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Development of Intrinsic IPT Scintillator

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Abstract

We report on the development of a new polystyrene based plastic scintillator. Optical absorption, fluorescence and light output measurements are presented. Preliminary results on radiation damage effects are also given and compared to the effects on a commercial plastic scintillator, NE 110.

1 Introduction

In order to develop new plastic scintillators, a program to investigate the photophysics of polystyrene (PS) based systems has been underway at Fermilab for the past year and a half. We have focused our development on polystyrene based scintillators since we perceived the major application for these new scintillators to be in the form of Plastic Scintillation Fiber (PSF). Polystyrene is easily drawn into fibers and can thus form the core material for stepped index plastic optical fiber. We have prepared a number of test scintillators using 2-(2'-Hydroxyphenyl)-benzothiazole (HBT) or a derivative of HBT as the only dopant. Absorption, fluorescence, and light output measurements were then performed.

2 Physics of the Scintillation Process in PS

2.1 Intrinsic Fluorescence - Scintillation

In aromatic compounds like polystyrene, it is the excitation of π -orbital electrons that leads to fluorescence. Fluorescence is defined as the radiative transition from the first excited singlet state to the ground state,

$$S_1 \rightarrow S_0$$

with the emission of a photon. Excitation of π -electrons by ionizing radiation and the subsequent fluorescence of the excited states is the primary energy transfer process in organic scintillators. The primary scintillation efficiency,

P, is just the fraction of the energy deposited in the scintillator that goes into π -electron excitation. For most aromatics $P \simeq 0.1$. However, not all of this excitation energy leads to fluorescence. A number of non-radiative de-excitation processes can compete with fluorescence. Internal quenching, in which the excitation energy is dissipated non-radiatively, has a large rate constant in polystyrene and thus the radiative quantum yield (probability of fluorescence) in polystyrene is only 7%. [1]

2.2 Energy-Couplers

Solutions of PS plus an efficient fluorescent dopant can give a system with close to unity quantum yield. Quantum yield is defined here as the probability that an excited state in the polymer leads to the emission of a photon by a dopant. A theory of non-radiative energy transfer between molecules in solution has been developed by Förster. [2] The energy transfer is described by a dipole-dipole interaction in which non-radiative energy transfer occurs between the first excited π -singlet state of the solvent and the solute (dopant). The strength of this interaction is

$$k = \frac{1}{(\tau_{0s})_0} \left(\frac{R_0}{r} \right)^6$$

where $(\tau_{0s})_0$ is the natural fluorescence lifetime of the solvent, r is the mean separation between solvent and solute molecules and R_0 is a constant proportional to the overlap integral between the solvent fluorescence distribution and the solute absorption, i.e.:

$$R_0^6 \propto \int_0^\infty f_s(\nu) \varepsilon_d(\nu) \frac{d\nu}{\nu^4}.$$

ν is the wavenumber, $f_s(\nu)$ the solvent fluorescence distribution and $\varepsilon_d(\nu)$ the absorption distribution of the solute. Typical values for R_0 in PS systems are between 5 and 30 Å.[3] At high dopant concentration (r small compared to R_0) this process can dominate over emission or quenching of the solvent. Thus if the dopant's radiative quantum yield is close to unity, the number of photons emitted per solvent molecule π -electron excitation can approach one even though the radiative quantum yield of the solvent may be small.

2.3 Single vs. Multiple Step Systems

Dopants added in high concentration ($\simeq 1\%$) that couple to the primary scintillation of the solvent are primary dopants. They both raise the scintillation photon yield (the number of photons emitted per unit energy deposited in the solvent) and shift the mean wavelength of the final fluorescence to longer wavelength. A binary system, solvent (PS) plus primary dopant, can be considered a single step or primary scintillator because the dopant couples directly to the primary scintillation on a distance scale of Angstroms.

Secondary dopants may also be added, but their functioning is qualitatively different from that of the primary. Secondary dopants are typically added in low concentration ($\simeq 0.01\%$) and only shift the mean fluorescence wavelength further into the red. They do not increase the intrinsic photon yield of the scintillator. Energy transfer between the primary and secondary dopant is through the emission and reabsorption of a photon (the trivial process). The best one can do in this process is to maintain the photon yield of the primary. Secondary dopants increase the technical photon yield

of a scintillator, however. By shifting the fluorescence emission to longer wavelength, more of these photons can escape from finite sized scintillators and self-absorption by the scintillator is thus reduced. Most primaries used to date in PS based scintillator fluoresce in the deep blue, $\lambda_p \simeq 350 - 390$ nm. As can be seen in figure 1, PS absorbs quite strongly in this spectral region. Without the use of a secondary dopant much of the light produced by the primary is reabsorbed within a few centimeters. Although the use of a secondary waveshifter does increase the technical quantum yield of a scintillator, the process of emission by the primary followed by absorption by the secondary and finally by emission from the secondary does not give unity photon yield. Self absorption by the primary and by the secondary lead to a decrease in yield since rarely do these dopants have quantum yields of one. It is the finite overlap between the absorption and emission spectra of the various dopants that lead to these efficiency losses. In particular, for very large path lengths within the scintillator self absorption losses by the secondary can become quite substantial.

2.4 Intra-Molecular Proton Transfer Compounds

Ideally one would like to use waveshifters whose emission and absorption spectra have no overlap. Compounds which undergo intra-molecular proton transfer upon excitation exhibit this property.[4] Renschler and Harrah first reported using 3-Hydroxy Flavone in PVT based scintillator.[5] In their studies 3-HF was used as an intermediate waveshifter between the primary and the terminal waveshifter. It was then proposed that since 3-HF's absorption

spectrum overlapped the fluorescence emission distribution for polystyrene, 3-HF (or other IPT compounds with appropriate absorption spectra) could be used as the primary dopant in polystyrene based scintillator if it could be added in sufficient concentration. [6] In addition, since the fluorescence distributions for these types of compounds have emission peaks at wavelengths often longer than 500nm., no secondary dopant would be required. For the application of PSF this situation is ideal. We have a single step system (binary) in which the light produced by ionization is localized along the track trajectory to within approximately 10-20 Å. Energy transfer is very efficient since the only transfer is via the Förster mechanism and there should be little self-absorption by the dopant. Also the final fluorescence is in a wavelength region where PS is extremely transparent. In our studies we have chosen the compound 2-(2-Hydroxyphenyl)-benzothiazole (HBT). It has properties similar to 3-HF in terms of absorption and fluorescence, but is less prone to oxidation effects and is easier to purify. A number of derivatives of HBT have also been studied.

