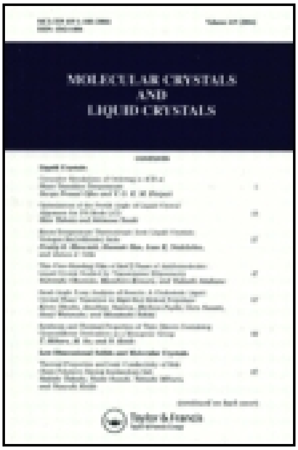

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HOLOGRAPHY AS A NEW TOOL FOR INVESTIGATING PHOTOCHEMICAL REACTIONS IN THE SOLID STATE

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In general holography[1] is known as a technique to produce a threedimensional picture which can be stored in a twodimensional photographic film. To do this an object wave, carrying all information about the object in its intensity and phase distribution, is overlapped with a reference wave at the surface of a photographic film (see Figure 1a). Since both waves are mutually coherent in space and time they produce an interference pattern. This interference pattern is impressed photochemically into the film. The photochemically stored interference pattern is called the hologram. If such a hologram is illuminated by the reference wave only (see Figure 1b) the stored interference fringes diffract part of the reference wave in such a way that an exact reconstruction of the object wave occurs. Since not only the intensity but also the phase of the object wave are reconstructed correctly a three-dimensional picture is reproduced. During the past decade the applications of holography[2] have increased strongly in-

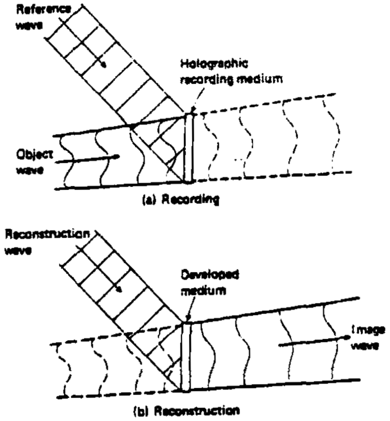

FIGURE 1. a) Writing and b) reading of a hologram.

cluding for example holographic interferometry, optical memories and holographic optical elements. In this article a new application will be described which uses the connection between the growth of a hologram and the photochemical impressed interference pattern to detect the photochemistry going on in the holographic film. The techniques[3-8] developed so far will be described shortly.

Developing holography as a new tool for investigating photochemical reactions it is reasonable to use one of the simplest holograms, i.e. a plane wave hologram in order to reduce complications. The construction of such a plane wave hologram is shown in Figure 2. Two coherent waves (reference and object wave) with equal intensity I_0 are overlapping at the holographic sample. Since both waves are plane waves the interference pattern is a simple modulation of the intensity I(x) in x-direction across the sample with a fringe distance Λ :

$$I(x) = 4 I_0 \cos^2 \left(\frac{\pi}{\Lambda} x\right) \qquad (1)$$

If the holographic sample contains a photochemically active material (as a solute in a polymer film or any other glassy or crystalline matrix), this material will react at the bright parts of the sample but not at the dark parts. Thus a spatial variation of the photochemical product formation P = f(x,t) occurs in which kinetic parameters are reflected in the additional time dependence f(t). This product formation changes the optical properties of the sample because the index of refraction n and the absorbance a of the product differ from those of the starting material. Therefore a modulation of the index of refraction and/or the absorbance is produced with an amplitude $n_1 = f(P)$ and/or $a_1 = f(P)$. In the first case we have a phase hologram whereas in the second case an amplitude hologram occurs. The formation of such holograms can be measured by the diffraction efficiency η :

$$\eta = \frac{I_1}{I_0} = f(n_1, a_1) = f(P) \qquad (2)$$

To obtain η , the hologram is illuminated only with the reference wave of intensity I_0, and the intensity I_1 of the beam deflected in the original direction of the object wave (reconstruction of the object wave by the hologram) is measured. According to Eq. (2) the ratio of both intensities gives the diffraction efficiency η . This has to be a function of n_1 and a_1, i.e. a function of the product formation. Therefore the observation of $\eta = f(t)$ should contain the kinetics of the photochemistry occurring in the holographic sample. A quantitative treatment[8] for a simple reaction, where A reacts photochemically to product P with an overall reaction rate k ($A \xrightarrow{k} P$) leads to the formula:

