

LUMINESCENCE OF SOME ORGANIC COMPOUNDS
UNDER X-RAY EXCITATION

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Plates XI-A and XI-B

ABSTRACT. The luminescence spectra of uranyl nitrate, triphenyl-methane, naphthalene, diphenyl and mixtures of anthracene and naphthalene excited by X-ray have been reported in this paper. The spectra of naphthalene and diphenyl show a greater number of bands than were reported earlier. The mixtures of anthracene and naphthalene emit separate band systems of both the constituents, though shifts in position as well as changes in relative intensities are observed. Triphenyl-methane, which shows a measurable afterglow, has got no special feature in its luminescence spectrum distinguishing it from other molecular phosphors.

The results of investigations on the luminescence spectra of some of the well known molecular compounds have been reported in this paper, which include the repetition of some of the earlier works (Bose, 1945) with improved technique yielding increased intensity of luminescence and greater precision.

The luminescence spectra of organic compounds by X-ray excitation has attracted little attention up till now. Excitation in these cases takes place through the intermediary of photo-electron produced inside the crystal by the incident photons so that it is possible to assume a large number of photo-electrons of different energies inside the crystal at any instant; besides, it is quite possible that in these cases emission takes place in molecules already ionised by the primary X-rays, which fact is expected to be reflected in the spectra. In ultra-violet excitation, direct excitation of the optical levels takes place; difference in the probabilities of excitation of optical levels by photons and photo-electrons, if there be any, should tell upon the intensity distribution of the spectra. Moreover, the incident photons being of very high energy compared to that of the optical levels the intensity of different lines should depend only on the corresponding transition probabilities. These features are expected to make the study of X-ray luminescence spectra interesting and of important consequences.

RESULTS AND DISCUSSIONS

The results of the present measurement are shown in Table I the spectrograms and some of the microphotographs are given in plates XI-A and XI-B. As expected the spectra in all cases consist of a number of bands; the width

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of the bands are not same throughout and it is possible that some of them are composed of more than one component. The width in general increases perceptibly on the higher energy region. This can also be easily understood from our ideas about the energy states of these molecular crystals. In these crystals, optical transition takes place within the same molecular group, whose energy levels are very little affected by the crystalline field; the levels remain rather sharp, observed breadth being due to either the thermal vibration of the lattice or superposition of one or more lines. In spite of the fact that the molecular character of the energy states are preserved in these crystals, the higher energy part of the spectra in which the higher energy levels are involved, will be comparatively more affected by the surrounding neighbours.

TABLE I
Peaks of the luminescence spectra in ÅU

| | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) |
|---------------------------------|------|------|------|------|------|------|------|------|------|------|
| Uranyl nitrate | 6208 | 5913 | 5635 | 5370 | 5137 | 4962 | | | | |
| Triphenyl methane | 6000 | 5780 | 5390 | 5250 | 4710 | 4620 | 4490 | 4290 | | |
| Naphthalene | 6300 | 5900 | 5850 | 5410 | 5000 | 4640 | 4355 | 4135 | | |
| Diphenyl | 6306 | 6210 | 6035 | 5700 | 5360 | 5160 | 4950 | 4580 | 4290 | 4150 |
| Anthracene + 10% of Naphthalene | 6285 | 5830 | 5392 | 5073 | 4740 | 4560 | | | | |
| Naphthalene + 10% of Anthracene | 5720 | 5295 | 4945 | 4670 | 4465 | | | | | |

The emission due to uranyl nitrate (Plate XI-A f) consists of six almost equidistant well separated bands. These agree in position very closely with those obtained by ultraviolet excitation in the solid state and in solution. The emission thus takes place entirely within the molecular group UO_2 to which is attributed the optical behaviour of uranyl compounds. Excitation in the present case takes place through the intermediary of the photo-electrons which are produced by the incident X-rays inside the crystal in large number and of different energies. Absence of any afterglow in this case is also due to the same reason. There is, however, one important difference between ultraviolet and X-ray excitation. In former, fluorescence, though weak, is observed even in solution whereas in latter case fluorescence, ceases when the lattice breaks up in all substances. The existence of absorption and fluorescence under ultraviolet radiations indicates that the corresponding energy states of the molecular group remain intact, as is expected. This only indicates that photo-electrons produced inside the crystal can no longer excite the said electrons in the absence of the crystalline field, at least probability of such in elastic collisions is very much reduced. Whatever may be the reason, the presence of crystalline field greatly facilitates the inelastic colli-

sions of the photo-electrons moving through the crystal, with the optical electrons of the said molecular groups, which is necessary for emission; whenever the lattice breaks up, either on melting or in solution, the photo-electrons lose their energy mostly by other non-radiative processes (elastic collision, etc.).

The luminescence spectrum of tri-phenyl methane, shown in Plate XI-A (e) is similar to those of other molecular compounds and consists of a number of bands which extend throughout the entire visible region and (possibly in the ultraviolet region also) generally increase in width with frequency. Tri-phenyl methane is the only organic phosphor so far obtained, which shows a measurable afterglow under X-rays, which should make its study all the more interesting.

The spectra of naphthalene and diphenyl show a marked improvement in intensity and an increase in the number of bands; the distribution of the bands throughout the visible region makes us believe that the spectra extend into the ultraviolet region.

