

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

FINAL REPORT

on

HOLOGRAPHIC RECORDING MATERIALS DEVELOPMENT

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LANGLEY RESEARCH CENTER

NASA Contract NAS1-12324

Period Covered:
May 29, 1974 to March 24, 1975

(NASA-CR-132672) HOLOGRAPHIC RECORDING
MATERIALS DEVELOPMENT Final Report, 29 May
1974 - 24 Mar. 1975 (Battelle Columbus
Labs., Ohio.) 45 p HC \$3.75 CSCL 14C

N75-23930

Unclas

G3/35 22200



BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

ABSTRACT

Research during the contract period has produced several significant advances in the area of organic cis-trans photoisomerization systems for holographic memory applications. These studies have utilized representative indigo and thioindigo derivatives in addition to the stilbene derivative used during the previous contract period, and have led to the following achievements:

- The successful writing of phase holograms in the stilbene/polymer gel system.
- The successful writing of phase holograms in the thioindigo/polymer gel system.
- The successful writing and erasing of phase holograms in both the indigo/polymer gel system and in the indigo/solid polymer systems studied.

The chemical research effort included photochemical studies of the stilbene, indigo, and thioindigo derivatives in solution and in a variety of polymer matrix materials, in an effort to optimize the photorefractive behavior of the chemical system as a whole. The optical physics research effort, utilizing lithium niobate, encompassed studies of the writing and reading efficiencies of thick phase holograms with writing wavelengths different from the read wavelength. Both plane wave holograms and Fourier-Transform holograms were employed, and a number of reconstruction techniques are discussed.

The results achieved to date have clearly demonstrated the possibility of using the cis-trans photoisomerization of appropriate organic chemicals as the basis for a holographic recording system. The current status of the materials examined is discussed, and a rationale for improving the performance of future candidate materials is outlined.

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD.	1
SUMMARY	2
PHOTOCHEMISTRY.	3
Stilbene Derivatives	3
Holography.	4
Degradation	10
Sensitization	10
Thioindigo Dyes.	11
Holography.	12
Refractive Index Studies.	13
Matrix Studies.	13
Indigo Dyes.	14
Holography.	14
Refractive Index Studies.	14
Matrix Studies.	15
Analysis of Isomeric Composition	16
Calculation of Absorption Spectra	20
Continuing Studies	20
MULTIPLE HOLOGRAM STORAGE IN THICK <u>cis-trans</u> MATERIALS.	28
Angular Selectivity of Plane Wave Gratings	29
Angular Selectivity of Fourier Transform Holograms of Transparency Objects	30
Effects of Reading and Writing With Differing Wave- lengths.	34
Alternative Reconstruction Techniques.	39
REFERENCES.	40

LIST OF TABLES

Table 1. Comparison of Data Taken in Laser/Optical Studies of Organic Systems and Comparison to LiNbO ₃ System.	9
---	---

LIST OF FIGURES

	<u>Page</u>
Figure 1. Screw Type Cell Designed to Limit Evaporation of Solvent From Gel Matrices.	6
Figure 2. Laser-Optical Setup for Writing of Holograms by <u>cis-trans</u> Isomerization in Organic Material.	8
Figure 3. Schematic of Laser/Optical Setup for Writing a Hologram by Photoisomerization	17
Figure 4. Schematic Drawing of Laser/Optical Setup for Reading a Hologram	18
Figure 5. Schematic Drawing of Laser/Optical Setup for Erasing Hologram by Photoisomerization	19
Figure 6. Computer Program for Calculation of Extinction Coefficients from Spectral Data for Three Photostationary States.	21
Figure 7. Absorption Spectra of Three Photostationary States of N,N'-Diacetylindigo Used for Calculation of Absorption Spectra of the Pure Isomers	22
Figure 8. Calculated Absorption Spectra for N,N'-Diacetylindigo	23
Figure 9. Calculated Absorption Spectra for Pure Isomers of N,N'-bis-(p-Trifluoromethylbenzoyl) Indigo	24
Figure 10. Schematic Illustrations of Possible Effects of Wavelength on Optimizing Refractive Index Differences.	25
Figure 11. Diffracted Light Intensity from a Simple Holographic Phase Grating as a Function of the Angle of Incidence of the Read Beam. The Sample Thickness is 3 mm.	31
Figure 12. Angular Acceptance of Simple Holographic Gratings as a Function of Grating Thickness. Theory (—) and Experimental Data (x).	32
Figure 13. Experimental Arrangement for Producing a Fourier Transform Hologram	33

LIST OF FIGURES
(continued)

	<u>Page</u>
Figure 14. Diagram of Experimental Scheme for Producing a Fully Illuminated Image from a Fourier Transform Hologram of a Transparency Object ($\lambda_T \neq \lambda_W$). Refraction at the Sample Surface has been Ignored in the Figure.	35
Figure 15. Diffraction Efficiency of a F-T Hologram <u>vs.</u> Angular Extent of Reconstruction Beam. The Exact Shape of the Curve is not Fully Understood, but the Peak is seen to Coincide with the Prediction of Eq. (2).	37

FOREWORD

This report was prepared by Battelle, Columbus Laboratories, under Contract No. NAS1-12324. This project is monitored by Marvin Beatty of the Flight Instrumentation Division, NASA-Langley Research Center. The program coordinator for the research is C. M. Verber of the Solid State and Optical Sciences Section. Other contributors are R. A. Nathan, P. J. Perry, R. E. Schwerzel, N. E. Klosterman, J. A. Hassell, A. R. Bunk, W. J. Mueller, and N. F. Hartman.

SUMMARY

The research performed during this contract period has resulted in the successful writing of thick phase holograms in three chemically different cis-trans isomeric systems. These include the stilbene derivative studied last year, a thioindigo derivative, and an indigo derivative. In addition, the holograms have been written using a variety of polymeric matrix materials. These results clearly demonstrate the possibility of using the photochemical cis-trans isomerization of organic materials for holographic recording, although the diffraction efficiencies and writing sensitivities obtained to date are far from optimal. Finally, the problems of reconstructing thick holograms with light of a wavelength different from the writing wavelength have been considered in detail, using doped lithium niobate for experimental studies. Several reconstruction strategies have been investigated.

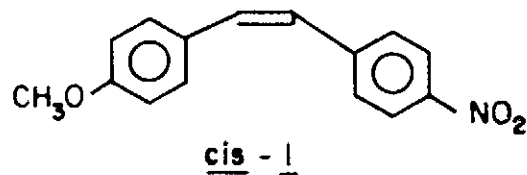
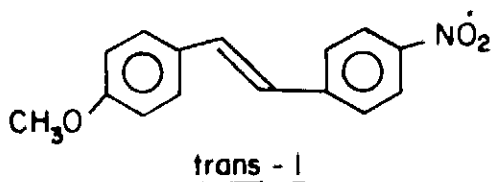
PHOTOCHEMISTRY

The photochemical research performed during this contract period continued the studies of 4-methoxy-4'-nitrostilbene initiated in the previous contract period. This compound can be photoisomerized efficiently in solution, and produces a significant change in refractive index upon photoisomerization. Thick phase holograms were written successfully using this compound in a polymeric gel matrix; the holograms could not be erased, however, and there is reason to suspect that under the conditions used the stilbene underwent a photochemical reaction with the gel matrix.

Subsequent research with thioindigo and indigo derivatives, which undergo cis-trans photoisomerization analogously to stilbenes, led to the successful writing and erasing of thick phase holograms with the indigo in several matrix materials. In addition, a computer program was written which permits the calculation of the absorbance spectra of the pure trans and cis isomers on the basis of the spectra of cis-trans mixtures for systems such as the thioindigos and indigos, for which the individual isomers are not readily available. Finally, these studies have provided an accumulation of data and expertise which should greatly accelerate the screening of improved candidate materials during the next contract period.

Stilbene Derivatives

During the previous contract period several stilbene derivatives were considered, and one compound, 4-methoxy-4'-nitrostilbene (compound 1) was selected for further study on the basis of its favorable refractive



index properties. The initial studies carried out during this contract period therefore continued the evaluation of this derivative, and were directed toward the following goals:

- Adjustment of the stilbene concentration so as to optimize the absorbance in the visible range.
- Demonstration of reversible photoisomerization in a solid matrix.
- Writing and erasing of phase holograms in a solid matrix.
- Estimation of long-term stability and recycling capabilities.

Holography

Previous research carried out under this contract had demonstrated that 4-methoxy-4'-nitrostilbene (1) could be isomerized from trans to cis both in solution and in a benzene/polymer gel system by irradiation with an appropriately filtered xenon arc lamp. The first attempts to write holograms, however, were unsuccessful. These experiments utilized compound 1 in a viscous benzene solution of low molecular weight polyisobutylene, contained between glass slides by a 1 mm thick Teflon spacer. It seems most likely that the failure to write a hologram under these conditions resulted from there being insufficient laser power to isomerize the stilbene at the wavelength used (350 nm). For this reason a more powerful laser (argon ion) was utilized for the bulk of these studies. The laser line at 488 nm was used.

The absorption maximum of trans-1 (the trans form of compound-1) is near 400 nm, but the absorption tails out to nearly 500 nm so there is a small, but finite, extinction coefficient at the 488 nm argon ion laser wavelength. Increasing the stilbene concentration did result in measurable trans to cis isomerization upon irradiation at 488 nm. A stilbene solution of such high concentration (0.10 M) however, had excessive absorbance at the laser wavelengths suitable for erasure; no light was transmitted. Thus, while the cis to trans erasure isomerization may have taken place at the cell's surface, not enough light was transmitted to convert molecules deeper

within the sample. This difficulty serves to emphasize the importance of maximizing the refractive index difference ($\Delta n/mole$) between the two isomers; the use of high concentrations to compensate for a small $\Delta n/mole$ (to permit multiple hologram recording) can lead to unfavorable absorbance properties.

During this phase of the research, a threaded sample cell (Figure 1) was designed to eliminate shrinkage of the gel matrix materials due to slow evaporation of benzene. In this cell, which replaced the glass-slide/Teflon spacer devices, the sample was contained between circular quartz windows by a cylindrical, 1 mm thick Teflon spacer. Evaporation of solvent was minimized by use of rubber spacers and the screw-type construction. This system greatly limited the problem of evaporation as well as eliminating the possibility of contamination of the sample by the benzene-soluble epoxies and sealants used on the glass slide/teflon spacer cell.

Three different polymeric gels, swelled with benzene, were then evaluated as matrix materials:

- Butyl rubber (light sulfur cure) - this gel proved to be soluble in benzene, and was therefore unsatisfactory.
- Ethylene-propylene copolymer (dicumylperoxide cure) - this material was readily swelled in benzene and formed optically clear gels.
- Ethylene-propylene-diene terpolymer (dicumylperoxide cure) - this material also was readily swelled in benzene and formed optically clear gels. As this polymer was the more easily handled, it was used for most of the subsequent studies.

The gels were purified prior to extraction over a period of several days, using a Soxhlet extractor and graded series of solvents ranging from pure benzene to benzene/methanol mixtures to pure methanol. Discs of the purified gels swelled in benzene were placed in concentrated benzene solutions of trans-1 for 24 hours to allow diffusion of the photo-reactant into the matrix. Irradiation with a filtered Eimac xenon arc lamp (cutoff below 315 nm) followed by ultraviolet spectroscopy yielded little evidence of degradation.

