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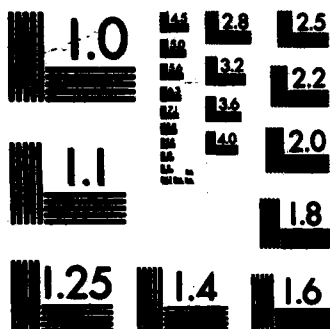
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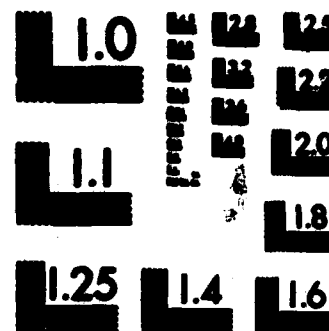
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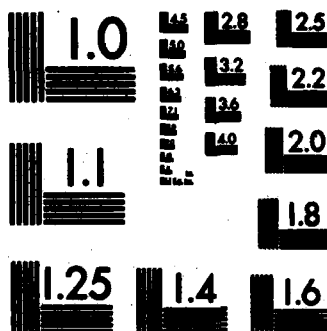
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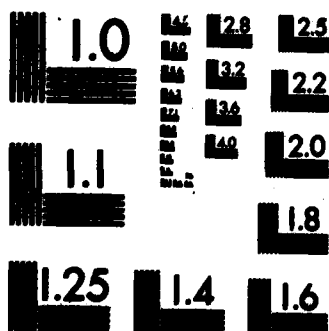
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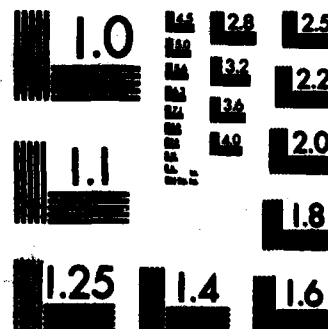
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2	2. GOVT ACCESSION NO. AD-A120787	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) APPLICATIONS OF HOLOGRAPHY IN THE INVESTIGATION OF PHOTOCHEMICAL REACTIONS		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Donald M. Burland		8. CONTRACT OR GRANT NUMBER(s) N00014-81-C-0418
9. PERFORMING ORGANIZATION NAME AND ADDRESS International Business Machines Corp. San Jose Research Laboratory 5600 Cottle Road, San Jose, CA 95193		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 051-782
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Code 413 800 N. Quincy Street Arlington, VA 22217		12. REPORT DATE October 7, 1982
		13. NUMBER OF PAGES 30
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES To be published in Accounts of Chemical Research		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Holography, photochemistry, triplet-triplet absorption		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The use of holography to investigate photochemical reactions is described. The experimental and theoretical bases for the technique are treated. Several specific applications are discussed including determination of the number of photons involved in a photochemical process, unraveling of a complex sequence of photochemical reactions and investigation of photochemistry that occurs from higher triplet states.		

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OFFICE OF NAVAL RESEARCH

Contract N00014-81-C-0418

Task No. NR 051-782

TECHNICAL REPORT NO. 2

**Applications of Holography in the
Investigation of Photochemical Reactions**

by

Donald M. Burland

Prepared for Publication

in the

Accounts of Chemical Research

**IBM Research Laboratory
San Jose, California 95193**

October 7, 1982

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RJ 3637 (42433) 10/7/82
Chemistry

APPLICATIONS OF HOLOGRAPHY IN THE INVESTIGATION OF PHOTOCHEMICAL REACTIONS

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ABSTRACT: The use of holography to investigate photochemical reactions is described. The experimental and theoretical bases for the technique are treated. Several specific applications are discussed including determination of the number of photons involved in a photochemical process, unraveling of a complex sequence of photochemical reactions and investigation of photochemistry that occurs from higher triplet states.

I. GENERAL INTRODUCTION

Holography is a method of photography that results in three-dimensional images of the object being photographed.¹ An example of a typical arrangement for producing a hologram is shown in Figure 1. Light from a single coherent source, almost always a laser, is divided into two beams; an object beam that is scattered off the object being photographed and a reference beam. An interference pattern resulting from the overlapping of these two beams is formed in the plane of a photographic plate. As a result of photochemical reactions that occur in the photographic plate, the optical properties of the plate are changed and a permanent record of the interference pattern is produced. To read the hologram a reconstruction beam, identical to the reference beam, is directed at the recording plate. A portion of this reconstruction beam is diffracted by the recorded hologram and produces a virtual image of the original object. An observer looking at this diffracted light sees a three-dimensional image of the original scene.

Much experimental effort has gone into the development of efficient holographic recording materials.² These investigations have primarily been concerned with improving the holographic recording process and only secondarily with the underlying photochemistry. In this paper, these priorities will be reversed and the use of holography as a tool for investigating photochemistry will be discussed. Of course, it is sometimes difficult to draw a sharp distinction between the two approaches. Interesting photochemical results have emerged from the search for holographic materials³ and new approaches to holographic recording have resulted from the photochemical investigations.⁴

It would, of course, not be particularly wise to attempt to study photochemistry by studying the time development of holograms of toy trains. The arrangement actually used is much simpler and is shown in Figure 2. The hologram is produced by the interference of

two mutually coherent plane waves. The interference pattern is thus a simple sinusoidal variation of light intensity across the sample. The resulting photochemistry causes a corresponding modulation of the optical properties of the recording medium producing what is essentially a diffraction grating. When a single reconstruction beam strikes the sample at the appropriate angle, a portion of the beam is diffracted by the grating. By following the growth in intensity of this diffracted probe beam with time, one can monitor the temporal progress of the photochemistry. A technique similar to the one to be discussed here where the light source producing the hologram is pulsed and where the grating is transient has been used to study a variety of diffusion processes in solids and is known by several names; four wave mixing, the transient grating technique and forced Rayleigh scattering.⁵

Why would one want to use a holographic technique for following photochemical reactions? What advantages does it possess over other methods? First the technique is essentially a zero-background one, that is the diffracted light intensity grows from an initial value of zero as photochemistry proceeds. This is in contrast to, for example, direct absorption measurements where a small change in a large background signal must be detected. As a result the holographic technique is capable of detecting very small photochemical changes. This assertion will be given a more quantitative significance elsewhere in the paper.

Second the technique may be used for investigating photochemical reactions where the absorption spectra of reactants and products overlap. Since, as will be shown, hologram growth depends on changes in the index of refraction of reactants and products as well as on differences in their absorption coefficients, one can observe a photochemical hologram even when reactants and products have their absorptions intimately intertwined.

The technique is useful for investigating solid state photochemistry. It can thus be used to study such industrially important processes as photopolymerization and photodegradation in a routine manner.

And finally it is important to emphasize the simplicity of the holographic technique. One tends to think of holographic experiments as taking place on super stable tables isolated from vibrations by tons of granite and concrete or floating on air cushions. For high resolution holographic photography such precautions may indeed be necessary. For the holographic photochemistry experiments discussed here one only needs stability comparable to that necessary for any moderate resolution spectroscopic experiment.

The remainder of this paper will be devoted to a more detailed discussion of holographic photochemistry. In the next section the experimental and theoretical bases of the technique will be described. Then three specific applications will be treated. These are determination of the number of photons involved in a photochemical process, unraveling of a complex sequence of photochemical reactions and investigation of photochemistry that occurs from higher excited triplet states.

II. THE TECHNIQUE OF HOLOGRAPHIC PHOTOCHEMISTRY

A. A Typical Experimental Arrangement

Figure 3 illustrates one possible experimental set-up for investigating photochemistry using holography. The light from a laser (either cw or pulsed) is divided into two beams. These beams are then recombined at the sample being investigated to produce an interference pattern. In most cases the sample is a thin ($\sim 200\mu$) sheet of a polymer host containing as a dissolved guest the molecule whose photochemistry is of interest. A low power HeNe laser is used to probe the growth of the hologram continuously. A fraction of the probe laser beam

is diffracted by the grating into a photodetector. An aperture blocks the laser beam that produces the hologram from reaching the photodetector but permits the HeNe laser beam to pass. Additional elimination of scattered light is accomplished by placing a narrow band pass filter before the monochromator allowing only 632.8 nm light to reach the detector.

The HeNe laser beam has very little divergence so that one can eliminate interference from unwanted scattered light simply by moving the detector well away from the sample. Additional improvements in the detection system can if needed be made by chopping the HeNe beam and using a phase sensitive detector to monitor the photodiode signal. With such an experimental arrangement, efficiencies (diffracted intensity/incident intensity) as low as 10^{-9} can be detected. More elaborate experimental arrangements can improve the sensitivity by several more orders of magnitude.^{5b}

B. The Relationship Between Hologram Growth and Photochemistry

A hologram is produced in the recording medium as a result of changes in the index of refraction and absorption coefficient brought about by the photochemistry. To see this relationship more clearly, consider the hypothetical system represented in Figure 4a. In this system a reactant A is photochemically converted into a product B. The absorption spectrum of A consists of a very intense band in the far UV ($\epsilon_{\text{max}}=50,000$ l/mole cm) at 200 nm, a strong band ($\epsilon_{\text{max}}=10,000$) at 250 nm and a much weaker band ($\epsilon_{\text{max}}=100$) at 400 nm. The product B of the photochemical reaction is assumed to retain only the single very strong band ($\epsilon=50,000$) at 200 nm. Such spectral changes are typical of those that might occur when a ketone, having a weak $n\pi^*$ transition in the visible or near UV and a strong $\pi\pi^*$ transition in the UV, undergoes hydrogen abstraction to yield a ketyl radical.⁶

The index of refraction dispersion corresponding to the absorption spectra of Figure 4a can be calculated from the absorption spectrum using the Kramers-Kronig relationship.⁷ The results of such a calculation are shown in Figure 4b. If the index of refraction change is monitored with a HeNe laser at 632.8 nm, these calculations indicate an overall change Δn of 2.2×10^{-3} when a molar concentration of A is completely converted to a molar concentration of B.

