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# Frequency-domain gratings by simultaneous absorption of two photons

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## Abstract

We study frequency-domain coherence gratings produced by interference in process of simultaneous absorption of two photons in an inhomogeneously broadened medium. In our experiment, we create a grating at a visible wavelength by illuminating an organic dye-doped polymer at low temperature with phase-locked pairs of 100-fs laser pulses at a near-infrared wavelength equal to two times the transition wavelength. We show that two-photon excited coherence can be detected either by measuring the spectrum of fluorescence or, after prolonged illumination, by observing spectrally modulated persistent spectral hole. We analyze the phase and contrast of the grating at different temperatures and obtain, for the first time to our knowledge, temperature dependence of Debye–Waller factor and phonon spectrum of two-photon transition of organic molecule in presence of large inhomogeneous broadening. We also study wavelength dependence of absolute two-photon absorption cross-section in a series of porphyrins and show that at some wavelengths in porphyrin B-band region the cross-section is resonantly enhanced by nearby one-photon allowed Q-transition. These experiments indicate that large organic molecules such as porphyrins are promising candidates for further investigation of multi-photon excitation of coherence. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Study of coherent nonlinear optical effects such as time-and-space-domain holography, photon echo, spectral hole burning, multi-photon absorption, electromagnetically induced transparency, stopping (and accelerating) of light pulses in a

nonlinear medium etc. gives valuable insights into the physics of the interaction between atoms (or molecules) and light. This research is also paving a road for future advances in technology, especially in high-speed high-capacity data storage, ultra stable frequency- and time standards, as well as new ways of performing computations.

The principle of time-and-space-domain holography is based on frequency-domain interference, which occurs due to coherence excited in an absorbing medium, by time-delayed object- and reference pulses [1–8]. Depending on the relative phase between different components of the field

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amplitude, either constructive or destructive interference may take place, thus enhancing or suppressing absorption at particular instants of time and (or) frequencies. If a sequence of pulses is applied to such a system, a grating in frequency domain will be created, provided that the duration of the sequence does not exceed the homogenous dephasing time,  $\Delta\tau < T_2$ . The resulting spatial-spectral pattern of interference is recorded by an absorption-induced permanent change of complex index of refraction of the medium. The change of the medium absorption is proportional to the amount of energy absorbed, and the associated process is known as persistent spectral hole burning (SHB) [9,10].

So far, coherent optical transient effects have been studied mostly in the case, where the ground electronic state is coupled to an excited electronic state via a resonant one-photon transition.

It may be expected that by using two- or three-photon coherent processes instead of the usual one-photon transition, one can greatly increase the variety of nonlinear optical effects useful for optical storage and processing of information.

If an atom or molecule is excited via a two-photon transition, then two quanta of electromagnetic field of different wavelengths may be absorbed simultaneously. Two-photon absorption (TPA) has been used earlier 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 [11]. Since the sample is transparent for each beam separately, only at their intersection one gets the TPA, which results in photochemical reaction of molecules doped to the polymer. It has been shown that an addition of the third spatial dimension increases the capacity of optical memory device (3D memory) by several orders of magnitude. One can expect that combining of this effect with a spectral grating hole burning can provide even higher data storage density.

Two-photon absorption of shaped femtosecond pulses was studied recently for narrow atomic absorption lines [12,13], revealing several interesting nonlinear interference effects. In case of an excitation with a spectrally broad ultrashort pulse, only

the sum of the energy of the two photons has to add up to the energy of the transition, while the energy of each photon taken separately may be arbitrary.

In this paper we study two-photon excited coherence in an inhomogeneously broadened medium consisting of organic dye-doped polymer at low temperature. In our experiment, we create a grating at a visible wavelength by illuminating the sample with phase-locked pairs of 100-fs laser pulses at a near-infrared wavelength equal to two times the transition wavelength. We perform experiments where the two-photon excited coherence is detected in two independent ways—either by measuring the spectrum of fluorescence or, after prolonged illumination, by observing spectrally modulated persistent spectral hole. We analyze the detailed shape of grating at different temperatures and show that this information can be used to deduce temperature dependence of Debye–Waller factor and phonon spectrum of the two-photon electron–phonon transition in the presence of large inhomogeneous broadening.

It has been observed that in organic molecules such as porphyrins, typically used for SHB experiments, the probability of simultaneous absorption of two photons is rather small, even if high intensity laser pulses are applied. At the same time, molecules known to have a large TPA cross-section often lack properties required for SHB. A further goal of this paper is investigating new materials for multi-photon frequency-selective SHB recording. So far, there has been only a limited number of communications on absolute TPA cross-sections of porphyrin-like molecules [14–18]. To obtain further insight into structure-property relationships of TPA in prospective SHB materials, we perform measurements of absolute cross-section in series of octaethyl-, tetraphenyl-, and tetrabenzo-substituted porphyrins, and analyze how nonlinear absorption parameters are linked to linear absorption parameters of the molecules.

## 2. Theoretical description of coherence excited by simultaneous absorption of two photons

Previous treatments of coherent interaction of a sequence of short pulses with a two-photon

absorbing medium [12,13] have been based on an assumption that the duration of the illuminating pulses is much shorter than inverse homogeneous- and inhomogeneous line width of the medium,  $t_p < \Gamma^{-1}$ . Since, under such condition, the frequency-domain interference is restricted to a narrow bandwidth of the TPA medium, in previous approaches the interference occurred only if the time delay between the pulses was varied. Below we analyze the case of a strongly inhomogeneously broadened medium, such that the overall width of the TPA spectrum is larger than the inverse duration of the pulses.

