CHAPTER - V

RESULTS AND DISCUSSION

Figures - 1 and 2

The excitation and emission spectra for the monomer specimen A, have been presented in Figures 1 and 2. The excitation spectra recorded for the emission at 430 nm, display two excitation bands at 240 and 280 nm respectively. Both these excitations exhibit a prominent emission band at 430 nm alongwith a shoulder at 520 nm.

It can further be noted that the intensity of 430 nm emission is favoured by the excitation of 280 nm.

Figures - 3 and 4

The results presented in Figures 3 and 4, correspond to the excitation and emission spectra for the as-received polymer specimen A_1. The emission spectra corresponding to 280 nm excitation shows prominent bands at 320 and 480 nm alongwith a shoulder at 420 nm [Figure-3(b)]. It is interesting to note that for the excitation of 296 nm [Figure-4(b)], the 480 nm emission diminishes in its intensity and suprisingly a new prominent emission at 520 nm appears, alongwith the well defined 320 nm emission. Emission at 420 nm can also be observed with reduced intensity.

The intensity of emission spectra at 320 nm has been considerably enhanced for 296 nm excitation compared to the 280 nm excitation.

Figure - 5

It is observed that the present polymer specimen A_2 exhibits a single excitation band at 280 nm for the corresponding emission. The emission spectra recorded for the excitation of 280 nm exhibits a well defined, high intensity peak at 320 nm, alongwith other emissions at 420, 480 and 520 nm.

Figure - 6

Figure-6 exhibits the excitation and emission spectra for the polymer specimen A_3. It can be observed that the emission spectra shows two bands at 320 and 480 nm, alongwith a shoulder at 420 nm for the excitation of 280 nm.

It is noteworthy that the intensity of 320 nm emission is suppressed compared to the intensity of 480 nm emission.

Figures - 7 and 8

The polymer specimen A_4 has been studied for its luminescence behaviour. The results are presented in Figures 7 and 8. The The emission spectra for 280 nm excitation results in a well defined isolated peak at 560 nm and a weaker peak at 320 nm. Alongwith these two, additional bands at 420 and 480 nm are also observed in the form of humps [Figure-7(b)].

It is interesting to observe from Figure-8, that for the emission of 560 nm, the excitation spectra at 280 nm is identical to that for the emission of 480 nm except for the notable increase in the intensity. This indicates that 280 nm excitation is characteristic to 560 nm emission.

Figures - 9 and 10

Figures 9 as well as 10 include the study of fluorescence spectra of polymer specimen A_5. Two excitation spectra obtained at 272 and 280 nm wavelengths are presented in Figures 9 (a) and 10 (a) respectively. The emission spectra obtained by excitation into 272 nm band [Figure-9(b)] exhibit well defined peaks at 320 and 560 nm alongwith two humps at 420 and 480 nm. Figure-10(b) shows the emission spectra for 280 nm excitation. It is observed that the emission spectra are identical to each other for 280 as well as 272 nm excitations.

It is interesting to note from Figure 10 (b) that 320 nm band appears well defined and more pronounced compared to the other bands under 280 nm excitation.

Comparison of the intensity of the emission band at 320 nm in the two Figures 9 (b) and 10 (b) clearly indicates an appreciable increase in intensity for 280 nm excitation. However, the 560 nm emission shows similar intensity level for both the excitations.

Figures - 11 and 12

The results obtained in the case of monomer specimen A compressed to a pellet are presented in Figures 11 and 12. Figure

11 (a) shows the excitation spectra of the specimen A, when compressed to a pellet at the emission of 430 nm. The emission spectra stimulated by 240 nm excitation is seen in Figure 11 (b). Figure 12 shows the emission spectra for 260 nm excitation. An enhancement in intensity can be seen for 260 nm excitation compared to the 240 nm excitation. The emission spectra exhibit two bands at 360 and 430 nm.

Figure - 13

The excitation spectra for the mechanically deformed specimen A at 460 nm emission shows, a band at 225 nm [Figure 13 (a)]. This is over and above the 240 and 260 nm excitations. The emission spectra for the excitation of 225 nm has been presented in Figure 13 (b). Here also two emission bands exist at 360 and 430 nm.

Figures - 14 and 15

The results presented in Figures 14 and 15 correspond to the excitation and emission spectra for the mechanically deformed specimen of polymer A_1. It is seen from Figure 14 (a) that two excitation bands at 252 and 272 nm are observed for 420 nm emission. For each excitation, emission spectra exhibit three bands namely, 350, 420 and 460 nm.

Figures - 16 and 17

The excitation and emission data presented in Figures 16 and 17 relate to the mechanically deformed polymer specimen A_2. The emission spectra for 252 nm excitation is seen in Figure 16 (b).

Figure 17 shows the emission spectra for 272 nm excitation. The emissions exhibited in these figures are 350, 420 and 460 nm respectively. It is observed that higher excitation intensity enhances the intensity of all the emission bands.

Figures - 18 and 19

Figure 18 (a) exhibits the excitation spectra recorded for the mechanically deformed specimen A_3 at 420 nm emission. Corresponding emission spectra for the excitations of 252 nm and 280 nm have been presented in Figures 18 (b) and 19 respectively.

Both the emission spectra show three emissions at 350, 420 and 460 nm.

Figures - 20 and 21

The fluorescence spectra of the polymer specimen A_4 in the form of pellets are shown in Figures 20 and 21. The excitation spectra shows two bands namely at 252 and 270 nm for the 420 nm emission [Figure 20 (a)]. Emission spectra excited by 252 nm is presented in Figure 20 (b), while Figure 21 shows the same for 270 nm excitation. The emission spectra show bands of moderate intensity at 350, 420 and 460 nm for both the above excitations. In the emission spectra, one observes a prominent band at 420 nm while 350 and 460nm bands are found to be weaker in nature.

Figure 22

Figure 22 exhibits the emission and excitation spectra of the mechanically deformed specimen of polymer A_5. The emission band stimulated by 252 nm excitation exhibits three emission bands namely 350, 420 and 460 nm. The 350 nm emission band becomes more prominent compared to all other polymers in the form of pellets.

Figures 23, 24 and 25

The luminescence spectra for the monomer specimen A annealed at 100°C for 2 hours in the silica boat and then air-quenched to room temperature are presented in Figure 23. Three excitation bands appear namely at 240, 248 and 272 nm for the emission of 420 nm. It is observed from the figure that for each excitation, emission spectra gives a band at 420 nm. Further, it is observed that for the higher excitation, there has been a considerable increase in the emission intensity.

The emission at 420 nm appears to be a prominent one. The emission spectra corresponding to the three excitations wavelength show exactly identical features, except their intensities.

Figures 26 and 27

The excitation spectra for the polymer specimen A_1 obtained after annealing and quenching under the similar conditions as those for specimen A, at the emission wavelength of 440 nm has been presented in Figure 26 (a). Two excitation bands namely 240 and 256 nm have been observed. Excitation into 240 and 256 nm bands result in a emission with maxima at 440 nm with a hump at 500 nm. The spectra are identical in both excitations, as can be seen from Figures 26 (b) and 27.

Figures 28 and 29

Figures 28 and 29 present the excitation and emission spectra of polymer specimen A_2, after the thermal treatment. The excitation spectra for 440 nm emission shows two bands at 240 and 256 nm respectively. The emission spectra for the specimen excited by 240 and 256 nm are identical in nature as exhibited in Figure 28 (b) and 29, both exhibit the well defined emission at 440 nm with a weaker one at 500 nm. The intensity is higher for higher excitation wavelength.

Figures 30 and 31

The excitation and emission data presented in Figures 30 and 31 relate to the specimen A_3, after annealing and quenching. It is obvious from the Figure 30 (a) that the excitation spectra recorded for 440 nm emission exhibits two bands at 240 and 270 nm respectively. The emission bands recorded corresponding to 240 270 nm excitation show identical spectra with the emission at 440 nm. Here, the emission spectra corresponding to 270 nm shows enhancement in intensity compared to that for 240 nm excitation. [Figure 30 (b) and 31].

Figure 32

The luminescence spectra for annealed and quenched polymer specimen A_4 has been presented in Figure 32. It is obvious from the Figure 32 (a) that the excitation spectra for the specimen shows a single dominant band at 240 nm. The emission spectra induced by this excitation also displays a single prominent band at 440 nm.

The intensity of emission seems to be much larger compared to the emission intensity in case of other specimens, presented earlier.

Figures 33 and 34

Figure 33 (a) illustrates the excitation spectra while Figure 33 (b) as well as Figure 34 represent the emission spectra for the annealed and quenched polymer specimen A_5. Examination of the excitation spectra shows two bands at 240 and 270 nm respectively. From the emission spectra excited by these excitations, one can observe a prominent band at 440 nm and subsidiary emission at 500 nm.

It is noteworthy that the intensities of the excitation or emission bands are not significantly high compared to those for specimens A_3 and A_4.

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Figure-1 : (a) Excitation spectra of as received specimen A for 430 nm emission.

(b) Emission spectra of as received specimen A for 240 nm excitation

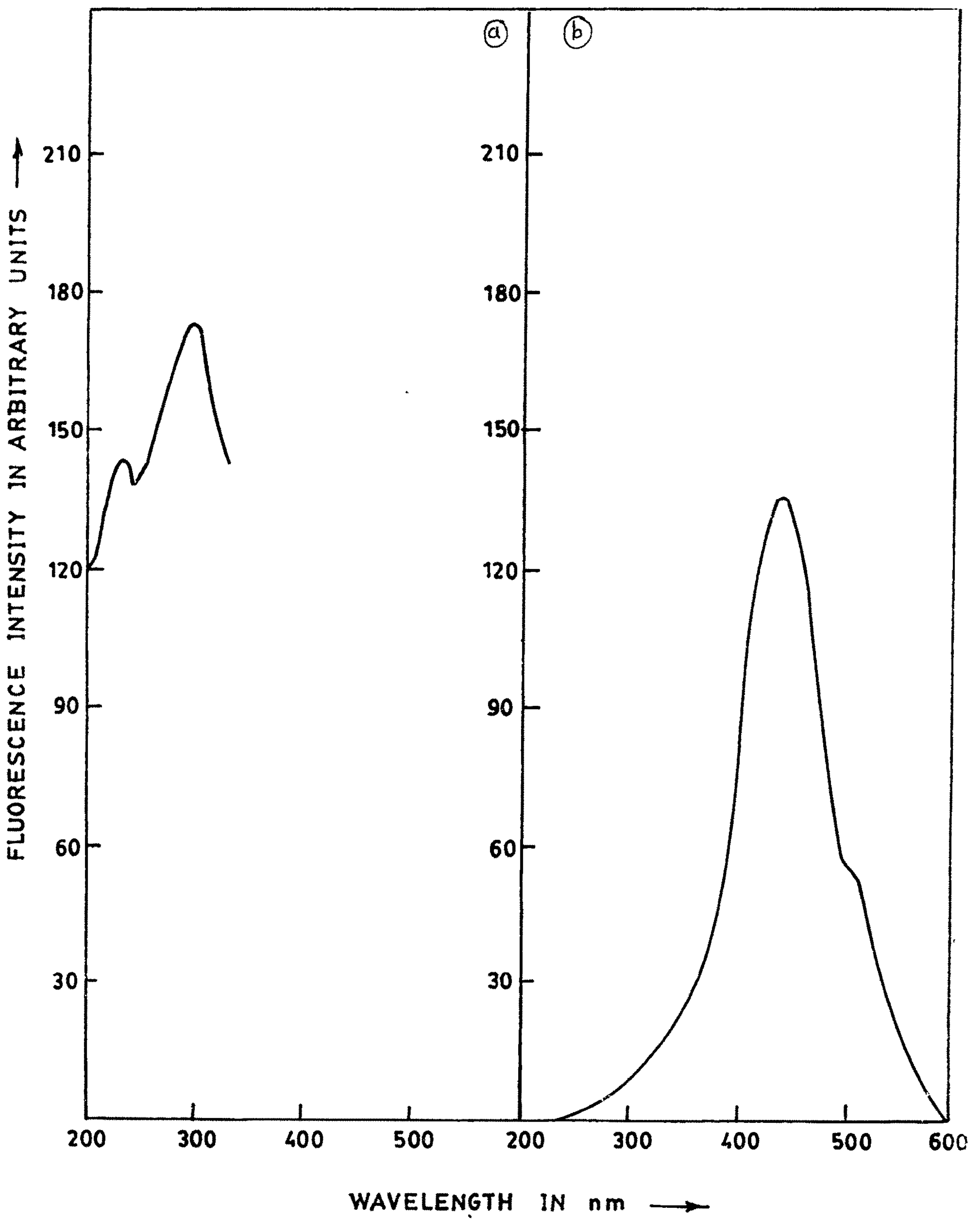
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FIGURE 1

Figure-2 Emission spectra of as received specimen A for 280 nm excitation.

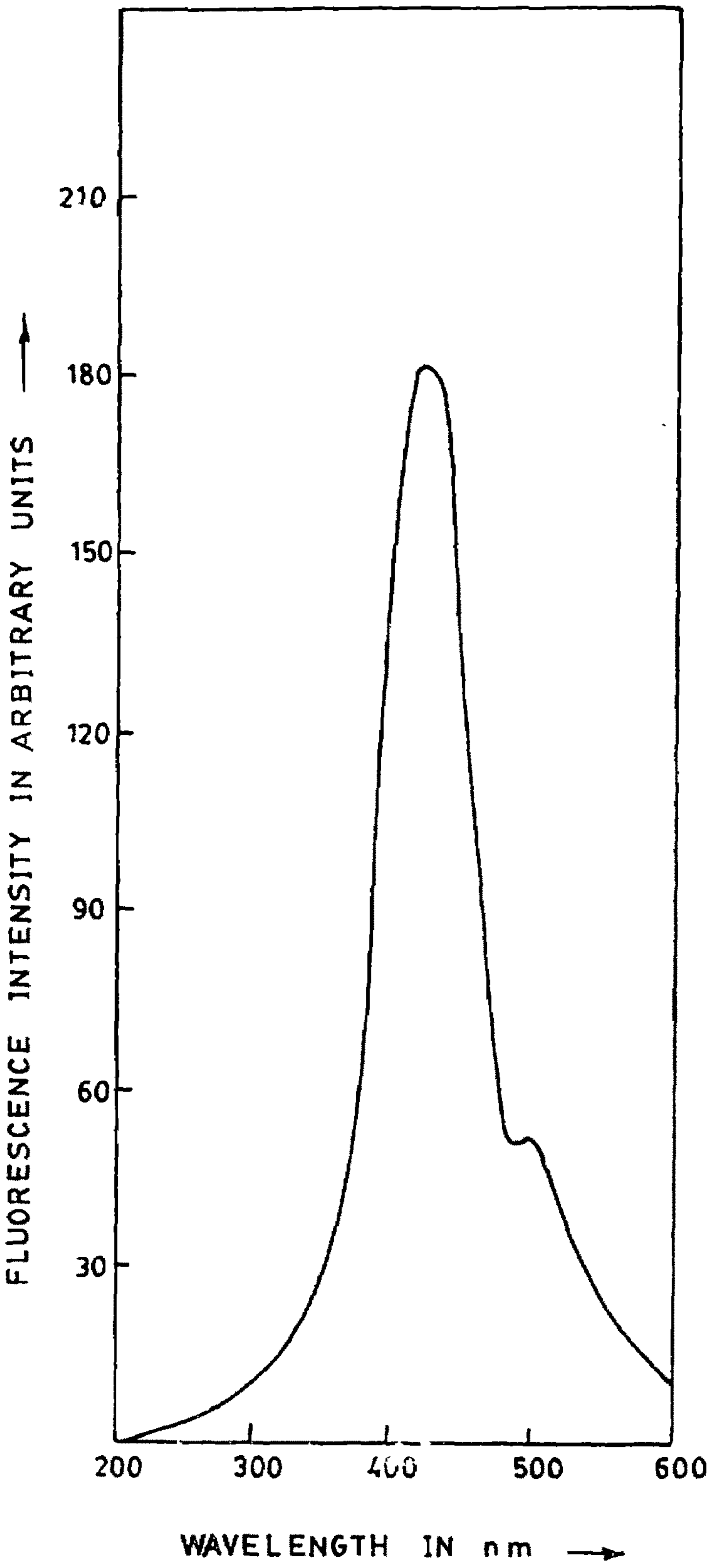
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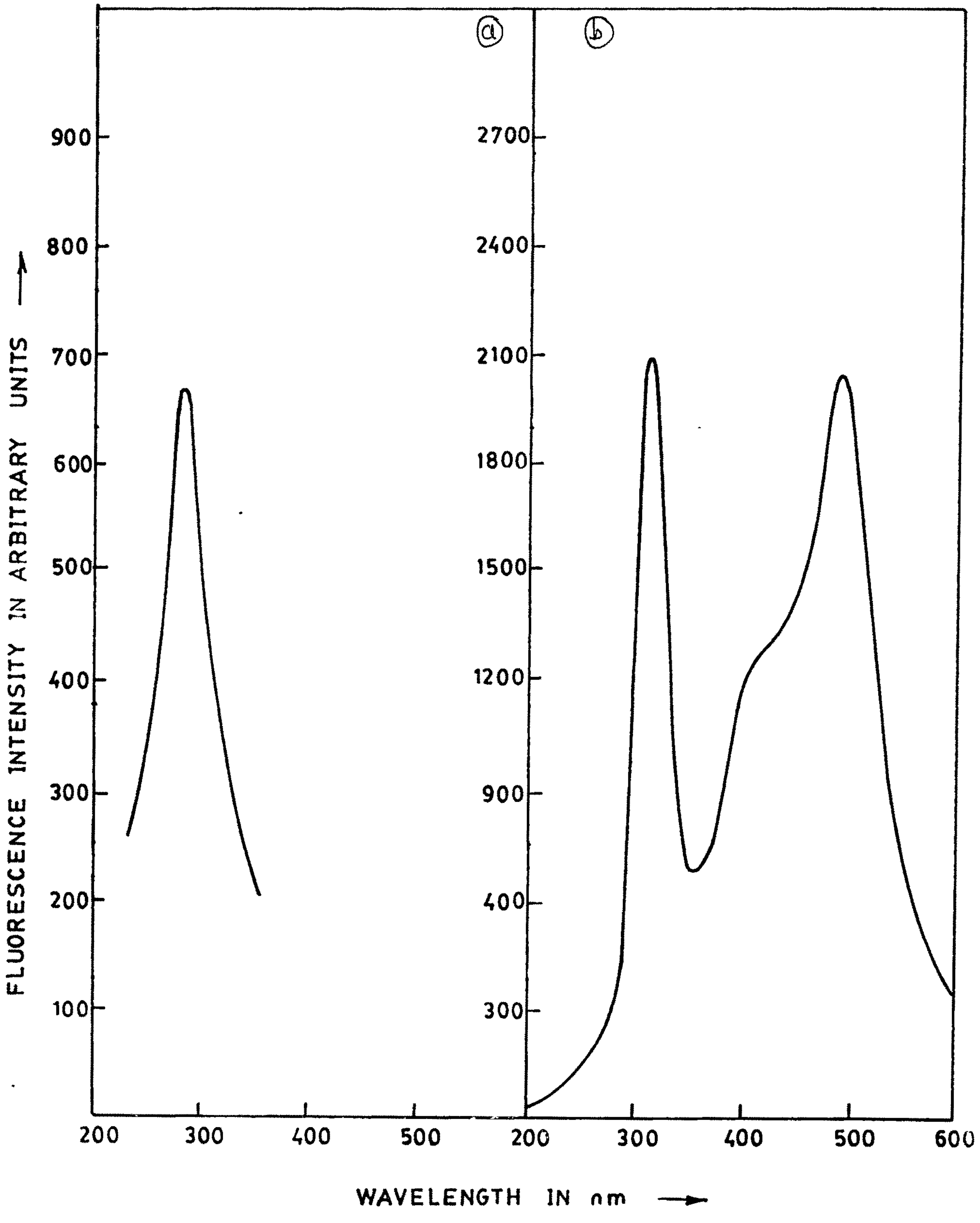
FIGURE 2

Figure-3 : (a) Excitation spectra of as received specimen A_1 for 480 nm emission.

(b) Emission spectra of as received specimen A_1 for 280 nm excitation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WAVELENGTH IN nm →

FIGURE 3

Figure-4 : (a) Excitation spectra of as received specimen A_1 for 520 nm emission.

