FINAL REPORT

on

HOLOGRAPHIC RECORDING MATERIALS DEVELOPMENT

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LANGLEY RESEARCH CENTER

NASA Contract NAS1-12324
Requisition No. 1-17-3638

Period Covered:

May 29, 1973 to May 28, 1974

BATTELLE
Columbus Laboratories
505 King Avenue
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ABSTRACT

Research during this contract period led to significant new develop-
ments in the area of organic cis-trans isomerization systems for holographic
memory applications. These studies of a stilbene derivative in a polymer gel
matrix strongly indicate that the system can be further developed to provide the
following benefits:

- Reduction of energy required for forming holograms, permitting
  the use of compact, economical and reliable lasers,

- Large refractive index difference, allowing multiple hologram
  superposition,

- Adaptability for use of convenient laser wavelengths,

- Potential, through "materials engineering", for control of
  optical properties and hologram thickness.

The chemical research effort consisted of photochemical studies leading to the
selection of a stilbene derivative and a polymer matrix system which have greatly
improved refractive index differences between the cis and trans isomers as well
as demonstrated efficiency of the photoisomerization process. In work on lithium
niobate effects of sample stoichiometry and of read and write beam polarizations
on recording efficiency were investigated. Effects of stoichiometry are not
negligible, at least in samples of low iron content. $LiNbO_3$ was used for a
study of angular sensitivity and of capability for simultaneous recording of
extended objects without interference. The current status of $LiNbO_3$ as a
holographic recording material is summarized.

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FOREWORD

This report was prepared by the 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 this work is C. M. Verber of the Solid State and Optical Sciences Section. Other contributors are R. A. Nathan, P. J. Perry, J. A. Hassell, A. R. Bunk, V. E. Wood, D. R. Grieser, and N. F. Hartman.

SUMMARY

The major innovation from research during this contract period is the development of a workable cis-trans isomerization system for holographic digital storage. In addition, a series of studies of the recording utility of doped lithium niobate systems was performed. Work on the organic isomerization system proceeded from synthetic studies through theoretical and experimental considerations of refractive index, photochemistry, and matrix materials. The prototype system of 4-methoxy-4'-nitrostilbene in polyisobutylene/benzene gel is currently ready for irradiation studies.

Significant accomplishments in the last year's work were the increase of refractive index difference between isomers by several orders of magnitude to a projected value of 0.15 and laser induced photoisomerization of a substituted stilbene in a solid matrix.

RECOMMENDATIONS

Results of research with the 4-methoxy-4'-nitrostilbene system have provided substantial evidence of its potential for high-speed, high-capacity holographic memories. Continued work is needed to optimize such factors as sensitivity, cyclability, bit density, thermal-chemical stability, and diffusion in the gel matrix. Extensive theoretical studies have already indicated possible solutions. Major advances during the past year give reason to believe that continued studies, as discussed later in this report, should be performed to develop further this promising system. Further studies are desirable to determine ultimate noise and crosstalk limitations on the number of phase holograms of digital data that may be simultaneously stored in a given volume of recording material. Some additional work on $LiNbO_3$ to determine the nature of the recording mechanism and the ultimate capabilities of the material is also desirable.

cis-trans SYSTEM

Chemical research for this phase of the program began with synthetic studies of a prototype stilbene, 4-methoxy-4'-nitro-α-methylstilbene, and proceeded to development of an organic gel matrix system with high photoisomerization efficiency for a related compound, 4-methoxy-4'-nitrostilbene.

Major areas of study included theoretical and experimental investigations of refractive index, photochemistry, synthesis, and matrix systems for the stilbenes. Data from each study contributed to the establishment of parameters for maximizing refractive index differences between cis- and trans-isomers, optimizing the efficiency of the photoisomerization reaction and development of a solid format for the stilbene which would allow efficient isomerization while limiting migration of the stilbene molecules.

Refractive Index Studies

Theoretical

Before any experimental work was carried out, careful consideration was given to anticipated refractive index differences between cis and trans isomers of substituted stilbenes. This resulted in an initial selection of candidate stilbenes for the holographic system. Refractive index is dependent upon the compound's electron polarizability which in turn is a function of the π-bond conjugation. Therefore, a difference in refractive index between cis and trans isomers is dependent upon a change in polarizability. The conjugation in the π-electron system is much less effective in the non-planar cis-isomer than in the trans-isomer, which is usually close to a planar configuration. This results in a predictably lower polarizability of the cis-isomer of any cis-trans pair. Increasing polarizability or refractive index differences between the cis and trans isomers depends upon increasing the polarizabilities of the individual isomers, an effect easily accomplished by adding polar groups to the molecule. In such cases, the refractive index of the trans-isomer generally increases to a greater extent than that of the cis-isomer, thus increasing the magnitude of the refractive index difference. The combination of nitro (NO_2) and methoxy (CH_3O) groups at opposite ends of the molecule is particularly effective since under these conditions these groups tend to delocalize electrons in a reenforcing fashion (one toward, one away from the central π-electron system).

Such considerations eventually contributed to the shift of emphasis away from the α-methylstilbenes because the α-methyl group causes a decrease in planarity of the trans-compounds and thus a corresponding decrease in their polarizability. This would be expected to decrease refractive index differences. Experimental evidence supported this theory.

A molecule to be considered in future work is the 4-dimethylamino-4'-nitrostilbene, which is planar and contains a dimethylamino group which delocalizes the electrons toward the ring system to an even greater extent than does the methoxy group.

Experimental

A Brice-Phoenix Differential Refractometer, Model BP-1000-V, was used in the experimental phases of refractive index studies. Primary application was in comparison of the refractive index differences between 4-methoxy-4′-nitrostilbene and its α-methyl analogue. Each isomer was measured against the solvent, chloroform, in five different concentrations and against its complementary isomer at each concentration. Graphs of the latter set of data showed a strikingly linear relationship between refractive index difference between isomer solutions (Δn) and molar concentration. The steeper slope of the curve for the 4-methoxy-4′-nitrostilbene (Figs. 1 and 2) gave evidence for its predictably greater Δn.

From the data obtained by measuring solutions of each isomer against chloroform, absolute refractive index values for each were calculated and plotted against molar concentration to provide further illustration (Figs. 3 and 4) of the greater Δn for 4-methoxy-4′-nitrostilbene. Figure 5 shows the values we have estimated for Δn versus molar concentration for 4-dimethylamino-4′-nitrostilbene. These values were estimated on the basis of the known electronic effects of the substituent dimethylamino group as compared to methoxy. Such linear relationships were extrapolated to illustrate potential Δn for a 50% (5.85 M) solution for the 4-methoxy-4′-nitrostilbene in a matrix. Assuming that 1) such extrapolation is valid, 2) the quantum yield (events/photon absorbed) for trans to cis conversion is 0.5, and 3) the system can be fabricated so that 1/3 of the writing light is absorbed in producing a hologram of a given thickness, a series of calculations outlined below predicted a Δn_{max} of 0.15 and that 1.0×10^{-3} J/mm^2 of blue light would be required to write a 1% efficient hologram.

The index of refraction change required to produce a hologram with a 1% diffractive efficiency is determined from the expression

$$\eta = T \sin^2 \left(\frac{\pi \, \Delta n \, t_o}{2 \, \lambda \, \cos \theta} \right)$$

where   T is the transmission (2/3),

η is the diffraction efficiency, taken as 1%,

t_o is the hologram thickness, taken as 1 mm.

