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A New Class of Materials for Holography in the Infrared

A new class of holographic materials is described. These materials undergo four-level two-photon photochemistry. The holograms recorded in these materials are self-developing and are not erased during reading. Furthermore, the recording process may be gated off and on by using an auxiliary incoherent light source. As a specific example of such a system, holograms formed using samples of an α-diketone dissolved in poly(cyanoacrylate) are described. Gated holograms have been recorded in this material at 752 and 1064 nm.

Introduction

It is well known that coherent optical wavefronts can be recorded and later reconstructed by the technique of holography [1]. In the most general case, as illustrated in Fig. 1(a), the hologram of a complicated object wave is formed by recording the interference pattern created between this wave and a reference wave. The object and reference wave must be mutually coherent both spatially and temporally in order to provide an interference pattern that is stationary during the recording period. The stationary interference pattern is impressed in a photosensitive recording medium as a modulation of the absorption and/or index of refraction to form a hologram. If the hologram is illuminated by a reconstruction wave that is identical to the original reference wave [see Fig. 1(b)], the recorded fringes will diffract a portion of the reconstruction wave to form an image wave that is an exact replica of the original object wave.

Holograms can be used in a variety of applications. One can rely on the sensitivity of the interference pattern to small spatial variations in an object wave to provide a means of measuring small dimensional changes in an object of interest. At present this technique, known as holographic interferometry, is perhaps the most widely used holographic technique [2]. A great amount of effort has gone into the assessment of the potential usefulness of holograms in optical memories [3]. In this application, holograms containing binary information are produced in a two- or three-dimensional spatial array. To date, the promise of holographic optical memories has, however, exceeded their performance.

Perhaps in the future holograms will be most widely used for the production of a variety of kinds of optical elements for the deflection and focusing of light. Holographic optical elements (HOEs) utilize the fact that a hologram is capable of transforming a family of incident waves. The simplest example of a HOE is the holographic grating formed by the interference of plane object and reference waves. Another example is the holographic lens that is formed by the interference of a spherical object wave with a spherical or plane reference wave. Figure 1(c) shows the recording geometry for the production of an off-axis holographic lens. The properties and application of HOEs have been the subject of several recent reviews [4–6]. HOEs have so far found applications as diffraction gratings [7], visual displays involving overlapping scenes [4], laser light deflector/scanners [8], in the correction of optical system aberration [9], and in the simulation of optical system performance [10]. In addition, HOEs are currently being considered for applications requiring matched optical elements, and for use as continuously variable dichroic beamsplitters, light-weight laser upcollimators, integrated optics input/output couplers

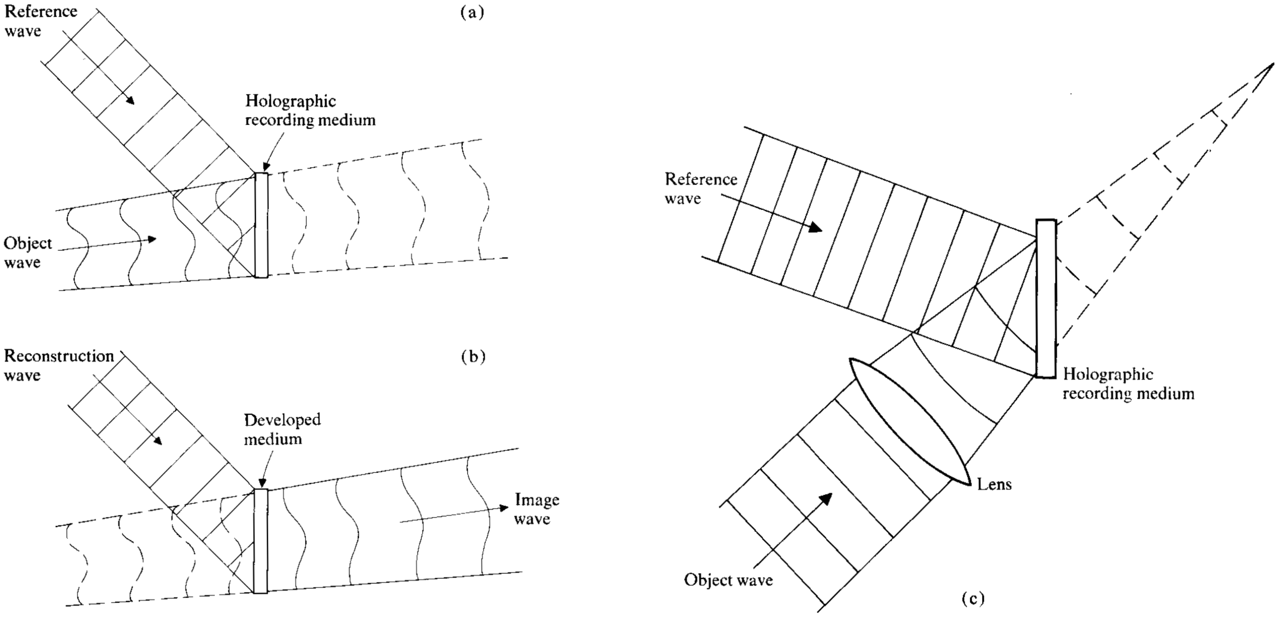

Figure 1 Schematic representations of holographic (a) recording and (b) reconstruction procedures, and (c) the arrangement of the coherent light waves necessary to record the holographic image of a lens.

with focusing properties, and wavefront-correcting elements directly matched to individual laser sources.

