Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Chemical Physics Letters 485 (2010) 11-15

Contents lists available at ScienceDirect





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



UV-photoexcitation of encounter complexes of oxygen O_2-O_2 as a source of singlet oxygen $O_2(^1\Delta_g)$ in gas phase

Aleksandra P. Trushina^{a,b}, Veniamin G. Goldort^c, Sergei A. Kochubei^c, Alexey V. Baklanov^{a,b,*}

^a Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk 630090, Russia ^b Novosibirsk State University, Pirogova Str. 2, Novosibirsk 630090, Russia ^c Institute of Semiconductor Physics, Lavrentiev Ave. 13, Novosibirsk 630090, Russia

ARTICLE INFO

Article history: Received 14 October 2009 In final form 24 November 2009 Available online 27 November 2009

ABSTRACT

The photogeneration of singlet oxygen $O_2(a^1\Delta_g)$ resulted from the photoexcitation at 248 nm of gaseous oxygen at elevated pressure (3–80 atm) has been investigated. Singlet oxygen monitored by its IR-luminescence at 1.27 µm was found to appear via two processes which are identified to be due to absorption of individual O_2 molecules and encounter complexes O_2-O_2 , respectively. The one-quantum absorption of complexes gives rise to appearance of oxygen in Herzberg III state $O_2(^3\Delta_u)$ which is supposed to be a triplet sensitizer responsible for singlet oxygen $O_2(a^1\Delta_g)$ production observed in our experiments.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The photo processes in oxygen are very important for chemistry of atmosphere, oxidative organic photochemistry as well as for oxygen assisted photobiochemistry. The photoabsorption of 'isolated' O2 molecules is very weak within the whole IR-UV spectral region where all electronic transitions of ground state O2 molecule are spin and/or orbital symmetry forbidden. The photochemistry of oxygen resulting from the excitation of oxygen via forbidden transitions in UV has been discussed by Parker [1]. Following this overview we should mention that three forbidden transitions into the $A^{3}\Sigma_{u}^{+}$, $c^{1}\Sigma_{u}^{-}$ and $A'^{3}\Delta_{u}$ states, named as the Herzberg I, II and III states, govern the discrete absorption of oxygen in UV-region from 242 to 290 nm which can be deconvoluted into three Herzberg I, II and III bands. Below in wavelength the so-called Herzberg continuum is located between 242 and 200 nm. The main contribution into the UV-absorption is provided by transition into Herzberg I state. Since long ago the dramatic effect of molecular environment giving rise to enhancement of optical absorption by oxygen is well known. Wulf [2] and then Finkelnburg [3] observed the diffuse bands with triplet structure in UV-absorption of oxygen in the region 240-290 nm which overlaps with discrete Herzberg absorption. Finkelnburg revealed the quadratic pressure dependence of this absorption [3]. Now these bands are named the 'Wulf-bands' or 'high-pressure bands'. The shape of these bands which are the diffuse triplets with splitting due to spin-orbit coupling allowed the authors of papers [4,5] to assign these bands as governed by transition into Herzberg III $A'^{3}\Delta_{u}$ state. On the basis of pressure

E-mail address: baklanov@kinetics.nsc.ru (A.V. Baklanov).

dependence analysis the same conclusion has been made for the 'enhanced' absorption in Herzberg continuum region [6,7]. The overview of the experimental and theoretical data devoted to the collisional enhancement of Herzberg III transition is presented in paper by Minaev et al. [8]. The measurements of the absorption within Wulf-bands with high spectral resolution were carried out by Bernath et al. [9]. The authors of this Letter revealed that the spectrum of the Wulf-bands absorption of oxygen when normalized on the same O2 concentration does not change qualitatively and semiquantitatively with change in the row of collision partners Ar, N₂ and O₂. So the authors concluded that the collision-induced absorption (CIA) is a mechanism responsible for Wulf-band appearance. In spite of the name 'high-pressure bands' the contribution of CIA governed by absorption of encounter complexes O₂- O_2 and O_2 - N_2 is comparable with linear absorption of oxygen at atmospheric conditions already [6] and that makes it to be of atmospheric interest [9,10]. The measurements of collision-induced absorption in oxygen have been carried out for many collision partners which demonstrate the wide spread in efficiency of absorption 'enhancement' [7,11]. The 'dramatic' effect of complex partner on photophysics and photochemistry of oxygen was revealed when the velocity maps of O atoms arising from the photodissociation of van der Waals complexes X-O₂ were investigated [12]. The photoexcitation of encounter complexes of oxygen O_2 -O₂ is followed by new photochemistry as well which is discussed in the review by Koda and Sugimoto [13]. The excitation with quantum energy above the threshold for dissociation of O₂ gives rise to oxygen atoms. Even the excitation below threshold provides the chemical changes which firstly were observed by Slanger et al. who detected formation of ozone after irradiation of oxygen at 248 nm [14]. This process has well defined pressure-dependent contribution due to the excitation of encounter complexes which

^{*} Corresponding author. Address: Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk 630090, Russia.