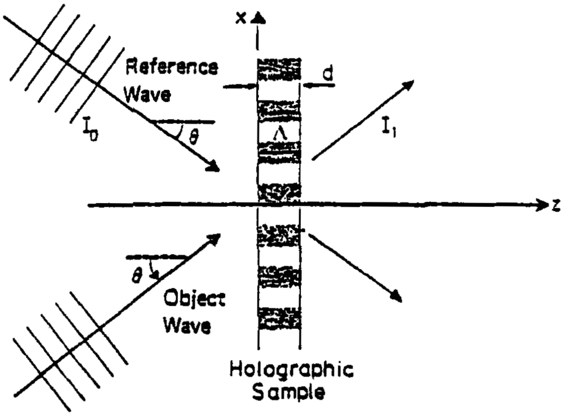

FIGURE 2. The hologram of two plane waves.

$$\eta = (F \cdot C)^2 \cdot k^2 \cdot t^2 \tag{3}$$

In Eq. (3) F and C are known constants. F contains all geometric parameters like the thickness d of the hologram, the wavelength λ and the angle of incidence Θ :

$$F = \frac{\pi \cdot d}{\lambda \cdot \cos\Theta} \tag{4}$$

whereas C contains the average index of refraction n, the starting concentration $C_A(0)$ of A and the change in molar refractivity ΔR_{AP} from A to P:

$$C = \frac{(n^2 + 2)^2}{6000\ n} \cdot \Delta R_{AP} \cdot C_A(0) \tag{5}$$

Since the values of F and C are known for a holographic sample the observation of $\eta = f(t)$ gives the overall rate constant k.

Experimentally[3-8] $\eta = f(t)$ is obtained with an apparatus shown in Figure 3. The light of an argon laser is split in a reference and object wave which produce the interference pattern at the sample. The formation of the hologram can be

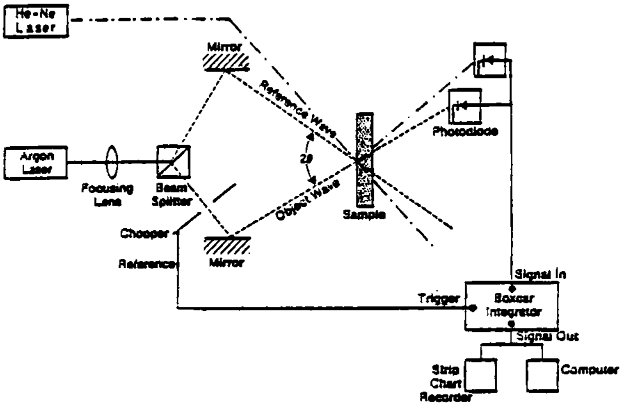

FIGURE 3. A schematic representation of the apparatus for the detection of holographic growth curves.

observed in two ways. First a helium neon laser can be used. If the light of this second laser strikes the sample at the correct Bragg angle it will be deflected by the hologram (plane wave hologram = holographic grating). The intensity of the deflected beam can be measured with a photodiode and electronically recorded. It is directly proportional to the diffraction efficiency η and shows the hologram growth as a function of time. Since normally the red light (633 nm) of the helium neon laser is not absorbed by the sample a pure phase hologram (a and a_1 = 0 at 633 nm) is observed. A second way of detection is to use the light of the argon laser itself. In this case a chopper is used in the object beam. When the chopper shuts the object beam only the reference wave strikes the sample. Then light of this wave is deflected into the direction of the object wave according to the formation of the hologram and can be detected with a photodiode which is connected to a boxcar integrator. The reference of the chopper opens the gate of the signal input of the boxcar integrator only during the dark periods of the object beam so that hologram growth (open period of the chopper) and hologram detection (closed period) follow each other with the frequency of the chopper. In this way hologram growth curves η = f(t) can be easily obtained as shown in Figure 4. According to Eq. (3) these curves show a quadratic time behaviour.