Because the image quality and diffraction efficiency can rapidly degrade as the reconstruction wavelength departs from the wavelength of the original object and reference waves, HOEs, optical memories, and holographic interferometers have narrow spectral bandwidths. Thus, holograms are most useful with laser reading and writing sources, but their use is restricted to wavelength regions where currently available holographic materials have response. This constraint sharply limits the number of possible laser sources that can be used directly. A variety of holographic recording materials have been considered [11, 12]. One of the best and most widely used holographic recording materials currently available is dichromated gelatin [5, 13]. Holograms cannot be produced in dichromated gelatin at wavelengths longer than 550 nm. Responses to wavelengths as long as 748 nm have been obtained using recording material with less desirable properties, such as Kodak 649F or 120-01 photographic film [14]. Attempts to spectrally sensitize dichromated gelatin or holographic-quality photographic film to longer wavelengths have so far produced unsatisfactory results. At present, no single-photon volume holographic recording material with response to wavelengths longer than 750 nm exists. Thus, holograms cannot be directly fabricated for use with important longer-wavelengths lasers such as GaAlAs (800–850 nm), Nd:YAG or Nd:glass (1.06 μm), or GaInAsP (1.2–1.6 μm).

In this paper we discuss a new technique involving *four-level two-photon photochemistry* [15] for the production of holograms in the red and infrared. We illustrate the technique by describing a new class of materials in which it is possible to record holograms directly in the wavelength region beyond 1 μm [16]. These materials also have the advantage that, unlike dichromated gelatin and silver halide films, they are self-developing and require no fixing step. Furthermore, the hologram formation can be gated off and on by utilizing an auxiliary light source.

This new class of holographic recording materials opens up the possibility of many interesting applications. HOE upcollimators and wavefront correctors matched to individual GaAlAs and GaInAsP lasers would be useful for the production of small and lightweight all-solid-state laser sources with beams of diffraction-limited quality. Applications would be for laser scanning, integrated optics, and coupling light into or out of optical fibers. HOEs for Nd lasers would make possible the production of lightweight upcollimators, dichroic beamsplitters, aberration correctors for optical systems, and efficient light collectors. In the remainder of this paper, we first discuss the concept of four-level two-photon photochemistry, and then illustrate the concept with specific experimental examples, α-diketones in cyanoacrylate polymers.

Four-level two-photon photochemistry

By far the largest number of holographic recording materials are linear in laser light intensity [11, 12]; *i.e.*, the rate of the photochemical process responsible for recording the hologram has a linear dependence on light intensity. An energy-level diagram for such a system is shown in Fig. 2(a). In such a system, a molecule in its ground state (denoted A_1) absorbs a photon and is converted to an excited state A_2 from which photochemistry occurs with a quantum yield ϕ. If σ is the absorption cross section for the process $A_1 \rightarrow A_2$ and I (W/cm^2) is the exciting light intensity, the rate of production of photochemical products (s^{-1}) is given by

$$W = \phi\sigma I/\hbar\omega \tag{1}$$

and is linear in I as previously indicated; ω is the frequency of the writing beam (rad/s).

Now consider using such a linear one-photon medium for holographic recording. The spatial variations in light intensity are impressed on the holographic medium as corresponding spatial variations in the absorption coefficient and/or index of refraction as a result of the photochemistry. The reconstruction wave is then diffracted during the reading process by this recorded interference pattern to form a replica of the object wave (see Fig. 1). If, however, as will generally be desirable, the reading light source is at the same wavelength as the writing source, the reading source can also produce photochemistry and this photochemistry will result in gradual erasure of the hologram. This is indeed an undesirable situation, and there are two ways of eliminating or minimizing the effect of erasure during reading for one-photon materials. The first and less satisfactory method is simply to reduce the reading light intensity so that the photochemistry that occurs during reading is reduced to an acceptable level. This is difficult to do, particularly in those cases where the hologram is meant to be semi-permanent, as for example in a HOE. The most commonly used method of eliminating erasure is to fix the holographic image permanently. This is done in dichromated gelatin and silver halide films by wet chemical processes.

Another disadvantage of one-photon materials arises when one considers extending their sensitivity into the red and infrared regions. All of the energy used to produce the photochemistry necessary to record the hologram is provided by the absorbed photon. Very few systems undergo efficient photochemistry in the red or infrared, and those few systems that do also tend to be thermally unstable.

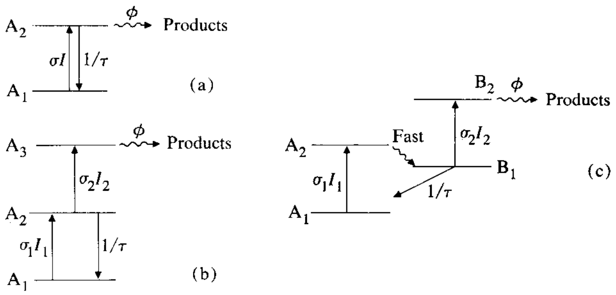

Figure 2 (a) A two-level one-photon energy-level scheme. (b) A three-level two-photon energy-level scheme. (c) A four-level two-photon energy-level scheme.