3 Results with HBT and HBT Derivatives

In addition to HBT, the following derivatives were synthesized and used as primary dopants in PS: 3-Chloro-HBT, 4-Methyl-HBT and 5-Methyl-HBT. All scintillator samples were prepared by mixing 1 wt. % of the solute with vacuum distilled styrene monomer. The solution was degassed by repeated freeze, pump, thaw cycles and polymerized at 125° C. Samples were then

cut and polished. Absorption measurements were made on a HP 8451 diode array spectrophotometer. In all cases pure PS was used as the reference. Fluorescence measurements were made with UV excitation ($\lambda_{ex} = 254 \text{ nm.}$) in this case using the 8451 as a fluorimeter. Absorption and emission spectra for the above samples are given in figures (2-6). The scintillation light output from the samples was determined using the 1.06 MeV electron from ^{207}Bi . The samples were excited by the bismuth and the light output was monitored using a calibrated Hamamatsu R669 PMT coupled to a LeCroy Model 3001 qVt multi-channel analyzer. The samples were in the form of 1 cm. cubes. The ratio of the intrinsic light output (Q.E.corrected) for the samples HBT, 3CHBT, 4MHBT and 5MHBT is 1.0:1.28:0.95:0.82. In addition, the light output ratio for HBT vs. NE 110 was determined to be 1.0:3.0. Although the coupling to the PS primary excitation is efficient in these IPT systems, all the compounds studied thus far have relatively low radiative quantum yields, $\eta_f \simeq 0.30 - 0.35$, vs. quantum yields for the more standard scintillator dopants of between 0.90 and 0.95.

4 Preliminary Radiation Damage Studies

4.1 Gamma exposures of IPT Scintillators

Samples of IPT scintillator (HBT, 3CHBT and 5MHBT) were irradiated in the gamma facility at Idaho Falls. All samples received a total dose of approximately 1 MRad ($\pm 10 \%$) where E_γ^{av} is approximately 0.7 MeV. During irradiation the samples were maintained in a Nitrogen atmosphere. In addi-

tion to the IPT samples, a sample of NE 110 and a sample of undoped PS were included in this exposure. The results are summarized in figures (7-10). These figures show transmission curves before and after irradiation for each sample (1.2 cm path length) referenced to unexposed pure PS. The fluorescence emission is also included. After irradiation the light output from each sample was measured with ^{207}Bi . The light output was reduced to 98, 89, 91 and 70 percent of their pre-irradiated values for HBT, 3CHBT, 5MHBT and NE 110 respectively. The PS fluorescence was measured with a quartz window PMT (RCA 31000M) and after irradiation dropped to approximately 20-30 % of its initial value.

In order to try to understand why the IPT scintillators have better radiation resistance, a number of UV excitation studies were performed. In these studies the sample was front surface (surface facing collection optics) excited with narrow band UV light ($\lambda_{\text{ex}} = 254 \text{ nm}$). This light is absorbed very close to the surface and since only light immediately leaving the sample is monitored, we do not see effects due to bulk absorption. What we have observed is quite interesting. With the sample that showed the most degradation after irradiation (Ne 110), the fluorescence intensity distribution from the dopants is essentially unchanged when measured with front surface excitation (figure 11). This curve shows fluorescence from both the primary and secondary dopants used in NE 110. Since PS is very absorbing at 254 nm., the majority of the incident radiation is absorbed by the PS. Even after irradiation, however, there is efficient coupling to the primary dopant and then to the secondary. An undoped sample of PS was also studied in this

way. Figure 12 shows the before and after excitation spectra for a sample of PS, $\lambda_{ex} = 254$ nm. Again to within our measurement error (± 10 %) there is no change in the PS output for front surface UV illumination, even though the signal from Bismuth was drastically reduced. What these measurements seem to indicate is that the light loss in PS scintillator from irradiation is primarily due to optical absorption in the polymer and that the radiative quantum yields of the polymer and dopants are not affected. The reason why the IPT scintillators show less degradation than NE 110 is because their fluorescence has been further shifted into the red where radiation coloring effects in PS are much less pronounced.¹

5 Conclusion

We have developed a new type of plastic scintillator with acceptable light output and an improved radiation resistance as compared to NE 110. The major effects of radiation on these types of PS scintillator appear to be due to coloring (transmission losses) of the base polymer. The dopants do not appear to be degraded nor is the transfer efficiency between the PS intrinsic excitation and the primary dopant significantly changed.

¹It should be noted that NE 110 is a PVT based scintillator. We have also looked at the coloring of PVT vs. PS due to irradiation. In Nitrogen atmospheres the losses in transmission for the two polymers are quite similar.

References

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- [3] J.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Second ed., (Academic Press, New York), (1971).
- [4] David L. Williams and Adam Heller, *Journal of Physical Chemistry*, Vol. 74, No. 26, 1970, pg. 4473.
- [5] Clifford L. Renschler and Larry A. Harrah, *Nucl. Inst. and Methods*, A235, 1985, pg 41.
- [6] A.D. Bross in *Proceedings of the Workshop on New Solid State Devices for High Energy Physics*, October 20-30, (1985), LBL 22778.

Figure Captions

Figure 1. Absorption curve for polystyrene, reference air. The vertical scale is in absorption units, $AU = -\log(\frac{I}{I_0})$, path length = 1 m.

Figure 2. Absorption and fluorescence for HBT doped PS, path length = 1.2 cm.

Figure 3. Absorption and fluorescence for 3CHBT doped PS, path length = 1.2 cm.

Figure 4. Absorption and fluorescence for 4MHBT doped PS, path length = 1.2 cm.

Figure 5. Absorption and fluorescence for 5MHBT doped PS, path length = 1.2 cm.

Figure 6. Absorption and fluorescence for NE 110, path length = 1.2 cm.

Figure 7. HBT radiation study. Transmission before and after irradiation. The fluorescence distribution is included for reference. Path length for transmission measurements = 1.2 cm.

Figure 8. 3CHBT radiation study. Transmission before and after irradiation. The fluorescence distribution is included for reference. Path length for transmission measurements = 1.2 cm.

Figure 9. 5MHBT radiation study. Transmission before and after irradiation. The fluorescence distribution is included for reference. Path length for transmission measurements = 1.2 cm.

Figure 10. NE 110 radiation study. Transmission before and after irradiation. The fluorescence distribution is included for reference. Path length for transmission measurements = 1.2 cm.

Figure 11. Fluorescence distribution from front surface excitation, $\lambda_{ex} = 254$ nm. for NE 110. Curves shown are for pre and post irradiation.

Figure 12. Front surface excitation spectra for PS, pre and post irradiation.

