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Resonance enhancement of two-photon absorption in porphyrins

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Abstract

Two-photon absorption spectra in absolute cross-section values are presented for a number of octaethyl-, tetraphenyl-, and tetrabenzo-substituted porphyrins. In excitation spectral region of 710–810 nm, the two-photon absorption efficiency is resonantly enhanced due to nearby Q(0–0) one-photon transition. The cross-section value calculated directly from the ground- and excited-state absorption parameters in a single intermediate level approximation, agrees well with that measured in experiment. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Special optical properties of porphyrins make them attractive for various photonic applications such as holographic data storage [1–4], optical power limiting [5–9] and photodynamic therapy [10,11]. Typically, in the applications listed above, the first step of the light–molecule interaction consists in linear one-photon absorption. In analogy to other organic photonic materials [12], one may suggest that the utility of porphyrins could be substantially increased by using instead of the

linear, one-photon absorption a nonlinear process of simultaneous absorption of two photons. If the efficiency of the two-photon absorption (TPA) could be made, at least at some excitation wavelengths, comparable to that of the one-photon process, then this will open a possibility for many new applications.

So far, however, there has been only a limited number of communications on measurement of the absolute TPA cross-section at selected wavelengths [13–17], TPA spectra in relative values [18,19], and absolute TPA spectra [20–22] in porphyrins. On the other hand, there have been detailed investigations of one-photon absorption properties of porphyrins, including absorption from the excited electronic state. If one could find a relationship between the nonlinear TPA cross-section and one-photon absorption parameters, then this will considerably facilitate a search for new porphyrins with enhanced TPA properties.

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The goal of this Letter was, first, to present the TPA spectra in absolute cross-section values for a number of porphyrins with gradually varying optical properties, and, second, to search for a relationships 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 observance 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.

2. Experimental

2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine Zinc(II) (ZnOEP) and 5,10,15,20-Tetraphenyl-21H,23H-porphine (H_2 TPP) were purchased from Aldrich. Tetrabenzoporphine (H_2 TBP) was purchased from Porphyrin Products (Logan, UT). 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) were synthesized and purified by A.M. Shul'ga (Minsk, Belarus).

Our experimental setup comprises a Ti:sapphire regenerative amplifier (CPA-1000, Clark MXR), which was operated at 1 kHz repetition rate and produced 150 fs pulses at 0.8 mJ energy per pulse. These pulses were parametrically down-converted using the optical parametric amplifier, OPA (TOPAS, Quantronix), which yielded 100 fs pulses in the wavelength range from 1.1 to 1.6 μ m. TPA spectra were obtained by tuning the OPA with second harmonic crystal at the output and registration of one-photon fluorescence. Absolute TPA cross-sections were measured by comparing fluo-

rescence intensity under one- and two-photon excitations, (see [17, and references therein for details]).

In these measurements we employed the fundamental laser wavelength for two-photon excitation and its second harmonics for corresponding one-photon excitation. In both cases, a central part of the beam's spatial cross-section was selected with a pinhole and passed through a 1-cm cell with sample solution. Fluorescence was collected and focused on the entrance slit of a Jobin-Yvon TRIAX 550 monochromator with a spherical mirror or onto CCD array of a Xillix PMI 1400 camera with an objective. Special care was taken to geometrically eliminate the possible reabsorption effects.

3. Results and discussion

Fig. 1 shows TPA cross-section of three compounds – ZnOEP, H_2 TBP, and ZnTPTBP as a function of twice the excitation laser frequency. Linear absorption spectra in the region of the Soret (B) band are presented for comparison. For all the experimental points shown in Fig. 1, we attested that the two-photon-excited fluorescence intensity had a quadratic dependence on laser power. At higher excitation frequencies, the fluorescence intensity dependence gradually transformed into linear one because the one-photon absorption in Q-band started to compete with TPA.

