



# Photon energy upconversion in porphyrins: one-photon hot-band absorption versus two-photon absorption

M. Drobizhev<sup>a,1</sup>, A. Karotki<sup>a</sup>, M. Kruk<sup>a,2</sup>, A. Krivokapic<sup>b</sup>,  
H.L. Anderson<sup>b</sup>, A. Rebane<sup>a,\*</sup>

<sup>a</sup> Department of Physics, Montana State University, Bozeman, MT 59717-3840, USA

<sup>b</sup> Dyson Perrins Laboratory, Chemistry Department, University of Oxford, South Parks Road, Oxford OX1 3QY, UK

Received 25 August 2002; in final form 28 December 2002

## Abstract

We study the porphyrin  $S_1 \rightarrow S_0$  fluorescence and the photosensitized singlet oxygen  $^1\Delta_g \rightarrow ^3\Sigma_g$  phosphorescence, both originating from absorption of photons with energy less than the porphyrin  $S_0 \rightarrow S_1$  transition energy. By measuring the excitation intensity dependence of fluorescence at lowered sample temperatures, we are able to discriminate between two parallel processes of one-photon hot-band absorption (HBA) and simultaneous two-photon absorption (TPA). When the HBA and TPA contributions are comparable in magnitude, we use this new method to determine absolute TPA cross-section. We also demonstrate for the first time a singlet oxygen photosensitization via HBA in porphyrin.

© 2003 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Optical excitation of molecules with photons possessing lower energy than the energy of the first pure electronic transition presents an important task for basic molecular physics and various applications. The first example of such a process is a

‘hot-band’ absorption (HBA), where a molecule is excited from vibrationally populated state and then fluoresces at shorter wavelength (anti-Stokes fluorescence). Provided the fluorescence quantum yield is close to unity, HBA can be used for laser cooling of matter [1,2]. Another example is the simultaneous two-photon absorption (TPA), in which case two photons are absorbed at once in such a way that their energies add up to the molecular transition energy. This effect finds use in up-conversion lasing, 3D-memory and 3D-micro-fabrication, fluorescence microscopy, photo-medicine and several other areas (see [3,4] and references therein).

Anti-Stokes excitation of tetrapyrrole molecules is important because of potential applications in medical imaging and photodynamic therapy, and

\* Corresponding author. Fax: +1-406-994-4452.

E-mail address: [Rebane@physics.montana.edu](mailto:Rebane@physics.montana.edu) (A. Rebane).

<sup>1</sup> Permanent address: Lebedev Physics Institute, Leninsky pr., 53, 119991 Moscow, Russia.

<sup>2</sup> Permanent address: Institute of Molecular and Atomic Physics, National Academy of Sciences, 70 F. Skaryna Ave., 220072 Minsk, Belarus.

especially because the use of red-shifted excitation wavelength has a benefit of deeper penetration in biological tissues [5,6]. However, the effect of fluorescence wavelength up-conversion in tetrapyrroles has not received the attention it deserves. We can refer to only [7], where the reverse of absorption, i.e., spontaneous emission from thermally populated electronic excited state was observed in phthalocyanine molecules. In our recent papers [8–10] we have studied simultaneous two-photon absorption in porphyrins and have shown that this process can be applied for optical recording [9] as well as for photosensitization of singlet oxygen [8].

In this Letter, we show that one-photon up-conversion in new *meso*-tetra-alkynyl-porphyrins is mainly determined by a transition originating from thermally populated vibrational state of the ground electronic state. We also demonstrate that by using a properly selected excitation power and wavelength of femtosecond pulses (or sample temperature) one can simultaneously observe both HBA and TPA. This allowed us to propose a new simple yet reliable method of evaluation of molecular TPA cross-section which is based upon the measurement of power dependence of anti-Stokes spontaneous fluorescence. For a non-fluorescent Pb-porphyrin, we demonstrate that hot-band one-photon absorption can be used for photosensitization of singlet oxygen in solution. Temperature-dependent measurements of porphyrin absorption and singlet oxygen luminescence present a confirmation of the hot-band mechanism of excitation and also allow us to obtain the temperature dependence of quantum efficiency of singlet oxygen photosensitization by this porphyrin.

## 2. Experimental

Our laser system comprises a Ti:sapphire oscillator laser (Coherent Mira 900) which can be operated either in cw- or in mode-locked regime. In the latter case, its 76-MHz, 150-fs output pulses are used for seeding a Ti:sapphire regenerative amplifier (CPA-1000, Clark MRX), which is operated at 1-kHz repetition rate and produces 150-fs pulses at 0.8 mJ energy per pulse. These pulses can

be parametrically down converted in the optical parametric amplifier, OPA (TOPAS, Quantronix) which yielded 100-fs pulses in the spectral range from 1.1 to 1.9  $\mu\text{m}$  (in the form of either signal or idler photons).

Porphyrin fluorescence was collected at 90° and focused with a spherical mirror on the entrance slit of a Jobin–Yvon TRIAX 550 monochromator. To obtain regular porphyrin fluorescence spectra we used a He–Ne laser as excitation source and a Hamamatsu PMT for detection. In quantitative measurements of relative intensity, the spectra were corrected to the sensitivity of our PMT. For anti-Stokes fluorescence intensity measurements at one particular (maximum) wavelength, special selective filters were placed before the entrance slit of monochromator to cut off laser scattered light when it was spectrally close to fluorescence. The signal was detected with a nitrogen-cooled CCD. Singlet oxygen luminescence was detected in the same configuration, but with a nitrogen-cooled IR Ge-detector coupled with a lock-in amplifier.

