

ment to a phenol, while electron-withdrawing groups retard the reaction. In fact, with Pyrex-filtered light, rearrangement is completely suppressed with an acyl substituent at C(8) or C(9) in **22**. A carbonyl substituent at C(4) seems to facilitate photorearrangement, and we have already noted that trans-fused hexa-

hydrodibenzofurans are unreactive (e.g., **21**). The origin of electronic and steric effects as well as the synthetic potential of benzodihydrofuran photochemistry is currently under investigation in our laboratory.

Concluding Remarks

In this Account I have focused attention on our own studies of photochemical six-electron heterocyclization reactions. Potential for stereochemical control, the possibility of intercepting ylide intermediates by dipolar cycloadditions (inter- and intramolecular), and the potential for incorporation of a variety of heteroatoms suggest that photochemical heterocyclizations will provide a rich area of organic chemistry for future consideration.

It is a pleasure to acknowledge the contribution of graduate and postdoctoral students who participated in this research effort; their names are recorded in the references. Continued support from the National Institutes of Health, the National Institute on Drug Abuse, and most recently the National Science Foundation is appreciated. Early support from the Research Corporation, the Petroleum Research Fund, administered by the American Chemical Society, and a Du Pont Young Faculty Grant was instrumental in the initiation of this research program.

Applications of Holography in the Investigation of Photochemical Reactions

DONALD M. BURLAND

IBM Research Laboratory, K64/282, San Jose, California 95193

Received September 30, 1982 (Revised Manuscript Received January 20, 1983)

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 with 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

Donald M. Burland received an A.B. degree from Dartmouth College and a Ph.D. degree from Caltech. He spent 2 years at the Kamerlingh Onnes Laboratory in the Netherlands before joining IBM in 1971. He is currently the manager of the optical materials group. His research interests include photoconductivity and energy transfer in organic crystals and applications of laser techniques to photochemical investigations.

These investigations have primarily been concerned with improving the holographic recording process and only secondarily with the underlying photochemistry. In this account, 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

(1) J. B. DeVelis, and G. O. Reynolds, "Theory and Applications of Holography", Addison-Wesley, Reading, MA, 1967.

(2) W. J. Tomlinson, and E. A. Chandross, *Adv. Photochem.*, **12**, 201 (1980).

(3) W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde, and A. A. Lamola, *Appl. Opt.*, **11**, 533 (1972); A. Bloom, R. A. Bartolini, and D. L. Ross, *Appl. Phys. Lett.*, **24**, 612 (1974); A. Bloom, R. A. Bartolini, P. L. K. Hung, and D. L. Ross, *ibid.*, **29**, 483 (1976).

(4) C. Bräuchle, U. P. Wild, D. M. Burland, G. C. Bjorklund, and D. C. Alvarez, *Opt. Lett.*, **7**, 177 (1982); *IBM J. Res. Dev.*, **26**, 217 (1982).

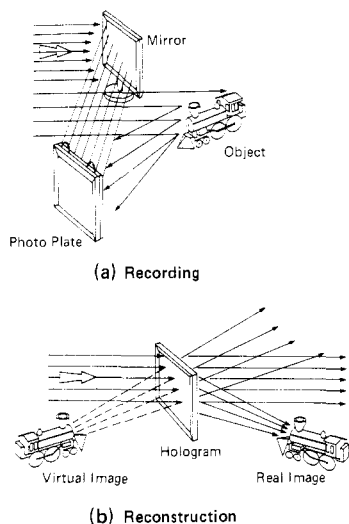


Figure 1. Recording and reconstruction of a holographic image. The virtual image is the one that is normally considered to be the holographic image.

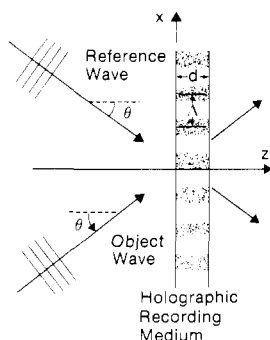


Figure 2. The formation of a hologram in a recording medium by the interference of two plane waves. The darkened areas in the recording medium indicate the regions where the two beams destructively interfere and little photochemistry is produced. The lighter areas are regions of constructive interference.