In the spectral range presented in Fig. 1, the two-photon absorptivity does not reproduce any feature of the linear Soret band, which 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 – 10^2 GM) than near Q-transition (< 10 GM [20–22]). 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 [23–27]

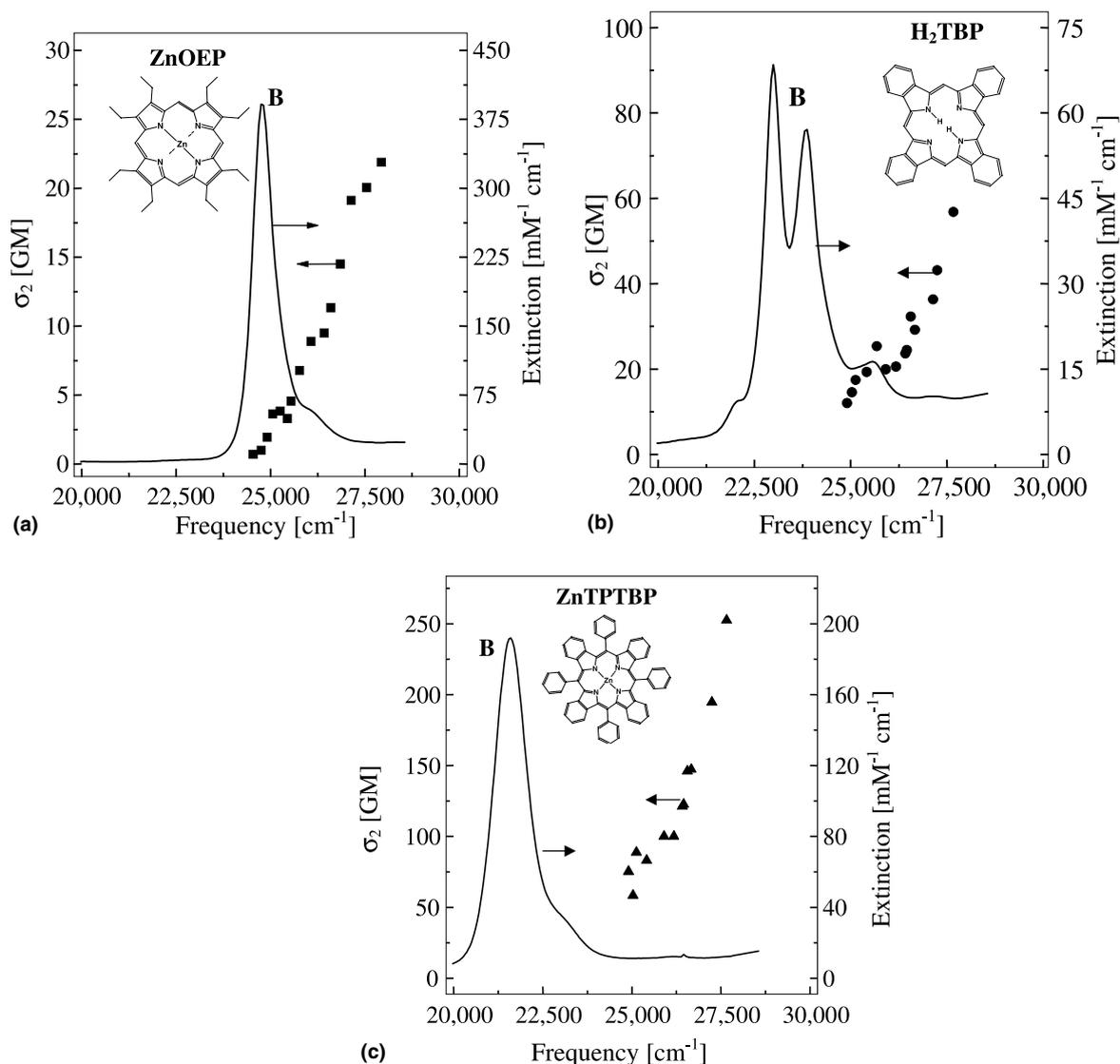


Fig. 1. Two-photon (symbols) and one-photon (solid line) absorption spectra of ZnOEP in dichloromethane (a), H₂TBP in pyridine (b) and ZnTPTBP in toluene (c). The *x*-axis corresponds to the transition frequency for both linear and two-photon spectra.

predict the existence of a number of such states, the lowest one lying somewhere in the range 24 000–28 600 cm⁻¹. Furthermore, measurement of transient stepwise absorption in several porphyrins, including ZnOEP and ZnTPTBP, [7,14] shows no distinct S₁ → S₂ band in the energy region (recalculated with respect to the ground state) from 26 000 to 32 000 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 TPA, this absorption tail can be attributed to overlapping of several spectrally broad and relatively weak *g* → *g* transitions [14].