Figure 1

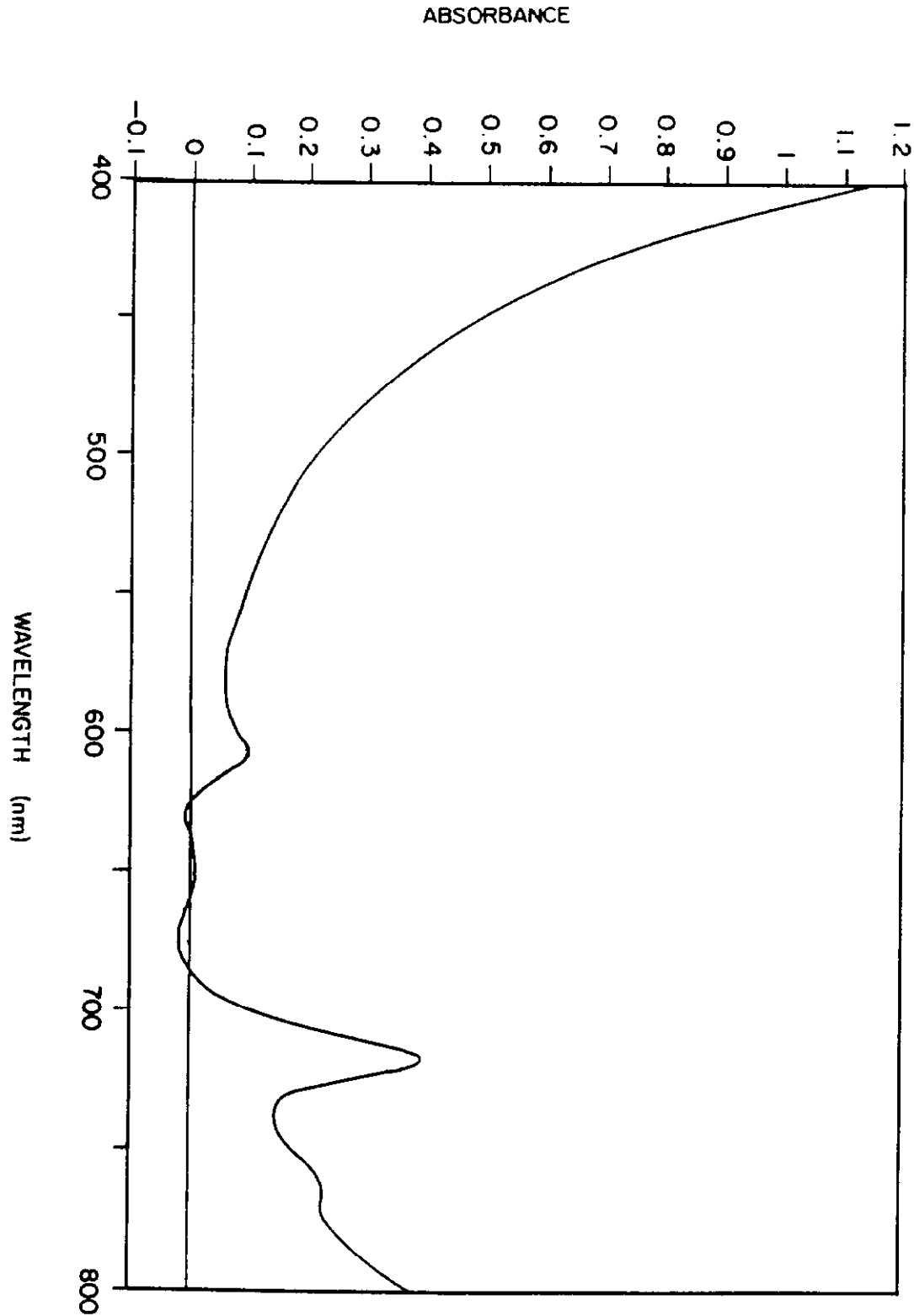


Figure 2

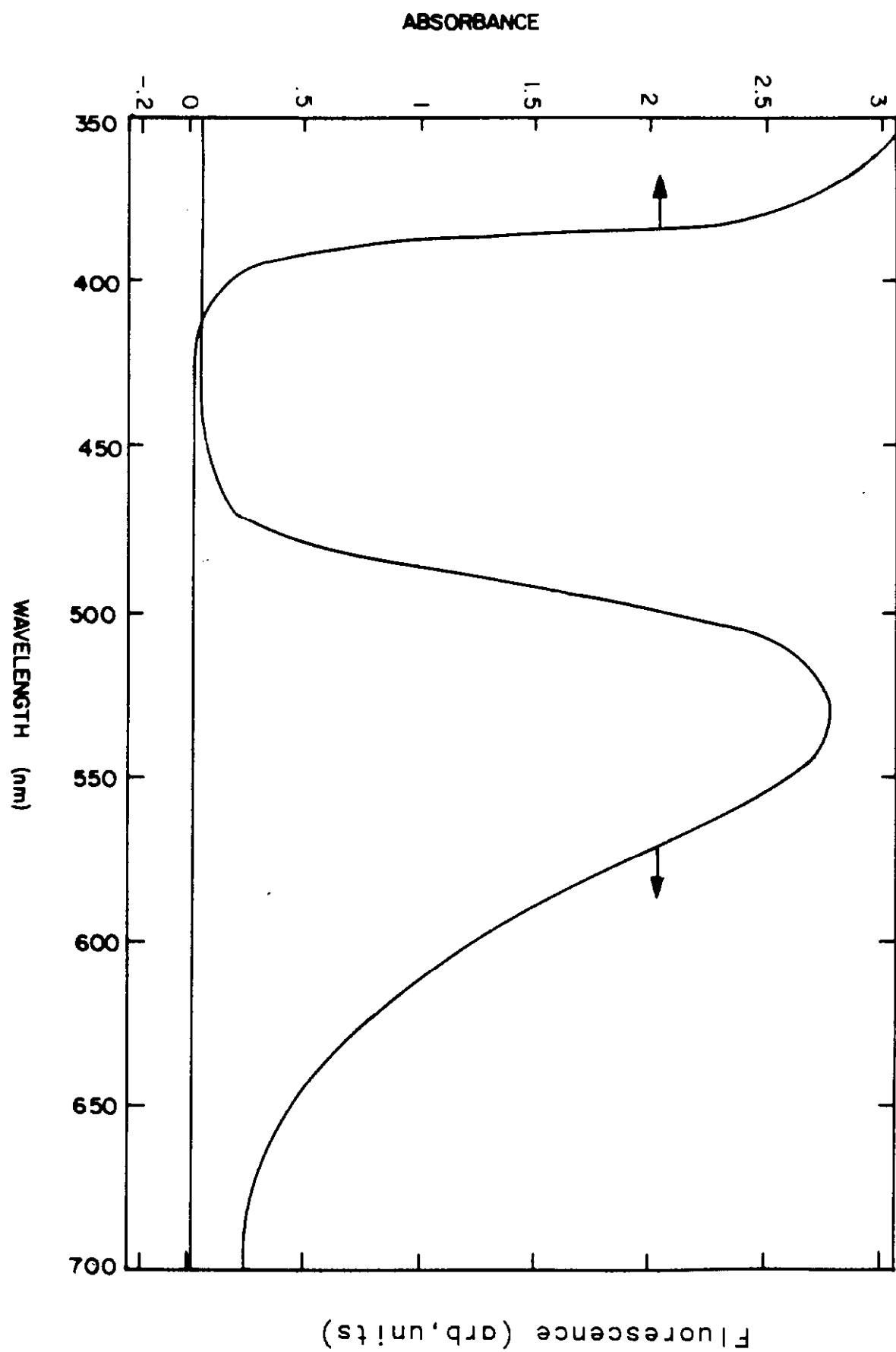