Low-temperature measurements were carried out in an optical cryostat (Kiev, Ukraine), which was operated with liquid nitrogen. Porphyrin fluorescence was collected at 45° from a poly-(vynyl-butylal) (PVB) polymer film placed in the cryostat. Singlet oxygen luminescence was collected at 90° from a 1-cm airtight optical cell. Temperature dependence of optical density was measured with the same cryostat placed in the sample compartment of a Lambda 900 Perkin–Elmer spectrophotometer. In this case, a temperature sensor was immersed in the cell with the porphyrin solution. Temperature stabilization in the cryostat was  $\pm 1$  K.

## 3. Theoretical background

Consider short laser pulses illuminating a solution of fluorescing molecules at a frequency  $\nu$ , less than the frequency of the first pure electronic transition. At low sample absorption and at low pulse intensity, the probability that light is absorbed in two-photon process is much less than the probability of conventional one-photon absorption. However, because TPA increases quadratically with incident power, at a higher illumination

intensity the one- and two-photon absorption processes can have a comparable probability. In this case, one can describe the observed fluorescence intensity as a sum of two contributions

$$F = K\sigma_1(v) \int I(t) dt + \frac{1}{2}K\sigma_2(v) \int I^2(t) dt. \quad (1)$$

Here constant  $K$  includes collection and recording efficiency, fluorescence quantum yield and molecular concentration, and because the one- and two-photon excitation is carried out in single experiment,  $K$  is the same for one- and two-photon terms.  $I(t)$  designates the instantaneous photon flux (in photons  $\text{s}^{-1} \text{cm}^{-2}$ ) in a laser pulse with a rectangular spatial shape (The last is ensured in experiment by placing a small-aperture pinhole before the sample). An instantaneous photon flux is related to an average (measured) photon flux  $P$  as follows:  $\int I(t) dt = P/r$ , where  $r$  is the pulse repetition rate and integration here and in (1) is carried out over the time period, covering one single pulse. For the Gaussian temporal profile of the excitation pulse,  $\int I^2(t) dt = 0.66P^2/r^2\tau$  [11], where  $\tau$  is the pulse duration (FWHM). Therefore,

$$\begin{aligned} F(P) &= K'\sigma_1(v)P + 0.33K' \frac{\sigma_2(v)}{r\tau} P^2 \\ &= aP + bP^2, \end{aligned} \quad (2)$$

where  $K' = K/r$ . Note that the ratio,  $a/b$ , corresponds to a particular average photon flux,  $P^*$ , at which the one- and two-photon absorption have equal probability

$$\frac{a}{b} = \frac{\sigma_1(v)r\tau}{0.33\sigma_2(v)}. \quad (3)$$

From the latter relation we can express the TPA cross-section as follows:

$$\sigma_2(v) = \frac{\sigma_1(v)r\tau}{0.33(a/b)}. \quad (4)$$

Here the molecular linear,  $\sigma_1$ , and nonlinear,  $\sigma_2$ , absorption cross-sections are measured at the same frequency,  $\nu$ . In principle, one could find  $a/b$  from experimental power dependence measurement, and then use (4) to find the value of TPA

cross-section. Unfortunately, such experiments require that linear absorption is rather weak, which makes direct measurement of  $\sigma_1$  difficult.

However, if the linear absorption takes place from vibrationally excited ground state, the cross-section of HBA can be easily evaluated as a probability of vibronic transition at frequency  $\nu$ :

$$\sigma_1(\nu) = \sigma_1(\nu_{\max}) \exp\left(-\frac{\nu_{\max} - \nu}{kT}\right) \frac{FC(\nu)}{FC(\nu_{\max})}, \quad (5)$$

where  $\sigma_1(\nu_{\max})$  is the cross-section at the band maximum (which corresponds in the case of porphyrins to the 0–0 transition maximum),  $FC(\nu)$  and  $FC(\nu_{\max})$  are the Franck–Condon factors for vibronic and 0–0 transitions, respectively. The ratio  $FC(\nu)/FC(\nu_{\max})$  can be independently measured either from fluorescence spectrum as the ratio of intensities at  $\nu$  and at fluorescence maximum (if the Stokes shift between absorption and fluorescence 0–0 transitions is small) or from absorption spectrum as the ratio of absorption at  $2\nu_{\max} - \nu$  and at  $\nu_{\max}$ . Consequently,  $\sigma_2$  value can be evaluated from (4) and (5).