Although the above considerations are providing a qualitative explanation of the TPA spectra, a quantitative description of the absolute TPA cross-section values is not readily available. 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.

Our goal is to clarify whether the increase of TPA cross-section is indeed due to a resonance enhancement or to some other reason, e.g. particular spectral distribution of the $g \rightarrow g$ transitions. For this purpose we present in Fig. 2 the

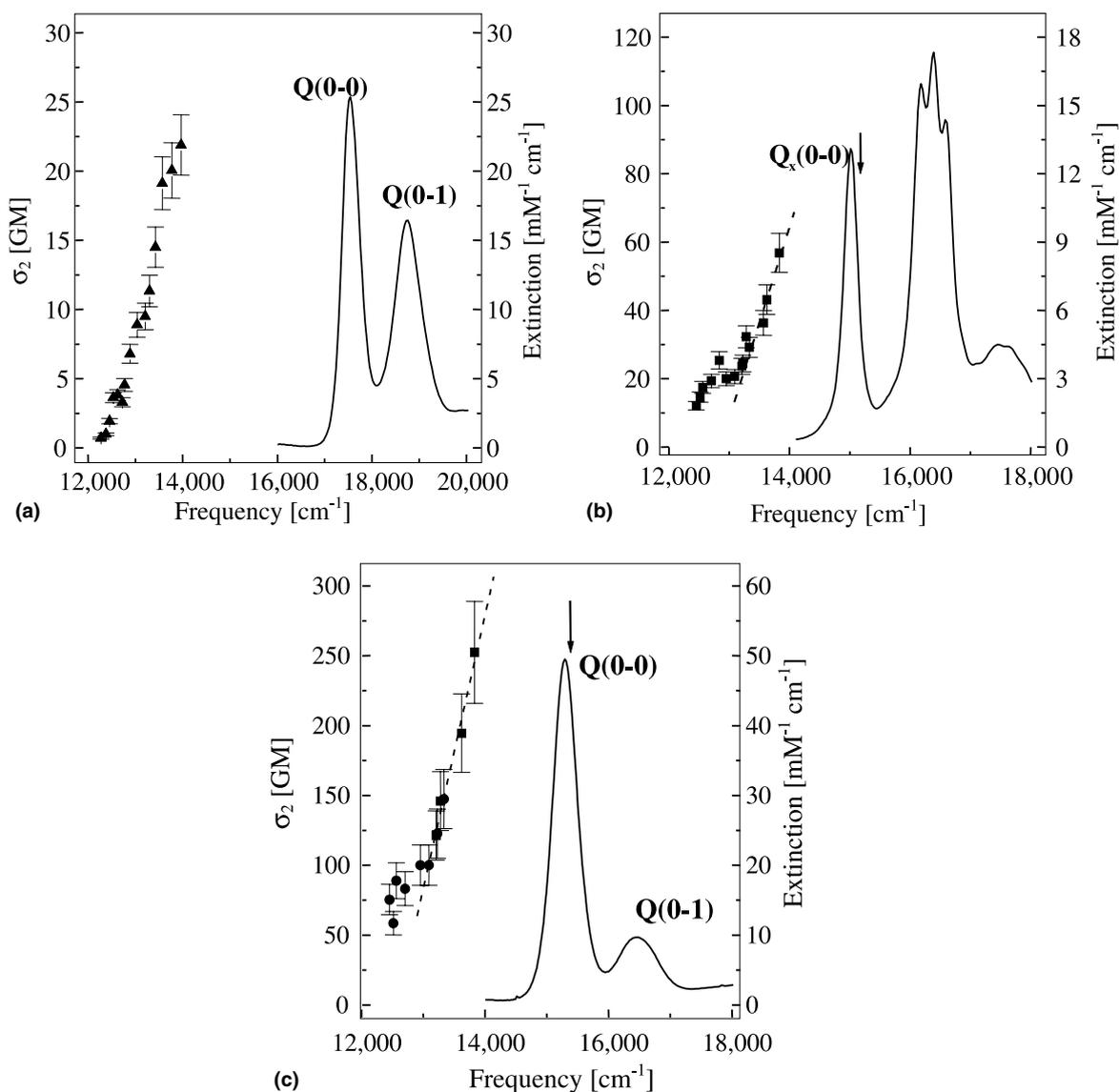


Fig. 2. Two-photon (symbols) and one-photon (solid line) absorption spectra of the same molecules, as in Fig. 1. The x-axis corresponds to photon energy (one-half of transition energy in case of TPA). Dashed lines in (b) and (c) show the linear fits to high-frequency regions of TPA spectra. Arrows on one-photon spectra in (b) and (c) demonstrate the expected frequency of enhancing one-photon transition, obtained according to (5).

same TPA data points as in Fig. 1, but now plotted as a function of laser frequency. The role of the nearby one-photon Q(0–0) transition, shown in Fig. 2, will be elucidated from the following analysis. The perturbation theory result for the TPA cross-section (in $\text{cm}^4 \text{s photon}^{-1}$) reads as follows [12,25,28, and references therein]:

$$\sigma_2 = \frac{(2\pi)^4 v_p^2 L^4}{(ch)^2 n^2} \langle |S_{f0}|^2 \rangle g(2v_p). \quad (1)$$

This expression is obtained for the degenerate case when both photons have the same frequency v_p (in Hz). Here subscripts 0 and f designate ground and final excited states, L is the local field factor, calculated by the Lorentz local field as $L = (n^2 + 2)/3$, n is the refractive index of medium, $g(2v_p)$ is the normalized line shape function (in Hz^{-1}), proportional to the cross-sectional contour of the final state. $\langle \rangle$ denotes the average over the molecular orientation. $|S_{f0}|^2$ represents the molecular two-photon tensor

