



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Full length article

Photonics of dissolved oxygen molecules. Comparison of the rates of direct and photosensitized excitation of oxygen and reevaluation of the oxygen absorption coefficients

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ARTICLE INFO

Article history:

Received 15 March 2016
 Received in revised form 17 June 2016
 Accepted 24 June 2016
 Available online 25 June 2016

Keywords:

Molecular oxygen
 Singlet oxygen
 Photosensitizers
 Direct oxygen excitation

ABSTRACT

The rates of photooxygenation of singlet oxygen traps (1,3-diphenylisobenzofuran, tetracene and rubrene) were compared in air-saturated carbon tetrachloride upon porphyrin-photosensitized and direct excitation of oxygen molecules. At equal power of incident radiation, the ratio of oxygen excitation rates normalized to porphyrin absorbance was found to be $\sim 10^4$. Continuous and pulse (peak power $\leq 20 \text{ MW/cm}^2$) laser radiation of equal average power caused similar rates of direct oxygen excitation. Improved procedure of data analysis was developed and accurate values of absorbance A_{max} , molar absorption coefficient ϵ_{max} and the cross section of light absorption σ_{max} were obtained for the oxygen absorption maxima at 1273, 765 nm and 1073 nm. The results were employed for reevaluation of the absorption coefficients of oxygen in other solvents, which were studied using carbon tetrachloride as the reference. It was found that the ratios A_{1273}/A_{765} ; $\epsilon_{1273}/\epsilon_{765}$ and $\sigma_{1273}/\sigma_{765}$, which were equal to 7/1 in carbon tetrachloride, decreased in polar solvents and reached 1.5/1 in water. This effect was shown to be due to the decrease of ϵ_{1273} and σ_{1273} on going from non-polar solvents to water, whereas ϵ_{765} and σ_{765} are less sensitive to solvents and slightly increased with the increase of solvent polarity. The obtained data are important for dosimetry of laser radiation in biomedical experiments and suggest that the radiation at 765 nm is more appropriate for oxygen excitation in biological systems since its efficiency is similar to that of the radiation at 1273 nm, but dark red light penetrates deeper into tissues and causes weaker heating of water.

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1. Introduction

It is known that oxygen molecules have triplet ground state ($^3\Sigma_g^-$) and two relatively low-lying singlet $^1\Delta_g$ and $^1\Sigma_g^+$ levels (Fig. 1). These transitions are highly forbidden therefore reliable spectrophotometric detection of the absorption bands of dissolved oxygen is only possible under very high pressure 50–140 atm. Under this pressure, oxygen dimols (O_2)₂ are known to dominate [1–5]. Direct photoexcitation of oxygen dimols at oxygen pressure 130–140 atm was shown to lead to formation of the $^1\Delta_g$ singlet oxygen, which causes oxygenation of the added organic singlet oxygen traps, aminoacids, proteins and other molecules (see [2,4] and refs therein).

In solvents saturated with air at normal atmospheric pressure, oxygen molecules are mostly monomeric but their absorption bands are so weak that they cannot be recorded using conventional spectrophotometers. Nevertheless some time ago an idea was advanced that direct laser excitation of intrinsic oxygen molecules of living cells might be a reason for biological action of laser radiation. Evidence was also presented that this effect might be applied to destruction of cancer cells in vitro and in animal and human organisms ([6–8] and refs therein).

These papers caused heated discussions. Although biological action of IR lasers was clearly demonstrated [6–11] there was no crucial evidence showing that laser damage of tumor cells was due namely to oxygen excitation. In this connection, a decade ago our group started work on mimicking these effects in solutions of singlet ($^1\Delta_g$) oxygen traps in organic solvents and water at normal pressure and temperature. It was shown using tetracene, 1,3-diphenylisobenzofuran (DPIBF) and uric acid as traps that under normal conditions, laser radiation of moderate power (0.03–2 W)

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causes oxygenation of these compounds [12–19]. The oxygenation was inhibited by singlet oxygen quenchers – β -carotene and sodium azide [12–14]. The photoreaction was not observed after purging with argon or nitrogen. After purging with pure oxygen the photoreaction rates increased 5-fold compared to air-saturated solutions [12]. The main maxima of the photooxygenation action spectra were found at 765 and 1273 nm (Fig. 2) [12–16,18]. Thus, evidence was obtained that under ambient conditions, monomeric oxygen molecules can work as photosensitizers of oxygenation reactions similarly to the oxygen dimols appearing at high oxygen pressure. Judging by the maxima of the action spectra, absorption bands of oxygen in the solution phase are slightly shifted to longer wavelengths compared to the maxima of the absorption spectrum of monomeric oxygen in the rarified gas [1] (Fig. 1).

These observations were recently supported by Courtade's group in France [20–23]. In addition, it was shown by this group that if one uses narrow laser beams (of about 0.1 mm) and reaches very high density of laser power ($\sim 200 \text{ W/cm}^2$), direct oxygen excitation by IR laser radiation causes photodamage of cancer cells with the maximum of the action spectrum at 1273 nm [22]. Even stronger effect was reported when narrow laser beams and nanosecond laser pulses were used together [24]. Apparently, above experiments in model systems and cells provide a basis for development of real clinical methods for laser therapy of tumors.