In contrast to our approach, the standard fluorescent technique for measurement of absolute TPA cross-section is based on comparison of fluorescence intensity upon two- and one-photon excitation [12–14] at fixed intensities. Two-photon excited fluorescence signal is calibrated to a combination of several unknown experimental factors (including collection and recording efficiency, fluorescence quantum yield, molecular concentration, etc.) by measuring fluorescence intensity in exactly the same conditions, but upon linear one-photon excitation of one of the high-lying allowed electronic transitions. Provided that Vavilov–Kasha's rule works (each molecule excited higher than the first excited singlet level relaxes to that level without emission) and molecular absorption cross-section at excitation frequency,  $\sigma_1(\nu)$ , is known, the TPA cross-section can be calculated. Note that this standard technique implies that the two-photon excitation is carried out with photon energy very far from any linear absorption band. This requirement is understandable because, otherwise, one-photon absorption will strongly dominate the fluorescence response. In our previous papers [8,10], we have observed that upon approaching

the linear Q(0–0) transition of porphyrins from the low-energy region, the power dependence of fluorescence signal starts to decline from quadratic and quickly transforms into linear one. Similar transformation of power law was previously observed in other molecular systems [15].

The new method, proposed here, has an advantage of possibility to measure  $\sigma_2$  close to one-photon resonance. It is particularly useful for studying resonance enhancement effect and it also lifts problems connected with a dissimilarity of experimental geometry factors, arising in the case of different excitation wavelength (or even source) used for one-photon calibration.

## 4. Experimental results and discussion

### 4.1. Two-photon absorption cross-section in meso-tetra-alkynyl-porphyrins

Fig. 1 shows the molecular structures of porphyrins studied along with their regular absorption and fluorescence emission spectra in toluene solution. Note that Pb-TTIPS (Fig. 1c) possesses almost no detectable fluorescence. This is not surprising, because it shows very high quantum efficiency of intersystem crossing,  $\phi_{ST} \sim 1$  [16]. We use this specific property for photosensitization of singlet oxygen as described in the next section.

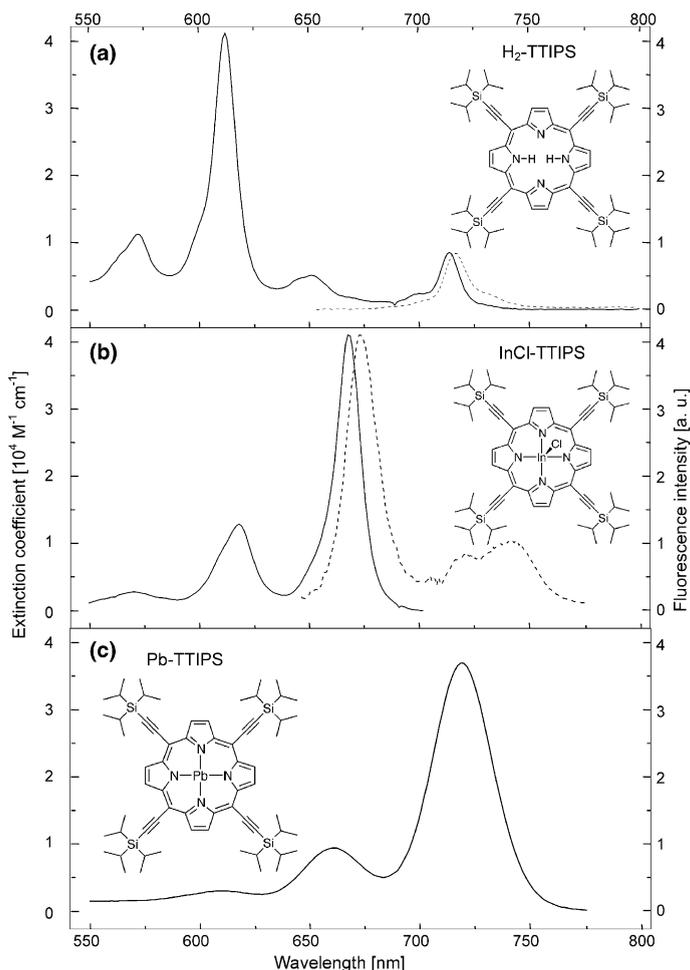


Fig. 1. Absorption and fluorescence spectra of H<sub>2</sub>-TTIPS (a), InCl-TTIPS (b), and Pb-TTIPS (c) in toluene solutions.

The maxima of the lowest one-photon transition of  $\text{H}_2$ -TTIPS and InCl-TTIPS are at 714 and 666 nm, respectively, see Fig. 1. In the case of InCl-TTIPS, the excitation wavelength (786 nm) is sufficiently detuned from the absorption peak, such that the fluorescence intensity reveals a purely quadratic dependence on the excitation power. This allows us to measure the TPA cross-section at room temperature by a standard method, comparing one- and two-photon fluorescence, excited at two different wavelengths. As a result, we obtain  $\sigma_2 = 60 \pm 10 \text{ GM}$  ( $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ ).

In the case of  $\text{H}_2$ -TTIPS, the detuning is much less and we observed almost linear dependence of fluorescence intensity on excitation power in the entire tuning range of Ti:sapphire amplifier (760–810 nm) at room temperature. This can be explained by a domination of one-photon hot-band

Q(1–0) transition (see below) belonging to vibronic manifold of the first Q-band centered at  $\nu_{\text{max}} = 714 \text{ nm}$ . Only when the excitation was detuned to 903 nm using second harmonic of the OPA idler output, we obtained quadratic fluorescence dependence. The standard method gave TPA cross-section at this wavelength,  $\sigma_2 = 40 \pm 10 \text{ GM}$ , which is comparable to the value found in InCl-TTIPS at 786 nm.