$$|S_{f0}|^2 = 4 \left| \sum_j \frac{(\mathbf{p} \cdot \boldsymbol{\mu}_{j0})(\boldsymbol{\mu}_{fj} \cdot \mathbf{p})}{v_{j0} - v_p + i\Gamma_j} \right|^2, \quad (2)$$

where \mathbf{p} is the unit vector defining the laser polarization, v_{j0} and Γ_j are the frequency and the homogeneous linewidth, respectively, associated with the j th state, $\boldsymbol{\mu}_{nm}$ are the transition dipole moments between states m and n (if $m \neq n$) or permanent dipole moments (if $m = n$). In the single intermediate state approximation, $j = i$, and in the case when $\boldsymbol{\mu}_{i0}$ and $\boldsymbol{\mu}_{fi}$ are parallel and exciting light is linearly polarized, Eqs. (1) and (2) reduce to

$$\sigma_2 = \frac{4}{5} \frac{(2\pi)^4 v_p^2 L^4}{(ch)^2 n^2} \frac{|\boldsymbol{\mu}_{i0}|^2 |\boldsymbol{\mu}_{fi}|^2}{(v_{i0} - v_p)^2 + \Gamma^2} g(2\omega_p). \quad (3)$$

The single intermediate state (or three-level) approximation holds for centrosymmetric molecules and in spectral range where the detuning $v_{i0} - v_p$ is sufficiently small. All the molecules studied in this Letter are centrosymmetric or quasi-centrosymmetric (i.e. if they are unsymmetrically substituted, the substituent groups only slightly perturb the whole conjugated π -system). This suggests the absence of permanent dipole moments in ground and excited states and makes accounting for the initial and final states unnecessary ($m \neq n$ in (2)

always) [29]. Also, Fig. 2 demonstrates the proximity of v_{i0} to v_p thus qualitatively suggesting the validity of small detuning.

