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THE USE OF DYNAMIC FILTERING AS A MEANS OF LASER EYE PROTECTION, by

Alan H. Blumenthal, Robert W. Anderson, Jr., and James J. Mikula. (Frankford
Arsenal Technical ~~Pitman-Dunn Laboratory~~ Symposium paper.)

ABSTRACT

With the growing uses and new developments in the field of laser radiation, it has become increasingly vital to perfect an eye protection device for the safety of industrial workers and combat troops.

It is possible to devise a static filter which will provide protection at one wavelength. This; however, is not acceptable because laser light can be tuned to cover the entire visible spectrum. If a series of broadband static filters are used in conjunction, it may offer protection from damage; however, no light would penetrate such a filter and therefore this is an unsatisfactory solution.

An ideal dynamic filter would have high visible transmittance at ordinary light levels and high optical density at increased laser powers. This is accomplished with a three level system. Absorption of laser radiation would populate an excited singlet state. If the decay to the ground state is slow and a higher excited singlet, of the proper energy separation, exists with a sufficiently large extinction coefficient, then dynamic filtering will take place.

Heptaphene, phthalocyanine aluminum chloride, Sudanblack B, and Indanthrone have shown an increase in optical density over that of the ground state when subjected to a Q-switched laser. Up to a twenty fold increase in optical density has been demonstrated with increasing laser power. Measurements have been done at 5300Å and 6943Å showing the feasibility of dynamic filtering for eye protection.

INTRODUCTION

Because of the need for a suitable eye protection device against laser radiation in the range of the visible spectrum, and the inadequacy of a static filter, we have undertaken the task of evaluating the feasibility of employing dynamic filtering of intense laser radiation as a means of achieving eye protection without limiting visibility.

Any transient increase of absorption of laser light during a giant pulse must be based upon the production by the pulse of an excited species having a greater extinction coefficient for the laser light than the ground state. The use of triplet-triplet absorption for laser eye protection may in some cases serve as a suitable means of achieving the desired goal but in many cases the response times of such systems would appear to be too slow to provide protection against Q-switched lasers with pulse durations of 30 nanoseconds or less. A more promising approach is based on excited singlet-singlet absorption since the energy transfer rate constants are generally more favorable.

For dynamic filtering we considered a three level energy system with energies E_1, E_2, and E_3. This is shown in Figure 1.

In this model absorption occurs from level 1 (ground state singlet) to level 2 (excited singlet) with extinction coefficient ϵ_{12} and from level 2 to level 3 (higher excited singlet state) with extinction coefficient ϵ_{23}. Downward transitions from level 3 to 2 are assumed to occur instantaneously ($1/k_{32}$ is much less than the pulse duration of a Q-switched laser).

Two necessary requirements for potential laser dynamic filter materials are that they absorb weakly at the laser frequency in the visible region (small ϵ_{12}) from the ground state and more strongly from the excited state. That is, a sufficiently rapid population of an excited singlet or triplet state. Three polycyclic hydrocarbons had been synthesized which meet these requirements. They have weak ground state absorptions in the visible region of the spectrum at the argon ion laser frequencies (4880Å and 5145Å) and the neodymium glass doubled frequency at 5300Å. They also show fairly strong transient absorption bands over the same visible region of the spectrum when the excited singlet states are pumped with 3472Å light from a frequency doubled ruby laser operating in the pulsed mode. These three compounds are heptaphene, 1,2,8,9-dibenzoperopyrene and 1,2,3,4,8,9,10,11-tetrabenzopentacene (structures are shown in Figure 2).

In addition to these hydrocarbons, a search of the literature has also opened up other possible sources of eye protection based on dynamic filtering.

A dimeric form of phthalocyanine aluminum chloride has been shown[1] to decrease in transmissivity with an increase in light flux. Indanthrone[2] and Sudanblack B[3] have also been reported to undergo increased optical absorption with increasing Q-switched laser power.

EXPERIMENTAL

Optical densities were determined with both a Cary 14 spectrophotometer and a Q-switched laser apparatus. The laser apparatus is shown in Figure 3.