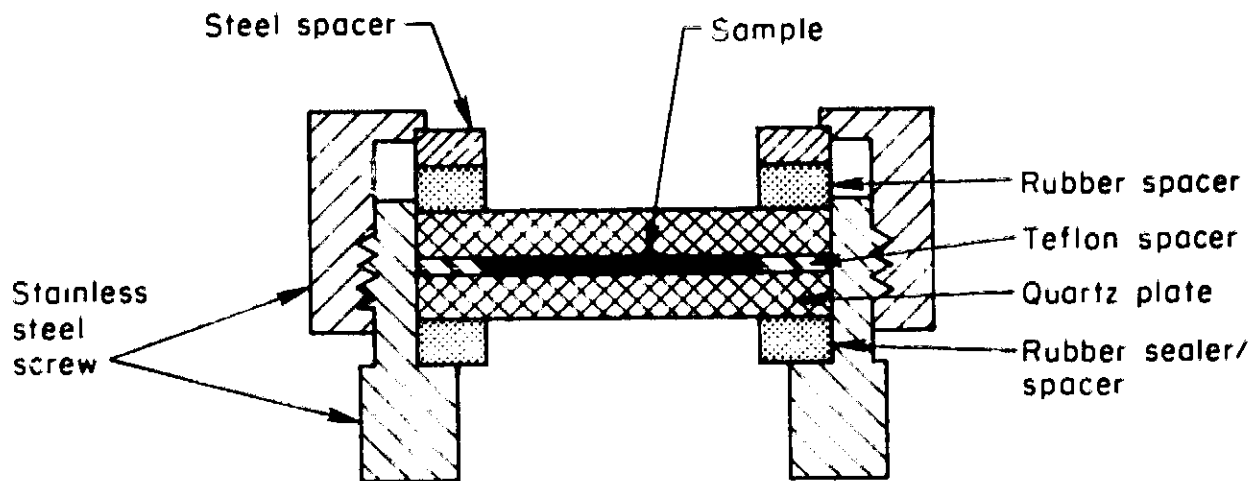


FIGURE 1. SCREW TYPE CELL DESIGNED TO LIMIT EVAPORATION OF SOLVENT FROM GEL MATRICES

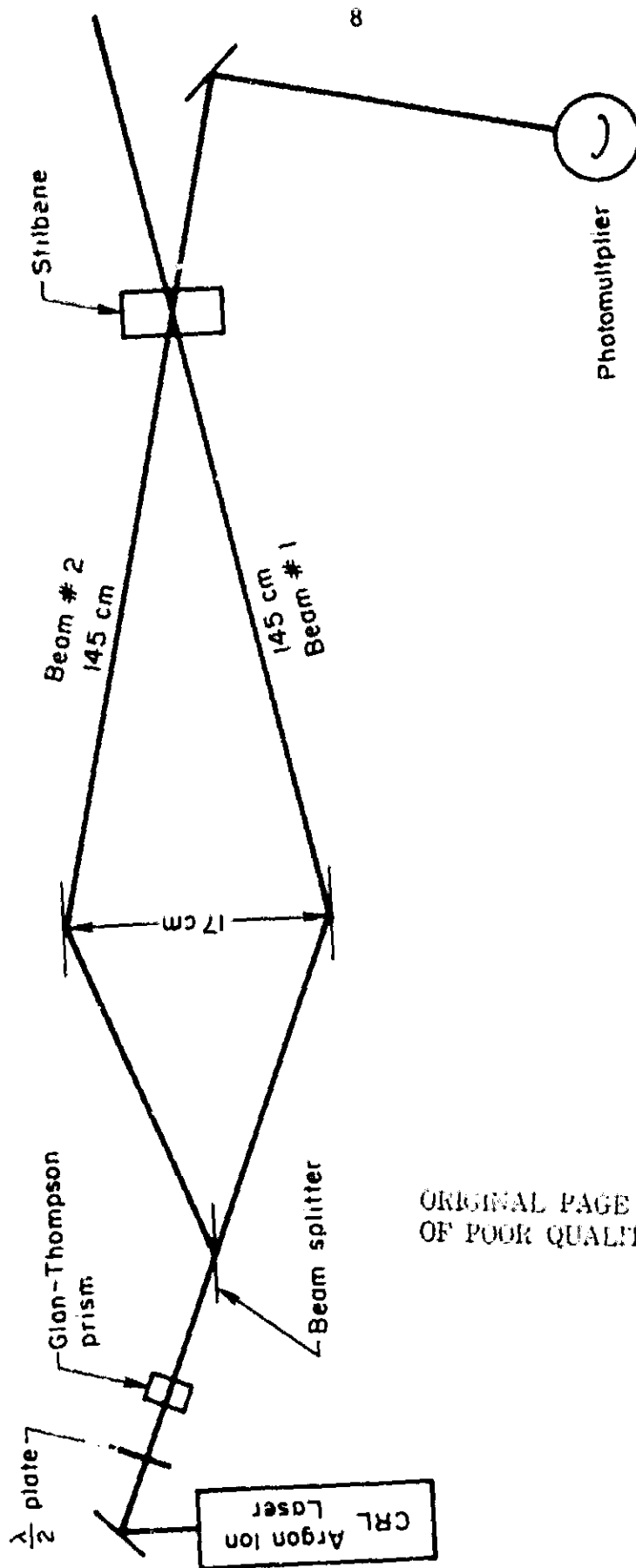
ORIGINAL PAGE IS
OF POOR QUALITY

Attempts to obtain high stilbene concentrations (ca. 0.1 M) in the new gels, for continued experiments with 488 nm irradiation, were unsuccessful. There appeared to be a limit to the amount of stilbene which would diffuse into the individual gel discs. When discs of the gels were soaked in aliquots of a benzene solution of known stilbene concentration, and analyzed spectroscopically after equal immersion times, it was found that the stilbene concentration varied from sample to sample, even among discs of the same gel. However, stilbene concentrations of ca. 0.03 M could be reproducibly obtained, as determined from the absorption spectra of several samples.

These samples were used to write the first holographic gratings in October 1974, using the 488 nm line from the Coherent Radiation argon-ion laser. The presence of the diffracted beam could be observed after approximately three minutes' exposure time. The power of each beam was 3 mw and the beam diameter was 2-3 mm. The approximate half-width of the acceptance angle was 4 minutes, close to the expected value.

The holographic recording capabilities of compound 1, and all subsequent compounds, were evaluated by recording plane wave diffraction gratings in a test sample. A conventional holographic setup (Figure 2), consisting of a laser beam split into two components which then intersected at the site of the recording medium, was used to produce the spatial pattern to be recorded. In all cases the polarization of the writing beam was perpendicular to the plane of incidence.

The process of writing the diffraction grating was recorded, in real time, by introducing a second beam, of a wavelength different from that of the writing beam, and monitoring the intensity of its diffracted portion as a function of writing time and energy. As Table 1 indicates, relatively high diffraction efficiencies could be obtained, particularly with the stilbene/terpolymer gel system at a writing wavelength of 457.9 nm. However, it was noticed that none of the holograms written with this system could be erased, and that a brownish spot inevitably appeared at the point of irradiation with the laser beams. These observations strongly suggested that degradation of the system occurred under the conditions of irradiation with the



ORIGINAL PAGE IS
OF POOR QUALITY

FIGURE 2. LASER-OPTICAL SETUP FOR WRITING OF HOLOGRAMS BY
cis-trans ISOMERIZATION IN ORGANIC MATERIAL

ORIGINAL PAGE IS
OF POOR QUALITY

TABLE 1. COMPARISON OF DATA TAKEN IN LASER/OPTICAL STUDIES OF ORGANIC SYSTEMS AND COMPARISON TO LiNbO_3 SYSTEM

Sample	Read (Write) (λ)	Absorption at Write (%)	$\frac{\theta}{2}$	Max. D.E.	$\frac{1}{e}$ erase ($\frac{\text{joules}}{\text{cm}^2}$)	Write Energy* for 1% D.E. (for 0.1% D.E.)	Write Power Density**	$\Delta n = \frac{2 \cos(\theta_0)}{\pi^2} \sin^{-1}(\tau^{1/2})$
4-Methoxy-4'-nitrostilbene in benzene	4579 (4579)	~ 61%	4.1°	31%		2.2 $\frac{\text{joules}}{\text{cm}^2}$ (.34 $\frac{\text{joules}}{\text{cm}^2}$)	.009 W/cm ²	1.62 x 10 ⁻⁴
4-Methoxy-4'-nitrostilbene in benzene	4579 (4579)	~ 61%	26°	0.8%			0.2 W/cm ²	2.6 x 10 ⁻⁵
Terpolymer gel matrix	6328 (6328)	22%	4.1°	.082%	20 $\frac{\text{joules}}{\text{cm}^2}$	(~160 $\frac{\text{joules}}{\text{cm}^2}$)	1.36 W/cm ²	1.15 x 10 ⁻⁵
6-6'-Diethoxythioindigo	4579 (4579)	16%	4°	0.55%		(14 $\frac{\text{joules}}{\text{cm}^2}$)	0.65 W/cm ²	2.15 x 10 ⁻⁵
0.1% Fe doped LiNbO_3	6328 (4880)	70%	20°	76%	113 $\frac{\text{joules}}{\text{cm}^2}$	~ .07 $\frac{\text{joules}}{\text{cm}^2}$ (~ .007 $\frac{\text{joules}}{\text{cm}^2}$)	.044 W/cm ²	4.26 x 10 ⁻⁴

* The write energy includes only that absorbed by the sample. The energy reflected and transmitted is not included in this table.

** Power density at the incident surface.

lasers, and it is not known whether the holograms observed with this system resulted from the presence of the desired cis isomer or from the degradation products responsible for the brown spot. However, it is clear from the high diffraction efficiency, that a phase, rather than an absorption, hologram was written.

Degradation

The failure of the samples to undergo erasure could be due, in part, to the strong absorbance of the samples at the wavelengths suitable for erasure, as was mentioned above. The inevitable presence of a brown spot at the point of laser irradiation made it seem quite likely that compound 1 had undergone a photo-induced degradation reaction of some type. The degradation of the stilbene was strikingly confirmed by the disappearance of the absorbance spectrum of the stilbene as the irradiation proceeded. This was thought at first to result from the presence of impurities in the system. However, neither the use of a less unsaturated (and therefore less reactive) gel, high molecular weight ethylene-propylene copolymer (purified by repeated solvent extraction as before), nor the use of photochlorinated benzene,* served to reduce the degradation of the stilbene. High pressure liquid chromatography and ultraviolet spectroscopy gave little evidence of the expected trans to cis isomerization, and provided no clues as to the composition of the brown spot. One may speculate that the degradation is due to the photochemical reactivity of the nitro group of the stilbene, but this is only conjecture. In the hope that the undesired reactivity associated with the direct irradiations might be avoided, efforts were then made to write holograms by means of the sensitized isomerization of the stilbene.

Sensitization

Biacetyl and acridine orange were selected as possible sensitizers because their singlet and triplet energies are in the appropriate range for

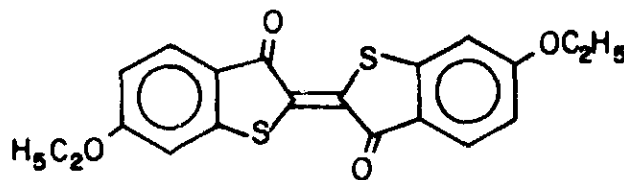
* Ultrapure benzene can be prepared by brief irradiation of commercial benzene saturated with chlorine gas; (1) this converts any olefinic aliphatic, or heterocyclic impurities to high boiling chlorinated compounds which may be removed by chromatography and distillation.

the stilbene isomerization. The biacetyl was distilled to remove gross impurities, but was then found to have no absorbance at 488 nm. Acridine orange is insoluble in benzene and had to be added to the system dissolved in a small amount of acetonitrile. Irradiation studies of the sensitized system showed both degradation of the stilbene and changes in the absorbance of the acridine orange. The sensitizer apparently undergoes photochemical reactions with the polymer, or perhaps with the stilbene. Attempts to prove this by irradiation of the sensitizer alone and by chemical tests were inconclusive, and attempts to derivatize the sensitizer to a less chemically reactive form were not successful.

In view of these problems with compounds of this type, it was felt that further work with this stilbene derivative would not be productive and that other potentially useful cis-trans systems should be investigated.

Thioindigo Dyes

The first alternative cis-trans system examined was 6,6-diethoxythioindigo (compound 2). This compound was suggested as a possible candidate



2

material by the work of D. L. Ross,⁽²⁾ which refers to use of this compound for the writing of relatively inefficient absorption holograms. A sample of this compound, which has been known in the open literature for a number of years, was kindly provided to us by Prof. G. M. Wyman of the University of North Carolina.

Holography

The initial holographic experiments were carried out using compound 2 in the benzene/terpolymer gel system. As anticipated, holograms were successfully written in this system, both by trans to cis isomerization (using the 514.5 nm argon ion line) and by cis to trans isomerization (using the 457.9 nm argon ion line). Because compound 2 absorbs blue and green light rather strongly, the thioindigo/gel samples were sensitive to room light and gave a mixture of cis and trans isomers when prepared or handled under room light. The trans to cis photo-isomerization of compound 2 is also thought to be strongly quenched by oxygen.⁽³⁾ The samples were therefore prepared under argon, either in the dark or under red safe-lights. The desired starting isomeric composition could then be obtained simply by irradiating the sample with an appropriately filtered xenon arc lamp; a Corning CS5-58 blue filter gave trans-rich samples, while a Corning CS3-69 cutoff filter gave cis-rich samples.