(b) Emission spectra of as received specimen A_1 for 296 nm excitation

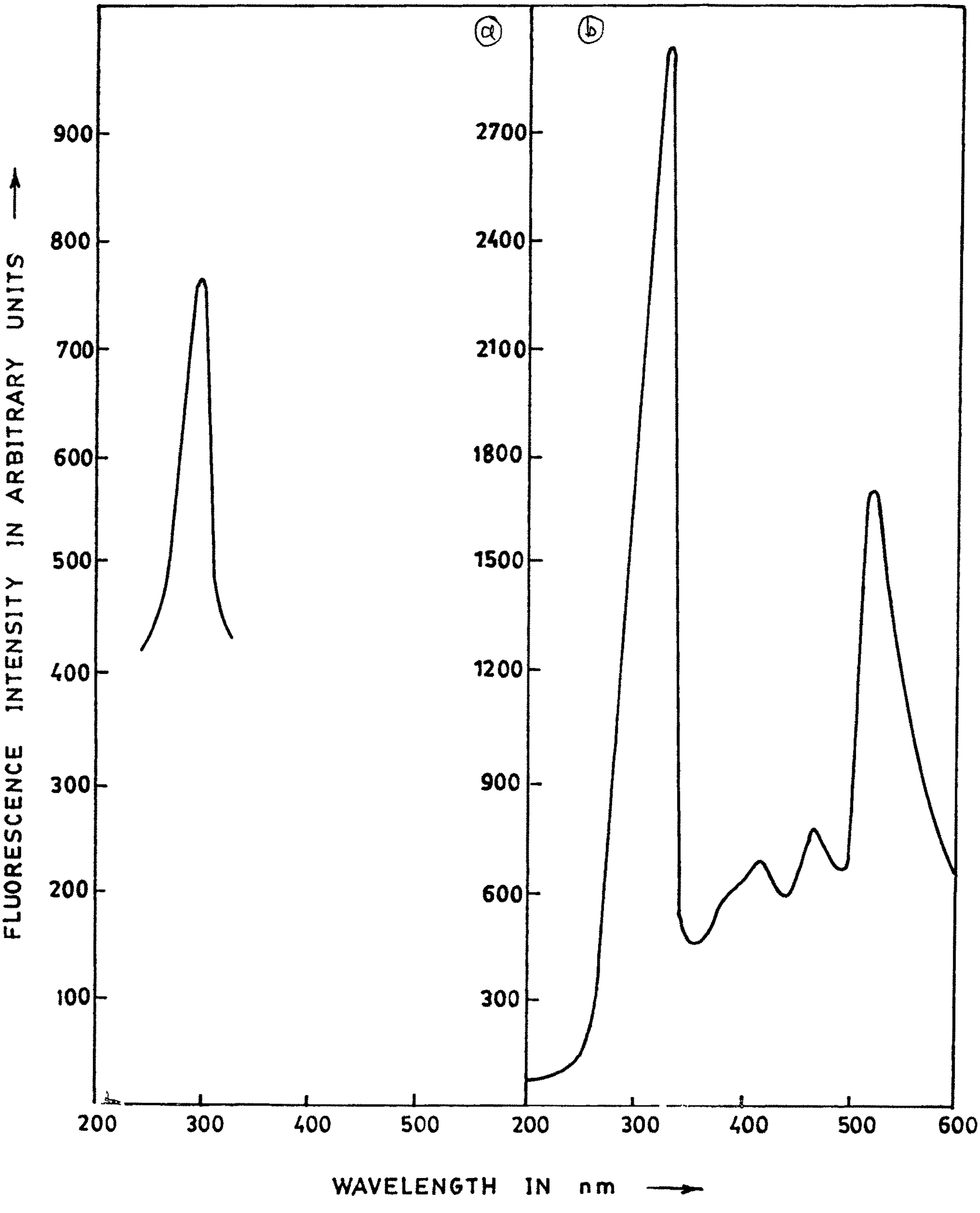
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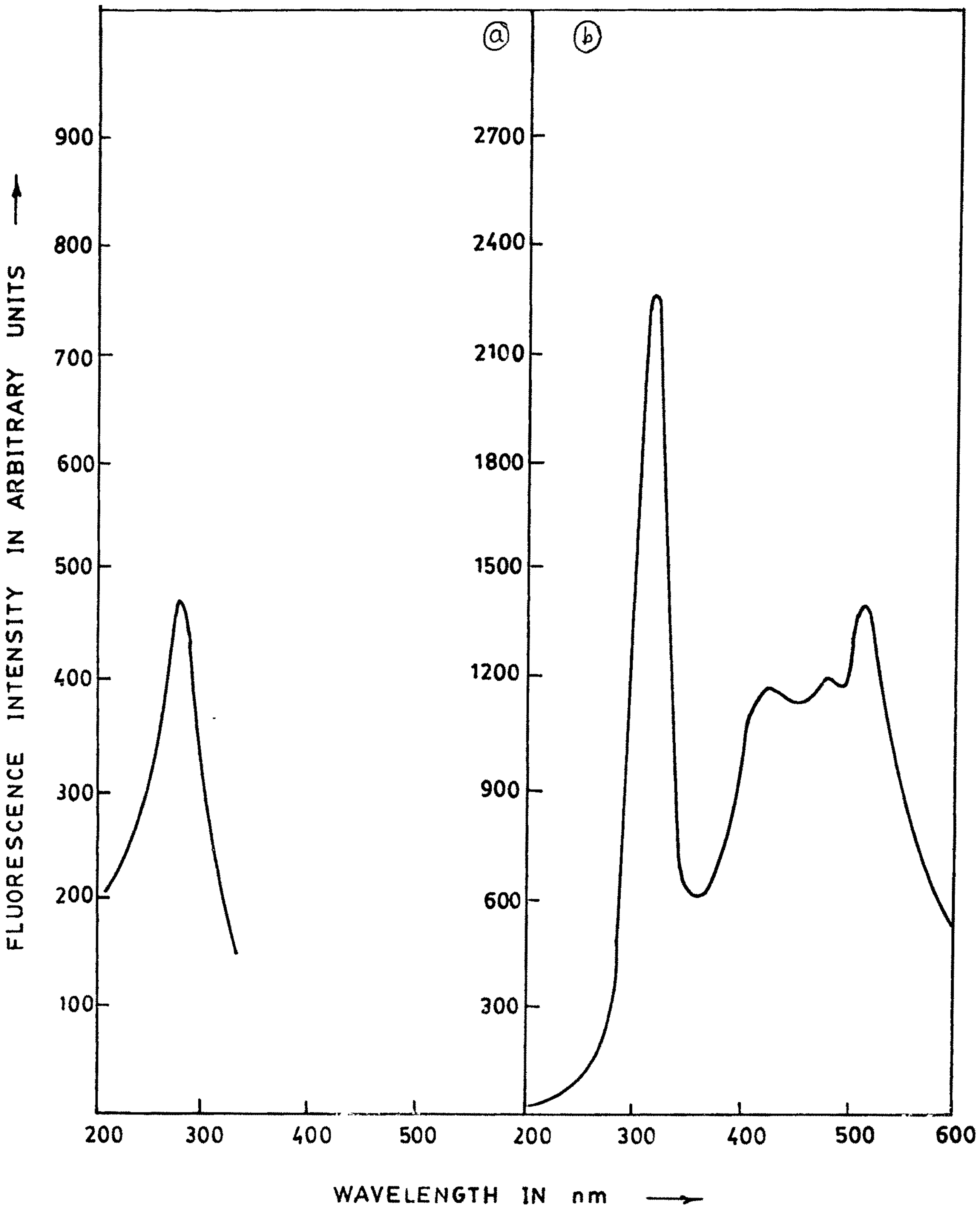
FIGURE 4

Figure-5 : (a) Excitation spectra of as received specimen A_2 for 480 nm emission.

(b) Emission spectra of as received specimen A_2 for 280 nm excitation.



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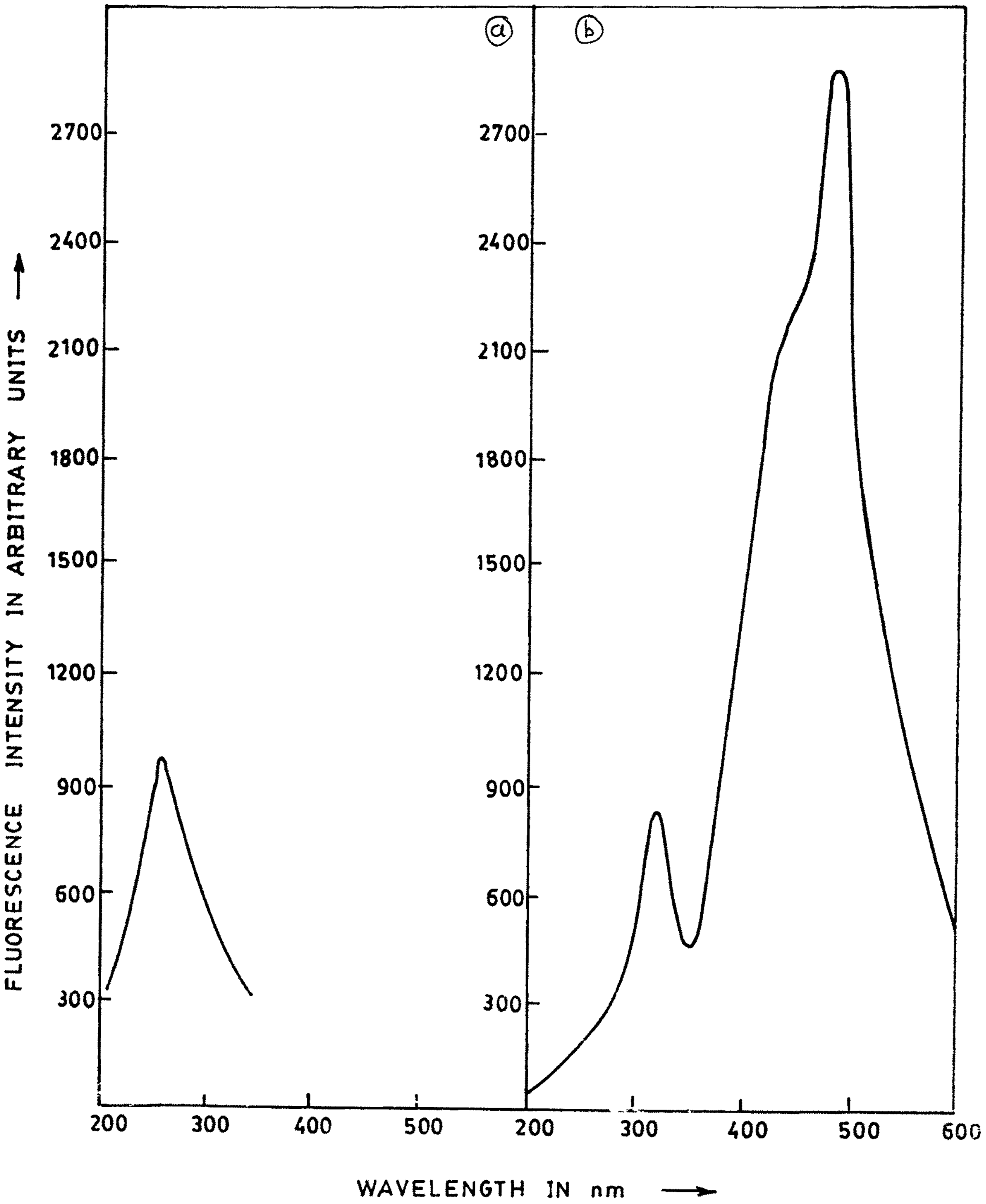
WAVELENGTH IN nm

FIGURE 5

Figure-6 : (a) Excitation spectra of as received specimen A_3 for 480 nm emission.

(b) Emission spectra of as received specimen A_3 for 260 nm excitation.



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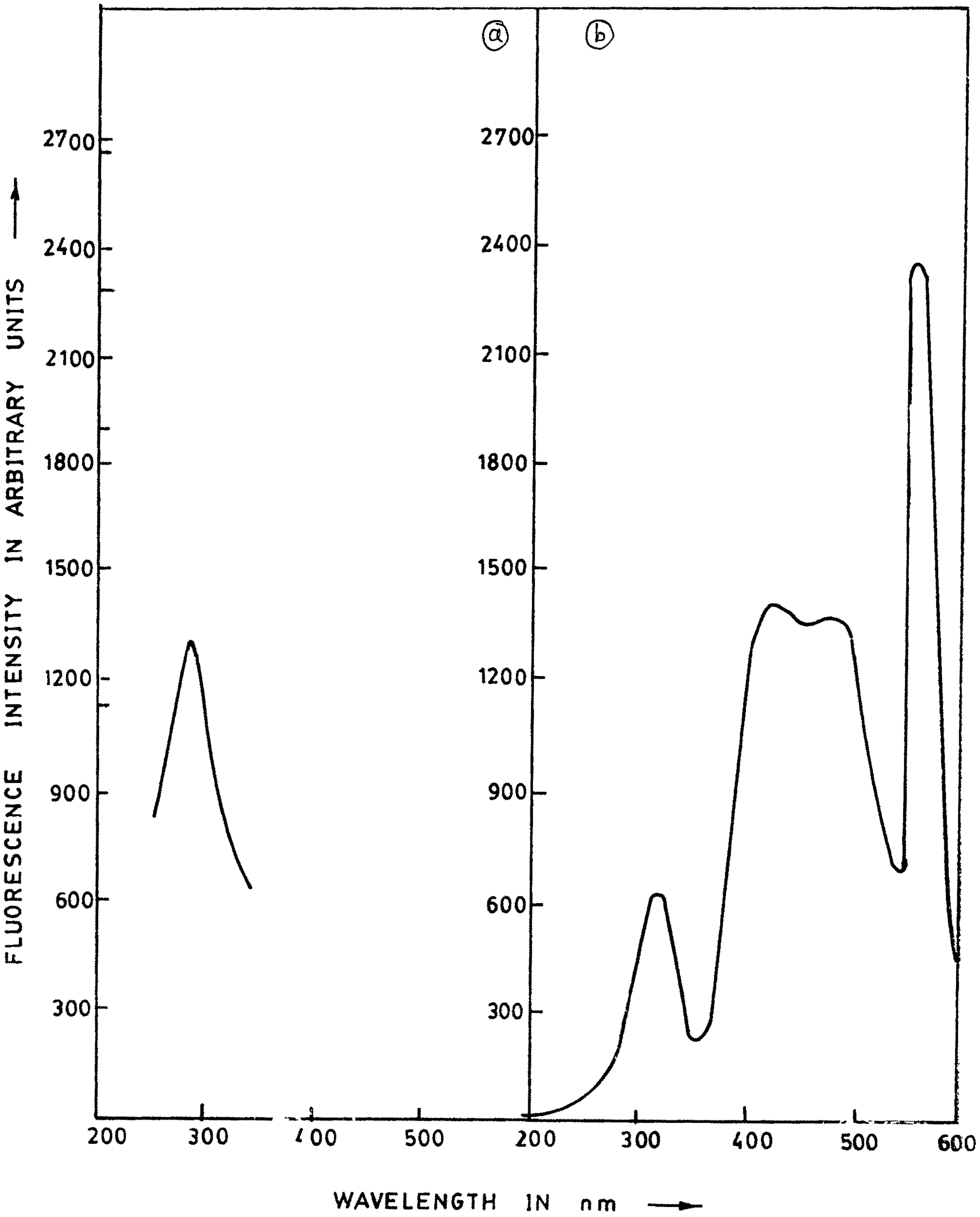
WAVELENGTH IN nm →

FIGURE 6

Figure-7 : (a) Excitation spectra of as received specimen A_4 for 480 nm emission.

(b) Emission spectra of as received specimen A_4 for 280 nm excitation.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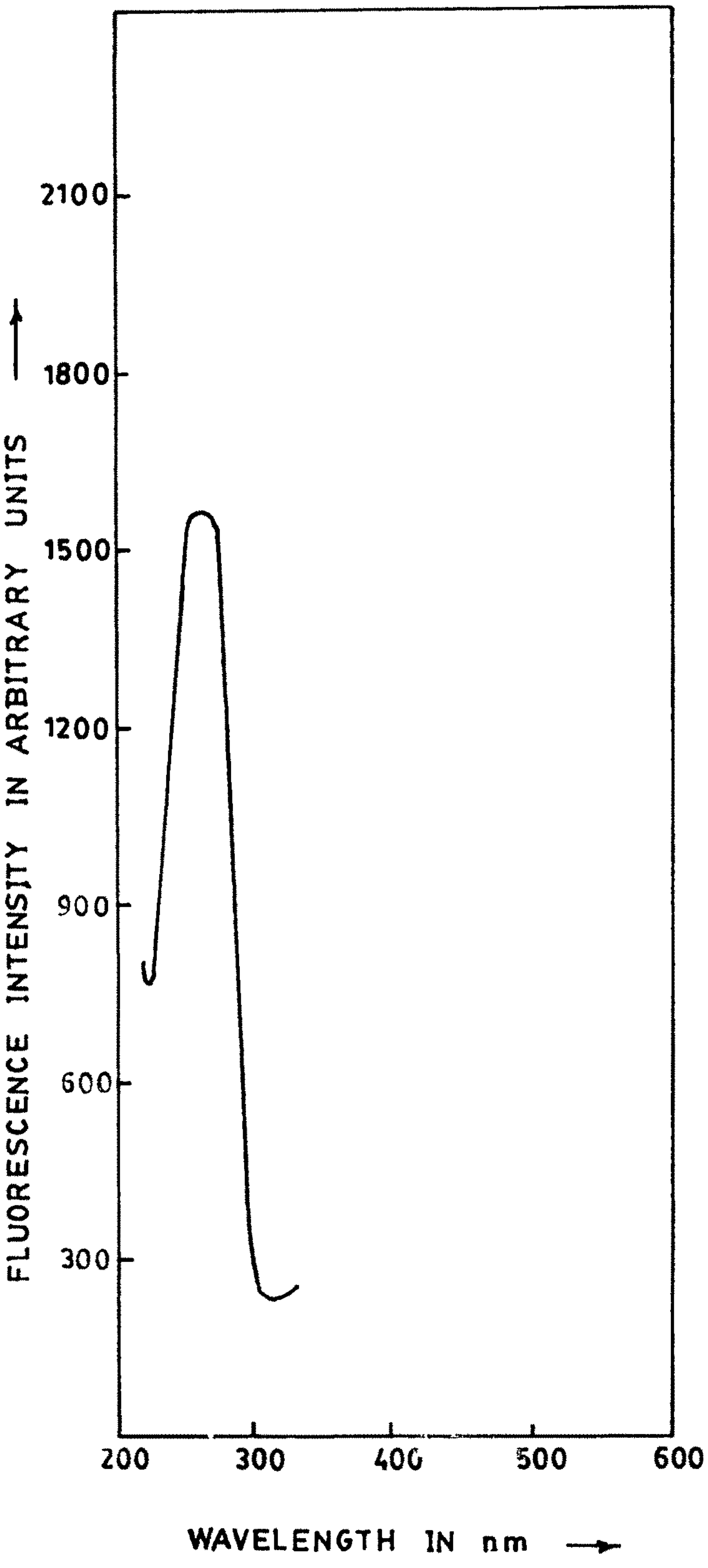
WAVELENGTH IN nm →

FIGURE 7

Figure-8 : Excitation spectra of as received specimen A_4 for 560 nm emission.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FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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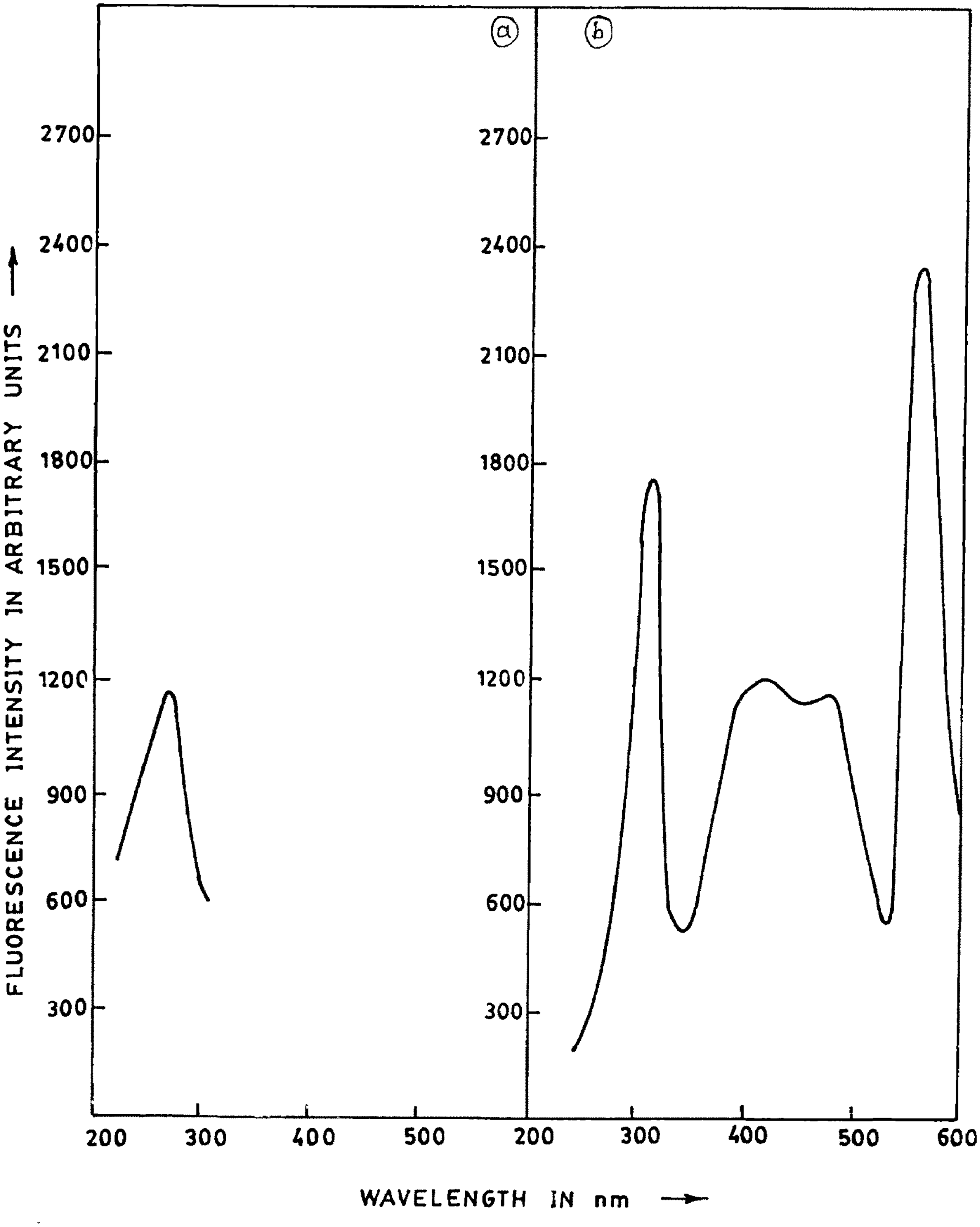
WAVELENGTH IN nm

FIGURE 8

Figure-9 : (a) Excitation spectra of as received specimen A_5 for 480 nm emission.