A holographic experiment on such a hypothetical system might consist of irradiating the sample in its weak absorption band at 400 nm with two interfering laser beams. The resulting interference pattern would produce a sinusoidally modulated intensity distribution

$$I = 2I_1 \left[1 + \cos \left(\frac{2\pi}{\Lambda} x \right) \right] \quad (1)$$

assuming both beams are of equal intensity. Here I_1 is the incident intensity in either beam, x is defined in Figure 2 and Λ is the fringe spacing given by

$$\Lambda = \frac{\lambda}{2n \sin \theta} \quad (2)$$

For an angle 2θ between the two beams of 2° , Λ is on the order of 10μ . n is the total index of refraction and is around 1.5 for most polymer hosts.

As a result of this nonuniform illumination of the sample, photochemistry will proceed at a nonuniform rate and the distribution of reactants A and products B will be correspondingly nonuniform. Since the index of refraction and absorption coefficient depend on the concentrations of A and B, these parameters will be similarly modulated and the depth of modulation will increase as the reaction proceeds. Kogelnik⁸ has shown that when the

index of refraction modulation has the form

$$n = n_0 + n_1 \cos \left(\frac{2\pi}{\Lambda} x \right) \quad (3)$$

and when the hologram thickness d is much larger than the fringe spacing,⁹ the efficiency in the absence of absorption may be written

$$\eta = \sin^2 \left(\frac{\pi n_1 d}{\lambda' \cos \theta'} \right) \quad (4)$$

where λ' is the reading wavelength and where the reading beam is assumed to strike the holographic grating at the Bragg angle θ' . (Note that n_1 in Eq. (3) is half Δn the total amplitude of the index of refraction change.)

For the hypothetical example being considered we use the following values

$$n_1 = 1.1 \times 10^{-3}$$

$$\theta' = 0$$

$$\Lambda' = 632.8 \text{ nm}$$

$$d = 200\mu$$

and obtain the result that when a molar concentration of A has been entirely converted into B in a 200μ thick sample the hologram efficiency is 79%. As has been mentioned previously hologram efficiencies of 10^{-9} can easily be measured. For the hypothetical example, this means that reactions involving concentration changes of less than $10^{-4}M$ can be followed easily in a 200μ sample. To follow such a reaction in direct absorption at 400 nm would require the detection of transmittance changes of 0.0005.

To see how one can obtain useful photochemical information from the experiment described above, we will reconsider Eq. (4) in the limit of small efficiencies. This is always the case at early times in the hologram growth process. In this limit

$$n_1 \approx \left(\frac{n_0 \epsilon \phi I}{\lambda \cos \theta} \right)^2 \quad (5)$$

The only factor in Eq. (5) that is significantly affected by photochemistry is n_1 . For the simple photochemical reaction



this dependence can be made explicit by expressing n_1 in terms of δn_A and δn_B the index of refraction change per mole for substances A and B, respectively:

$$n_1 = [\delta n_B - \delta n_A] \quad (6)$$

where $[\delta]$ is the concentration of substance A. Considering early times in the photochemical reaction one obtains the relationship

$$n_1 = [A]_0 (\delta n_B - \delta n_A) \phi \epsilon I t \quad (7)$$

$$n_1 = [\delta n_B - \delta n_A]^2 \phi^2 \epsilon^2 I^2 t^2 \quad (8)$$

where $[A]_0$ is the concentration of A at $t=0$, ϕ is the quantum yield for the reaction, ϵ the extinction coefficient at the recording wavelength and I the recording light intensity. From Eq. (8) it is clear that information concerning the photochemical reaction can be obtained by following the temporal growth of the hologram.

III. APPLICATIONS OF THE HOLOGRAPHIC TECHNIQUE

A. Determination of the Intensity Dependence

In many cases, particularly when lasers are involved, one would like to know how many photons must be sequentially absorbed to produce a photochemical reaction.¹¹⁻¹⁴ This is particularly simple to determine by the holographic technique. Equation (8) can be generalized in a straightforward manner to yield;¹⁰

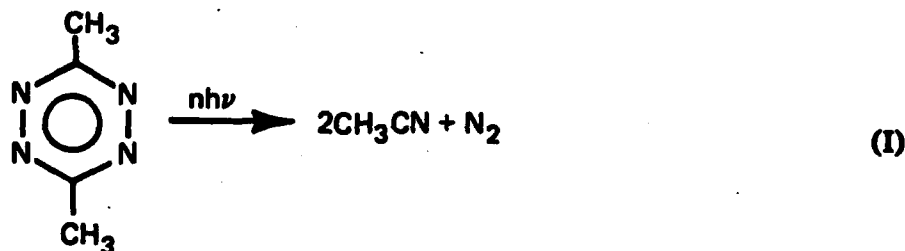
$$\eta = a(I)t^2 \quad (9)$$

where $a(I)$ has the functional form

$$a(I) = bI^{2n} \quad (10)$$

Here b is a constant and n is the number of photons involved in the photochemical reaction.

As an example consider the photodissociation of the molecule dimethyl-s-tetrazine (DMST):

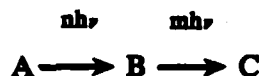


It has been demonstrated by direct absorption experiments¹³ that this molecule requires the stepwise absorption of two photons for the reaction in Scheme (I) to proceed. To verify this result using the holographic technique one obtains a series of hologram growth curves at various laser intensities. Such a set of growth curves is presented in Figure 5 for DMST in a polyvinylcarbazole (PVK) host.

The first thing to notice from these growth curves is that they are nonlinear as predicted by Eq. (9). They can in fact be shown to depend quadratically on time as expected. For each of the individual growth curves a value of $a(I)$ may be determined. From a log-log plot of $a(I)$ versus I , as shown in Figure 6, one can obtain a value for n . The results show that within experimental uncertainty the photodissociation of DMST in PVK is a two-photon process. Also shown in Figure 6 are results for the hydrogen abstraction reaction of camphorquinone in PVK.¹⁰ This reaction is known to require only one photon and as expected we find from the holographic experiments that n is very nearly unity.

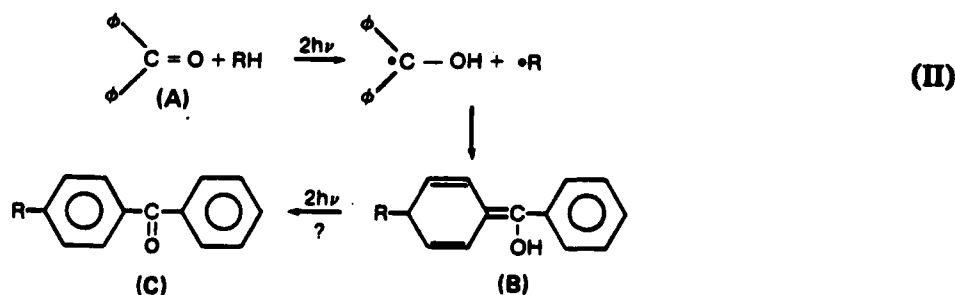
B. Investigation of Complex Reaction Sequences

Frequently photochemical reactions occur in several distinct steps. The initial reactants are converted into products that themselves absorb radiation and are converted into secondary products. Reaction sequences of this type might be represented schematically in the following way:



where n and m are the number of photons involved in each step. As a specific example of such a system consider the photochemistry undergone by benzophenone dissolved in PMMA.

The reaction may be written



The initial step in this reaction scheme is hydrogen abstraction by benzophenone from the polymer host RH resulting in a ketyl radical and a radical on the polymer chain $\cdot R$. In solid phases this reaction has been shown by the holographic technique just discussed to require the sequential absorption of two laser photons.¹⁶ The first step is benzophenone hydrogen abstraction and will be discussed in more detail later.

The two radicals produced in the first step are held by the polymer host in close proximity and can react to produce the species B. B absorbs in the same wavelength region as A so that light that produced the first step in the reaction can also be absorbed by B. B then photochemically reacts to yield a final product C. The chemical structure drawn for species C is speculative but it does seem to be consistent with the observed changes in the absorption spectrum.

Consecutive reaction schemes like this have characteristic hologram growth curves. Such a curve for benzophenone in polymethylmethacrylate (PMMA), produced and monitored using the UV lines from an Ar^+ laser, is shown in Figure 7a. The hologram grows in intensity, reaches a maximum, fades away to zero and then begins to grow again.