The distinctive property of our approach is that the delay is constant, and the interference occurs directly in the frequency dimension.

Consider a sequence of two linearly polarized, temporally nonoverlapping laser pulses, described by electric field:

$$E(t) = E_1(t)e^{-i\omega_L t} + E_2(t - \Delta\tau)e^{-i\omega_L(t - \Delta\tau)}, \quad (1)$$

where  $E_i(t)$  ( $i = 1, 2$ ) is the pulse envelope,  $\omega_L$  is the carrier frequency of the pulse and  $\Delta\tau$  is delay of the second pulse. In case of holographic recording, one of the pulses serves as an object pulse and the other as a reference pulse [5]. If all molecules are in the ground electronic state before the pulses are applied, then after one-photon resonance excitation by the pulses, the probability of finding molecule with transition frequency  $\omega_k$  in the excited state is proportional to the intensity of the spectral component of the incident light at this frequency:

$$P(\omega_k) \propto |\hat{E}(\omega_k)|^2, \quad (2)$$

where  $\hat{E}(\omega)$  is Fourier transform of the electric field:

$$\hat{E}(\omega) = \int E(t)e^{i\omega t} dt. \quad (3)$$

As has been shown by several authors before, by choosing a suitable reference pulse shape, power spectrum (3) contains all necessary information about the object pulse.

In case of two-photon absorption, however, there is no such linear correspondence of the excitation probability and the power spectrum of the pulses. To find this relation for TPA we need to

consider the process of absorption in some more detail. Let  $|g\rangle$  denote the molecule's ground state,  $|i\rangle$  the single intermediate state (which is out of resonance with 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  $\omega_k$ . At time  $t$ , after the pulse sequence,  $(t - \Delta\tau) \gg t_p$ , the wave function of a particular molecule with transition frequency  $\omega_k$  will be

$$|\Psi_k(t, \omega_k)\rangle = |g\rangle + a_k(t, \omega_k)|e_k\rangle, \quad (4)$$

where the probability amplitude  $a_k(t, \omega_k)$  is given by

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

where  $Q_{g,k}$  is the two-photon transition operator,

$$Q_{g,k} = \frac{\langle e_k | \mu | i \rangle \langle i | \mu | g \rangle}{\hbar(\omega_i - \omega_L)} \quad (6)$$

and

$$\hat{E}^2(\omega) = \int E^2(t) e^{i\omega t} dt \quad (7)$$

is the Fourier transform of the square of electric field.

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

$$a_k(t, \omega_k) = \frac{i}{\hbar} Q_{g,e_k} e^{-i\omega_k t} \hat{E}_1^2(\omega_k - 2\omega_L), \quad (8)$$

where  $\hat{E}_1^2(\omega)$  is the Fourier transform of the square of electric field envelope of the first pulse.

Eq. (8) shows that the first pulse creates a polarization in the excited state oscillating at  $\omega_k$ . Note that each subset of molecules from the inhomogeneous distribution oscillates at its own resonant frequency.

If the time delay  $\Delta\tau$  between the first and second pulses is less than the homogeneous optical dephasing time  $T_2$ , then an interference between polarizations induced by the two pulses will occur. If we consider a simplified situation, where the two temporarily nonoverlapping pulses have identical envelopes,  $E_1(t) = E_2(t - \Delta\tau) = E_0(t)$ , the probability amplitude after two pulses is:

$$a_k(t, \omega_k) = \frac{i}{\hbar} Q_{g,k} e^{-i\omega_k t} \hat{E}_0^2(\omega_k - 2\omega_L)(1 + e^{i\omega_k \Delta\tau}). \quad (9)$$

Since the probability of finding a molecule in the excited state is proportional to  $|a_k|^2$ , the excited state population created by two-photon excitation, is proportional to the “effective power spectrum”,  $\hat{E}_0^2(\omega_k - 2\omega_L)$ , modulated by periodic function,

$$f(\omega_k) = (1 + \cos \omega_k \Delta\tau). \quad (10)$$

This result demonstrates that for a fixed  $\Delta\tau$  value, the constructive or destructive interference conditions can be obeyed for a predetermined set of transition frequencies within inhomogeneous band. Namely, in 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  $\omega_k$ , one will have a constructive interference of this pulse with a polarization induced by the first pulse at this frequency.

Experimentally, in 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 the pair of pulses, also delayed by  $\Delta\tau$ . We underline, however, that grating is created at an optical frequency, which is double the actual carrier frequency of the pulses illuminating the medium.

### 3. Experimental

Our laser system comprised a 1 kHz repetition rate Ti:sapphire regenerative amplifier system (Clark MRX CPA-1000) seeded by a mode-locked Ti:sapphire femtosecond laser (Coherent Mira 900). The amplified pulses had a duration of 150 fs and energy of 0.8 mJ at 780 nm. TOPAS (Quantronix) optical parametric amplifier (OPA) was used to convert 780 nm pulses into near infrared pulses tunable in the range 1100–1800 nm. The IR pulses were nearly Fourier-transform limited, had duration 100 fs and energy 0.1–0.2 mJ. Glass color filters were used to cut off any residual visible light from the laser.