Optical density measurements were carried out at 6943Å with a Holobeam Q-switched laser containing a ruby rod capable of delivering up to 3.5 joules in 24 nsec.

In order to perform measurements of 5300Å the ruby rod was replaced by a neodymium glass rod capable of delivering up to 3.5 joules in 15 nsec. The second harmonic was generated by frequency doubling the primary radiation using a KD*P crystal. The two wavelengths were separated by a green filter, A.O. 595, which has an optical density greater than 17 at 10,600Å, thus allowing only the green light to pass through.

The laser beam passed through an aperture so that the beam diameter on the sample was approximately 1.3 cm. The incident laser pulses were detected with an S-1 surface photomultiplier tube, which was later replaced by Holobeam HPD-1 photodetectors. The signal was received through a T125/T50 adaptor terminated with 50 ohms into a Tektronix 556 oscilloscope, with the data obtained in the form of oscillograms. The reference detector was calibrated by replacing the sample detector with a Quantronix Model 504 Energy Meter, and measuring the energy as a function of the reference pulse height. The lasers were calibrated by measuring the reference voltage and the sample voltage for a series of Fish-Shurmann neutral density glass filters. A plot of sample optical density as a function of -log(Sample Voltage/Reference Voltage) should yield a straight line with a slope of one.

The optical densities were determined from the oscillograms in the following manner:

In the absence of a sample

$$\left(\frac{VD_1}{VD_2}\right) = \left(\frac{K_1 I_o}{K_2 I_o}\right) = K$$

VD_1 = peak amplitude from detector 1
VD_2 = peak amplitude from detector 2
K = constants which are functions of the optical system
I_o = intensity of initial laser pulse

If a sample is placed in front of detector 1, then

$$\left(\frac{VD_1}{VD_2}\right) = \left(\frac{TK_1 I_o}{TK_2 I_o}\right) = TK$$

T = fraction of the pulse transmitted through the sample

therefore,

$$T = \left(\frac{VD_1}{VD_2}\right) = \frac{1}{K}$$

$$OD = -\log_{10} T$$

RESULTS

Heptaphene

Of the three polycyclic hydrocarbons, we were able to demonstrate dynamic filtering with one of them, namely, heptaphene.

A solution of heptaphene in tributyl phosphate was prepared. This solution was found to have an optical density which is power dependent. The ground state absorbance of a 10^{-6}M solution in a 10cm cell was found to be 0.01 at 5300Å using a Cary 14 spectrophotometer whereas the laser induced absorbance ranged from 0.1-0.2 as the incident laser power density was varied from 3-12 MW/cm^2.

In addition to the experimental procedures described in the above, we also approached the problem of dynamic filtering on a theoretical basis. A detailed theoretical analysis is reported elsewhere[4]. This was done in order to estimate the molecular parameters (lifetimes, cross-sections, etc.) needed in the design of practical dynamic filters.

According to the suggested model, the ratio of the extinction coefficients for the excited state and ground state transitions, which is referred to as θ, $\left(\theta = \frac{\epsilon_{23}}{\epsilon_{12}}\right)$, should be large in order to obtain a great change in optical density. A lower limit of ten has been estimated for θ in heptaphene by Dr. Windsor at Washington State University. We have found that agreement between our results on heptaphene and our proposed Monte Carlo calculations are achieved if the fluorescence rate constant is between 10^8-10^9 sec^{-1} and θ has a value of 100. This magnitude for θ would place the value of the excited state extinction coefficient ϵ_{23} at 55,000 liters/mole cm. Since this was a theoretically estimated value for θ based on an assumed value for the fluorescence rate constant of heptaphene we proceeded to verify this value by measuring the actual lifetime of heptaphene using a photon counting technique.