It has been recognized by previous workers that many of the problems with one-photon systems are either not present or are significantly reduced in importance when the hologram-forming photochemical process is nonlinear in I, *i.e.*, when the absorption of two or more photons is involved [17, 18]. Such a multi-photon system is illustrated by the three-level scheme shown in Fig. 2(b). In a three-level system, the recording medium is simultaneously exposed to radiation at two different optical frequencies, ω_1 and ω_2, with respective intensities I_1 and I_2. In this case, the steady-state rate for low laser powers is given by

$$W = \phi\tau \frac{\sigma_1 I_1}{\hbar\omega_1} \frac{\sigma_2 I_2}{\hbar\omega_2}, \tag{2}$$

where τ is the lifetime of the intermediate level A_2. The recording process has a low energy threshold $\hbar\omega_{th}$. For total photon energies $(\hbar\omega_1 + \hbar\omega_2)$ less than this threshold, no photochemical reaction can occur. If the optical frequencies are chosen so that $\omega_1 + \omega_2 > \omega_{th}$, $\omega_1 > \omega_{th}/2$, and $\omega_2 < \omega_{th}/2$, the recording process can be initiated by the simultaneous absorption of an ω_1 or ω_2 photon (Case I) or by the absorption of two ω_1 photons (Case II). The absorption of two ω_2 photons, being below threshold, has no effect. In Case I, the rate of the photochemistry according to Eq. (2) is proportional to I_1I_2, while for Case II, it is proportional to I_1^2.

Case II two-photon holograms would be recorded in the same fashion as are one-photon holograms (see Fig. 1). Holographic materials of this type would have two advantages over one-photon materials. First, since the photochemistry is proportional to I_1^2, any reduction in the laser intensity during reading would have its effect on hologram erasure reduced by the square of this factor. Second, since the energy to produce photochemistry is now supplied by two laser photons, it might be possible to find thermally stable two-photon photochemical systems that could be used with red or infrared radiation.

Two-photon holographic recording media corresponding to Case I are perhaps even more interesting. A typical geometry for recording in this case is shown in Fig. 3. The recording medium is illuminated by reference and object beams at frequency ω_2, as well as by an additional uniform beam at frequency ω_1. The ω_2 source must be coherent, while an incoherent source can be utilized to provide the ω_1 radiation. The intensity modulation of the ω_2 field in the recording medium is created by the interference of the object

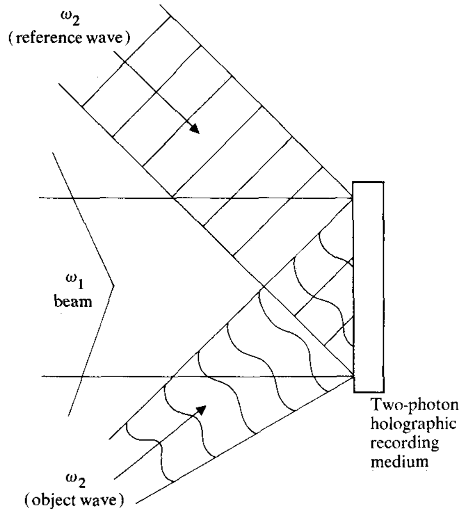

Figure 3 Schematic representation of the holographic recording process for a two-photon recording medium.

and reference beams. Since the rate of this process is proportional to $I_1 I_2$ and since I_1 is uniform, the fringe pattern of the ω_2 field will be linearly recorded. Reconstruction of the holographic image is accomplished by illuminating the hologram with a single beam of ω_2 radiation identical to the original reference wave.

HOEs formed by this type of two-photon recording have several advantageous properties. Like the Case II materials, these materials can be written with red or infrared lasers. Most of the energy needed to produce photochemistry can be supplied by the ω_1 photons which can be in the ultraviolet (uv). Another important advantage is that the recording medium is sensitive to the ω_2 radiation only when ω_1 radiation is present. Thus, during the reconstruction of the image for readout, when the HOE is illuminated only by ω_2 radiation, no additional deleterious exposure of the recording medium takes place. Also, temporal or spatial gating of the HOE recording can be achieved by masking or modulating the ω_1 beam.

The first demonstrations of two-photon holographic recording were in $LiNbO_3$ and KTN ($KTa_xNb_{1-x}O_3$), where the recording process was the multi-photon photorefractive effect [17, 18]. The basis of this effect involves the excitation of carriers within the crystal lattice to produce a macroscopic polarization change that induces a modulation of the index of refraction via the electro-optic effect. The formation of HOEs for integrated optics by two-photon holography in out-diffused $LiNbO_3$ waveguides has been demonstrated [19]. The major disadvantage of $LiNbO_3$ and KTN media is the lack of real intermediate energy levels between the ground and final states. Since the resonant enhancement from these intermediate levels is not present, the two-photon absorption processes are extremely weak, and peak exposure intensities greater than 5 MW/cm^2 are necessary. Thus, in order to produce HOEs with 1-cm dimensions, high-power pulsed lasers are necessary. A factor-of-100 improvement in the sensitivity was demonstrated by doping the $LiNbO_3$ crystal with Cr^{+3}, thereby converting the intermediate level [A_2 in Fig. 2(b)] from a virtual to a real level with a 500-ns lifetime [20]. The resulting sensitivity, however, was still several orders of magnitude too low for cw two-photon holography.

The limitations of three-level two-photon systems, represented by Fig. 2(b), can be seen by considering the role played by the intermediate state A_2 and by a closer look at Eq. (2). For optimum production of photochemical products, one wants the population of the state A_2 to be as large as possible. This means that the absorption cross section σ_1 should be large and the lifetime of this state τ should be long. However, σ_1 and τ are not independent quantities. The largest value that τ may have is its radiative value τ_{rad}, *i.e.*, its value when there are no additional nonradiative processes to deplete the intermediate level;

$$\tau = \tau_{\text{rad}} = \frac{m}{e^2}\frac{c^3}{2\omega_1^2}\frac{1}{f} = \frac{5.33 \times 10^{22}}{\omega_1^2 f}, \tag{3}$$

where f is the oscillator strength for the transition between the ground state and intermediate level, m and e are the electron mass and charge, and c is the velocity of light all in CGS units, and ω is in units of rad/s. The oscillator strength and the absorption cross section are related to each other in the following way:

$$\sigma_1 = \frac{e^2}{m}\frac{4\pi}{c}\frac{f}{\Delta\omega} = 1.06 \times 10^{-1}\frac{f}{\Delta\omega}, \tag{4}$$

where $\Delta\omega$ is the width of the intermediate level. Combining Eqs. (3) and (4) we obtain

$$(\sigma_1\tau)_{\max} = \frac{2\pi c^2}{\omega_1^2\Delta\omega} = \frac{5.65 \times 10^{21}}{\omega_1^2\Delta\omega}. \tag{5}$$