Figure 3

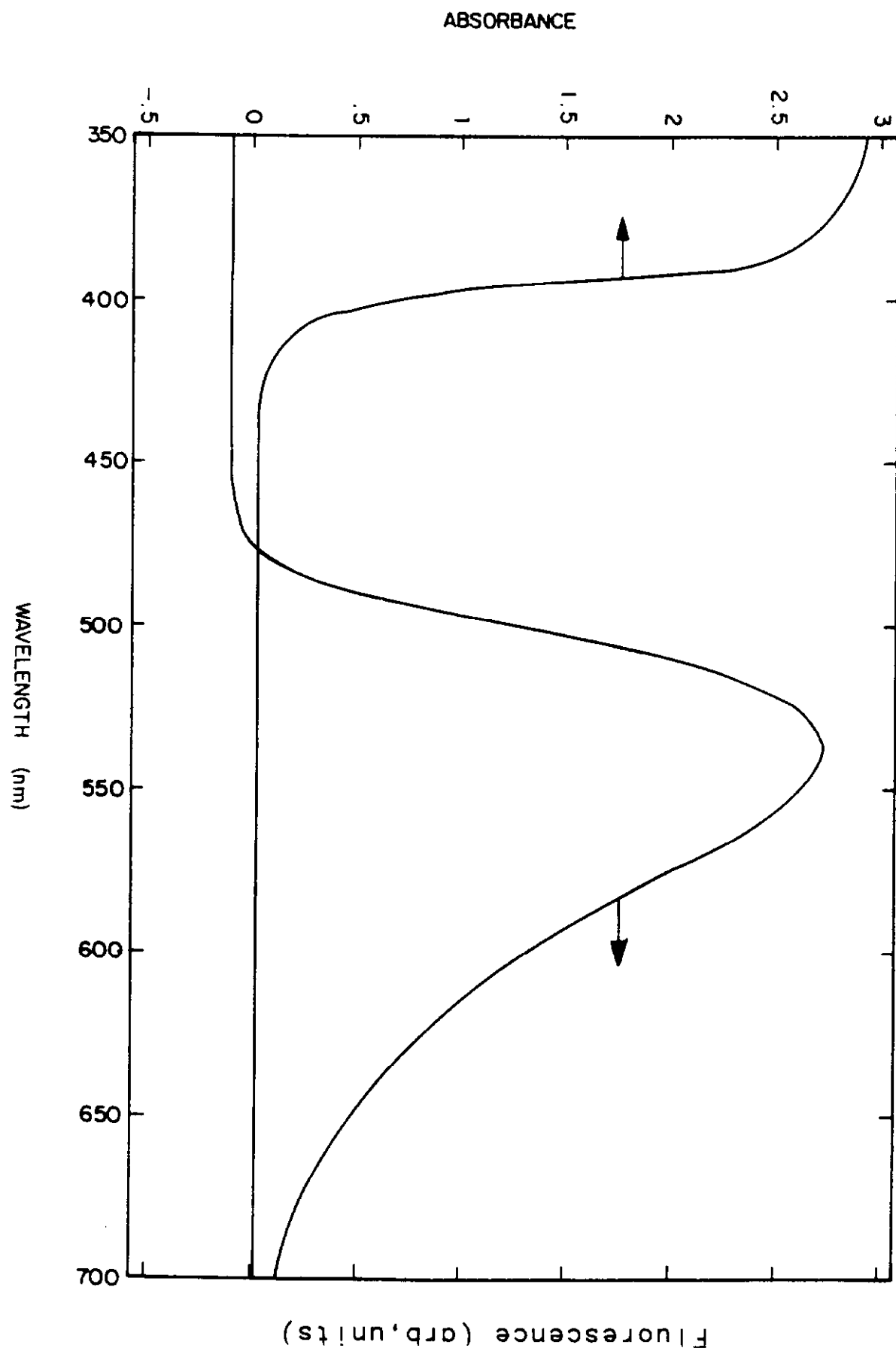


Figure 4

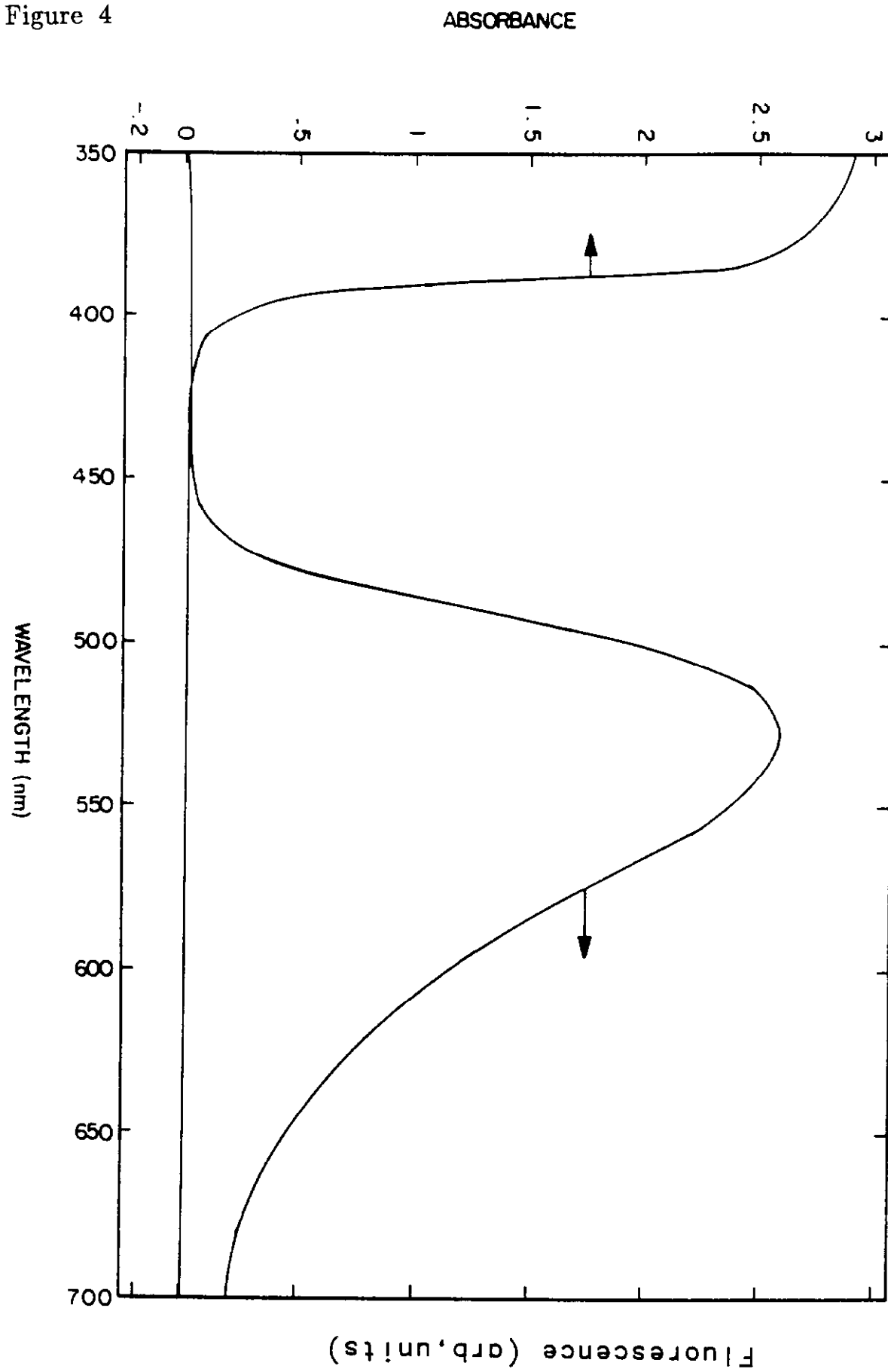