An Ortec nanosecond fluorescence spectrometer was used to compute the lifetime of a 10^{-6}M solution of heptaphene in tributylphosphate at 5200Å and 5600Å. These wavelengths correspond to the fluorescence maximum of heptaphene which we have previously noted using a Perkin-Elmer Fluorescence Spectrophotometer. The monitoring was done at two wavelengths as a test of the purity of the sample. The calculated rate constant from these lifetime observations was identical at both wavelengths and the value of .3 to 1 x $10^8 sec^{-1}$ was in excellent agreement with our assumed value in the Monte Carlo calculation.

Heptaphene as well as the other two polycyclic hydrocarbons are extremely insoluble in most organic solvents. In order to get heptaphene into a system that would be more practical for an eye protection device, we attempted to incorporate it into a plastic matrix. Because of its excellent optical properties the polymer of choice was polymethyl methacrylate. A sample of polymethyl methacrylate containing heptaphene was prepared by adding heptaphene crystals to methyl methacrylate syrup composed of 20% polymer dissolved in 80% monomer, and polymerizing the resulting mixture. Although some heptaphene remained undissolved, the polymer sample has a yellow cast with respect to polymer prepared under identical conditions without the addition of heptaphene. It was anticipated that a higher concentration of heptaphene could be obtained in this fashion than would be possible with most common organic solvents. The concentration of heptaphene in this sample could not be accurately determined since a correction for the absorbance due to the plastic alone would have to be known, and no suitable matching blank was available for such purposes. However, using an extinction coefficient for the ground state absorption of heptaphene of 550 liters/mole cm and some reasonable estimates the concentration is believed to be approximately 5 x 10^{-4}M. The normal optical density measured with a Cary 14 spectrophotometer was 0.05 at 5300Å.

Operating in the pulsed mode, a frequency doubled neodymium laser was used to test for dynamic filtering. Between 0.03 and 1.0 MW/cm^2 the optical density was approximately constant at about 0.15, a threefold increase over that measured with the Cary 14. As the laser power increased the optical density continued to show small increases. At 2.9 MW/cm^2 the O.D. was 0.20 and at 5.27 MW/cm^2 it was 0.24. To achieve even higher powers a condensing lens was used in conjunction with the laser. This focused the beam to a smaller area thus increasing the power density. Using this technique the polymethyl methacrylate containing heptaphene was tested at power densities up to 178 MW/cm^2. The measured optical density remained constant (at about 0.24) throughout this range. It is interesting to compare $\frac{\text{OD max}}{\text{OD low light level}}$ for samples of heptaphene in solution and PMMA. The ratios are 20 and 4.8, respectively. According to the preceeding theoretical discussion this ratio is θ. These differences are probably due to changes in the ϵ_{23} in going from solution to polymethyl methacrylate since in most cases ϵ_{12} does not change that drastically.

Similar experiments in which heptaphene was dissolved in methyl methacrylate monomer were carried out. The heptaphene crystals were heated in methyl methacrylate until it appeared that a saturated solution was formed. The concentration of this solution was calculated to be 7.9×10^{-5}M. The optical density obtained on a conventional spectrometer was 0.095 using a 5 cm cell.

With a Q-switched laser the optical density was shown to increase with increasing power density. At 0.29 MW/cm^2 the optical density was 0.15. This increased to 0.18 at 7 MW/cm^2. A condensing lens was then used to increase power density. The rise in optical density was still apparent. The O.D. increased to 0.49 as the power increased to 40 MW/cm^2. These results are summarized in Table I.

Phthalocyanine Aluminum Chloride

The work of Bryaznov[1] led us to the study of phthalocyanine aluminum chloride as a possible solution of the dynamic filter problem. He noted a decrease in transmissivity with an increase in light flux. This effect was noted at an intensity of about 2 MW/cm^2 for a 3.2×10^{-6}M solution of the dimeric form of phthalocyanine aluminum chloride. The optical density increased tenfold with powers up to 30 MW/cm^2.

To more fully investigate this, samples of phthalocyanine aluminum chloride were obtained. The complex was sulphonated in order to increase its solubility which otherwise is extremely low.