Our next step was to demonstrate the effect of simultaneous one- and two-photon up-conversion in  $\text{H}_2$ -TTIPS and the possibility to measure  $\sigma_2$  close to one-photon resonance. For this purpose we have measured the power dependence of fluorescence of  $\text{H}_2$ -TTIPS embedded in PVB-film at lowered temperatures. Fig. 2 shows these data obtained at two selected temperatures with excitation frequency fixed at  $\nu = 12820 \text{ cm}^{-1}$  (780 nm).

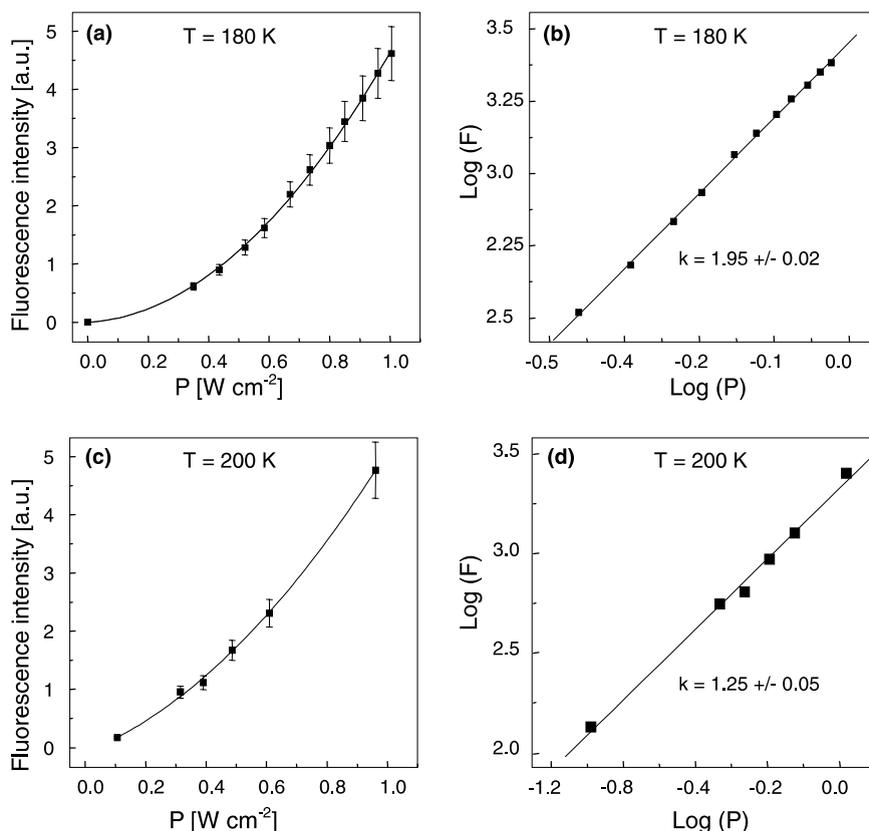


Fig. 2. Power dependence of fluorescence intensity of  $\text{H}_2$ -TTIPS in PVB-film upon anti-Stokes excitation at 780 nm at 180 K (a,b) and 200 K (c,d) presented in linear (a,c) and double logarithmic scale (b,d). The exponent of the power dependence  $k$  is presented in (b).

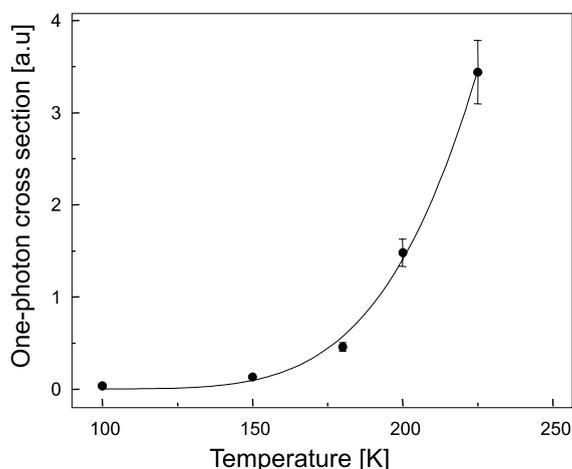


Fig. 3. Temperature dependence of one-photon absorption cross-section of  $H_2$ -TTIPS in PVB-film at 780 nm. Continuous line shows the best fit to the Boltzmann function with frequency detuning from 0–0 transition,  $\Delta\nu = 1170 \text{ cm}^{-1}$ .

At  $T < 180 \text{ K}$ , the dependencies are described by quadratic function, i.e., the TPA dominates. In the temperature range 180–250 K, the power dependence has an exponent lying in between 1 and 2 and is well described by Eq. (2) in all the cases. Relative one-photon absorption cross-section, proportional to coefficient  $a$  in (2), is plotted in Fig. 3 as a function of temperature. Continuous line presents a simulation of data with Boltzmann function,  $C \exp(-\Delta\nu/kT)$ , where only  $C$  was varying, and  $\Delta\nu$  was fixed equal to the difference between the frequencies of the Q(0–0) maximum and the laser:  $\Delta\nu = \nu_{\max} - \nu = 1170 \text{ cm}^{-1}$ . Excellent agreement between the experimental data and fitting function unambiguously demonstrates that the one-photon absorption of  $H_2$ -TTIPS at 780 nm

is completely determined by a hot transition from some thermally populated vibrational level (or levels) of the ground electronic state.