Each curve in Figure 4 is obtained for a special intensity. Taking $\sqrt{\eta}$ = f(t) gives for each curve and thus for each intensity I a separate overall rate constant k(I). In a steady

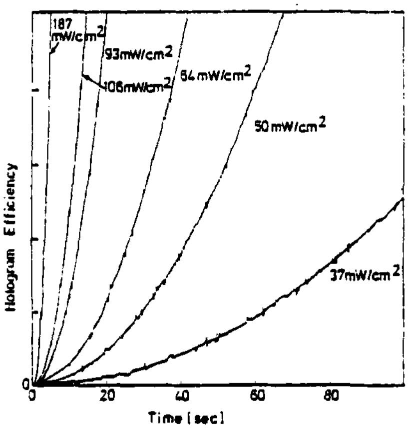

FIGURE 4. Hologram growth curves for different light intensities.

state approximation it can be easily shown that k is related to the intensity I according to

$$k = \xi \cdot I^r \qquad (6)$$

where r gives the number of the mechanistically necessary photons and ξ contains all the other interesting photophysical and photochemical constants. It can be shown[6,8] that for a one photon process (r = 1, left side of Figure 5)

$$\xi = 2303 \cdot \varepsilon_1 \cdot \phi_p \qquad (7)$$

ε_1 = extinction coefficient

ϕ_p = photochemical quantum yield

whereas for a two photon process (r = 2, right side of Figure 5)

$$\xi = (2303)^2 \cdot \varepsilon_1 \cdot \varepsilon_2 \cdot \tau_2 \cdot \phi_2 \cdot \phi_p \tag{8}$$

ε_1, ε_2 = extinction coeeficients for the two absorption steps

τ_2 = lifetime of the state A_2

ϕ_2 = quantum yield of population of A_2

ϕ_p = photochemical quantum yield

Since plotting lg k as a function of lg I gives r as the slope and lgξ as the intercept according to Eq. (6), it is possible to get out the photochemical quantum yield ϕ_p if one knows some simple photophysical parameters like the extinction coefficient ε_1 in the one-photon case. Thus r tells us something about the photophysical and photochemical reaction scheme (see Figure 5) whereas gives us a detailed value about the ratio of the photochemical step versus the

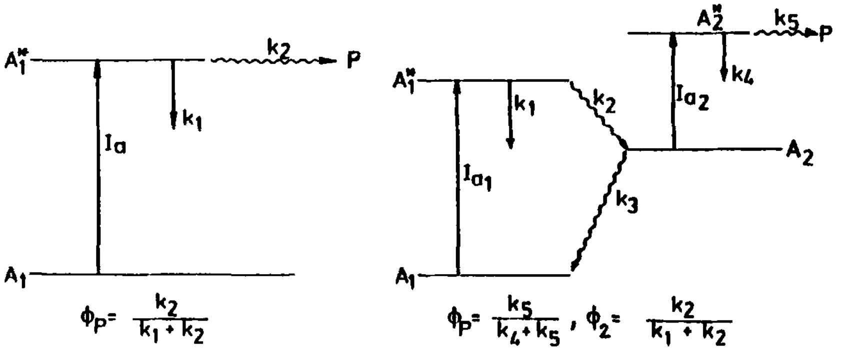

FIGURE 5. Energy-level schemes for one and two-photon processes.

photophysical relaxation. (Without a detailed description it shall only be mentioned here that holography with pulsed lasers[9] can give directly the rate constant for the photochemical step, e.g. k_2 for the one-photon process and k_5 for the two-photon process (see Figure 5), however not the quantum yield. Therefore both methods are complementary.) An extensive experimental study[8] has shown excellent agreement between values of r and ϕ_P determined by holography as compared to values determined by other methods like absorption spectroscopy. The summary at the end of this article will show the advantages of the holographic technique as compared to absorption spectroscopy.

Besides getting out information about r and ϕ it is also possible to distinguish under certain circumstances more complex reaction schemes[4,6] like consecutive and parallel reactions by the shape of the hologram growth curves. Here only one example shall be mentioned briefly. For benzophenone (BP) dissolved in a polymethylmethacrylate film the hologram growth curve shown in Figure 6 is observed.[4] There a hologram grows very fast from (1) to (2), then disappears (3) and grows again slowly (4). It is easy to show that the formation of the two holograms corresponds to two consecutive photoreactions as indicated in the figure. However, the question arises why the first hologram disappears, i.e. why the hologram formation is subtractive and not additive. To answer this question one has to investigate more thoroughly the mechanisms of hologram production. Figure 7 shows the