Figure 5

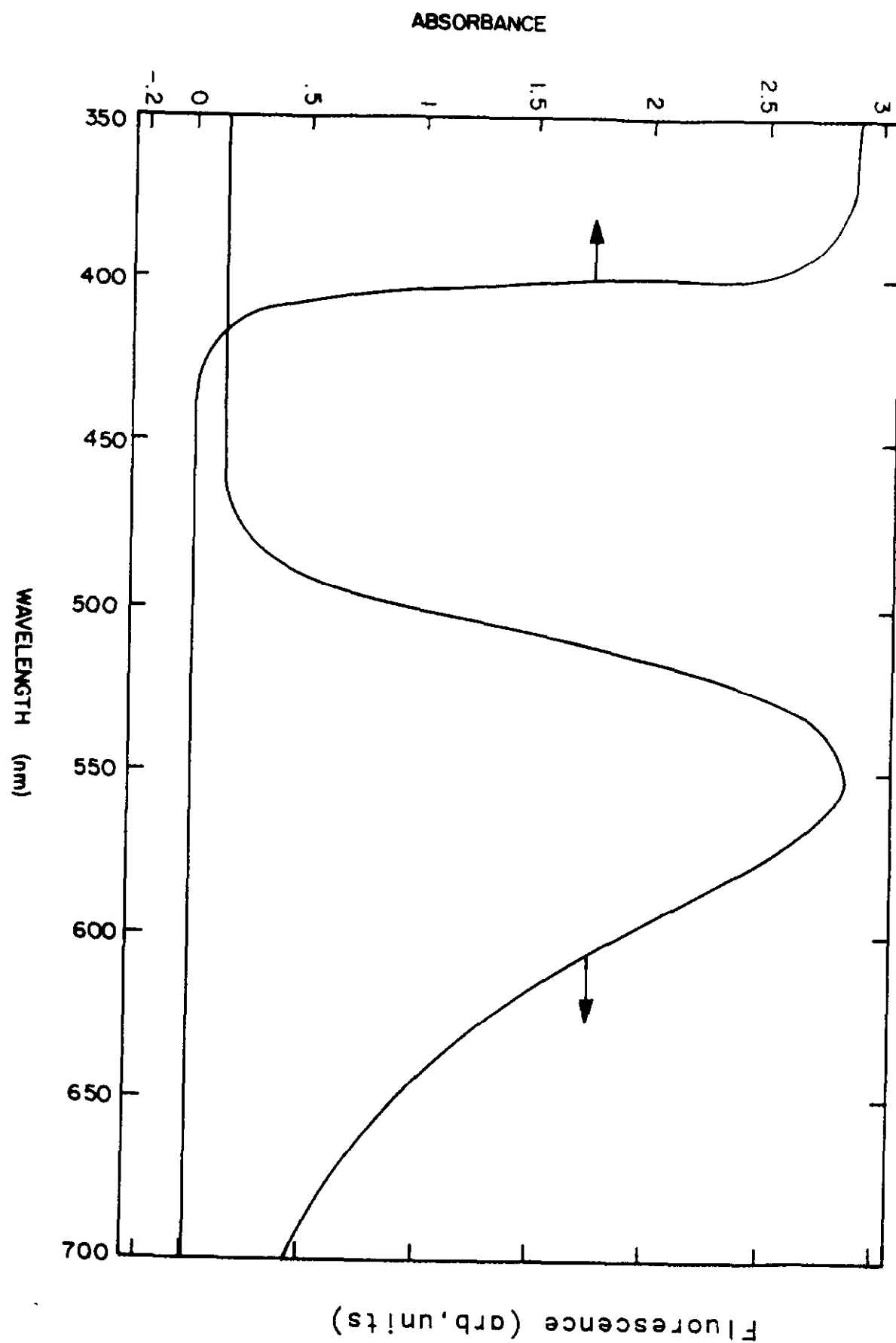


Figure 6

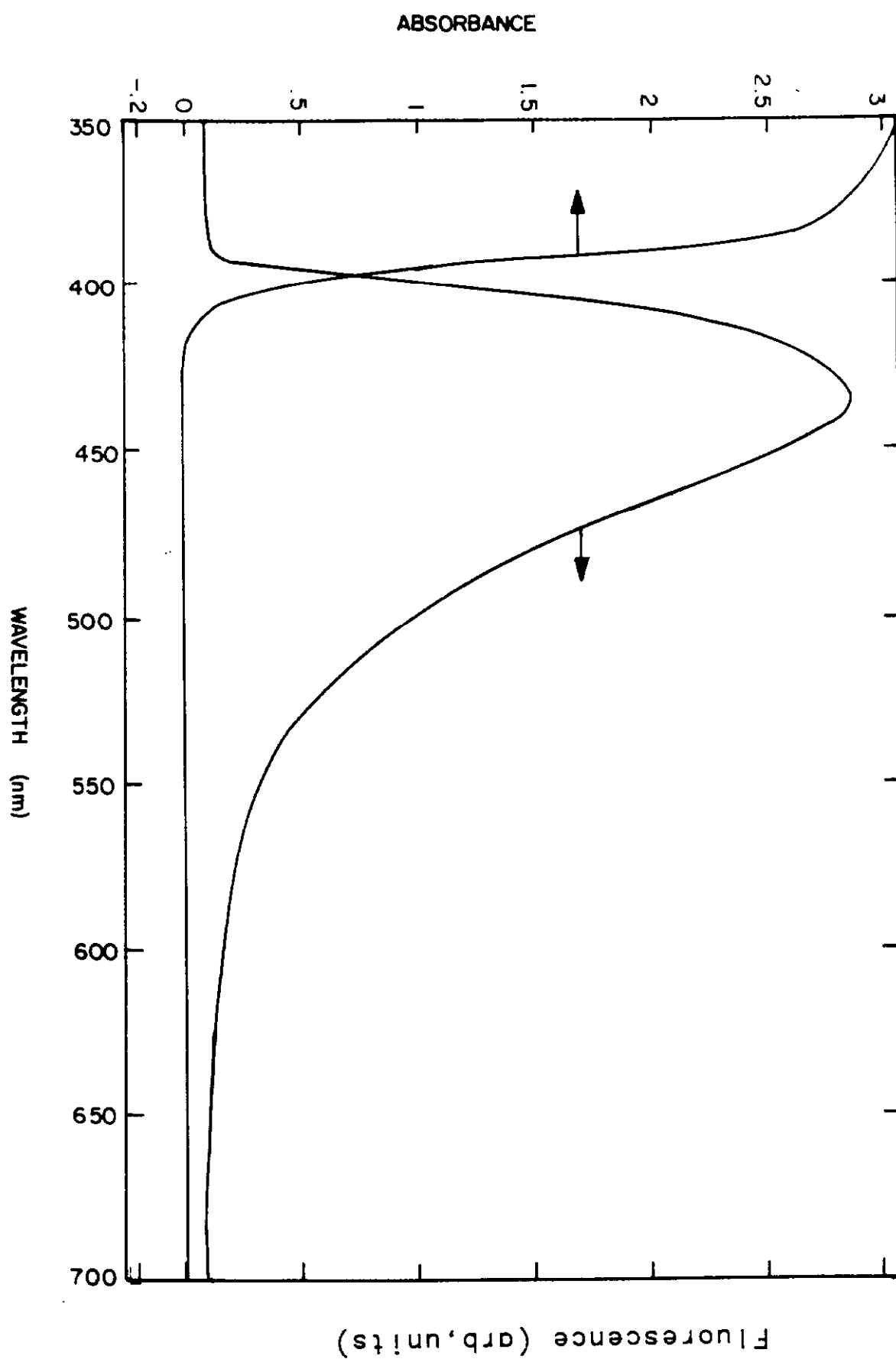