The observed diffraction efficiencies of the holograms written in the thioindigo/gel system were considerably less than those observed for the 4-methoxy-4'-nitrostilbene system. Values of ca. 0.55% were typically obtained for the thioindigo, as compared to values as high as 31% for the stilbene (see Table 1).

It was observed that under the conditions employed, the holograms could not be erased, despite the fact that they would be written both from trans to cis and from cis to trans. Unlike the stilbene, there was no evidence of chemical degradation in these samples. It is felt that the failure to erase the holograms resulted from insufficient power in the erasing beam and the fact that it requires much more energy to erase than to write a weak grating. The holograms did undergo slow, spontaneous thermal erasure over periods of several hours in the dark. This may have been due to catalysis of the (normally very slow) thermal cis to trans isomerization by acidic impurities in the system, or to the physical diffusion of isomerized molecules within the pores of the gel matrix.

Refractive Index Studies

Attempts were made to measure the refractive index difference (Δn /mole) between the trans and cis isomers of compound 2, as had been done for the stilbene. Compound 2 is of sufficiently low solubility in benzene, however, that the refractive index of a saturated solution differed too little from that of benzene alone to permit accurate measurements using the Brice-Phoenix differential refractometer. An estimate of the effective Δn based on the diffraction efficiency data is given in Table 1.

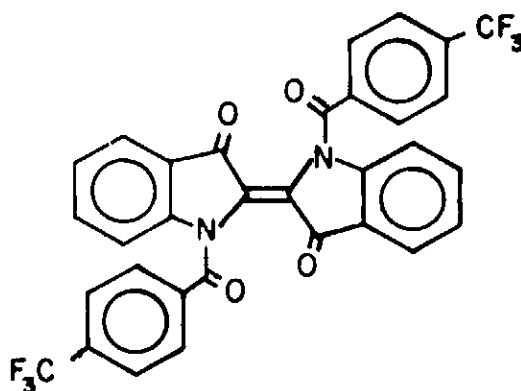
Using the effective Δn data obtained from diffractive efficiency measurements and a knowledge of the optical energy required to produce the observed $\Delta\mu$, an effective quantum yield can be determined provided Δn /mole has been determined independently. This effective quantum yield may be significantly less than the true quantum yield as determined from the true bulk measurements. Resolution problems, molecular migration, scattering, and instabilities in the optical system used to write the diffraction grating all can reduce the diffraction efficiency even though isomerization is occurring. Thus, the effective quantum yield and the true quantum yield may differ by several orders of magnitude. We plan to use this fact to study loss mechanisms in the future.

Matrix Studies

Several unsuccessful attempts were made to incorporate compound 2 into solid polymeric matrix materials to test the claim by Ross that isomerization does occur in solid plastics. Compound 2 proved to be nearly insoluble in monomers such as styrene and methyl methacrylate, precluding the use of polystyrene and polymethylmethacrylate matrices. While the "water white epoxy" referred to by Ross was not available for this work, compound 2 proved essentially insoluble in several nearly white commercial epoxy resins. Thus, while holograms were successfully written in the thioindigo/gel system, the solubility problems associated with compound 2 were so severe that it was decided to examine a more soluble material.

Indigo Dyes

The indigo dyes were a logical next choice for investigation, as their photochemistry resembles that of the thioindigos and their solubility properties are far superior. A proprietary indigo derivative, N,N'-bis(4-trifluoromethylbenzoyl) indigo (compound 3) was obtained for trial evaluation from a proprietary source.

3

ORIGINAL PAGE IS
OF POOR QUALITY

This compound proved to be far more soluble than compound 2, and was successfully incorporated in several solid matrices.

Holography

As with the thioindigo compound 2, the initial holographic experiments with compound 3 were carried out in the benzene/terpolymer gel system. Holograms were readily written, as anticipated, although with somewhat less efficiency than was obtained with compound 2. Having verified that compound 3 was suitable for holography, attention was then given to measuring the refractive index properties of the compound and to incorporating it in solid matrix polymers.

Refractive Index Studies

Solutions of compound 3 in benzene were irradiated with the filtered output of an Elmac xenon arc lamp to produce photostationary state mixtures with differing cis-trans isomeric ratios. The analysis of these mixtures,

which required the calculation of the absorption spectra of the individual cis and trans isomers, is described in a following section. The refractive index of each mixture was measured relative to the benzene solvent (as for the stilbene), using the Brice-Phoenix differential refractometer. A plot of the measured refractive index values versus the concentration of cis isomer produced a straight line, the slope of which gave the value of Δn between the two isomers at the total concentration (cis plus trans) used. From this it was determined that $\Delta n/\text{mole}$ for this indigo is ca. 3.4×10^{-3} , compared to ca. 4×10^{-2} for compound 1.

Matrix Studies

The solubility of the indigo derivative made it an attractive candidate for incorporation into solid polymers. Attempts to use epoxy resins were unsuccessful. Epon 828 epoxy resin was used, cured with amines, amides, aldehydes, and peroxides. All of the compositions tried reacted irreversibly with compound 3 to give a variety of highly colored products which could not be photoisomerized.

Incorporation of compound 3 into melamine methacrylate (Monsanto 720 melamine and Ashland methacrylate) was accomplished by mixing the dye into the liquid resin mixture, and then heat curing the resulting solution. While photoisomerization did occur in this matrix, the solid was cloudy and was not used further.

Compound 3 was successfully incorporated into both polystyrene and polymethylmethacrylate. Dow 666 polystyrene was dissolved in benzene to give a 20% (W/W) solution. The indigo was then added (0.3%, W/W) and the solvent removed in vacuo. This material could be heated and molded with no adverse effect on the indigo. Reversible photoisomerization was verified in this system, using the Eimac xenon arc lamp in conjunction with a monochromator.

Commercial (Eastman) polymethylmethacrylate, purified to remove stabilizers, was also used successfully. The indigo was dissolved in purified monomer, mixed with the purified polymer, and treated with a small

amount of dicumylperoxide catalyst. The resulting dye-impregnated polymer was hard and clear, and could be cut and polished into optically clear discs (melting and extrusion molding are also possible with this polymer). Reversible photoisomerization of the dye was verified in the cut, polished discs of polymethylmethacrylate. These discs were then utilized to achieve the successful writing and erasing of holographic gratings, using the 632.8 nm line of a helium-neon laser for writing and the 488.0 nm argon line for erasure. Schematic drawings of the write, read, and erase modes are presented in Figures 3-5. The diffraction efficiencies achieved with these holograms was disappointingly small, ca. 0.08% (Table 1). However, the holograms obtained with compound 3 certainly result from the trans-cis photoisomerization of 3 and not from degradation of the system.

Analysis of Isomeric Composition

Because refractive index of solutions varies with concentration as well as with the cis to trans isomer ratio, it is essential to know both the total concentration of the solute and the isomer ratio for each photo-stationary state used for Δn measurements. These values can be calculated easily from the observed absorption spectra and extinction coefficient data for the pure isomers using the following simultaneous equations, which are based on Beer's Law:

$$A_1 = A_1^t + A_1^c = \epsilon_1^t l C_t + \epsilon_1^c l C_c$$

$$A_2 = A_2^t + A_2^c = \epsilon_2^t l C_t + \epsilon_2^c l C_c$$

where the subscripts 1 and 2 refer to two different wavelengths on the absorption spectrum, and the notation c and t refers to properties of the cis and trans isomers, respectively. A is the absorbance (or optical density), ϵ is the molar decadic extinction coefficient, l is the optical path length, and C is molar concentration of the solute. Extinction coefficient data are not available for many indigos and thioindigos, nor is it always possible to separate the pure isomers. For this reason, it is necessary to calculate the absorption spectra for the pure isomers of these compounds.

ORIGINAL PAGE IS
OF POOR QUALITY

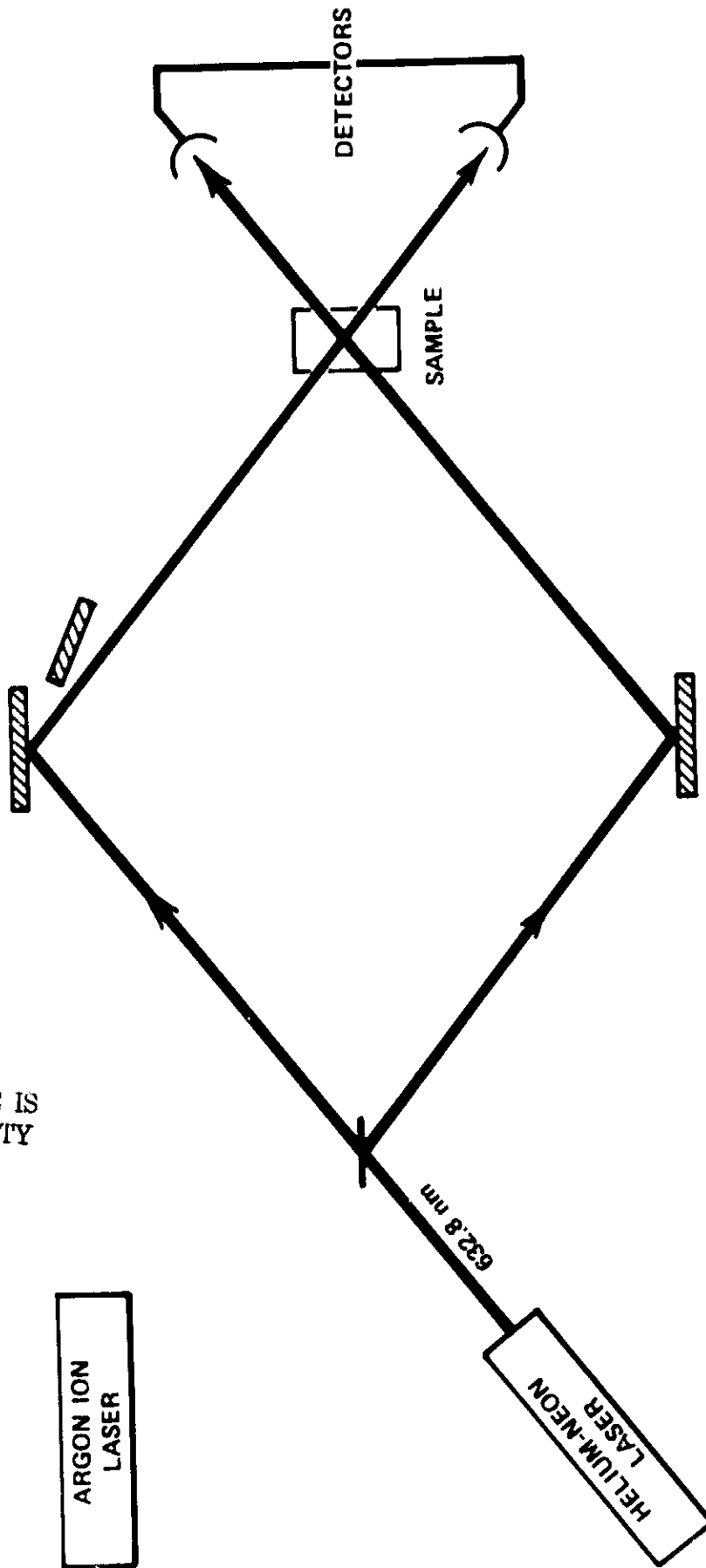
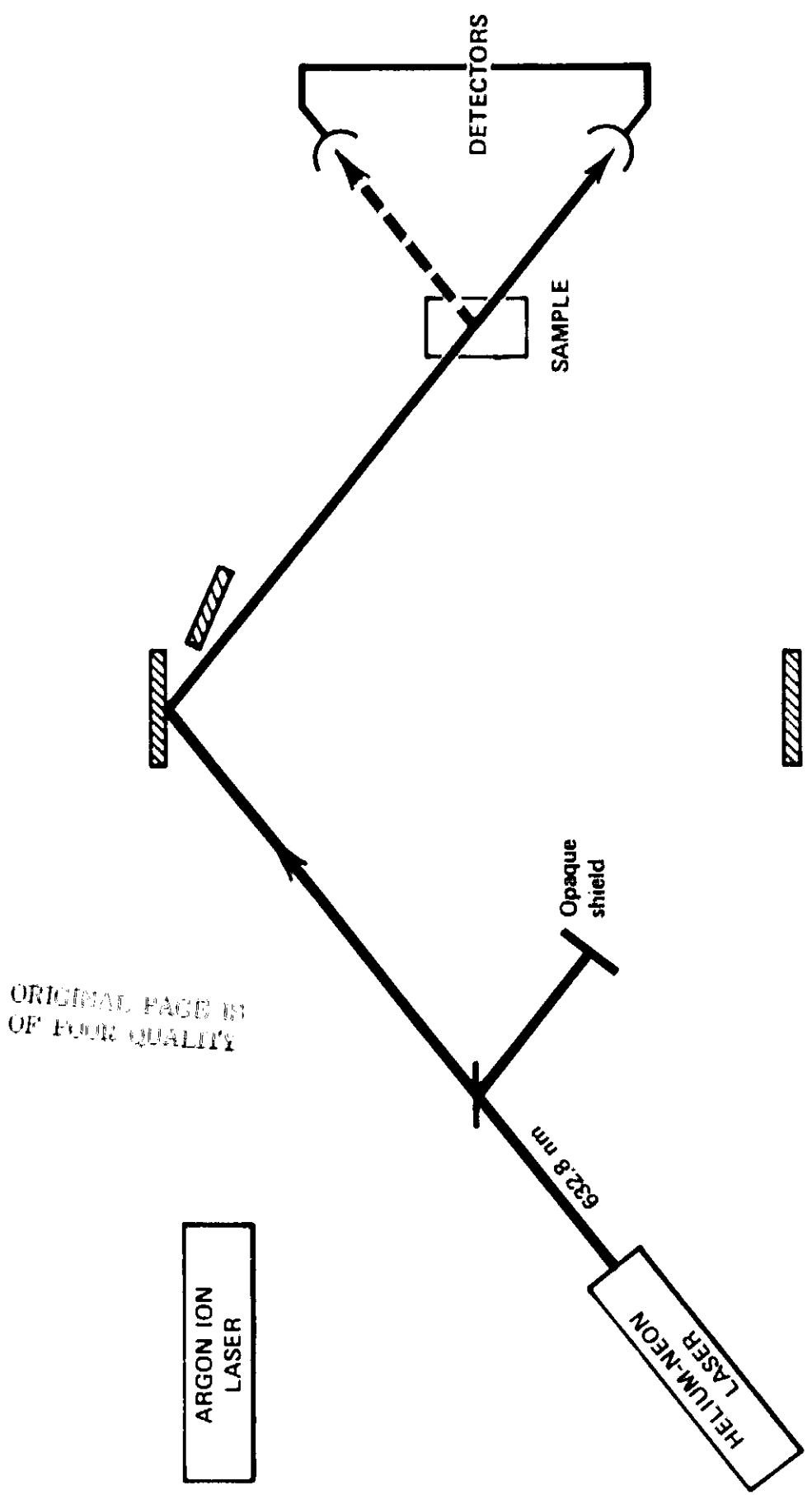