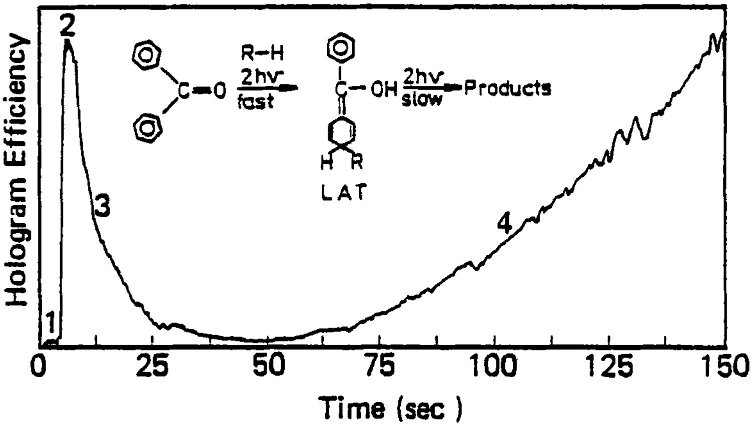

FIGURE 6. The hologram growth curve of benzophenone/polymethylmethycrylate.

change of the molar refractivity R as a function of wavelength for the three consecutive compounds of the reaction (BP, LAT = Light Absorbing Transient, Prod. = final product). If the reaction is observed with the argon laser lines around 350 nm a positive change of R occurs for the first reaction (BP ⟶ LAT) whereas a negative change follows when the second reaction (LAT ⟶ Prod.) starts to grow. The second reaction first cancels the amplitude modulation n_1 produced by the first reaction and then forms again such a modulation but in opposite direction. This corresponds to the cancellation of the first hologram and the formation of the second hologram. The correctness of this interpretation can be checked by the prediction that according to Figure 7 the observation of the hologram with e.g. the 488 nm line of an argon laser

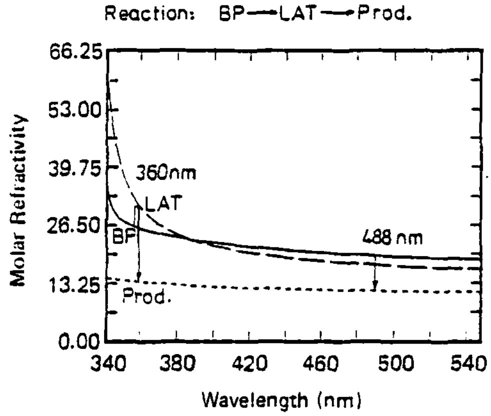

FIGURE 7. The molar refractivity as a function of wavelength for benzophenone (——), LAT (--) and the product (•••).

should result in an additive behaviour of the two holograms because the molar refractivity changes in the same direction throughout the reaction. Experimentally this prediction is verified. Knowing the correct interpretation of the shapes of hologram growth curves in correspondence to the underlying reaction scheme it is possible to develop a quantitative theory and make a computer simulation of the curves.[6] The result for such a calculation is shown in Figure 8 for a consecutive reaction observed at 350 nm (Figure 8a) and 488 nm (Figure 8b). The additive behaviour of a first small, but fast growing hologram and a second slowly growing hologram is seen very clearly in Figure 8b. In the interpretation of the shapes of hologram growth curves discussed so far only the contribution of the phase hologram was taken into account. This is a very good approximation because it can be shown[6] that for detection wavelengths in regions of not too strong absorption the contribution of the amplitude hologram can be neglected.

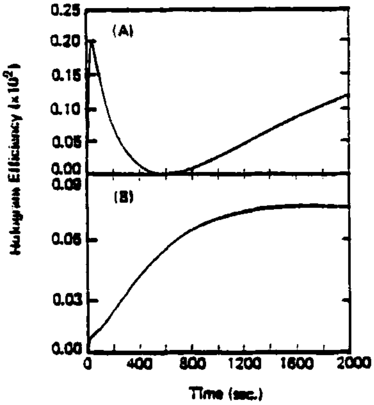

FIGURE 8. Calculated hologram growth curves for a consecutive reaction observed at a) 350 nm and b) 488 nm.