FIGURE 1.   REFRACTIVE-INDEX DIFFERENCE
AS A FUNCTION OF MOLAR CONCENTRATION
OF cis AND trans ISOMERS OF 4-METHOXY-4'-
NITRO-α-METHYLSTILBENE IN CHLOROFORM
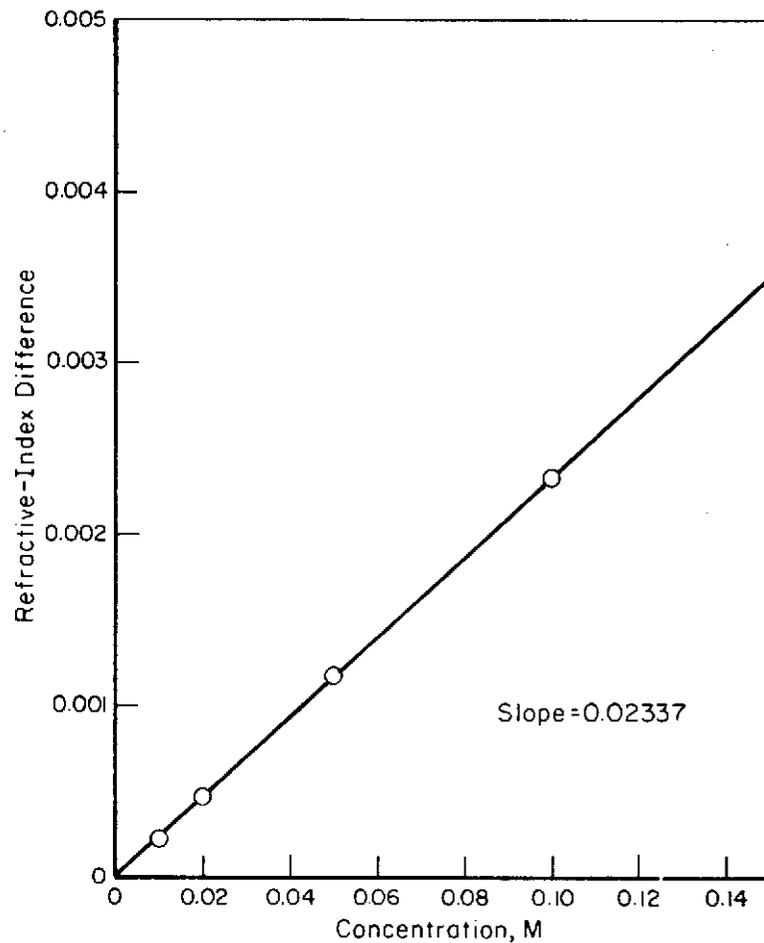
FIGURE 2.   REFRACTIVE-INDEX DIFFERENCE AS
A FUNCTION OF MOLAR CONCENTRATION OF cis
AND trans ISOMERS OF 4-METHOXY-4'-
NITROSTILBENE IN CHLOROFORM
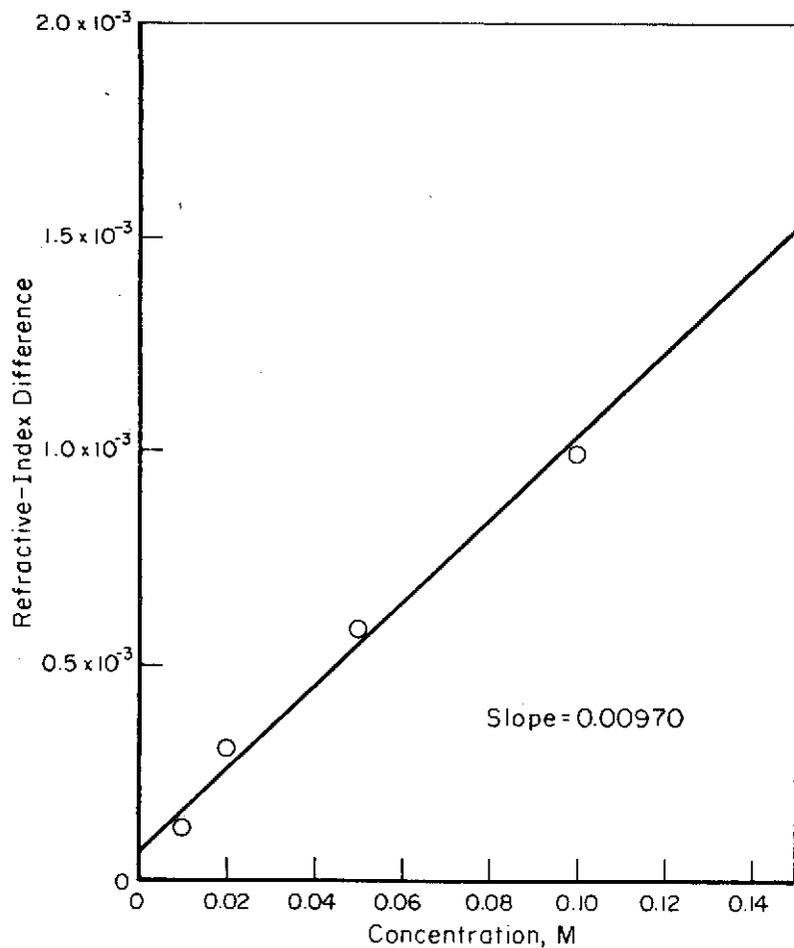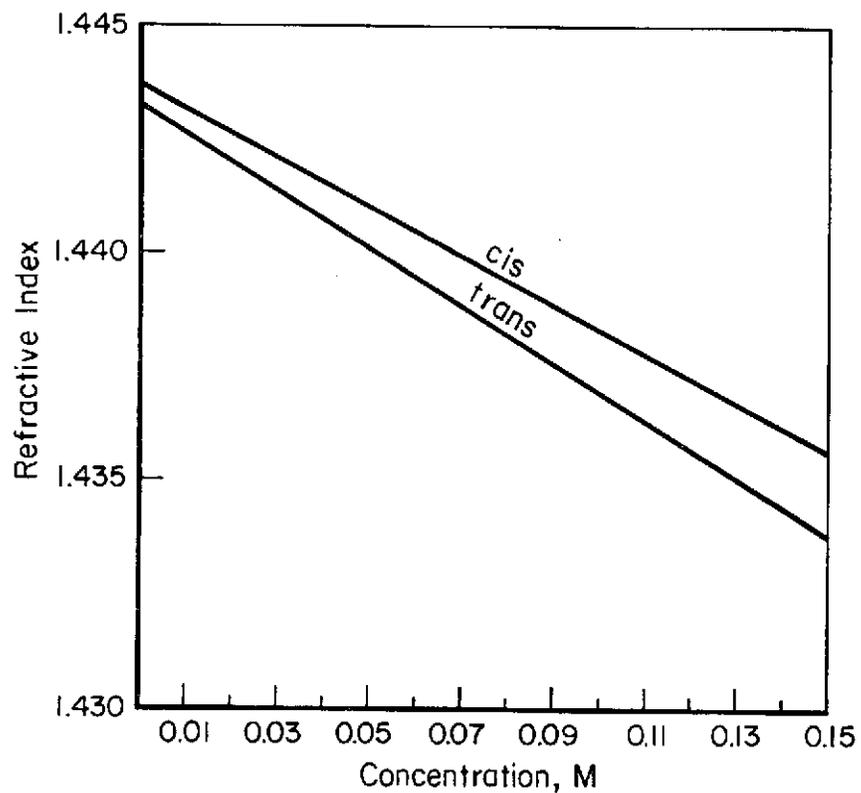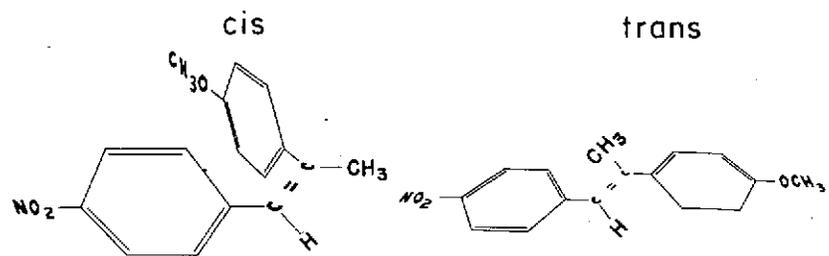
FIGURE 3. REFRACTIVE INDEX AS A FUNC-
TION OF CONCENTRATION OF cis AND trans
ISOMERS OF 4-METHOXY-4'-NITRO-α-
METHYLSTILBENE
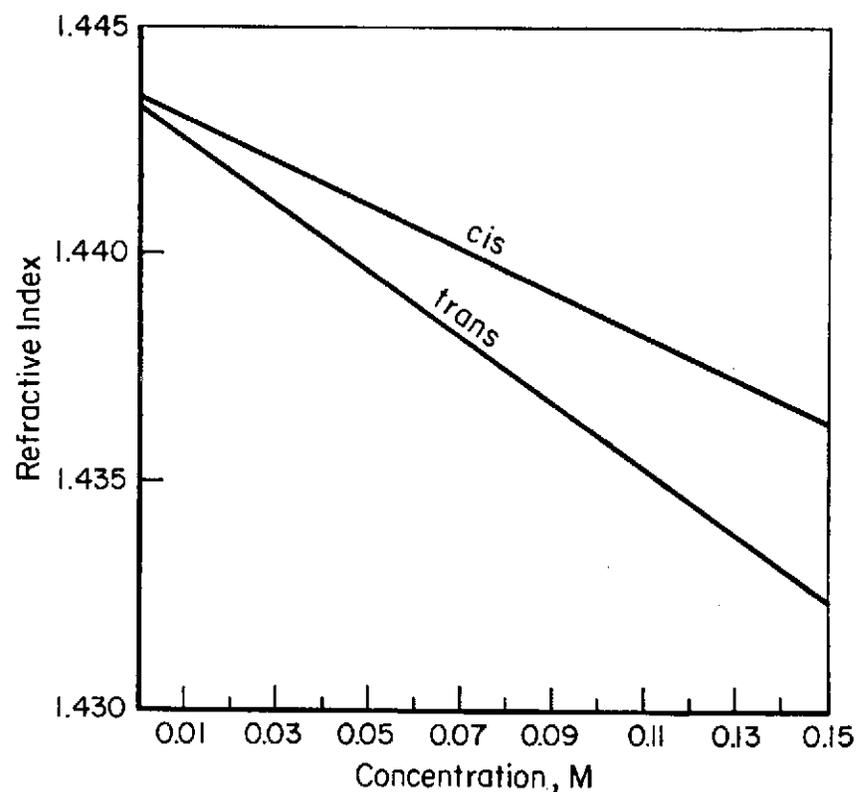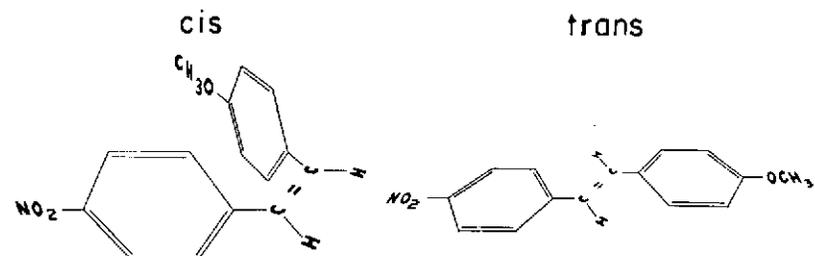
FIGURE 4. REFRACTIVE INDEX AS A FUNCTION OF
CONCENTRATION OF cis AND trans ISOMERS OF 4-
METHOXY-4'-NITROSTILBENE

8
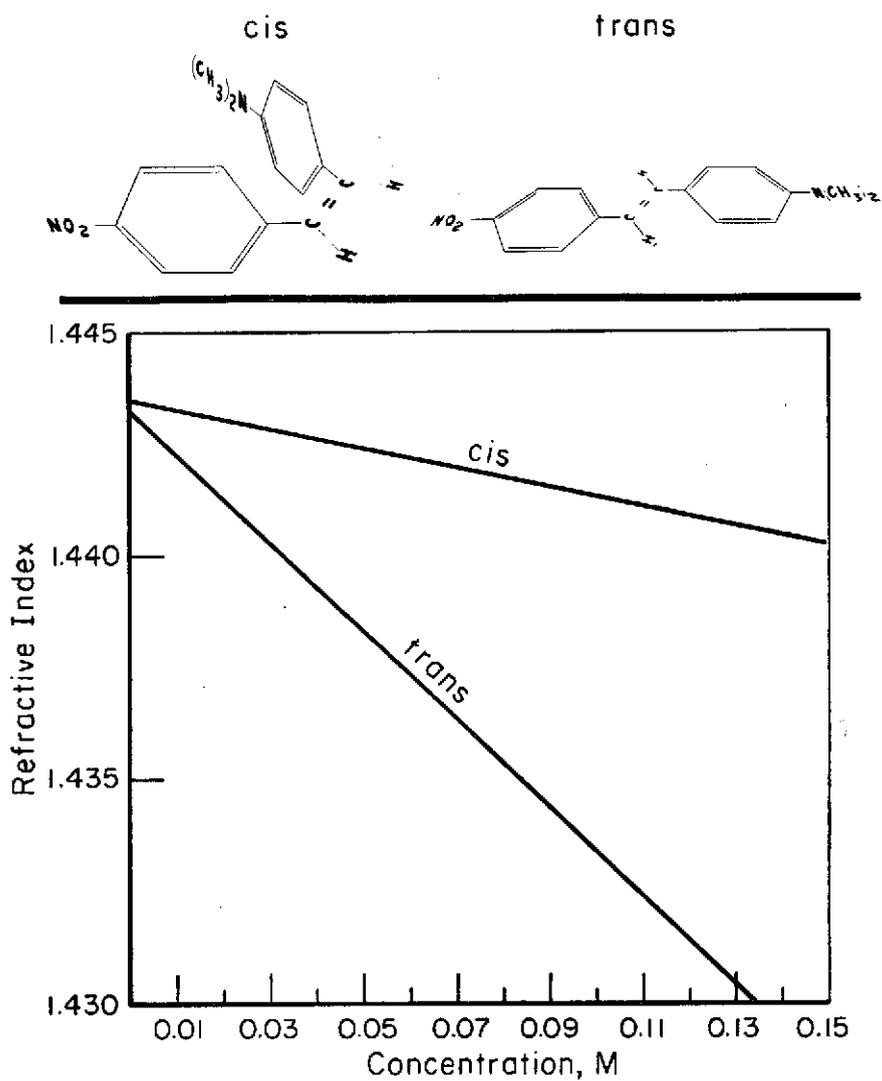
FIGURE 5. ESTIMATED REFRACTIVE INDEX AS A FUNCTION OF
CONCENTRATION OF cis AND trans ISOMERS OF 4-
DIMETHYLAMINO-4'-NITROSTILBENE

λ = 0.5 μm is the assumed wavelength of the read beam, and θ is half the angle between the write beam and the reference beam; we assume θ = 30°.

The required index change is

$$\Delta n = \frac{2\lambda \cos \theta}{\pi\ t_0}\ \sin^{-1}\ (\eta T^{-1})^{1/2}$$

$$= 3.39 \times 10^{-5}$$

From Figure 2, it can be shown that to effect this index change in 4-methoxy-4'-nitrostilbene requires that 1.45 x 10^{-9} moles/mm^3 of the material be switched. The number of molecules which have to undergo the <u>cis</u> to <u>trans</u>-conversion to achieve the required index change is

$$N_m = 6.02 \times 10^{23}\ \text{molecules/mole} \times 1.45 \times 10^{-9}\ \text{moles/mm}^3\ ,$$

or $\qquad N_m = 8.72 \times 10^{14}\ \text{molecules/mm}^3\ ,$

for a 1 mm^3 hologram recording volume.

Assuming a quantum yield of 0.5, allowing for absorption of only 1/3 of the light, and noting that molecules in only one-half of the volume are isomerized in forming a typical hologram, it can readily be seen that

$$2 \times 3 \times 1/2 \times N_m\ \text{photons} \times 3.97 \times 10^{-19}\ \text{J/photon}$$

must be incident on the one square millimeter front face, or an energy density (both beams) of 1.0 x 10^{-3} J/mm^2. The factor of three improvement in refractive index change per molecule predicted for 4-dimethylamino-4'-nitrostilbene would reduce this to about 3.5 x 10^{-4} J/mm^2 as shown in Table 1.

Because of the consistently linear relationships obtained between Δn and molar concentration, it was speculated that refractive index might be a valuable method for quantifying isomeric ratios.

TABLE 1

MATERIALS COMPARISON FOR HOLOGRAPHIC RECORDING

Materials	Δn_{max}	Energy Density to Write 1% Efficient Hologram (J/mm^2)	Bit Density** $(Bits/mm^2)$
4-methoxy-4'nitro-α-methylstilbene	5×10^{-2}*	2.4×10^{-3}	10^6
4-methoxy-4'-nitrostilbene	1.5×10^{-1}*	1.0×10^{-3}	10^6
4-dimethylamino-4'-nitrostilbene	5×10^{-1}*†	3.5×10^{-4}	10^6
Typical doped lithium niobate	1.25×10^{-3}	8×10^{-4}	6×10^{4}***

  * For 50% loading in matrix
 ** Assuming a maximum of 100 holograms per recording site, a 1% diffraction efficiency per hologram and a 10^4 bit page composer.
*** Presently insufficient for multiple hologram recording
 † Estimated value

A linear reference curve was obtained from standard mixtures of the two isomers, but repeated trials to test the data yielded parallel lines lying above and below the original. No explanation was found for such shifts and the method was abandoned as unreliable for that purpose. These observations did lead to a checking of Δn values previously obtained. Slopes remained the same, yielding the same overall Δn figures.

Photochemical Studies

Theoretical

Several photochemical parameters are particularly important for maximizing the efficiency of the holographic recording system. These include high and consistent percentage of conversion, freedom from side reactions, ease of recyclability and a distinct separation of wavelengths for the trans→ cis and cis→ trans isomerizations. In addition, the whole system must be tailored to specific, available laser wavelengths.

