Single femtosecond exposure recording of an image hologram by spectral hole burning in an unstable tautomer of a phthalocyanine derivative

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We demonstrate, for what we believe is the first time, recording of a femtosecond image hologram by illumination with a single pair of high-intensity femtosecond pulses in a broad inhomogeneous bandwidth spectral hole-burning material consisting of a polymer film doped with anthraceno-phthalocyanine dye molecules. High efficiency of spectral hole burning is achieved by preillumination of the sample at a low temperature to convert the dye molecules into an unstable tautomer form.   © 2000 Optical Society of America

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Pulsed femtosecond holography is potentially an important tool for investigating complex nonlinear optical phenomena, such as self-focusing, self-phase modulation, and optical breakdown induced by high-intensity ultrashort pulses,[1,2] time-gated imaging through a scattering medium,[3] and time-resolved spectroscopy of molecules and solids.[4] However, because femtosecond pulses have a short coherence length, capturing a high-resolution holographic image on a femtosecond time scale is generally an exceedingly difficult task. For example, a conventional hologram recorded with 100-fs-duration pulses comprises fewer than $\sim$100 interference fringes. For an image hologram, such marginal temporal coherence gives rise to defects and aberrations, which severely degrade the resolution and the field of view of the hologram.[5] A drawback, of course, is that ultrashort pulses possess a spectral bandwidth that typically is larger than $\Delta\nu_p > 4$ THz. Such a broad bandwidth encompasses many optical frequencies, each of which may produce a different interference fringe pattern. A conventional light-sensitive material such as a photoplate does not distinguish among the various frequencies and, consequently, all the different fringe patterns are added and in the end average to zero.

In a method called spectral holography, the frequency components of the femtosecond pulse are separated in space by use of a dispersing optical element such as a diffraction grating or a prism.[3,6,7] Each frequency can now record its own set of interference fringes. Note, however, that such spatial separation of the frequency components inevitably occupies at least one lateral spatial dimension of the recoding medium. Therefore it is still practically impossible to capture a full two-dimensional image hologram.

Spectral hole burning (SHB) offers an entirely different approach to recording a hologram by utilizing an inhomogeneously broadened ensemble of absorbing molecules in a solid to capture holograms simultaneously at a range of frequencies.[8] The spectral resolution in this case is given by the width of the homogeneous zero-phonon line, Γ_{hom}, which in certain organic chromophores such as porphyrins

at liquid-helium temperature may be as narrow as $\Gamma_{hom} < 100$ MHz (and even much narrower for some rare-earth ions in crystals). The inhomogeneous broadening comes about because the intrinsic imperfection of the solid influences each individual molecule differently, resulting in a random shift of the zero-photon frequency. In a strongly disordered solid such as an organic polymer the inhomogeneous bandwidth may be as large as $\Gamma_{inh} > 4$ THz. This fact was used previously to demonstrate recording of image holograms with a femtosecond laser.[9] However, because of the low quantum yield of the SHB process (typically of the order of $\varphi \sim 10^{-3}$ or less), in all earlier experiments the writing exposure had to be repeated many times to accumulate the diffraction efficiency of the SHB hologram.[8–10] For imaging of nonlinear phenomena in which the spatial–temporal wave front is not reproduced from one laser shot to another, it is essential that the hologram writing exposure consist of a single femtosecond pulse rather than of an accumulated train of pulses. Here we introduce a new procedure for increasing the recording efficiency of the SHB material and use it to demonstrate, for the first time to our knowledge, a femtosecond image hologram captured by illumination with a single pair of high-intensity femtosecond pulses.

The experimental arrangement comprised a regenerative-amplified Ti:sapphire laser (Clark MRX CPA-1000), which produced pulses with 0.4 mJ of energy and a duration of 150 fs at a repetition rate of 500 Hz at a wavelength of $\lambda = 764$ nm. The spectral bandwidth of the laser was $\Delta\lambda = 5$ nm. The output laser beam was expanded to 2-cm diameter, and only its central part with a flat intensity profile was used. A 50% beam splitter divided the beam into object and reference beams. The two beams overlapped at an angle of $\Theta = 5°$ on the sample, which was positioned inside an optical cryostat. The object beam was delayed 10 ps with respect to the reference beam. At the sample, both beams had a diameter of 1 cm, and their combined average energy in a 1-cm^2 area was 0.15 mJ/laser pulse. The hologram recording exposure was controlled by means of a mechanical

shutter that opened and closed the output beam of the amplifier. The sample consisted of a 0.1-mm-thick polyethylene film doped with anthraceno-triphthalocyanine (AnPc$_3$) molecules at a concentration of $\sim 10^{-3}$ mol/L.[11] During the experiment the polymer film was immersed in superfluid helium at a temperature $T = 2$ K. For readout of the holograms, the object beam was blocked and the reference beam was attenuated by a factor of 10^4 with a neutral-density filter. Images were recorded with a cooled CCD camera (Xillix Microimager). Absorption spectra were measured with Perkin-Elmer Lambda 900 spectrophotometer.