To see the origin of this hologram growth pattern, consider a calculation of the index of refraction dispersion from the absorption spectra of species A, B and C. The results of such a calculation are shown in Figure 8.¹⁷ To obtain these results prudent guesses have been made concerning the details of the absorption spectra of species B and C. The calculated dispersion curves thus have qualitative but not quantitative significance. A straightforward extension of Eq. (6) yields the following expression for the index of refraction modulation

n_1

$$n_1 \propto [B]\delta n_B + [C]\delta n_C - ([B] + [C])\delta n_A. \quad (11)$$

Referring to Figure 8 for values of δn_A , δn_B and δn_C , we note that during the initial stages of the reaction A is being converted into B. Since the reaction is being monitored at about 350 nm and since at 350 nm $\delta n_B > \delta n_A$, n_1 from Eq. (11) will be positive. But as the reaction proceeds further B is replaced by C and C has $\delta n_C < \delta n_A$. This means that n_1 must eventually become negative. Following n_1 as a function of time then, we find that n_1 begins at zero grows positively for a while, then decreases passing through zero, eventually becoming negative. Since the hologram efficiency depends on the square of the quantity n_1 , the expected hologram growth pattern is exactly the pattern observed experimentally in Figure 7a.

Next consider what would happen if, instead of reading the hologram at 350 nm, we used 514.5 nm radiation. At this wavelength we have the relationship $\delta n_A > \delta n_B > \delta n_C$. n_1 is thus negative throughout the reaction. In this case we expect the hologram to grow initially at a rate characteristic of the A $\rightarrow$ B reaction but to eventually grow with the B $\rightarrow$ C rate. That this is exactly what happens is shown in Figure 7b.

Various portions of the holographic growth curve can be correlated with changes in the absorption spectrum of the sample. This can be seen by comparing Figures 7 and 9. Initially, before any photochemistry has occurred, one sees two bands corresponding to a $\pi\pi^*$ (249 nm) state and an $n\pi^*$ (338 nm) state of benzophenone in PMMA. As the hologram grows, the benzophenone spectrum disappears. This can be seen by following the disappearance of the $\pi\pi^*$ absorption. The benzophenone spectrum is replaced by a strong absorption in the vicinity of 333 nm. This spectral change has been observed by a number of other workers in a variety of host materials¹⁸ and seems to be a general feature of benzophenone photochemistry. The growth of the second step in the hologram corresponds to a decrease in the absorption of this intermediate.

C. Reactions from Higher Excited Triplet States

In 1944, Lewis and Kasha¹⁹ speculated that photochemistry might occur when a molecule in its lowest metastable triplet state is excited to a higher triplet state. Since that time several examples of reactions of this type have been studied.²⁰ The holographic technique is particularly useful for studying such processes because it can be used even in cases where an interfering reaction occurs from the lowest triplet state.⁴

To illustrate the use of holography in this case, we will consider the photodissociation of carbazole.²¹⁻²³ Figure 10 shows the lower energy levels of the carbazole molecules. Neither the lowest singlet nor the lowest triplet state has sufficient energy to permit dissociation of the N-H bond.²⁴ Dissociation will occur, however, if the carbazole is first excited to its lowest triplet state with a photon of frequency ω_1 and then to a higher triplet state via triplet-triplet absorption with a second photon at ω_2 . ω_1 and ω_2 may, of course, be equal in energy.

To see how one might use holography to investigate this type of photochemistry, consider the experimental arrangement shown in Figure 11. Light of frequency ω_1 from a lamp or a laser illuminates the sample preparing carbazole molecules in their lowest triplet state. This light need not be coherent and it does not produce a hologram. If simultaneously the sample is illuminated with two coherent beams at a lower frequency ω_2 , a hologram can be produced as a result of the photochemistry that occurs from T_n . Frequently the ω_2 radiation is too low in energy to be absorbed by the ground state of the system. This means that no hologram will be produced when only ω_2 radiation strikes the sample. Figure 12 clearly shows the gating on and off of the hologram growth by the ω_1 beam.²¹

The frequency of the ω_2 radiation can be varied and referring to Eqs. (7) and (8) one can measure the product $\phi\epsilon$ as a function of wavelength. By comparing this wavelength dependence with the triplet-triplet absorption spectrum we can infer the wavelength variation of the quantum yield. Results for carbazole are shown in Figure 13 and one can conclude in this case that the quantum yield is independent of wavelength.²²

An example where the product $\phi\epsilon$ does not simply reproduce the triplet-triplet absorption spectrum is provided by the solid-state hydrogen abstraction reaction of benzophenone, the first step of Scheme (II).¹⁶ In solution this process occurs irreversibly from the lowest triplet state, an $n\pi^*$ state. When confined in a solid matrix, however, the products of the abstraction reaction are held in close proximity. They thus may efficiently recombine to reform the reactants and no irreversible photochemistry occurs. When excited with two-photons, however, into a higher triplet state, irreversible photochemistry does occur and the reactions shown in Scheme (II) can proceed.

Using the holographic technique the wavelength dependence of this photochemistry can be investigated. The results are summarized in Figure 14. We clearly see that excitation of the absorption band at 320 nm results in observable photochemistry, while excitation of the band with a maximum at 520 nm does not. The short wavelength triplet-triplet absorption band has been assigned to an $n\pi^*$ state, as has the lowest triplet state and the long wavelength band is attributed to a $\pi\pi^*$ state.¹⁵ If this assignment is correct then the photochemistry can be understood in the following simple terms. A fundamental characteristic of ketone photochemistry is the difference in reactivity between $n\pi^*$ and $\pi\pi^*$ triplet states.⁶ $n\pi^*$ states are known to undergo hydrogen abstraction reactions while $\pi\pi^*$ states do not. Benzophenone seems to behave in a way consistent with this pattern.

IV. CONCLUDING REMARKS

The holographic technique has proven to be a simple but sensitive technique for investigating photochemical reactions in the solid state. Since it is a zero-background technique it can be used to follow photochemical changes that are too small to detect by other means. Reactions that do not result in holograms are not detected by the technique and their presence does not interfere with the results.

The technique can be extended in a variety of ways. By chopping the coherent light source and measuring the transient holograms one might hope to follow photochemistry in liquids. The hologram growth can be followed as a function of temperature in order to measure activation energies for photochemical reactions. This would be particularly useful in the case of higher triplet states. One can think of a variety of other circumstances in which the holographic technique may prove useful.

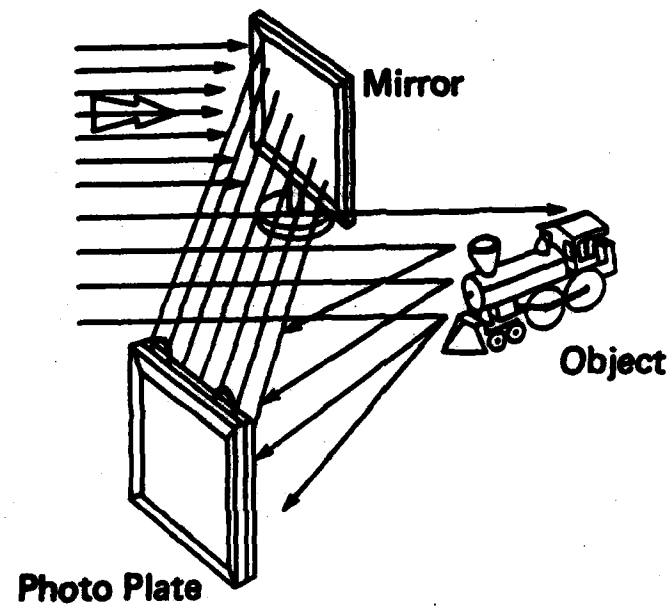
ACKNOWLEDGMENTS

I am deeply indebted to all of my coworkers whose names appear in the references cited in this paper for their contributions to the development of the holographic technique. I am also grateful to G. C. Bjorklund and H. E. Hunziker for their critical reading of the manuscript. In addition I would like to acknowledge the partial financial support of the Office of Naval Research and the U.S. Army Research Office.

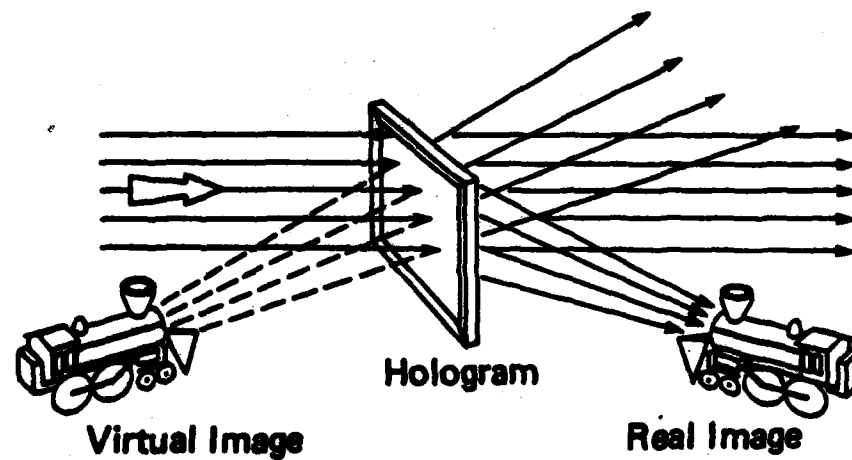
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(a) Recording



(b) Reconstruction

Figure 1. Recording and reconstruction of a holographic image. The virtual image is the one that is normally considered to be the holographic image.

