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On the Fluorescence Spectra of Naphthacene in Solid Solution of Anthracene for Different Exciting Wave-Lengths

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The fluorescence of green anthracene crystal (naphthacene in solid solution of anthracene) has been studied with exciting light of different wave-lengths and the long wave-length limit for excitation has been found. From the study of the fluorescence and absorption spectra an attempt has been made to interpret the mechanism of the fluorescence phenomenon in this crystal.

INTRODUCTION

THE naphthacene molecule fluoresces brilliantly when it is in the state of a solid solution in anthracene. E. J. Bowen attempted to interpret the mechanism of this fluorescence. Owing to its high brilliance, the fluorescence of this solid solution has attracted the attention of different workers¹ in the field of the study of fluorescence. Naphthacene has both absorption and fluorescence bands in the visible spectrum; its absorption and fluorescence bands remain the same in solid, solution, and vapor states except for a little shift depending upon the medium surrounding the molecule; the absorption and fluorescence bands are like object and image in a mirror. In consideration of the above facts the substance is quite suitable for studying the influence of frequency of the incident radiation. When studying fluorescence, usually ultraviolet light from the Hg arc is used as the source of exciting radiations and by suitable filter the wave-lengths longer than the exciting radiation are cut off. By using incident radiation of this nature, it is therefore not possible to observe the relation between the incident and fluorescent radiation critically. We have used white light as the source of radiation and from its spectrum we have chosen the exciting radiation we wish. This has the advantage over mercury or any other arc spectrum in that we can have any desired wave-length, which may not be available in the arc spectrum.

EXPERIMENTAL

The experimental arrangement for studying the fluorescence bands of the crystal was as

¹ K. S. Krishnan and P. K. Seshan, *Acta Phys. Polon.* **5**, 289 (1936); E. J. Bowen, *Nature* **142**, 1081 (1938).

follows: The light from a coiled-coil lamp, rendered convergent by a lens, illuminated the slit of the spectrograph. The spectrum was received on a screen with a movable slit. The light passing through the slit was converged by another lens and the crystal was illuminated. The fluorescent light issuing from the crystal together with the exciting light was received by a lens at a suitable angle, and was received on the slit of another spectrograph. The crystal was excited by radiation of wave-length 460, 475, 490 $m\mu$ where the first and last are within the absorption bands of the crystal and 475 is in the non-absorbing interval. The spectra were taken under identical conditions. Time of exposures were the same. Photographs were taken on the same plate. The current was kept fairly constant in all the three exposures.

RESULTS

The absorption spectra of the crystal shows a continuous absorption band shorter than 405 $m\mu$, which is owing to anthracene and absorption bands at 435, 460, and 491 $m\mu$ which are owing to naphthacene (Fig. 1). The absorption spectra were taken in the usual way. Pure naphthacene absorbs at 425, 453, and 485 $m\mu$. In this crystal naphthacene molecule fluoresces, having the positions of the bands at 498, 533, 574 $m\mu$. By using monochromatic exciting radiation of various wave-lengths, we find the following results.

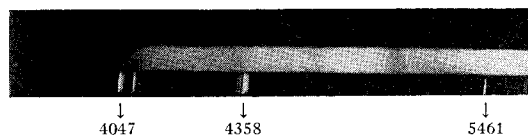


FIG. 1. Absorption spectra of the crystal of anthracene containing traces of naphthacene.

1. The crystal does not give any fluorescence if the incident radiation is of wave-length longer than the longest absorption band of the crystal.

2. The positions and number of the fluorescence bands of naphthacene are independent of the exciting wave-length, as long as the wave-length is not longer than its lowest absorption band.

3. With the change of frequency of the incident radiation, we find a change of intensity of the fluorescence bands; the intensity is greater when the incident light wave is an absorption band of the substance. The change of intensity is practically the same for all the fluorescence bands of the substance (Fig. 2).

4. If the crystal is excited by strong ultraviolet radiation from a Hg arc (3650, 4047Å), in addition to the characteristic fluorescence bands of naphthacene we get four more fluorescent bands at 400, 414, 440, 468 $m\mu$ which are the characteristic fluorescent bands of anthracene (Fig. 3).

The variable distribution of the energy of the spectrum from which monochromatic beam has been isolated cannot be the reason of the difference of intensity at 460, 475, 490 $m\mu$. The

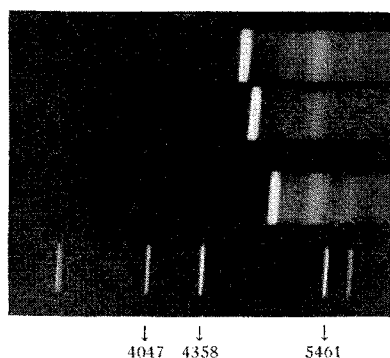


FIG. 2. Fluorescence spectra of naphthacene, excited by $\lambda 4910$, $\lambda 4750$, $\lambda 4600$.

incandescent lamp used had a perfectly continuous spectrum and the difference of intensity between two neighboring points 460, 475, and again between 475, 490 $m\mu$, is not sufficient for the considerable fall of intensity in the first case and considerable rise of intensity in the latter case.