Figure 7

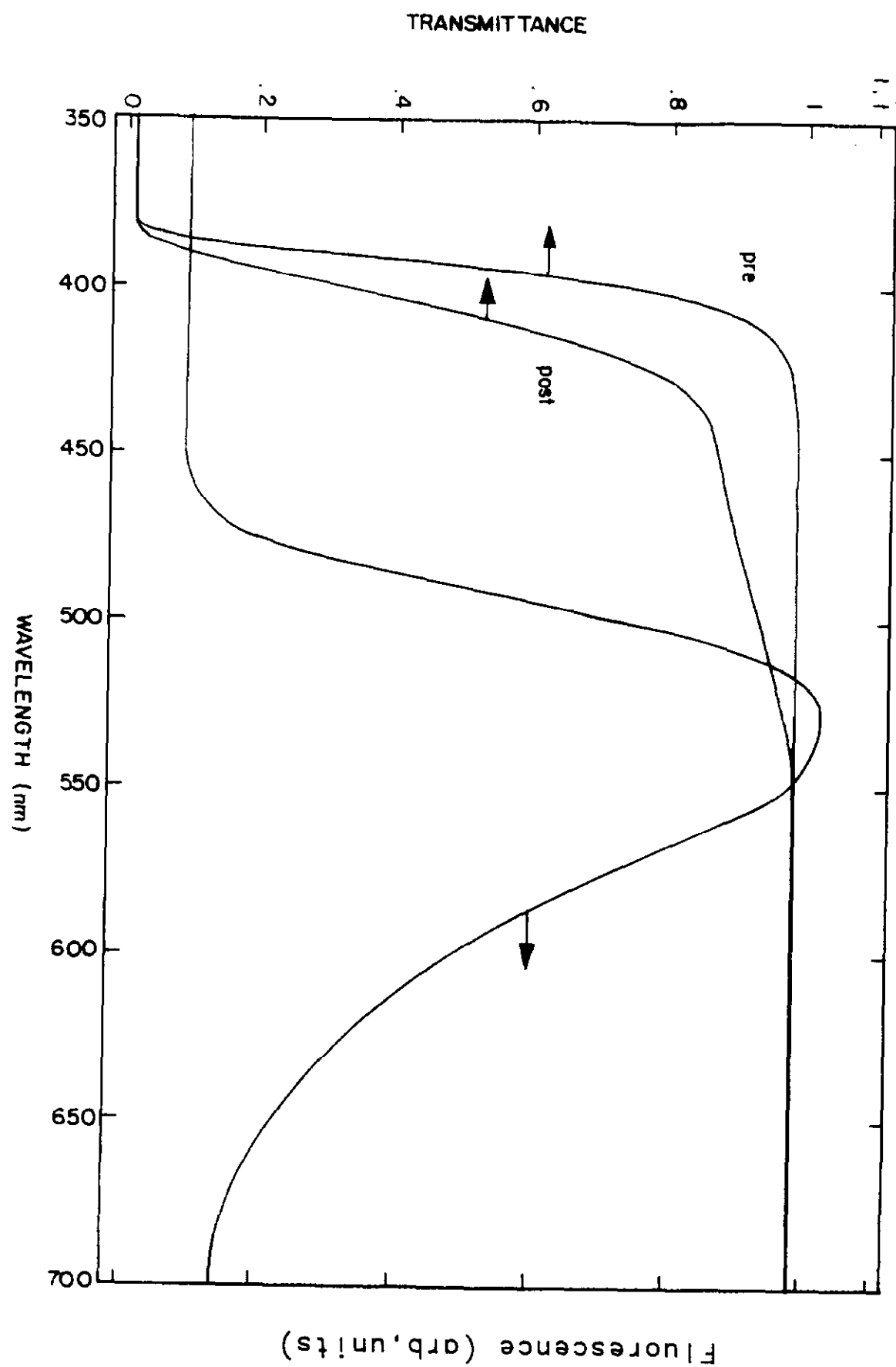


Figure 8