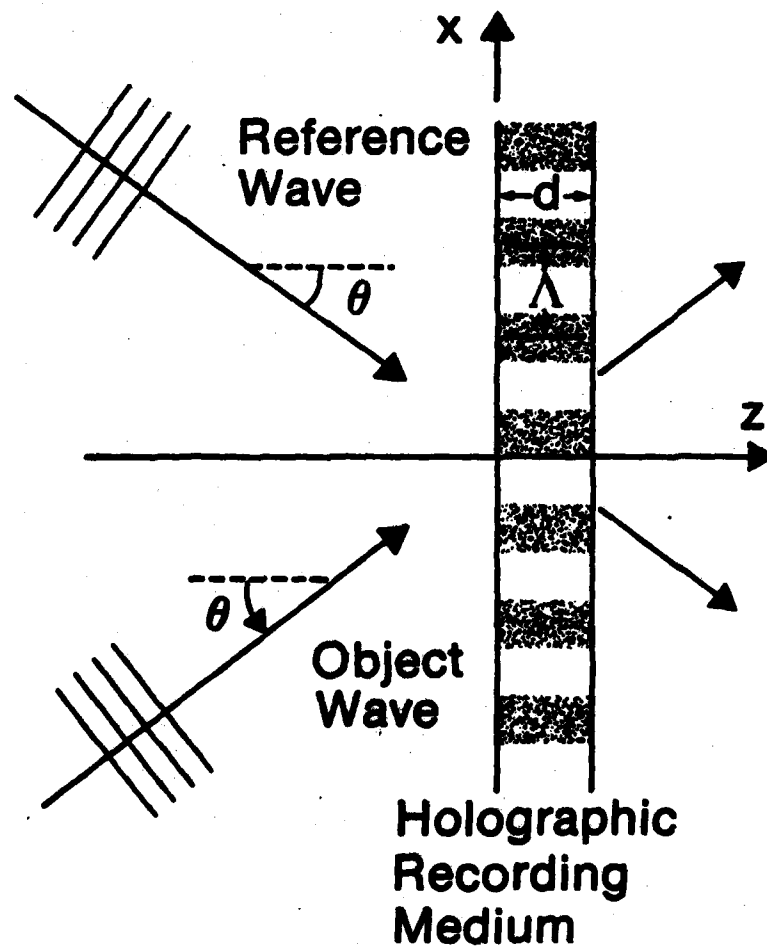


Figure 2. The formation of a hologram in a recording medium by the interference of two plane waves. The darkened areas in the recording medium indicate the regions where the two beams destructively interfere and little photochemistry is produced. The lighter areas are regions of constructive interference.

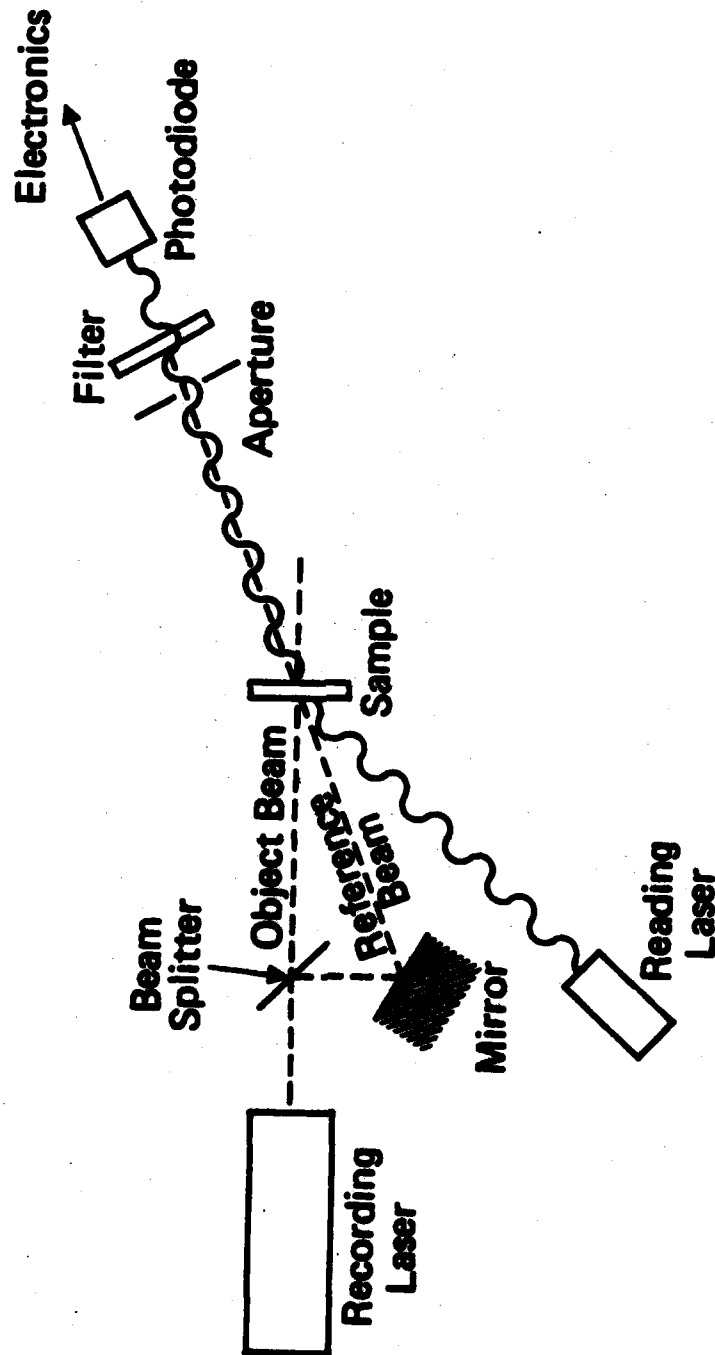


Figure 3. One possible experimental arrangement for the recording of holographic growth curves.

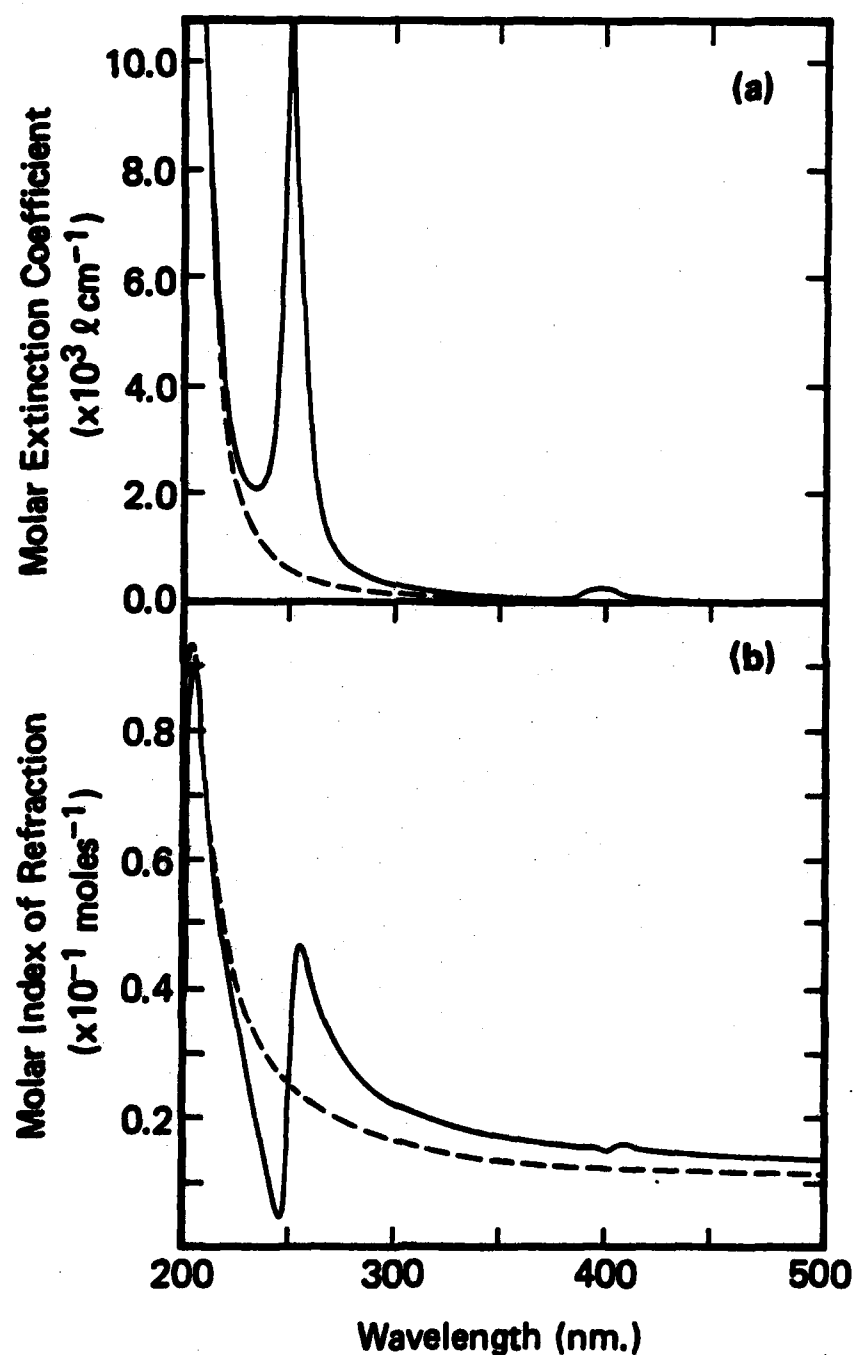


Figure 4. a) Absorption spectra for the hypothetical system described in the text. The solid line is the spectrum of species A and the dashed line of species B. Each absorption band is assumed to have a full width at half maximum of $25\text{\AA}$. b) The molar index of refraction dispersion for the absorption spectra in a) calculated using the Kramers-Kronig relationship.