^{0009-2614/\$ -} see front matter @ 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.cplett.2009.11.058

has been studied in a series of papers and the results are summarized in the review [13]. Koda and Sugimoto conclude that the most probable mechanism of O_3 formation involves the collisioninduced absorption with transition of oxygen into Herzberg III state $A'^3 \Delta_u$ and bimolecular reactions like $O_2(A') + O_2 \rightarrow O_3 + O$ giving rise to ozone. Similar processes of odd oxygen species formation were also assumed to be responsible for the laser-induced oxidation of hydrocarbons in the hydrocarbon/ O_2 /supercritical CO₂ mixtures at 248 nm also considered in the review [13].

In the current Letter we describe the experimental results which reveal the new photochemical process resulting from the excitation within Wulf-band of encounter complexes of oxygen O_2-O_2 and giving rise to singlet oxygen $O_2(^{1}\Delta_g)$ formation. The possible mechanism of this process is also discussed.

2. Experimental

The experimental setup involves the high-pressure cell, laser source of UV-radiation, detector of IR-luminescence and digital oscilloscope for the control of the signal.

The gas was let into the cylindrical cell made of stainless-steel which was designed to withstand pressure more than 100 atm. The cell was T-shaped with three quartz windows of 10 mm in thickness and 13 mm in diameter. Pressure was measured by a pressure gauge and throughout the experiments it was varied within the range 3–80 atm. Gaseous oxygen with content $O_2 = 99.999\%$ was used in the experiments. For the estimation of kinetic parameters the values of oxygen concentration *n* were used. These values have been obtained from the pressure values *P* via the equation $n = \frac{P}{2RT}$ with taking into account the non-ideality of oxygen. In this equation *R* is gas constant, *z* is oxygen compressibility at temperature *T* = 300 K, taken from [15]. The difference between so calculated non-ideal and ideal-gas oxygen concentrations makes roughly 1–1.85%.

The gas in the cell was irradiated by the second harmonic (248 nm) of nanosecond excimer-pumped dye laser (Coumarin 102 in ethanol) generated in nonlinear crystal of barium β -borate (BBO). UV-pulse energy was 1 mJ. The second harmonic was separated from the fundamental by a prism and directed into the gas cell by dielectric mirrors and a lens of 25 cm in focus length with a focus beyond the cell. In order to measure pulse energy was attenuated with the use of the set of UV-VIS Neutral Density Filters. The laser pulse passed through the cell and at the output it was detected by photodiode providing control of pulse energy and external triggering for signal recording. In some experiments KrF excimer laser has been used as a source of exciting radiation with wavelength of 248.5 nm. Its pulse energy was 1.5 mJ.

The singlet oxygen $O_2(^1\Delta_g)$ has been detected by its luminescence at the wavelength 1.27 μ m. The luminescence was registered transversely to the laser beam direction with the use of InGaAs photodiode G6126 (Hamamatsu). To register a narrow spectrum region around 1.27 μ m, interference filter (transmission peak at 1.27 μ m, transmittance in maximum – 92.5%, transmission half-bandwidth – 30 nm) and silicon plate of 0.4 mm in thickness were used. Luminescence signals have been obtained by averaging of results of 30–500 laser shots (1 Hz repetition rate). If needed, background signal recorded with the empty cell was subtracted from the luminescence signals.

To evaluate the contribution of O_2-O_2 complexes in the general absorption and control the laser-radiation absorption during the experiments, the absorption spectra of oxygen at various pressure values were recorded on the UV–VIS spectrophotometer (Shimadzu).

3. Results and discussion

3.1. Production of $O_2(^1\Delta_g)$

Fig. 1 represents the temporal profile of singlet oxygen luminescence at 1.27 nm which has been detected after excitation of gaseous oxygen at elevated pressure. The luminescence signal follows the concentration of singlet oxygen. The absolute value and temporal profile of this signal did not depend on the number of laser pulses. So we can exclude effect of any accumulated products. We have fitted the experimental time-profile of this signal by the equation

$$S = \frac{A \cdot k_1}{k_2 - k_1} \cdot [\exp(-k_1 t) - \exp(-k_2 t)], \tag{1}$$

with parameters A, k_1 and k_2 being the result of the least squares fitting of measured profiles. The variation of oxygen pressure P within the range 3–80 atm resulted in the change of A – the amplitude and k_2 – the temporal characteristic of the signal decay. The parameter k_1 – the temporal characteristic of the rising part of the profile does not change in our conditions and is governed by frequency response characteristic of the photodiode. The parameter k_2 is the rate constant of the pseudo-first order process of $O_2({}^1\Delta_g)$ quenching which will be discussed later.