TABLE I

Optical Density as a Function of Laser Power Measured at 5300Å for a 5 cm Cell Containing 7.9 x 10^{-5}M Solution of Heptaphene in Methyl Methacrylate Using a Condensing Lens

Power (MW/cm^2)	Optical Density
Cary 14	0.095
1.3	0.15
6.1	0.23
14.3	0.24
21.4	0.28
40.0	0.49

The solubility was tested in a variety of solvents with the results varying from insoluble in water to very soluble in acetone, ethanol, chloroform, THF, and ethylene dichloride. The solubilities of the sulphonated sample are summarized in Table II.

The ground state absorption spectra provides a convenient way of distinguishing between the monomeric and dimeric species. It is necessary to have the dimeric species since the monomer shows an increase in transmittance with increased light intensity whereas the dimeric form decreases in transmittance. The absorption spectra of the monomer consists of a narrow intense band at 693 nm. The dimer has two broad nearly symmetrical bands of almost equal intensity at 590 and 825 nm.

Thus far in all of our attempts we have only been able to isolate the monomeric species. This spectrum is shown in Figure 4, along with the reported dimer spectrum.

Spectra were obtained with a variety of solvents at varied concentrations. It was expected that chlorinated hydrocarbons would lead to a dimeric species; however, the monomer was still the only form present with ethylene dichloride and with chloroform. Concentrations were varied above and below the reported concentration without any change in the spectra. Phthalocyanine aluminum chloride was also incorporated into a cellulose propionate plastic matrix, but the monomer was still the only form present as determined by the absorption spectra.

Indanthrone and Sudanblack B

Based on the work of Huff and DeShazer[2] and Hess[3] we started preliminary investigations on the indanthrone dyes as possible dynamic filters.

Initial experiments were done with a mode locked picosecond laser. We were successful in finding the probable excited state which is necessary for dynamic filtering in these materials. Preliminary picosecond laser measurements were also performed to test the effect of power on optical density. A solution of Sudanblack B in chlorobenzene was measured for optical density at picosecond powers between 500-1000 MW/cm^2. The result was a slight increase in optical density from 0.31 to 0.39. Indanthrone in chlorobenzene did not show any increase of optical density up to 300 MW/cm^2 with a mode locked laser. These results did not offer a great deal of promise; however, because of the differences in mode locked lasers and Q-switched laser pulses,

TABLE II

Solubility of Phthalocyanine Aluminum Chloride

Solvent	Solubility
Acetone	very soluble
Ethanol	very soluble
Methanol	soluble
Toluene	soluble
Isopropanol	soluble
Water	insoluble
Ethylene Glycol	insoluble
Ethylene Dichloride	very soluble
Chloroform	very soluble
THF	very soluble
Butyl Acetate	soluble
Ether	insoluble
Petroleum Ether	insoluble
Benzene	very slightly soluble

which could greatly effect the response of a given compound, we decided to continue testing of these samples with Q-switched laser pulses. Beside the possible differences in responses with different laser radiation, the choice of solvent could also play a role in the ultimate behavior.

A solution of Sudanblack B in acetic acid was prepared with an optical density of 0.29. When subjected to a Q-switched, neodymium doubled, 5300Å pulse in a one cm cell, the optical density increased from .31 at .69 MW/cm^2 to .44 at 28.9 MW/cm^2. Indanthrone in water was also subjected to a Q-switched pulse. The initial Cary 14 optical density was 0.22. This value increased to 0.62 at 26.8 MW/cm^2. The two dyes were also tested at 6943Å with a Q-switched ruby laser pulse also in one cm cells. Sudanblack B in ethanol remained constant over the range of power tested up to ~56 MW/cm^2. The choice of solvent was changed because Sudanblack B appeared to undergo decomposition in acetic acid. Indanthrone in water showed a dramatic change in optical density. The O.D. changed from an initial value of 0.20 to 1.27 at ~54 MW/cm^2. This is an increase in optical density of about 600%. These results are summarized in Tables III and IV.