Figure 1 shows the absorption spectrum of anthraceno-triphthalocyanine molecules in polyethylene at low temperature immediately after cooling from room temperature to 2 K (thin solid curve). All molecules are in stable tautomer form (educt), with the maximum of the $S_1 \leftarrow S_0$ electronic transition at 780 nm and inhomogeneous bandwidth $\Gamma_{inh} \sim 4.6$ THz ($\Delta\lambda = 8.8$ nm). The homogeneous zero-phonon linewidth is $\Gamma_{hom} < 1$ GHz, which corresponds to an optical dephasing time of $T_2 > 400$ ps. The oscillator strength of the electronic transition is $f \sim 0.14$.[11]

The dashed–dotted curve in Fig. 1 shows the transformation of the absorption spectrum as a result of 5-min illumination with 10-mW cm^{-2} average intensity in the wavelength range 775–785 nm. We produced the broadband light by blocking the Ti:sapphire oscillator and using the remaining free lasing output of the amplifier. The illumination transformed the entire 780-nm band into a new absorption band with its maximum at 764 nm. It is known that free-base porphyrins and phthalocyanines may undergo photochemical tautomerization reactions at low temperature, which switches the position of the two NH protons in the center of the tetrapyrrolic ring.[12] Typically the probability (quantum efficiency) of such a photoreaction in the excited state S_1 is $\sim \varphi_e = 10^{-3}$–10^{-4}. Here the new band at 764 nm corresponds to the $S_1{}^* \leftarrow S_0{}^*$ transition of the product tautomer form of anthraceno-triphthalocyanine. The other spectroscopic parameters of this transition, such as Γ_{inh}, Γ_{hom}, and f, are within a few percent of that of the educt. However, the probability (quantum efficiency) of tautomerization in the product's excited state $S_1{}^*$ is an order of magnitude higher than that in the educt. The reason for such a large difference in quantum efficiency is most probably related to the observation that the product tautomer is much less stable and that it exists only at low temperature, $T < 100$ K. We use this fact to increase the efficiency of recording of femtosecond hole-burning holograms. For this we preilluminate the sample in the way discussed above, creating the product absorption spectrum shown in Fig. 1. After the preillumination, the holograms are recorded in a normal way by illumination at 764 nm.

As a first setup we studied the efficiency of phototransformation of the product band under illumination with high-intensity 150-fs pulses at 764 nm. The power spectrum of the pulses is shown in Fig. 1. The dotted curve shows the absorption spectrum after illumination with 250 pulses of 150-μJ cm^{-2}

intensity. First let us note that, in illumination with a single femtosecond pulse with a duration much less than optical dephasing time $t_p \ll T_2$, each molecule may be excited only once (or not excited at all). The average probability of excitation may be derived from numerical solution of the density-matrix equation of a two-level atom. Using the known absorption cross section,[11] we estimate that, at our illumination intensity, every pulse should excite the molecules with a probability close to 100%. Assuming that the quantum efficiency is $\varphi_p \sim 10^{-2}$, we expect that exposure to 250 pulses will transform nearly all molecules back into the educt form. However, the actual measured absorption change is only 25%, from which it follows that each pulse bleaches out only $\sim 0.1\%$ of the molecules. We can explain this apparent discrepancy by considering that in our experiment not all molecules were in equally optimum conditions for excitation. First, because of the high value (O.D. ~ 1.7) of the optical density of the sample, the excitation intensity decreases exponentially with the penetration depth into the sample, leading to an average excitation probability of $\sim 30\%$. Furthermore, because of the finite spectral width of the laser pulses, only those molecules that were close to the maximum of the laser spectrum are optimally excited. Combinations of these factors lead to the situation in which each laser pulse excites on average only $\sim 10\%$ of the molecules.

As the next step we measured the dependence of the diffraction efficiency of the hologram on the number of exposures (Fig. 2). Every single exposure contained a pair of object and reference pulses with a median intensity of 150 μJ cm^{-2}. As described above, each such exposure burned out $\sim 0.1\%$ of the product band. The figure represents the diffraction efficiency obtained after subtraction of the background scattering signal and by averaging of the recalled object intensity over a certain image area. A simulation based on numerical solution of Maxwell–Bloch equations (solid curve) predicts that under our conditions we may expect a
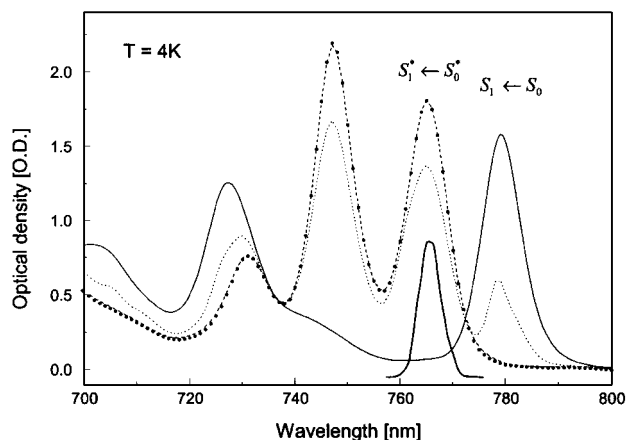

