

Two-photon excited coherence gratings in inhomogeneously broadened organic solid

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Abstract. For the first time a frequency-domain grating is observed in the visible region as a result of coherence excited by two-photon absorption of time-delayed near-IR femtosecond pulses in an inhomogeneously broadened organic solid-state system. The grating appears in chlorin (2,3-dihydroporphyrin)-doped polymer film at low temperature and is detected in two different ways. First, modulation is observed in the pure electronic fluorescence band upon 'resonant' two-photon excitation with laser carrier frequency equal to one-half of the fluorescence band maximum. Second, upon long exposure time at half of the transition frequency, a persistent spectral hole with periodic structure is observed. The two-photon absorption spectrum of the chlorin molecule in the spectral range 1130–1310 nm is also presented for the first time.

1. Introduction

In recent years, a great deal of attention has been paid to the coherent control of atomic and molecular systems with specifically modulated ultrashort laser pulses [1–3, and references therein]. The electric fields of these pulses can be shaped in such a way that it contains complicated amplitude, frequency or phase modulation. Depending on the relative phase between different components of the complex field, either constructive or destructive interference may take place, thus enhancing or suppressing light–matter interaction at particular instants of time and (or) frequencies. It should be emphasized that, because the phase is given as the product of time and frequency, a particular interference condition, e.g. $\Delta\phi = \pi$ or 2π , can be attained in both time and frequency domains, with the complementary variable being fixed. So far, the vast majority of papers have addressed interference in the time domain, and have neglected interference in the frequency domain. This is because most experiments use spectrally narrow atomic or molecular transitions, which, even in the case of broadband pulse excitation, select a particular resonance frequency from the laser spectrum. For example, coherent control of molecular systems including selective manipulation of molecular structures or breaking specific bonds was demonstrated [4] with trains of short pulses by adjusting the

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time delay (phase difference) between them, but keeping the carrier frequency in resonance with a particular transition. Other applications included ultrahigh resolution spectroscopy with short pulses [5–8], forcing or inhibition of one- and two-photon absorption [9, 10] or ionization [11].

Interference in the frequency domain was proposed as a method for fast optical data storage, processing, and time-and-space domain holography [12, 13]. In this alternative approach, one makes use of the fact that some dye-doped polymer systems possess very broad inhomogeneous bands, comprising narrow and high peak intensity zero-phonon lines. If a sequence of pulses is applied to such a system, a grating will be created in the frequency domain, provided that the duration of the sequence does not exceed the homogeneous dephasing time, $\Delta\tau < T_2$. One of the most important advantages of such spectrally selective systems is that the spectral grating can be 'engraved' into the inhomogeneous absorption band using a persistent spectral hole burning effect (SHB). This provides a unique possibility for recording holograms of very fast events [14, 15]. While SHB-based frequency gratings have been demonstrated previously [16, 17], they were based on direct one-photon excitation of the lowest singlet–singlet transition. In this paper the possibility of creation of such spectral gratings via simultaneous absorption of two photons is demonstrated. Preliminary results on the possibility of SHB via simultaneous two-photon absorption (TPA) are communicated in [18].

One important advantage of a two-photon process consists in the possibility of unrestricted penetration and focusing of laser radiation in the depth of bulky samples. Two-photon absorption has been used to demonstrate conventional, spectrally nonselective, recording in photochromic materials by focusing two perpendicularly directed laser beams (with photon energies $\hbar\omega_1$ and $\hbar\omega_2$) onto one spot [19]. Since the sample is transparent for each beam separately, one obtains the TPA only at their intersection, which results in a photochemical reaction of molecules doped in the polymer. It has been shown that addition of the third spatial dimension increases the capacity of optical memory devices (3D memory) by several orders of magnitude [19]. Combining this effect with spectral grating hole burning can provide an even higher density of stored data. Another possible application is recording and studying the effects of photon correlations in nonclassical light. This is based on the effect that the TPA probability is proportional to the fourth-order correlation function of the electric field. Suppression of TPA at some wavelengths and enhancement at others could also find use for TPA spectral filtering and selective power limiting.