CONCLUSIONS

Although heptaphene may not be practical as an eye protection device, it served a great purpose in demonstrating the feasibility of dynamic filtering. Its extremely low solubility is a severely limiting factor for all practical purposes. There appeared to be a problem in forming a true solution at higher concentrations. The concentration in PMMA was higher than in methyl methacrylate monomer, yet the absorption on the Cary 14 was less. The reason that no dynamic filtering was noted on the polymethyl methacrylate at higher laser powers may have been due to the change in θ, as was previously stated.

Phthalocyanine aluminum chloride shows promise as a dynamic filter and is worthy of more attention. The immediate problem is the obtainment of a dimeric species. In the solubilized form which we investigated, only the monomer was present. This indicates that work should be done on the non-solubilized species. Its low solubility should be tested in other solvents, considering such factors as temperature and pH. Different methods of preparing a solubilized form of phthalocyanine aluminum chloride should be investigated, and also other phthalocyanine compounds should be considered. Until the dimeric form of this species is secured, it is impossible to ascertain its full potential as a laser eye protection device.

The Indanthrone dyes appear to show the greatest promise for protection against laser radiation. They are readily soluble in many solvents including water, they are not considered relatively dangerous,

TABLE III

Optical Density as a Function of Laser Power Measured at 5300Å for Indanthrone and Sudanblack B in a One cm Cell

Power (MW/cm^2)	Optical Density
Sudanblack B	
Cary 14	0.29
0.7	0.31
2.8	0.31
7.4	0.36
28.9	0.44
Indanthrone	
Cary 14	0.22
0.6	0.20
2.9	0.23
7.6	0.35
26.8	0.62

TABLE IV

Optical Density as a Function of Laser Power Measured at 6943Å for Indanthrone and Sudanblack B in a One cm Cell

Power (MW/cm^2)	Optical Density
Sudanblack B	
Cary 14	.43
1.6	.43
5.7	.40
55.2	.42
Indanthrone	
Cary 14	.20
1.6	.21
5.8	.39
54.3	1.27

and they show a marked increase in optical density with increasing Q-switched laser power over a range of frequencies.

A full scale investigation should be carried out on these compounds. Careful measurements must be performed to determine the concentration at which the optimum protection could be achieved without unduly limiting visibility. Since the Indanthrone dyes exhibit dynamic filtering over a wide spectral range, the feasibility of shifting the absorption maximum toward the red should be investigated. This could conceivably increase visibility under normal conditions without greatly effecting the dynamic filtering properties under Q-switched laser radiation.

The results of these experiments demonstrate to us the feasibility of dynamic filtering as the answer to the problem of safe laser eye protection.

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3. Personal communication from LaVerne D. Hess, Member Technical Staff, Laser Department, Hughes Research Laboratories.
4. Anderson, R. W., et al, Department of the Army, Frankford Arsenal Report R-2044.