The luminescence spectrum of anthracene with ten per cent of naphthalene dissolved in it and that of naphthalene with ten per cent. of anthracene dissolved in it are shown in Plate XI A (a) and (b), respectively. The two compounds in each case emit almost independently; slight changes in positions and in intensity distribution take place. Absence of the weaker bands in each case does not indicate any characteristic quenching. The measurements reported by Pringsheim, in the case of ultraviolet excitation are also of the same nature (Pringsheim, 1939).

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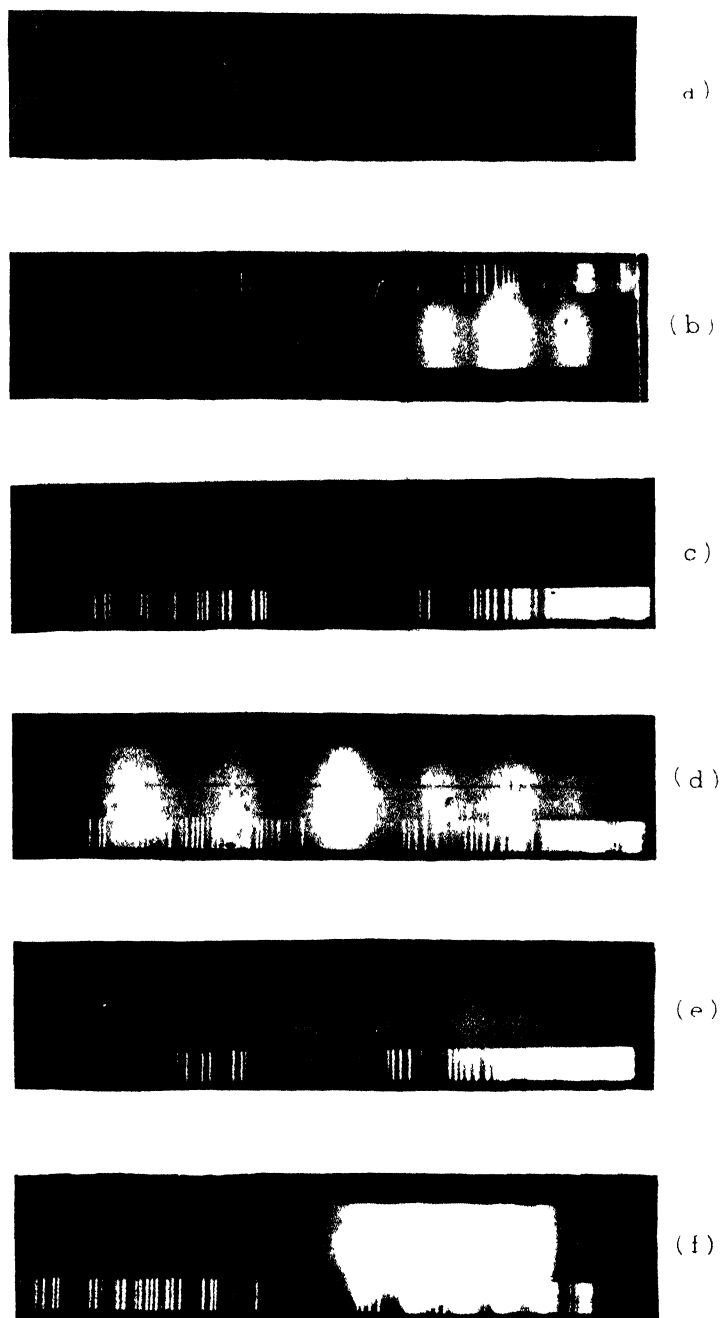


Fig 1

Luminescence Spectra

- (a) Naphthalene + 10% anthracene
 (b) Anthracene + 10% naphthalene
 (c) Diphenyl (d) Naphthalene
 (e) Triphenyl methane (f) Uranyl nitrate.

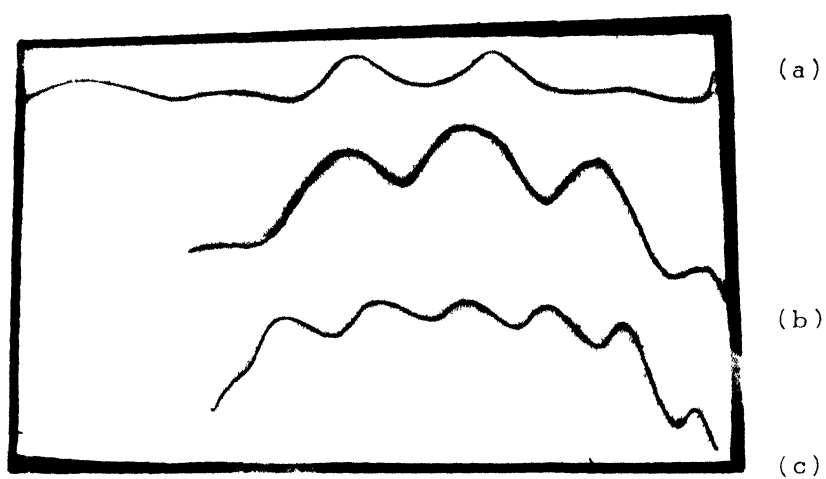


Fig 2

Microphotometric curves of the luminescence spectra (reduced)

- (a) Naphthalene + 10% of anthracene
- (b) Anthracene + 10% of naphthalene
- (c) Uranyl nitrate