(b) Emission spectra of as received specimen A_5 for 272 nm excitation.



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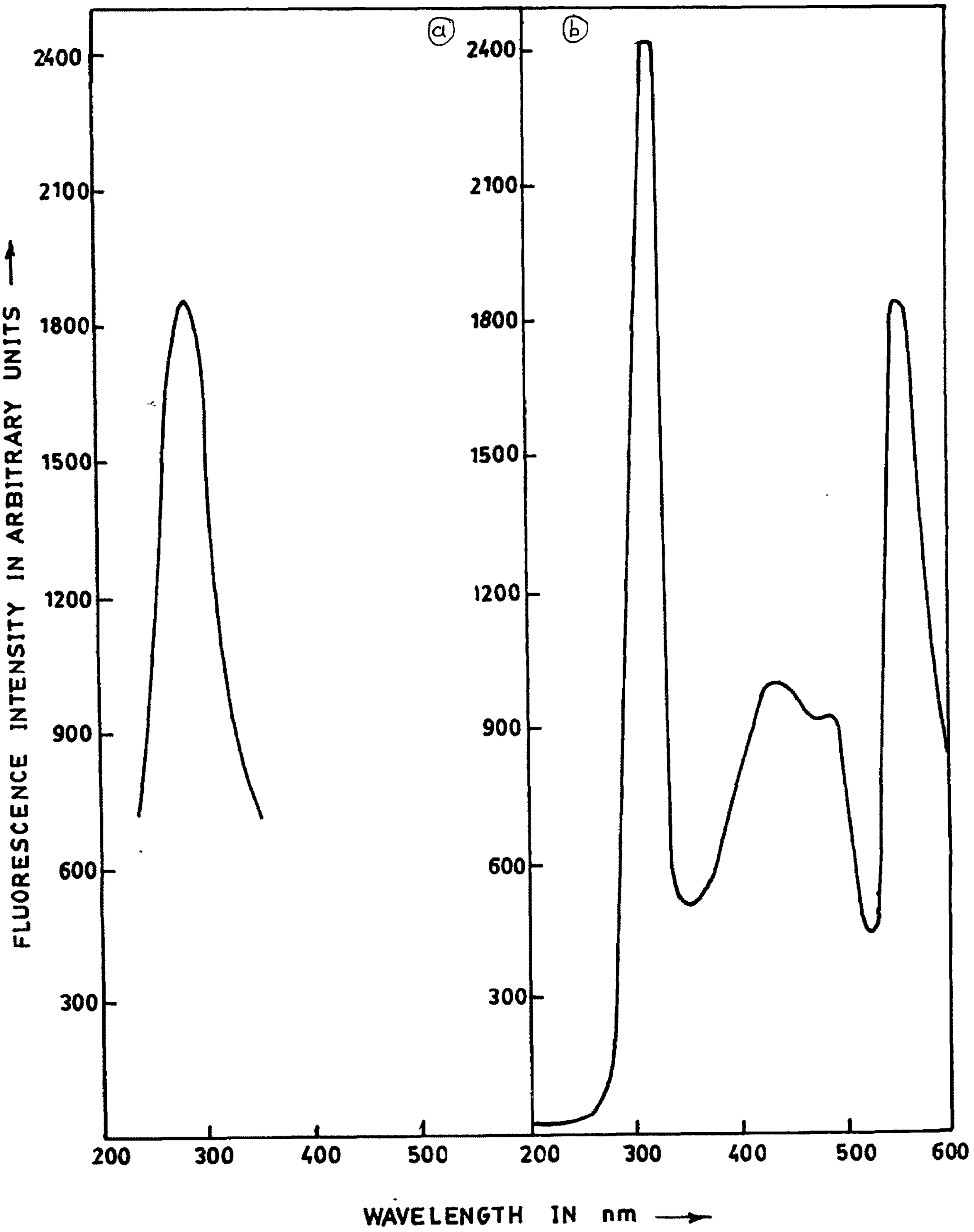
WAVELENGTH IN nm →

FIGURE 9

Figure-10 : (a) Excitation spectra of as received specimen A_5 for 560 nm emission.

(b) Emission spectra of as received specimen A_5 for 280 nm excitation.



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WAVELENGTH IN nm

FIGURE 10

Figure-11 : (a) Excitation spectra of mechanically deformed specimen A for 430 nm emission.

(b) Emission spectra of mechanically deformed specimen A for 240 nm excitation.

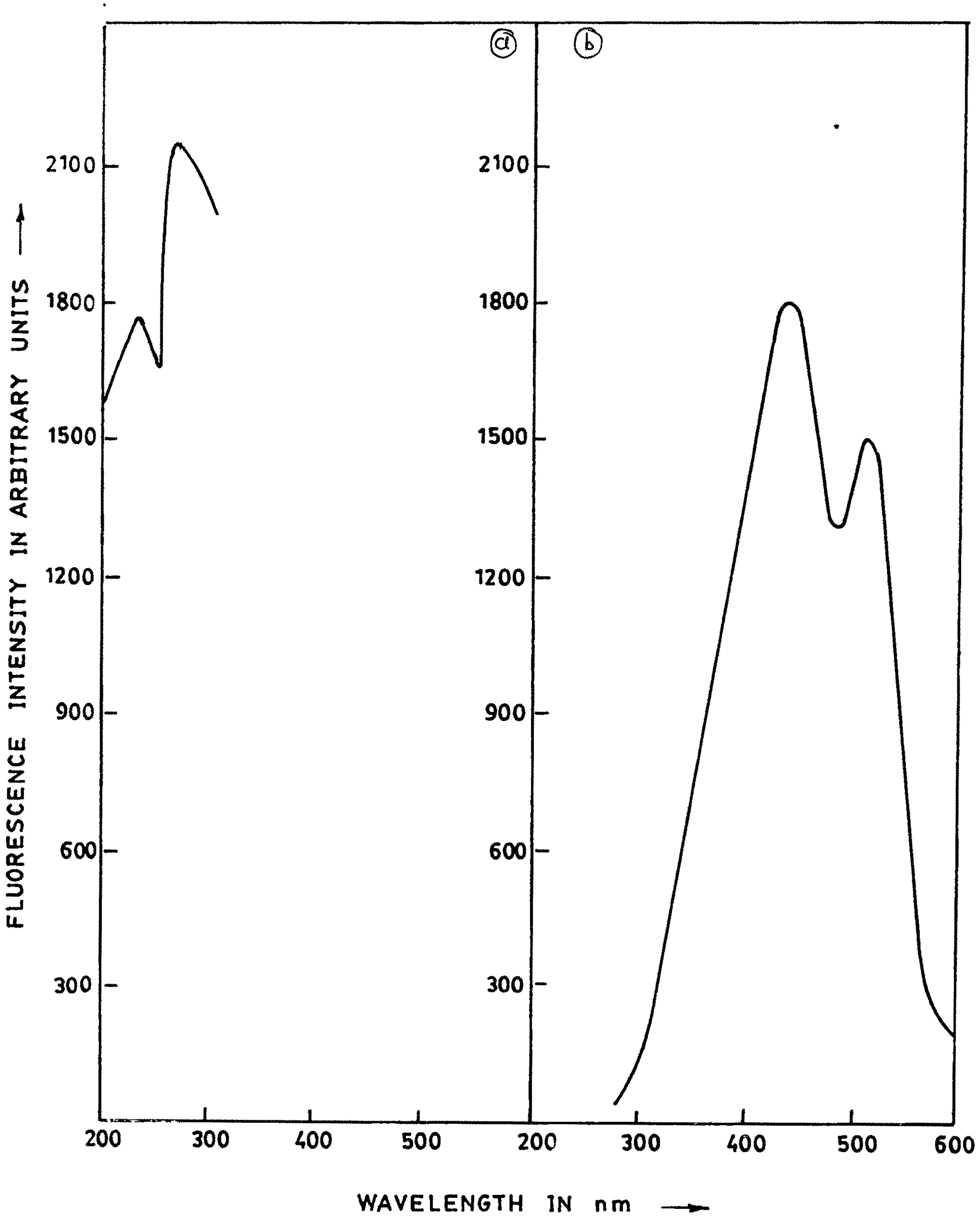
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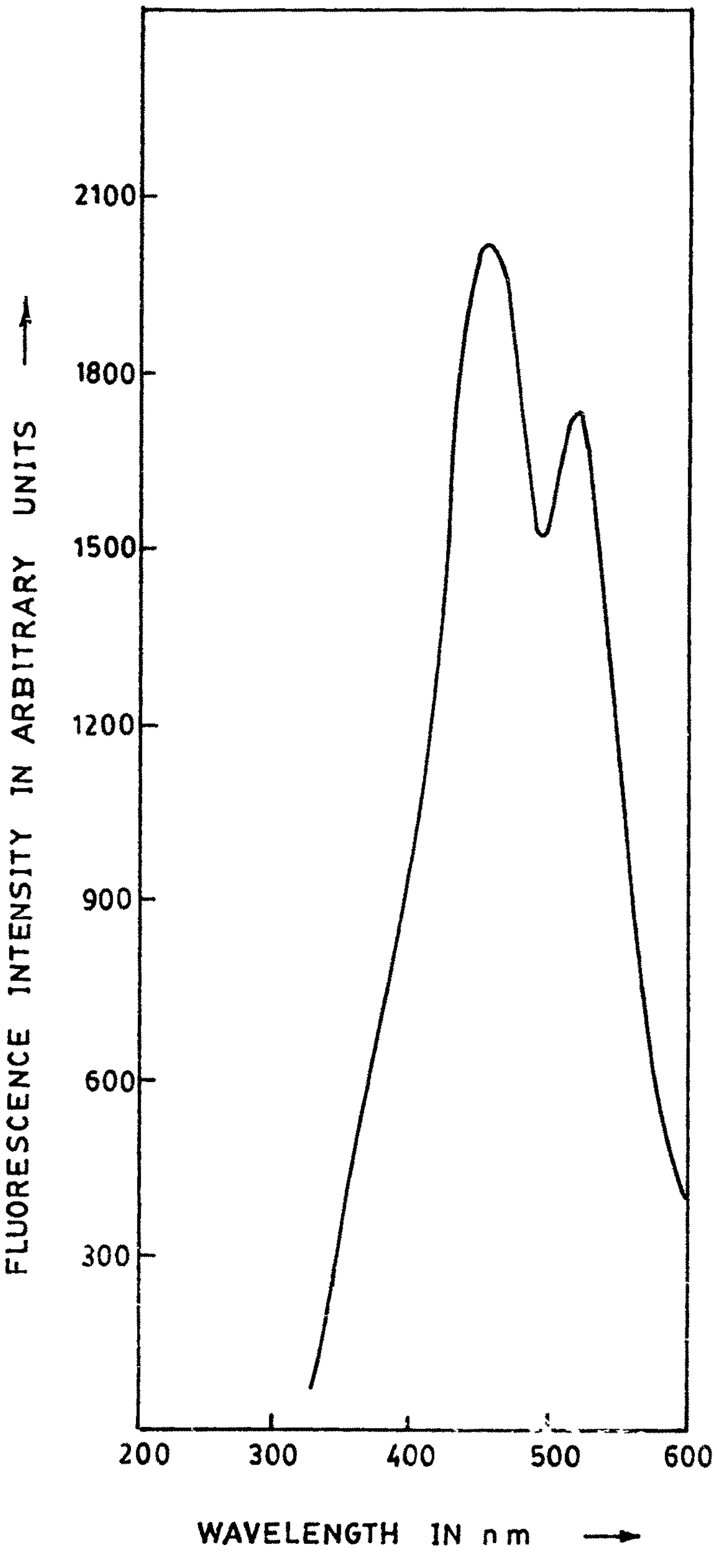
FIGURE 11

Figure-12 Emission spectra of mechanically deformed specimen A for 260 nm excitation.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FLUORESCENCE INTENSITY IN ARBITRARY UNITS →
200
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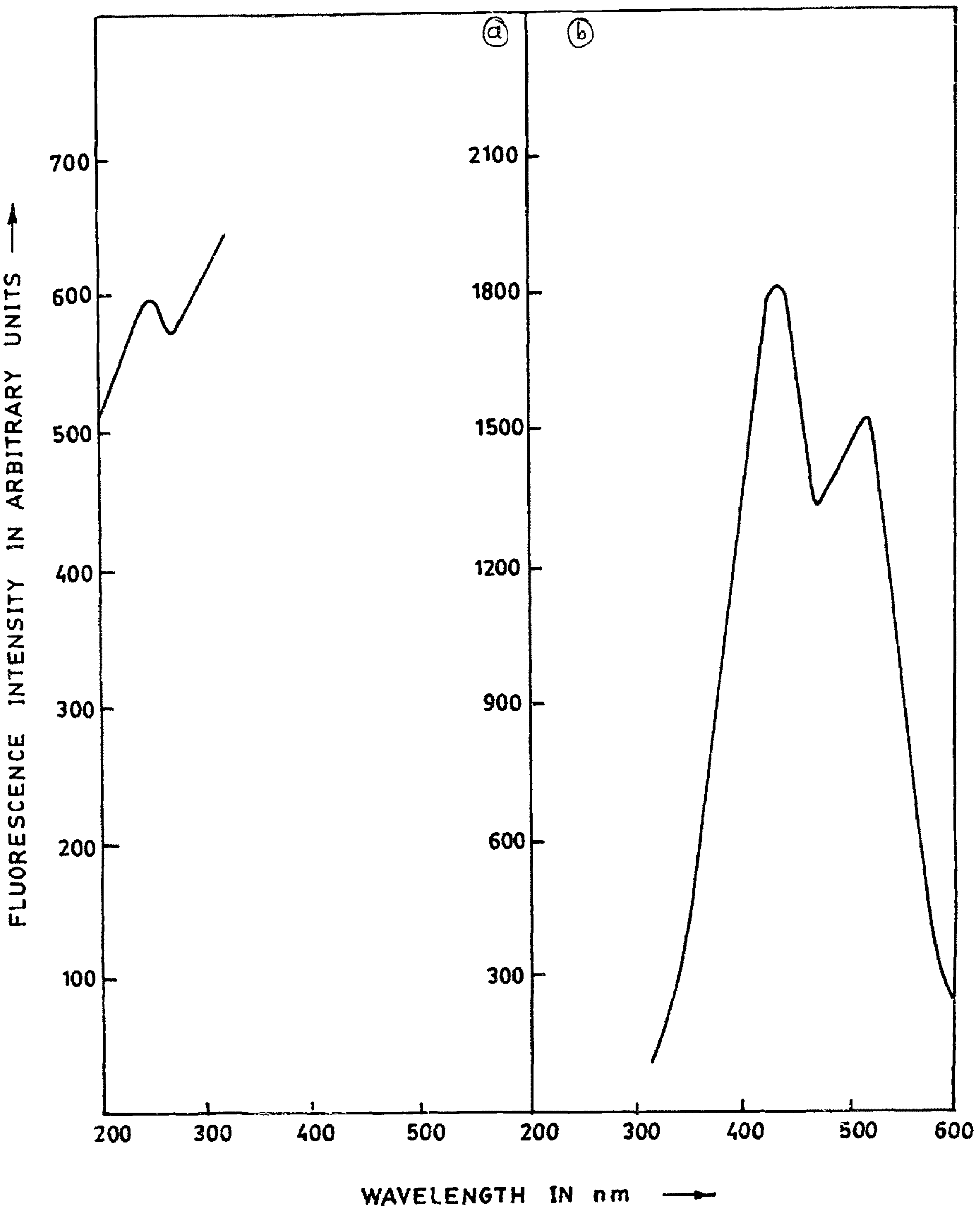
WAVELENGTH IN nm →

FIGURE 12

Figure-13 : (a) Excitation spectra of mechanically deformed specimen A for 460 nm emission.

(b) Emission spectra of mechanically deformed specimen A for 225 nm excitation.