Fig. 1 shows experimental set-up used for two-photon excited fluorescence measurement. Slightly modified set-ups were used for two-photon hole

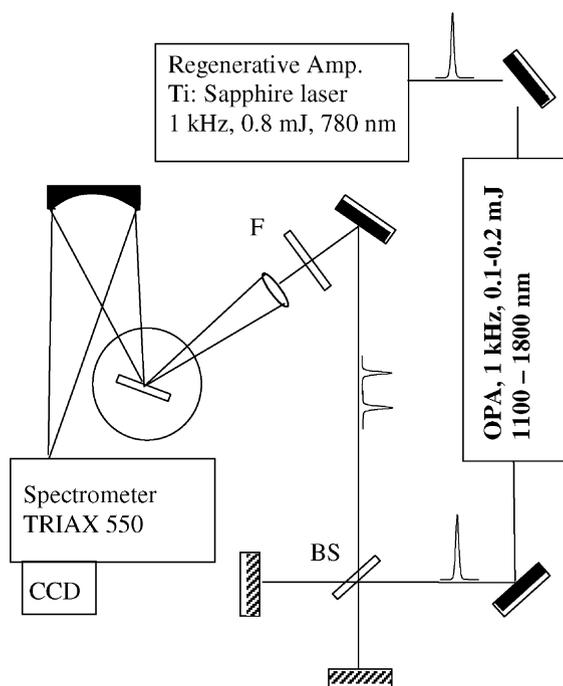


Fig. 1. Schematic of experimental set up for two-photon-excited fluorescence measurements. PM—photomultiplier; F—set of infrared filters; BS—beam splitter.

burning and absolute cross-section measurements, and are described in detail in Ref. [18]. A Michelson interferometer divided the OPA beam into two spatially overlapped but time-delayed beams. The time delay between the two pulses was  $\Delta\tau \approx 100$ –1000 fs, and was adjusted by translating one of the mirrors. The pulses were focused with a  $f = 500$  mm lens onto a sample positioned inside a variable-temperature helium bath cryostat ( $T = 2$ –300 K). Laser spot size was estimated to be about  $2.5 \times 10^{-3}$  cm<sup>2</sup>. The pulse peak intensity at the sample was varied from 20 to 80 GW cm<sup>-2</sup> by neutral density filters. In the hole burning experiment, a mask with  $1 \times 0.6$  mm opening was placed just before the sample to ensure that the same exact spot was irradiated and probed.

Fluorescence was collected with a spherical mirror and focused on the entrance slit of a Jobin-Yvon TRIAX 550 spectrometer equipped with a N<sub>2</sub>-cooled CCD array detector.

In the frequency domain grating experiments, we used 0.2 mm thick polyvinylbutyral (PVB) films activated with 7,8-Dihydroporphyrin (chlorin) or Silicon-2,3-naphthalocyanine dioctylxide (SiNc) molecules at a concentration of about  $10^{-4} \text{ mol l}^{-1}$ . In the TPA cross-section experiments the sample was a porphyrin solution in dichloromethane or toluene at room temperature. SiNc, 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine Zinc(II) (ZnOEP) and 5,10,15,20-Tetraphenyl-21H,23H-porphine ( $\text{H}_2\text{TPP}$ ) were purchased from Aldrich. Tetrabenzoporphine ( $\text{H}_2\text{TBP}$ ) was purchased from Porphyrin Products, Inc. (Logan, Utah). Zn-5-Monophenyl-tetrabenzoporphyrin (ZnMPTBP), Zn-5,15-Diphenyl-tetrabenzoporphyrin (ZnDPTBP), Zn-5,10,15-Triphenyl-tetrabenzoporphyrin (ZnTriPTBP) and Zn-5,10,15,20-Tetraphenyl-tetrabenzoporphyrin (ZnTPTBP) and chlorin were synthesized and purified by A. M. Shul'ga (Minsk, Belarus).

In the TPA spectra measurements, we employed the second harmonic of OPA output as well as fundamental Ti-sapphire amplifier wavelength for two-photon excitation and the second harmonic of the latter for one-photon excitation. Central part of the beam's spatial cross-section was selected with a pinhole and passed through a 1 cm cell with sample solution. Special care was taken to geometrically eliminate the possible re-absorption effects.

#### 4. Two-photon excited spectral gratings detected by resonance fluorescence and persistent spectral hole burning

The first observation of energy-selective two-photon excitation of organic molecule was reported by Kohler [19]. In Ref. [20], Small and co-authors burned a hole by usual one-photon excitation mechanism, and detected it in TPA fluorescence excitation spectrum. Recently Takeda et al. demonstrated two-photon excited fluorescence line narrowing for several dyes with no inversion symmetry [21]. In the earlier 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 the scattered laser light near the transition frequency, which provides the unique possibility of recording pure electronic zero-phonon line in fluorescence.

Fig. 2 shows fluorescence spectrum of chlorin in PVB at  $T = 4 \text{ K}$ , recorded in the region of inhomogeneously broadened 0–0 transition near 630 nm, at the time when the sample was illuminated with infrared pulses at a wavelength of 1270 nm. Illumination with single pulses led to a smooth fluorescence profile (dashed curve). However, if the sample was illuminated with pairs of phase-locked pulses (solid curve), the center part of the spectrum showed a distinct periodic modulation. The period of fluorescence intensity modulation is  $50 \text{ cm}^{-1}$ , which corresponds to the inverse delay between the pulses,  $\Delta\tau = 670 \text{ fs}$ . Dotted curve at the bottom of the figure presents frequency-doubled spectrum of the laser, obtained by passing the pulse pairs through a SHG crystal at phase matching angle. Note that the light reaching the sample contained no second harmonic. Although SHG approximately corresponds to the TPA spectrum, we underline that, in general, one cannot deduce the modulation structure in the TPA-excited fluorescence signal from that in the SHG spectrum.