To show that the TPA spectra in Fig. 2 reflect indeed a resonance enhancement due to nearby one-photon transition, we performed the following simple analysis. One can easily see from Eq. (3) that if $\Gamma \ll v_{i0} - v_p \ll v_p$, the normalized spectral derivative of the two-photon molecular absorptivity depends only on the value of detuning:

$$\frac{1}{\sigma_2} \frac{d\sigma_2}{dv_p} = \frac{2}{v_{i0} - v_p}. \quad (4)$$

Therefore we can obtain from the measured TPA spectrum an expected frequency of the most important one-photon transition as follows

$$v_{i0} = v_p + 2 \frac{\sigma_2}{d\sigma_2/dv_p}. \quad (5)$$

From the experimental point of view, this approach is rather reasonable because we have in our disposal only a narrow part of TPA spectrum, which is nevertheless sufficient for estimation of derivative at a particular frequency. An advantage of this approach consists also in using only relative values of TPA (one does not need to measure absolute cross-sections). The derivative was calculated for H_2TBP and ZnTPTBP by accomplishing a simple linear regression of a high-frequency segment of spectrum around $v_p = 13520 \text{ cm}^{-1}$, see Fig. 2. The corresponding values of $(1/\sigma_2)(d\sigma_2/dv_p)$ are 1.197×10^{-3} and $1.055 \times 10^{-3} \text{ cm}$, which according to (5) gives $v_{i0}(\text{H}_2\text{TBP}) = 15190 \text{ cm}^{-1}$ ($\lambda = 658 \text{ nm}$) and $v_{i0}(\text{ZnTPTBP}) = 15420 \text{ cm}^{-1}$ ($\lambda = 648 \text{ nm}$). More accurate calculations, which take into account the finite values of $\Gamma \approx \Delta\nu$, (see Table 1 for the spectral linewidths $\Delta\nu$), give $\lambda(\text{H}_2\text{TBP}) = 659 \text{ nm}$ and $\lambda(\text{ZnTPTBP}) = 650 \text{ nm}$. Note that real lowest one-photon transitions lie for these two molecules at 666 and 654 nm, respectively. (We note also that the closer v_p to Q(0–0) resonance, the better is the correspondence between v_{i0} estimated from (5) and the real one.) This fairly close correspondence of expected and real frequencies suggests that the TPA spectral features presented in Fig. 2 really result from resonance enhancement due to nearby lowest Q(0–0) transition.

Table 1
Linear and nonlinear optical properties of several porphyrins

Porphyrin	Solvent	λ_{\max} (nm)	$\bar{\nu}_{i0}$ (cm^{-1})	$\epsilon_{i0}(\max)$, ($\text{mM}^{-1} \text{cm}^{-1}$)	$\Delta\bar{\nu}$ (cm^{-1})	ϵ_{fi} (532 nm) ($\text{mM}^{-1} \text{cm}^{-1}$)	σ_2^a GM
ZnOEP	CH_2Cl_2	571	17 510	13	550	8 ^b [14]	4.4
H ₂ TPP	Toluene	647	15 500	3.4	470	15 [14]	15
ZnTPP	Toluene					16 [5]	
	CH_2Cl_2					16 [14]	
	Toluene					18 [5]	
H ₂ TBP	Pyridine	666	15 015	13	310		20
MgTBP	EP					15 [8]	
ZnMPTBP	Toluene	628	15 924	66	325		67
ZnDPTBP	Toluene	632	15 810	56	370		50
ZnTriPTBP	Toluene	641	15 600	86	460		130
ZnTPTBP	Toluene	650	15 385	49	510		90
	Benzene					19 [7]	

Maximum wavelength, λ_{\max} , frequency, $\bar{\nu}_{i0}$ extinction coefficient, $\epsilon_{i0}(\max)$, and spectral band width (FWHM), $\Delta\bar{\nu}$, of the Q(0–0) linear absorption band; the lowest excited singlet extinction coefficient ϵ_{fi} (532 nm) measured at probe wavelength of 532 nm; the two-photon absorption cross-section σ_2 , measured at 780 nm.