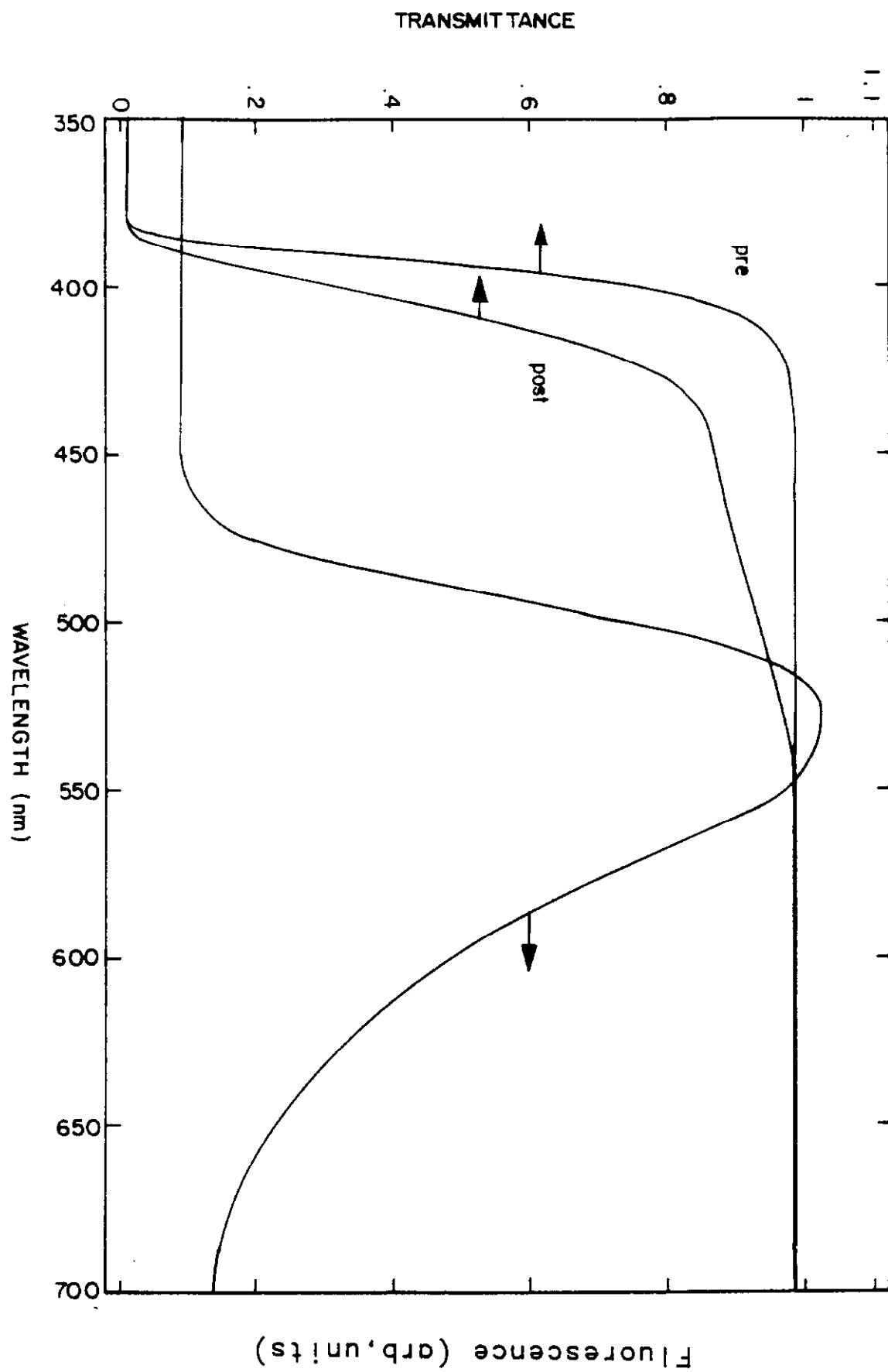


Figure 9

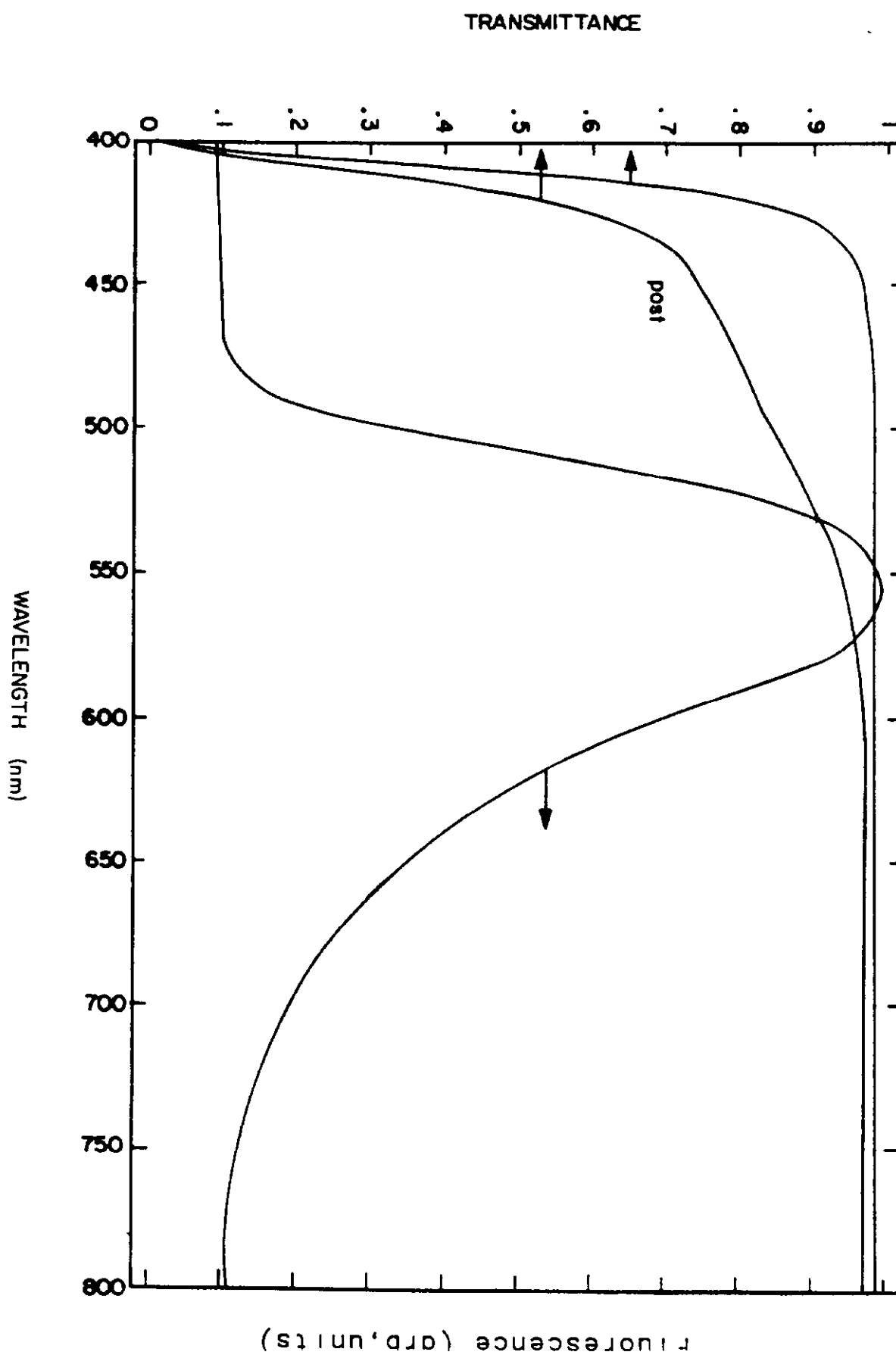


Figure 10