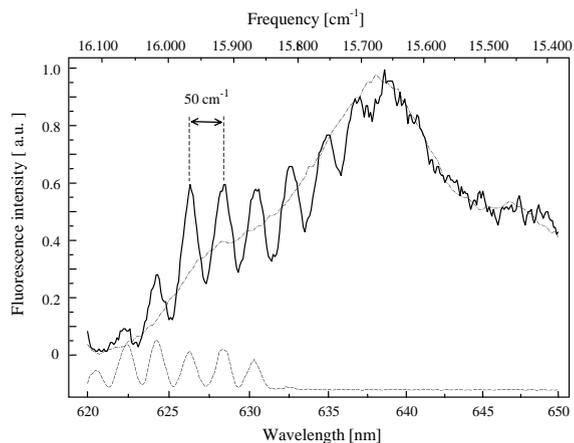


Fig. 2. The frequency-domain modulated ( $\Delta\nu = 50 \text{ cm}^{-1}$ ) fluorescence spectrum of chlorin (7,8 dihydroporphyrin) in PVB film (—). The spectrum obtained with one closed arm of Michelson interferometer (- · - · -) is normalized with respect to the previous one. The spectrum of laser second harmonics is presented for comparison (- - -).

It is known that at liquid helium temperature, the homogeneous one-photon zero-phonon line of chlorin is much narrower,  $\Gamma_{\text{hom}} < 0.3$  GHz, than the inhomogeneous broadening,  $\Gamma_{\text{inh}} > 5$  THz [22]. Our measurement shows that the same is true for two-photon transition in chlorin.

Our next step is a demonstration of “engraving” of the above spectral modulation via persistent SHB. Since the rate of TPA-induced excitation in chlorin was still rather low, then for this experiment it was critical that the quantum efficiency of photochemical transformation is as large as possible. However, our attempts to induce a detectable change in the absorption of the  $Q_x$  band of chlorin molecule’s stable tautomer (T1-form) were failed even for irradiation times as large as several hours. The main reason is in very small quantum efficiency of photo-transformation  $\sim 10^{-4}$ – $10^{-3}$  [23,24]. Fortunately, we found another opportunity in using reverse photochemical reaction from chlorin’s unstable tautomer form. It is known that at room temperature chlorin molecule exists in a form with N–H ... H–N axis parallel to the reduced C–C bond [25]. At liquid helium temperatures it undergoes photo-induced tautomerization yielding perpendicular direction of N–H ... H–N axis with respect to the reduced bond (T2-form) [26]. One-photon SHB has been shown in both educt and photo-product tautomers of chlorin in Shpolskii matrices [26], and polymer films [22–24]. As compared to T1  $\rightarrow$  T2 photo-transformation, a drastic increase of the rate of back T2  $\rightarrow$  T1 process has been observed [23,24,26], giving rise to 10% quantum efficiency of this process in polymer matrices. This value is probably the highest one known for monomolecular SHB systems. Tautomer T2, as well as its stable counterpart T1, has no center 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  $1000\text{ cm}^{-1}$  [24,26], 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 [23,24], nevertheless, it is known that its inhomogeneous band has a certain degree of spectral selectivity.

With this information in hand, we started by preparing the molecules in T2-form by illuminating the sample at 4K for 20 min with 633-nm pulses, obtained by frequency doubling of the OPA output 1265 nm. After that, we tuned OPA to 1134 nm, which corresponded to half of the frequency of the T2 band at 567 nm. Fig. 3 shows the changes in the visible absorption, as a result of irradiation of the sample with pairs of 1134 nm pulses with a constant time delay. Experimental dots (closed and open) were obtained as follows. 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 experimental differential spectrum and the result was smoothed with standard method using 10 adjacent points. The closed and open dots correspond to the 45s and 285s irradiation times, respectively. The experimental modulation period is  $230 \pm 30\text{ cm}^{-1}$ , which coincides with theoretical expectation within experimental error.

In conclusion of this section we note essential difference between TPA-initiated SHB and the known process of photon-gated SHB [27]. The latter implies sequential absorption of two photons with the first one in resonance with molecule absorption, whereas TPA occurs via a purely virtual intermediate level.

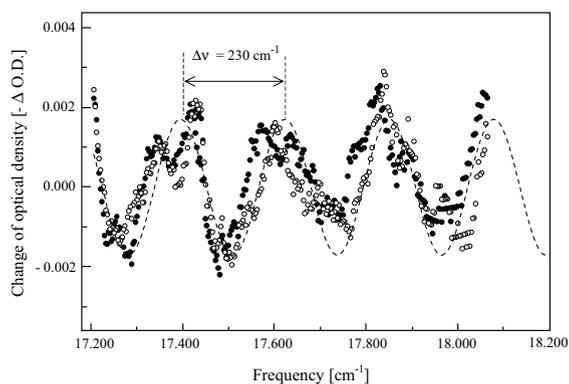


Fig. 3. Spectral modulation in unstable phototautomer of chlorin absorption band after prolonged illumination with pairs of pulses with 180-fs time delay between them after irradiation time of 45 (●) and 285s (○),  $I = 3\text{ W cm}^{-2}$ . — represents a cosine fitting function with a period of  $230\text{ cm}^{-1}$ .