In this paper we first measure the two-photon absorption spectrum of chlorin (7,8-dihydroporphin) molecule doped into polyvinylbutyral film. Then we describe a spectral grating in the chlorin fluorescence spectrum created by TPA from phase-locked pairs of femtosecond pulses. Finally, we demonstrate spectrally selective hole burning in unstable chlorin tautomer by direct two-photon excitation.

2. Experimental

A laser system was used comprising a mode-locked Ti:sapphire femtosecond laser (Coherent Mira 900) and a 1 kHz repetition rate Ti:sapphire regenerative amplifier system (Clark MRX CPA-1000). The amplified pulses had a duration of

150 fs and energy of 0.8 mJ at 780 nm. An optical parametric amplifier, OPA (TOPAS, Quantronix), converted these pulses to near infrared (1100–1800 nm), nearly Fourier-transform limited, 100-fs-duration pulses with energy 0.1–0.2 mJ. Glass colour filters were used to cut off any residual visible light from the laser. The laser spectrum was recorded with either a Lambda 900 Perkin Elmer spectrophotometer coupled with a light-collecting fibre or with a TRIAX 550 Jobin Yvon/Spex spectrometer. Pulse duration and its temporal profile for both amplifier and OPA were measured with an autocorrelator.

Figure 1 shows schemes of the experimental setup for two-photon excited fluorescence measurement (a), and two-photon hole burning (b). In both cases, a Michelson interferometer divided the OPA beam into two spatially overlapped but time-delayed beams. The time delay between the two pulses was $\Delta\tau \approx 670$ fs for fluorescence measurements, and $\Delta\tau \approx 180$ fs for hole burning. Infrared pulses were focused with a lens, $f = 50$ cm, on a sample inside a cryostat. In the case of hole burning a mask with a 1×0.6 mm opening was placed just before the sample to ensure that the same spot of the sample was irradiated and probed. Laser spot size was estimated to be about 2.5×10^{-3} cm². The pulse peak intensity at the sample was varied from 20 to 80 GW cm⁻² by a variable neutral density filter. In both experiments a chlorin-doped 0.2 mm thick polyvinylbutyral (PVB) film was used as a sample. The sample was contained in a helium cryostat at temperature $T = 4$ K, which was stabilized by temperature regulator UTRECS K41.

For measurement of transmission spectra (figure 1(b)), chopper-modulated light from a filament lamp was dispersed in a TRIAX 550 Jobin Yvon/Spex spectrometer and then collected with a lens on the mask opening before the sample. The transmitted signal was recorded with a Hamamatsu photomultiplier coupled with a lock-in amplifier.

3. Results and discussion

Figure 2 presents the two-photon absorption cross-section of chlorin in PVB film at room temperature, as a function of excitation laser wavelength in the region 1130–1310 nm. To perform this measurement, the resulting fluorescence intensity was detected by a digital CCD camera (Xillix Microimager). Absolute values of the TPA cross-section were determined by scaling the spectrum obtained with the value $\sigma_2 = 0.5$ GM (1 GM = 10^{-50} cm⁴ s photon⁻¹ molecule⁻¹) at 1270 nm, which was recently reported in [18]. Figure 2 shows also the conventional one-photon absorption spectrum of the sample along with the fluorescence spectrum measured at room temperature by excitation with a green laser (532 nm). A strong band at 633 nm in the one-photon spectrum corresponds to the pure electronic transition, $Q_y(0-0)$, polarized along the reduced C–C bond, and a weak band near 585 nm belongs to the vibronic satellite $Q_y(0-1)$. The TPA spectrum shows the same two transitions, but at twice the wavelength. The fact that the position of the maxima in the TPA spectrum coincide with those of the linear spectrum means that one-photon and two-photon transitions are simultaneously allowed. This is because electronic levels of molecules without inversion symmetry have a mixed parity [20]. The chlorin molecule has no inversion symmetry owing to a reduced double bond in one of the pyrrole rings. The slightly larger value of bandwidths in the TPA spectrum presented is due to the rather large spectral width (150 cm⁻¹) of the OPA, which is comparable to the bandwidth of the chlorin absorption bands.