The potential of a compound to absorb light and isomerize efficiently at a given wavelength is, of course, a function of the electronic energetics of the compound itself. Extensive conjugation, for example, increases absorbance and gives a maximum absorbance at longer wavelengths than less conjugated systems. Addition of substituents to the parent molecule which interact with the π-electron system also tends to shift absorbance maxima to longer wavelengths.

Side reactions with trace contaminants or normally inert solvents are a principal problem with the electronically excited states of molecules in a photochemical system. This necessitates thorough consideration of all possible chemical reactions of the system.

Sensitizers are the primary means of controlling a reaction to insure consistent isomer ratios upon conversion and to adapt the system to different wavelengths. Photochemical sensitization is dependent upon the principle that molecules of certain organic compounds can be excited to their triplet energy states by photons of a specific energy (light wavelength) range.

Energy from this excited electron state can then be transferred to molecules
of another compound which has a lower triplet energy state. Therefore, a
sensitizer can be selected, using tabulated data in existing literature,
which will absorb light efficiently in a range including the wavelength of
the laser with which one wants to work. Consideration of the triplet energies
of the two isomers can allow selection of a sensitizer combination which will
give the desired trans → cis conversion of the stilbene at one wavelength
and cis → trans at another, even when the stilbene might not absorb well at
either wavelength. A major advantage of sensitized systems is the obser-
vation that at the photostationary state (the stable state reached by a
photochemical system after prolonged irradiation at a specific wavelength)
the ratio of cis to trans isomers depends on the sensitizer employed. While
a stilbene isomer might absorb well at one laser wavelength and theoretically
require no sensitization, the use of a particular sensitizer will allow
better control of the steady state cis-trans ratio.

Thus, photochemistry introduces a new set of considerations for
the selection of an appropriate stilbene; it must have the capability either
of absorbing strongly at a given wavelength or of being sensitized to react
there. Several wavelengths which will be readily available for our study
are 351.0 nm, 488.0 nm, 514.5 nm, 632.8 nm, and 647.1 nm.

Sensitization studies of the 4-methoxy-4'-nitrostilbene system
are still in the theoretical stages and are discussed here as such. A
major disavantage of the system now being studied is its unsensitized absor-
bance at wavelengths below those of most useful lasers. There is also a
small, 10 nm, span between absorbance maxima of the two isomers. trans → cis
Photoisomerization will occur at 350 nm with a low-powered laser beam.
Spectral analyses for triplet energies of the isomers of 4-methoxy-4'-nitro-
stilbene are not complete, but benzophenone, a classic sensitizer for stilbene
work, absorbs well near 350 nm, transfers energy efficiently and will be a
strong choice once conditions are optimized for the unsensitized system.
The next conveniently obtained laser wavelength at the long end of the absorption
spectrum for this stilbene is 488 nm. Potential sensitizers in this range
might be acridine orange and tetracene. The same sensitizer combination
would be even more efficient with the proposed 4-dimethylamino-4'-nitrostilbene

system since that stilbene absorbs weakly at the two suggested wavelengths (Fig. 6).

Experimental

Photochemical experimentation began with initial attempts to prepare quantities of the cis-isomers for study. Wavelengths of ultra-violet absorbance maxima of the trans-isomers were used to predict suitable wavelengths for irradiation. While the efficiency of the system was not great (20% yield of the cis-isomer as discussed under "Preparation and Isolation of Pure cis-Isomers"), quantities obtained were sufficient and a greater emphasis on purity than on quantity limited further development work in the photochemical reaction at this point.

Irradiation of a 0.1 M solution of 4-methoxy-4'-nitrostilbene in benzene at 350.7 nm using a low powered (8.0-17.5 mW) krypton laser was performed in a cuvette equipped for stirring and degassing by constant bubbling with nitrogen. Exposure for five hours gave qualitative (thin layer chromatographic) evidence of conversion but the small amount of cis-isomer could not be isolated. Additional irradiation for longer time periods yielded qualitative evidence of greater conversion. Subsequent photochemical experimentation was performed with consideration being given to the matrix system, as discussed next.

Matrix Studies

Theoretical

The occurrence of photoisomerization in stilbene solutions being established, adaptations of the reaction for holography require methods of restricting diffusion of the stilbene molecules. A matrix system designed to allow recording of a reproducible image must be rigid and transparent with the capacity for restricting the stilbene migration while allowing solvation of the compound and enough internal space or flexibility for the geometric change occuring in the isomerization process. Various concepts have been considered for the matrix, including
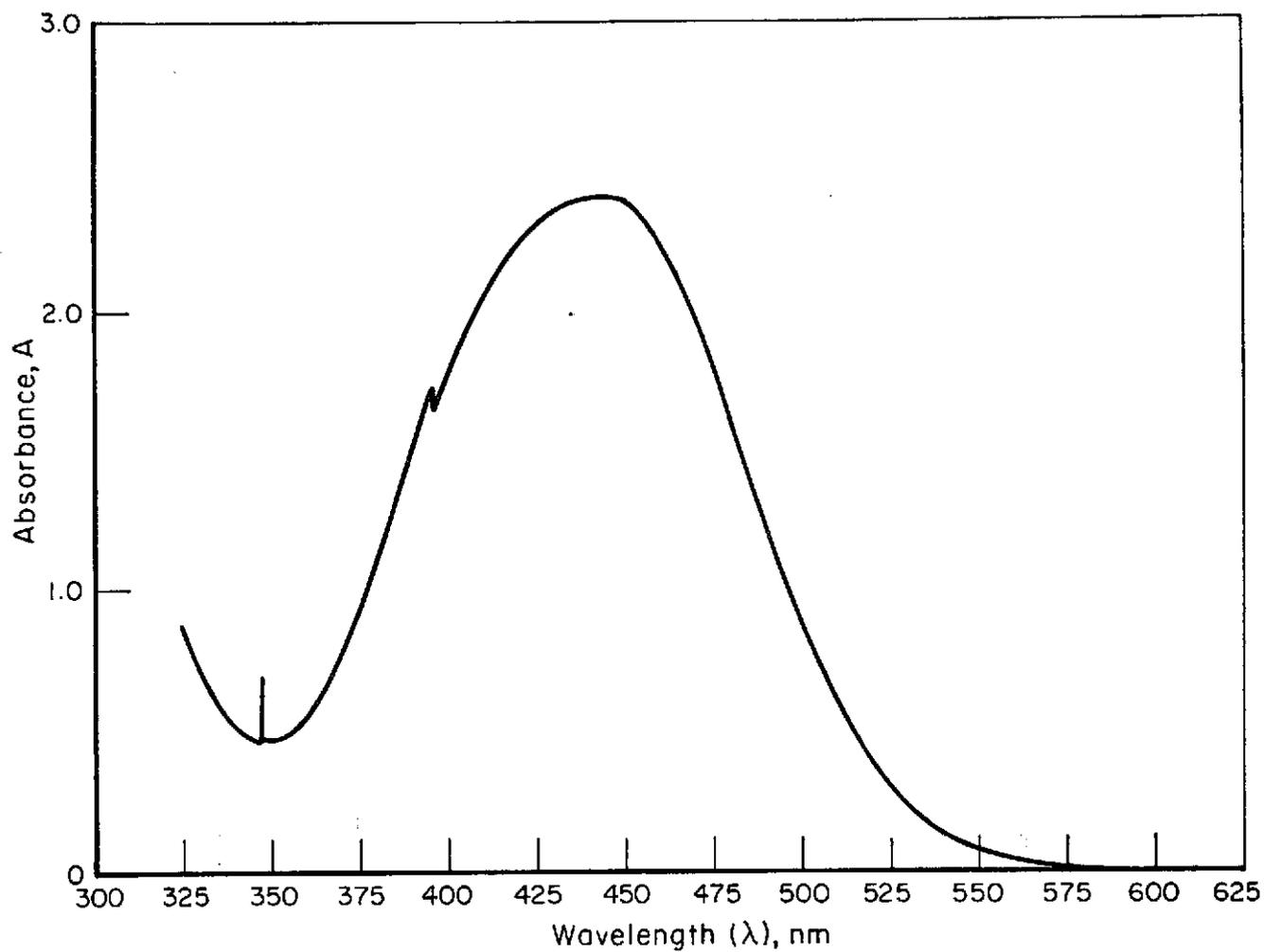
FIGURE 6. ABSORBANCE SPECTRUM OF trans-4-DIMETHYLAMINO-4'-
NITROSTILBENE

1.0×10^{-4} M in chloroform, recorded at 1.0 nm/sec

o Glass plate laminates

o Gels

o Microencapsulation

o Microvoids

o Bulk polymers

o Polymer-stilbene molecular engineering.

Glass plates. The simplest concept would be use of two glass plates containing a film of stilbene solution. The glass would provide the structural integrity and confine the liquid. However, diffusion of the stilbene in the solution would still be a problem and a thicker layer is required than could be obtained in this way. The diffusion might be limited, however, by using a high viscosity solution or even a gel.

Gels. A high viscosity solution would retard the diffusion of an image, but a better method would be to prevent the migration by using a gelled matrix. The gel is a three-dimensional solvent-swelled system. A gel traps the solvent preventing it from migrating. If the gel structure is strong enough and the solvent "cells" (the solvent trapped areas between the gel structure) are tight enough, then the stilbene will be trapped in these cells and its diffusion will be restricted.

Such a system could easily provide the desired resolution of 10^3 lines/mm since the entire molecular diameter (and therefore intramolecular space) of the high-molecular-weight polymers being considered falls well within the five micron dimension necessary.

Many gel systems occur in nature but are water based. In the context of stilbene and its photo-induced isomerization, water-based systems cannot be used until a modified stilbene has been produced. Studies of the properties of salts of 4,4'-dinitrostilbene-2,2'-disulfonic acid, water-soluble compounds, are in progress.

Several techniques can be utilized to provide a non-aqueous gelled system. A gel can be made from a synthetic polymer by taking a long chain polymer and lightly crosslinking it. Ideally the polymer would be dissolved in a solvent containing stilbene and then crosslinked; however, the cross-linking is a chemical reaction and would probably cause chemical change in the

stilbene which may not be tolerable. Another method for producing the gel would be to lightly crosslink the polymer and swell it to its maximum extent in a solvent containing the stilbene. Some of the solvent can then be pumped off, trapping the solvent and stilbene in the polymer.

Microencapsulation or Microvoids. Microencapsulation is the generation of small spheres which could be used to confine the stilbene solution by a rigid capsule wall. This method is ideal for providing a stable, nonmigrating system. However, the wall material and the matrix material must be matched so as not to interfere with the optical response. The microvoid is a matrix containing finite voids, like a foam, which are filled with the stilbene solution. Again the system must be designed to provide good optical properties.

Polymers. A solid, long-chain polymer would provide an ideal matrix material for the stilbene and sensitizers allowing intermolecular spaces for the geometric conversion of the stilbene and for the interaction of stilbene and sensitizer. The polymer could then be shaped into any desired shape, a film for instance. The greatest difficulty in this concept is the prevention of the planar stilbene molecule from associating with the polymer chain. This association can prevent optical isomerization by sterically hindering the stilbene aromatic ring movement or by the transfer of energy, via optical absorption, to the polymer without causing the isomer change.

Polymer Molecular Engineering. The surest way of limiting the stilbene migration and preventing strong interaction with the polymer is through polymer molecular engineering in which stilbene molecules are chemically bonded onto a polymer chain. The bonding would be through a chemical reaction at a site on the stilbene which did not influence its efficiency for photoisomerization. An example of such a reaction has been reported by some Czechoslovak chemists[1]. This system has the obvious advantage of being single-phase, nonsolvent-based and self-contained. A polymer could be formed into any shape without the threat of loss of integrity, evaporation of solvent or migration of the image. However, such a system would require considerable development before it would be ready for use in the optical memory.

Experimental

The first matrix materials considered were solids, primarily
medium to high molecular weight polymers. The limited success obtained with
photoisomerization of stilbenes in these compounds led to a brief investi-
gation of irradiation of stilbenes in viscous solvents. Studies of polymeric
gel matrices followed and the successful isomeric conversion observed in
these systems is now being optimized. Results of current studies are expected
to be applied in two areas, establishing conditions for successful photo-
isomerization in a solid matrix and molecular engineering of a polymer
containing bonded stilbene groups.