As a last example for the use of the holographic technique in photochemical investigations the separation of photochemical steps which are interweaved into each other shall be demonstrated. So for example in the case of the reaction of benzophenone to LAT a two-photon process was observed.[4] The first photon is used for the absorption $S_0 \longrightarrow S_1$ and the second photon for the absorption within the triplet system (see Figure 9). Here the question arises which of the higher triplet states does react to the LAT. Using in a continuous wave (cw) illumination UV-light for the $S_0 \longrightarrow S_1$ absorption

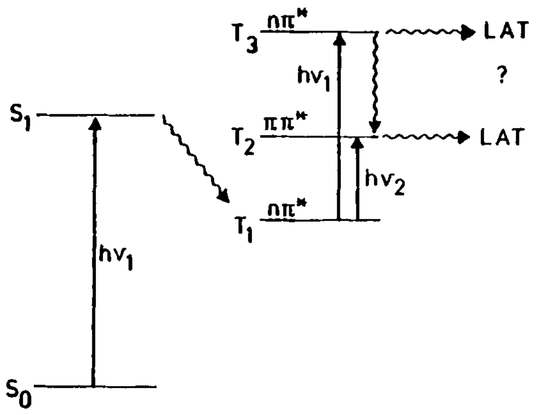

FIGURE 9. Reactive states of benzophenone ⟶ LAT.

this light will populate energetically high lying triplet states (e.g. T_3) and by relaxation lower lying triplet states (e.g. T_2). Thus a distinction between T_2 and T_3 as reactive states seems to be not possible in a cw-method because of the overwriting of the first absorption process with respect to the second. However if one uses for the first absorption step $S_0 \longrightarrow S_1$ incoherent light from e.g. a Hg-lamp and for the second absorption step two coherent beams as reference and object waves (see Figure 10) and changes the wavelength of these two beams in the range of the absorption $T_1 \longrightarrow T_2$ and $T_1 \longrightarrow T_3$ the production of a hologram at a special wavelength should indicate the reactive state. So a separation of the two different absorption processes is possible using incoherent light (not able to produce a hologram) for the one process and coherent light (showing a hologram in case of photochemistry) for the other process. It is obvious that in this way it is also possible to get a photoaction spectrum[5] of a short lived intermediate (excited state or chemical species) and indicate the reactive states of this intermediate.

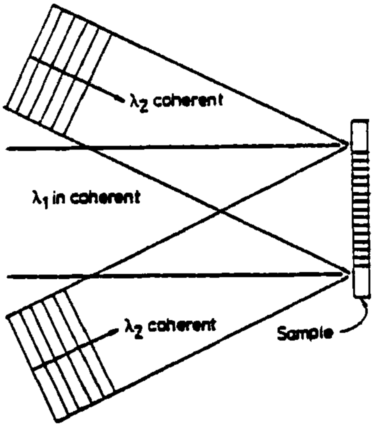

FIGURE 10. A three beam experiment using one incoherent and two coherent waves.

Making a summary some of the advantages and disadvantages of the holographic technique as compared to absorption spectroscopy shall be mentioned. 1) First of all the holographic technique is in contrast to the absorption spectroscopy a zero-background technique because the hologram grows out of the dark. Thus it has high sensitivity and high accuracy. 2) One has the free choice of the detection wavelength because one can detect the phase hologram and is therefore <u>not</u> restricted to the range of absorption. So one can do dispersion spectroscopy instead of absorption spectroscopy. This has the practical advantage that overlapping absorption bands do not prevent the investigation of the kinetics of a reaction and that complicated reaction schemes (e.g. $A \longrightarrow B \longrightarrow C$) can be observed at one wavelength and without interrupt even when the reaction compounds have different absorption spectra. Further the detection wavelength can be chosen in a spectral range where the detection system has high sensitivity. 3) One has the free choice of the intensity of the detection beam because in a pure phase hologram this beam is only deflected but not absorbed. Thus using very high power in the detection beam does not destroy the sample but gives high sensitivity in the detection. 4) The shape of a hologram growth curve can be related to the underlying reaction scheme and a computer modelling can help to prove the reaction mechanism. 5) The observation of a photoaction spectrum is possible, i.e. a differentation between the absorption spectrum of an intermediate and the wavelengths which convert this intermediate to photochemical products.

The disadvantages of the holographic technique are 1) that lasers are expensive and 2) that an identification of the photoproducts is not possible so far. Because of characteristic absorption bands for different compounds an identification of photoproducts with absorption spectroscopy can be done in some cases.

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