Thus, there is an upper limit placed on the rate W that can be obtained for a three-level two-photon system. This limit occurs because the intermediate level A_2 must perform two not-completely-compatible functions. There is only a limited extent to which the requirements for both σ and τ to be large can be met. For typical solid state systems, $\omega_1 \approx 5 \times 10^{15}$ rad/s, $\Delta\omega \approx 1 \times 10^4$ rad/s, and thus $(\sigma_1\tau)_{\max}$ is on the order of 2.3×10^{-28} cm^2/s.

To produce nonlinear holographic systems that can be used with cw laser sources, one must circumvent the constraints expressed by Eq. (5). One way of doing this is illustrated in Fig. 2(c). Here we use a *two-photon four-level* *system.* There are now two intermediate levels A_2 and B_1. Level A_2 may have a large oscillator strength with respect to transitions from the ground state, while level B_1 may have a long lifetime. Thus, for this type of energy level structure, τ and σ_1 are free parameters, and it is possible to find both two-photon four-level systems with which one can produce holograms using only a few milliwatts of cw laser power and an improvement of 10^6 in the sensitivity.

A variety of organic molecules have energy-level systems arranged as shown in Fig. 2(c). States A_1 and A_2 in general are the lowest ground state and an excited singlet state of the molecule, respectively; B_1 may represent an isomeric form of the original molecule produced by a distortion of the excited singlet state. The isomer then undergoes irreversible photochemistry when excited to B_2. If a second photon is not absorbed during the lifetime of B_1, the system returns to the ground state A_1. The photochemistry of the substituted tetrazines is believed to occur in this way, and tetrazines embedded in polymer matrices have been used to produce nonlinear holograms [21]. The energy levels B_1 and B_2 may also represent excited triplet states. In systems of this type, the molecule undergoes irreversible photochemistry from a higher triplet state B_2. Holographic materials of this type have been produced using benzophenone [22] and carbazole [15] as the photochemically active molecules.

For the remainder of this paper we describe experiments on four-level two-photon holographic systems based on the photochemistry of α-diketones dissolved in various α-cyanoacrylate polymers. In these systems, it is possible to record holograms at wavelengths beyond 1 μm. Although both the α-diketones [23] and cyanoacrylate polymers [24] have been used as holographic materials, they have not previously been used as two-photon holographic materials.

Experimental details

- *Samples and sample preparation*

A variety of combinations of α-diketones dissolved in alkyl-α-cyanoacrylates were used in this investigation. The systems studied are listed in Table 1. For convenience, a particular system, *e.g.*, biacetyl in poly(methyl-α-cyanoacrylate), will be represented as BA/Me-CAc.

Two sources of monomeric α-cyanoacrylates were used. By far the largest amount of work was done with cyanoacrylate obtained from the commercial adhesive Krazy Glue®. Analysis of this material by gas-phase liquid chromatography (glc) revealed it to be primarily ethyl-α-cyanoacrylate (Et-CAc), probably with small amounts of acidic stabilizers, polymerization inhibitors, and plasticizers. Before use, the Krazy Glue was vacuum distilled over SO_2. This *distilled* cyanoacrylate is referred to in Table 1 as CAc. The pure methyl (Me-), ethyl (Et-), and iso-butyl (ISB-) cyanoacrylates were obtained from Polyscience and used without further purification. The biacetyl (BA) was obtained from Fluka AG (*puriss.*) and kept refrigerated until needed. The camphorquinone (CQ), obtained from Eastman Chemical Co., was recrystallized from hexane and sublimed before use. Benzil (BE) from Matheson, Coleman & Bell was used without further purification.

Table 1 Diketone/poly(cyanoacrylate) combinations used.

	CAc	*Me-CAc*	*Et-CAc*	*Isb-CAc*	*PMMA*
Biacetyl (BA)	X	X	X	X	X
Camphorquinone (CQ)	X				
Benzil (BE)	X				

CAc = cyanoacrylate, Me = methyl, Et = ethyl, Isb = Isobutyl, and PMMA = poly(methyl methacrylate)—degassed.

To show that the presence of dissolved oxygen in the samples was not an important factor in the photochemistry necessary to produce the holograms, and to demonstrate holographic growth in polymer hosts other than the poly(cyanoacrylates), a degassed BA/poly(methyl methacrylate) (PMMA) sample was prepared. The sample was prepared by dissolving BA in methyl methacrylate monomer and then degassing the solution by successive freeze-pump-thaw cycles. The degassed sample was then sealed under vacuum and polymerized by heating at 60°C for several days. No qualitative differences were observed between this BA/PMMA sample and the other samples used.

The major reason for choosing cyanoacrylate polymers over other polymeric hosts was the ease with which samples of good optical quality can be prepared from these polymers. This fact has previously been noted by Friesem *et al.* [24]. These workers used poly(methyl-α-cyanoacrylate) sensitized with p-benzoquinone to produce efficient linear holograms. The α-cyanoacrylate monomers undergo rapid anion-initiated polymerization when squeezed between two surfaces. In the present work, solutions of guest α-diketones in the cyanoacrylate monomer were squeezed between two glass microscope slides with spacers $\approx$200 μm thick. The polymerization begins immediately after squeezing. Samples with an area of $\approx$5 cm^2 and of excellent optical quality could be prepared in this way.