FIGURE 3. SCHEMATIC OF LASER/OPTICAL SETUP FOR WRITING A HOLOGRAM BY PHOTOISOMERIZATION



ORIGINAL PAGE IS
OF FOUR QUALITY

FIGURE 4. SCHEMATIC DRAWING OF LASER/OPTICAL SETUP FOR READING A HOLOGRAM

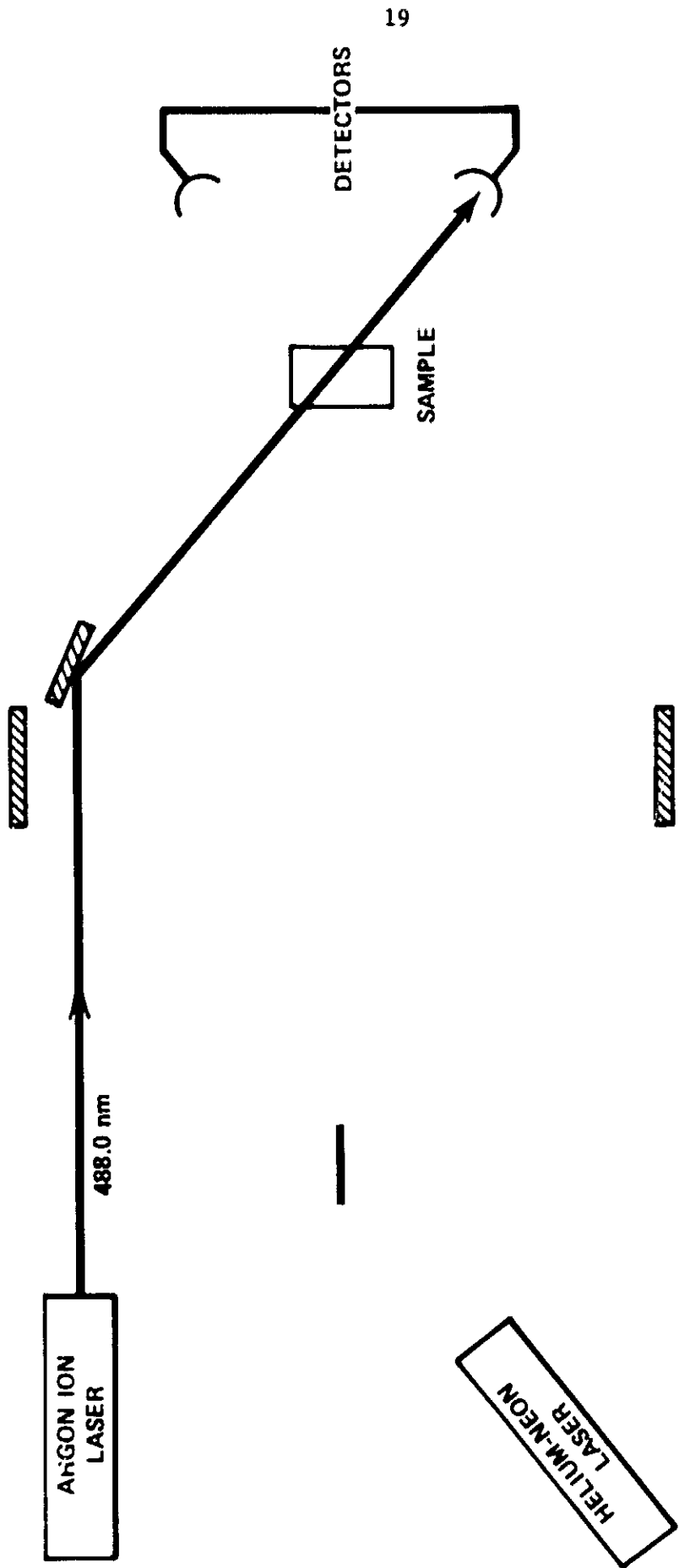


FIGURE 5. SCHEMATIC DRAWING OF LASER/OPTICAL SETUP FOR ERASING HOLOGRAM BY PHOTOISOMERIZATION

Calculation of Absorption Spectra

A method for carrying out the calculation of the absorption spectra of the cis and trans isomers of such systems, based on measured spectra of three photostationary states obtained by irradiation at three different wavelengths, has been published by G. N. Wyman.⁽⁴⁾ A computer program was written for this purpose (Figure 6). N,N'-diacetylindigo (Figure 7) for which literature references⁽⁵⁾ are available, was used to test the computer program and calculation method. The calculated absorption spectra for the cis and trans isomers of the diacetylindigo (Figure 8) were consistent with the literature. Similarly, the spectra calculated for N,N'-bis-(p-trifluoromethylbenzoyl) indigo (Figure 9) were consistent with expectations.

Having such curves available permitted the calculation of cis-trans ratios for various photostationary states of solutions of known molarity. The computer program has proved to be of great value for this purpose, as the calculation of the absorption spectra by hand is a tedious, time-consuming process.

Continuing Studies

The main objective of future work will be to obtain materials and material combinations which exhibit larger Δn values than those obtained thus far with the indigo and thioindigo derivatives. Continuing research will include both the measurement of the dispersion spectra of those systems (shown schematically in Figure 10) so as to identify the optimum reading and writing conditions, and the screening of other cis-trans photoreactive compounds for desirable photorefractive properties.

The research performed to date has indicated that the most useful compounds are those in which the electron polarizability of one isomer is substantially greater than that of the other isomer. The polarizability can be thought of as a measure of how readily the electron cloud surrounding a molecule can respond to the electric field of a photon. A highly polarizable

```

0005 DATA .110, .220, .150, .440, .210, .400, .500, .440, .350, .400, .500, .100, .000
0010 READ I=1, N, L, B, D, C, A, S, E, H, I, J, K, L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z
0011 PRINT 'IF YOU WANT CALCULATED E VALUE, IF NOT ENTER 0.'
0012 INPUT I
0013 IF I=0 GO TO 100
0014 PRINT
0015 GO TO 100
0020 K=1.19E-12/L**2
0030 FOR J=1 TO 3
0040 E=I+K*(J-1)*(J-1)+.5*(J-1)**2
0045 E=I+INT(E-1)*10**4+.5*10**4
0050 NEXT J
0055 IF I=0 GO TO 100
0060 H=2*(E-1)*L**2-E*(J-1)*L*(J-1)*L**2
0065 H=2*INT(H-1)*10**4+.5*10**4
0070 J=1
0075 E=I+K*(J-1)*(J-1)+.5*(J-1)**2
0080 H=I+INT(H-1)*10**4+.5*10**4
0090 H=H*(K**2-E)
0095 H=2*INT(H-1)*10**4+.5*10**4
0100 FOR I=1 TO 3
0110 E=I+K*(J-1)*(J-1)+.5*(J-1)**2
0115 E=I+INT(E-1)*10**4+.5*10**4
0120 TO I=INT(E-1)*10**4+.5*10**4
0125 NEXT I
0130 IF I=0 GO TO 100
0135 PRINT 'QUANTUM FIELD RATIO FOR WAVELENGTH'
0140 PRINT WAVELENGTH
0145 PRINT 'NEW WAVELENGTH IF YOU ENTER 0.'
0150 INPUT WAVELENGTH
0155 PRINT
0160 IF WAVELENGTH=0 GO TO 100
0165 PRINT 'E VALUE CALCULATED FROM WAVELENGTH OF '
0170 WAVELENGTH
0175 I=0
0180 FOR J=1 TO 3
0190 PRINT 'E=I+K*(J-1)*(J-1)+.5*(J-1)**2'
0195 PRINT 'H=I+INT(H-1)*10**4+.5*10**4'
0200 PRINT
0205 NEXT J
0210 PRINT 'TO CALCULATE ADDITIONAL E VALUE, TYPE 1; IF NOT TYPE 0.'
0215 PRINT
0220 INPUT I
0225 IF I=0 GO TO 100
0230 I=I+1
0235 IF I=1 GO TO 200
0240 PRINT 'ENTER REFERENCE DATA FOR TWO PHOTOIONIZATION STATES'
0245 PRINT 'AT EACH WAVELENGTH (A) INDICATED AND WRITE E VALUE.'
0250 PRINT
0255 PRINT 'ENTER D=1.00E-10 (A) WAVELENGTH'
0260 INPUT D=1.00E-10
0265 PRINT
0270 E=I+K*(J-1)*(J-1)+.5*(J-1)**2
0275 E=I+INT(E-1)*10**4+.5*10**4
0280 PRINT
0285 PRINT 'WAVELENGTH = 1000*(D**2)/(E-1)**2'
0290 PRINT 'E=I+K*(J-1)*(J-1)+.5*(J-1)**2'
0295 PRINT
0300 GO TO 100
0305 END

```

ORIGINAL PAGE IS
OF POOR QUALITY

FIGURE 6. COMPUTER PROGRAM FOR CALCULATION OF EXTINCTION COEFFICIENTS FROM SPECTRAL DATA FOR THREE PHOTO-STATIONARY STATES