Table 1, lines 4–6, presents the values of  $\sigma_2$  for  $H_2$ -TTIPS in PVB film calculated according to Eqs. (4) and (5) by using the fitting parameters  $a$  and  $b$ , obtained at each temperature and Franck–Condon factors, determined from the corrected fluorescence spectrum. The same table presents also the  $\sigma_2$  values obtained by standard procedure (lines 1–3). One can see that in contrast to one-photon absorption, the two-photon absorption cross-section of  $H_2$ -TTIPS in PVB film does not strongly depend on temperature. To make sure that the results provided by this method are reliable, we have also measured  $\sigma_2$  value with the standard fluorescence procedure. In this case, the one-photon transition at 388 nm was excited in the same sample but at 77 K, i.e., where TPA completely dominates. As is evident from Table 1, (cf. line 3 with lines 4 and 5) the results obtained by these two methods indeed coincide within experimental error.

From these data the following conclusions can be drawn. The TPA cross-sections obtained for both molecules fall in the range of values usually observed in this spectral region for neutral (in terms of charge-transfer substitution) porphyrins, i.e., 10–100 GM [17]. An average TPA cross-section of  $H_2$ -TTIPS measured in different conditions, is found to be  $\sigma_2 \approx 30 \pm 10 \text{ GM}$ . Effects of temperature, excitation wavelength, and matrix result in deviations of  $\sigma_2$  within  $\sim 30\%$  in all cases, see Table 1, lines 2–6.

A three-fold increase of  $\sigma_2$  in InCl-TTIPS as compared to  $H_2$ -TTIPS (cf. lines 1 and 6), obtained in the wavelength region near 785 nm can

Table 1

Two-photon absorption cross-sections measured in InCl-TTIPS and  $H_2$ -TTIPS at different experimental conditions

Exp. no.	Molecule	$\lambda$ (nm)	$T$ (K)	Matrix	$\sigma_2$ (GM)
1	InCl-TTIPS	786	300	Toluene	$60 \pm 10$
2	$H_2$ -TTIPS	903	300	Toluene	$40 \pm 10$
3	$H_2$ -TTIPS	782	77	PVB-film	$22 \pm 5$
4	$H_2$ -TTIPS	782	200	PVB-film	$20 \pm 5$
5	$H_2$ -TTIPS	782	225	PVB-film	$17 \pm 5$
6	$H_2$ -TTIPS	782	77–225	PVB-film	$20 \pm 3$

be explained by the effect of resonance enhancement of TPA [17].

#### 4.2. Singlet oxygen photosensitization via hot-band absorption in Pb-meso-tetraethynyl-triisopropylsilyl-porphyrin

Despite extensive studies related to the singlet oxygen photosensitization with tetrapyrrole molecules [18], this effect has, to our knowledge, not been shown for an excitation of hot vibronic transition. Here we present such data obtained with Pb-TTIPS. This porphyrin has been chosen because it shows very efficient intersystem crossing [16].

First of all, we measured the quantum efficiency,  $\Phi_{\Delta}$ , of singlet oxygen photosensitization by Pb-TTIPS molecule. In this measurement we used direct (Stokes) excitation by means of a 532-nm cw-Nd:YAG laser and recorded an emission peak at 1.27  $\mu\text{m}$ , which is a distinctive feature of the  ${}^1\Delta_{\text{g}} \rightarrow {}^3\Sigma_{\text{g}}$  singlet oxygen ( ${}^1\text{O}_2$ ) luminescence. By calibrating our recording system to the  ${}^1\text{O}_2$  luminescence signal obtained with the free base tetraphenylporphyrin in air-saturated toluene ( $\Phi_{\Delta} = 0.68$ ), we obtained  $\Phi_{\Delta} = 1.0 \pm 0.1$  for Pb-TTIPS at room temperature. Such a high value of  $\Phi_{\Delta}$  could not be obtained but for the intersystem crossing efficiency is close to unity. It also suggests almost a 100% of energy-transfer efficiency from the porphyrin triplet state to molecular oxygen ( $S_{\Delta} = 1$ ).

Upon excitation of an air-saturated toluene solution of Pb-TTIPS with a CW radiation from Ti:sapphire oscillator at  $\lambda = 780$  nm, we also observed the characteristic singlet oxygen luminescence band, centered at 1.27  $\mu\text{m}$ . We present in Fig. 4 an excitation spectrum of this luminescence, which is obtained by tuning laser throughout the long-wavelength tail of the lowest absorption band of Pb-TTIPS. For comparison, the same figure presents a corresponding part of the molecule absorption spectrum (continuous line). One can see that after appropriate normalization, both spectra coincide quite well. This demonstrates that  ${}^1\text{O}_2$  is indeed generated as a result of excitation of the long-wavelength ‘tail’ of the first allowed transition. Note that in general this long-wavelength ‘tail’ can result from hot vibronic transitions or