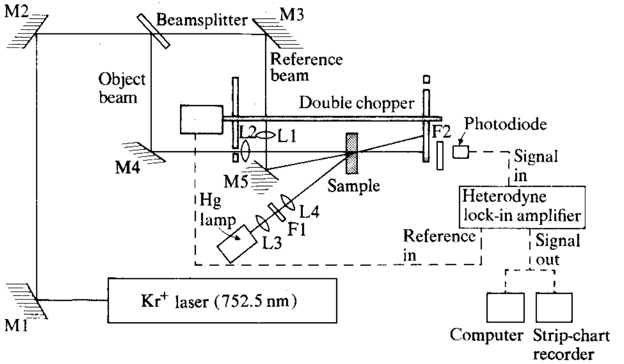

Figure 4 Diagram of the experimental apparatus used to record four-level two-photon holograms. M1–5 are mirrors, L1–4 are lenses, F1 is either a 7-54 or 5-60 Corning glass filter, and F2 is a 2-64 filter. The solid line indicates the light path and the dashed line the electrical path.

- *Apparatus*

A typical experimental arrangement used in this work is shown in Fig. 4. The first photon ω_1 was supplied by a 200-W Hg lamp. Corning glass filters [7-54 (240–400 nm) and 5-60 (350–500 nm)] were used to restrict the wavelength of ω_1. When used in conjunction with the glass microscope slides, the actual sample was not exposed to radiation of wavelength $\lesssim$300 nm. The power density of the Hg lamp at the sample, not including absorption by the microscope slide, was 1.02 W/cm^2 when the 7-54 filter was used and 1.75 W/cm^2 when the 5-60 filter was used.

In most of the experiments described here, the second photon ω_2 was provided by a Kr$^+$ laser at 752.5 nm. The laser beam was tightly focused at the sample and the power density normally used was 96 W/cm^2. Holograms have also been obtained with laser power densities as low as 1.6 W/cm^2.

The beam from the Kr$^+$ laser is split into two beams, an object and reference beam, of approximately the same intensity. The two beams are recombined at the sample at an interference angle of about 10 mrad. The object beam is periodically turned off and on by a double chopper. The reference beam continuously illuminates the sample. When the object beam is blocked, the second chopper wheel is open, allowing the photodiode to detect the light from the hologram that is being read by the reference beam. Both choppers are open or closed 50% of the time. The Hg lamp continuously illuminates the sample. The electrical signal from the photodiode is amplified by a heterodyne lock-in amplifier. The amplifier detects only those signals that are at the same frequency as the light chopper. The signal from the amplifier is then either digitized and recorded in an IBM Series/1 computer or displayed on a strip chart recorder.

In one set of experiments the Kr$^+$ laser was replaced by a pulsed Nd:YAG laser. In these experiments the holograms were recorded at 1064 nm. The laser had a 10-Hz pulse rate and was focused to a spot size of $\approx$8 mm^2. The average laser power was 42.8 mW. A small HeNe laser was used to make the hologram visible to the naked eye.

Holograms that make use of α-diketones in poly(cyanoacrylate)

- *α-diketone energy-level structure and photochemistry*

The α-diketones seemed to be good candidates to undergo four-level two-photon photochemistry, for a variety of reasons. First, as for most ketones, the intersystem crossing from the first excited singlet state S_1 to the lowest triplet state T_1 is fast and results in the observation of room-temperature phosphorescence in many α-diketones [25]. Second, the lifetime of T_1, which is an important parameter in the rate of the two-photon photochemistry [see Eq. (2)], is on the order of 1 ms in the α-diketones [26]. Finally, the triplet-triplet absorption spectrum, corresponding to the second step in Fig. 2(c), has a broad band in the 600–1100-nm wavelength region [27]. This is an ideal range for a holographic medium to be used with GaAs- or Nd-type lasers. In Fig. 5, Curves 1–3 show the absorption spectra of the three α-diketones studied. Curves 1 and 4 provide a comparison between the $S_0 \rightarrow S_n$ absorption spectrum for Step I in the process outlined in Fig. 2(c), and the $T_1 \rightarrow T_n$ absorption spectrum for Step II. The spectrum shown in Curve 4 is that of biacetyl, but corresponding spectra, at least for camphorquinone, are similar [27].

In environments with a suitably abstractable hydrogen [25], α-diketones undergo hydrogen abstraction reactions from their lowest triplet states. It is presumably this reaction from T_1 that is used to form one-photon holograms in these materials [23]. In the present multi-photon case, this reaction from T_1 is an undesirable side reaction. For use as a four-level two-photon system, it is necessary for the system to undergo reaction from a higher triplet state T_n. As we shall see, a reaction does occur from T_n, although at present we are unable to say what the reaction is. In fact, one of the useful features of these holographic investigations is the fundamental information one can obtain about photochemical reaction mechanisms [28]. We hope in the future to use the holographic technique to investigate details of reactions of α-diketones from higher triplet states.

- *Two-photon holograms*

A clear confirmation that a given hologram is growing by the stepwise absorption of two laser photons is the observation of gating. To observe gating, the holographic sample is simultaneously illuminated by an incoherent broadband Hg lamp. The uv light from the Hg lamp excites the diketone to its S_1 state, which is then rapidly converted to the T_1 state by intersystem crossing. Even if photochemistry does occur as a result of this initial excitation, no hologram can be produced from this single incoherent illumination source. The hologram is produced by the interference of two coherent beams at 752 nm that cause a spatially modulated excitation of the $T_1 \rightarrow T_n$ transition. This 752-nm radiation is not absorbed by the α-diketone molecule in its ground state. Hologram growth can thus only occur when the uv source is on.