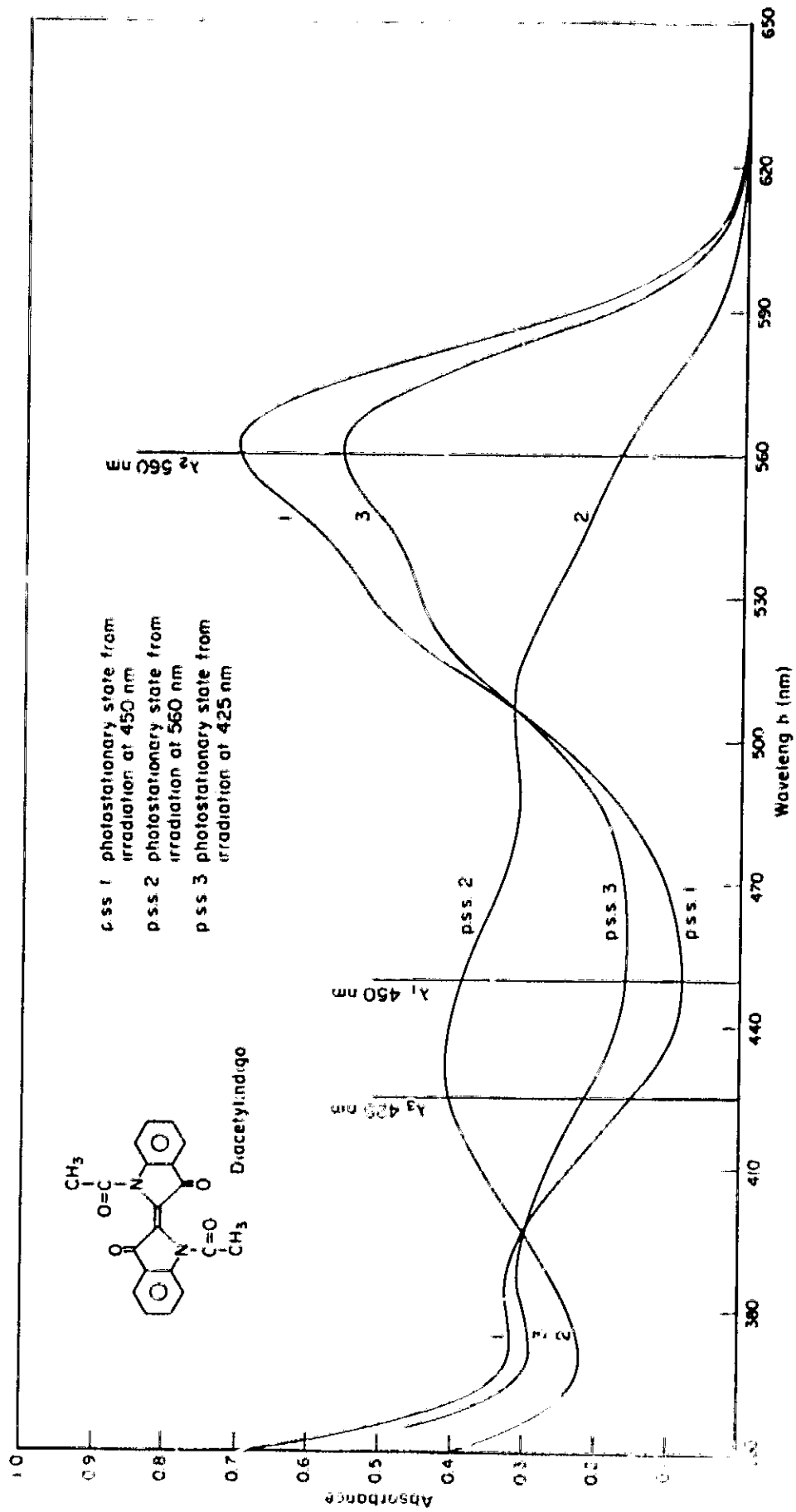
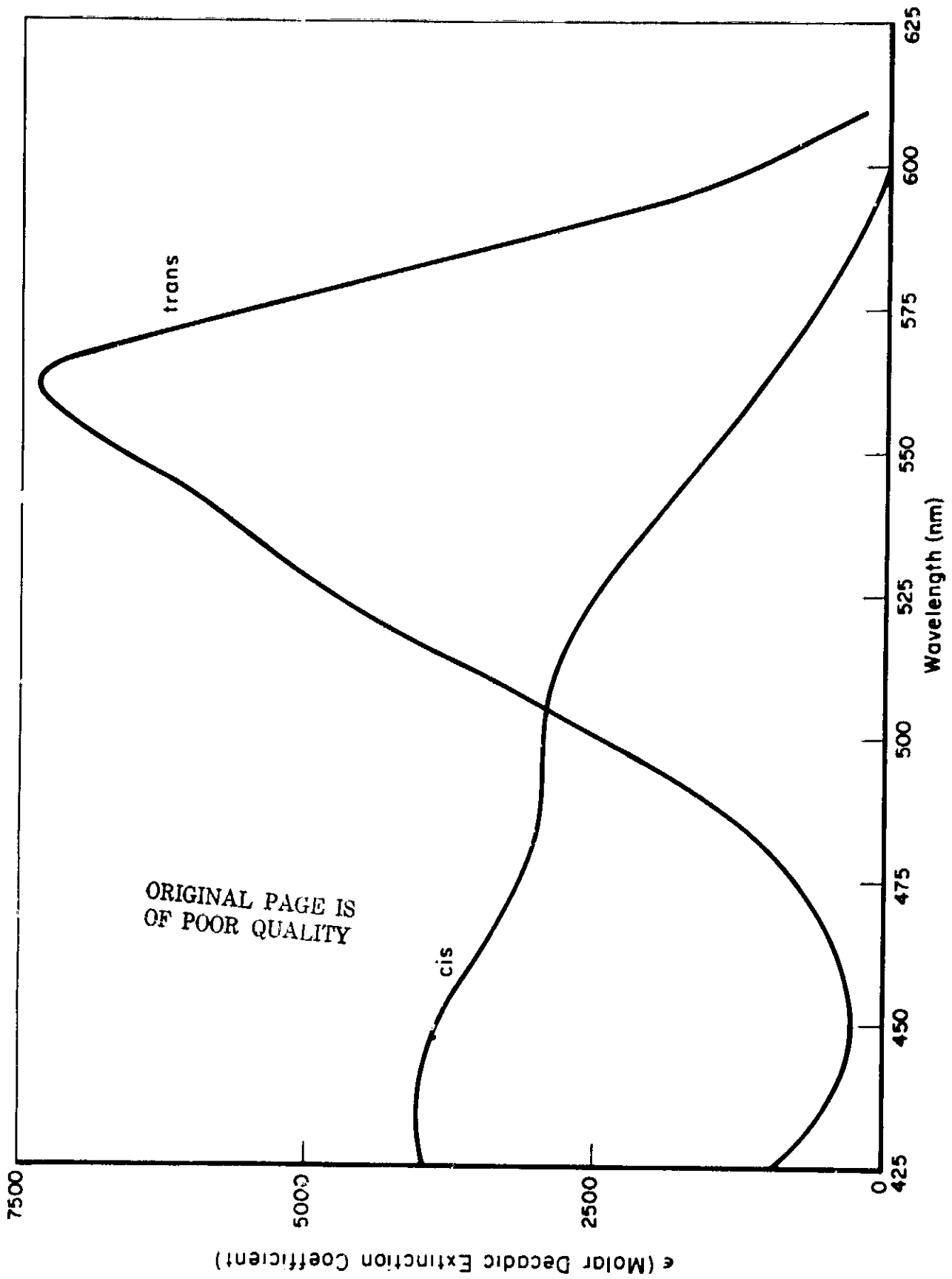


FIGURE 7. ABSORPTION SPECTRA OF THREE PHOTOSTATIONARY STATES OF N, N'-DIACETYLINDIGO USED FOR CALCULATION OF ABSORPTION SPECTRA OF THE PURE ISOMERS