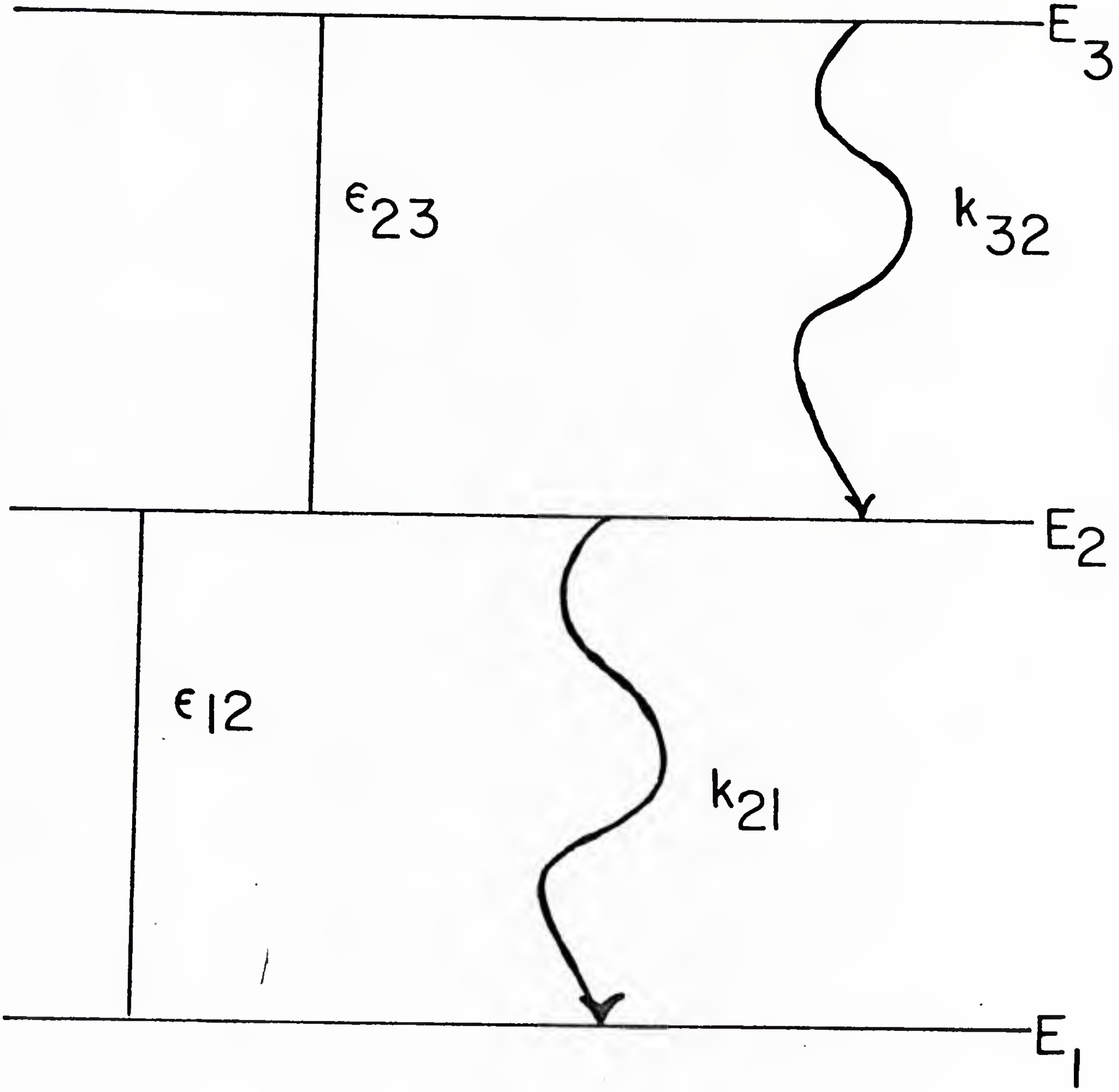
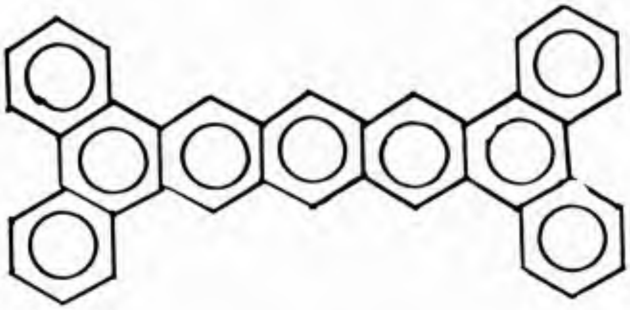
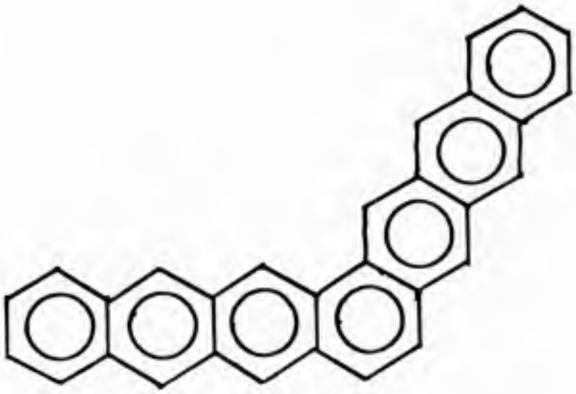