Solids. Several polymers were selected on the basis of inter-
molecular spaces and possible structural flexibility for use as the solid
matrix into which to put the stilbene; however, only a few exhibited
satisfactory transparency and solvating capabilities. A methylmethacrylate/
styrene/alkyd terpolymer reacted with melamine formaldehyde (83:17 ratio in
solids) in the presence of the p-toluene sulfonic acid was investigated most
thoroughly. Films of the polymers were spread on glass slides. Qualitative
analysis was performed by dissolving films in a 1:1 solution of methylethylke-
tone and toluene and spotting the solutions on thin layer chromatographic
(TLC) plates eluted with a 1:1 ether/hexane solution. Initial irradiation
studies with trans-4-methoxy-4$'$-nitrostilbene (0.1% by weight in polymer)
gave evidence of extensive isomerization with and without irradiation. This
reaction was determined to be resulting from simple acid catalysis and sub-
sequent samples of the polymer were made without the acid catalyst.

Timed studies of the dark reaction of the trans-isomer in the non-
catalyzed polymer showed slight conversion to the cis-isomer, a stable state
being reached within one hour. Irradiation with a krypton laser (λ=350.7 nm)
produced little detectable isomerization though the small diameter of the beam
made any isomerization difficult to detect by thin layer chromatography of a
solution of the irradiated area of polymer in solvent. Use of a PEK short arc
lamp filtered to exclude wavelengths shorter than 305 nm produced substan-
tial stilbene degradation as detected by ultraviolet spectroscopy and thin layer
chromatographic methods (Fig. 7). This was probably due to photo-induced
chemical reactions involving oxygen incorporated in the polymer upon curing.
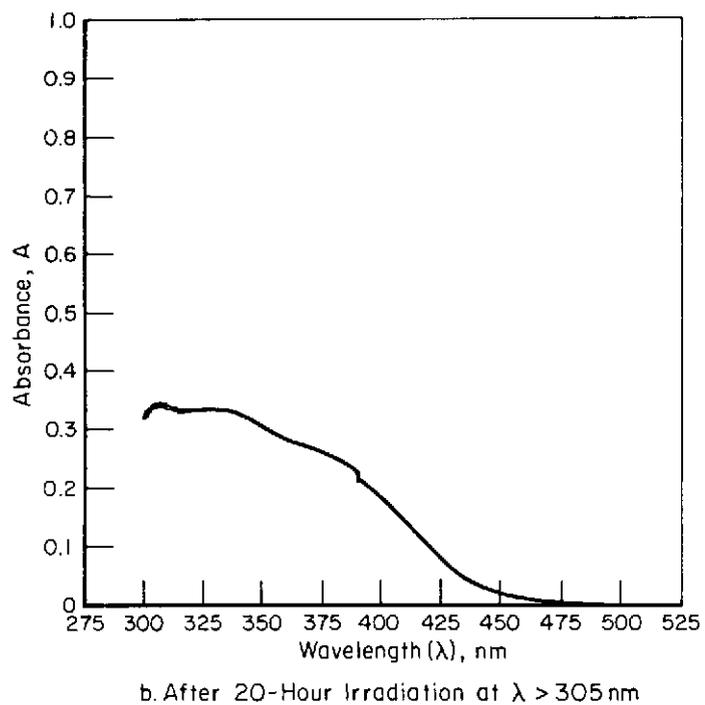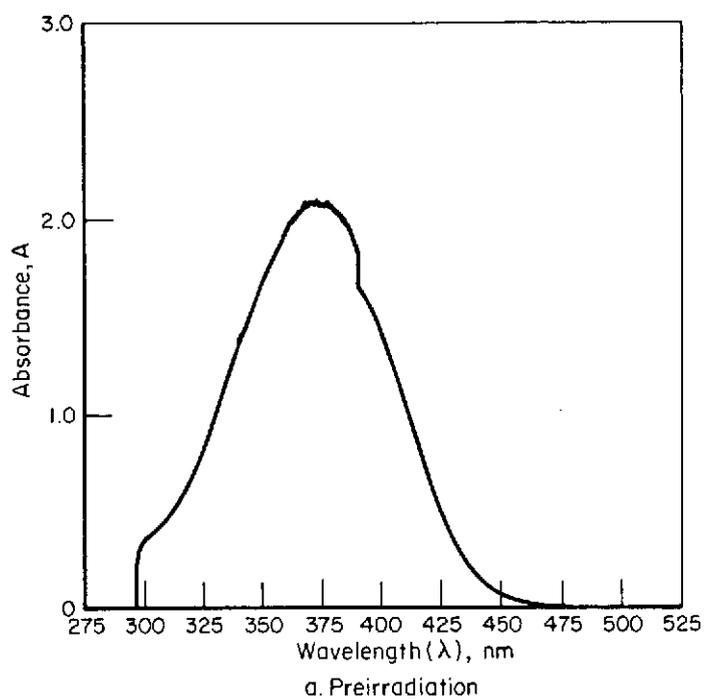
a. Preirradiation

b. After 20-Hour Irradiation at $\lambda > 305\,nm$

FIGURE 7. ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-NITROSTILBENE IN SOLID ALKYD TERPOLYMER MATRIX

1.0×10^{-4} M, recorded at 0.5 nm/sec

Argon degassing prevented curing of the polymer. In an effort to determine whether the side reactions were due primarily to the solvent or polymer, attempts were made to identify side reaction products by infrared spectroscopy. These were abandoned because the complex spectrum of the polymer obscured that of the stilbene and no method had been developed for separating the stilbene from the polymer. Solvent or matrix impurities are other likely causes for such degradation, particularly in the lower concentrations of stilbenes in films employed as solids for ultraviolet spectral analysis.

A series of high molecular weight acrylics, identified as acryloid B-66, B-44, and A-101, also had suitable transparency and solvating characteristics. Irradiation of stilbenes in these polymers produced a darkening of the exposed area and evidence by thin layer chromatography of degradation without conversion.

Other solid polymers considered were BASF Wyandotte urethane latex 1023 and Vistanex LM/MH (low molecular weight polyisobutylene rubber). The former was extremely cloudy and required a water-soluble stilbene (sodium salt of 4,4'-dinitrostilbene-2,2'-disulfonic acid was used) with which little photochemical work had been done. The second would solvate only trans-stilbene and remained too sticky to handle conveniently.

An attempt was also made to cocrystallize the trans-4-methoxy-4'-nitrostilbene with adamantane, an organic solid which has large spaces in its well-ordered crystal lattice. This was primarily aimed at investigating the potential of the stilbene to isomerize without a solvent, a valuable property for both solid matrix studies and polymer-stilbene molecular engineering. Infrared spectra gave evidence of cocrystallization, but irradiation of the crystals yielded no cis-isomer.
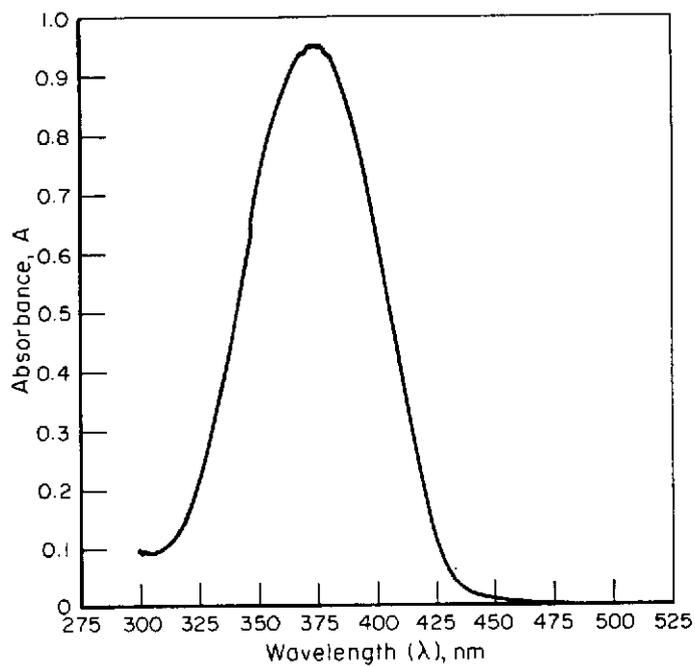
Viscous Solvents. Before proceeding with solids, new studies were begun to determine optimal conditions for photoisomerization in systems closer to liquid. Samples of the trans-4-methoxy-4'-nitrostilbene were dissolved separately in heated glycerin (viscosity 1,490 cp) and ethylene glycol (viscosity 19.9 cp). Solutions were degassed with argon and irradiated 20 hours.

Some conversion was noted in the ethylene glycol by thin layer chromato-graphy (1:1 ether/hexane elution) but not in glycerin. The poor success of these studies resulted in decisions to perform optimization studies in low viscosity solvents. Organic polymer gels, which can provide spaces filled with solvents such as benzene, were thought to be promising materials.

Polymeric Gels. A relative abundance of water-soluble gels encouraged more photochemical work with the sodium salt of 4,4'-dinitrostil-bene-2,2'-disulfonic   acid, but the most constructive study, in terms of developing a workable system, was performed with organic gels of polyiso-butylene (Vistanex MM/L-120 and L-140) in toluene and benzene. Toluene gels were soon disregarded as irradiation even in pure toluene produced substantial stilbene degradation (Figs. 8 & 9). This was attributed to photochemical reduction of the nitro group in the presence of toluene methyl group leading to low-molecular-weight polymerization of the stilbene. Subsequent work with benzene also indicated that the observed degradation might result from or be increased by impurities in the toluene.

The most concentrated effort to increase photoisomerization efficiency began with the development of a polyisobutylene/benzene gel matrix for the 4-methoxy-4'-nitrostilbene holographic system. At a concentration of 1.0×10^{-4} M, chosen for detectability by ultraviolet spectroscopy, degradation of the stilbene was extensive, both in the gel and in benzene alone (Figs. 10 & 11). Degassing benzene with argon and preparing the gel under argon decreased this effect, but only slightly at low concentrations. Further trials established 1.0×10^{-2} M as a minimal concentration for clean conversion (Fig. 12). A simple cell was designed using two glass microscope slides separated by a 1 mm thick aluminum spacer and clamped with spring clips. In the first attempt to write a hologram using a low powered laser at $\lambda = 350.7$ nm with this system, all light was absorbed by the stilbene, thus preventing read out of any hologram formed.

Parameters for the system were then reconsidered and fixed at: 1) maximum absorbance (A) of one third of the light, 2) maximum pathlength (ℓ) of 0.0274 cm (the thickness of available teflon sheet for spacer), and 3) extinction coefficient (ϵ) of the stilbene from UV spectral data of 2.07×10^4 at 350.7 nm. Using Beer's law for the absorbance,

a. Preirradiation

b. After ½-Hour Irradiation at λ > 305 nm

FIGURE 8.   ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-
NITROSTILBENE IN VISTANEX MM/ L-120/ TOLUENE
CELL

1.0×10^{-4} M recorded at 1.0 nm/ sec
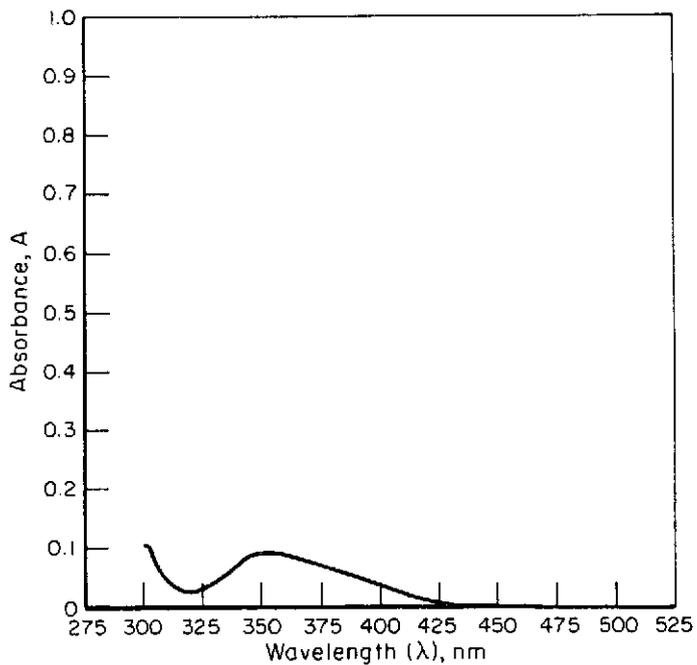
a. Preirradiation