FIGURE 8. CALCULATED ABSORPTION SPECTRA FOR N,N' -DIACETYLMINDIGO

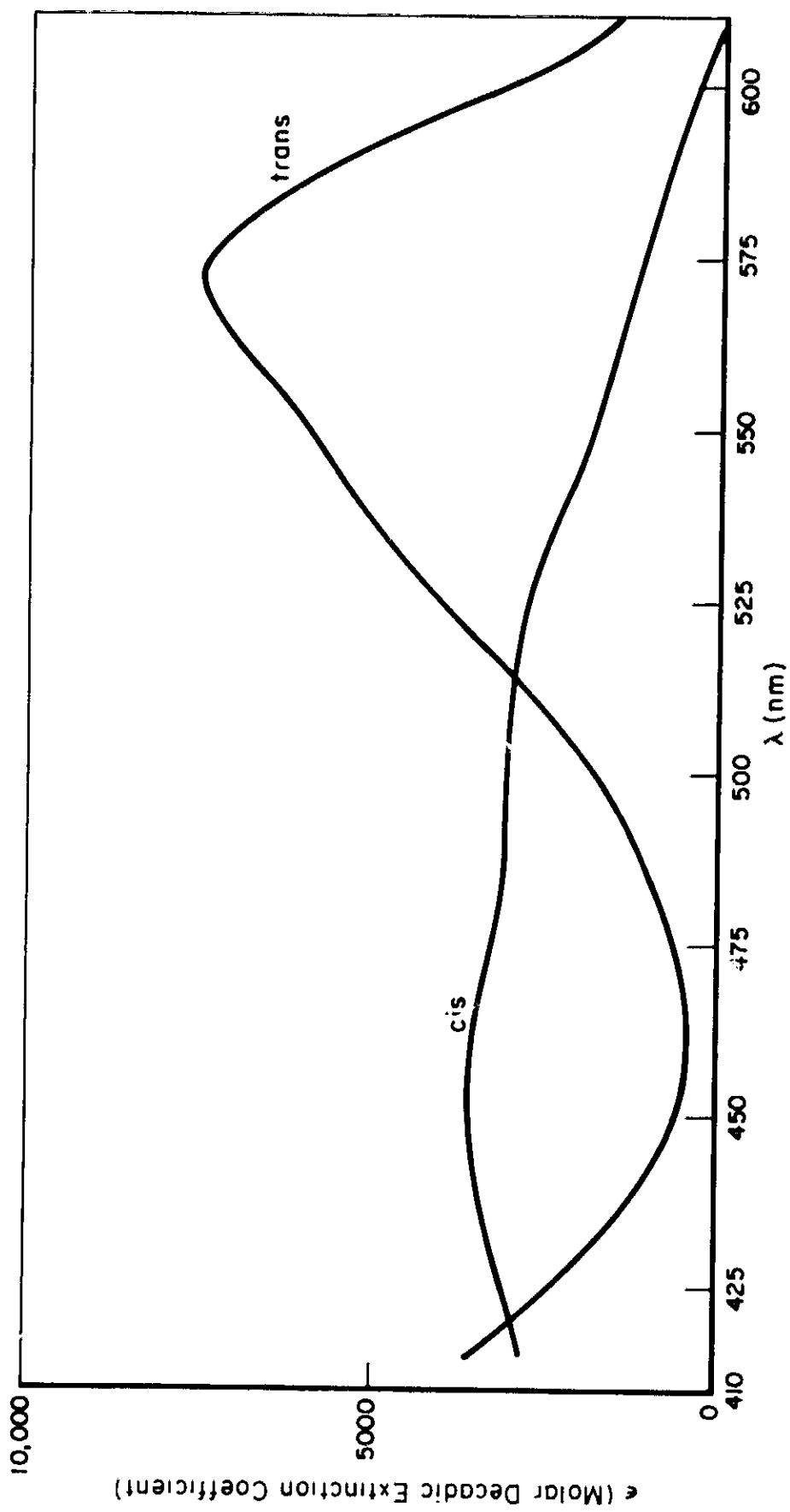


FIGURE 9. CALCULATED ABSORPTION SPECTRA FOR N, N'-bis-(p-TRIFLUOROMETHYLBENZOYL) INDIGO

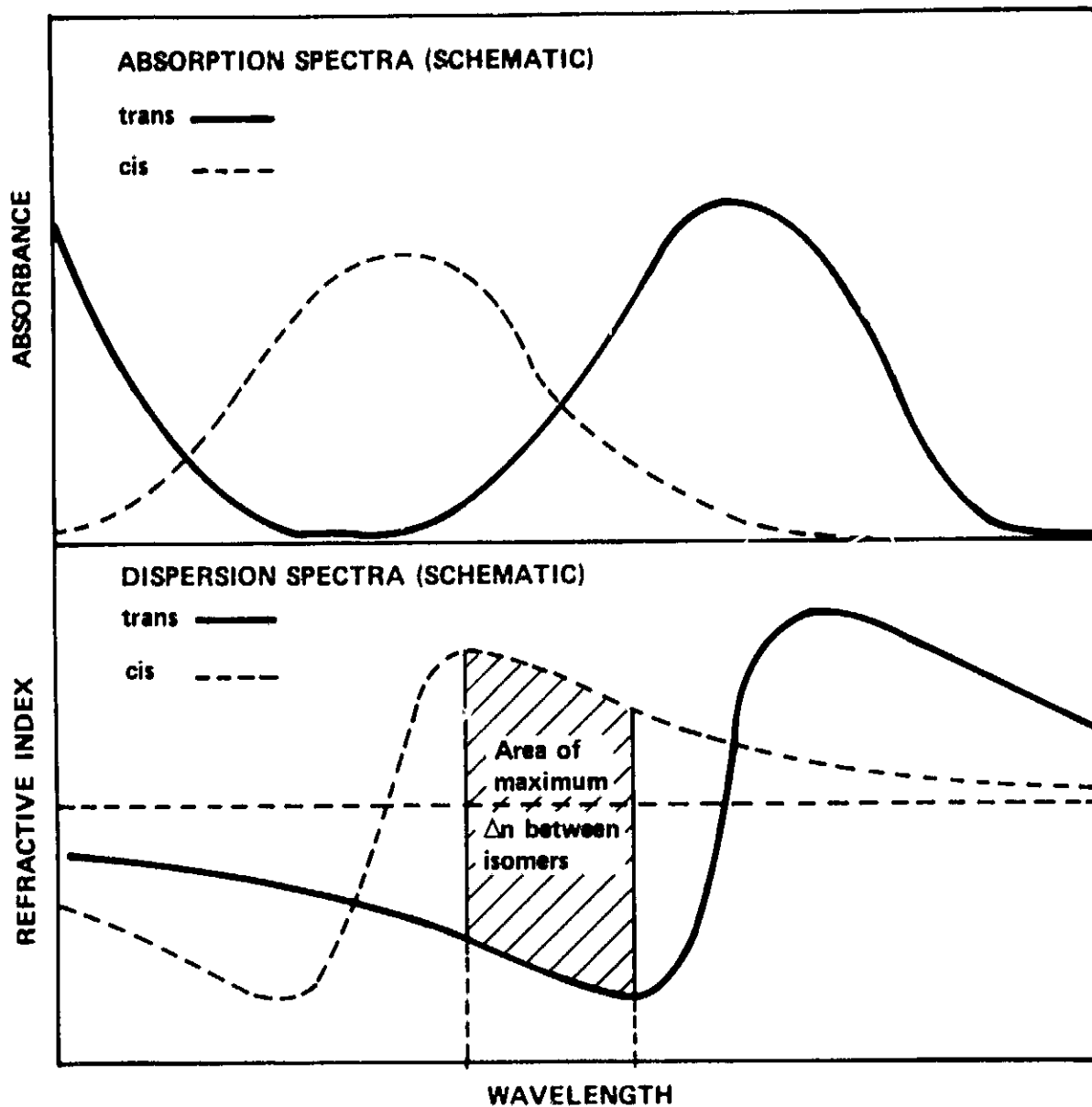
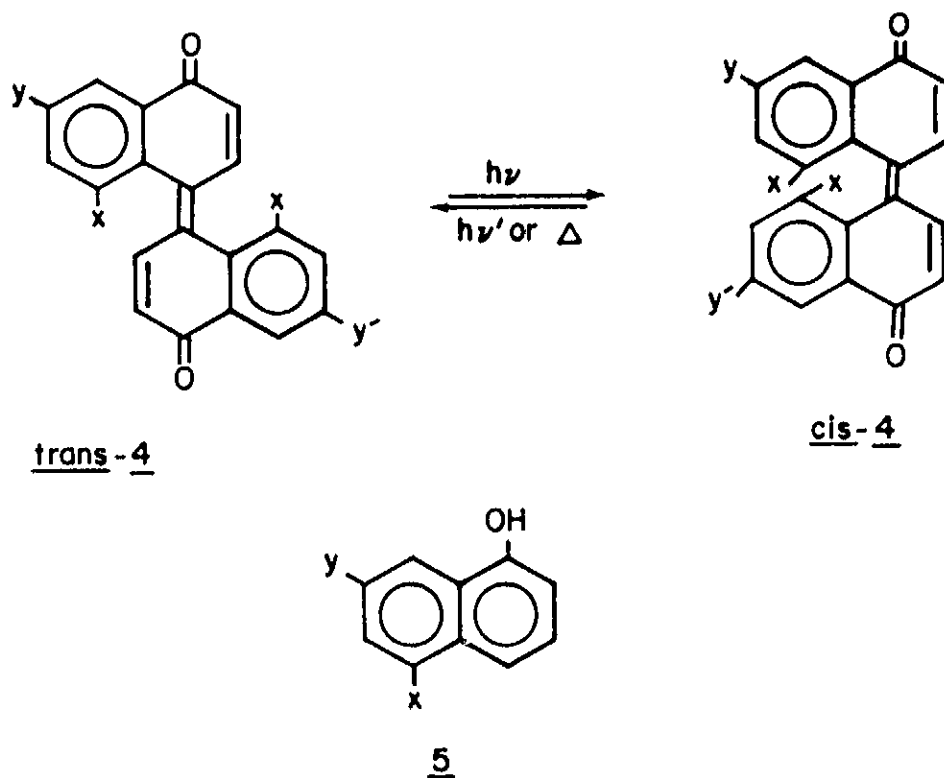


FIGURE 10. SCHEMATIC ILLUSTRATIONS OF POSSIBLE EFFECTS OF WAVELENGTH ON OPTIMIZING REFRACTIVE INDEX DIFFERENCES

ORIGINAL PAGE IS
OF POOR QUALITY

electronic structure is fairly "loose" and is therefore easily perturbed by a photon (even when the photon is not absorbed); such materials have a high index of refraction.

Should the indigoid dyes prove to be unsatisfactory for efficient holographic recording, it may be possible to utilize another class of cis-trans materials, the naphtho-bisquinones, represented by structure 4. These compounds are easily prepared by oxidation of the corresponding naphthols (structure 5).



The cis isomers of structure 4 tend to undergo internal cyclization when irradiated unless the positions indicated by *x* are substituted with some group other than hydrogen. In conjunction with the cis-trans photoisomerization, the photorefractive properties of these compounds might be enhanced by choosing the substituents *y* and *y'* so as to provide a charge-transfer interaction between the adjacent aromatic rings in the cis isomer.

It is known⁽⁶⁾ that the refractive index is sensitive to charge-transfer interactions, so this phenomenon could be quite useful for the purpose of holographic recording.

MULTIPLE HOLOGRAM STORAGE IN
THICK cis-trans MATERIALS

The primary motivation for the development of cis-trans materials for holographic recording media has been for use in a contemplated page-oriented, high-capacity, digital memory. In order to achieve the high bit density which is one of the unique features of this system, it is necessary to superimpose up to 100 individual holograms in each of the cells of the memory. Each of these holograms can be reconstructed individually by virtue of the high angular and wavelength selectivity exhibited by thick holograms.

The angular or wavelength resolution of thick holograms increases as the thickness of the holographic recording material is increased. To achieve the storage densities required by the memory system, a thickness of approximately 1 mm is desired. Unfortunately, this thickness causes severe complications in the reconstruction of the holographic image. This complication arises from the fact that the preferred mode of readout employs a wavelength λ_{read} which differs from the write wavelength, λ_{write} .

If a collimated read beam of wavelength $\lambda_{\text{read}} \neq \lambda_{\text{write}}$ is used, then a hologram consisting of a simple diffraction grating can be read out with high efficiency by having the read beam incident at the Bragg angle appropriate to its wavelength. However, inserting additional information into the stored hologram results in a set of superimposed gratings of differing orientation whose Bragg condition can no longer be satisfied by any single angle of incidence unless $\lambda_{\text{read}} = \lambda_{\text{write}}$. Readout at wavelengths other than λ_{write} results in distortion and loss of information. The severity of this problem increases with the hologram thickness, so the very property which allows multiple hologram storage interferes with high quality reconstruction unless $\lambda_{\text{read}} = \lambda_{\text{write}}$.

In light of these problems there must be compelling reasons to retain the $\lambda_{\text{read}} \neq \lambda_{\text{write}}$ mode of operation with thick holograms. There are two principle reasons for wanting to do this. First, the cis-trans materials cannot be fixed. They are therefore always sensitive to radiation at the writing wavelength and repeated reading at this wavelength will degrade the stored information. Second, the materials are most efficiently

used as phase rather than amplitude holograms. To read at the write wavelength would reduce their diffraction efficiency since, in order to use the write energy effectively, the absorption of the material at this wavelength must be reasonably high. It is obvious that by limiting the number of times a particular memory element is read, and by accepting some reduction in writing efficiency and/or diffraction efficiency, the cis-trans materials could be used in a $\lambda_{\text{read}} = \lambda_{\text{write}}$ mode. However, the advantages of using different wavelengths for the two functions are sufficiently great to justify a more detailed investigation of the problems involved in so doing. The remainder of this section deals with this problem. The discussion starts with the angular selectivity properties of simple gratings and then proceeds to the more complicated case of a hologram of an extended transparent object.

Angular Selectivity of Plane Wave Gratings

The angular selectivity of thick plane wave gratings can be evaluated using an approximation of the equations developed by H. Kogelnik.⁽¹⁾ The resulting equation has the form

$$2\Delta\theta_{1/2} \approx n \frac{\lambda}{d} = \frac{\lambda_a}{2 d \sin(\theta_i)} \quad (1)$$

where λ_a = wavelength in air
 θ_i = Bragg angle in the medium
 d = thickness

and $2\Delta\theta_{1/2}$ = angular half power band-width of the acceptance curve in air. The equation indicates that the angular half power band-width is inversely proportional to both the sine of the Bragg angle and the thickness of the grating. The dependence of the angular selectivity on the latter parameter was examined experimentally and shown to agree with the predicted values. For these measurements, LiNbO_3 slabs of varying thickness were used as the recording medium. The gratings were written with the 4880 Å output of an argon laser and the included angle between the writing beams was 60 degrees.

The angular measurements were performed using a rotary table with a resolution of 3 arc-secs.

The angular half power band-width was determined from the angular acceptance curves produced by monitoring the diffracted intensity as the reconstruction beam was varied about the Bragg angle. A typical recording is shown in Figure 11 with the half power band-width noted. Using this technique, the half power band-width was evaluated for several thicknesses. The experimental data are presented in Figure 12 along with the prediction of Kogelnik's equations. The agreement between the predicted and experimental values is within the experimental error involved in measuring the half width of the curve.

If, for the sake of argument, we assume a system in which the reference beam angle can be positioned at any of 100 discrete positions in a 0.1 radian ($\sim 6^\circ$) range, then we see that the minimum hologram thickness for separate readout of individual plane wave holograms is 0.28 mm.

Angular Selectivity of Fourier Transform Holograms of Transparency Objects

The previous results can be extended to the case of Fourier Transform holograms of a transparency. This special case is important in that it simulates as many of the designs for holographic read-write memory systems based on the page composer concept.

An experimental arrangement for recording a Fourier Transform (F-T) hologram is illustrated in Figure 13. The object beam is a converging beam of angular extent δ_0 while the reference beam has a planar wavefront. In practice the object beam can be represented by spectrum of plane waves having a maximum angular spread of δ_0 . The recorded hologram can be considered to be composed of a superposition of many plane wave gratings all of which were constructed with the same reference beam. As a result the Bragg condition can then be satisfied simultaneously for all components of the hologram when the illuminating beam is identical to the reference beam. The half power band-width for any plane wave grating component is given approximately by Equation (1) where $\theta_i = \theta_0$, if $\delta_0 \leq \frac{1}{5} \theta_0$. Thus, the