Fig. 1. Absorption spectrum of the sample at low temperature ($T = 4$ K). Thin solid curve, stable tautomer form before illumination; dashed–dotted curve, unstable tautomer form produced by illumination with spectrally broad light at 780 nm; dotted curve, after exposure to 250 pulses with 150-μJ cm^{-2} intensity at 764-nm wavelength; thick solid curve, power spectrum of the pulses.
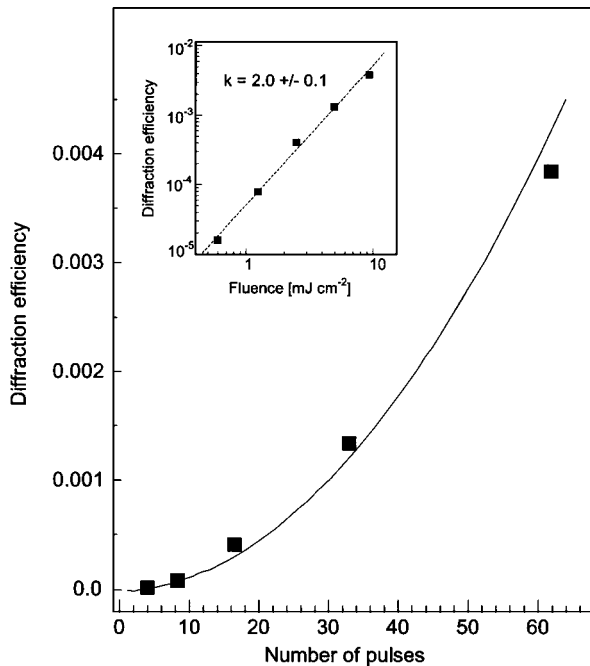
Fig. 2. Dependence of the hologram's diffraction efficiency on the number of exposures. One exposure corresponds to illumination with one pulse pair of femtosecond object and reference pulses with an average intensity of 0.15 μJ cm^{-2}. Solid curve, numerical simulation based on our experimental conditions. Inset, the same data points on a logarithmic scale; dotted line, a fit to the quadratic dependence.
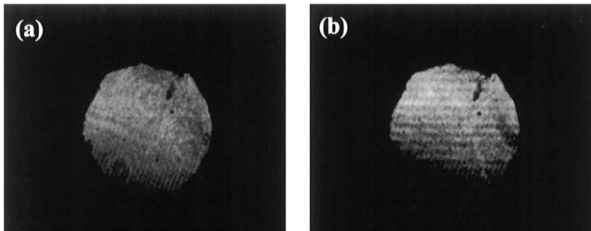

Fig. 3. Interference hologram recorded with a single femtosecond exposure. Hologram image (a) before and (b) after exposure. Horizontal interference fringes appear as the result of interference between the reference hologram and the single-exposure hologram. The reference-beam direction of the single-pulse exposure is slightly tilted in the vertical direction.

quadratic dependence of the relative diffraction efficiency on the number of exposures. Our experimental data closely follow this predicted dependence.

The smallest diffraction efficiency at which hologram images were clearly detected after the background was subtracted was $\sim 2 \times 10^{-5}$. The limitation originated from the relatively high background-scattering signal level of 10^{-4} because the polyethylene film of the sample comprised small inclusions of microcrystals. Taking into account the noise caused by the background scattering, we were able to reliably detect holograms that resulted from two exposures. To detect single-exposure holograms we used an interference approach proposed earlier.[13] For that case we first recorded a relatively strong plane-wave reference hologram by accumulating 80 exposures. After that we exposed the sample for one more laser pulse but now with a slightly tilted reference-beam direction. Figure 3 shows readouts of such double-exposure holograms; the single-shot exposure is clearly seen in the form of a horizontal interference fringe pattern. In our future experiments we plan to exploit this interferometric technique to measure quantitatively the spatial and spectral dependence of the phase of the femtosecond pulse.[14]

In conclusions, we have demonstrated the feasibility of recording femtosecond image holograms by illumination with a single exposure of 150-fs pulses. We made use of the broad inhomogeneous bandwidth of an organic spectral hole-burning material and of the fact that the spectral hole-burning efficiency is higher in the photochemically unstable product of anthraceno-phthalocyanine molecules. We have also demonstrated the possibility of obtaining double-exposure interference holograms with femtosecond pulses, which will facilitate precision time–space amplitude and phase analysis of ultrashort phenomena.

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