b. After $1\frac{1}{2}$-Hour Irradiation at $\lambda > 305$ nm
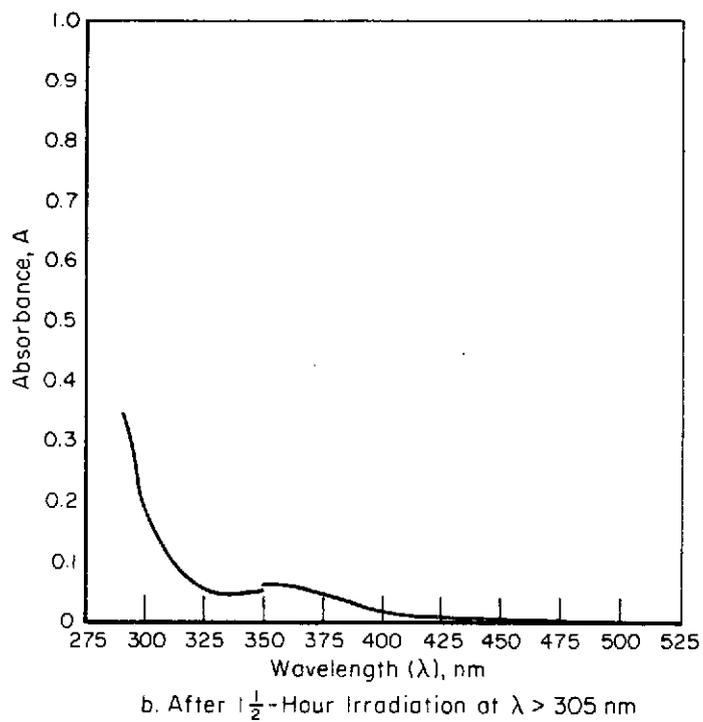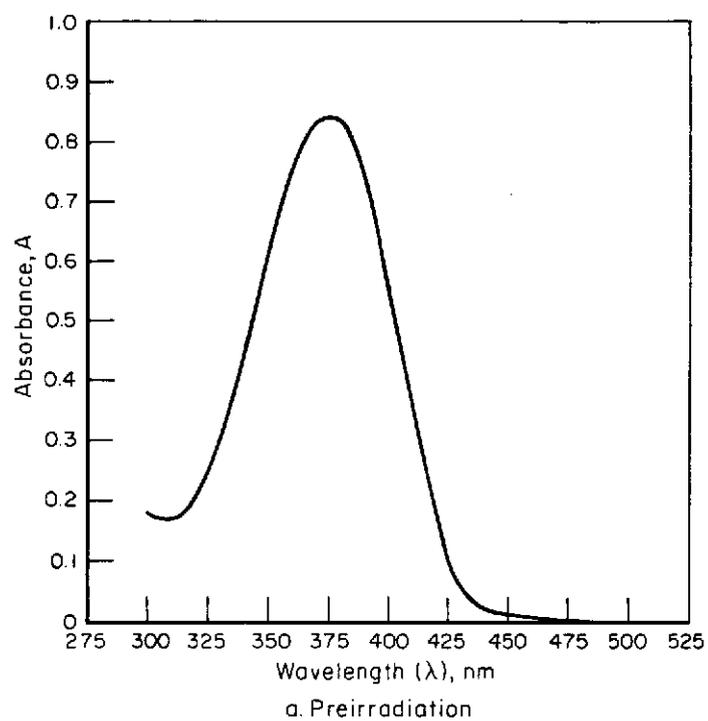
FIGURE 9.   ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-NITROSTILBENE IN TOLUENE

3.0×10^{-5} M,   recorded at 1.0 nm/sec

a. Preirradiation

b. After 1-Hour Irradiation at λ > 305 nm
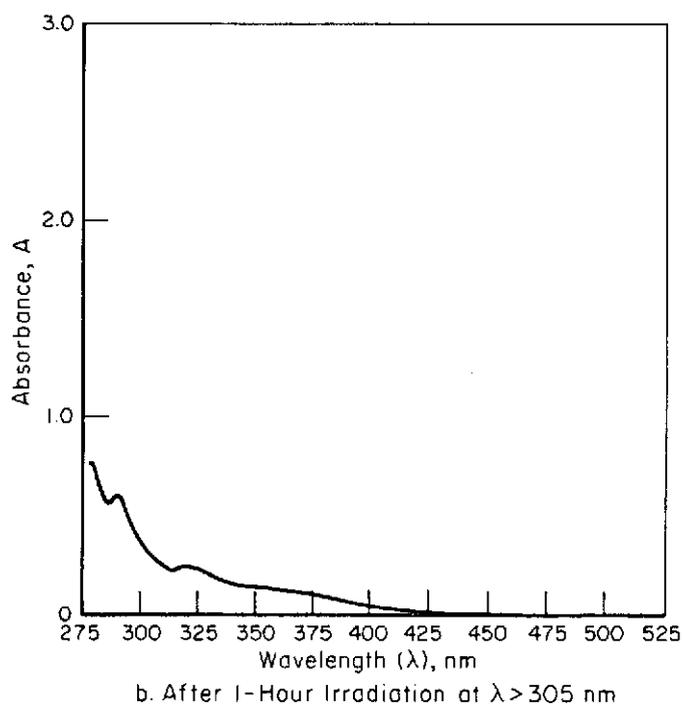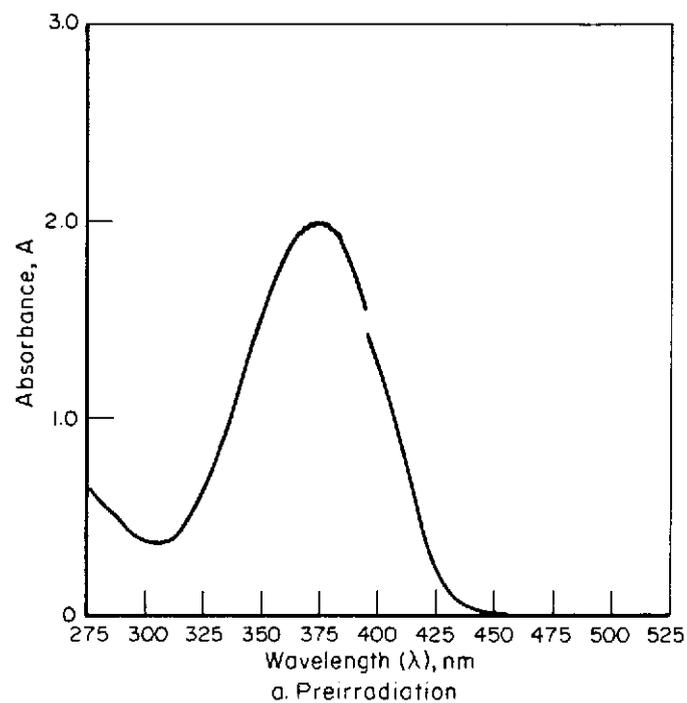
FIGURE 10. ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-NITROSTILBENE IN VISTANEX MM/L-120 BENZENE GEL

1.0×10^{-4} M, recorded at 1.0 nm/sec

a. Preirradiation

b. After 1-Hour Irradiation at λ>305 nm

c. After 3-Hour Irradiation at λ > 305 nm

FIGURE 11. ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-NITROSTILBENE IN BENZENE DEGASSED WITH ARGON

1.0×10^{-4} M, recorded at 1.0 nm/sec

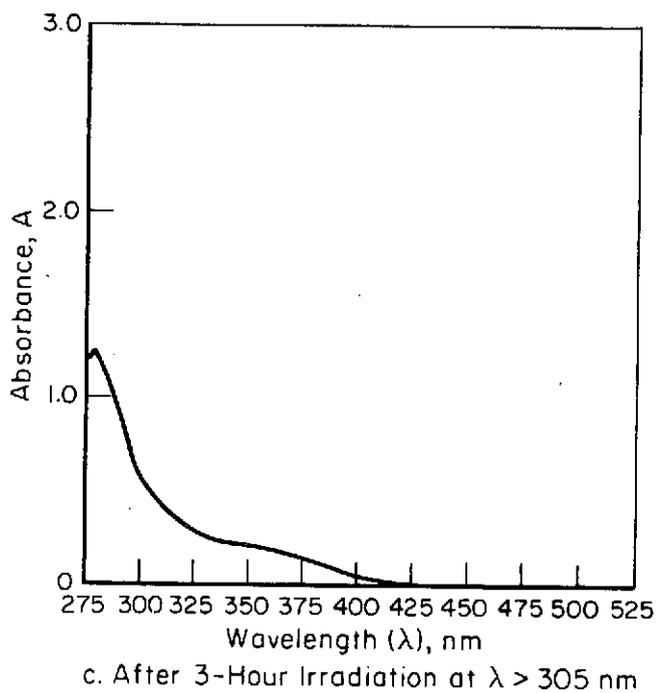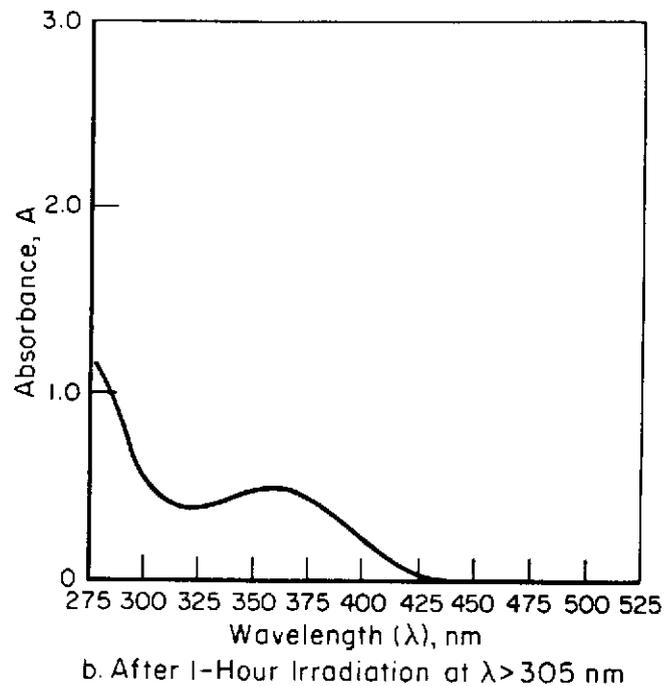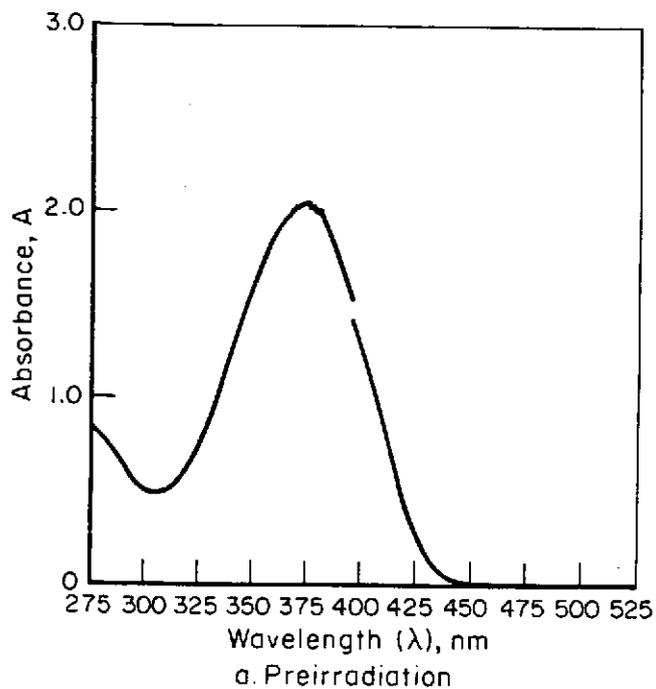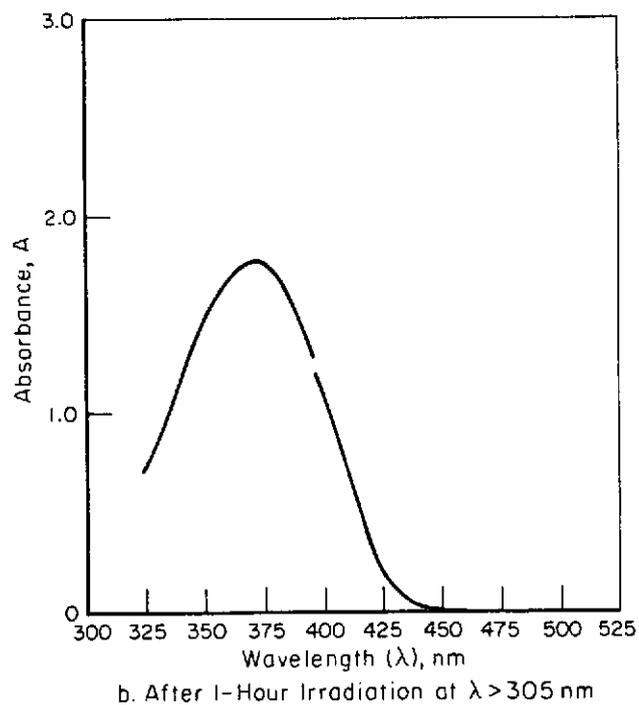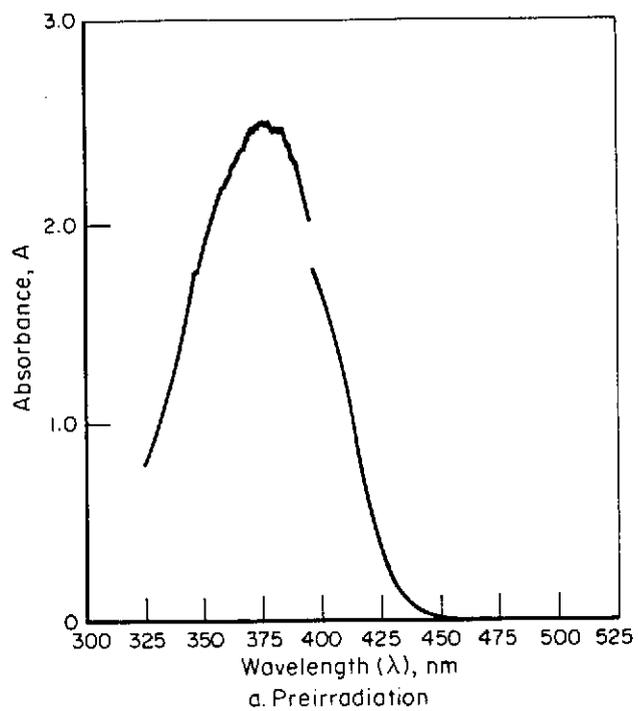FIGURE 12. ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-NITROSTILBENE IN BENZENE, DEGASSED WITH ARGON

1.0×10^{-2} M diluted to 1.0×10^{-4} M for analysis, recorded at 1.0 nm/sec

$$A = \log \frac{I_o}{I} = \epsilon \ell c \quad ,$$

where I_o is the radiant power of the incident beam (light in) and I is the radiant power of the transmitted beam (light out), the necessary concentration is 3.1×10^{-4}M. A trial irradiation in benzene under these conditions resulted in the stilbene degradation at concentrations below 10^{-2}M.