The bold-lined curve in Fig. 6 shows the gating of the hologram growth in a 200-μm-thick sample of 15% (by weight) BA/CAc. The uv light is from a 200-W Hg lamp with a 7-54 Corning filter with a power density of 1.02 W/cm^2. Initially the efficiency η of the hologram, *i.e.*, the intensity of the light deflected into the hologram divided by the incident light intensity, is zero even though the sample is irradiated by the interfering 752-nm beams. After 8 min the uv lamp is turned on and the hologram begins to grow. When the uv lamp is again turned off, hologram growth stops. As the figure shows, this cycle can be repeated several times. The hologram efficiency has been followed with the uv source off for up to 14 h with no measurable change in efficiency. This is expected since the ir light used to read the hologram (752-nm line of a Kr$^+$ laser at 96 W/cm^2) is not absorbed by the sample and thus has little effect on it. Gating curves such as this were obtained with CQ, BE, and BA in all of the hosts indicated in Table 1.

If the 5% BA/CAc sample used for the lighter-line curve in Fig. 6 was pressed between glass plates as described in the previous section and allowed to stand for over 24 h before use, somewhat different results were obtained than with fresh CAc samples. In the figure the growth of a BA/CAc sample one half hour old is shown. Hologram growth continues, albeit at a reduced rate, even when the uv light is off. In fact, the hologram growth continues when the 752-nm beams are also off. This self-enhancement effect has been previously reported for cyanoacrylate systems in which p-benzoquinone was the photochemically active species and in which a single-photon mechanism [Fig. 2(a)] was operative [24]. Friesem *et al.* [24] attribute this self-enhancement to a cross-linking reaction between the benzoquinone and the host polymer chains. This explanation has recently been criticized by Tomlinson and Chandross [12], who point out that the results are also consistent with a photon-induced residual polymerization. The polymerization is induced by the benzoquinone photochemistry but continues in the dark.

Residual polymerization also explains our results, as can be seen from Fig. 7(a). Here, the maximum efficiency $\eta_{\max}$ of a hologram produced t hours after the sample was prepared is plotted as a function of t. Typically, one observes an initial period of time within which no hologram forms, followed by

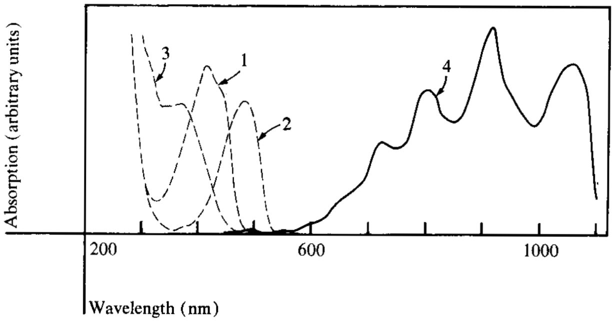

Figure 5 Absorption spectra of 15% BA/CAc (Curve 1), 15% CQ/CAc (Curve 2), 15% BE/CAc (Curve 3); all samples 200 μm thick. Curve 4 shows the $T_1 \rightarrow S_n$ absorption spectrum of biacetyl (3.9×10^{-2} mole/liter solution in carbon tetrachloride [27]).

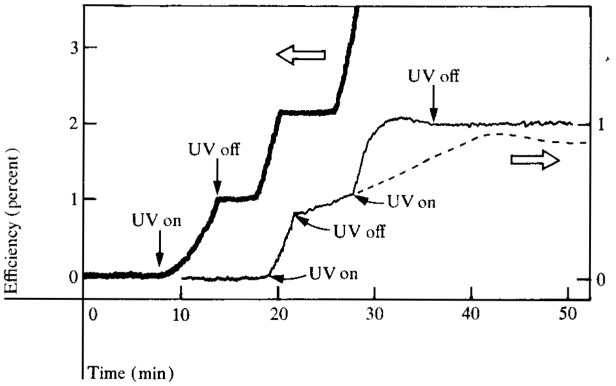

Figure 6 Bold-line curve: Gating of a hologram in a 200-μm 15% BA/CAc sample used 12 h after preparation; see text for details. Lighter-line curve: A hologram grown in 5% BA/CAc under the conditions specified for the 15% BA/CAc sample, except that this sample was used only 30 min after preparation. The dotted line represents the course of the self-enhancement reaction in the dark.

a steep rise to $\eta_{\max}$, and finally a small leveling off to a constant value. The initial period reflects the fact that polymerization of the host must proceed to the point where the sample viscosity is high enough to sustain a spatial record of the hologram before any hologram can be observed. After the induction period, hologram formation occurs as a result of two mechanisms. First, the reaction of the diketone itself causes changes in the sample absorption and index of refraction that lead to hologram formation. Second, the products of this initial photochemistry can induce additional host polymerization. For samples used less than ten hours after preparation, both processes can occur and one observes self-enhancement, as was the case in the 30-min sample (lighter-line curve) of Fig. 6. For older samples, the second process becomes less and less important