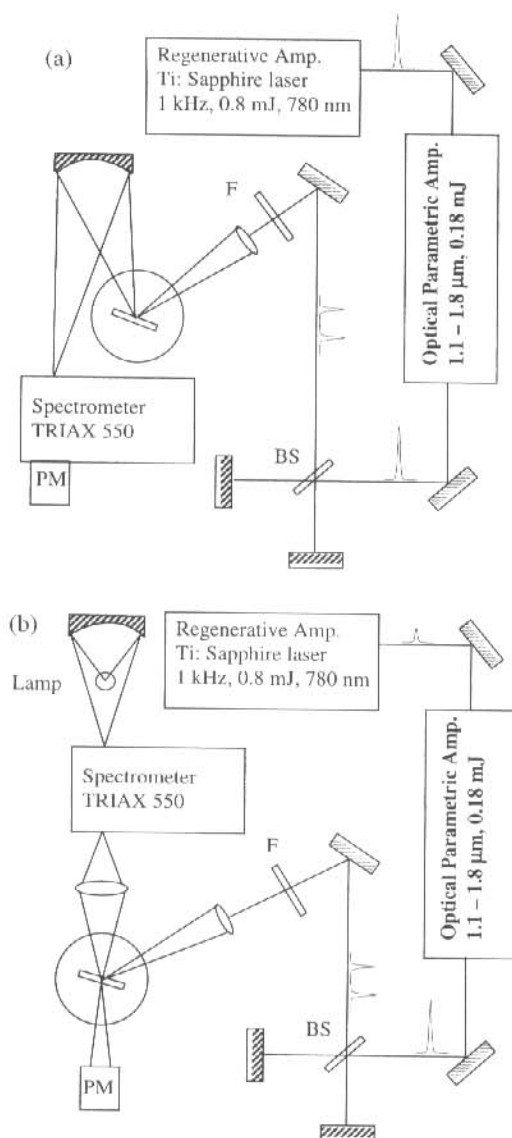


Figure 1. Schematic of experimental setup for the two-photon excited fluorescence measurements (a), and two-photon hole burning (b). Lamp—filament lamp; PM—photomultiplier; F—set of infrared filters; BS—beam splitter.

Therefore, the TPA spectrum in figure 2 is actually a convolution of the 'real' absorption profile and the laser spectrum. To the best of our knowledge, this is the first report of the TPA spectrum of the chlorin molecule.

Note that the ratio of purely electronic and vibronic peaks is quite different in one- and two-photon spectra of chlorin: for the one-photon process the pure electronic band dominates, while for the two-photon process the vibronic satellite is much stronger. The closely related chlorophyll *a* molecule also reveals coincidence of one- and two-photon absorption maxima and a similar relation between the two peaks [21]. This fact matches well with the communication [22] and data

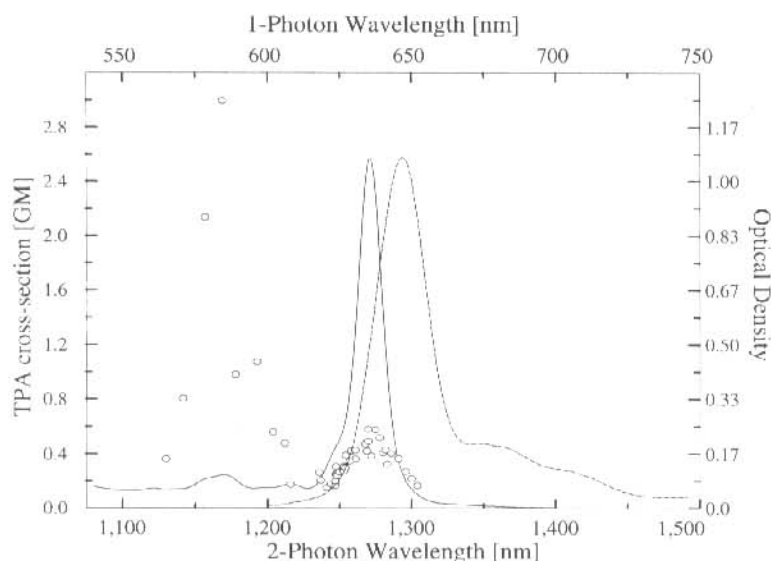


Figure 2. Two-photon absorption (○), one-photon absorption (—) and fluorescence spectra (---) of chlorin in PVB film.

for the TPA spectra of several tetrapyrrolic molecules measured in solutions and polymer films. In all cases the intensity of the vibronic band in the TPA spectra was found to be higher than that of the pure electronic transition. A detailed discussion of this phenomenon will be given elsewhere.