Benzene Purification Concentration dependence of the degradation side reaction indicated possible involvement of some impurity in the Burdick and Jackson distilled-in-glass benzene. A 500 ml sample was purified by photo-chlorination[2] in an Ace Glass photochemical reactor fitted with a Friedrich condenser, water-jacketed 450 watt medium pressure Hanovia mercury lamp and a fritted glass tube for chlorine admission. Chlorine was bubbled through the magnetically stirred solvent during a brief irradiation period. Any impurities which would tend to react photochemically with stilbene or polymer would react with the chlorine to produce filterable solids. The benzene was washed with base and water, dried over Drierite, filtered through neutral alumina and re-fluxed before distilling. This product was used to make a gel in which 90% conversion to the cis-isomer was noted in a 1.0×10^{-4}M solution after one hour irradiation at wavelengths greater than 305 nm (Figs. 13 & 14). Thus impurities were not only reacting to reduce the amount of stilbene available for isomerization, but were also limiting the extent of conversion, probably by promoting the reverse isomerization. Obviously, the clean benzene system is very reactive and care will need to be taken in handling to avoid exposure to stray light prior to laser irradiation.
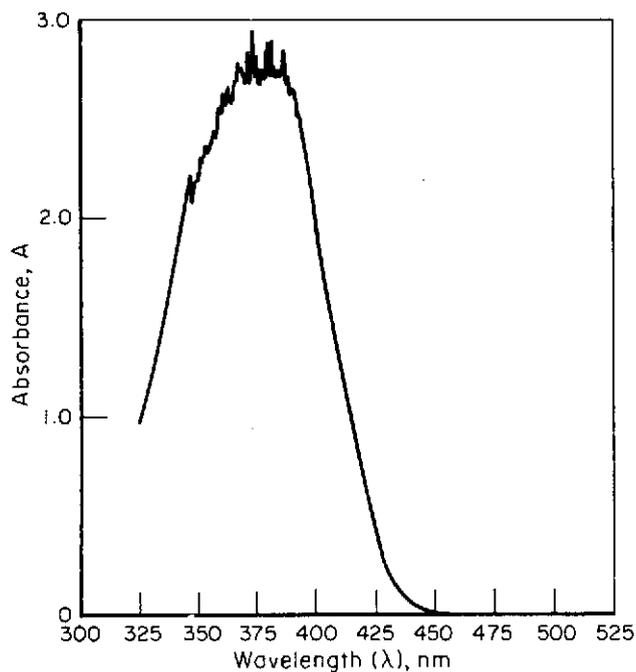
FIGURE 13.   ABSORBANCE SPECTRUM OF trans-4-METHOXY-
4'-NITROSTILBENE IN BENZENE PURIFIED BY
PHOTOCHLORINATION, DEGASSED WITH ARGON,
PREIRRADIATION

3.1 x 10^{-4} M diluted to 1.0 x 10^{-4} M for analysis,
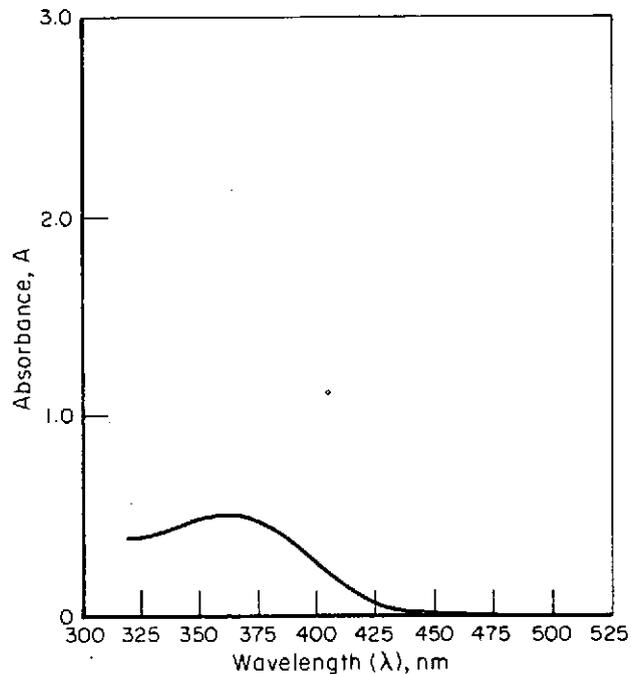recorded at 1.0 nm/sec

FIGURE 14.   ABSORBANCE SPECTRUM OF 4-METHOXY-4'-NITROSTILBENE
IN POLYISOBUTYLENE/PURIFIED BENZENE GEL,   PREPARED
UNDER ARGON,   AFTER 1-HOUR IRRADIATION AT λ>305 NM

3.1 x 10^{-4} M diluted to 1.0 x 10^{-4} M for analysis recorded at
1.0 nm/sec

Synthesis

To date, the following stilbenes have been prepared for evaluation.

1.   trans-4-Methoxy-4'-nitrostilbene. This compound was easily prepared following the method of Pfeiffer[3]. Nitrophenylacetic acid was reacted with 4-methoxybenzaldehyde in the presence of piperidine. This was heated with refluxing for one hour and recrystallized several times from hot acetic acid. Excess acid was removed by slurrying a chloroform solution of the stilbene with a weak aqueous sodium carbonate solution for several hours. Evaporation of the chloroform from the organic layer was followed by recrystallization from hot ethanol. Yield was 60%, melting point 130-132 C.

2.   cis and trans-4-Methoxy-4'-nitro-α-methylstilbene. The original synthetic work with this compound involved a Meerewein-diazonium coupling of p-methoxy-α-methylstyrene and p-nitroaniline. This long procedure gave, at best literature report, only 30% yield. Synthetic studies of this compound for this phase of the program, therefore, concerned alternate methods for obtaining the stilbene in higher yields.

The most promising method was a Wittig reaction described by Ketcham, Jambotkar and Martinelli[4]. Under very dry conditions, nitrophenylmethylenetriphenylphosphorane, a primary precursor, was prepared by reaction of nitrophenylchloromethyltriphenylphosphorane with sodium dimethylsulfonate (DMSO heated with sodium hydride) in benzene. This product was reacted with 4-methoxyacetophenone for 8 hours. Crude product was extracted from a bright orange solid with petroleum ether and recrystallized from hot ethanol. A 55% yield of the desired bright yellow product was verified by infrared spectroscopy. Efforts to scale up the synthesis were shelved when the superior refractive index properties of the more easily prepared 4-methoxy-4'-nitrostilbene became apparent. The cis/trans ratio of the product was not established.

3.   4,4'-Dinitrostilbene-2,2'-Disulfonic Acid. This material was obtained as a crude commercial sample from American Cyanamid Corporation and

recrystallized from hot aqueous ethanol with the use of decolorizing char-
coal. The resulting bright yellow salt was soluble in water to the extent
of 73% and had a melting point greater than 360 C.

4. <u>trans-4-Methoxystilbene</u>. This was prepared, primarily for
spectral reference, after the method of Orekhoff and Tiffeneau[5]. The
starting compound, 4-anisylbenzylcarbinol was prepared by Grignard reaction
of tolylmagnesium chloride (from α-chlorotoluene and magnesium) and 4-methoxy-
benzaldehyde. This was then dehydrated using sulfuric acid and the product
was recrystallized from hot ethyl acetate. The snow white crystals melted
at 134-135 C. Yield 60%.

Preparation and Isolation of Pure cis-Isomers

Since the synthesized compounds were predominantly the <u>trans-</u>
isomers, photochemical methods for producing the <u>cis</u>-isomers had to be
employed on a preparative scale.

The <u>cis</u>-isomer of 4-methoxy-4'-nitro stilbene was prepared by irra-
diating 500 ml of a 5.0×10^{-3}M solution of the <u>trans</u> isomer in benzene in an
Ace Glass photochemical reactor using a 450 watt medium pressure Hanovia
mercury lamp in a quartz glass shield ($\lambda > 360$ nm). The irradiated sample
was concentrated by vacuum. Isomers were separated by column chromato-
graphs on neutral alumina using ether/hexane (1:1) elution. Chilling of the
<u>cis</u>-eluate prior to solvent evaporation in vacuo gave bright yellow crystals
which did not require the difficult recrystallization from hot ethanol. This
method gave 20% yield of a product, 95% <u>cis</u>-isomer as verified by high pressure
liquid chromatography (HPLC). It is expected that yield of <u>cis</u>-isomer may
be increased by using a slightly basic alumina column to prevent acid-
catalyzed isomerization to the <u>trans</u> form.

Only chromatography separation on alumina followed by recrystal-
lization from hot ethanol was necessary to isolate a reasonable quantity of
the <u>cis</u>-isomer from the mixed isomeric product of the 4-methoxy-4'-nitro-
α-methylstilbene synthesis. Methods are still under development for the
isolation of the water-soluble irradiation products of 4,4'-dinitrostilbene-
2,2'-disulfonic acid by high pressure liquid chromatography methods.

Gel permeation chromatography has also been used to separate a mixture of stilbene isomers from polymeric matrix solutions and may be combined in a single system with high pressure liquid chromatography.

Analysis

Due to instrument breakdown, alternative methods to nuclear magnetic resonance spectroscopy (NMR) were investigated. While NMR was found most valuable in earlier work for verification of compound structure and isomeric content, several other analytical methods were found to be acceptable in providing not only reliable information pertaining to ratios of cis-trans-isomers in mixtures and to isomeric purity, but also in providing absorbance data which could be applied to many phases of the program. The three major techniques employed were ultraviolet and infrared spectrophotometry, and high pressure liquid chromatography (HPLC). Thin layer chromatography and refractive index were used as simple qualitative methods.

Ultraviolet Spectroscopy

A Beckman ACTA III spectrophotometer was most extensively used because of its ability to scan a large range of the spectrum to determine maximum absorbances of the compounds and individual isomers. Using reference spectra of pure cis and trans isomers (Figs. 15 & 16), and the fact that the absorbance (A) of a mixture of components absorbing in the same region is the summation of the absorbances of the contributing species, the composition of a mixture could be calculated.

Typical running conditions included chart scale 25 nm/in., absorbance span 0–3.0, sample concentration 1.0×10^{-4}M. Shifts in wavelength and height of absorbance peaks could indicate changes in isomer ratios and degradation due to side reactions. The obvious drawback to this method is the necessity of having pure samples for reference spectra. Absorbance values obtained, however, are extremely valuable in establishing parameters of the matrix system for the holographic process.