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, since the diffracted light intensity grows from an initial value of zero as the 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 sig-

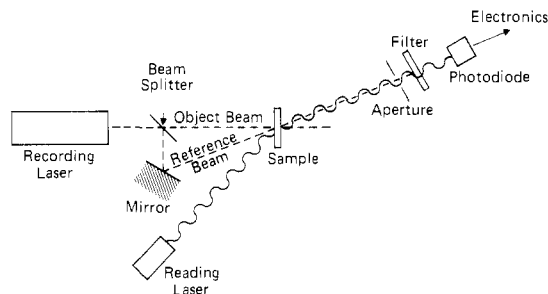


Figure 3. One possible experimental arrangement for the recording of holographic growth curves.

nificance elsewhere in this account. A second advantage of the technique is that it 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 also 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. 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.

Typical Experimental Arrangement

Figure 3 illustrates one possible experimental setup 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 ($\sim 200 \mu\text{m}$) 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 and by moving the detector well away from the sample. 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}

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 ab-

(5) (a) H. J. Eichler, *Opt. Acta*, **24**, 631 (1977); *Festkörperprobleme*, **18**, 241 (1978); (b) D. W. Pohl, *IBM J. Res. Dev.*, **23**, 604 (1979).

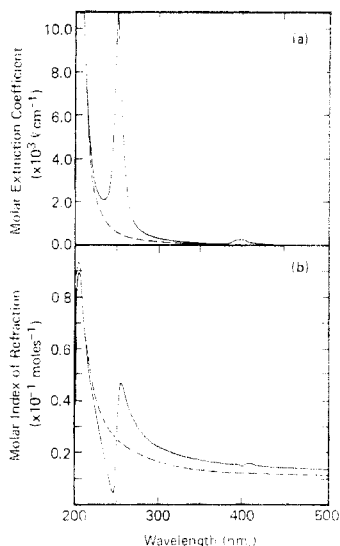


Figure 4. (a) Absorption spectra for the hypothetical system described in the text. The solid line is the spectrum of species A and the dashed line of species B. Each absorption band is assumed to have a full width at half-maximum of 25 Å. (b) The molar index of refraction dispersion for the absorption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

sorption 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 ($\epsilon_{\max} = 50\,000$ l/mol cm) at 200 nm, a strong band ($\epsilon_{\max} = 10\,000$) at 250 nm, and a much weaker band ($\epsilon_{\max} = 100$) 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-ultraviolet and a strong $\pi\pi^*$ transition in the UV, undergoes hydrogen abstraction.^{6,7}

The index of refraction dispersion corresponding to the absorption spectra of Figure 4a can be calculated from the absorption spectrum by using the Kramers–Kronig relationship.⁸ 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

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

assuming both beams are of equal intensity. Here I_i 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 $10 \mu\text{m}$. 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. Kogelnik⁹ 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,¹⁰ 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

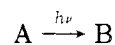
$$\begin{aligned} n_1 &= 1.1 \times 10^{-3} \\ \theta' &= 0 \\ \lambda' &= 632.8 \text{ nm} \\ d &= 200 \mu\text{m} \end{aligned}$$

and obtain the result that, when a molar concentration of A has been entirely converted into B in a $200\text{-}\mu\text{m}$ -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 $200\text{-}\mu\text{m}$ 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 discussed 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

$$\eta \approx \left(\frac{\pi n_1 d}{\lambda' \cos \theta'} \right)^2 \quad (5)$$

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



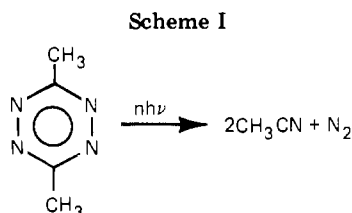
(6) P. J. Wagner, *Top. Curr. Chem.*, **66**, 1 (1976).

(7) C. Bräuchle, D. M. Burland, and G. C. Bjorklund, *J. Phys. Chem.*, **85**, 123 (1981).

(8) R. W. Ditchburn, "Light", Academic Press, London, 1976, pp 733–736.

(9) H. Kogelnik, *Bell Syst. Tech. J* **48**, 2909 (1969).

(10) T. K. Gaylord, and M. G. Moharam, *Appl. Opt.*, **20**, 3271 (1981).



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 molecules A and B, respectively:

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

where [B] is the concentration of molecule B. Considering early times in the photochemical reaction, one obtains the relationship¹¹

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

or

$$\eta \propto [A]_0^2(\delta n_B - \delta n_A)^2\phi^2\epsilon^2 I^2 t^2 \quad (8)$$

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.