FIGURE 1. Energy Level Diagram for Dynamic Filtering



1,2;3,4;8,9;10,11-Tetravenzopentacene



Heptaphene

1,2;8,9-Dibenzoperopyrene

FIGURE 2. Polycyclic Compounds for Possible Use as Dynamic Filters

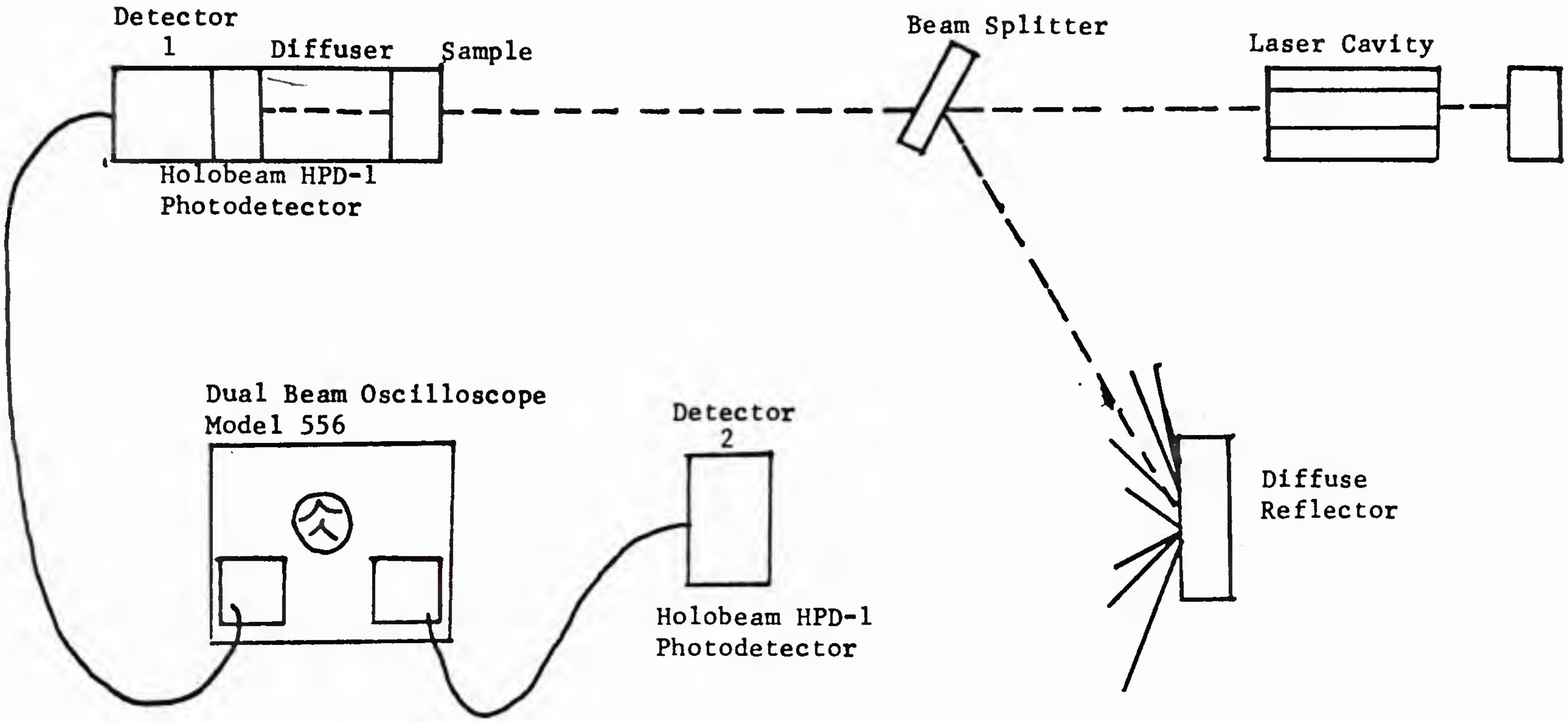


FIGURE 3. Laser Apparatus for O. D. Measurements

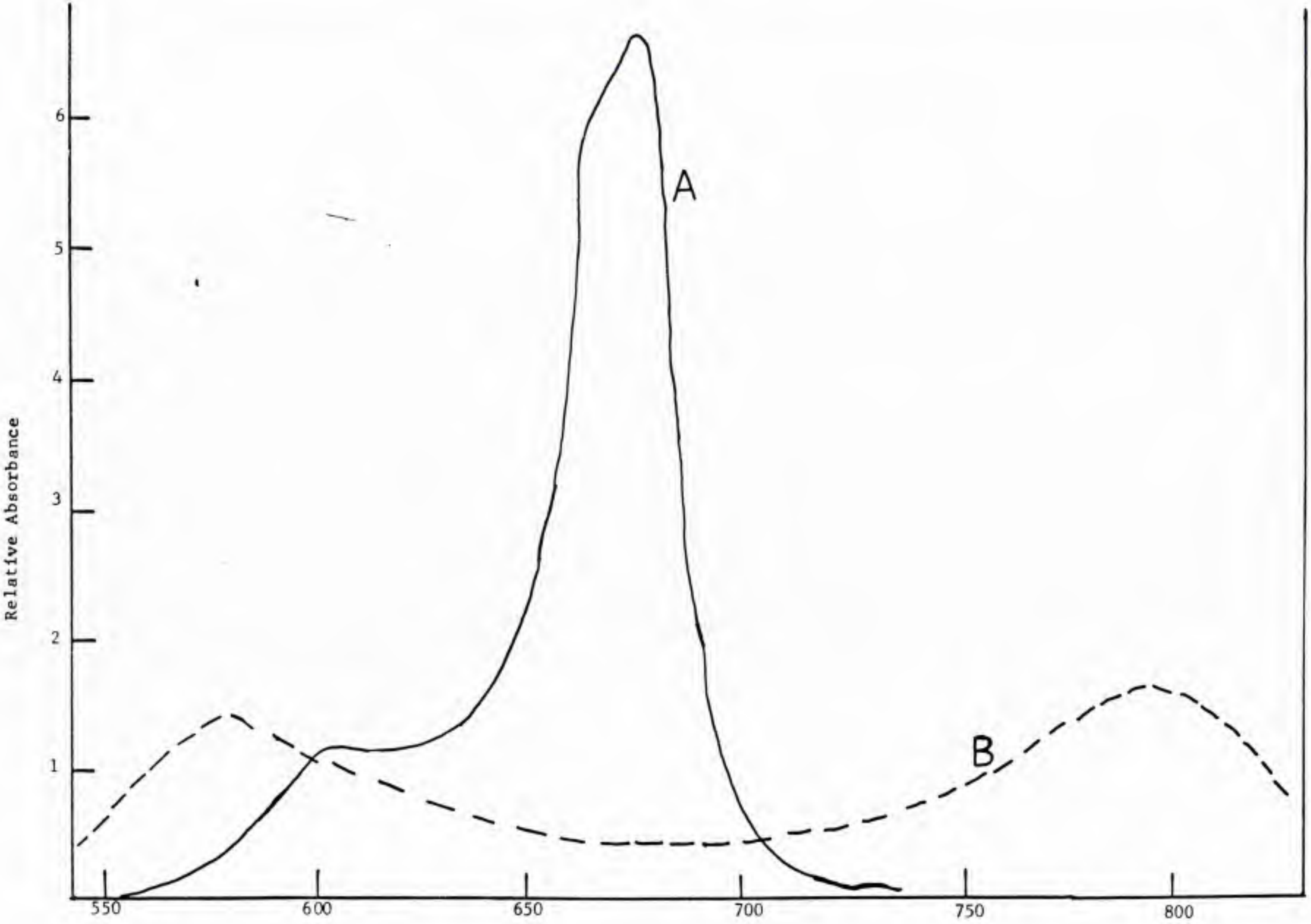


FIGURE 4. Ground State Absorption Spectra of Phthalocyanine Aluminum Chloride