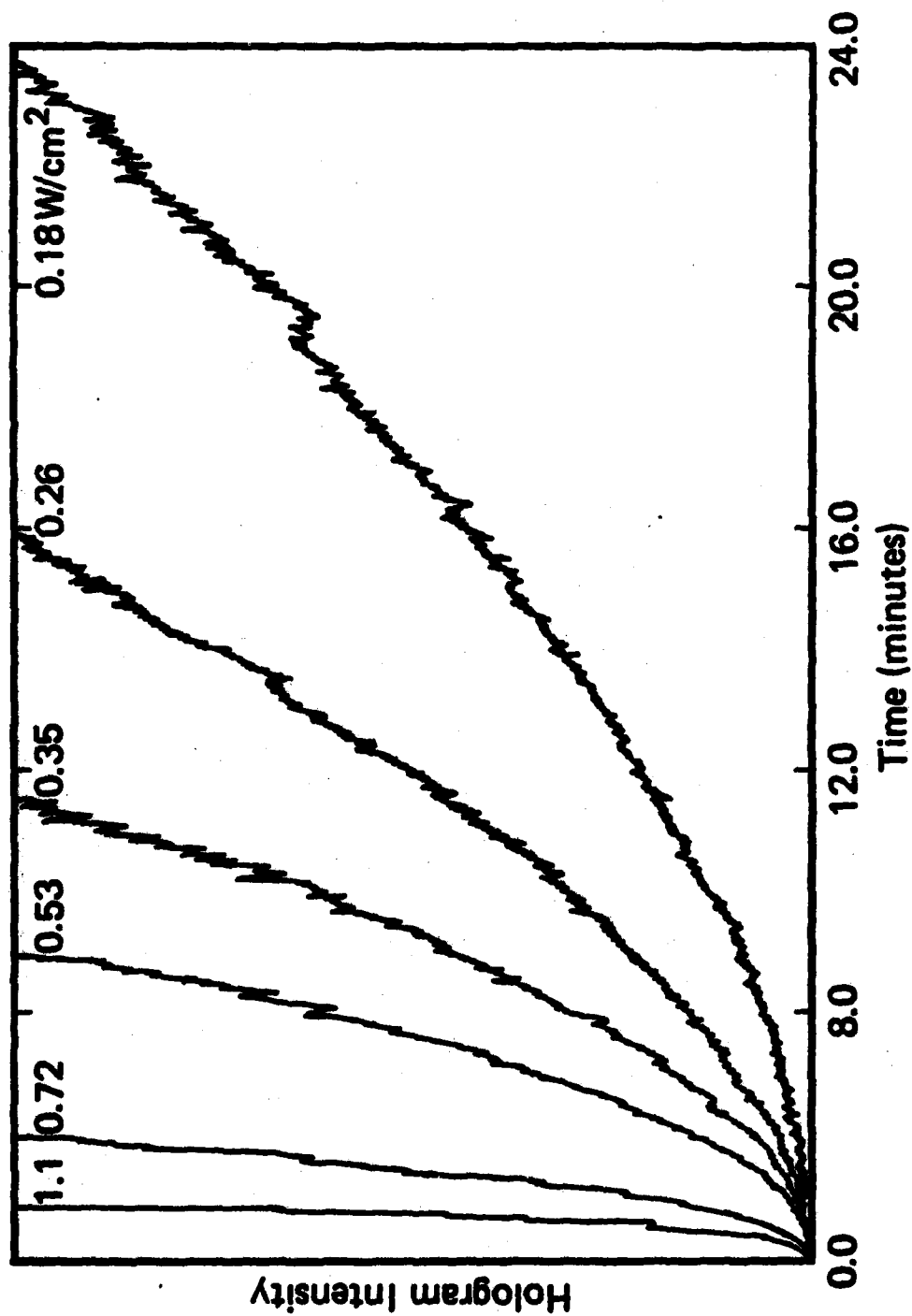


Figure 5. Holographic growth curves for DMST in polyvinylcarbazole (PVK) using the 514.5 nm line from an argon ion laser. Next to each curve is indicated the laser power density used to produce the hologram.

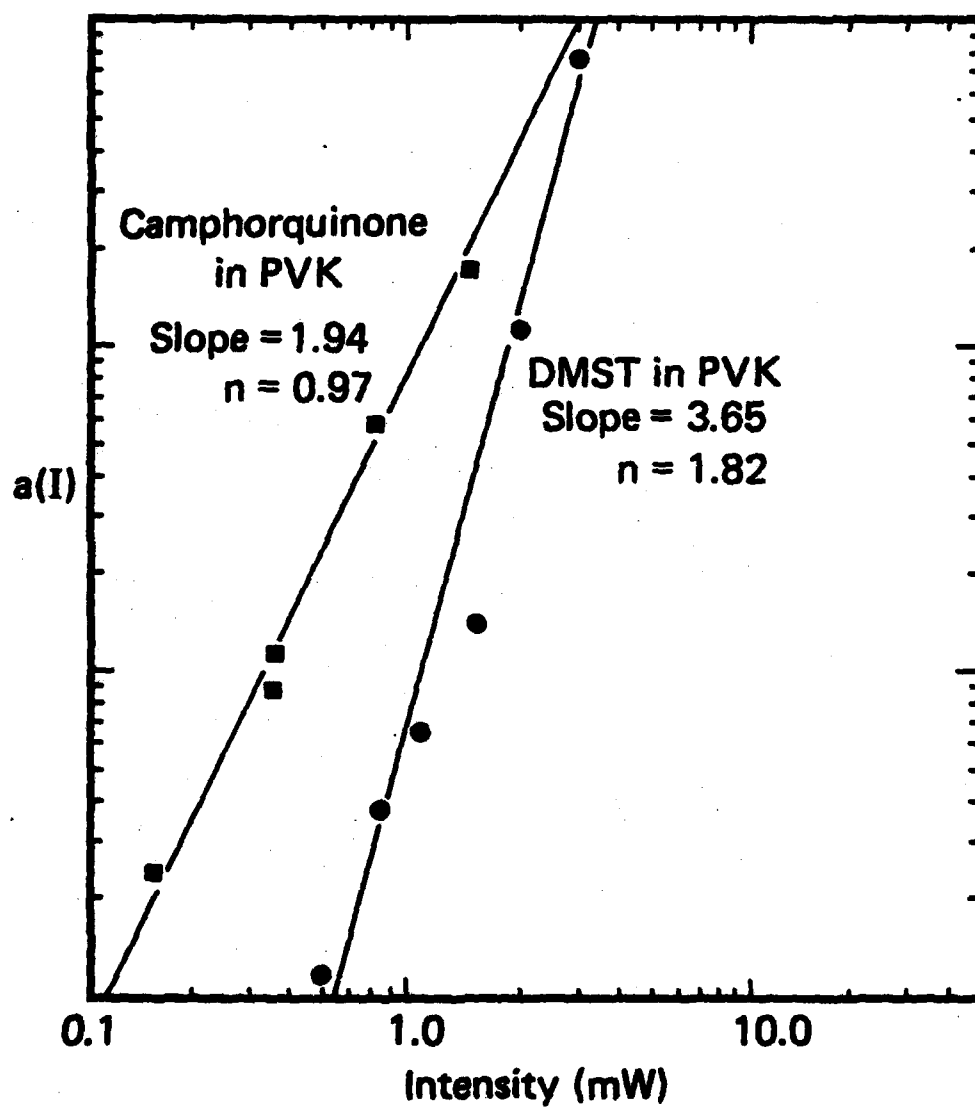


Figure 6. The factor $a(I)$ defined in Eq. (9) as a function of laser intensity. The DMST points were obtained from the data shown in Figure 5. The camphorquinone points were obtained from similar families of curves recorded using the 488 nm line from an argon ion laser.