On the other hand, from the mechanistic point of view biomedical effects caused by laser excitation of oxygen molecules should be directly proportional to the rate of $^1\text{O}_2$ production by laser radiation, which in turn, depends on laser power (I_{las}) and the fraction of laser light absorbed by oxygen molecules ($1-10^{-A_{\text{ox}}}$), where A_{ox} is oxygen absorbance ($A_{\text{ox}} \ll 0.01$). Hence:

$$\text{Biological effect} \sim I_{\text{las}} (1-10^{-A_{\text{ox}}}) = I_{\text{las}} \times 2.3 \times A_{\text{ox}} \quad (1)$$

Thus, reliable information on A_{ox} and absorption spectroscopy of oxygen molecules under natural conditions is of great importance for dosimetry of IR laser radiation in biomedical experiments and laser therapy.

Previously, our group proposed several methods for estimating absorbance (A_{ox}), absorption cross section (σ_{ox}) and molar absorption coefficients (ϵ_{ox}) of dissolved oxygen from analyses of the experimentally measured oxygenation rates under laser irradiation [13–19]. The first results were reported in Ref. [13], in which tetracene served as a singlet oxygen trap and carbon tetrachloride was a solvent. In further papers this system was used as the standard (actinometer) for estimation of spectroscopic

parameters of oxygen in other solvents [14–17]. Relative values of ϵ_{ox} obtained in organic solvents and water were found to correlate with relative rate constants of $^1\text{O}_2$ radiative deactivation [14–18]. Initially, to simplify calculations we suggested that molar absorption coefficients of the traps (ϵ_{tr}) and rate constants of $^1\text{O}_2$ reactions with traps did not depend on solvents. Also, when relatively broad-band diode lasers were used, degree of overlapping (overlap integral) of laser emission bands and absorption bands of oxygen were not accounted for [14–18]. Recently, more accurate analytical procedures were developed. The overlap integrals were calculated using laser emission bands and excitation spectra of trap photooxygenation [19]. The use of the rate constants of trap oxygenation was ruled out due to comparing the rates of singlet oxygen production by direct and photosensitized oxygen excitation [18]. An alternative procedure was proposed by Sivery et al. [21,23] who analyzed the time course of photooxygenation of the traps under prolonged laser irradiation, suggesting that the rate of this process is not influenced by accumulating degradation products. Application of different analytical methods caused scattering in the reported A_{ox} , ϵ_{ox} and σ_{ox} .

In the present work, we reconsider results of the prior studies of our group [13–19] dealing with direct laser excitation of oxygen molecules in order to obtain the accurate absorption coefficients of oxygen, which could be a solid basis for dosimetry of IR laser radiation in biomedical systems and for analyses of basic photochemical and photophysical properties of oxygen. The following strategy was used. New experiments were limited by one solvent - CCl_4 and by oxygen absorption bands at 1273 and 765 nm. The photooxygenation rates were compared for three different traps (tetracene, rubrene and DPIBF) upon direct and photosensitized excitation of oxygen and, than analyzed using recently developed analytical procedures [18,19]. It was found that all traps yielded similar value of A_{ox} . New value of A_{ox} was applied for reevaluation of the results obtained previously in a few other solvents, for which the solutions of the traps in CCl_4 served as the reference [13–18]. Corrected results are compared with those of the French group [21,23] and our recent studies [19]. All data are presented in similar units. Besides, in view of the fact that some data were obtained using laser pulses, the rates of trap oxygenation under continuous and pulsed laser radiation were compared. The latter work is of interest in view of the recent paper suggesting that oxygen excitation by pulsed lasers is more efficient in cell killing [24].

2. Materials and methods

As a source of steady-state radiation, diode lasers LAMI Gelios were applied (firm "Surgical innovation technologies", Moscow), having the emission band at 1267 and 762 nm with the half band width 7–12 and 4–5 nm respectively. Laser light was focused into a fiber light guide with the diameter of 1 mm. The eliciting light power was controlled by the power meter Ophir ORION-TH with the sensor head 20C-SH (Israel). For pulsed excitation of oxygen, two IR laser generators assembled at the Institute of Physics of Russian Academy of Science were applied. One was a pulse wavelength-tunable forsterite laser pumped by an acousto-optically Q-switched Nd-YAG laser. The pulse repetition rate was 20 kHz. The duration of individual pulses was $200 \pm 20 \text{ ns}$. The wavelength of laser radiation was set to be 1273 nm. The bandwidth was 3 nm. The average output power was 100 mW. The diameter of the laser beam at the surface of the cuvette was 4 mm, therefore the peak power of individual pulses was about 25 W. Another source of pulse radiation was the second Stocks component of a Raman laser on a crystal $\text{KGd}(\text{WO}_4)_2$ pumped by Q-switched Nd-YAG laser [25]. The wavelength was 1272 nm, the

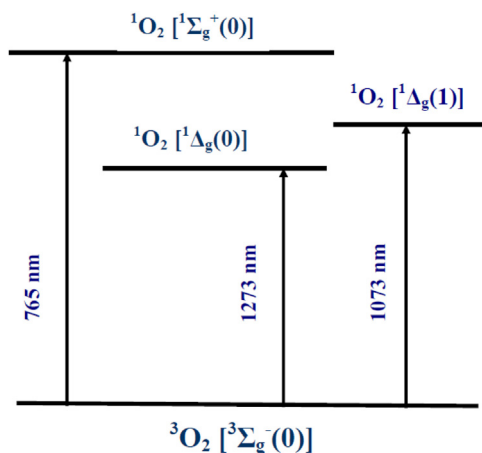


Fig. 1. The main electronic transitions in monomeric oxygen molecules in the solution phase. The vibrational sublevels and multiplicity of the states are shown in brackets. In the gas phase at low pressure all maxima are known to be shifted 3–5 nm to shorter wavelengths [1].

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