(a)
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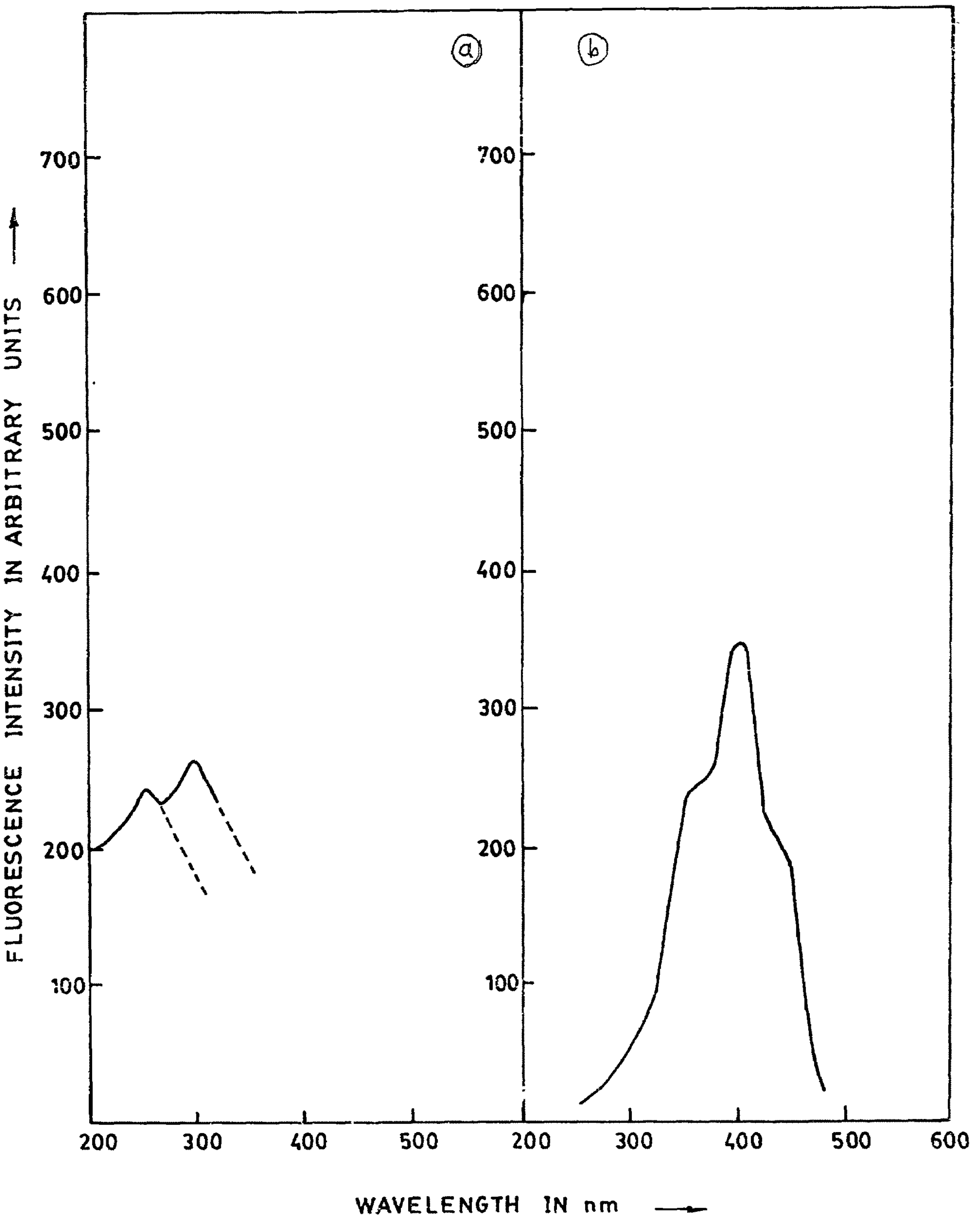
WAVELENGTH IN nm

FIGURE 13

Figure-14 : (a) Excitation spectra of mechanically deformed specimen A_1 for 420 nm emission.

(b) Emission spectra of mechanically deformed specimen A_1 for 252 nm excitation.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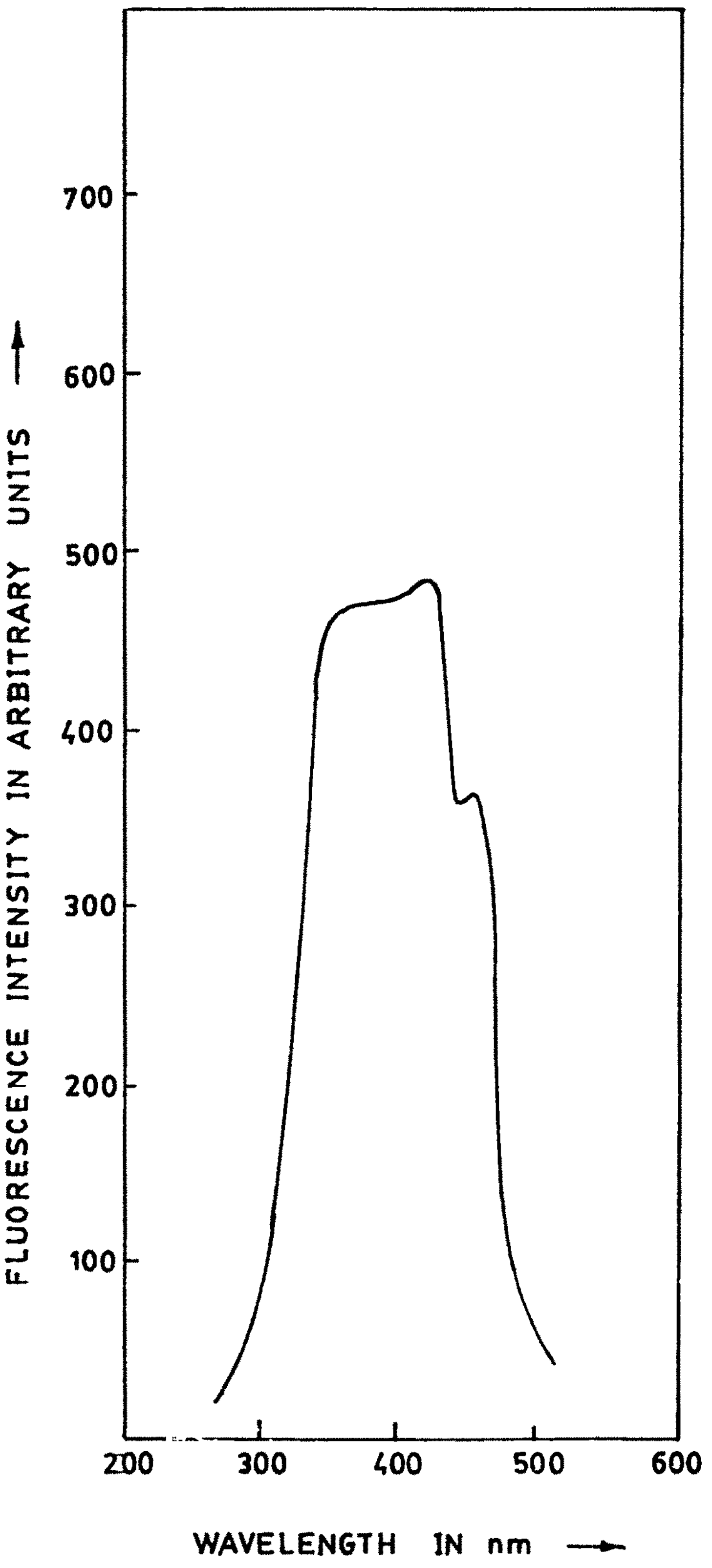
WAVELENGTH IN nm

FIGURE 14

Figure-15 Emission spectra of mechanically deformed specimen A_1 for 272 nm excitation.


FLUORESCENCE INTENSITY IN ARBITRARY UNITS
700
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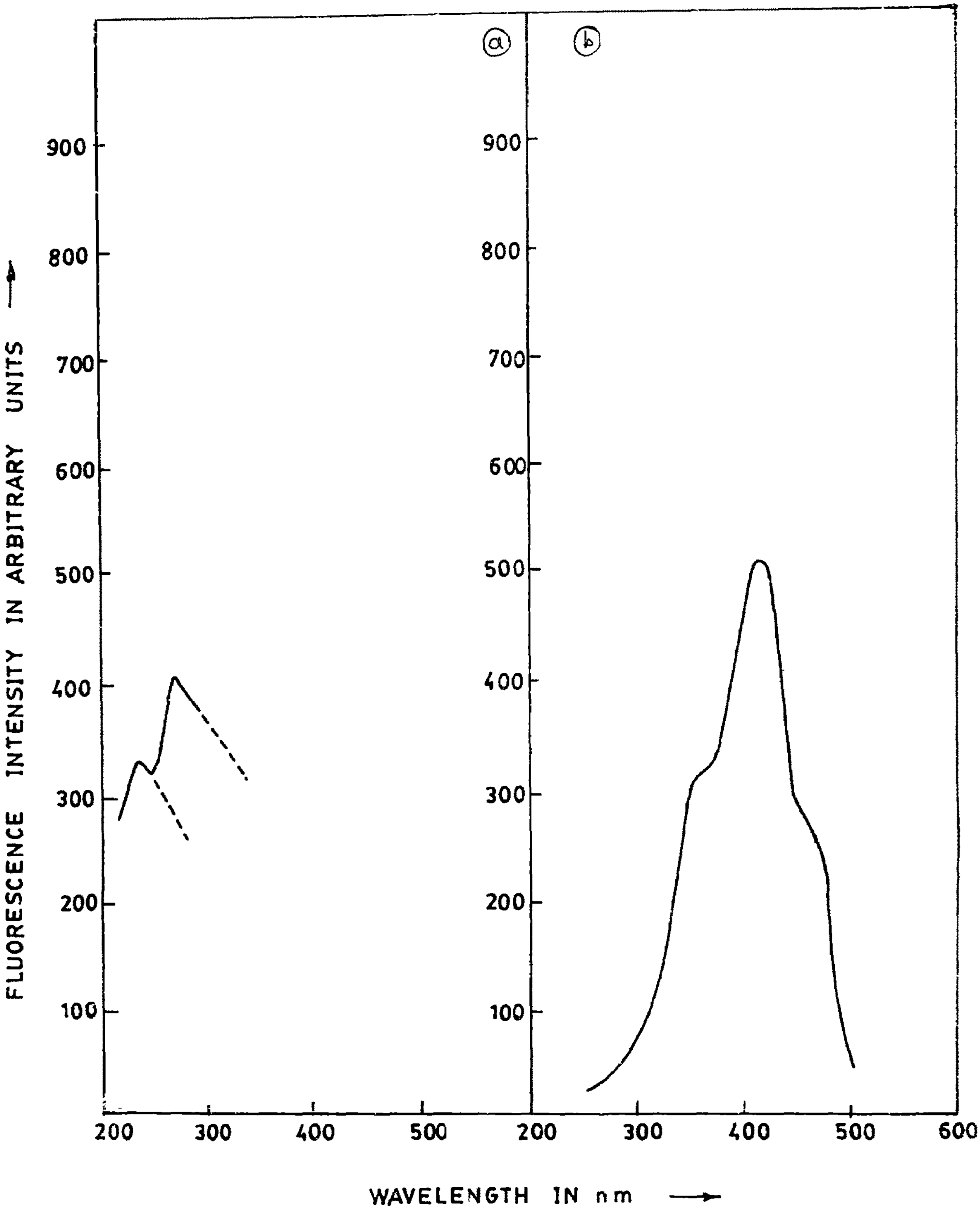
600
WAVELENGTH IN nm

FIGURE 15

Figure-16 : (a) Excitation spectra of mechanically deformed specimen A_2 for 420 nm emission.

(b) Emission spectra of mechanically deformed specimen A_2 for 252 nm excitation.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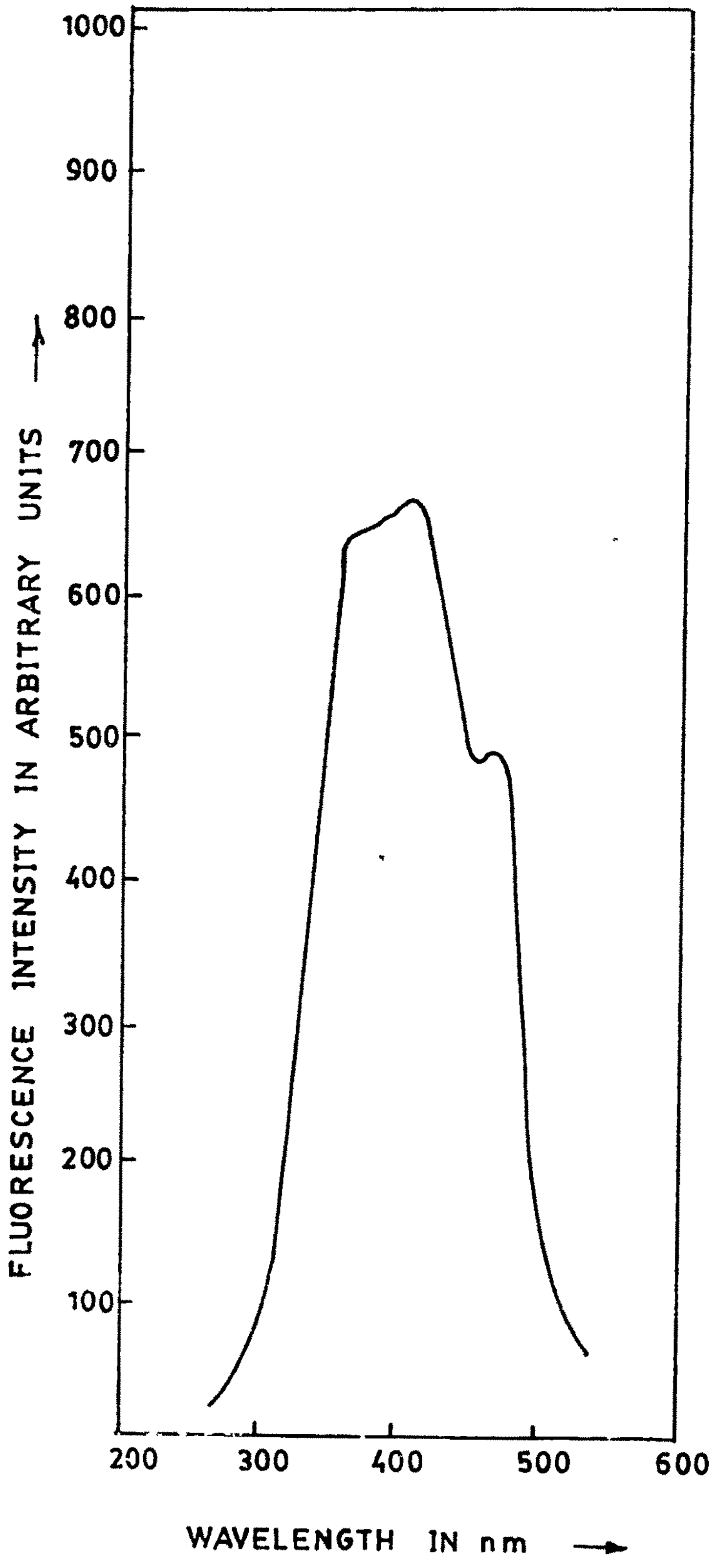
WAVELENGTH IN nm

FIGURE 16

Figure-17 : Emission spectra of mechanically deformed specimen A_2 for 272 nm excitation.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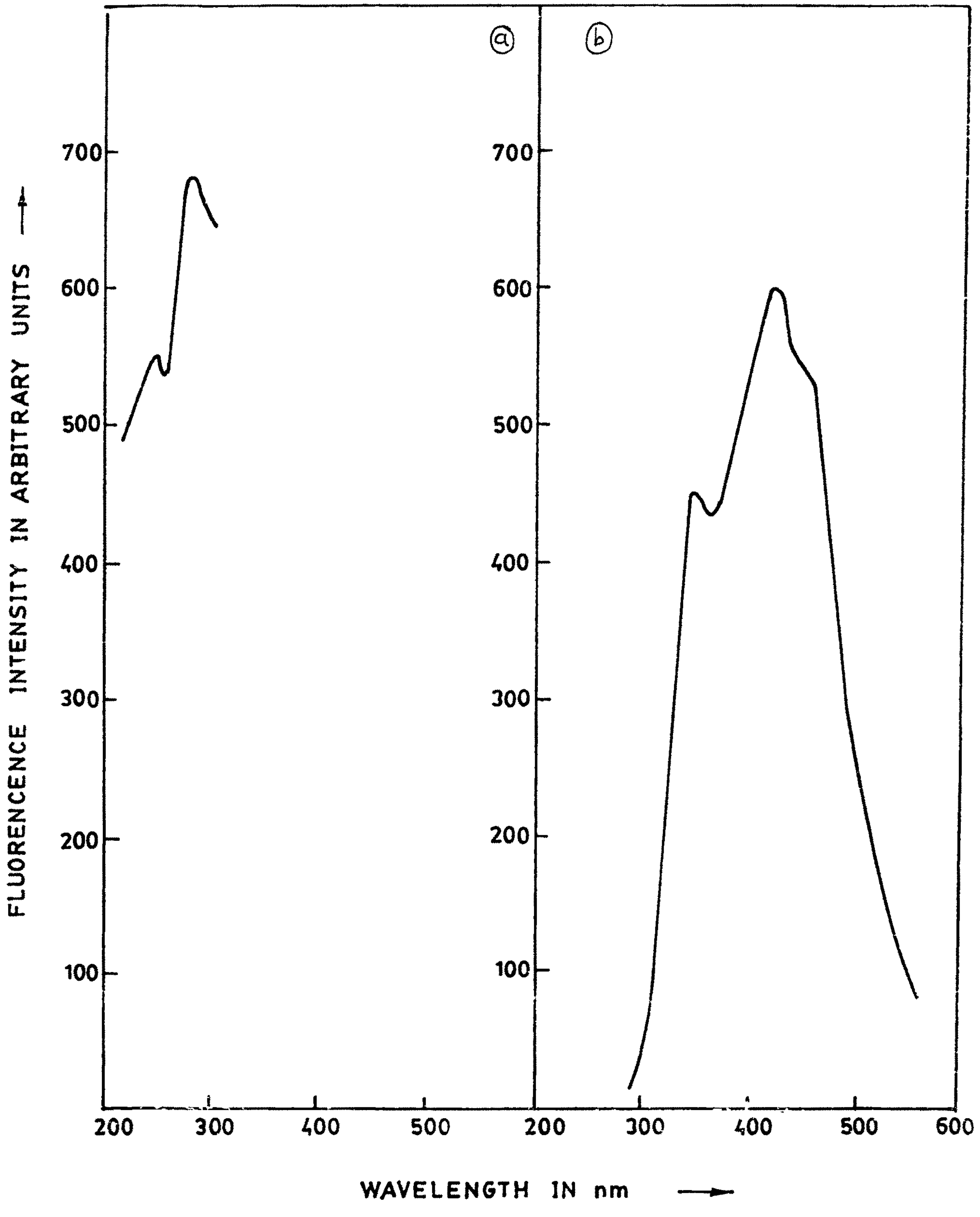
WAVELENGTH IN nm

FIGURE 17

Figure–18 : (a) Excitation spectra of mechanically deformed specimen A_3 for 420 nm emission.

(b) Emission spectra of mechanically deformed specimen A_3 for 252 nm excitation.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FLUORENCENCE INTENSITY IN ARBITRARY UNITS
100
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WAVELENGTH IN nm
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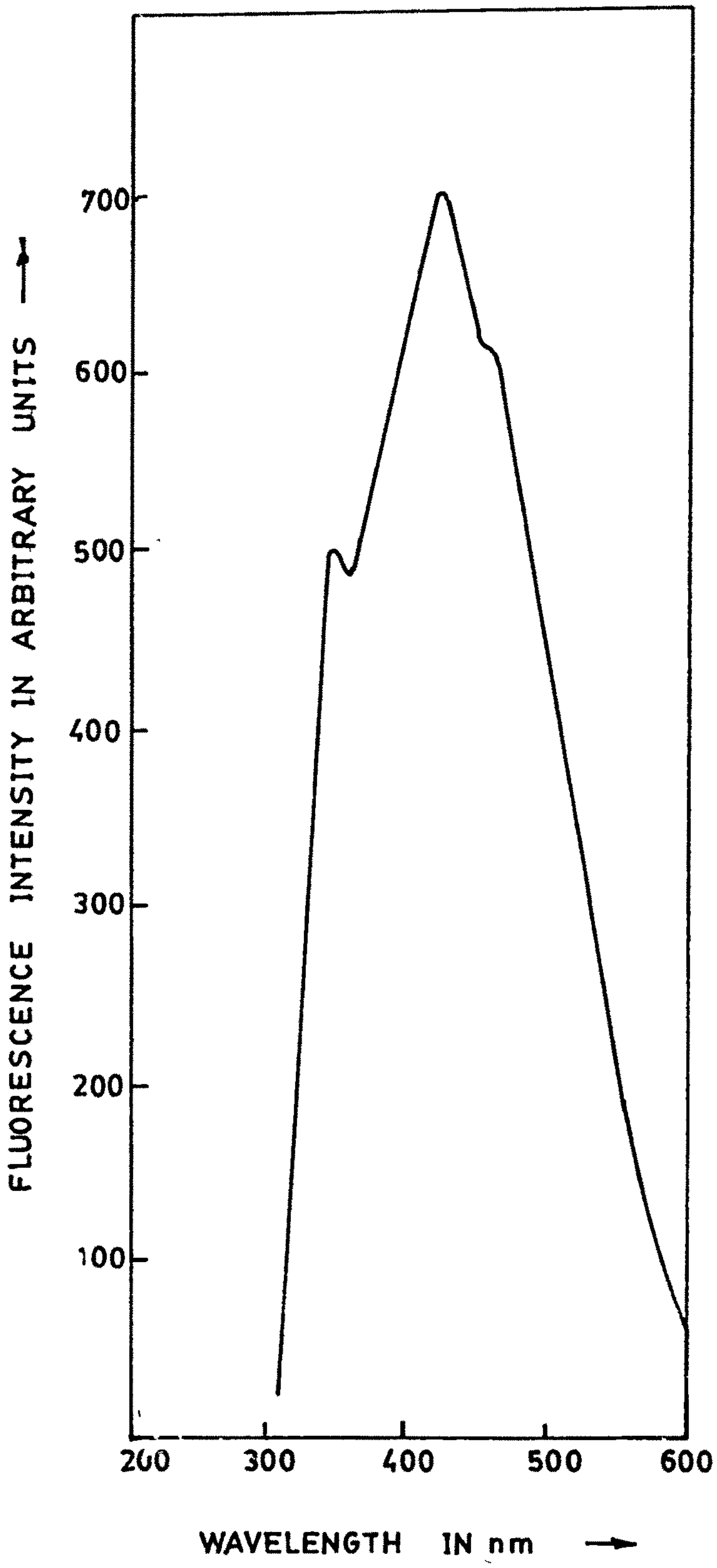
FIGURE 18

Figure-19 Emission spectra of mechanically deformed specimen A_3 for 280 nm excitation.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200
100
FLUORESCENCE INTENSITY IN ARBITRARY UNITS →
200
300
400
500
600
WAVELENGTH IN nm →

FIGURE 19

Figure-20 : (a) Excitation spectra of mechanically deformed specimen A_4 for 420 nm emission.