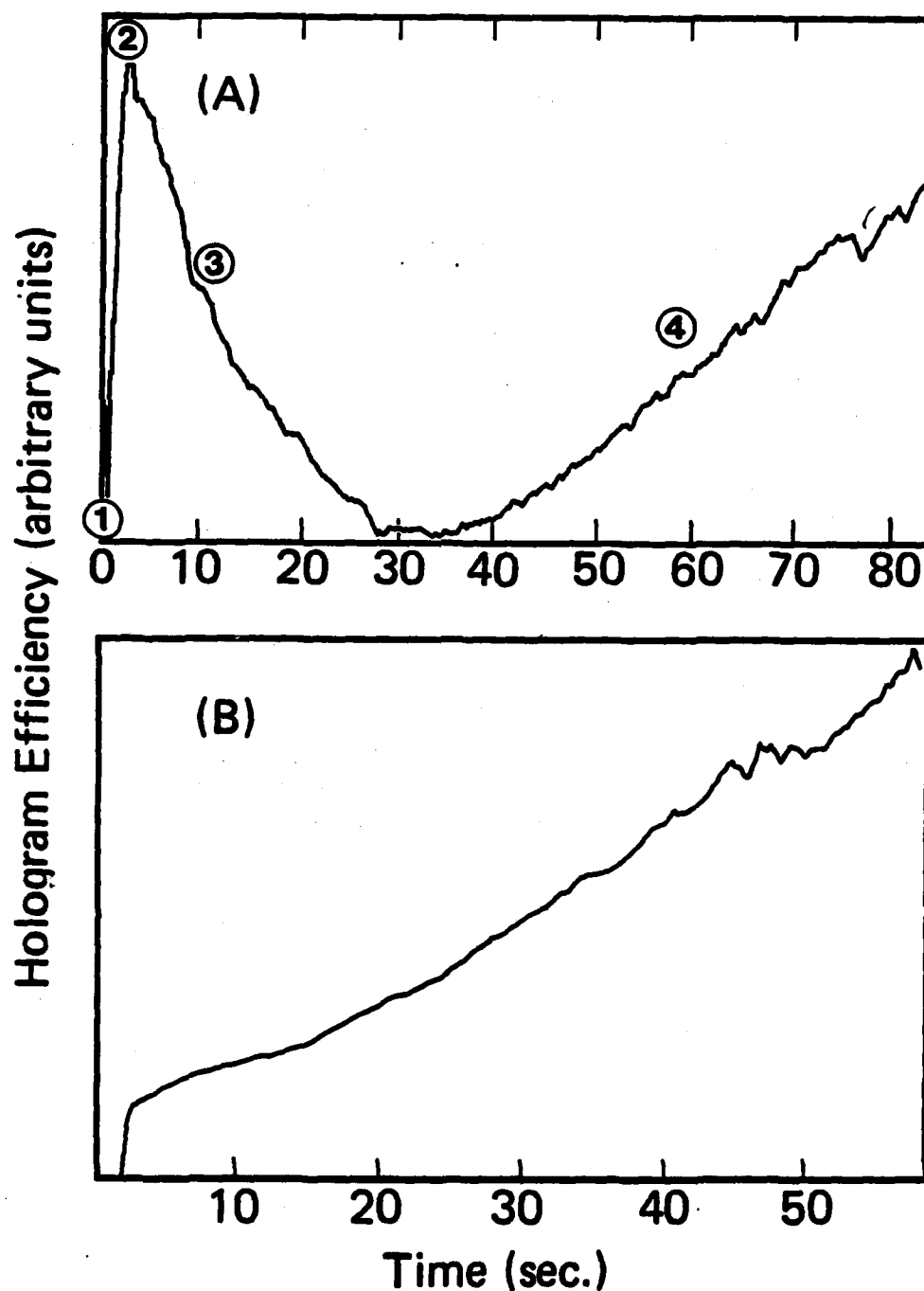


Figure 7. Hologram efficiency versus time for benzophenone in PMMA. a) Hologram produced and read using argon ion laser UV lines. The numbers next to the curve refer to points at which the spectra in Figure 9 were taken. b) Hologram produced using argon ion laser UV lines and read at 514.5 nm. Note that the start of the hologram growth has been shifted from zero time to make it more readily visible.

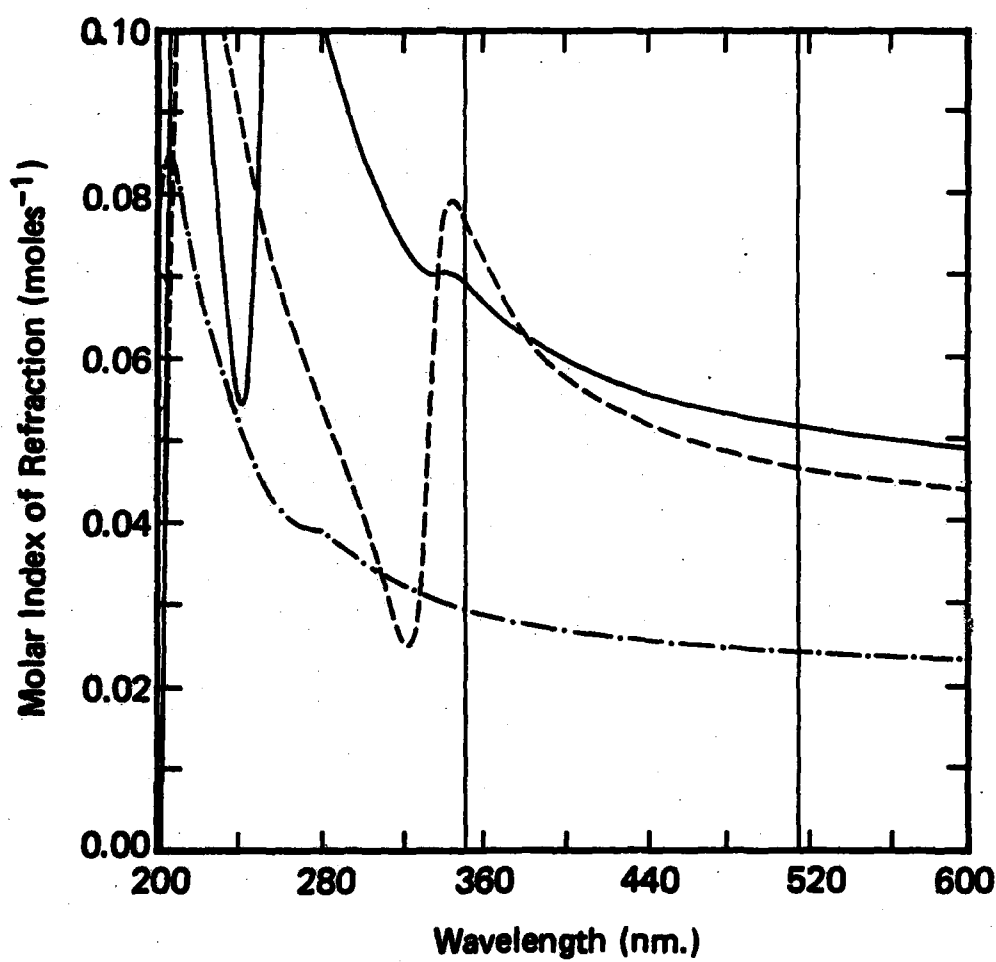


Figure 8. Calculated molar index of refraction dispersion. The three curves are for the three species involved in the benzophenone photochemistry. — A (benzophenone), --- B, - · - · C. The vertical lines at 350 and 541 nm indicate the two wavelengths at which holograms were read.