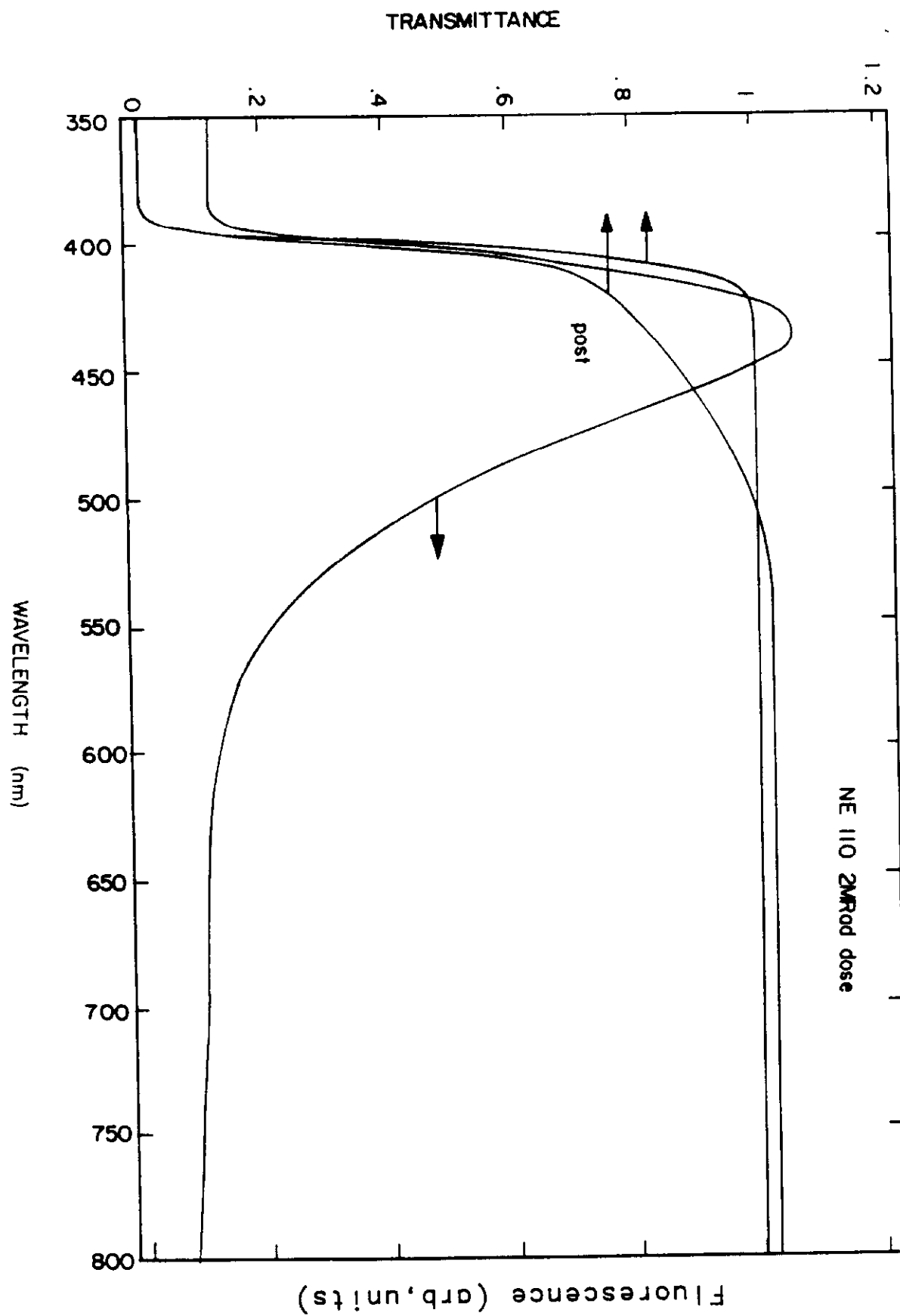


Figure 11

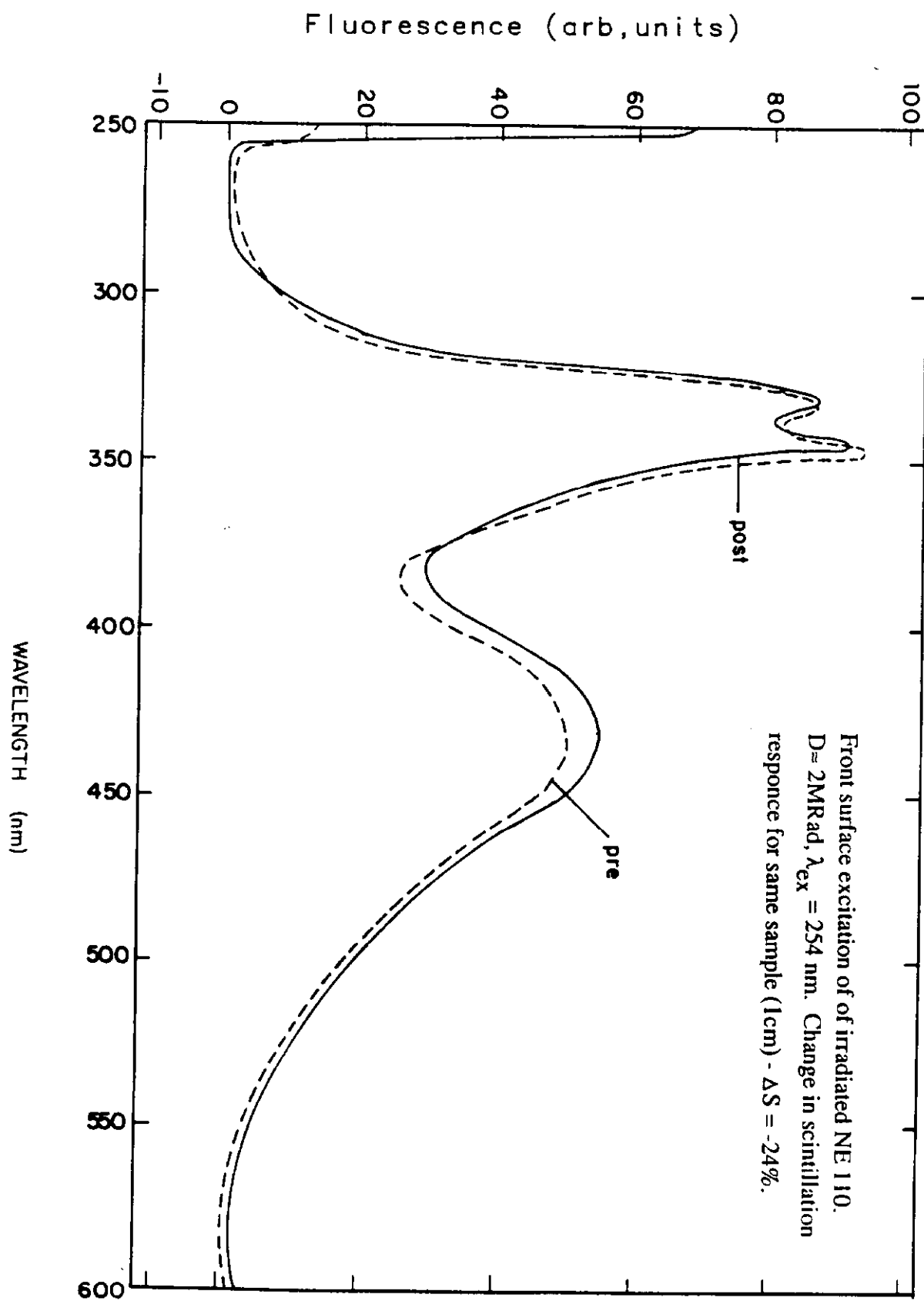


Figure 12