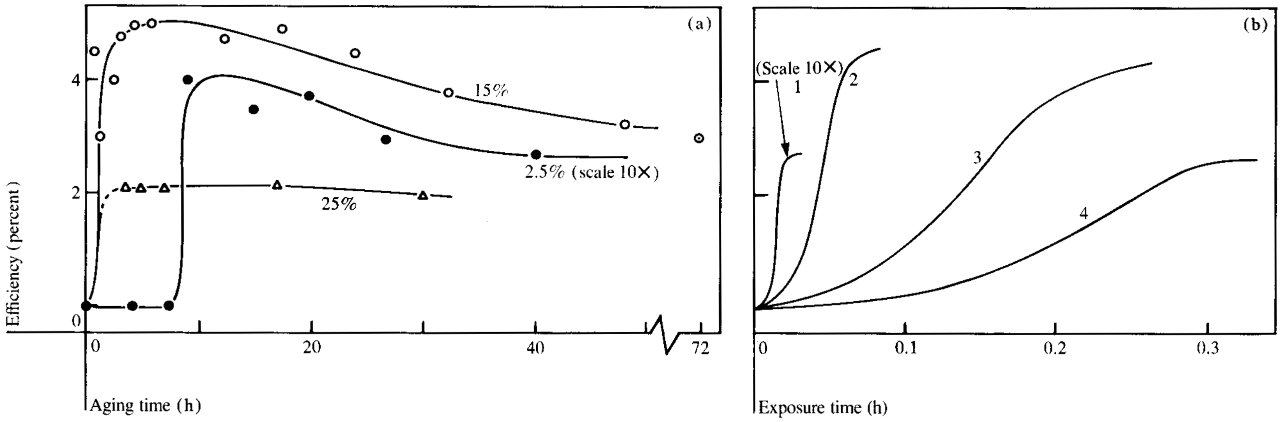

Figure 7 (a) Maximum hologram efficiency $\eta_{\max}$ as a function of age t for various concentrations of BA in CAc: ○, 15%; ●, 2.5%; △, 25%. The laser conditions were the same as specified in Fig. 6. All samples were 200 μm thick and $\geq$24 h old. (b) Typical curves of hologram efficiency η *vs.* photon flux for various concentrations of BA in CAc: Curve 1 (2.5%), Curve 2 (7.5%), Curve 3 (15%), Curve 4 (25%). The laser conditions were the same as specified in Fig. 6. All samples were 200 μm thick and 24 h old.

Table 2 Maximum efficiency $\eta_{\max}$ and normalized growth rate b/b_0 for various diketones in poly(α-cyanoacrylate).

	η_{max} (%)	b/b_0^*
15% BA/CAc	1.000	
15% CA/CAc	0.008	0.033
15% BE/CAc	—	0.01

*b_0 is the value of b for 15% BA/CAc.

as the cyanoacrylate host approaches complete polymerization. One thus observes no self-enhancement and a smaller maximum efficiency. These results are not consistent with the cross-linking model of Friesem *et al.* [24]. If cross-linking were responsible for self-enhancement of the hologram, it should be observed independently of the age of the sample. We should point out, however, that our α-diketone/poly(cyanoacrylate) system is not the same as that investigated by Friesem *et al.*, who used p-benzoquinone, and it is possible that the photochemistry involved is different from that of the α-diketones in the polymer host.

As a means of increasing the efficiency of holograms produced in cyanoacrylate polymers, this self-enhancement effect might be useful. However, it has the disadvantage in practice of requiring the holographic material to be prepared within 10 h of use. In the remainder of this paper we describe experiments performed on samples used more than 24 h after preparation that did not show self-enhancement.

The maximum hologram efficiency obtained in these four-level two-photon systems, 11%, was for a 800-μm-thick 20% BA/CAc sample. At 752 nm the lowest ir laser power density used was 1.6 W/cm^2 (1 mW in each of the two beams). Gating was also demonstrated at this power. Since the hologram efficiency in the present case grows with time t [28],

$$\eta = bI_1I_2t^2, \tag{6}$$

where b is a proportionality constant and I_1 and I_2 are the intensities of the gating beam and ir source, respectively, it is, of course, useful to use as high a laser intensity as possible to reduce the time necessary for experiments.

A comparison of $\eta_{\max}$ and normalized growth rate b/b_0 for CA, BE, and BA is shown in Table 2. All measurements were made under identical conditions. Clearly BA/CAc has a much higher $\eta_{\max}$ and b/b_0. For this reason, the BA/CAc system was used for the remainder of the experiments reported here. In Fig. 7(b) typical holographic growth curves for BA/CAc samples of various concentrations are shown. In all cases the initial growth is quadratic, as expected from Eq. (6). Eventually, the holographic efficiency reaches a maximum value as the BA begins to be depleted as a result of the photochemistry.

The $\eta_{\max}$ obtainable for a given concentration should increase as the diketone concentration is increased, since the hologram efficiency depends on the amplitude of the spatial modulation of the index of refraction and/or the absorption coefficient [28, 29]. This amplitude increases as [BA], the concentration of BA, increases. This increase is shown more clearly in Fig. 8, where $\eta_{\max}$ is plotted as a function of [BA]. The maximum efficiency initially increases with concentration as expected, but reaches a maximum value at a concentration of about 15%. The red beam was the 752-nm line from a Kr$^+$ laser with power density of 96 W/cm^2.

One explanation for this decrease in η at higher concentrations might be the onset of triplet energy migration among the BA molecules. This energy migration could result in a decrease in the triplet lifetime as a result of quenching of the BA molecule by bimolecular triplet-triplet annihilation, by O_2 impurities, or by other triplet traps. However, triplet-lifetime measurements over the 5–25% concentration range show no discernible decrease at higher concentrations. Another explanation for the concentration dependence is that at higher concentrations the uv light (300–400 nm) is almost completely absorbed near the surface of the sample. This means that the volume of overlap of the three beams is reduced, and one is effectively using less of the sample. This explanation is supported by measurements using filters that allow light in the 350–500-nm region to illuminate the sample. Referring to Fig. 5(a), this permits more radiation on the long-wavelength tail of the BA to enter the sample, thus increasing the effective spatial overlap of the three beams. As can be seen in Fig. 8, η_{max} with this longer wavelength illumination continues to increase at concentrations beyond 15%.