At liquid helium temperature, the homogeneous zero-phonon line of chlorin is much narrower, $\Gamma_{\text{hom}} < 0.3$ GHz, than the inhomogeneous broadening, $\Gamma_{\text{inh}} > 5$ THz, thus providing a high degree of spectral selectivity of absorption [23]. As already shown above, the first electronic transition is simultaneously accessible for both one- and two-photon excitation. These facts taken together make it suitable for spectrally selective two-photon excitation of this molecule.

The first observation of energy-selective two-photon excitation of an organic molecule was reported by B. E. Kohler and co-workers [24]. Recently Takeda *et al.* demonstrated two-photon excited fluorescence line narrowing for several dyes with no inversion symmetry [25]. In those papers, spectrally narrow (as compared to inhomogeneous broadening) pulsed lasers were used for excitation. Note that the important advantage of two-photon excitation is the absence of scattered light near the transition frequency, which provides the unique possibility of recording the pure electronic zero-phonon line in fluorescence.

In our approach we use pairs of 100-fs pulses with constant time delay, $\Delta\tau$. It is well known (see, for example, [16]) that in the case of one-photon excitation by a pair of time delayed pulses, the excitation power spectrum is determined by the square of the Fourier transform of the electric field, which is modulated with period $\Delta\nu = 1/\Delta\tau$. The spectral envelope function is determined by Fourier transform of an individual pulse.

The question of coherent interaction of TPA-absorbing medium with a sequence of phase-locked pulses was considered theoretically in [8, 26]. These considerations, however, dealt with interaction between light and atoms and molecules having spectrally narrow transitions. Here we present an extension of

this analysis to the case of inhomogeneously broadened medium. Let us consider a sequence of two identical, Fourier-transform-limited, linearly polarized laser pulses, delayed by $\Delta\tau$, which are described by the electric field $E(t)$:

$$E(t) = E_0(t)e^{-i\omega_L t} + E_0(t - \Delta\tau)e^{-i\omega_L(t - \Delta\tau)} \quad (1)$$

where $E_0(t)$ is the pulse envelope and ω_L is the carrier frequency of the pulse. Further, $|g\rangle$ denotes the ground, $|i\rangle$ the single intermediate state (which is out of resonance with the laser), and $|e_k\rangle$ the excited state. Index k here refers to a particular subset of molecules from an inhomogeneous ensemble, possessing transition frequency ω_k . As a result of light-matter interaction during the time t , the wave function of a particular molecule with transition frequency ω_k will be:

$$|\Psi_k(t, \omega_k)\rangle = |g\rangle + a_k(t, \omega_k)|e_k\rangle, \quad (2)$$

where the amplitude $a_k(t, \omega_k)$ is given, according to perturbation theory, by

$$a_k(t, \omega_k) = \frac{i}{\hbar} \int_0^t Q_{g,ek} E^2(t') e^{i(2\omega_L - \omega_k)t'} dt'. \quad (3)$$

Here $Q_{g,ek}$ is the two-photon transition operator,

$$Q_{g,ek} = \frac{\langle e_k | \mu | i \rangle \langle i | \mu | g \rangle}{\hbar(\omega_i - \omega_L)}. \quad (4)$$

After the first pulse passed through the medium, one will have:

$$a_k(t, \omega_k) = \frac{i}{\hbar} Q_{g,ek} e^{-i\omega_k t} \hat{E}_0^2(\omega_k - 2\omega_L). \quad (5)$$

Here,

$$\hat{E}_0^2(\omega) = \int E^2(t) e^{i\omega t} dt \quad (6)$$

is the Fourier transform of the square of electric field pulse envelope. Equation (5) shows that the first pulse creates a polarization in the excited state oscillating at ω_k . Note that each subset of molecules from the inhomogeneous distribution oscillates at its own resonant frequency. The excited state population is proportional to:

$$|a_k|^2 \propto |\hat{E}_0^2(\omega_k - 2\omega_L)|^2, \quad (7)$$

which represents a broad spectral envelope, determined by the Fourier transform of the pulse envelope squared.