^a The error of σ_2 values is about 15%.

^b Strong nearby absorption saturation (at 534 nm [14]) can introduce a large error in excited-state extinction value.

This important finding stimulated us to search for a simple empirical relationship between the TPA cross-section value and some usual linear absorption parameters of porphyrins. This kind of relationship, based on Eq. (3), could considerably facilitate a search and design of new porphyrins with strongly enhanced TPA. Experimental σ_2 values, obtained in this work for a number of porphyrins by using Ti-sapphire amplifier, operated at $\bar{\nu}_p = 12800 \text{ cm}^{-1}$, are presented in Table 1. Several linear absorption parameters measured in this work for Q(0–0) band are also presented in Table 1. Qualitatively, it is immediately apparent that among others, *meso*-phenyl-substituted tetrabenzoporphyrins show the highest TPA cross-sections. Eq. (3) predicts the σ_2 to be proportional to the linear transition dipole moment squared $|\mu_{i0}|^2$ over frequency detuning squared, provided that $|\mu_{fi}|^2 g(2\nu_p) \propto \epsilon_{fi}(2\nu_p - \nu_{i0})$ does not vary much from one molecule to another. An indirect evidence for this last assumption can be found in picosecond transient absorption data. The literature values of singlet excited state extinction ϵ_{fi} at $\lambda_{fi} = 532 \text{ nm}$ are collected in Table 1 for several porphyrins. It is evident that ϵ_{fi} (532 nm) does not

vary more than 25% upon transition from a free base tetraphenylporphyrin (H₂TPP) to metallo-tetraphenylporphyrins (ZnTPP and MgTPP) and to tetrabenzosubstituted porphyrins (MgTBP and ZnTPTBP). While we probe another spectral region in our simultaneous TPA experiment (corresponding to $\lambda_{fi} \sim 790\text{--}1100 \text{ nm}$), we assume that the corresponding extinction will stay more or less the same in a series of porphyrins studied, because the transient singlet-singlet absorption spectra of porphyrins consist of a very broad dominant peak centered at $\sim 440\text{--}510 \text{ nm}$ with similar width and very smooth tail in the region of $800\text{--}900 \text{ nm}$ [14].

Fig. 3 shows the dependence of TPA cross-section, measured at 780 nm, on the combination of linear absorption parameters: $\epsilon_{i0}(\max)\Delta\bar{\nu}/[\bar{\nu}_{i0}(\bar{\nu}_{i0} - \bar{\nu}_p)^2]$. The dependence is well fitted to a straight line, which indicates that there is indeed a correlation between σ_2 and $|\mu_{i0}|^2/(\nu_{i0} - \nu_p)^2$. This fact, from the one side, demonstrates one more time the effect of resonant enhancement of TPA in this spectral region and, from the other, supports our conclusion about small variations in $|\mu_{fi}|^2 g(2\nu_p)$ for porphyrins studied. Very illustrative in this sense is the behavior in a series of four

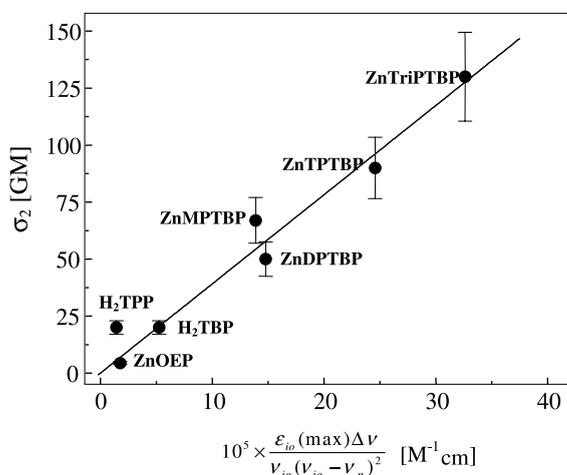


Fig. 3. Correlation between the two-photon absorption cross-section and a combination of linear absorption parameters for a number of porphyrins.

phenyl-substituted tetrabenzoporphyrins. As the number of phenyl substituents increases from one to four, the lowest absorption Q(0–0) band shifts to the red and its intensity increases, peaking for Zn-Triphenyl-tetrabenzoporphyrin, then slightly decreasing for Zn-Tetraphenyl-tetrabenzoporphyrin. Both these effects govern the TPA cross-section behavior, as evident from Fig. 3.