Infrared Spectroscopy

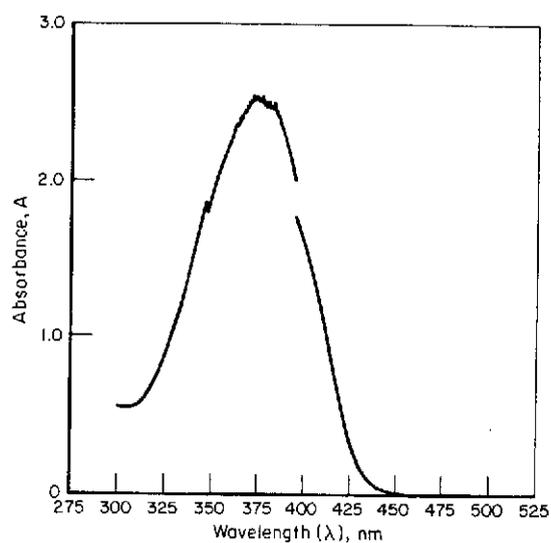A Perkin Elmer 521 grating infrared spectrophotometer was used for

FIGURE 15. ABSORBANCE SPECTRUM OF trans-4-METHOXY-4'-NITROSTILBENE IN VISTANEX NM/ L-120/ BENZENE GEL (1:9)

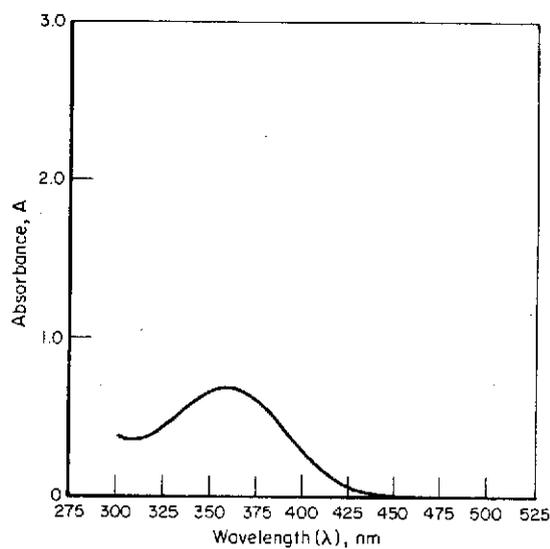trans Reference 1.0 x 10^{-4} M, recorded at 1.0 nm/sec

FIGURE 16. ABSORBANCE SPECTRUM OF cis-4-METHOXY-4'-NITROSTILBENE IN BENZENE

cis Reference 1.0 x 10^{-4} M, recorded at 1.0 nm/sec

identification and confirmation of synthetic and irradiation products. cis and trans impurities could be detected in samples prepared for ultraviolet spectral reference. The presence of side reaction products could also be verified.

High Pressure Liquid Chromatography

Varian's 4200 high pressure liquid chromatograph is being recognized as a valuable quantitative and qualitative tool. Impurities can be readily detected even in samples being used to establish quantitative curves. This is particularly valuable in compounds likely to degrade either thermally or photo-chemically. Quantitative work on mixed 4-methoxy-4'-nitrostilbene isomers has been satisfactorily reproducible (Figs. 17 and 18).

A major advantage is the necessity for pure reference samples of only one isomer. Small amounts of trans-isomer contamination in a cis-isomer reference sample can be quantified and compensated for to obtain a reliable quantitative reference curve.

Continuing Studies

Research on the present system must be directed to sensitization, discovery of a stiffer matrix, recyclability and stability. Selection of another stilbene derivative might be necessary, but the suggested alternate, 4-dimethyl-amino-4'-nitrostilbene, has been found to be difficult to isomerize.

Long range plans include further investigation of a polymer-stilbene synthetic product which would respond as desired under optimal conditions established in previous research.
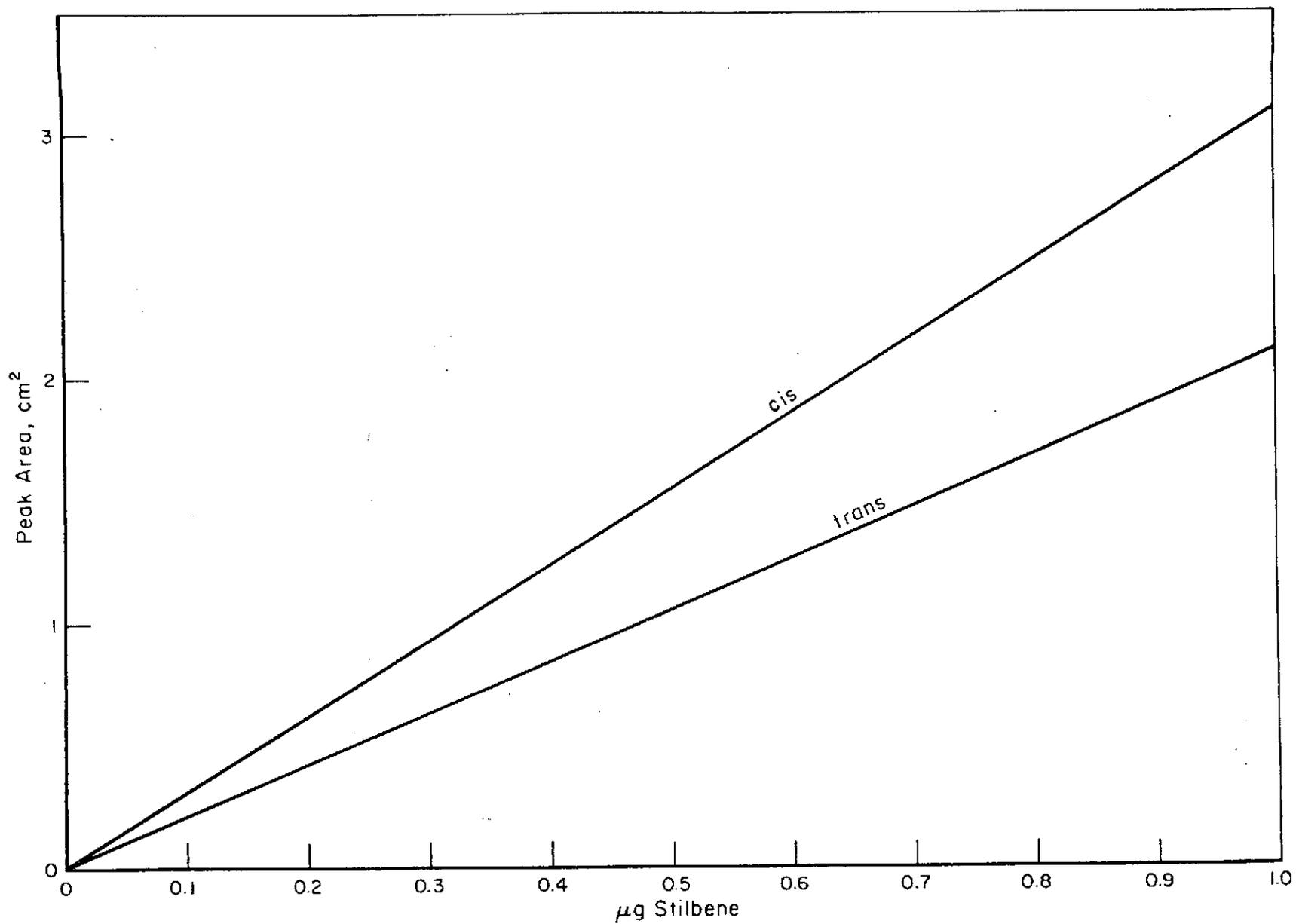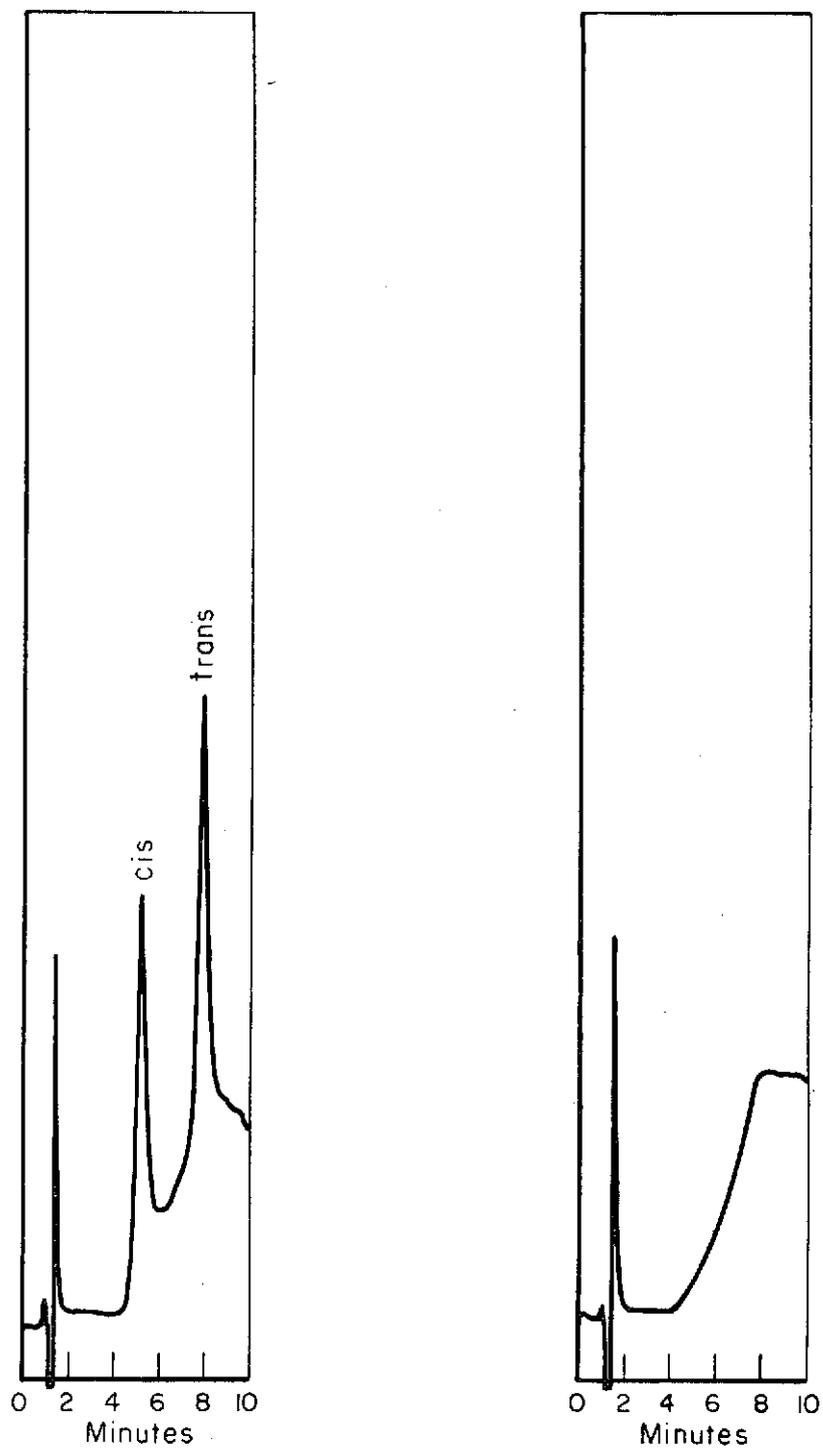
FIGURE 17.   HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC) QUANTITATIVE CURVE FOR
4-METHOXY-4'-NITROSTILBENE

a. HPLC spectrum of mixture
   of cis and trans isomers
   of 4-nitro-4'-methoxystilbene.

b. Gradient peak of solvent
   without stilbene.

FIGURE 18.   HPLC SPECTRA FOR ANALYSIS OF 4-METHOXY-
            4'-NITROSTILBENE

LITHIUM NIOBATE (LiNbO₃) STUDIES

Simultaneously with the work on the stilbenes, but at a much reduced level of effort, several tasks involving LiNbO₃ were carried out. These fell into two categories. First, a literature survey was made, and laboratory work was carried out to assess the present and potential capabilities of LiNbO₃ as a data storage material. Second, LiNbO₃ was used as a convenient recording medium to study experimentally the properties of thick holograms as they relate to high-density storage of digital data.

Summary of Relevant Characteristics of LiNbO₃

Over the past several years, much progress has been made in elucidating the writing mechanism in LiNbO₃. The role of impurities has been explored and in particular, the effect of iron and its valence state have been shown to be of considerable importance. One property of the crystal which has not received much attention is the stoichiometry. We have measured the relative writing sensitivity on a series of nominally pure (< 30 ppm of iron) LiNbO₃ crystals of differing stoichiometry, and found a striking variation in sensitivity among these crystals (Table 2).

TABLE 2. RELATIVE WRITING SENSITIVITY AND
MAXIMUM DIFFRACTIVE EFFICIENCY VS. STOICHIOMETRY

Li/Nb Ratio	Relative power to write 0.5% efficient grating	η Max.
0.4855	0.18	1.6%
0.4880	0.1	0.9%
0.4995	1	9.0%

The gratings were written with 4880Å and read with 6328Å. Stoichiometries were determined by comparison of the lattice parameters as measured by X-ray diffraction with the data of Lerner, Legras and Dumas[6]. It is not yet known whether the effect is a result of the stoichiometry variations controlling the valence of the residual iron impurities, or if the effect is more directly related to the stoichiometric variations. Other important results covering stoichiometry effects have recently appeared, and are

discussed below.