## 5. Temperature dependence of two-photon homogeneous absorption spectrum

In this section we study the dependence of the TPA-excited frequency-domain interference on homogeneous absorption (and emission) spectrum of the molecules. In this experiment we take full advantage of the fact that Rayleigh scattering is completely absent at the wavelength of TPA-excited emission. This allows us to measure resonance fluorescence spectrum with a high degree of fidelity, which may be quite challenging by other (linear) methods.

Fig. 4 shows spectra of  $S_1 \rightarrow S_0$  fluorescence emission of a chlorin in PVB polymer film

$$M(T) = \beta \sqrt{(A(T) + B(T)\cos\delta + C(T)\cos 2\delta)^2 + (B(T)\sin\delta + C(T)\sin 2\delta)^2} \quad (12)$$

obtained upon illumination with pairs of 1280 nm pulses at different temperatures. At low temperatures, one can clearly see a modulation with a period of  $45 \text{ cm}^{-1}$ , which corresponds to the inverse time delay between the pulses. With increasing temperature, the depth (contrast) of the modulation decreases, and the position of the grating maxima shifts to longer wavelengths.

Qualitatively, this behavior can be understood if one takes into account that the relative contribution of phonon side-band(s) to the homogeneous absorption and emission grows with temperature. For one-photon transitions it is well known that even at low temperatures, the real homogeneous spectrum is asymmetric due to a presence of phonon side-band, and that with increasing temperatures the contribution of the phonon side-band quickly increases [28]. In our case only the emission part of the measured spectrum is due to conventional one-photon transition, while the absorption is due to two-photon transition. Note that in general these two spectra do not possess mirror symmetry because of different selection rules in the two cases.

In the quantitative analysis presented below we assume that in the first approximation one- and two-photon spectra are symmetrical. We then take

the effective power spectrum in the form of a periodic function (10). By approximating the phonon wing of the homogeneous spectrum with a Gaussian (standard deviation  $\sigma(T)$  and Stokes shift  $\Delta$ ) we can express the fluorescence spectrum as,

$$F(\nu, T) = M(T)\cos[\nu\Delta\tau + \Delta\varphi(T)]. \quad (11)$$

Relation (11) shows that the spectral response of the medium (fluorescence spectrum in our case) can be presented by a harmonic function, where the amplitude,  $M(T) < 1$ , and the phase shift,  $\Delta\varphi(T)$ , both depend on temperature. Analytical expressions for these parameters are:

$$\Delta\varphi(T) = \text{arctg}\left(\frac{B(T)\sin\delta + C(T)\sin 2\delta}{A(T) + B(T)\cos\delta + C(T)\cos 2\delta}\right), \quad (13)$$

where  $\beta$  is the depth of the applied laser spectrum modulation and the following functions have been introduced:

$$A(T) = \alpha^2(T), \quad (14a)$$

$$B(T) = 2\alpha(T)[1 - \alpha(T)]\exp\left[-\frac{(-\Delta\tau\sigma(T))^2}{2}\right], \quad (14b)$$

$$C(T) = [1 - \alpha(T)]^2\exp[-(\Delta\tau\sigma(T))^2], \quad (14c)$$

where  $\delta = \Delta\tau \cdot \Delta$ .  $\alpha(T)$  is the Debye–Waller factor, which depends on temperature as:

$$\alpha(T) = \exp(-S_0 \text{cth}(\hbar\omega/2kT)), \quad (15)$$

and  $S_0$  is the Huang–Rhys factor,  $\omega$  is the effective phonon frequency and

$$\sigma(T) = \sqrt{\omega\Delta \text{cth}(\hbar\omega/2kT)}. \quad (16)$$

Figs. 5(a) and (b) present the experimental dependencies  $M(T)$  and  $\Delta\varphi(T)$ , along with corresponding theoretical fits (solid lines). Best fit to experimental data gives for the Huang–Rhys factor,  $S_0 = 0.6$ , Stokes shift,  $\Delta = 78 \text{ cm}^{-1}$ , and

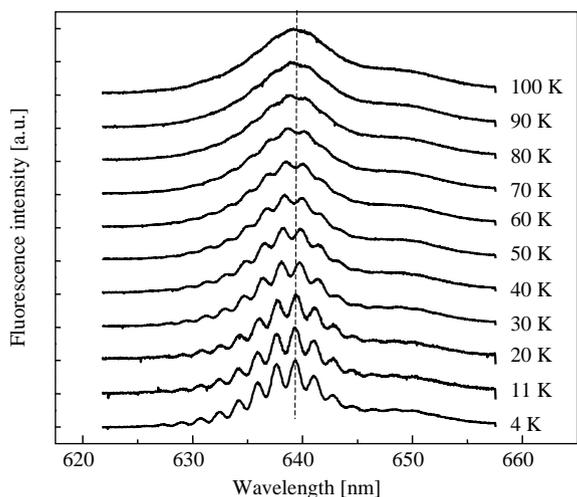


Fig. 4.  $S_1 \rightarrow S_0$  fluorescence emission spectra of a chlorin-doped polymer film obtained at different temperatures upon illumination with pairs of 1280 nm pulses. At low temperatures, one can clearly see a modulation with a period of  $45 \text{ cm}^{-1}$ , which corresponds exactly to the inverse time delay between the pulses. With increasing temperature, the grating shift to longer wavelengths and the depth (contrast) of the modulation decreases.