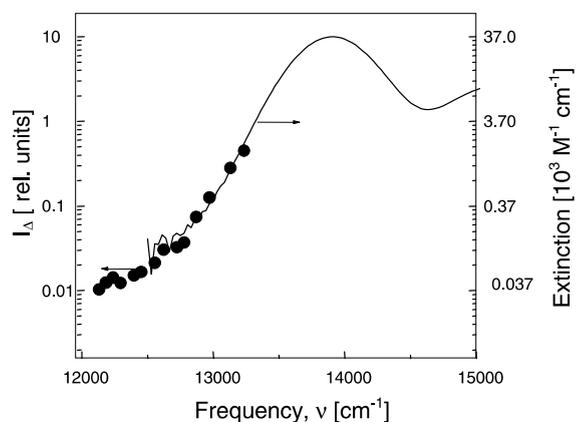


Fig. 4. Excitation spectrum (symbols) of singlet oxygen luminescence sensitized by Pb-TTIPS in air-saturated toluene. The corresponding part of absorption spectrum of Pb-TTIPS is also shown (continuous line). Note logarithmic scale of ordinate axis.

inhomogeneous and homogeneous broadening or either from some electronic transition hidden in the broad absorption band. Our next goal is therefore to elucidate the nature of this absorption tail. Since Pb-TTIPS is almost non-fluorescing, we study here the temperature dependencies of the porphyrin red tail absorption and singlet oxygen luminescence.

Fig. 5a shows the temperature dependence of the optical density of the Pb-TTIPS toluene solution measured at 766 nm. This wavelength corresponds to a 900  $\text{cm}^{-1}$ -detuning from the 0–0 transition. We observe a continuous decrease of the optical density upon decreasing temperature down to 260 K. The constant background observed at lower temperatures could be a scattering artefact due to porphyrin microcrystals or aggregates which start to precipitate at this point. Therefore, in our quantitative simulations, we consider only the temperature range  $T > 270$  K. In this range, the optical density can be well fitted to the following function:

$$OD(T) = A + Be^{-\frac{E_B}{kT}}. \quad (6)$$

The best fit gives  $A = 0.13 \pm 0.01$ ,  $B = 9 \pm 2$ , and  $E_B = 810 \pm 70$   $\text{cm}^{-1}$ . The corresponding curve is shown in Fig. 5a by a continuous line. As compared to the free base H<sub>2</sub>-TTIPS porphyrin

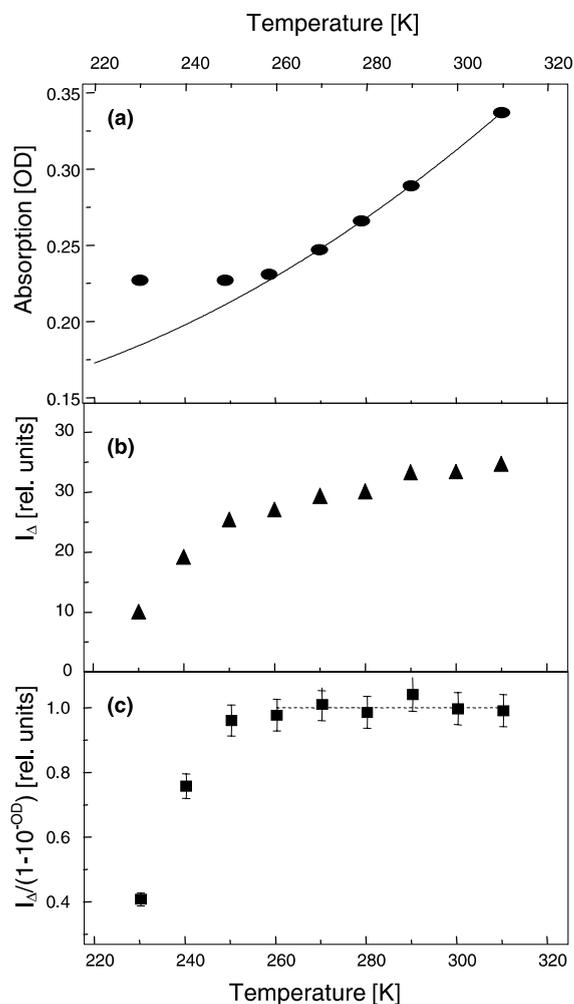


Fig. 5. (a) Temperature dependence of the optical density of Pb-TTIPS air-saturated toluene solution measured at 766 nm. (b) Temperature dependence of singlet oxygen luminescence intensity, measured upon anti-Stokes excitation of Pb-TTIPS in toluene at 766 nm. (c) Temperature dependence of quantum efficiency of singlet oxygen photosensitization, deduced from (a) and (b), see text for details.

(cf. Fig. 3), there is a prominent temperature-independent contribution (term  $A$  in (6)) in this case. We tentatively attribute this term to inhomogeneous broadening which does not vary with temperature. This assignment is also supported by a considerable broadening of the Q(0–0)-band in Pb-TTIPS as compared to H<sub>2</sub>-TTIPS. As for the temperature-dependent term, it can be expressed

as a product of the Boltzmann factor describing hot-band absorption and the temperature-dependent molar concentration, which is proportional to solvent density. The latter can be presented as  $\rho = \rho_0 \exp(E_{\rho}/kT)$ , with  $E_{\rho} = 70 \text{ cm}^{-1}$  for toluene in the studied temperature range. Taking a real detuning of the laser frequency from the 0–0 transition,  $\Delta\nu = 900 \text{ cm}^{-1}$ , we would expect an activation energy in (6) to be  $E_B = \Delta\nu - E_{\rho} = 830 \text{ cm}^{-1}$ . This value practically coincides with that obtained from Fig. 5a, thus confirming that the temperature-dependent part of the red-tail absorption is mainly determined by a thermal population of vibration states of the electronic ground state.