To see if one could produce holograms using this four-level two-photon technique in the ir beyond 1 μm, a set of experiments were performed with a pulsed Nd:YAG laser. Holograms were observed at 1.06 μm by using a laser energy of 4.3 mJ/pulse focused to a spot size of 0.8 cm^2 at a 10-Hz repetition rate. Holograms produced in this way could be gated off and on by a uv light source, demonstrating their two-photon nature. As expected, no hologram could be produced at this laser power level when only 1.06 μm radiation was used.

At the maximum pulse energy available from the Nd:YAG laser (700 mJ/pulse according to the manufacturer's specifications), it was possible to produce holograms using ir irradiation alone. These holograms were probably due to laser heating effects which resulted from low-level ir absorption by impurities in the samples or by the glass microscope slides. They had an entirely different growth pattern from the two-photon gated holograms described previously. Instead of growing slowly and steadily as the uv-gated holograms did, these high-laser-power holograms appeared suddenly after a brief induction period, and their appearance was accompanied by a pronounced increase in scattered light from the sample.

Finally, explicit mention should be made of one of the disadvantages of α-diketones in four-level two-photon holography: the deleterious effect of the one-photon photochemistry that occurs from T_1. When BA is used in Me-CAc, Et-CAc or ISB-CAc, one-photon holograms can be produced at 488 nm with maximum efficiency of from 30–70%. The most efficient two-photon system studied was an 800-μm-thick 7.5% BA/Et-CAc sample. This system gave holograms with efficiencies as high as 11%.

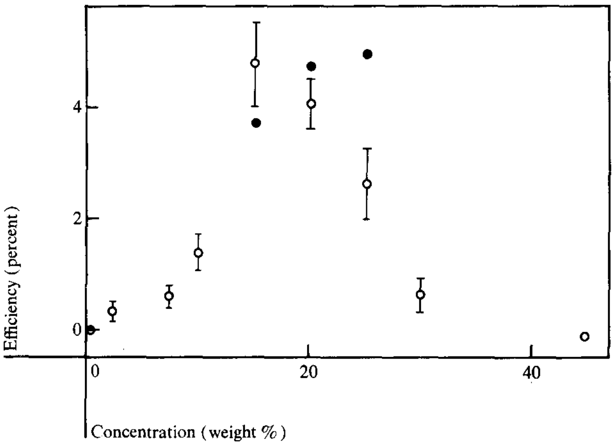

Figure 8 Maximum hologram efficiency for BA/CAc as a function of concentration. All samples were 200 μm thick and >24 h old; ○, Hg lamp plus 7-54 filter at 1.02 W/cm^2; ●, Hg lamp plus 5-60 filter at 1.75 W/cm^2. See text for details.

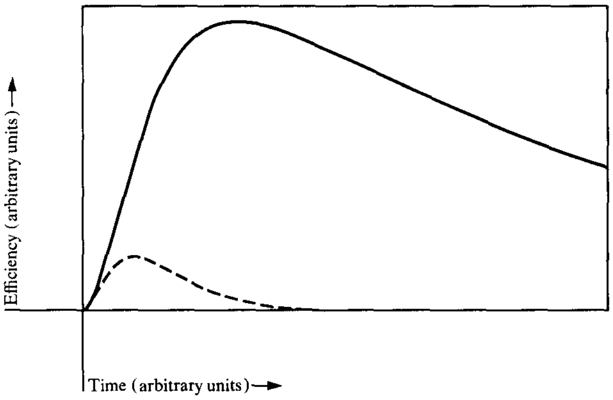

Figure 9 A plot of the calculated hologram efficiency as a function of time. The solid line represents the growth pattern with two interfering beams and the dashed line the pattern when a third incoherent beam illuminates the sample. Time and efficiency axes have arbitrary units.

One of the reasons for this lower efficiency in the two-photon systems is the depletion of the diketone by the uv beam as a result of one-photon photochemistry from T_1. The consequences of this unwanted photochemistry are shown in Fig. 9, in which the growth of two holograms has been simulated using a computer program, described in more detail elsewhere [30]. One of the curves shows the ideal growth of a hologram, assuming no interference from the uv source; the other represents the reduction in the maximum efficiency when a spatially uniform source of equal intensity in the two interfering beams is present. This uniform illumination of the sample causes a uniform reduction in the concentration of the photochemically active species. The result is a considerable reduction in the maximum hologram efficiency obtainable. Clearly, one could improve the efficiency of the two-photon four-level systems discussed here by eliminating this interfering one-photon process.

Conclusions

In this paper we have described experiments on holographic materials that can be used with low-power ir lasers beyond 750 nm. In fact, we have been able to record holograms with wavelengths as long as 1.06 μm. The holograms are recorded in cyanoacrylate polymers in which a photoactive α-diketone has been dissolved. Both polymer and dopant are readily available materials.

The technique used to record the holograms involves four-level two-photon photochemistry of α-diketones. Recording holograms in this way permits one to gate the hologram formation off and on using an auxiliary incoherent light source. In addition, the holograms are self-developing and are not erased during the reading process. Finally, it should be noted that the excited-state energy-level structure necessary for a molecule to undergo four-level two-photon photochemistry is rather common in organic molecules. There should be many systems in which it is possible to produce holograms in this way.

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