
..	4135	

At liquid oxygen temperature anthracene containing naphthacene shows afterglow. The decay of afterglow has been measured with a cathode oscillograph. The decay measurements were carried out separately for anthracene and naphthacene emissions isolated by suitable filters. It has been observed that the decay curves

are practically identical. In the glow curve for anthracene-naphthacene system, a very weak peak is observed.

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ABSTRACT.

The luminescence spectra of Naphthalene, Diphenyl, Phenanthrene, Triphenyl methane, Anthracene, etc., excited by X-rays and cathode rays at room temperature as well as at liquid oxygen temperature are reported in this paper. Most of these phosphors show a long period afterglow. The decay of the long period afterglow of some of these phosphors under cathode rays has been measured at liquid oxygen temperature; the glow curves for some of these samples have also been recorded.

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