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.¹²⁻¹⁵ This is particularly simple to determine by the holographic technique. Equation 8 can be generalized in a straightforward manner to yield,¹¹

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

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; Scheme I). It has been demonstrated by direct absorption experiments¹⁴ 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

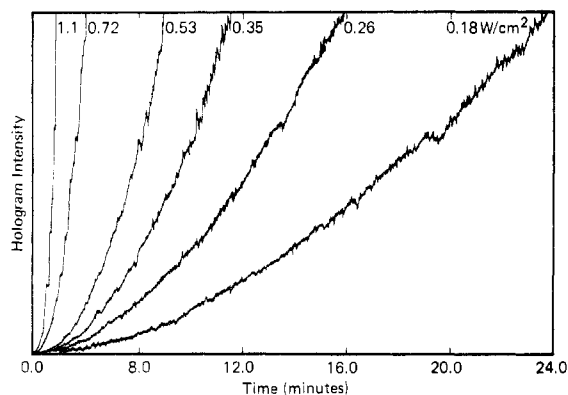
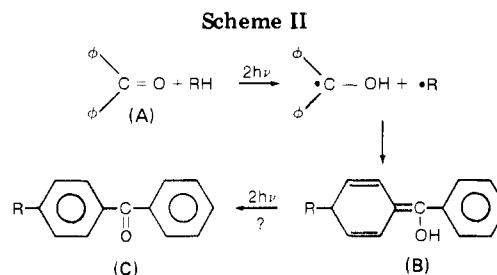


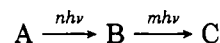
Figure 5. Holographic growth curves for DMST in polyvinylcarbazole (PVK) with use of the 514.5-nm line from an argon ion laser. Next to each curve is indicated the laser power density used to produce the hologram.



of $a(I)$ vs. I 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. For DMST in PVK these results indicate that the photodissociation is a two-photon process.

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 as shown in Scheme II. 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.⁷ 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.

(11) G. C. Bjorklund, D. M. Burland, and D. C. Alvarez, *J. Chem. Phys.*, **73**, 4321 (1980).

(12) S. Ishikawa, J. Nakamura, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **53**, 2476 (1980); K. Yokoyama, J. Nakamura, T. Kobayashi, and S. Nagakura *ibid.*, **53**, 3474 (1980).

(13) R. Lesclaux, and J. Jousset-Dubien, in "Organic Molecular Photochemistry", J. B. Birks, Ed., Wiley, London, 1973, Vol. 1.

(14) D. M. Burland, *Proc. Soc. Photo-Opt. Instrum. Eng.*, **133**, 151 (1977); D. M. Burland, F. Carmona, and J. Pacansky, *Chem. Phys. Lett.* **56**, 221 (1978); B. Dellinger, M. A. Paczkowski, R. M. Hochstrasser, and A. B. Smith, *J. Am. Chem. Soc.*, **100**, 3242 (1978).

(15) H. Murai, and K. Obi, *J. Phys. Chem.*, **79**, 2446 (1975).

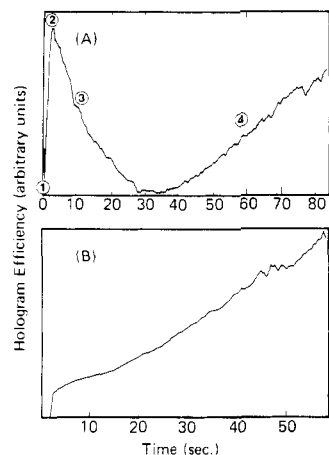


Figure 6. Hologram efficiency vs. time for benzophenone in PMMA. (a) Hologram produced and read with argon ion laser UV lines. The numbers next to the curve refer to points at which the spectra in Figure 8 were taken. (b) Hologram produced with argon ion laser UV lines and read at 514.5 nm. Note that the start of the hologram growth has been shifted from zero time to make it more readily visible.

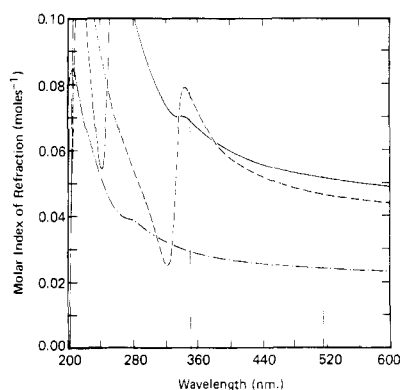


Figure 7. Calculated molar index of refraction dispersion. The three curves are for the three species involved in the benzophenone photochemistry: (—) A (benzophenone), (---) B, (-·-) C. The vertical lines at 350 and 541 nm indicate the two wavelengths at which holograms were read.