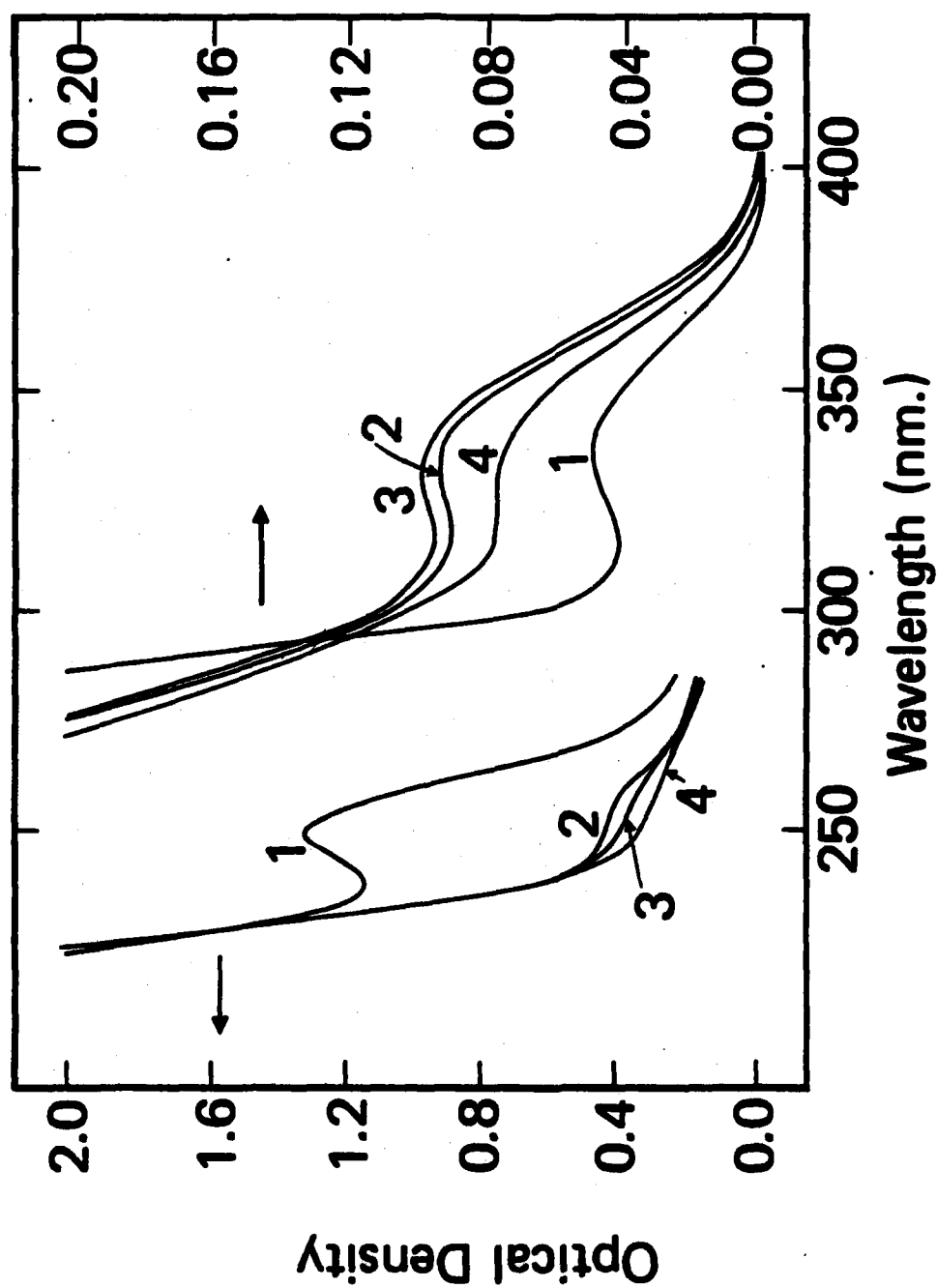


Figure 9. The absorption spectra of benzophenone in PMMA taken at various points during the growth of the hologram. The numbers next to the spectra refer to the times indicated in Figure 7.

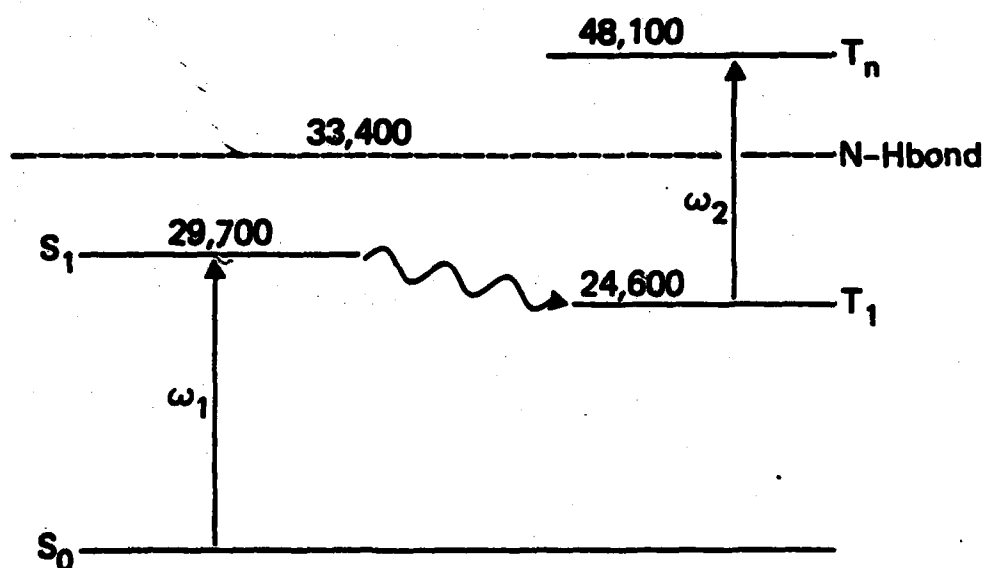
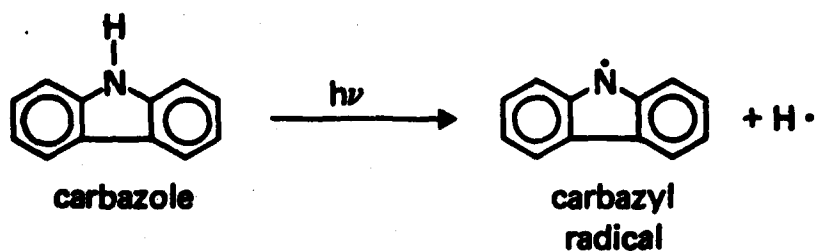


Figure 10. Photodissociation scheme and energy level diagram for carbazole. The position of the N-H bond dissociation energy is indicated in the figure by the horizontal dashed line.

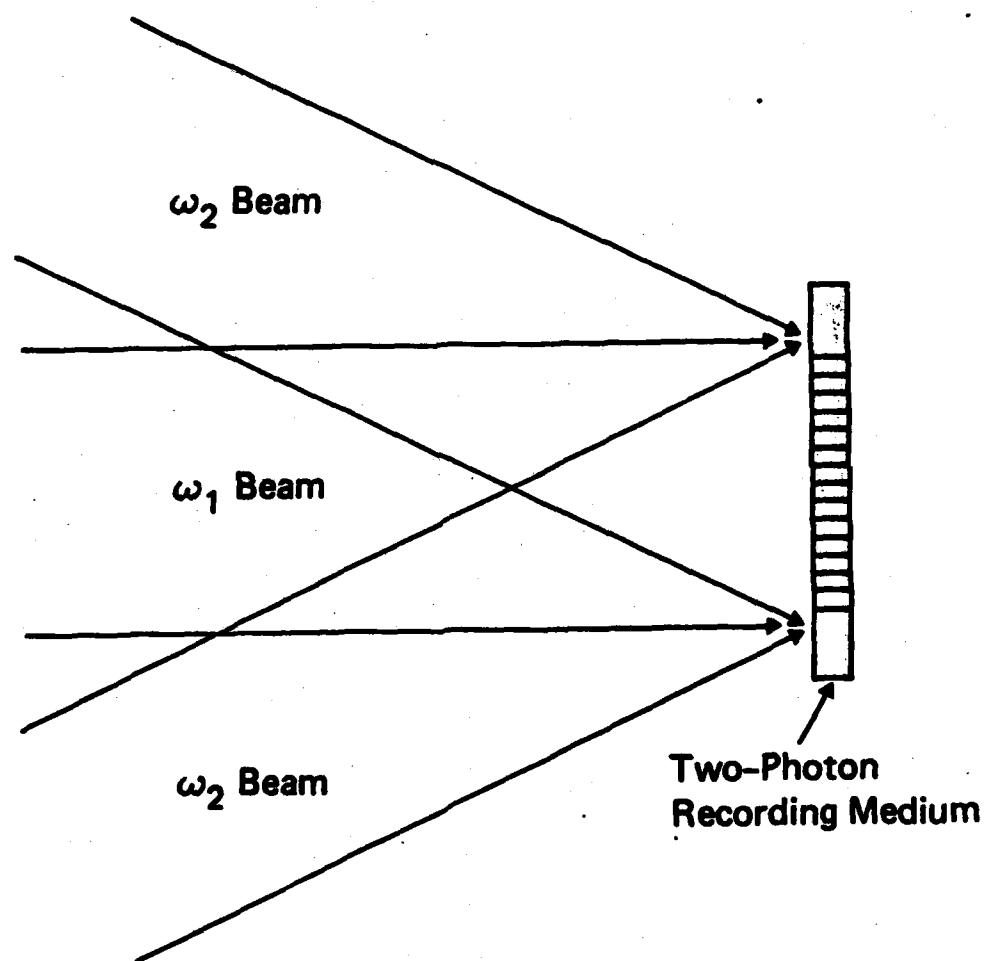


Figure 11. Experimental arrangement for following the photochemistry from higher triplet states.