Our next step is to elucidate the factors which can influence the efficiency of singlet oxygen photosensitization with Pb-TTIPS. Fig. 5b shows a dependence of the steady-state singlet oxygen luminescence on temperature upon anti-Stokes excitation with a CW Ti:sapphire laser at 766 nm. In general, the temperature dependence of this luminescence can be expressed as follows [19]:

$$I_{\Delta}(T) = D\Phi_{\Delta}(T)[1 - 10^{-OD(T)}]\varphi_R(T)c(T)n^2(T), \quad (7)$$

where  $D$  is a constant,  $\varphi_R$  is the quantum efficiency of singlet oxygen luminescence,  $c$  is the oxygen molar concentration, and  $n$  is the refraction index of solution. By measuring the temperature dependence of singlet oxygen luminescence,  $I_{\Delta}(T)$ , and normalizing it to absorption,  $1 - 10^{-OD(T)}$ , we can expect to obtain the temperature dependence of singlet oxygen photosensitization quantum yield,  $\Phi_{\Delta}(T)$ , as far as  $\varphi_R(T)$ ,  $c(T)$ , and  $n^2(T)$  are known from the literature. All the three last factors can be approximated by Arrhenius law with activation energies  $E_{\varphi}$ ,  $E_s$ , and  $E_n$ , respectively.  $E_{\varphi}$  was shown to be  $-0.2 \text{ kcal/mol}$  ( $\sim -70 \text{ cm}^{-1}$ ) in toluene in the same temperature range [20].  $E_s$  was measured to be almost negligible compared to its uncertainty for oxygen in toluene,  $E_s \sim 40 \pm 100 \text{ cm}^{-1}$  [21]. Taking the literature value of  $dn/dT = 5.7 \times 10^{-4} \text{ K}^{-1}$  for toluene, we estimate  $E_n = -50 \text{ cm}^{-1}$ . The total activation energy of the last three factors in (6) is thus less than  $100 \text{ cm}^{-1}$  and can be neglected. Therefore, the temperature

dependence of  $\Phi_{\Delta}(T)$  is to a high accuracy proportional to  $I_{\Delta}(T)/(1 - 10^{-OD(T)})$ . The last function is calculated by using the known best fitting function (6) for  $OD(T)$  and plotted in Fig. 5c. The main conclusion resulting from this plot is that the quantum yield of singlet oxygen photosensitization remains constant,  $\Phi_{\Delta}(T) = 1.0 \pm 0.1$  in the range 250–310 K, where Pb-TTIPS is present in monomeric form in solution.

Above, we have shown that the photosensitization of singlet oxygen can involve a vibronic transition from the ground electronic state. This phenomenon can in principle be applied for improving the efficacy of photodynamic treatment with near-infrared radiation. Note that the photodynamic action spectrum in biological tissues and tumors is red-shifted with respect to absorption spectrum in solution for several tetrapyrrole photosensitizers [22–26]. Previously this effect was interpreted as resulting from a particular interaction of photosensitizer with specific biological surrounding [24–27], leading to modification of absorption spectra [25,27] and fluorescence excitation spectra [24] in vivo. However, the effect of inner filter [28] as well as the strong wavelength dependence of the tissue optical properties cannot be ruled out either. This latter possibility is supported by the facts that the absorption peak of, for example, disulfonated aluminum phthalocyanine (AlS<sub>2</sub>Pc) in different homogeneous microenvironments never shows such a great shift as that was measured in tissue [27,29] and that the shift almost vanishes when lower loading concentrations of photosensitizer in vivo [30–32] or (and) optically more transparent cell cultures [33,34] are used. This could imply that the red side of absorption spectrum, consisting of HBA, is more pronounced in tissues.

Based on our results and on the above information, we can propose a new approach of enhancement of the photodynamic efficacy, involving population of vibrational states of the photosensitizer. The last can be achieved either by increasing temperature (thermal population) or by an active optical process, e.g., by coherent stimulated Raman process (non-thermal population). In both cases, it is also desirable to increase the corresponding Franck–Condon factors, which can be

achieved by appropriate chemical modification of the porphyrin structure.

## 5. Conclusions

We have demonstrated that at a particular excitation power range and wavelength, the probabilities of the one-photon anti-Stokes hot-band absorption and of the direct two-photon absorption in porphyrins can be of the same order of magnitude. We thus propose a new method of experimental evaluation of molecular TPA cross-section which is based upon the measurement of power dependence of anti-Stokes spontaneous fluorescence in this transient region. For non-fluorescing Pb-*meso*-tetraethynyl-triisopropylsilylporphyrin, we demonstrate that the hot-band one-photon absorption can be used to generate singlet oxygen in solution. Temperature-dependent measurements of the porphyrin absorption and singlet oxygen luminescence confirm the hot-band mechanism of excitation. We have also demonstrated that the quantum efficiency of singlet oxygen photosensitization remains close to unity even at lowered temperatures.

## Acknowledgements

We thank Prof. C.W. Spangler for useful discussions and Ms. Yu. Dzenis for technical assistance. This work was supported by AFOSR Grant F 49620–01-1-0406.