Consecutive reaction schemes like this have characteristic hologram growth curves. Such a curve for benzophenone in polymethylmethacrylate (PMMA), produced and monitored with the UV lines from an Ar^+ laser, is shown in Figure 6a. 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 7.¹⁷ 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 7 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

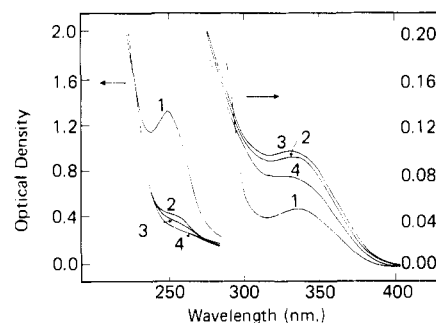


Figure 8. The absorption spectra of benzophenone in PMMA taken at various points during the growth of the hologram. The numbers next to the spectra refer to the times indicated in Figure 6.

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, and then decreases, passing through zero and 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 6a.

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 grow eventually with the $B \rightarrow C$ rate. That this is exactly what happens is shown in Figure 6b.

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 6 and 8. 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.

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 inter-

(18) N. Filipescu, and F. L. Minn, *J. Am. Chem. Soc.*, **90**, 1554 (1968); J. Chilton, L. Giering, and C. Steel, *ibid.*, **98**, 1865 (1976); S. A. Weiner, *ibid.*, **93**, 425 (1971); J. H. Hutchinson, M. C. Lambert, and A. Ledwith, *Polymer*, **14**, 250 (1973); P. Colman, A. Dunne, and M. F. Quinn, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2605 (1976).

(19) G. N. Lewis, and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(20) N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth, *Chem. Rev.*, **78**, 125 (1978).

(16) W. H. Melhuish, *Trans. Faraday Soc.*, **62**, 3384 (1966).

(17) D. M. Burland, and C. Bräuchle, *J. Chem. Phys.*, **76**, 4502 (1982).

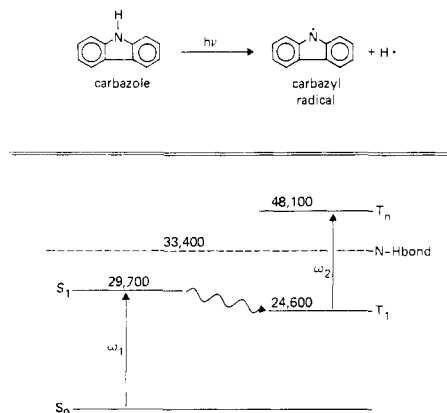


Figure 9. Photodissociation scheme and energy level diagram for carbazole. The position of the N-H bond dissociation energy is indicated in the figure by the horizontal dashed line.

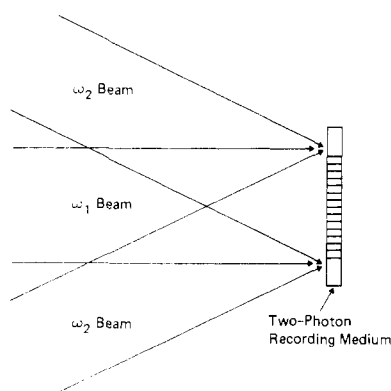


Figure 10. Experimental arrangement for following the photochemistry from higher triplet states.

fering 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 9 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 10. 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

(21) G. C. Bjorklund, C. Bräuchle, D. M. Burland, and D. C. Alvarez, *Opt. Lett.*, **6**, 159 (1981).

(22) U. Schmitt and D. M. Burland, *J. Phys. Chem.* **87**, 720 (1983).

(23) S.-A. Yamamoto, K. Kokuchi, and H. Kokubun, *Z. Phys. Chem.*, **109**, 47 (1978); M. Martin, E. Breheret, F. Tfibel, and B. Lacourbas, *J. Phys. Chem.*, **84**, 70 (1980).

(24) Pauling, L., "The Nature of the Chemical Bond", Cornell University Press, Ithaca, NY, 1960, p 85.

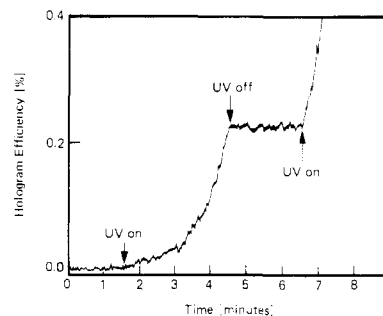


Figure 11. Growth curve of hologram diffraction efficiency for carbazole in PMMA.