If the time delay $\Delta\tau$ between the first and second pulses is less than the dephasing time T_2 of a medium, then interference between polarizations induced by the two pulses will occur. In such a case, the resulting amplitude $a_k(t, \omega_k)$ may be obtained by substitution of (1) into (3):

$$a_k(t, \omega_k) = \frac{i}{\hbar} Q_{g,ek} e^{-i\omega_k t} \hat{E}_0^2(\omega_k - 2\omega)(1 + e^{i\omega_k \Delta\tau}). \quad (8)$$

From this equation one can see that the excited state population, $|a_k|^2$, is proportional now to the envelope spectrum of a single pulse ($\sim E^2(t)$), modulated by the function $[1 + \cos(\omega_k \Delta\tau)]$. This result demonstrates that for a fixed $\Delta\tau$ value, constructive or destructive interference conditions can be obeyed for a predetermined set of transition frequencies within the inhomogeneous band.

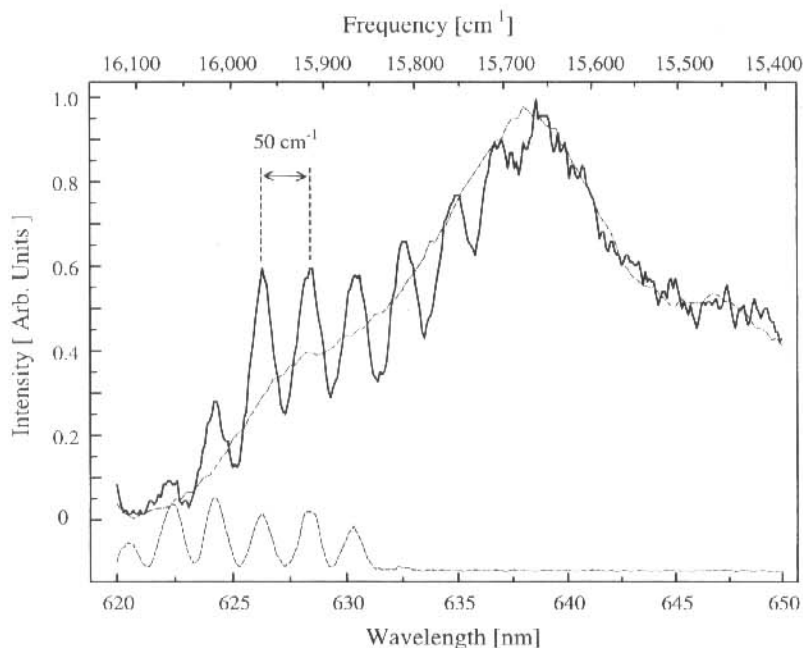


Figure 3. The frequency-domain modulated ($\Delta\nu = 50\text{ cm}^{-1}$) fluorescence spectrum of chlorin in PVB film (—). The spectrum obtained with one closed arm of the Michelson interferometer (---) is normalized with respect to the previous one. The spectrum of the laser second harmonics is presented for comparison (-.-).

Namely, in the case of constructive interference $\omega_k = 2\pi n/\Delta\tau$, ($n = 0, 1, 2, \dots$). In time domain language, this means that if the second pulse arrives with a phase delay $\Delta\phi = \omega_k \Delta\tau$ exactly equal to $2\pi n$ for a particular frequency ω_k , one will have constructive interference of this pulse with polarization induced by the first pulse at this frequency. Experimentally, in an inhomogeneously broadened medium one should observe a spectral grating with a period of $\Delta\omega = 2\pi/\Delta\tau$. Note that the period of modulation turns out to be the same as in the case of one-photon excitation with a pair of pulses, also delayed by $\Delta\tau$, but at double the frequency.