## References

- [1] R.I. Epstein, M.I. Buchwald, B.C. Edwards, T.R. Gosnell, C.E. Mungan, *Nature* 377 (1995) 500.
- [2] J.L. Clark, G. Rumbles, *Phys. Rev. Lett.* 76 (1996) 2037.
- [3] J.D. Bhawalkar, G.S. He, P.N. Prasad, *Rep. Prog. Phys.* 59 (1996) 1041.
- [4] M. Drobizhev, A. Rebane, A. Karotki, C.W. Spangler, in: *Recent Research Developments, Applied Physics*, vol. 4, Transworld Research Network, Trivandrum, India, 2001, p. 1.
- [5] W.-F. Cheong, S.A. Prael, A.J. Welch, *IEEE J. Quantum Electron.* 26 (1990) 2166.

- [6] S. Stolik, J.A. Delgado, A. Perez, L. Anasagasti, J. Photochem. Photobiol. B 57 (2000) 90.
- [7] H. van Mingroot, S. de Backer, J. van Stam, M. Van der Auweraer, F.C. de Schryver, Chem. Phys. Lett. 253 (1996) 397.
- [8] A. Karotki, M. Kruk, M. Drobizhev, A. Rebane, E. Nickel, C.W. Spangler, IEEE J. Sel. Top. Quantum Electron. 7 (2001) 971.
- [9] A. Karotki, M. Kruk, M. Drobizhev, A. Rebane, J. Mod. Opt. 49 (2002) 379.
- [10] M. Drobizhev, A. Karotki, A. Rebane, Chem. Phys. Lett. 334 (2001) 76.
- [11] C. Xu, W.W. Webb, J. Opt. Soc. Am. B 13 (1996) 481.
- [12] M.D. Galanin, Z.A. Chizhikova, JETP Lett. 4 (1966) 27.
- [13] A.P. Aleksandrov, V.I. Bredikhin, Opt. Spectrosc. 30 (1971) 37.
- [14] J.P. Hermann, J. Ducuing, Phys. Rev. A 5 (1972) 2557.
- [15] J. Krasinski, W. Majewski, M. Glodz, Opt. Commun. 14 (1975) 187.
- [16] A. Krivokapic, H.L. Anderson, G. Bourhill, R. Ives, S. Clark, K.J. McEwan, Adv. Mater. 13 (2001) 652.
- [17] M. Drobizhev, A. Karotki, M. Kruk, A. Rebane, Chem. Phys. Lett. 355 (2002) 175.
- [18] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 22 (1993) 113.
- [19] C. Grewer, H.-D. Brauer, J. Phys. Chem. 97 (1993) 5001.
- [20] A.A. Gorman, I. Hamblett, C. Lambert, B. Spencer, M.C. Standen, J. Am. Chem. Soc. 110 (1988) 8053.
- [21] L.R. Field, E. Wilhelm, R. Battino, J. Chem. Thermodyn. 6 (1974) 237.
- [22] C.J. Gomer, D.R. Doiron, N. Rucker, N.J. Razum, S.W. Fountain, Photochem. Photobiol. 39 (1984) 365.
- [23] G. Canti, D. Lattuada, E. Leroy, R. Cubeddu, P. Taroni, G. Valentini, Anti-Cancer Drugs 3 (1992) 139.
- [24] J. Griffiths, J. Cruse-Sawyer, S.R. Wood, J. Scholfield, S.B. Brown, B. Dixon, J. Photochem. Photobiol. B 24 (1994) 195.
- [25] R. Cubeddu, G. Canti, M. Musolino, A. Pifferi, P. Taroni, G. Valentini, J. Photochem. Photobiol. B 34 (1996) 229.
- [26] E. Ben-Hur, M.M. Zuk, M.E. Kenney, N.L. Oleinick, J. Mulvihill, B. Horowitz, Laser Med. Sci. 11 (1996) 221.
- [27] R. Cubeddu, G. Canti, C. D'Andrea, A. Pifferi, P. Taroni, A. Torricelli, G. Valentini, J. Photochem. Photobiol. 60 (2001) 73.
- [28] S. Dhimi, A.J. de Mello, G. Rumbles, S.M. Bishop, D. Phillips, A. Beeby, Photochem. Photobiol. 61 (1995) 341.
- [29] M. Ambroz, A.J. MacRobert, J. Morgan, G. Rumbles, M.S.C. Foley, D. Phillips, J. Photochem. Photobiol. B 22 (1994) 105.
- [30] R. Biolo, G. Jori, J.C. Kennedy, P. Nadeau, R. Porter, E. Reddi, G. Weagle, Photochem. Photobiol. 53 (1991) 113.
- [31] N. Bresseur, R. Oellett, S. Marengo, D. Houde, J.E. van Lier, J. Chim. Phys. 93 (1996) 29.
- [32] S.A. Blant, J.-F. Theumann, M. Forrer, G. Wagnieres, H. van den Bergh, Ph. Monnier, Laser Med. Sci. 12 (1997) 269.
- [33] J. Moan, K. Berg, J.C. Bommer, A. Western, Photochem. Photobiol. 56 (1992) 171.
- [34] L. Ma, J. Moan, K. Berg, Int. J. Cancer 57 (1994) 883.