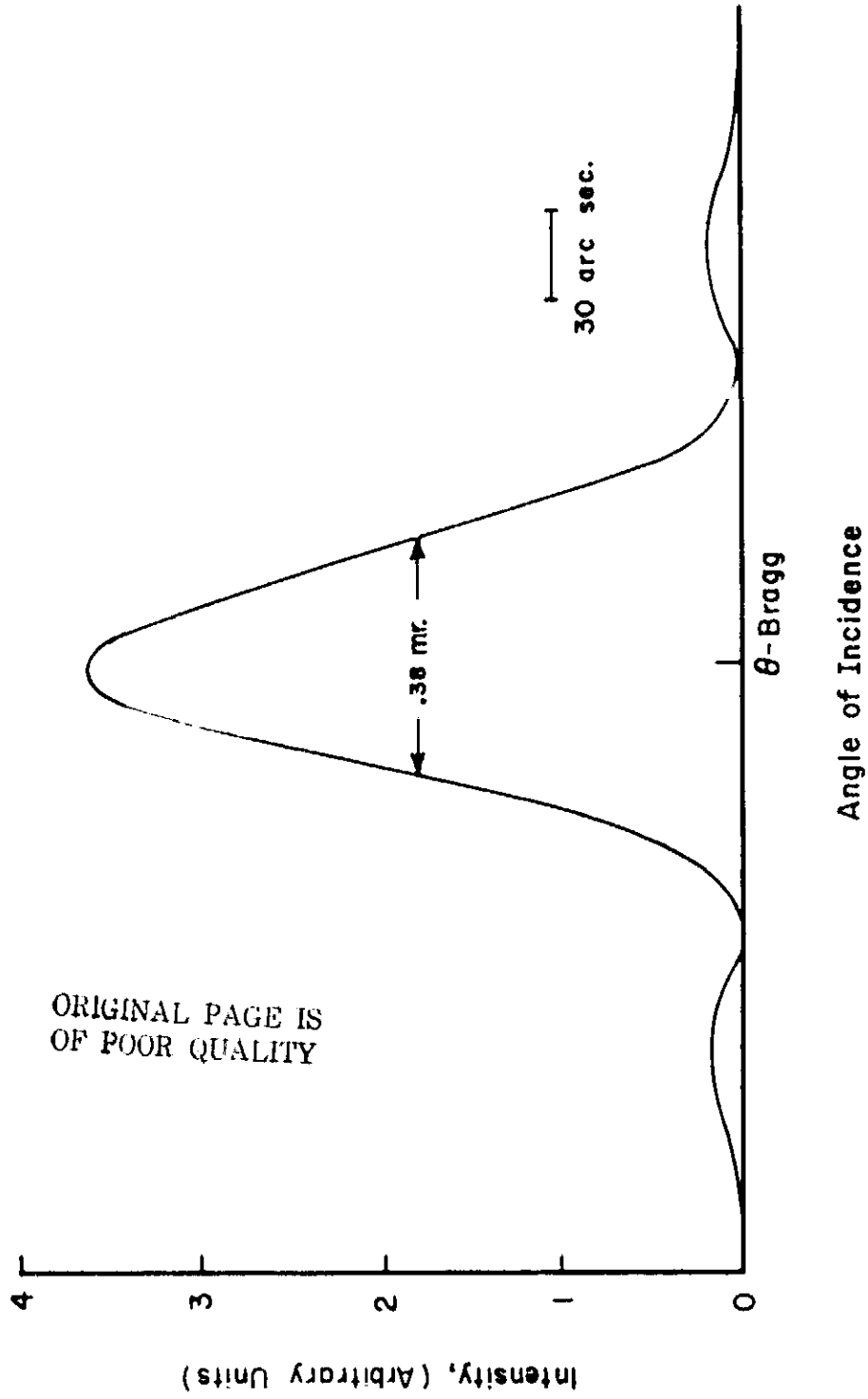


FIGURE 11. DIFFRACTED LIGHT INTENSITY FROM A SIMPLE HOLOGRAPHIC PHASE GRATING AS A FUNCTION OF THE ANGLE OF INCIDENCE OF THE READ BEAM. THE SAMPLE THICKNESS IS 3 MM.

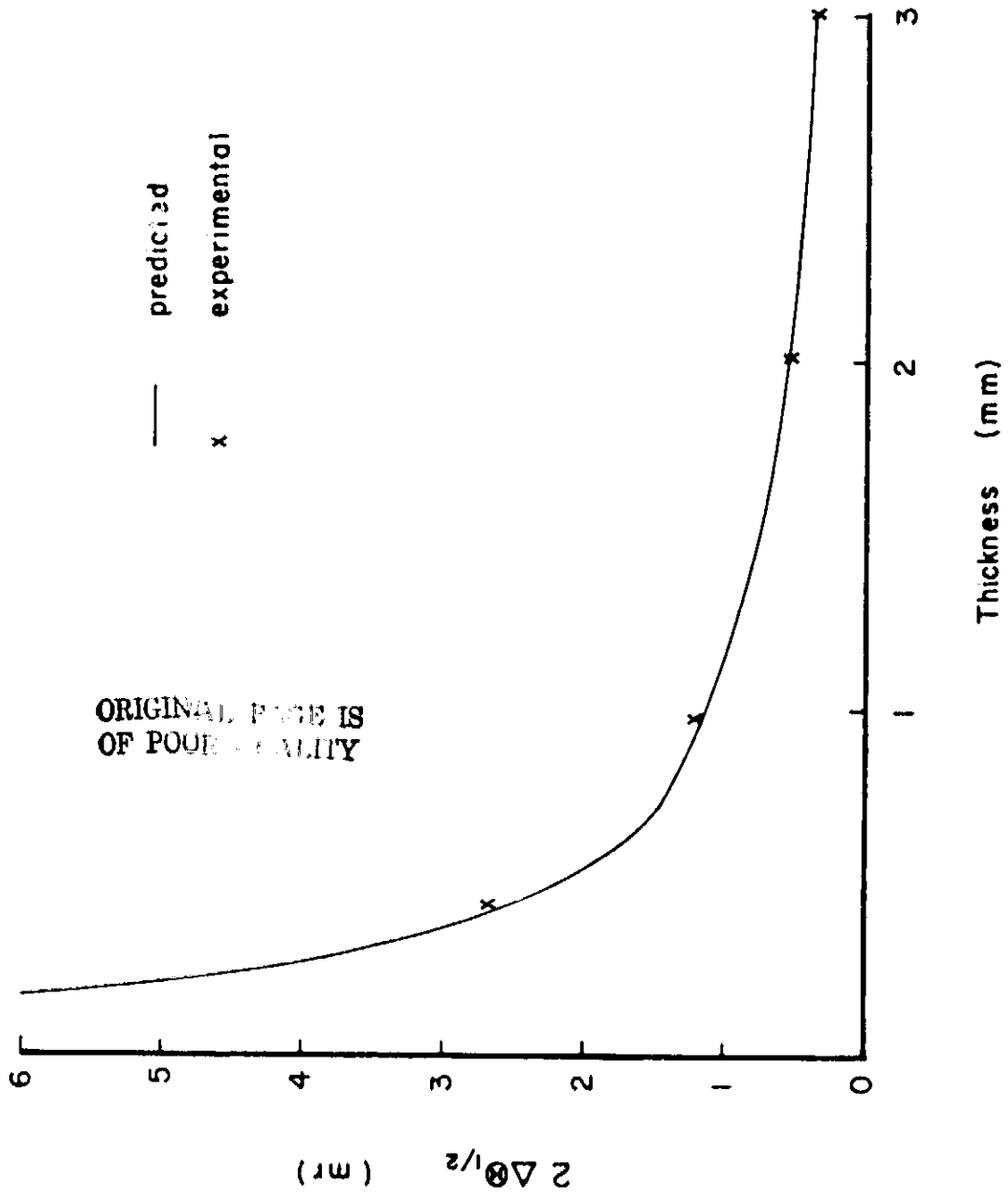


FIGURE 12. ANGULAR ACCEPTANCE OF SIMPLE HOLOGRAPHIC GRATINGS AS A FUNCTION OF GRATING THICKNESS. THEORY (—) AND EXPERIMENTAL DATA (x).

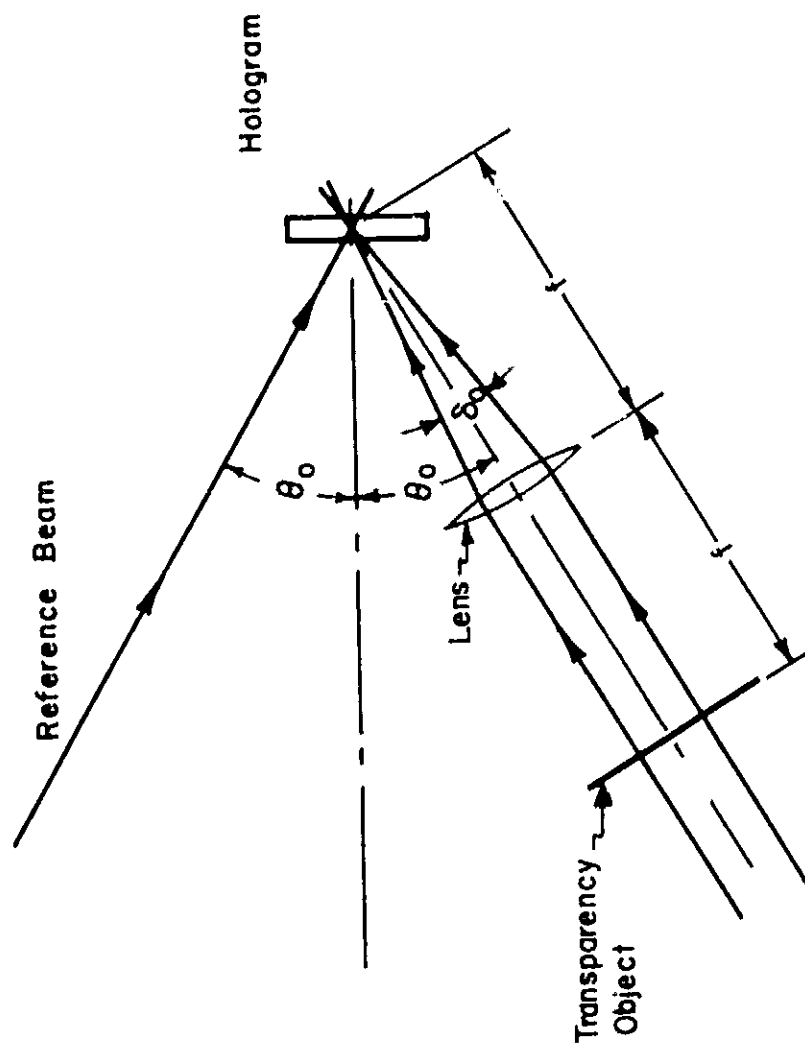


FIGURE 13. EXPERIMENTAL ARRANGEMENT FOR PRODUCING A FOURIER TRANSFORM HOLOGRAM

ORIGINAL PAGE IS
OF POOR QUALITY

acceptance curve for a Fourier Transform hologram is nearly identical to that of a plane wave grating when $\lambda_{\text{read}} = \lambda_{\text{write}}$. We have confirmed this by measuring the angular separation of adjacent minima (the full width of the acceptance curve) for a plane wave grating and a Fourier Transform hologram. Utilizing $\delta_0 = 30$ degrees for both the plane wave grating and a F-T hologram and $\delta_0 = 58$ mr for the F-T hologram the measured angular widths were found to be 3.38 mr and 3.22 mr, respectively, for $d = 1$ mm.

Effects of Reading and Writing With Differing Wavelengths

The previous results and discussions are still valid for the reconstruction of a plane wave grating with a wavelength differing from the writing wavelength. However, for $\lambda_{\text{read}} \neq \lambda_{\text{write}}$, a complication arises for the Fourier Transform hologram, which results in a decrease of its angular selectivity.

The use of an illuminating beam of differing wavelength requires an angular change to satisfy the Bragg condition. This condition is easily satisfied for gratings produced by two plane wavefronts. However, if the hologram is produced by an object beam composed of a spectrum of plane waves of angular extent δ_0 , the Bragg condition cannot be satisfied for all components simultaneously by a single collimated reconstruction beam. As a result, the image appears to be only partially illuminated. To form a completely illuminated image requires the use of a reconstruction beam composed of a spectrum of plane waves of angular extent given by

$$\Delta\theta_r = n_r \left\{ \sin^{-1} \left[\frac{\lambda_r}{\lambda_w} \frac{n_w}{n_r} \sin \left(\theta_i + \frac{\delta_i}{2} \right) \right] - \left[\sin^{-1} \left(\frac{\lambda_r}{\lambda_w} \frac{n_w}{n_r} \sin \theta_i \right) + \frac{\delta_i}{2} \right] \right\} \quad (2)$$

where

λ_r = read wavelength

λ_w = write wavelength

n_r = refractive index at λ_r

n_w = refractive index at λ_w

$\Delta\theta_r$ = angular extent of the reconstruction beam in air.

The angles θ_i and δ_i are defined as shown in Figure 14.