To observe this kind of spectral modulation, we first recorded the spectrum of resonance fluorescence of a chlorin-doped polymer film, kept at 4 K, in the region of inhomogeneously broadened 0-0 transition near 630 nm, figure 3, solid line. Excitation was carried out with pairs of infrared pulses with 670 fs time delay at a carrier wavelength of 1270 nm. The period of fluorescence intensity modulation is 50 cm^{-1} , which is exactly equal to the period of laser spectrum modulation. For comparison we also present in figure 3 the power spectrum of the second harmonic of the excitation light (---) obtained with a nonlinear crystal. The long wavelength side of the spectrum is distorted due to the narrow synchronism bandwidth of our thick nonlinear crystal. We checked that a change of delay time between infrared pulses resulted in a corresponding change in fluorescence modulation period. In all cases the period (measured in wavenumbers) of fluorescence modulation was equal to that of the laser spectrum. The modulation in

fluorescence spectrum disappeared (figure 3, ---) when one of the arms of the Michelson interferometer was blocked.

This validates the above theoretical considerations. Our next step is a demonstration of 'engraving' of the spectral modulation found above for TPA via persistent SHB in chlorin molecule. Generally, one can identify three key conditions, which need to be fulfilled to achieve this goal. (1) The lowest purely electronic transition should be accessible by TPA with reasonable cross-section, $\sigma_2 \sim 1 \text{ GM}$, to give a reasonable probability of excitation with existing laser sources. (2) This transition should be spectrally selective; i.e. the homogeneous spectrum (zero-phonon line plus phonon sideband) should be at least 10 times narrower than the inhomogeneous distribution. (3) Quantum efficiency of the photochemical transformation has to be sufficiently large for spectral changes to be observable at reasonable irradiation times.

As has been shown above, the first two conditions are satisfied for the Q_y band of the chlorin molecule. Although the TPA cross-section in this band is less than 1 GM , which requires rather high excitation powers, the transition can still be excited as observed above. However, attempts to induce a detectable change in absorption failed even for irradiation times as large as several hours. The main reason is the very small quantum efficiency of photo-transformation $\sim 10^{-4}$ – 10^{-3} [27, 28].

Fortunately, there is another opportunity. It is known that at room temperature the chlorin molecule exists in a form with the N–H...H–N axis parallel to reduced C–C bond (T1-form, figure 4) [29]. At liquid helium temperatures it undergoes photo-induced tautomerization yielding perpendicular direction of the N–H...H–N axis with respect to the reduced bond (T2-form) [30]. One-photon SHB has been shown in both educt and photoproduct tautomers of chlorin in Shpolskii matrices [30], and polymer films [7, 28, 30]. As compared to T1 \rightarrow T2 photo-transformation, a drastic increase of the rate of back T2 \rightarrow T1 process has been observed [27, 28, 30], giving rise to up to 10% quantum efficiency of this process in polymer matrices. This value is probably the highest known for monomolecular SHB systems. Tautomer T2, as well as its stable counterpart T1, has no centre of symmetry and, therefore, its lowest singlet electronic transition should be accessible for two-photon excitation. In addition, both chlorin tautomers are separated spectrally by more than 1000 cm^{-1} [27, 28, 30], providing the possibility of using femtosecond pulses for their independent excitation. One disadvantage is that T2 tautomer has a low Debye–Waller factor in polymer matrices [27, 28]; nevertheless, it is known that its inhomogeneous band has a certain degree of spectral selectivity [27]. Therefore, we turn to the metastable (at low temperatures) T2 tautomer to demonstrate the effect of two-photon SHB.