The pure effect of frequency detuning is clearly seen if we compare ZnOEOP and H₂TBP. Regardless of that ZnOEOP possesses the $\varepsilon_{i0}(\max)\Delta\bar{\nu}/\bar{\nu}_{i0}$ value 1.5 times higher than H₂TBP, the shift of one-photon transition from 571 to 666 nm when going from ZnOEOP to H₂TBP, results in rather strong increase (by 4.5 times) of σ_2 in the latter.

Finally, we are going to present an estimation of the absolute value of σ_2 for one of the molecules studied. Such estimation would prove the validity of Eq. (3) for further analysis of TPA in porphyrins. We have chosen ZnOEOP in CH₂Cl₂, because its transient absorption spectrum is known from literature [14] and it falls well into the linear regression presented in Fig. 3. Since the exact polarization of the $i \rightarrow f$ transition is not known, we assume for simplicity that μ_{i0} and μ_{fi} are parallel and use Eq. (3) directly. This will give us an upper estimation of σ_2 . We calculate $L^4 = 3.0$ for $n = 1.4$ in CH₂Cl₂, and $L^4/n^2 = 1.5$. $|\mu_{i0}|^2$ was found by integrating the corresponding absorption band, according to [30]

$$\begin{aligned}
 |\mu_{i0}|^2 &= \frac{3 \cdot \ln 10 \times 10^3}{(2\pi)^3} \frac{hc}{N_A} \frac{1}{\bar{\nu}_{i0}} \int \varepsilon d\bar{\nu} \\
 &\approx \frac{3 \cdot \ln 10 \times 10^3}{(2\pi)^3} \frac{hc}{N_A} \frac{1}{2\bar{\nu}_{i0}} \sqrt{\frac{\pi}{\ln 2}} \\
 &\quad \times \varepsilon_{i0}(\max)\Delta\bar{\nu},
 \end{aligned} \tag{6}$$

where N_A is the Avogadro number and absorption band is approximated to the Gaussian function. From independently measured linear absorption parameters (see Table 1) we got $|\mu_{i0}|^2 = 4.1 \times 10^{-36}$ (e.s.u.). It is easy to show that the product $|\mu_{fi}|^2 g(2\nu_p)$ in (3) can be replaced by

$$\frac{3 \cdot \ln 10 \times 10^3}{(2\pi)^3} \frac{h}{N_A} \frac{1}{\bar{\nu}_{fi}} \varepsilon_{fi}(2\bar{\nu}_p - \bar{\nu}_{i0}).$$

The only unknown value of the singlet excited state extinction $\varepsilon_{fi}(2\bar{\nu}_p - \bar{\nu}_{i0})$ was obtained by extrapolating the dependence $\varepsilon_{fi}(\bar{\nu})$ [14] to the working frequency $2\bar{\nu}_p - \bar{\nu}_{i0} = 8000 \text{ cm}^{-1}$, which gives $\varepsilon_{fi}(2\bar{\nu}_p - \bar{\nu}_{i0}) \approx 2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Substituting all the parameters in (3), we obtain $\sigma_2 = (4 \pm 1) 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} = (4 \pm 1) \text{ GM}$, which is in excellent agreement with the measured value of 4.4 GM. Therefore, the single intermediate state approximation described by Eq. (3) appears to quantitatively describe TPA for ZnOEOP and at least qualitatively for other porphyrins studied.

In conclusion, we have studied TPA absorption spectra in a series of octaethyl-, tetraphenyl-, and tetrabenzosubstituted porphyrins and have established, for the first time to our knowledge, that the TPA efficiency of porphyrins in 710–810 nm region is resonantly enhanced due to nearby Q(0–0) one-photon transition. We find 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.

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