(b) Emission spectra of mechanically deformed specimen A_4 for 252 nm excitation.

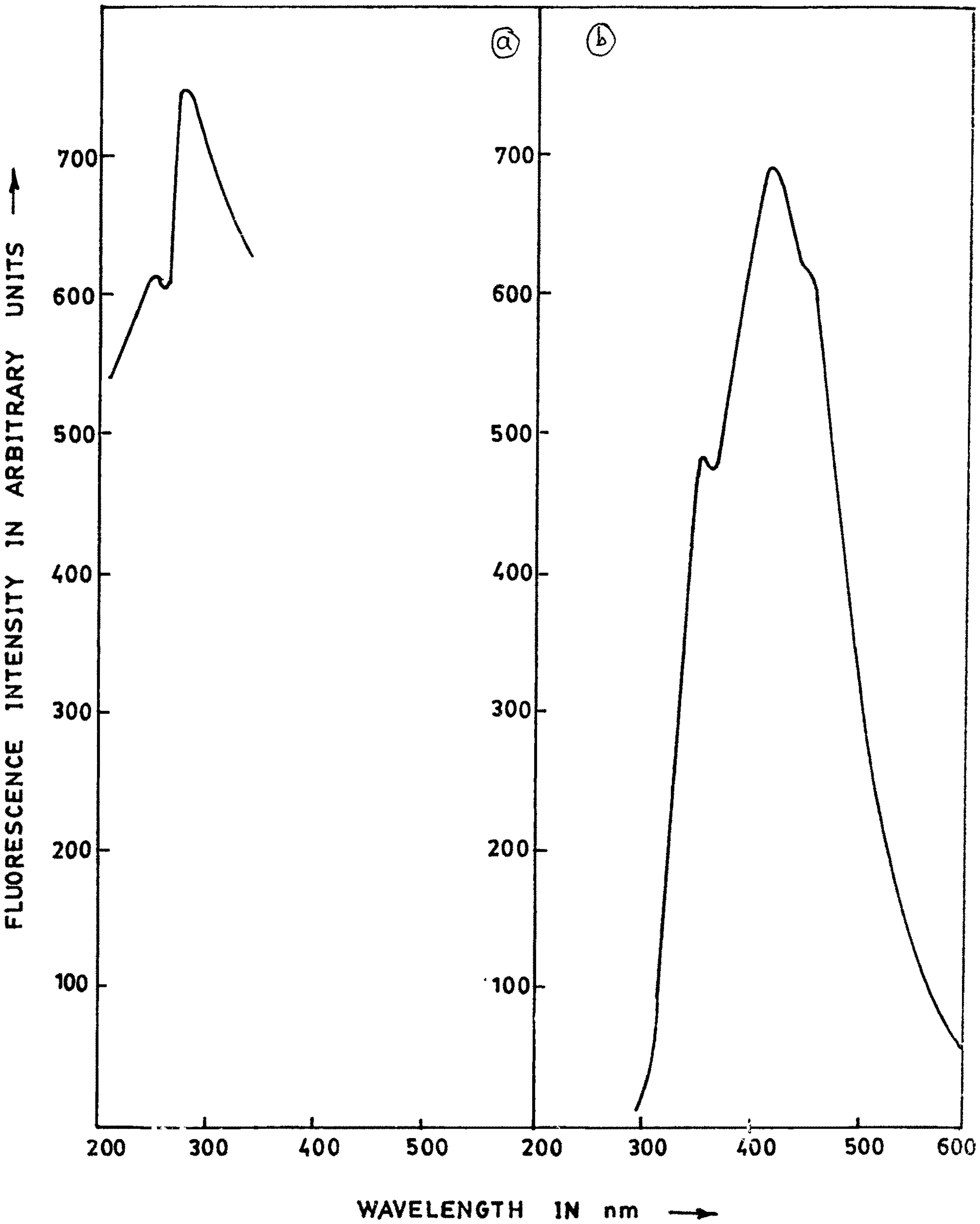
FLUORESCENCE INTENSITY IN ARBITRARY UNITS →
WAVELENGTH IN nm →
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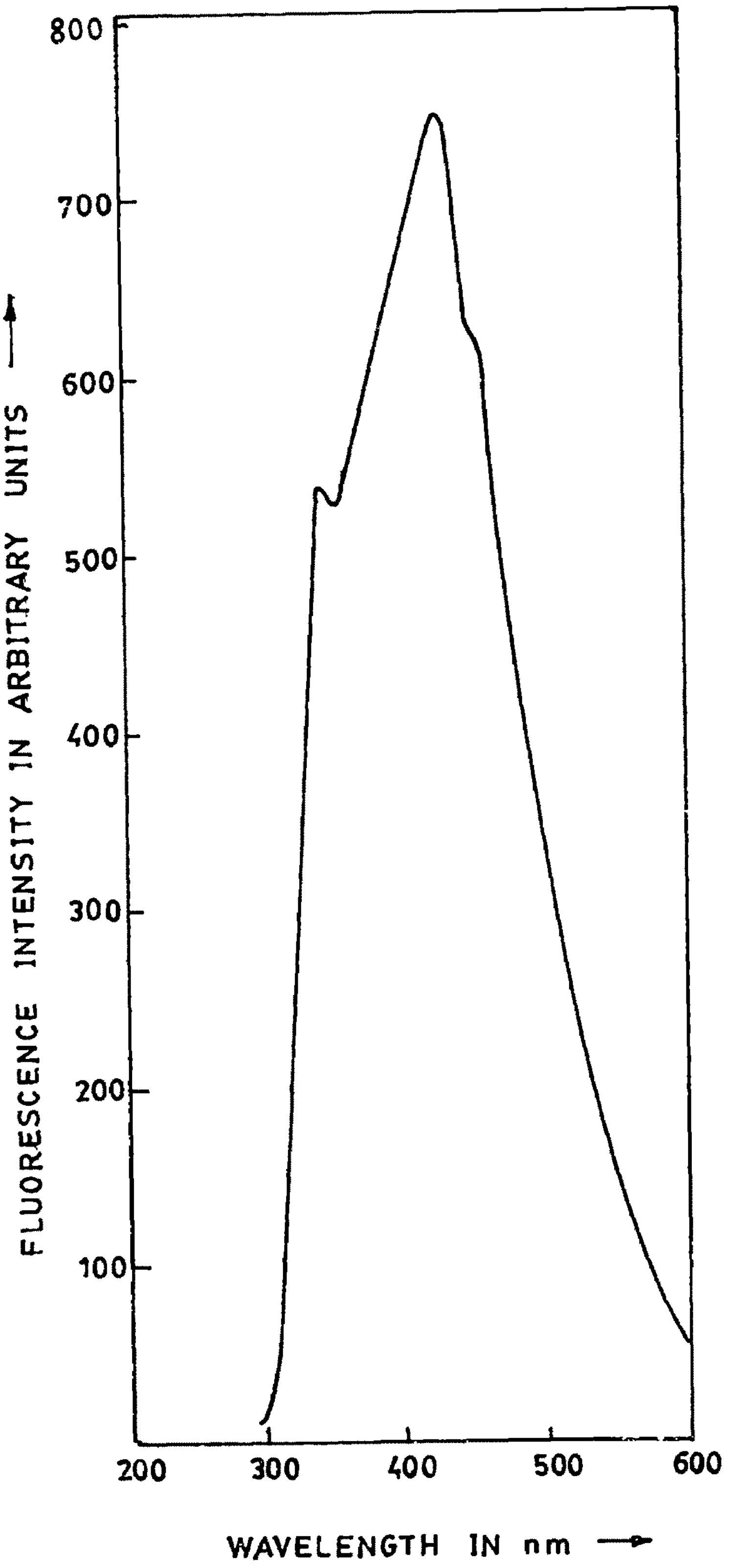
FIGURE 20

Figure-21 : Emission spectra of mechanically deformed specimen A_4 for 272 nm excitation.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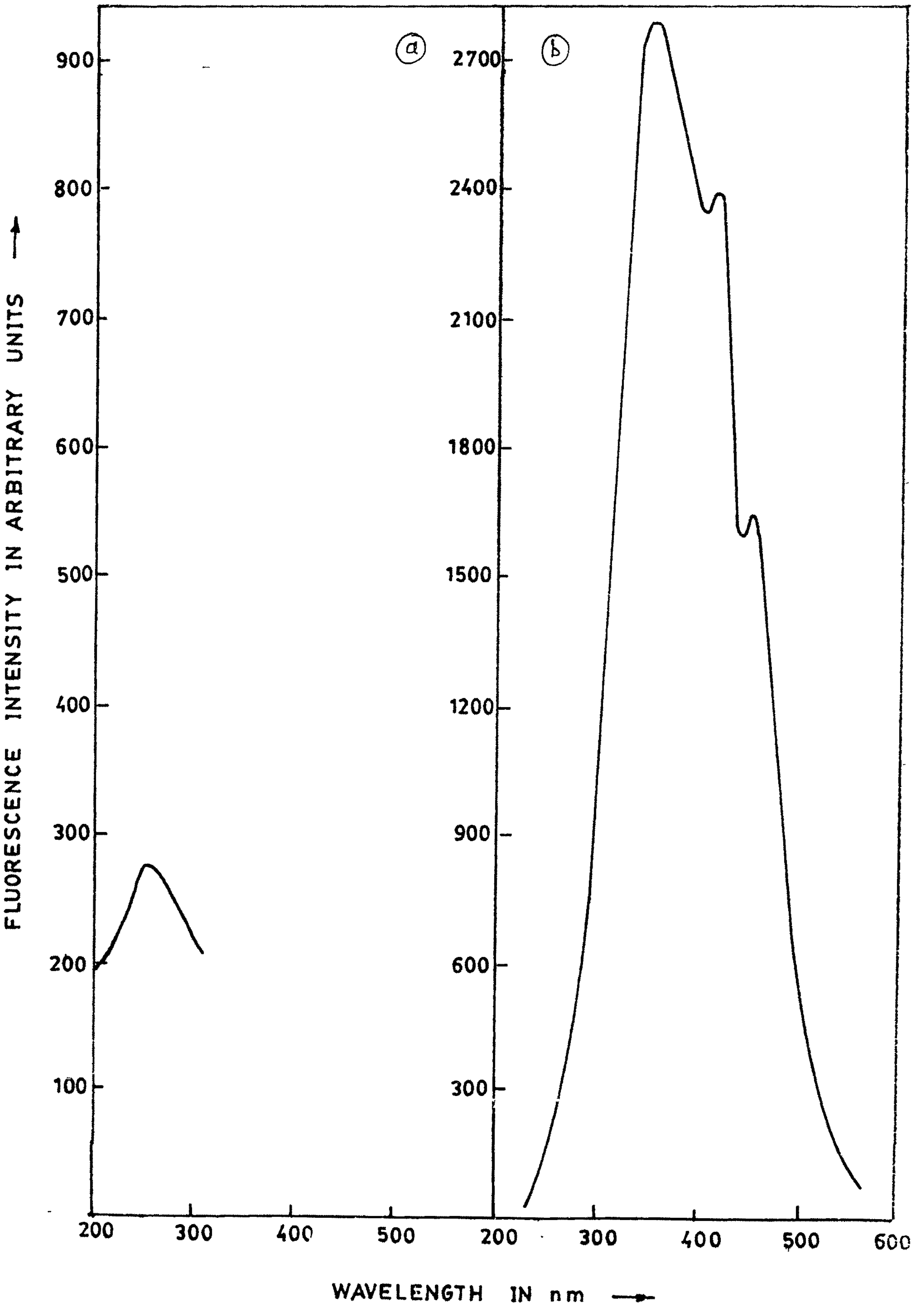
FLUORESCENCE INTENSITY IN ARBITRARY UNITS →
WAVELENGTH IN nm →

FIGURE 21

Figure-22 : (a) Excitation spectra of mechanically deformed specimen A_5 for 350 nm emission.

(b) Emission spectra of mechanically deformed specimen A_5 for 252 nm excitation.



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FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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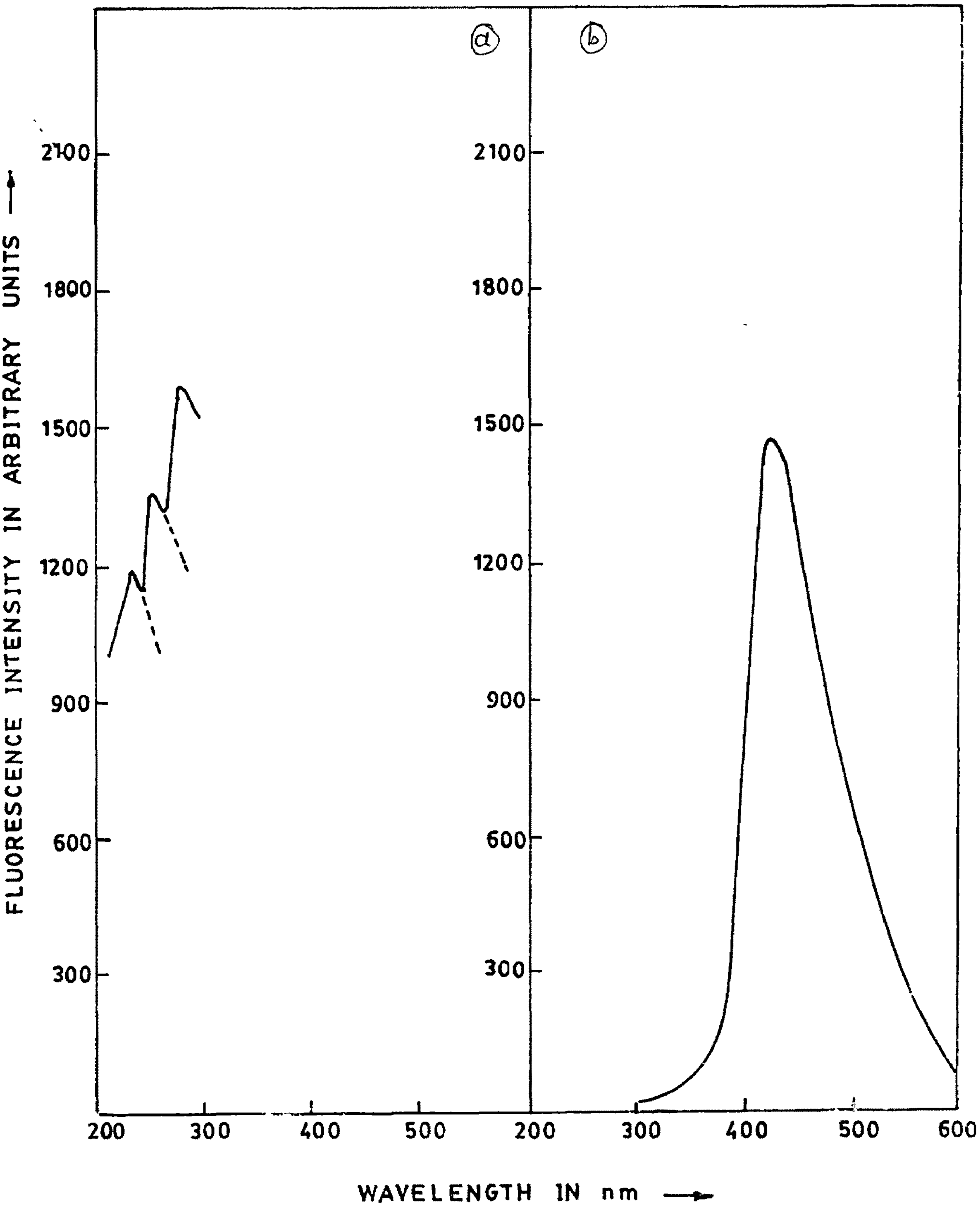
WAVELENGTH IN nm

FIGURE 22

Figure-23 : (a) Excitation spectra of annealed and quenched specimen A for 430 nm emission.

(b) Emission spectra of annealed and quenched specimen A for 272 nm excitation.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FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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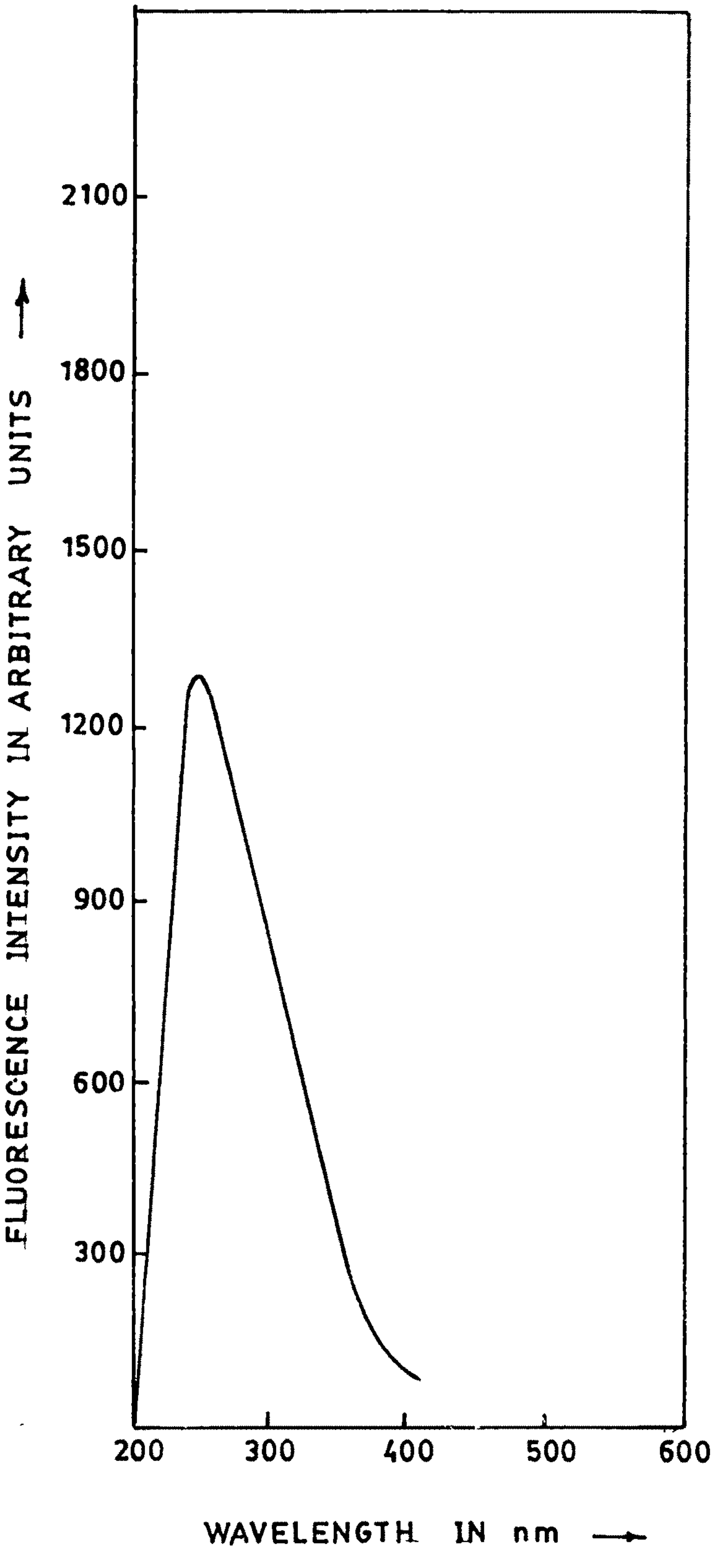
WAVELENGTH IN nm

FIGURE 23

Figure-24 : Emission spectra of annealed and quenched specimen A for 248 nm excitation.


FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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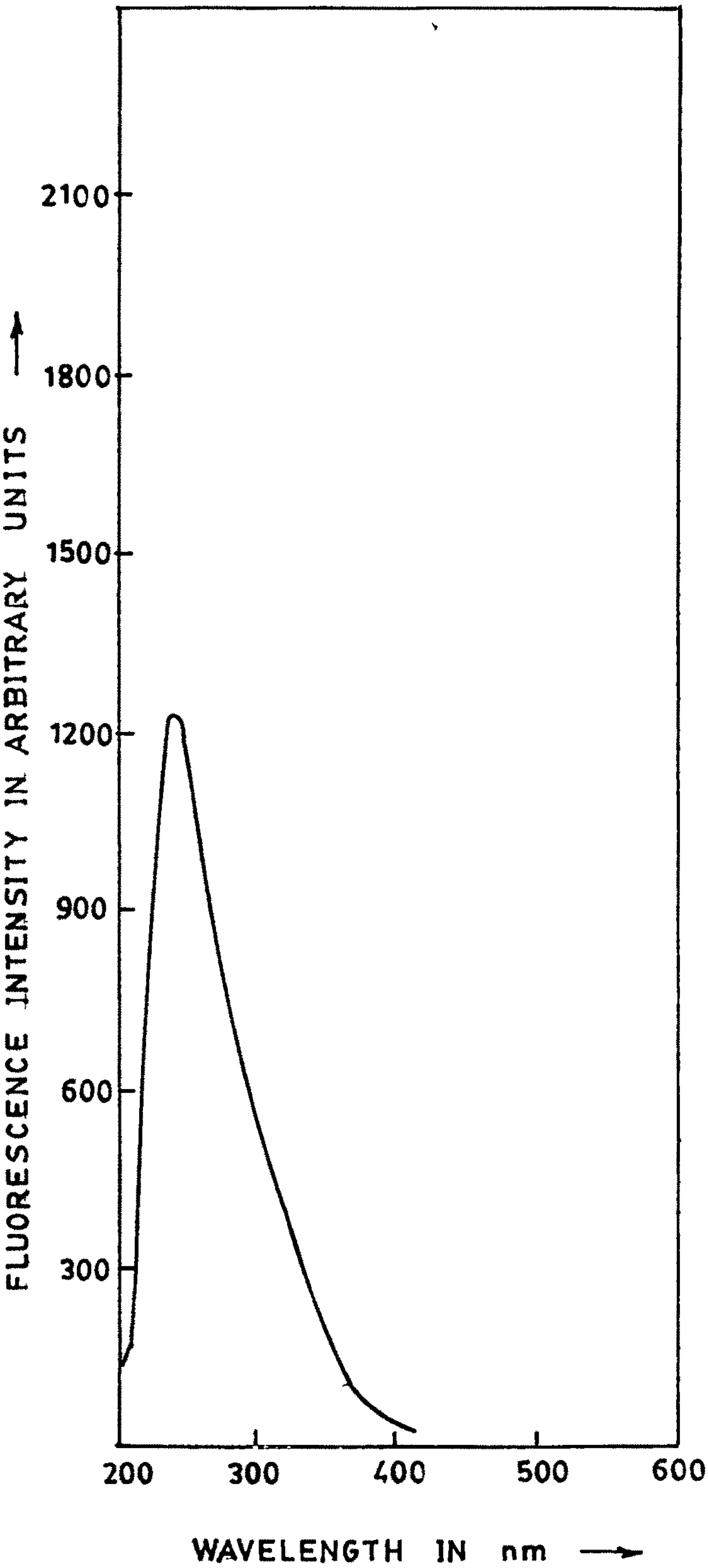
WAVELENGTH IN nm

FIGURE 24

Figure-25 : Emission spectra of annealed and quenched specimen A for 240 nm excitation.


FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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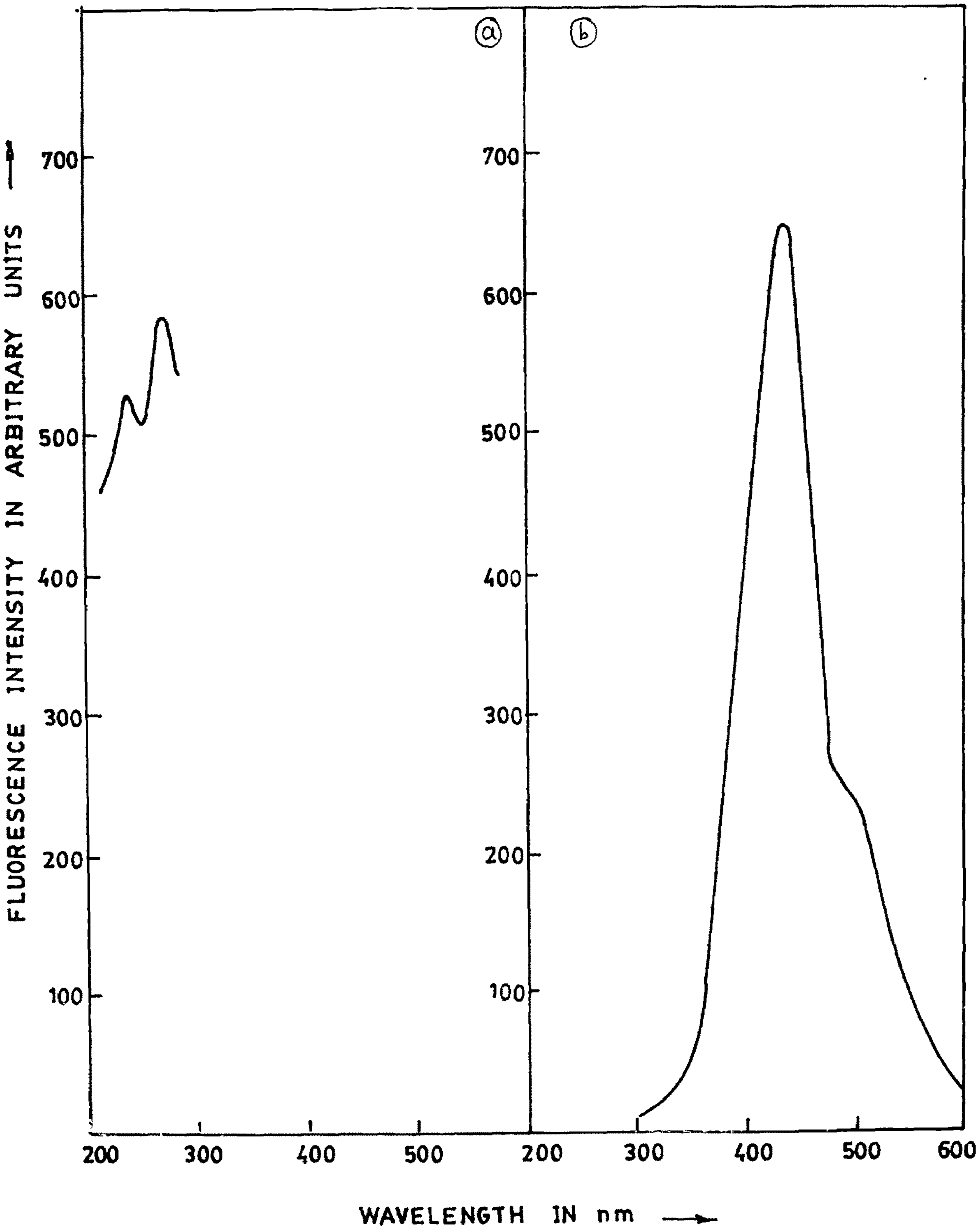
WAVELENGTH IN nm

FIGURE 25

Figure-26 : (a) Excitation spectra of annealed and quenched specimen A_1 for 440 nm emission.

(b) Emission spectra of annealed and quenched specimen A_1 for 256 nm excitation.



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FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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WAVELENGTH IN nm

FIGURE 26

Figure-27 : Emission spectra of annealed and quenched specimen A_1 for 240 nm excitation.

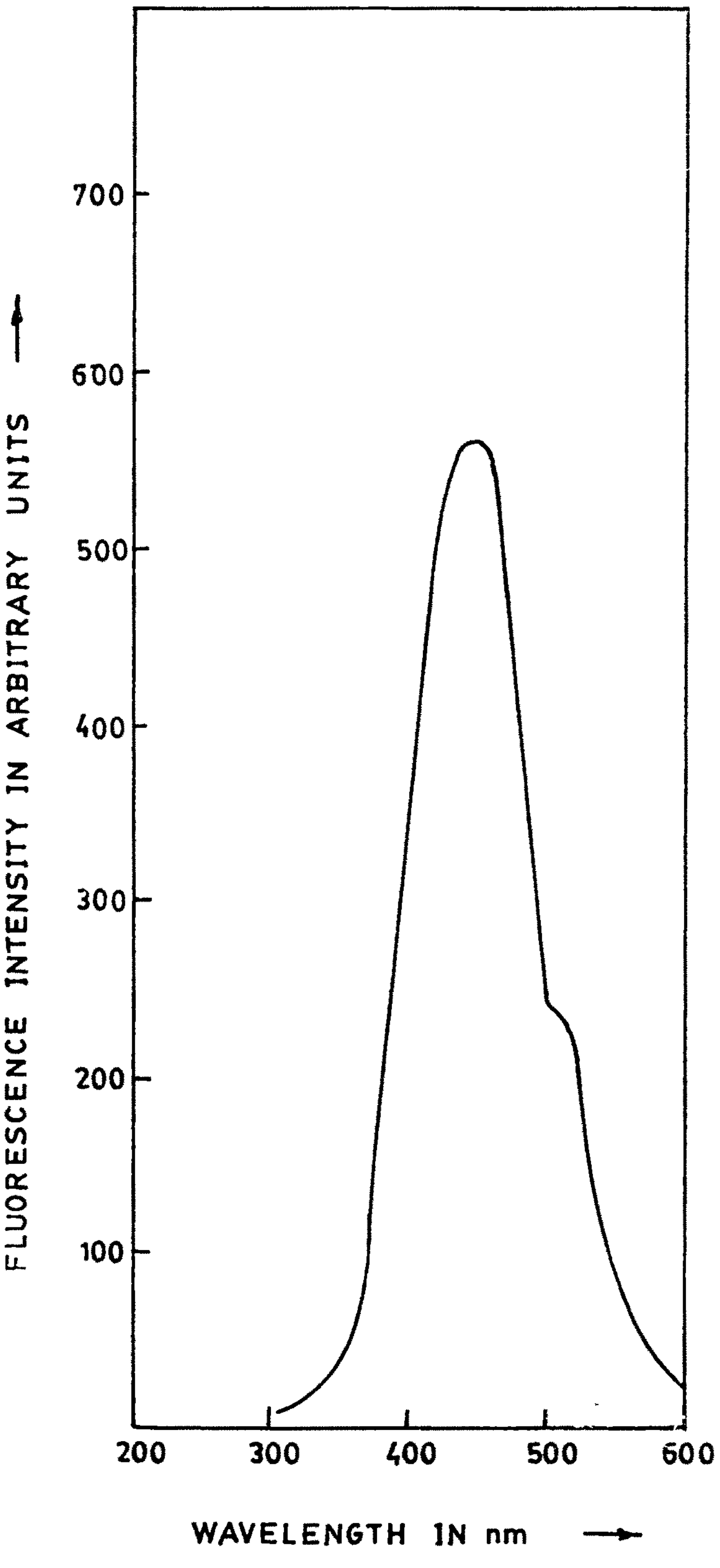
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FIGURE 27

Figure-28 : (a) Excitation spectra of annealed and quenched specimen A_2 for 440 nm emission.

(b) Emission spectra of annealed and quenched specimen A_2 for 256 nm excitation.

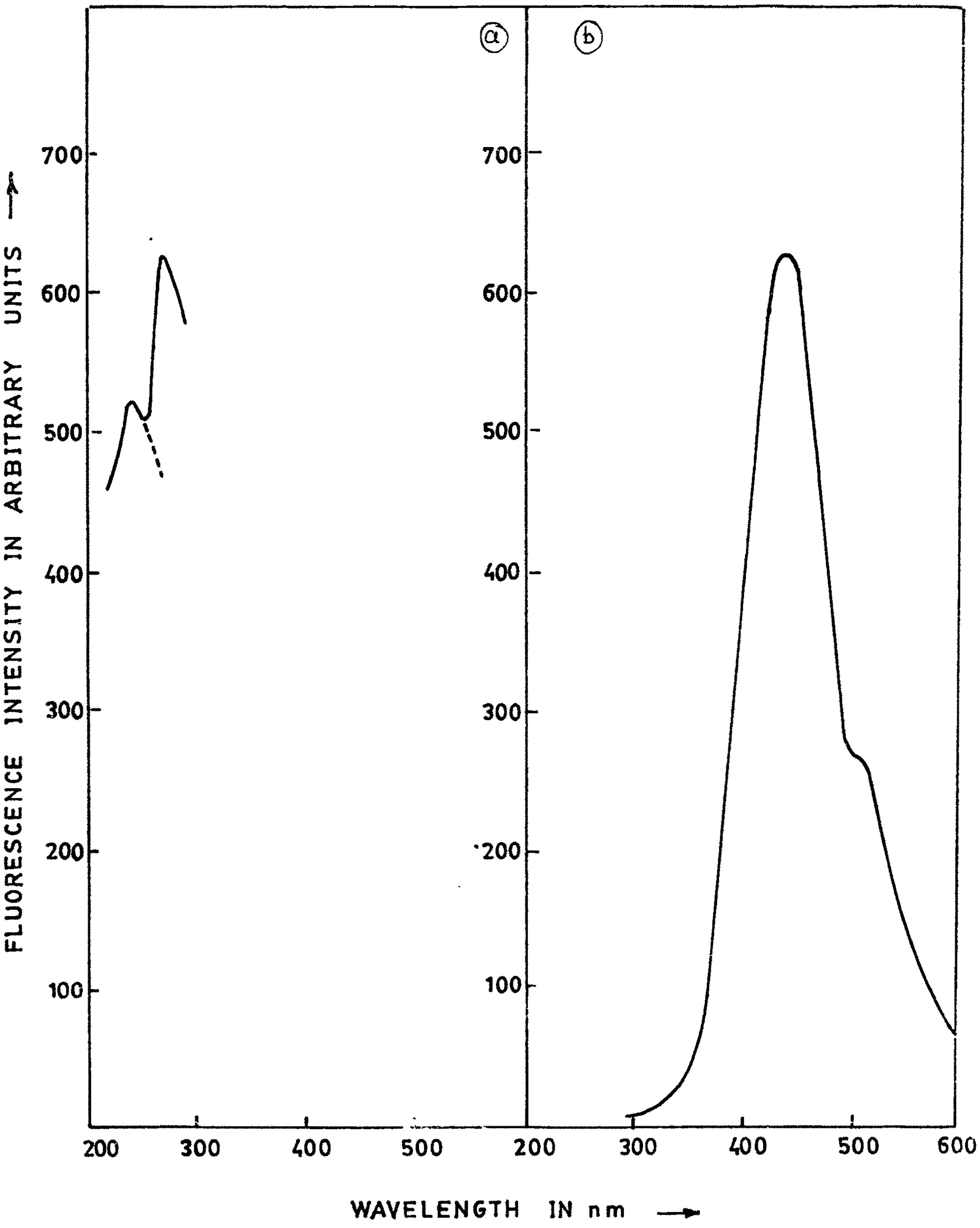

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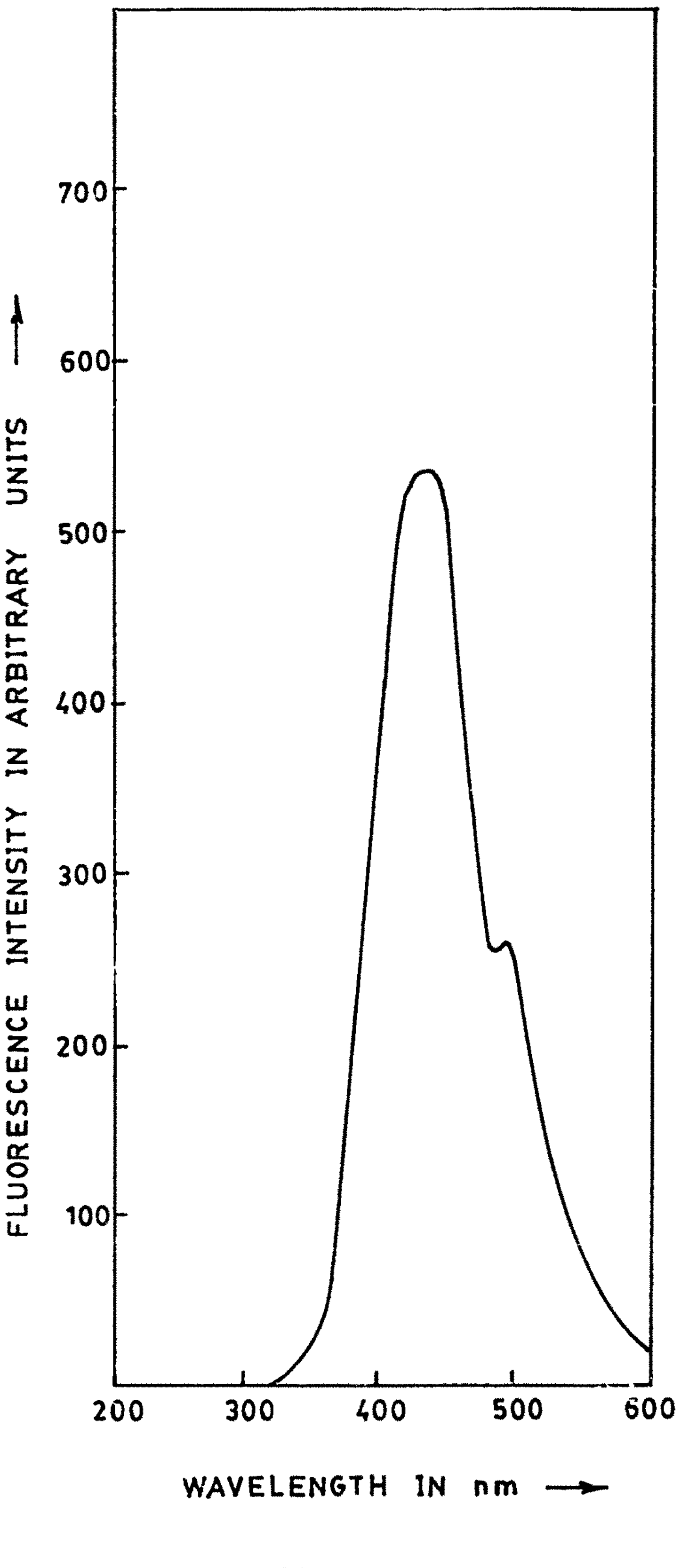
FIGURE 28

Figure- 29 : Emission spectra of annealed and quenched specimen A_2 for 240 nm excitation.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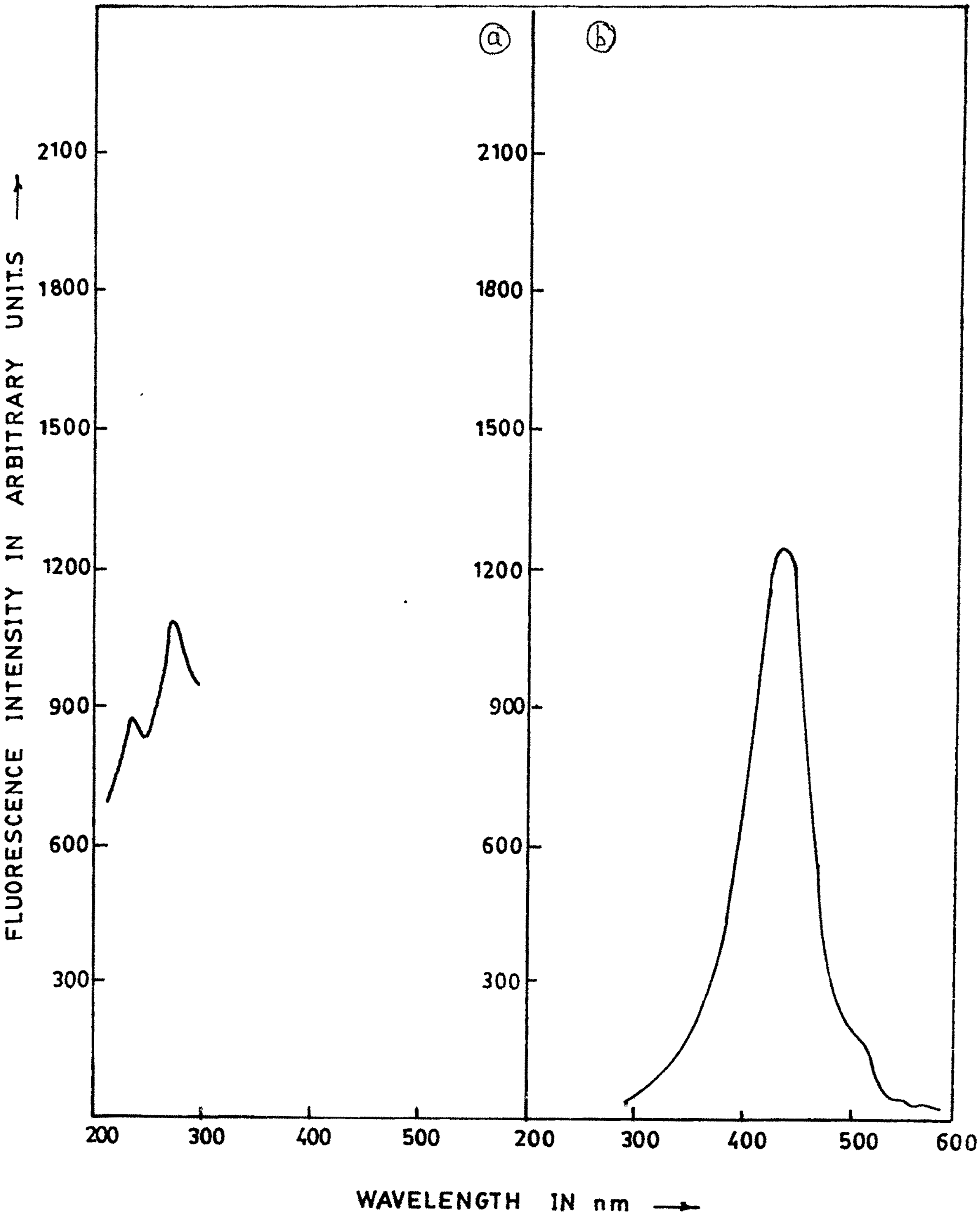
WAVELENGTH IN nm

FIGURE 29

Figure-30 : (a) Excitation spectra of annealed and quenched specimen A_3 for 440 nm emission.