The results are tabulated in Table I.

In order to find the critical wave-length of excitation we have changed the wave-length of the exciting light wave by changing the movable

slit of the monochromator. From the plate it is evident that so long as the exciting radiation lies inside the absorption band, its intensity is quite high and as it goes beyond it the intensity is diminished, and when it is well beyond the longest absorption band on the longer wave-length side, no fluorescence is observed (Fig. 4).

The crystal has two long limiting wave-lengths for excitation: one for anthracene and the other for naphthacene. If the exciting radiation lies

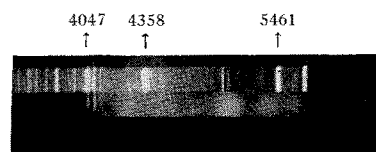


FIG. 3. Fluorescence spectra of the crystal of anthracene containing traces of naphthacene. Excited by $\lambda 3650$, and $\lambda 4047$ of the Hg arc.

within the longest absorption band of anthracene, both the fluorescent bands of anthracene and naphthacene are present, but if it is longer than the longest absorption wave of anthracene but shorter than or equal to the longest absorption wave of naphthacene, the fluorescent bands of naphthacene alone are present.

CONCLUSION

That all the fluorescence bands of naphthacene are excited by monochromatic radiation of any wave-length within the longest absorption band of naphthacene is interesting. As the exciting radiation is changed from one absorption band to the other through a non-absorbing interval, we find a change of intensity of the fluorescence bands in accordance with the change of absorption by the substance. We have not measured the intensities of the light emitted and absorbed, but we observe that when the exciting light wave coincides with the absorption band of naphthacene the intensity of fluorescence is increased. Naturally we have reasons to believe that the fluorescence yield depends upon the intensity absorbed. From the above facts and also from the study of its absorption bands we think that the mechanism of fluorescence of naphthacene is as follows: A naphthacene molecule by absorbing light energy is raised to various states of higher energy and all of them come to the lowest

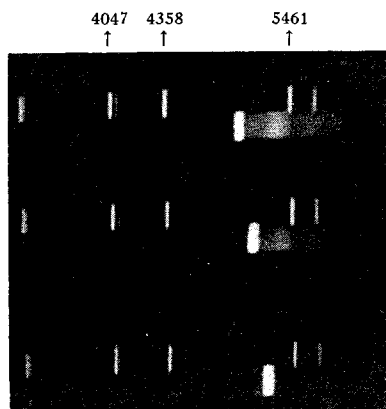


FIG. 4. Fluorescence spectra of naphthacene, excited by different wave-lengths. It shows the long wave-length limit for excitation.

vibrational level of the higher state. All the fluorescence of naphthacene comes from this level which is reached by degradation of electronic and vibrational energy.

Bowen² observed brilliant fluorescence of naphthacene in the solid solution of anthracene and compared it with the typical inorganic fluorescent solid such as zinc sulphide in presence of copper, etc. As the absorption bands of anthracene lie on the short wave-length side of those of naphthacene and the two do not overlap, there is reason to believe that in this crystal naphthacene molecules are the activators. Bowen sup-

² E. J. Bowen, *Nature* **142**, 1081 (1938).

posed that anthracene molecules after absorbing light energy give it to naphthacene and so naphthacene fluoresces. But our findings that the naphthacene fluoresces quite nicely even when the exciting light wave is longer than the longest absorption band of anthracene, and that the intensity of fluorescence of naphthacene depends only upon the quantity of light absorbed contradict the above suggestion.

It is interesting to note that the intensity of the fluorescence bands is stronger when the wave-length of the exciting radiation is $490\text{ m}\mu$ than when it is $460\text{ m}\mu$ though both of them are absorption bands of the crystal. From the plate

TABLE I.

Absorption bands	Relative intensity visual	Exciting radiation	Fluorescence bands	Relative intensity visual
435		460	498, 533, 574	2
460	2	475	498, 533, 574	1
491	3	491	498, 533, 574	3

it is evident that extinction coefficient of the absorption band at $490\text{ m}\mu$ is larger than that of $460\text{ m}\mu$. These facts qualitatively support the view that the efficiency is independent of exciting wave-length.

The author wishes to express his sincere thanks to Professor K. S. Krishnan for suggesting the problem and Professor K. Banerjee for helpful discussion and keen interest taken during the progress of work.