An initial absorption spectrum of the stable T1-form of chlorin at 4 K is shown in figure 4 (.....). This figure also shows the spectrum of the sample after illumination (20 min) with 633 nm pulses (second harmonic of OPA tuned to 1265 nm) (—). One can see the strong band appearing at 567 nm, which was observed earlier at low temperatures in the same system [27] and attributed to the chlorin T2 tautomer. Excitation of the sample now with 1134 nm pulses yields an orange fluorescence. Prolonged illumination results in a decrease of absorption at 567 nm and simultaneous increase of the initial band at 633 nm (---, ---, and ---- in figure 4). These facts confirm that the TPA of the photoproduct T2 takes place and leads to T2 \rightarrow T1 back-transformation. As can be seen in figure 4,

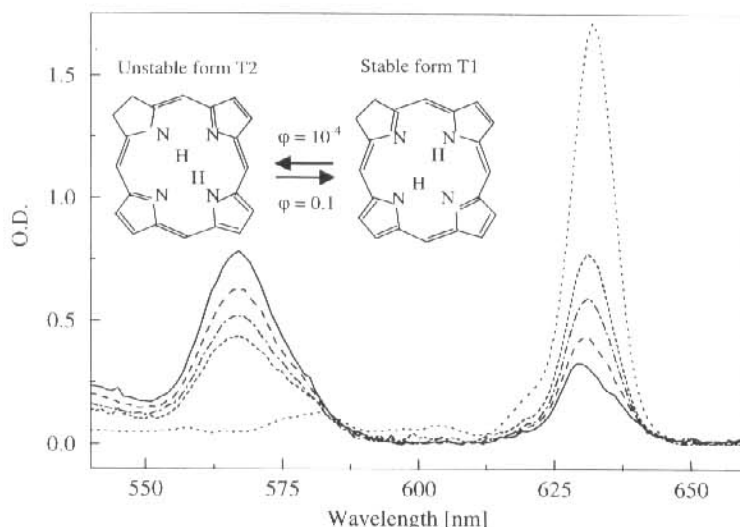


Figure 4. Absorption spectrum of stable chlorin tautomer T1 in PVB film at 4 K (.....). Spectrum of the sample after illumination with second harmonic of OPA (633 nm, 1 W cm^{-2} average power density at 1 kHz repetition rate) for 20 min (—). The band at 567 nm corresponds to unstable T2 tautomer; see inset for chemical structures. ---, - · - · -, and - - - - correspond to spectra after illumination of T2-form with 3.6, 4.7 and 6.1 kJ cm^{-2} total fluence of 1134 nm OPA pulses, respectively.

the changes in T2 spectrum are nonselective, i.e. the absorption band goes down as a whole, without SHB. This is due to the fact that the laser spectrum in this particular experiment has almost the same width and maximum as the inhomogeneous absorption band.

To obtain frequency-selective SHB, we used a Michelson interferometer again with a time delay of $\sim 180 \text{ fs}$. This resulted in a spectral modulation with $\Delta\bar{\nu} = 180 \pm 20 \text{ cm}^{-1}$. Figure 5 shows the change in the T2 absorption band of chlorin as a result of irradiation of the sample with pairs of pulses. Experimental results (• and ○) were obtained as follows. The absorption spectrum before burning was subtracted from that after burning. Then, this differential spectrum was approximated with a Gaussian envelope function. Finally, the Gaussian fit was subtracted from the experimental differential spectrum and the result was smoothed with a standard method using 10 adjacent points. • and ○ correspond to the 45 s and 285 s irradiation times, respectively. The experimental results show a modulation period for the holes of $230 \pm 30 \text{ cm}^{-1}$. This value coincides with the expected period within experimental error.

A poor contrast of the holes occurs because of a low Debye–Waller factor (< 0.1) [27, 28], which was mentioned above. However, it is known that for a broad inhomogeneous distribution function, exceeding both the phonon wing of the homogeneous spectrum and laser spectrum, one can still observe spectral selectivity [31, 32]. At low irradiation fluence, a relatively broad hole will appear exactly at the laser maximum frequency. During the burning process the hole will broaden and shift towards the maximum of the inhomogeneous distribution to coincide with it when almost all the centres are burnt. We can use this effect here as another