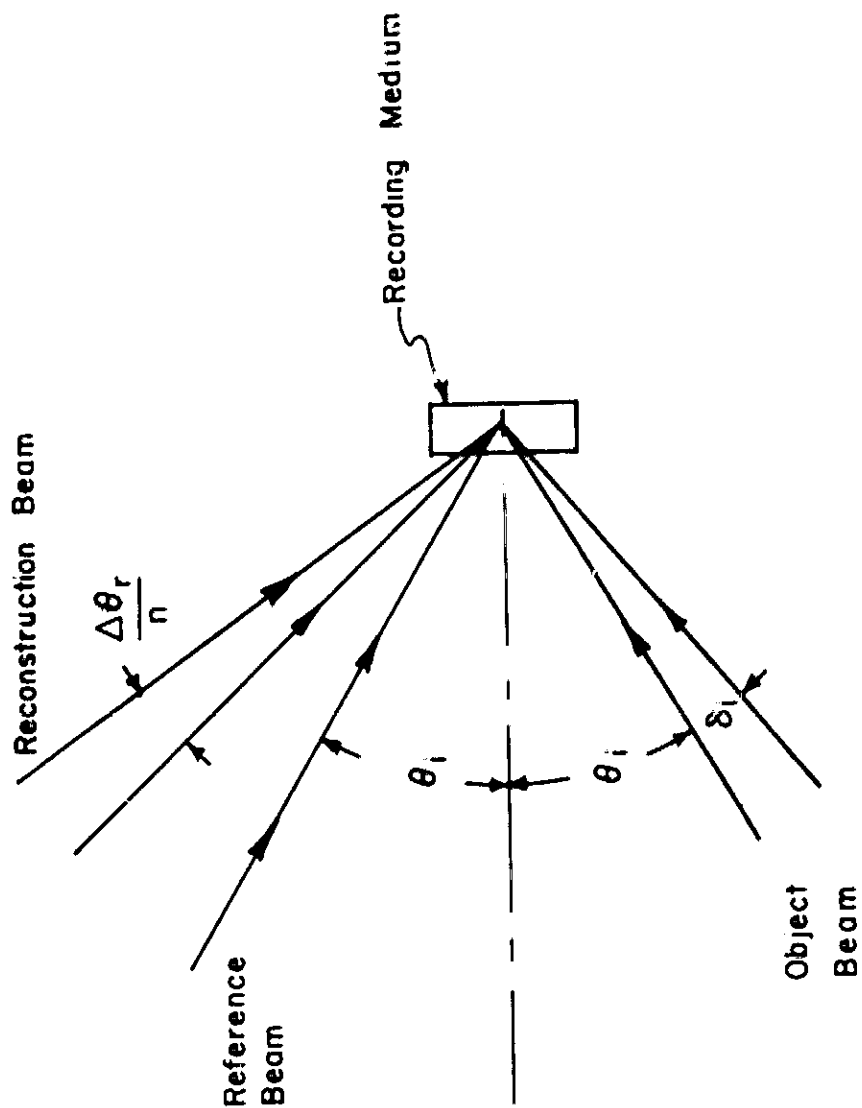


FIGURE 14. DIAGRAM OF EXPERIMENTAL SCHEME FOR PRODUCING A FULLY ILLUMINATED IMAGE FROM A FOURIER TRANSFORM HOLOGRAM OF A TRANSPARENT OBJECT ($\lambda_r \neq \lambda_w$). REFRACTION AT THE SAMPLE SURFACE HAS BEEN IGNORED IN THE FIGURE.

The simplest method of producing an illuminating beam of the appropriate angular extent is to use a converging or diverging beam focused at or near the hologram. Utilizing this procedure it was shown that a fully illuminated image occurred when the angular extent of the reconstruction beam was approximately that specified by Equation (2). This is shown explicitly in Figure 15 in which the diffraction efficiency is displayed as a function of the angular extent of the reconstruction beam for a Fourier Transform hologram constructed with $\theta_{air} \approx 26$ degrees and $\delta_o = 55$ mr. The peak of the curve is shown to coincide with the predicted value.

Although reconstruction with spherical wavefronts is useful for demonstrating the need for a beam of the appropriate angular extent to compensate for wavelength changes, it is not practical if a high resolution image is required. The use of an illuminating beam focused at or near the location of the hologram results in a severe loss of resolution, an observation which is consistent with that predicted using R. Meier's⁽²⁾ equations for third order aberrations. As an example, the equation for spherical aberrations of the virtual side band has the form

$$S = \frac{1}{Z_c^3} - \frac{\mu}{M^4} \left(\frac{1}{Z_r^3} - \frac{1}{Z_o^3} \right) - \frac{1}{Z_i^3} \quad (3)$$

where

Z_c = location of reconstruction point source

Z_r = location of reference beam point source

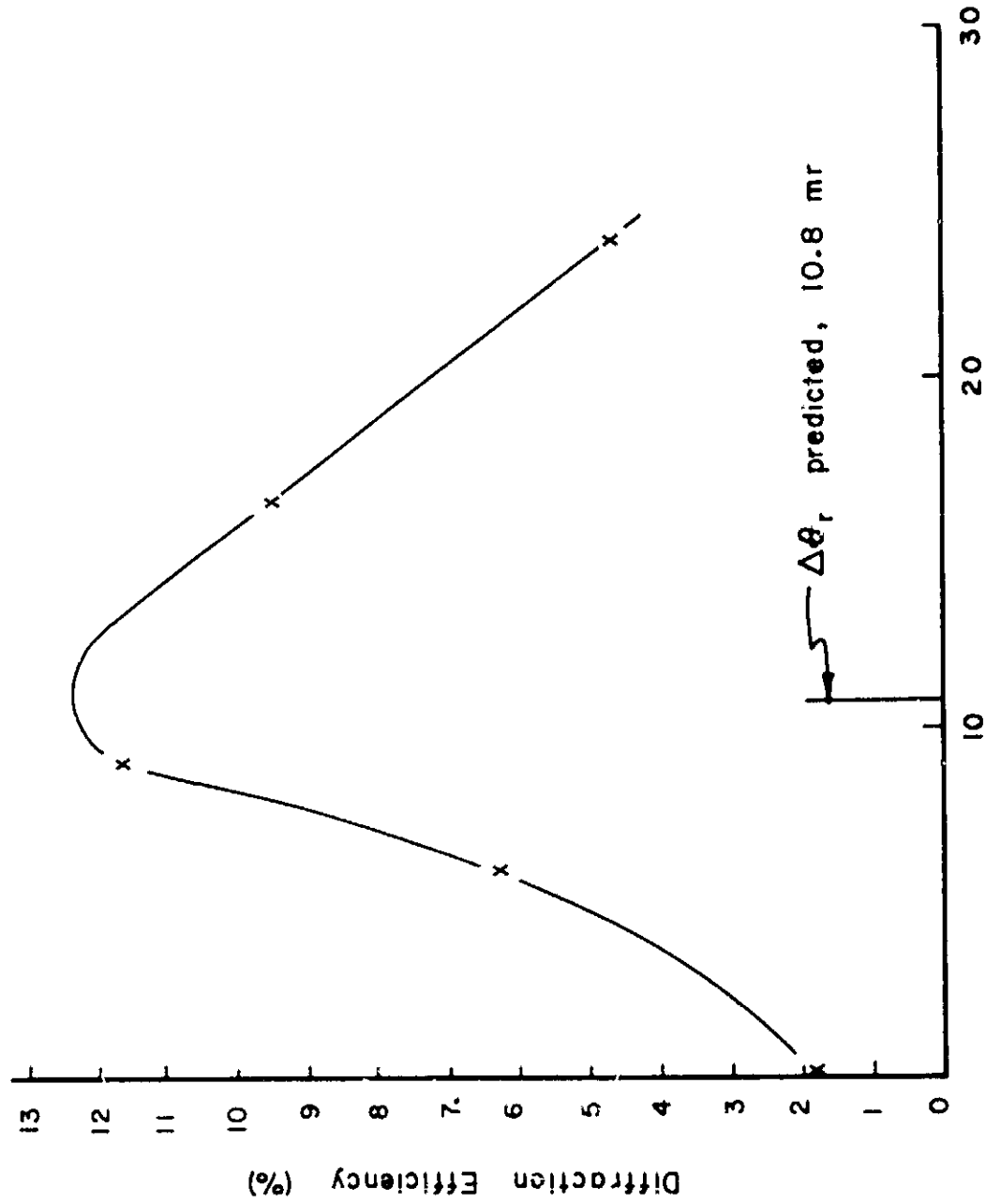
Z_o = location of the object point

Z_i = location of the image point

$\mu = \lambda_r / \lambda_w$

m = magnification

and S = magnitude of the spherical aberration.



Angular Extent of Reconstruction Beam, $\Delta\theta_r$ (mr)

FIGURE 15. DIFFRACTION EFFICIENCY OF A F-T HOLOGRAM VS. ANGULAR EXTENT OF RECONSTRUCTION BEAM. THE EXACT SHAPE OF THE CURVE IS NOT FULLY UNDERSTOOD, BUT THE PEAK IS SEEN TO COINCIDE WITH THE PREDICTION OF EQ. (2).

ORIGINAL PAGE IS
OF POOR QUALITY

For a Fourier Transform hologram reconstructed by an illuminating beam focused at the plane of the hologram the values of the various parameters are

$$\begin{aligned} Z_c &= 0 \\ Z_r &= \infty \\ Z_o &= 0 \end{aligned}$$

and

$$\frac{i}{Z_1} = \left(\frac{1}{Z_c} + \frac{\mu}{Z_o} \right)$$

Substituting the appropriate value for Z_1 in Equation (3) permits reducing it to

$$\begin{aligned} S &= \frac{1}{Z_c^3} + \frac{\mu}{Z_o^3} - \left\{ \frac{1}{Z_c} + \frac{\mu}{Z_o} \right\}^3 \\ &= \frac{1}{Z_c^3} + \frac{\mu}{Z_o^3} - \left\{ \frac{Z_o + \mu Z_c}{Z_c Z_o} \right\}^3 \\ &= \frac{1}{Z_c^3} + \frac{\mu}{Z_o^3} - \left\{ \frac{1}{Z_c^3} + \frac{3\mu}{Z_o Z_c^2} + \frac{3\mu^2}{Z_o^2 Z_c} + \frac{\mu^3}{Z_o^3} \right\} \\ S &= - \frac{3\mu}{Z_o Z_c} \left\{ \frac{1}{Z_c} + \frac{\mu}{Z_o} \right\} \end{aligned} \quad (4)$$

This form of the equation readily illustrates that the spherical aberration becomes very severe as Z_c and Z_o approach zero (focused near the location of the hologram). The equation for coma and astigmatism are of the same general form and thus exhibit the same behavior.

In addition to producing aberrations in the image, a Fourier Transform hologram reconstructed with an extended angle reference beam is also characterized by a decrease in the angular selectivity. Referring to the previous concept of a superposition of many plane wave gratings as representing a Fourier Transform hologram, any one component hologram can be reconstructed over the entire range of $\Delta\theta_r$. Thus the angular selectivity is reduced by a factor of

$$\frac{\Delta\theta_r + 2\Delta\theta_{1/2}}{2\Delta\theta_{1/2}}$$

For a hologram constructed with $\theta_o = 30_o$, $\delta_o = 58$ mr, writing wavelength of 4880 Å, a read wavelength of 6328 Å and a 1 mm thickness the reduction is a factor of approximately 15.

Alternative Reconstruction Techniques

The previous results have demonstrated that reconstruction of a F-T hologram with spherical wavefronts results in a reduction of the angular selectivity and loss of image resolution. While the reduction of angular selectivity is an inherent difficulty occurring because of the wavelength change, the primary cause of the resolution loss appears to be related to the difference in the degree of focusing or collimation of the reference and reconstruction beams. There are at least two available methods for reducing this difference. One is to reconstruct with a planar wavefront of the desired wavelength and sweep it thru the angle $\Delta\theta_r$ to produce a fully illuminated image. A second is to construct the hologram with a reference beam focused at or near the hologram and then reconstruct with an illuminating beam focused at the same position and having the same wavefront curvature. This geometry should provide a fully illuminated image with minimal aberrations. Both techniques are, however, expected to result of a loss in diffraction efficiency and angular resolution.

REFERENCES

- (1) J. Saltiel and L. Metts (Florida State University), personal communication to R. E. Schwerzel, 1971.
- (2) Daniel L. Ross, Appl. Opt. 10, 571 (March 1971); U.S. Patent No. 3,715,212 (February 6, 1973).
- (3) G. M. Wyman (University of North Carolina), personal communication to R. E. Schwerzel, (1974).
- (4) G. M. Wyman, Hol. Photochem. 2, 81 (1974).
- (5) D. L. Ross and J. Blanc, in Photochromism, G. H. Brown, Ed., Wiley Interscience, New York, 1971, Chapter 5.
- (6) H. E. Baur, et al, J. Phys. Chem. 73, 641 (1969).
- (7) H. Logelink, Coupled Wave Theory for Thick Hologram Gratings, The Bell System Technical Journal, 48 (9), (November, 1969).
- (8) R. W. Meier, Magnification and Third-Order Aberrations in Holography, Journal of the Optical Society of America, 55 (8), (August, 1965).