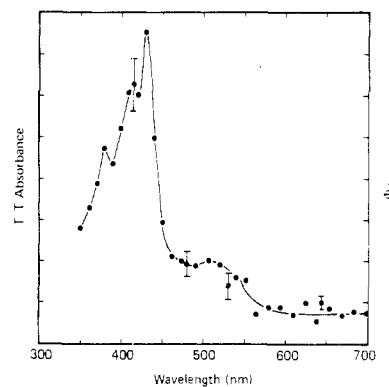


Figure 12. Triplet-triplet absorption spectrum of carbazole in PMMA at 77 K (solid line) and photochemical action spectrum from higher triplet state of carbazole/PMMA at room temperature (points with error bars).

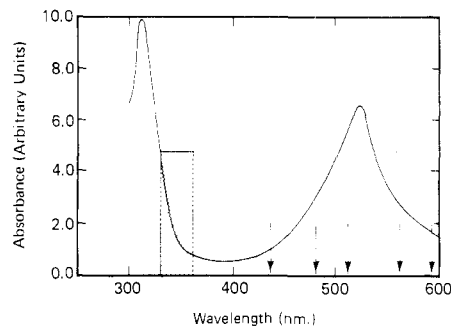


Figure 13. Triplet-triplet absorption spectrum of benzophenone in PMMA from ref 16. The arrows indicate wavelengths at which no higher triplet state reactivity was found.

the sample. Figure 11 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 eq 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 12, 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.⁷ 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.

With use of the holographic technique, the wavelength dependence of this photochemistry can be investigated. The results are summarized in Figure 13. 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.¹⁶

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. There are of course a variety of other circumstances in which the holographic technique may prove useful.

I am deeply indebted to all of my co-workers 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.

Chemical Applications of Picosecond Spectroscopy

E. F. HILINSKI and P. M. RENTZEPIS*

Bell Laboratories, Murray Hill, New Jersey 07974

Received July 12, 1982

Ever since the possibility of measuring the duration of light pulses emerging from mode-locked lasers existed, picosecond spectroscopy¹ has been developing as a field of science through which one may view fleeting elementary events. A powerful technique that permits direct observation of processes occurring in the range of 10^{-12} s has become an experimental reality. For understanding the physical and chemical changes that occur within a specific system, it is no longer necessary to probe the mechanism indirectly by frequently inconclusive kinetic arguments based upon chemical reactions. The primary events of most processes such as dissociation, photosynthesis, and polymerization, whose macroscopic significance are well realized, may be identified and understood by means of picosecond spectroscopy. Direct observation of intermediate species involved in chemical and biological processes and measurement of their formation and decay kinetics

can be made while the reaction proceeds by means of absorption, emission, and Raman picosecond spectroscopy.

The areas of chemistry, physics, and biology that have benefitted from picosecond studies are very large and continuously growing. The vast numbers of applications include studies of excited-state relaxation, cage effects, proton-transfer reactions, solvation of electrons, photosynthesis, vision, and nonlinear effects. This Account shall not even attempt to review this field of science but shall be restricted to some techniques and a few exemplary studies of chemical events that were performed primarily in our laboratories.

Experimental Methods

Picosecond laser systems in use today vary widely. Most commonly they are based on either solid-state oscillators, such as Nd^{3+} :silicate glass or Nd^{3+} :YAG, or synchronously pumped dye lasers. Each system possesses its own desirable features in terms of repetition rate, energy output, pulse width, and reliability. Nd^{3+} :YAG lasers, while producing pulses with a full width at half-maximum (FWHM) of ~ 20 – 40 ps, generate pulses with energy equal to that of a Nd^{3+} :glass oscillator but of narrower bandwidth (0.3 cm^{-1}) and permit repetition rates on the order of 10 Hz. Mode-locked dye lasers are capable of ~ 1 -ps pulses of low energy, which, in principle, can be tuned in wavelength over the range of the visible and ultraviolet spectrum,

Edwin Hilinski received his B.S. in Chemistry from Wilkes College. With Jerome Berson as his research advisor, he obtained his Ph.D. in 1982 from Yale University. Currently, he is a postdoctoral member of the technical staff at Bell Laboratories.

Peter M. Rentzepis is head of the Physical and Inorganic Chemistry Research Department at Bell Telephone Laboratories, Murray Hill, NJ. He is currently involved in picosecond spectroscopy research using lasers. Dr. Rentzepis holds over 25 patents and has published more than 200 articles. In addition to being affiliated with several universities as a visiting professor or advisor, he is editor of several technical journals and a fellow of the New York Academy of Science, the National Academy of Science, and the American Physical Society. He has been the recipient of three honorary doctorate degrees and has been accorded many awards, including the Scientist of the Year award in 1977 and the Peter Debye Award in Physical Chemistry in 1982.

(1) Rentzepis, P. M. *Chem. Phys. Lett.* 1968, 2, 37.