(b) Emission spectra of annealed and quenched specimen A_3 for 270 nm excitation.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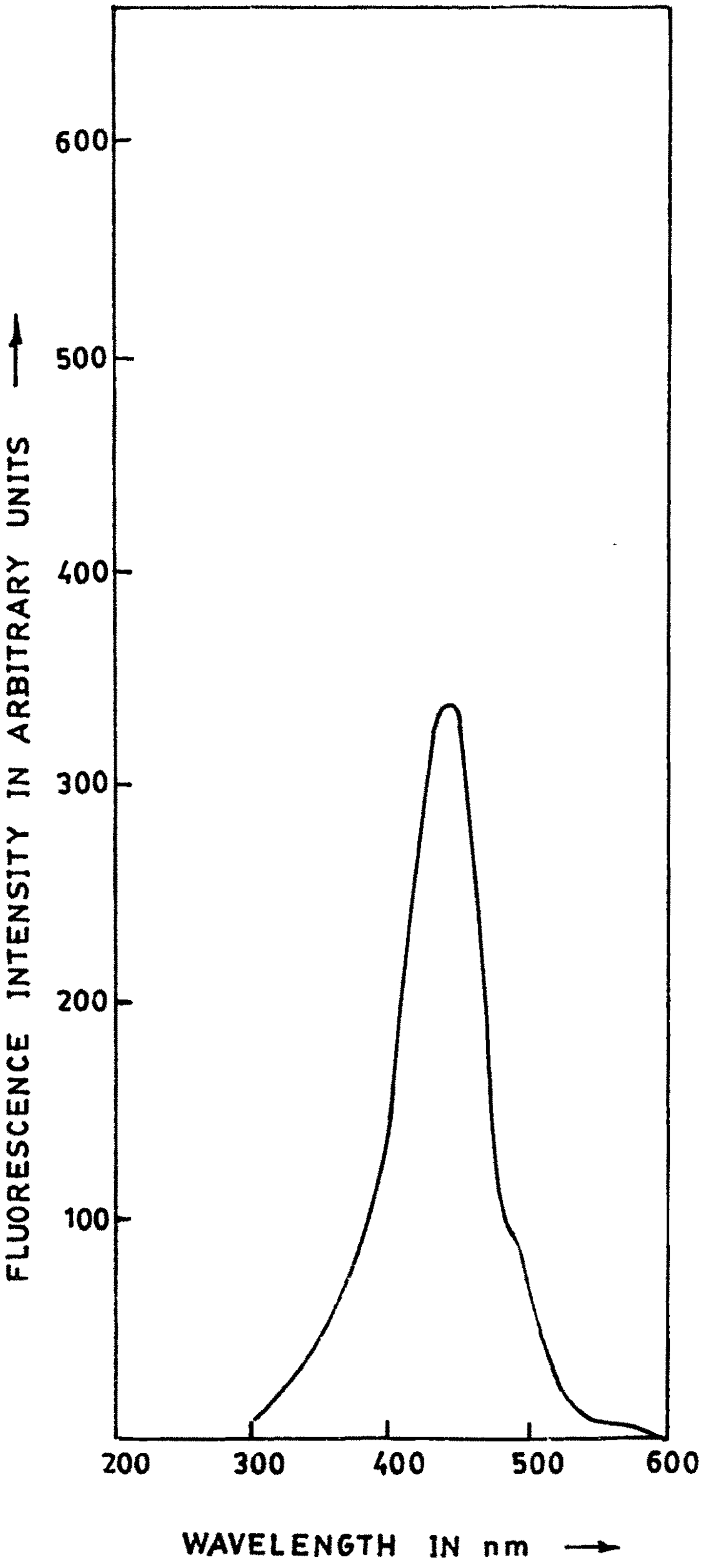
WAVELENGTH IN nm →

FIGURE 30

Figure- 31 : Emission spectra of annealed and quenched specimen A_3 for 240 nm excitation.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FLUORESCENCE INTENSITY IN ARBITRARY UNITS →
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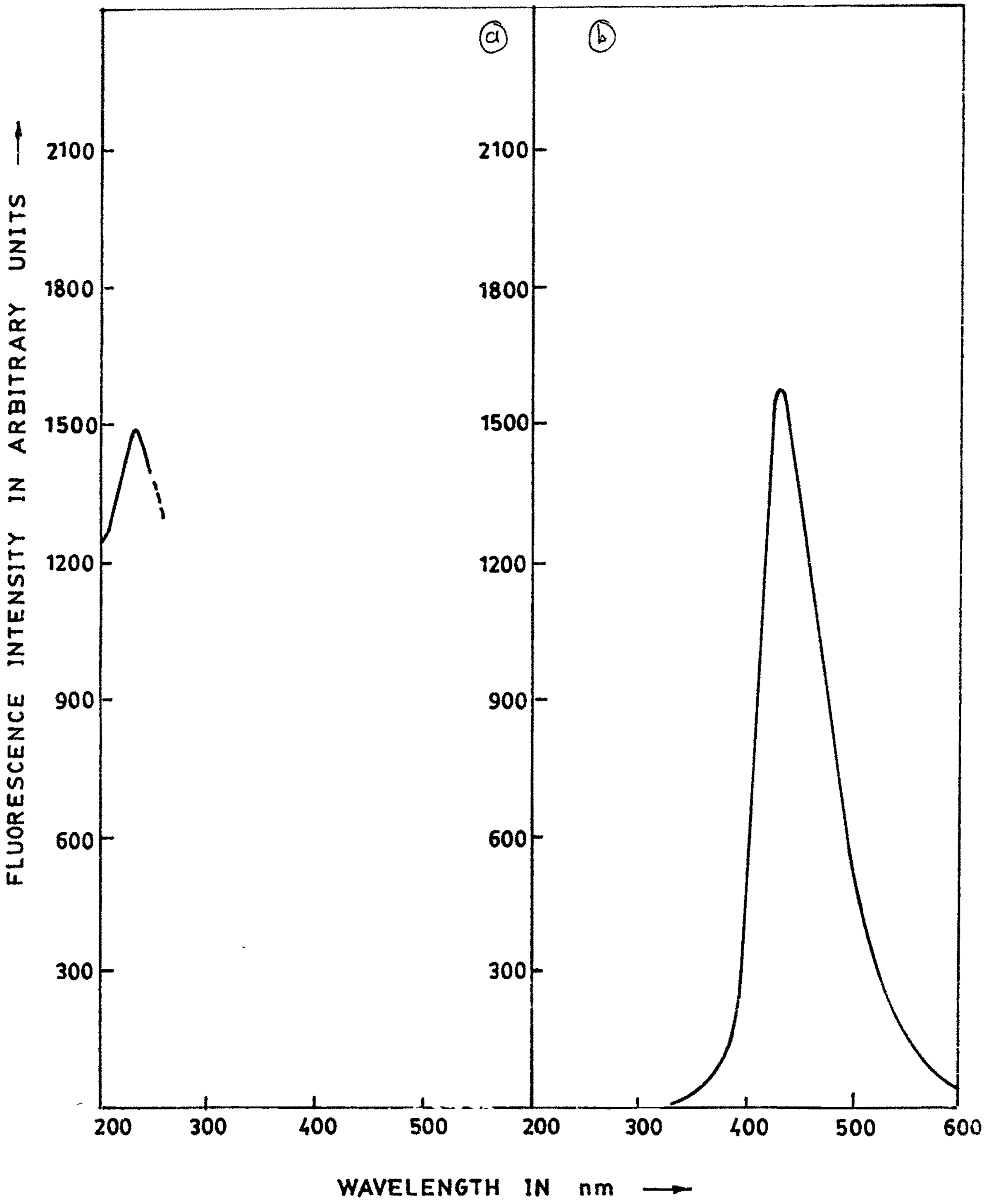
600
WAVELENGTH IN nm →

FIGURE 31

Figure-32 : (a) Excitation spectra of annealed and quenched specimen A_4 for 440 nm emission.

(b) Emission spectra of annealed and quenched specimen A_4 for 240 nm excitation.



(a)
(b)
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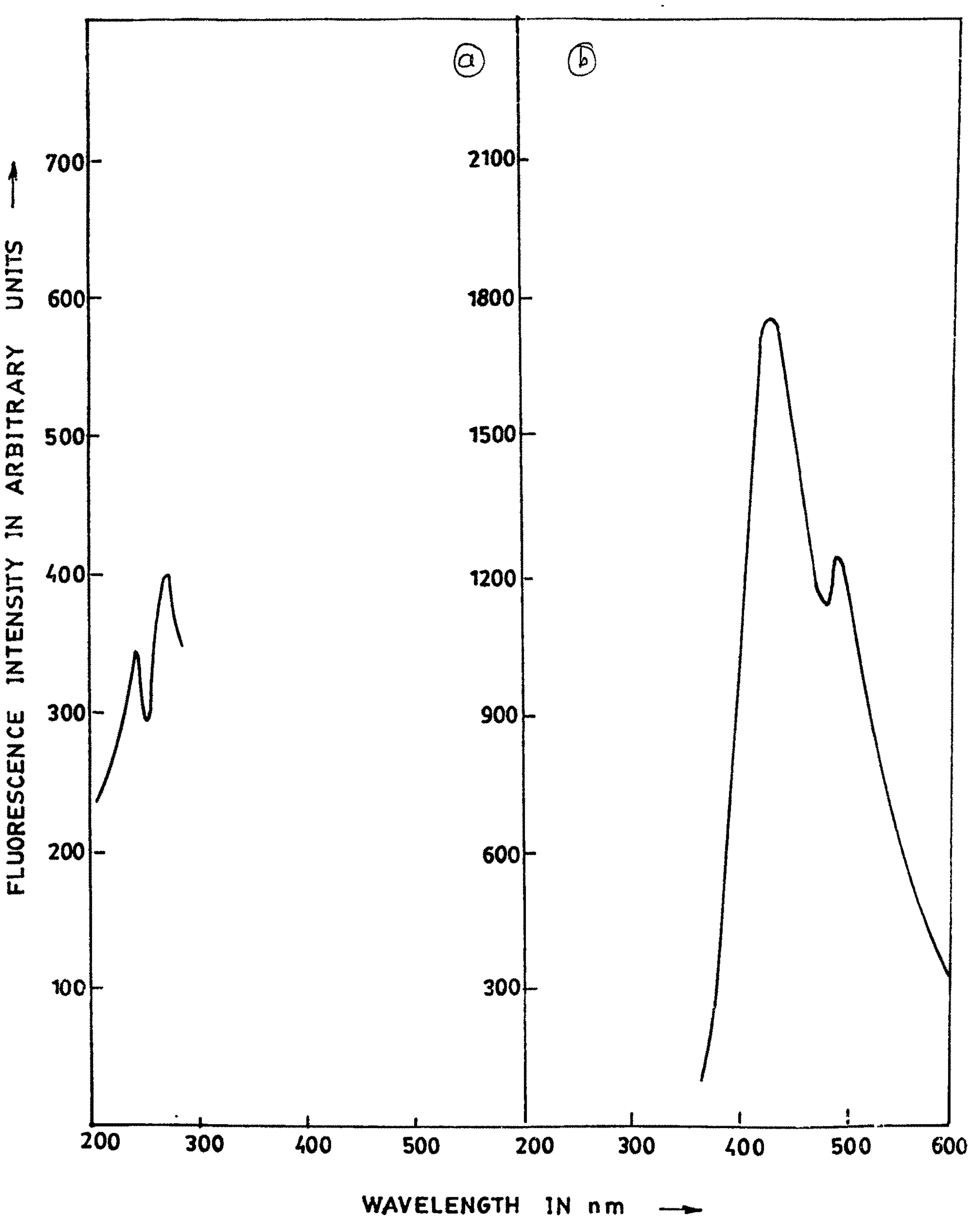
600
WAVELENGTH IN nm

FIGURE 32

Figure-33 : (a) Excitation spectra of annealed and quenched specimen A_5 for 440 nm emission.

(b) Emission spectra of annealed and quenched specimen A_5 for 270 nm excitation.



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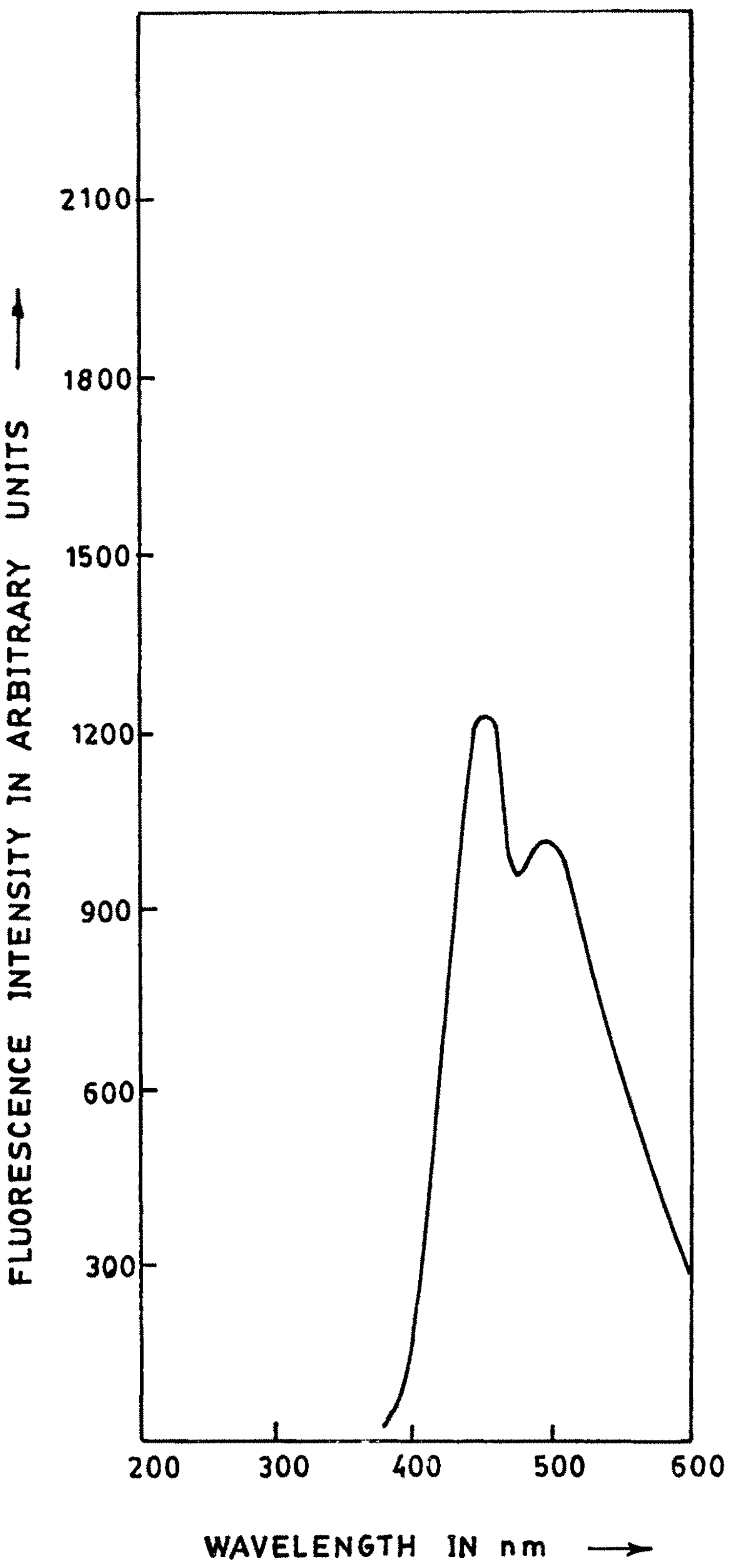
600
WAVELENGTH IN nm →

FIGURE 33

Figure- 34 : Emission spectra of annealed and quenched specimen A_5 for 240 nm excitation.


FLUORESCENCE INTENSITY IN ARBITRARY UNITS
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WAVELENGTH IN nm

FIGURE 34

DISCUSSION

The fluorescence efficiency of coumarins dependson the nature and position of a substituent in the parent molecule and also changes due to a change in the surrounding media. Though coumarin by itself does not exhibit fluorescence, many of the derivatives of coumarin are known to be fluorescent in nature. Further, in view of the use of coumarin derivatives in solar cells, the present study aims at examining the fluorescent spectra of some of the coumarin derivatives.

The fluorescence spectra, excitation and emission, has been recored at room temperature for the monomer specimen A and five polymer specimens A_1, A_2, A_3,$A_4$and A_5. The spectra presented for discussion are, for the specimens in as received condition in Figures 1 to 10, for the specimens after mechanical deformation in Figures 11 to 22 and for the specimens after the thermal treatment in Figures 23 to 34.

The emission spectra recorded in the specimens A and A_1 through A_5, exhibit four distinct bands at 320, 420, 480 and 520 nm respectively. The occurence and behaviour of each of these emission bands have been discussed in detail alongwith the changes which take place in position and intensity. Further, the discussion also includes the changes taking place in these emission bands after the mechanical deformation and thermal treatments. A energy level diagram of the electronic states and transitions have also been discussed at the end (Figure 35).

(a) 320 nm Emission Band

The emission band at 320 nm is observed in all the polymer specimens A_1, A_2, A_3, A_4 and A_5 examined in the present work, vide Figures : 3-7, 9 and 10. This emission is favoured by the excitation of the specimens into the band at 280 nm. The 320 nm band is conspicuous by its absence in monomer specimen A, vide Figures 1 and 2.