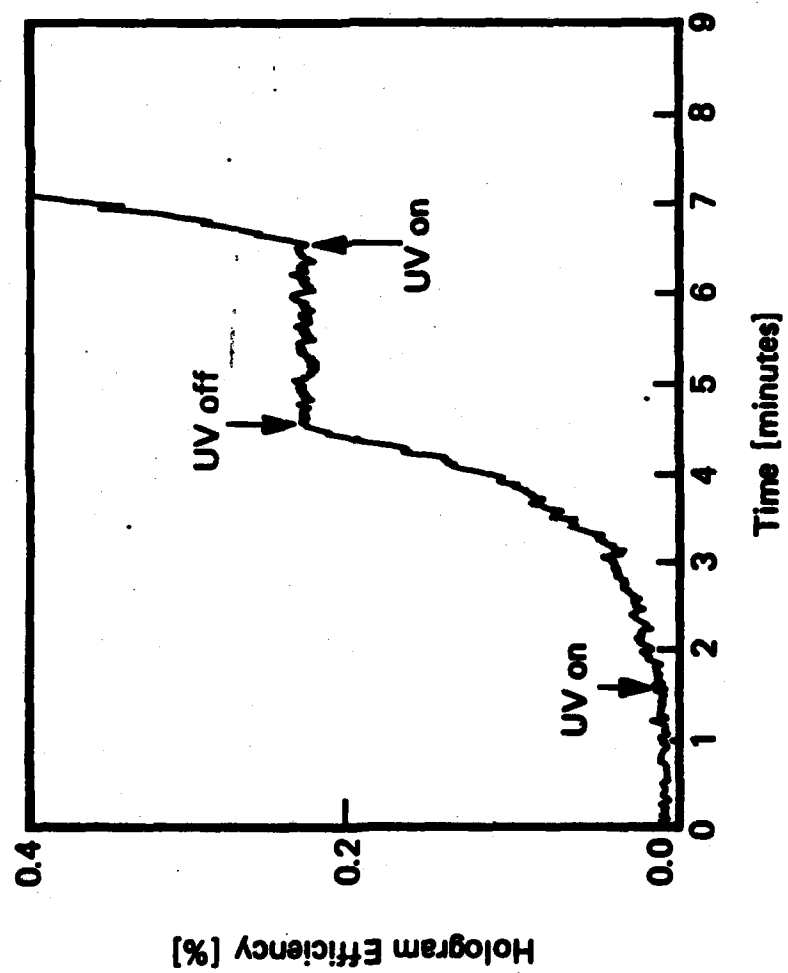


Figure 12. Growth curve of hologram diffraction efficiency for carbazole in PMMA.

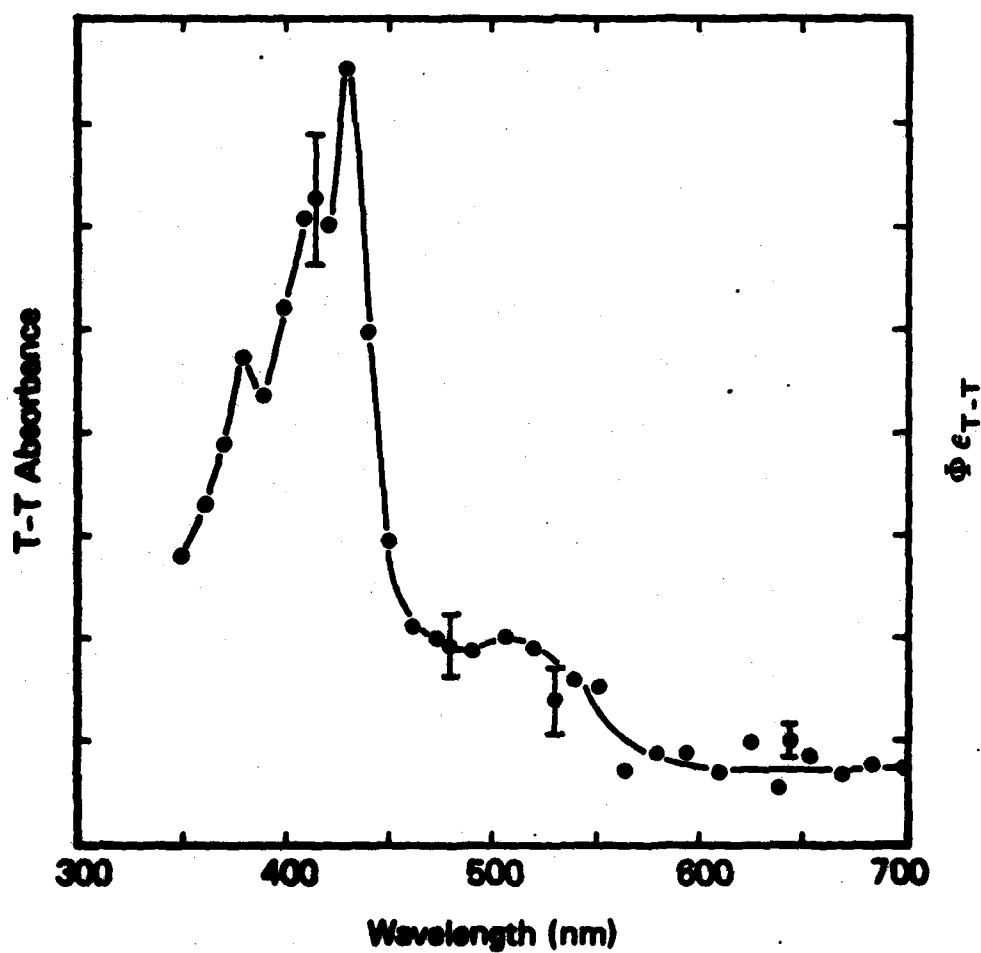


Figure 13. Triplet-triplet absorption spectrum of carbazole in PMMA at 77K (solid line) and photochemical action spectrum from higher triplet state of carbazole/PMMA at room temperature (points with error bars).

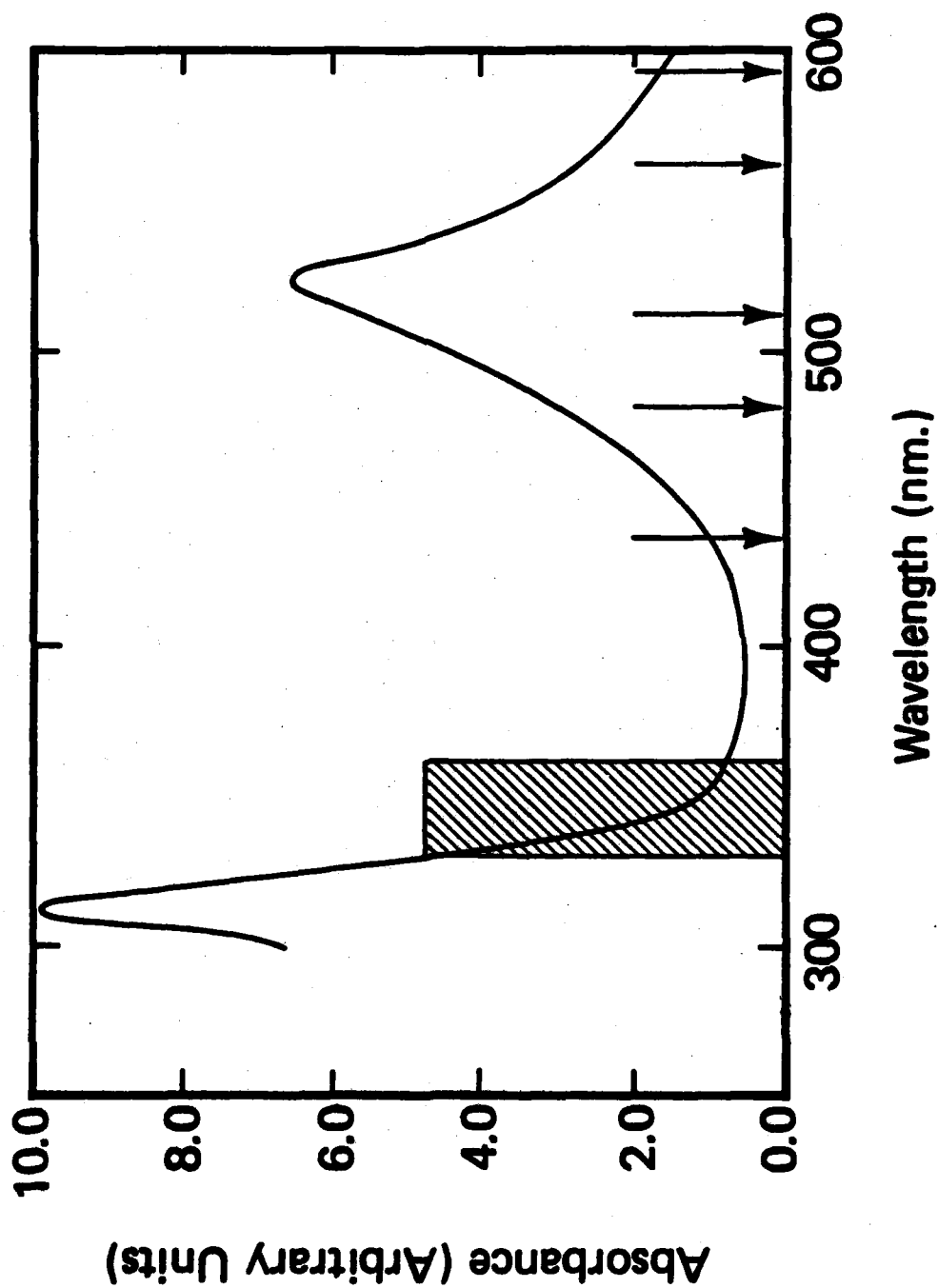


Figure 14. Triplet-triplet absorption spectrum of benzophenone in PMMA from Ref. 15. The arrows indicate wavelengths at which no higher triplet state reactivity was found.

END