Another variable which has a significant import on the writing sensitivity and maximum diffraction efficiency of $LiNbO_3$ holographic gratings is the polarization of the read and write beams. Representative data are presented in Table 3.

TABLE 3. EFFECT OF BEAM POLARIZATION ON
PEAK DIFFRACTION EFFICIENCY, Fe-DOPED ISOMET CRYSTAL

Read (653nm) / Write (488nm)	Horizontal	Vertical	Estimated energy to obtain 100% diffraction efficiency
Horizontal Vertical	53% 38.2	3.3% 23.1%	5 to 9 J/cm^2 50 J/cm^2

These data were taken with the c-axis of the crystal horizontal (i.e., in the plane of the writing beams). The experimental results show that this is also the preferred orientation for the read and write beam polarization. The reduced efficiency with vertical read beam polarization is simply a result of coupling to a smaller electrooptic coefficient. The origin of the reduced efficiency with vertical polarization of the writing beams is not as clear, but it may be at least in part due to somewhat lower optical absorption for this polarization in unreduced crystals[7]. (The Isomet crystal used was presumably oxygen-annealed according to their standard procedure[8]. It should be noted that there is a slight difference in grating spacing for the two write polarizations, arising from the crystalline birefringence.

An additional phenomenon which will be of importance under certain circumstances is that which we have called "twitching". This consists of sudden abrupt changes in diffraction efficiency when writing at high power levels in iron-doped crystals. Surveying the literature, we found a closely similar phenomenon had been mentioned briefly once before, by Peterson et al.[9]

They attributed the effect to dielectric breakdown, which seems much the most likely explanation. Since a "twitch" frequently (but not invariably) is observed as a strong, rapid reduction in diffraction efficiency, the existence of "twitching" may present an effective limit on the recording power level that can be used. A more thorough investigation into the circumstances under which it occurs thus might be of value. We have noted that the phenomenon occurs not only in the diffracted, but also in the scattered light. The gradual buildup of scattered light during recording in $LiNbO_3$ has been known for some time[10]; its origin is not clear, but it may not be inherent in the material, but rather result from interference effects occuring with the type of optical setup ordinarily used. In any event, when there is a twitch in the diffracted beam, there is a simultaneous twitch which strongly reduces the amount of scattered light, much as if one had changed the direction of the beam. This observation seems consistent with the proposed explanation of both the scattering and twitching effects. If there are incommensurable spatial frequencies in the recorded inter-ference pattern, one would expect there to be periodically spaced regions of particularly high charge density, in the vicinity of which dielectric breakdown would first occur.

Intensive work on $LiNbO_3$ has continued during the past year at a number of other laboratories. Some of the findings of relevance to NASA optical-computer interests will now be briefly reviewed.

Much has been done to elucidate the role of iron impurities in the optical damage process[7,11-14]. It has become clear that absorption by Fe^{2+} ions is responsible for generation of many of the photocarriers even in nominally pure crystals[13]. The extent to which retrapping is at Fe^{3+} sites[11,15] is not so clear, however[16]. Conversion of the available iron to the divalent state clearly improves the storage sensitivity, though. The effect is not simply one of increased absorption at the Fe^{2+} site[12], as was first pointed out by Peterson et al[9]. The erase sensitivity is also increased considerably[11]; one seems to pay a price in maximum attainable diffraction efficiency. In Rh-doped $LiNbO_3$, reduction also improves the efficiency[17]; but only vacuum reduction, which also drives off oxygen, has been tried.

In the most sophisticated work so far, Clark et al[7] attributed the photogeneration to a $Fe^{2+} \rightarrow Nb^{5+}$ intervalence transition on the basis of polarized optical spectra and EPR measurements. The activation energy for this charge-transfer transition was found to be about 0.9 eV. From crystal-field parameters it was tentatively suggested that iron impurities occupy the lithium site.

In connection with sensitivity improvements, the discovery[12], apparently in a routine shipment from Crystal Technology, Inc., of a highly sensitive Fe-doped $LiNbO_3$ crystal is of particular interest. Comparison of recording sensitivities of samples studied in different laboratories is made difficult by the varied experimental conditions used. Not all the relevant parameters are always reported, either. In the case of the data reported by Shah et al[12], there is an additional slight problem in that the recording sensitivity given in the text does not agree with that given on the graph. Finally, diffraction efficiency is frequently given as fraction of transmitted light in the diffracted beam. In the case of crystals of relatively high absorption at the read wavelength, this can be rather misleading. At any rate, we have reduced several recent measurements to a common basis in order to provide some basis for comparison. What we report (in Table 4) is the specific exposure* (energy density), entering the crystal at the front face, required to reach a diffraction efficiency of 1% in a crystal of 1mm thickness being written at 488 nm and read at 632.8 nm. The thickness is not necessarily the optimum for the assumed conditions and given doping levels, but is that which is generally considered in prototype system design work. It seems that the sample found by Shah et al is an order of magnitude or so more sensitive than previously reported, but just what is special about it is at present unknown, as are the ultimate capacities of $LiNbO_3$ as a recording material.

In the same paper[12], as well as in some previous work[18], data were provided on recording sensitivity vs. pulse duration, using doubled Nd:YAG and ruby pulse (Q-switched) lasers.

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* Shah et al[12] refer to this quantity as the recording sensitivity, but this terminology is not satisfactory, since the number is smaller the more sensitive the sample.

TABLE 4. RECENT DATA ON LiNbO$_3$ OF HIGH WRITING SENSITIVITY PLACED ON COMMON BASIS:

Read wavelength – 632.8 nm
Write wavelength – 488 nm
Thickness – 1 mm (not necessarily optimum for greatest sensitivity).

Exposure given in terms of light energy entering crystal at front face.

Reference	Impurity	Treatment	Specific exposure (mJ/cm^{-2}%)	Write beam polarization	Angle between object and reference beams
Staebler & Phillips (11)	"0.005% Fe"	Reduced in Ar at 1050 C	120	Horizontal (i.e., in plane of writing beams)	Not given
Mikami & Ishida (17)	0.1 wt% Rh (in melt)	Reduced in vacuum at 600 C, 5 min.	≥1600	Horizontal	30°
Shah et al (12)	0.05 mole% Fe (in melt?)	As received	13 (data in figure) 5.4 (data in text)	Vertical	28°

Small corrections for these experimental variables not made.

40

It was observed that the time constants associated with the recording process were much shorter than the shortest pulse lengths used (75 nsec at 531 nm, 30 nsec at 694.3 nm). Thus it appears that the ultimate speed of the recording process has not yet been approached.

A different, very interesting way to use pulse lasers was reported quite recently by von der Linde et al[16]. Using a mode-locked frequency-doubled Nd:YAG laser emitting a train of about 80 10 ps pulses, they found that at high intensity, substantial optical index changes could be induced in pure and doped $LiNbO_3$ by non-linear (two-photon) absorption. The transparency of the crystal at the fundamental frequency makes it possible, in principle, to achieve near 100% diffraction efficiency. Moreover, the nonlinear nature of the effect means that one can obtain rather high sensitivities by going to high peak power densities (say 0.5 GW/cm^2). For the standard conditions described above, except for writing now with the 2nd harmonic at 530 nm, we estimate from data given in Ref. [16] that the specific exposure required is about 150 mJ/cm^2-% at 0.5 GW/cm^2 input power. It remains to be seen whether high-power pulsed lasers of the type used here will ever be suitable for space applications, but in any event these experiments are important for what they reveal about $LiNbO_3$: Since the recording via the second harmonic is similar regardless of doping, the impurities are not essential as electron traps. It seems very likely that, as suggested by our experiment discussed above, stoichiometry-related traps are responsible for most of the retrapping, while impurity levels may be predominantly the source of the photogenerated carriers. This interpretation is somewhat at variance with that of Staebler and Phillips[11], and with their observation of increased erase sensitivity in crystals in which the amount of Fe^{3+} has been reduced. It is possible, of course, that their sample was of a different stoichiometry from that used in the two-photon experiments, and therefore chanced to have fewer stoichiometry-related defects. It is quite unfortunate that those workers who have studied impurities in $LiNbO_3$ have paid little attention to stoichiometry, while those who have done the most nearly complete studies of stoichiometry effects — such as Bollmann and Gernand[19] — have ignored possible effects of impurities.

Properties of Thick Holograms

A series of five undoped LiNbO$_3$ samples of varying thickness were supplied by NASA-Langley for a series of measurements on the dependence of holographic recording properties on sample thickness. Initially, the acceptance angle of gratings formed by plane waves was measured as a function of sample thickness and agreement with theory was established. Subsequent measurements were made on an extended object with the goal of determining the closest angular separation which could be used without unacceptable interference between the successive patterns. It was found that for a 1 mm thick hologram, successive recordings of an object of 50 mrad angular extent could be accomplished with no appreciable interference if the recording material was rotated by about 14 mrad. A schematic drawing of the apparatus used to make these measurements is shown in Figure 19.
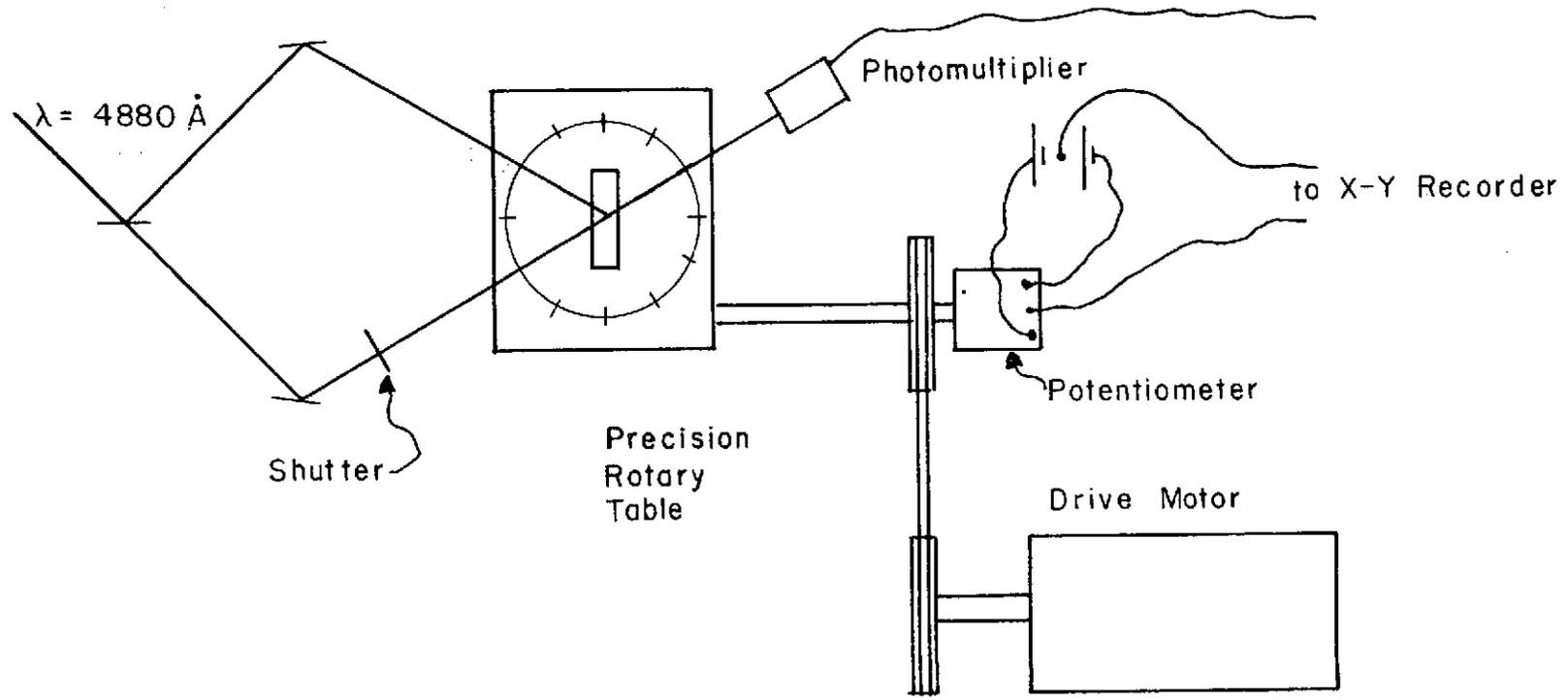
FIGURE 19

Experimental arrangement for studies of angular resolution and of

simultaneous recording of extended objects.

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