effective phonon frequency,  $\omega = 30 \text{ cm}^{-1}$ . Note that these parameters include the contribution from TPA homogeneous spectrum and therefore they are not necessarily equal to those, obtained in linear one-photon experiments (e.g. [23,24]). In

particular, while the Huang–Rhys factor and the effective phonon frequency values correspond well to those, known from one-photon homogeneous spectrum [23,24], the Stokes shift value seems to be larger than expected. Our conventional hole burning experiment gives  $\Delta = 15\text{--}20 \text{ cm}^{-1}$ . This experiment also shows that the phonon wing is much better described by the Lorentzian than by the Gaussian function. In the case of the Lorentzian phonon wing with half-width at half maximum  $\gamma$ , similar analytical results (with some modifications in Eqs. (14b), (14c) and (16)) were obtained and the corresponding best fit is shown in Fig. 5(a) and (b) by dashed line. In this latter case,  $S_0 = 0.86$ ,  $\Delta = 25 \text{ cm}^{-1}$ ,  $\omega = 29 \text{ cm}^{-1}$ , and  $\gamma(T=0) = 50 \text{ cm}^{-1}$ . Note that the phase shift (Fig. 5b) is fitted much better for Lorentzian phonon wing. Also, the Stokes shift is much closer to that obtained in the one-photon experiment. On the other hand, the Debye–Waller factor  $\alpha = \exp(-S_0) = 0.42$  is less than that obtained from homogeneous fluorescence spectrum,  $\alpha = 0.55$  [23]. This last result can be due to violation of the Franck–Condon approximation for two-photon transition and needs further investigation.

Thus, the presented method provides the unique possibility to obtain the parameters of homogeneous spectrum for simultaneous two-photon absorption in inhomogeneously broadened

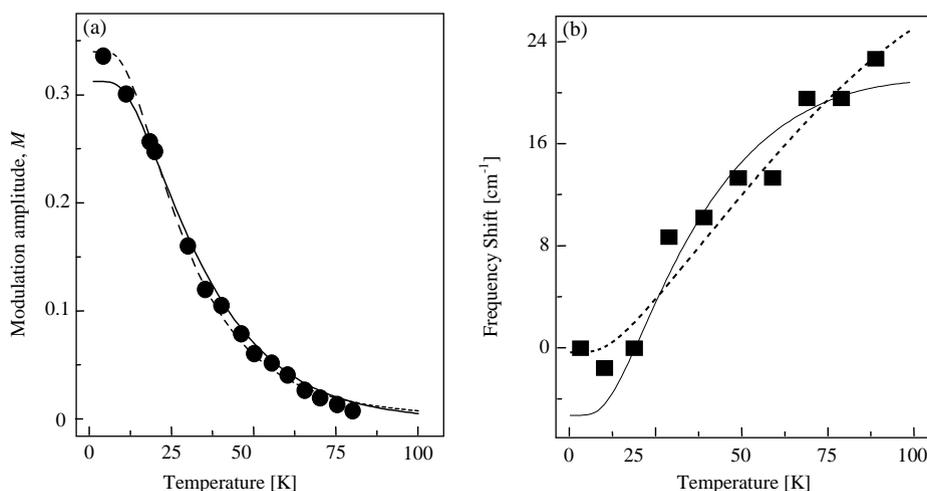


Fig. 5. Functions  $M(T)$  and  $\Delta\nu(T)$  found from the experiment. The best fit parameters,  $S_0 = 0.6$ ,  $\Delta = 78 \text{ cm}^{-1}$ ,  $\omega = 30 \text{ cm}^{-1}$ , are determined from model simulations, see text.

systems. This method can be easily expanded to an evaluation of spectral TPA-response of the medium to a complex pulse sequence such as used in time-domain holography.

Above we have mentioned that one- and two-photon transitions obey different selection rules, which may lead to asymmetry between two-photon absorption and one-photon emission spectrum.

This is clearly demonstrated in Fig. 6, where we present the temperature dependence of fluorescence spectra obtained at the same conditions, as in Fig. 4 but in centrosymmetric molecule, SiNc. As one can clearly see, here the grating does not shift with increasing temperature. This indicates that SiNc molecule does not possess the zero-phonon line in TPA homogeneous spectrum, because of pure electronic zero-phonon transition is strictly prohibited by symmetry. The fact that we still observe modulation at low temperatures may be entirely due to TPA with phonon creation, which slightly relaxes the selection rules by reducing the symmetry.

Another indication of reflection of the symmetry considerations in TPA can be found in Fig. 7, which presents two-photon absorption cross-section of chlorin in PVB film measured at room

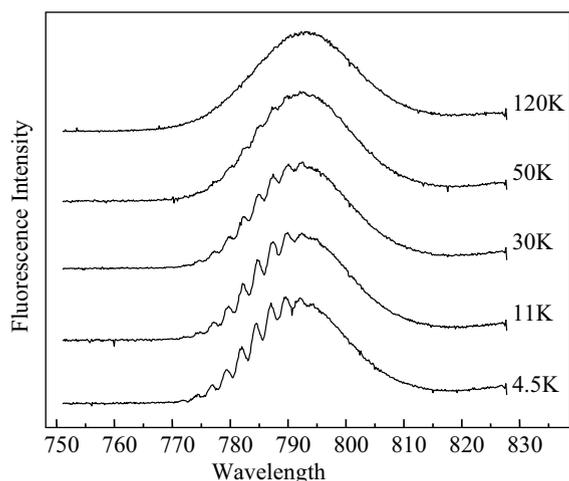


Fig. 6.  $S_1 \rightarrow S_0$  fluorescence spectra of a SiNc-doped polymer film obtained at different temperatures upon illumination with pairs of 1585-nm pulses. As compared to chlorine, see Fig. 4, there is no spectral shift of the grating, but only decrease of modulation depth.