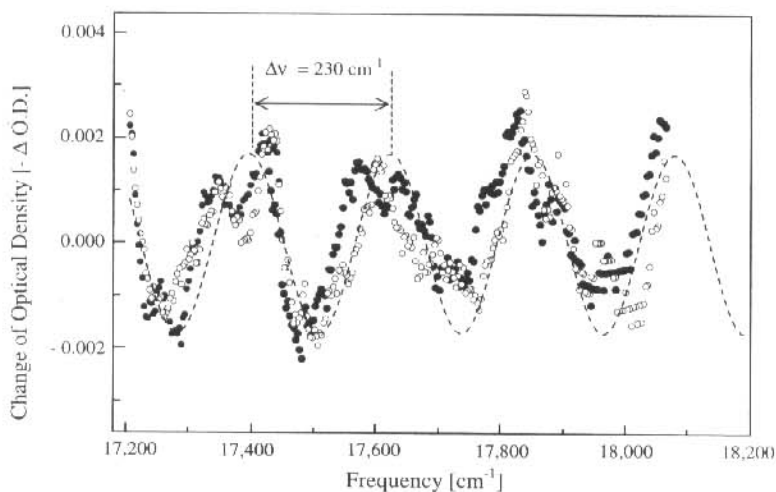


Figure 5. Spectral modulation in T2 absorption band induced by two-photon absorption from pairs of pulses with 180 fs time delay between them after an irradiation time of 45 (●) and 285 s (○), $I = 3 \text{ W cm}^{-2}$. --- represents a cosine function with a period of 230 cm^{-1} .

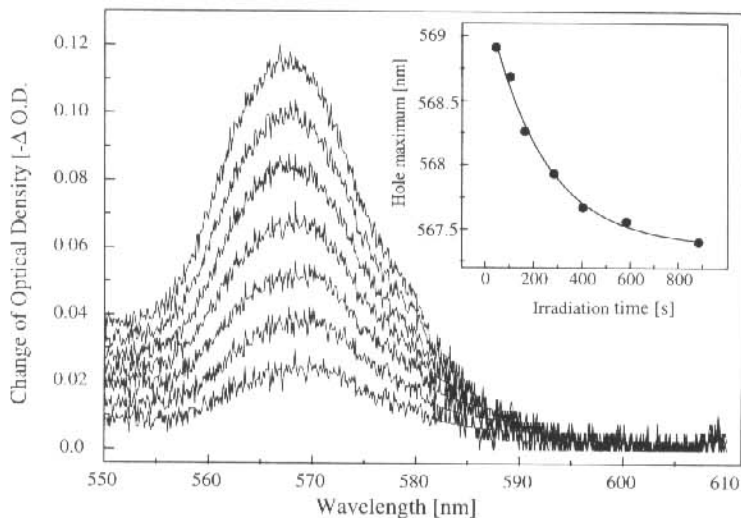


Figure 6. Spectral changes in T2 absorption band upon successive irradiation with pairs of pulses with carrier wavelength at 1138 nm, $I = 3 \text{ W cm}^{-2}$. Curves from bottom to top correspond to increasing irradiation time. Inset shows the position of the spectral envelope maximum of each curve as a function of that time (●) with exponential decay fit (—).

convincing demonstration of spectrally selective hole burning via simultaneous TPA. Successive changes of the hole shape as a function of irradiation time are shown in figure 6. One can definitely see that at the earlier stages the maximum of the broad envelope continuously shifts to the centre of the inhomogeneous distribution (567 nm). This is depicted in figure 6, inset. This experiment shows that during the burning process molecules with different transition frequencies become

involved in photo-induced reaction, which means that the system is spectrally selective.

Note that the effect of SHB via nonresonant TPA differs radically from the well-known photon-gated SHB [33]. The latter implies sequential absorption of two photons with the first one in resonance with molecule absorption.

4. Conclusions

This paper has demonstrated, for the first time, the interference of coherence in frequency-domain as a result of nonlinear two-photon absorption in an inhomogeneously broadened organic dye-doped polymer. It has been shown that two-photon spectral gratings may be detected in spontaneous fluorescence, as well as by means of persistent spectral hole burning at long exposure times. The spectral gratings observed in the present experiments are well described by a simple perturbation model of two-photon-induced coherence in a system with no real indeterminate level(s). Future work will focus on two-photon coherence in systems with a real intermediate level and will use shaped laser pulses to reveal the underlying dynamics of multi-photon coherence.

Acknowledgments

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