The structure of all the polymers differ from the monomer in the two aspects. One, two hydroxy groups are coverted to the two ester linkages and second, the coumarin moiety and the moiety of the diacid monomer repeats in the polymer chain. Due to this difference, of course, the polymeric systems will have higher polarizability compared to the monomer.

It seems that, a number of repeating units present in the long chains in polymer specimens are responsible for the present emission band of 320 nm. The absence of these repeating units in the monomer makes up for the absence of 320 nm emission in the monomer specimen A.

The band is observed in polymer specimens, which have the long chains. During the excitation of these specimen by ultraviolet light, the chains start vibrating, thereby causing the production of some low energy phonons. These phonons then interact with the excitation wavelength photons. This phonon-photon interaction creates a number of new photons having higher energies. This energy is equivalent to that which can take electron from π orbital to the excited state. These new photons releasing the energy and coming back to ground states are responsible for the 320 nm emission band.

In case of specimen A, no such long chain exists. Hence, no phonons are produced. Because of the non-availability of the phonons in specimen A, such a phenomenon of interaction does not take place and 320 nm emission band is not observed. Further, the large red shifts produced by the substitution of methyl and hydroxyl groups result into a higher wavelength band, which adds to the cause of missing 320 nm emission in specimen A.

Intensities of 320 nm emission band in specimens A_1 and A_2 are comparatively larger than in specimens A_3, A_4 and A_5. This can be explained on the basis of the quenching effect[1] taking place due to the substitution of an aromatic molecule as repeating unit in specimens A_3, A_4 and A_5. In case of specimens A_1 and A_2, the repeating units are aliphatic nuclei. In specimen A_5, the intensity of this peak is observed to increase comparatively, eventhough the intensity of another band at 560 nm is equally high. This increase in intensity of 320 nm emission can be attached to the symmetry observed in the aromatic attachment - along the axis joining the two ester groups, at para positions. No such symmetry is observable in the specimens A_3 and A_4.

Effect of Mechanical Deformation

The large pressure applied on the powder (as received) specimens to compress them into the pellet forms, will make the atoms come closer to each other. Although the links in polymer do not break, the atoms being close to each other, the interatomic separation reduces. The long chains of the specimens A_1 to A_5 will shorten, thereby making shorter length chains to vibrate after excitation. The shorter chains now give rise to phonons, which in turn will have the photon-phonon interaction with the excitation photons. The new photons generated have lesser energy now and give rise to the emission which shifts slightly from 320 nm to 350 nm in all the polymer specimens A_1 to A_5. In effect the chains have not broken into smaller chains, but have reduced their 'free motion' space. The constrain on the available space due to some of the planes of molecules going out of alignment and the mechanical pressure applied thereupon will make the polymer molecules fit into each others now, makes effect on the intensity of 350 nm which automatically reduces, compared to the intensity for the same specimen in powder form.

Effect of Thermal Treatment

In a few crystals, it has been possible to increase the fold length for macromolecular crystals. The annealing of the specimen to an elevated temperature, for two hours and then quenching them to room temperature is responsible for the breaking and remaking of the backbone chain bonds. This is so chaotic in nature, that the new molecules formed not only shorten in chain lengths by breaking into a large number of smaller chains, but may also become non-uniform in the distribution of masses over the chain lengths. The configuration of new molecules formed due to the breaking of chains at various sites and remaking them at some other sites; does not allow the earlier observed vibrations of long polymer chains. The vibrations caused due to these shortened but larger number of chains will produce the phonons with much lesser energy. Thus the photon-phonon interaction which now takes place, is not sufficient to cause new photons with larger energy observed earlier in specimens A_1 to A_5. This is mainly what makes the 320 nm emission band vanish from the spectra for polymer specimen A_1 to A_5. It is obvious that 320 nm emission band which is absent in monomer, as received specimen A, is also missing from spectra for annealed and quenched specimen A.

(b) 420 nm Emission Band

The emission band at 420 nm is observed in all the specimens examined here. The band is present in the monomer specimen A at 430 nm but in all the polymer specimens A_1 to A_5 at 420 nm (Figures 1-7 and 9-11).

This band is attributed to the attachment of the hydroxyl group alongwith the methyl group in the coumarin structure at 7-8 and 4 positions respectively. Coumarin shows a fluorescence maximum at 351 nm, which now shifts towards emission at 430 nm due to the substitution[2] with hydroxyl and methyl groups. This is the red shift observed in specimen A.

Specimen A also contains the intramolecular hydrogen bond. The absence of this bond[3,4] at 7-8 positions in specimen A_1 to A_5 is responsible for the shift from 430 nm to the emission at 420 nm.

The intensity of 420 nm emission increases sharply in specimens A_1 to A_5 compared to the specimen A. This is the effect of polymerization. The appreciable increase in the number of molecules forming the chains in the specimens A_1 to A_5 causes the intensity of this emission to increase. In the aliphatic compounds A_1 and A_2, the intensity in specimen A_2 is much larger compared to that in A_1. This is because of the difference in the repeating units in the two polymers. In case of polymer A_2, the repeating unit is -CH=CH- and in polymer A_1, it is eight ethylene units $-(CH_2)_8-$. The repeating double bonds in A_2 would contribute towards the increased polarizability of the molecules of A_2. Naturally, this will contribute towards the enhancement of the fluorescence intensity.

The comparison of intensity of specimen A_1 with the intensity of specimens A_3 to A_5 show that the latter specimens exhibit much larger intensity. This is because the specimens A_3 to A_5 have the aromatic nuclei as the repeating units. Instead specimen A_1 has the aliphatic methylene as a repeating unit. Here again, the π bond character of the aromatic nucleus will enhance the polarizability of the polymeric systems A_3 to A_5 compared to the A_1. The enhanced polarizability is reflected into the increased intensity of the above band. However, it is interesting to note that the intensity of the emission band is highest in the polymer specimen A_3. The symmetry aspect in the specimen should result into the highest intensity for the specimen A_5, which has been contrary to the observations. The careful analysis of the intensities for specimens A_3, A_4 and A_5 indicates that there is the enhancement in the intensity of the 420 nm emission band in the order from specimens A_5 to A_4 to A_3. This has been reflected into the steric factors of the polymer systems A_3 to A_5. The comparison of A_5 polymer system to A_4 and A_3, show the latter systems having higher steric interaction due to 1,3 and 1,2 substitution on the benzene ring of the di-acid repeat units. The steric interaction will be maximum in the specimen A_3 due to the phthalic acid ester (1,2 substitution) repeating units. It seems that to decrease the steric repulsion the aromatic ring might be going out of plane of the system, resulting into closer packing of the molecules of A_3 in the solid state, which in turn will result into the higher intensity of specimen A_3.

Effect of Mechanical Deformation

The mechanical compression of the specimen A as well as the specimens A_1 to A_5, show the emission at 430 nm for specimen A and 420 nm for polymer specimens. These specimens in the powder form also show the emissions at identical positions.

The specimens are now compressed together, thereby the interatomic separation being reduced. It is possible in case of polymer chains when compressed the different molecules may go out of plane, tilt and occupy lesser space. The chain lengths of the polymer specimen shorten and when such shorter chains vibrate, the effect is to produce smaller intensity for the same emission band. It is obvious now that the intensity of 430/420 nm band in the mechanically deformed specimens should be reduced compared to that in the powder form specimens. The emission band at 420 nm becomes sharper and dominent compared to the other bands in Figures 14 through 22. The characteristic excitation wavelength for the above emission of 420 nm seems to be 252 nm as observed in the Figures 15, 17, 18, 20 and 22. Further, for other excitation of 272 nm, the emission of 420 nm does not stand out as observed in Figures 14, 16, 19, 21.

Effect of Thermal Treatment

The annealing of the specimens at an elevated temperatures will make the atoms disperse from each other making the chains elongate, due to the absorption of heat energy. The interatomic separation which has been increased to a large extent can be expected to revert back to normal on cooling the specimens. However, the sudden cooling of these annealed specimens to room temperature will produce the configuration of the specimens other than the original ones. Further, the long polymeric chains may break into smaller chains. During this breaking and remaking of the polymeric chains, the basic structure of the molecule with methyl group and absence of hydroxyl group remains unchanged. This gives rise to the 420 nm emission. While in specimen A, the hydroxyl group and methyl group remain in the new configuration too, thereby giving the 430 nm emission. It must be noted that there are no long chains in specimen A; eventhough the number of molecules are large in the sample after the thermal treatment. The potential energy of the polymeric systems increase on the breaking of these chains. The dissipation of this energy into a larger number of smaller chains will make the specimen emit larger wavelength. There will now be new energy level corresponding to the ground state itself. The shift of the emission band from 420 to 440 nm can thus be explained. The intensity of 420 nm emission has grown in the specimens after the thermal treatment, compared to that for the specimens after the plastic deformation. This is due to the new elongated configurations to which the specimens come to after the thermal treatment and shortened configuration in the mechanically deformed specimen.

(c) 480 nm Emission Band

The emission band at 480 nm is present in all the specimens A_1 to A_5, however, it is absent in the specimen A. In specimen A, the positions at 7-8 have been occupied by hydroxyl groups, and ester group has been substituted in those positions for specimens A_1 to A_5. The substitution of the ester group in the repeating units is responsible for 480 nm emission in the above specimens. The absence of the ester group automatically makes up for the absence of 480 nm emission in specimen A.

The 420 nm emission band is attributed to the absence of hydroxyl group at 7-8 positions in the specimen A_1 to A_5. However, the band at 480 nm emission is caused due to the attachment of CO with O at these positions i.e. formation of esters. This attachment gives rise to a new energy level, the emission to which is responsible for 480 nm emission band. The two bands are thus closely related to each other and can be seen in the form of a doublet. Further, both these bands show more or less the same intensity for all the specimens. Further, it is observed from Figure 3(b), and Figure 6 (b), that 480 nm emission is prominent compared to 420 nm. One emission grows at the cost of other in the above doublet.

The intensity of 480 nm band in A_3, A_4 and A_5 specimen should be lesser than in specimens A_1 and A_2. This is because it is a known fact that substitution of aromatic[1] molecules diminish fluorescence. Specimens A_3, A_4 and A_5 show the successive drop in the intensity (Figures 6,7 and 9) as expected. The attachment of aromatic molecule have the ester group at ortho, meta and para positions in polymers A_3 to A_5. However, the intensity of 480 nm in specimen A_3 has suddenly shot up compared to those in A_1 and A_2 (Figures 6, 3 and 5). The reason is the closeness of the ester group in ortho positions for specimen A_3; which increases the intensity appreciably. This is the known sensitivity to the position of substitution.

The intensity pattern observed for 480 nm emission in the specimens of A_1 to A_5 agrees with the explanation provided for 420 nm emission on the basis of the structural changes taking place from specimen to specimen. Specimen A_2 contains double bond in aliphatic nuclei of -CH=CH- and also the closeness and symmetry factor for it compared to A_1 makes specimen A_2 show larger intensity than for the specimen A_1. The aromatic nuclei in the specimens A_3, A_4 and A_5 also explain the intensity pattern for 480 nm identical to 420 nm emission, based on the steric effect. This explanation is expected as 420 and 480 nm emissions are portrayed as the doublets.

Effect of Mechanical Deformation

The emission observed at 480 nm in the powder specimens A_1 to A_5 is attributed to the presence of ester group in them. This band now shifts to 460 nm after the specimens have been mechanically deformed into the pellets. Because 420 nm and 480 nm emissions are doublets, it is found from Figures 14, 16, 18, 19, 20 and 21, that whenever 420 nm becomes more pronounced it is at the cost of the intensity of 480 nm emission. In the above figures it can be observed that 480nm emission appears as a shoulder to the main emission at 420 nm.

The intensity for the 480 nm emission after plastic deformation in the specimens A_1 to A_5 is more or less similar to that in powdered specimens. Further, this emission is absent in specimen A, as is expected due to absence of ester group in the monomer specimen A.

Effect of Thermal Treatment

The specimen A does not contain the ester group, but contains hydroxyl group. The 480 nm emission corresponds to the absence of hydroxyl group and the presence of ester group in the specimens A_1 to A_5. Hence, this emission is not expected in specimen A as earlier in powdered specimens or the specimens after mechanical deformation.

In specimens A_1 thorugh A_5, the emission is observed at 500 nm. The shift from 480 nm to 500 nm is due to the configurational change in the polymer specimens. The chains being broken into smaller chains of large number, the shift of 480 nm is expected. However, the 420 nm being dominant in these specimens after the thermal treatment, it is obvious that the other emission namely 480 nm from the doublet is observable in the form of a weak peak.

The emission at 480 nm is not observed in the specimen A_4, where the only emission observed is 420 nm (440 nm). The intensity of this emission has been enhanced compared to all other specimens. This is at the cost of 480 nm emission. This is an additional point in favour of the statement that one of the emission grows at the cost of the other in the doublet.

(d) 520 nm Emission Band

The emission band at 520 nm is assumed to be due to the Carbonyl[5,6] group, in all the specimens were examined. This band is observed at 500 nm in the specimen A. Alkyl substitution[7] makes the small red shift in fluorescence causing the band to shift to 520 nm for specimens A_1 and A_2. However, the substitution of the aromatic molecule shifts the band further to 560 nm.

The carbonyl group is present in the monomer specimen A as well as in the polymer specimens A_1 through A_5. The emission band at 520 nm, which is observed at 500 nm in specimen A, is a weak band, in the form of a mere shoulder to the main spectra. However, in specimens A_1 thorugh A_5 it has increased in intensity as well as seen as a prominent one, because the specimens are long chains having large number of molecules, each containing the carbonyl group. The presence of the carbonyl group in the repeating units of the specimens make the weak band present in specimen A at 500 nm grow in intensity at 520 nm. Further, it seems to be favoured by selective excitation as seen from Figures 4 and 5. The 520 nm emission is exhibited for 296 nm excitation in the specimen A_1, but not for the excitation of 280 nm.

The emission is also missing from the emission spectra of specimen A_3, where the spectra is recorded for the 260 nm excitation and not for 296 nm, which seems to be the characteristic excitation into 520 nm emission. Secondly, the band is expected to be at 560 nm and not at 520 nm in specimen A_3. The specimens A_3, A_4 and A_5 are in a group with the aromatic nuclei substitution in place of aliphatic nuclei of specimens A_1 and A_2.

The absence of emission band at 520 nm in A_3 can also be explained as the intensity of 480 nm emission suddenly shoots up in the above specimen compared to the other specimens. The 480 nm grows at the cost of 520 nm emission.

In effect, the emission is caused due to the carbonyl group and it is a weak emission. It grows because of the presence of carbonyl group in the repeatative units. Further, whenever the emission is missing from the spectra, another emission at 480 nm enhances.

Effect of Mechanical Deformation

In the mechanically deformed specimens, the chains get entangled, shorten in length and also get out of plane in the configuration, thereby entering into one another. The new configuration now is responsible for the absence of this peak in the specimens A_1 to A_5. It is not possible for the weak emission to grow in intensity due to the constrain on the polymer chains.

However, the specimen A does not contain the long chains, which do not get affected by the mechanical deformation, hence, this peak is still observed in specimen A after mechanical deformation.

As other bands are missing, the 520 nm band stands out more in the emission spectra.

Effect of Thermal Treatment

It has been observed that the emission band at 520 nm is missing from all the specimens A and A_1 through A_5. The absence of this band can be explained here after the effect of the thermal treatment, wherein the long chains of polymers get broken into a large number of smaller chains. These smaller chains now are not capable of the emission energy, will correspond to the emission of 520 nm. The weak band does not grow in sufficient intensity to be recorded. Further, the emission band at 480 nm has appeared stealthily in all these specimens at 500 nm. Eventhough, the band at 480 nm which forms the doublet with the emission at 420 nm, is weak as observed in specimens here, the appearance of which is responsible for the missing 520 nm emission after the thermal treatment.

(e) Emission Spectra

The ground state corresponding to unsubstituted coumarin[2] is represented by π_c. This is red shifted to π_2 as a result of substitution of methyl and hydroxyl groups in the original coumarin, at 4 and 7-8 positions respectively. The electronic transition from lowest excited state to π_2 gives rise to the emission at 430 nm in specimen A. This is the transition ($\pi_2' \leftarrow \pi_1^*$). The absence of hydrogen

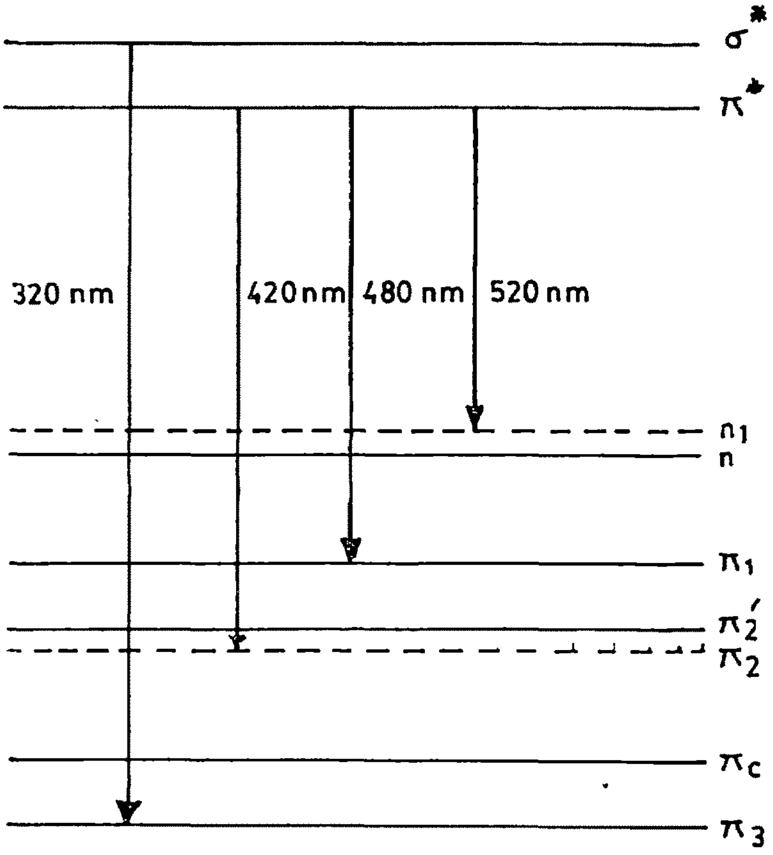

FIG. 35 SCHEMATIC ENERGY LEVEL DIAGRAM SHOWING ELECTRONIC STATES AND TRANSITIONS CORRESPONDING TO FEMISSION BONDS

bonding in specimens A_1 to A_5, blue shifts π_2' to π_2. The emission corresponding to ($\pi_2 \leftarrow \pi_1^*$) transition is 420 nm.

The attachment of R- CO to -O of hydroxyl group substituted in coumarin introduces a new ground state level π_1. The transition from lowest excited state to π_1 corresponds to 480 nm emission. This is the ($\pi_1 \leftarrow \pi_1^*$) shown in Figure 35. However, specimen A does not exhibit this emission because no such attachement is present in it.

The non-bonding electron present on the oxygens at 1 and 2 positions gives rise to a level n, called the non-bonding level. The transition to this level gives the emission at 500 nm in specimen A. However, the n level is red shifted to n_1 for the specimens A_1, A_2 and A_4, A_5. This is because of the substitution of aliphatic and aromatic structures in two groups respectively. The transition ($n \leftarrow \pi_1^*$) is responsible for the 520 nm band. The red shift is less for aliphatic substitution giving the 520 nm emission, while the aromatic substitution gives 560 nm, having larger red shift. The specimen A_3 is excited by a more energetic wavelength of 260 nm compared to other specimens A_1, A_2, A_4 and A_5. The electrons being more energetic, they return to π_1, level instead of n_1. This explains the high intensity of 480 nm and also the absence of 520 nm emission for the specimen A_3.

The excitation of polymer specimens produce phonons due to the vibrations of the molecular chains. These phonons interact with the excitation wavelength photons. This corresponds to a level π_3 .The transition from the lowest excited state to π_3 ($\pi_3 \longleftarrow \overset{*}{\sigma}$) contributes the 320 nm emission in specimens A_1 to A_5.

The absence of the long chains in specimen A, is responsible for the missing 320 nm emission. The production of phonons and thereby the interaction with photons is not feasible in specimen A. Hence, 320 nm emission is not observed in specimen A.

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