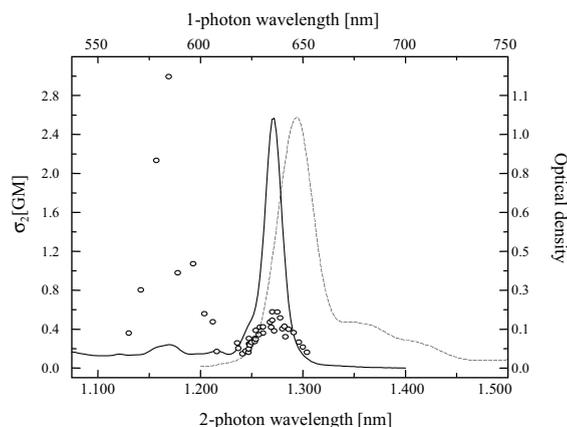


Fig. 7. Two-photon absorption ( $\circ$ ), one-photon absorption ( $\rightarrow$ ) and fluorescence spectra ( $-\ - -$ ) of chlorin in PVB film.

temperature, as a function of excitation laser wavelength in the region 1130–1310 nm. The absolute values of the TPA cross-section were determined by scaling the spectrum with the value  $\sigma_2 = 0.5 \text{ GM}$  ( $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ ) at 1270 nm, which was recently reported in [18]. The figure shows the TPA spectrum along with conventional one-photon absorption and fluorescence emission spectrum. 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  $Q_y(0-1)$ . Note that the TPA spectrum shows the same two transitions, but with opposite relative intensity.

## 6. Resonance enhancement of two-photon cross-section in near-infrared

In the previous sections we demonstrated excitation of coherence by a two-photon process, in which the frequency of  $S_1 \leftarrow S_0$  transition equals the sum of the frequency of two photons. It would be also of great interest to observe a related, Raman-like two-photon process, in which the transition frequency equals difference between the frequency of two pulses. Our initial attempts to excite coherence in a porphyrin sample by illuminating simultaneously with a pulse at green

wavelength and infrared wavelength were not successful. The main reason for that was most likely strong background fluorescence excited by the green wavelength, which was close to resonance with Soret band.

The goal of the following experiment was to investigate what effect a near-by resonance level has on the two-photon absorption process. We measure the TPA absolute cross-section values in the region of the Soret band for a number of porphyrins with gradually varying optical properties. This allows us to establish a relationship between TPA efficiency and several ground- and excited-state absorption parameters. For this purpose, we studied a series of tetrabenzoporphyrins with monotonically increasing number (from 0 to 4) of phenyl substituents in *meso* positions, as well as some other porphyrins. The choice of these porphyrins was motivated by the fact, that their excited-state absorption features do not vary much. This allowed us to find a simple relationship between the TPA cross-section and *only* linear ground-state absorption parameters. The observation of this relationship, which is based on a known single intermediate state approximation for TPA cross-section, demonstrates the effect of resonance enhancement of TPA efficiency in porphyrins by the presence of nearby one-photon-allowed Q-transition.

Fig. 8, left part shows TPA cross-section of ZnOEP as a function of laser frequency,  $\omega_L$ . The

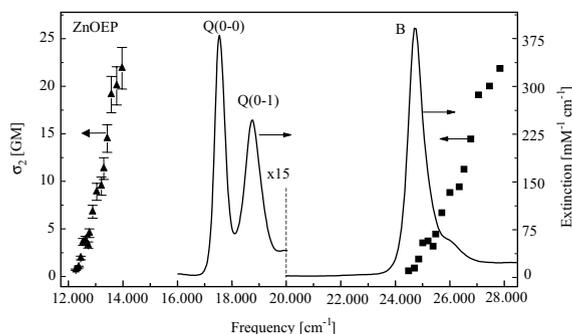


Fig. 8. Two-photon absorption (symbols) spectrum of ZnOEP in toluene. ▲, the  $x$ -axis values correspond to excitation (laser) wavelength. ■, the  $x$ -axis values correspond to transition (twice the laser) wavelength. Linear absorption bands are shown for comparison by solid lines. In this case the  $x$ -axis values always correspond to transition wavelength.

right part of the figure shows the same points but as a function of twice the laser frequency,  $2\omega_L$ . Linear absorption bands in corresponding regions are presented for comparison. For all the experimental points we attested that the two-photon-excited fluorescence intensity had a quadratic dependence on laser power. At higher excitation frequencies ( $> 14,000 \text{ cm}^{-1}$ ), the fluorescence intensity dependence gradually transformed into linear one because the one-photon absorption in Q-band started to compete with TPA.

We notice that the frequency dependence of  $\sigma_2$  in the frequency range studied does not reproduce any of the familiar features of the linear spectrum, such as Soret band. This may be explained by the fact that for centrosymmetric (or nearly centrosymmetric) molecules the selection rules for one- and two-photon dipole transitions are mutually exclusive. Also, one notices that the TPA cross-section values near Soret transition are considerably larger ( $10\text{--}10^2 \text{ GM}$ ) than near Q-transition ( $< 10 \text{ GM}$  [18,29,30]). Similar behavior was obtained for tetraphenylporphyrin ( $\text{H}_2\text{TTP}$ ) tetrabenzoporphyrin ( $\text{H}_2\text{TBP}$ ) and several phenyl-substituted Zn-tetrabenzoporphyrins.

Nearly monotonic increase of the TPA cross-section towards higher frequency as well as rather high cross-section values can be qualitatively explained by the presence of two-photon allowed g-states lying higher in energy than the Soret transition. Indeed, quantum mechanical calculations of porphyrins [31–35] predict the existence of a number of such states, the lowest one lying somewhere in the range  $24000\text{--}28600 \text{ cm}^{-1}$ . On the other hand, measurement of transient stepwise absorption in several porphyrins, including ZnOEP and ZnTPTBP, [15,36] show no distinct  $S_1 \rightarrow S_2$  band in the energy region (recalculated with respect to the ground state) from  $26000$  to  $32000 \text{ cm}^{-1}$ , but only a smooth absorption tail, monotonically increasing towards higher energies. Assuming that the selection rules are the same for stepwise and simultaneous two-photon absorption, this absorption tail can be attributed to overlapping of several spectrally broad and relatively weak  $g \rightarrow g$  transitions [15].

In [37] we have shown that one can obtain a quantitative description of TPA by considering

resonance enhancement via nearby linear Q-transition. It is well known that if in a multi-photon transition, the energy of one-photon approaches that of a real electronic level, the probability of the process may increase dramatically, even without populating the intermediate level. For porphyrins, there are several one-photon allowed transitions lying slightly higher in energy than the photon we use for two-photon excitation, the closest one being the first pure electronic Q(0–0) transition. In approximation where single intermediate state is considered, the TPA cross-section can be expressed as:

$$\sigma_2 = A \frac{|\mu_{i0}|^2 |\mu_{fi}|^2}{(v_{i0} - v_p)^2} g(2v_p), \quad (17)$$

where  $v_p$  is the photon frequency, subscripts 0,  $i$ , and  $f$  designate the ground, intermediate, and final excited state, respectively,  $g(2v_p)$  is the normalized line shape function,  $v_{i0}$  is the frequency of one-photon transition to intermediate state,  $\mu_{mm}$  are the transition dipole moments between states  $m$  and  $n$ ,

$$A = \frac{4}{5} \frac{(2\pi)^4 v_p^2 L^4}{(ch)^2 n^2}, \quad (18)$$

$L = (n^2 + 2)/3$ ,  $n$  is the refractive index of medium.

Fig. 9 shows the dependence of TPA cross section on the integrated intensity of the lowest Q-transition over the detuning squared, measured

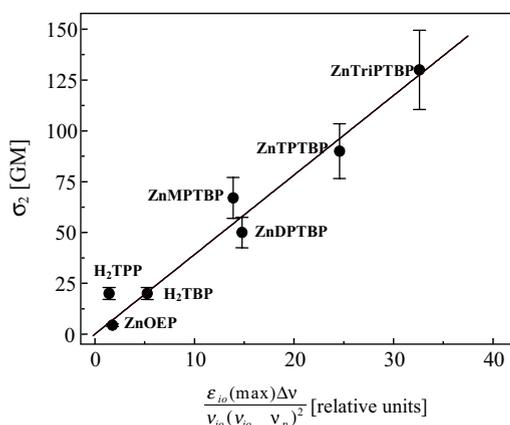


Fig. 9. Correlation between the two-photon absorption cross-section and a combination of linear absorption parameters for a number of porphyrins.

in several porphyrins at 780 nm. The dependence is well fitted to a straight line, which indicates the validity of the above model.

Another indication of resonance enhancement by Q-band can be found from the TPA spectrum. We showed that the frequency of one-photon intermediate transition, which can be found from Eq. (17), as

$$v_{i0} = v_p + 2 \frac{\sigma_2}{d\sigma_2/dv_p}, \quad (19)$$

coincides well with the real maximum of the Q-band.

We have also calculated the  $\sigma_2$  value for ZnOEP directly from (17) and (18), by taking all other parameters from independent measurements, and obtained a 10% correspondence with our experimental value.

The present semi-empirical relationship can be used to predict TPA cross-section value if certain linear absorption parameters are already known. This approach facilitates a search for new porphyrins with greatly enhanced nonlinear properties.

## 7. Conclusions

In this paper we have studied a formation of frequency-domain interference gratings in a multi-photon transition by excitation with time-delayed ultrashort pulses. We have demonstrated that at high illumination intensity, coherence can be created in an inhomogeneously broadened organic dye-doped polymer medium by a multi-photon, sum-frequency type process, rather than conventional one-photon process. We have 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 our present experiment are well described by a perturbation theory model of two-photon induced coherence in a system with no real intermediate level(s). By analyzing the phase and contrast of the grating at different temperatures we obtain, for the first time to our knowledge, temperature dependence of Debye–Waller factor and phonon

spectrum of a two-photon transition of an organic molecule. We have also studied wavelength dependence of absolute two-photon absorption cross section in a series of octaethyl-, tetraphenyl-, and tetrabenzo-substituted porphyrins and have established, for the first time to our knowledge, that the two-photon absorption efficiency of porphyrins in 710–810 nm region is resonantly enhanced due to nearby Q(0–0) one-photon transition. We found that the TPA cross-section can be directly calculated from ground- and excited-state one-photon absorption parameters in a single intermediate level approximation. We believe that this newly established relationship between the TPA and the linear absorption will facilitate a search for new porphyrins with enhanced nonlinear characteristics.

These results allow us to believe that large organic molecules such as porphyrins are not only promising candidates for practical applications such as high density two-photon data storage, fluorescence imaging, etc., but are also interesting objects for future experiments on multi-photon excitation of coherence. One of our further goals is to use the effect of two-photon coherence and SHB for detection of correlated photon pairs such as produced by spontaneous parametric down-conversion.

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