In Fig. 2 the pressure dependence of the signal amplitude *A* is shown. The dependence is well fitted by the sum of quadratic and cubic terms $A = C \cdot P^2 + D \cdot P^3$. To rationalize this dependence we should first discuss the process of IR-luminescence of singlet oxygen

$$O_2(a^1\Delta_g) \xrightarrow{1/\tau} O_2(X^3\Sigma_g^-) + h\nu \quad (\lambda = 1.27 \ \mu m). \tag{2}$$

This luminescence of unperturbed $O_2({}^1\Delta_g)$ molecules is forbidden process characterized by a very long radiative lifetime $\tau \approx 74$ min as derived from the Einstein coefficient $A = 2.256 \times 10^{-4} \text{ s}^{-1}$ extracted from the integrated absorption intensity for (0,0) band [17]. It is well known that the collision-induced perturbation

$$O_{2}(a^{1}\Delta_{g}) + O_{2}(X^{3}\Sigma_{g}^{-}) \xrightarrow{\kappa_{bl}} 2O_{2}(X^{3}\Sigma_{g}^{-}) + h\nu \quad (\lambda = 1.27 \ \mu\text{m})$$
(3)



Fig. 1. Time dependence of the $O_2(a^1\Delta_g)$ luminescence signal at O_2 pressure of 41 atm. The excitation wavelength is 248.3 nm. The line represents the least squares fit with the function $y = A \cdot k_1 \cdot (k_2 - k_1)^{-1} \cdot [\exp(-k_1 \cdot t) - \exp(-k_2 \cdot t)]$ (see text). On the inset the absorption spectrum of O_2 at the pressure of 100 atm (–) as measured in this work and low-pressure extrapolated absorption cross section of O_2 (**■**) as taken from paper [16] are presented. Arrow shows the wavelength used for excitation.



Fig. 2. Pressure dependence of the $O_2(a^1\Delta_g)$ luminescence signal amplitude (*A* value in the equation (1)). The excitation wavelength is 248.3 nm. Line corresponds to the fit of data by equation $A = C \cdot P^2 + D \cdot P^3$ with C = 0.00137 mV atm⁻² and D = 0.00057 mV atm⁻³ (see text).

accelerates this luminescence. The rate constant of this bimolecular luminescence has been measured by Wildt et al. [18] in the gas phase and found to be $k_{bl} = 3.4 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$. For our oxygen pressure conditions P = 3-80 atm (T = 300 K) this value of rate constant results in the radiative lifetime of τ = 6.7 min–15 s. This time is much shorter than the radiative lifetime of the unperturbed $O_2(^1\Delta_g)$ molecules. So for all our conditions the measured signal luminescence should be proportional to the first power of oxygen pressure P due to domination of collision-enhanced luminescence. The pure collision-induced nature of $O_2(^1\Delta_g)$ luminescence has been established for the oxygen pressure conditions similar to the ours by Furui et al. [19]. The quadratic and cubic terms in the pressure dependence of the signal amplitude A can be rationalized if the rate of excitation giving rise to singlet oxygen contains the terms which are linear and quadratic in pressure. The linear pressure dependence comes from unimolecular excitation process $O_2 \xrightarrow{h\nu} O_2(^1\Delta_g)$ and the quadratic term comes from excitation of encounter complexes of oxygen $O_2 - O_2 \xrightarrow{hv} O_2(^1\Delta_g)$ in the process of collision-induced absorption (CIA). So we can conclude that the photogeneration of singlet oxygen results from excitation of molecular oxygen O₂ itself and from excitation of encounter complexes O_2-O_2 . The ratio of contributions of encounter complexes O_2-O_2 and molecular oxygen O_2 itself is equal to $D \cdot P/C$, where D and C are the coefficients found for the pressure dependence shown in Fig. 2. This ratio at the maximal value of pressure (35 atm) in Fig. 2 is equal to about 15 and when extrapolated to P = 1 atm gives value 0.4. Fig. 3 plots the dependence of singlet oxygen signal on the laser pulse energy. The linear dependence indicates the one-quantum absorption to be responsible for $O_2({}^1\Delta_g)$ photogeneration. At the pressure used (68 atm) the ratio $D \cdot P/C$ is close to 30. This means that the conclusion on the one-quantum nature of singlet oxygen photogeneration in our conditions is relevant to the contribution of encounter complexes O₂–O₂. This allows us to discuss the mechanism of singlet oxygen photogeneration in more details.

3.2. Mechanism of singlet oxygen generation

The generation of singlet oxygen $O_2({}^1\Delta_g, \upsilon = 0)$ as a result of one-quantum absorption of UV-radiation by O_2 molecules at the low-pressure conditions (*P* = 10–100 Torr) was observed by Pejak-



Fig. 3. Double-logarithmic plot of the $O_2(a^1\Delta_g)$ luminescence signal magnitude *A* versus laser pulse energy at $\lambda = 248.5$ nm (KrF laser) measured at the pressure of oxygen *P* = 68 atm.

ović et al. [20]. These authors excited by laser the discrete spectrum of Herzberg I state $O_2(A^3\Sigma_u^+, v')$ and detected the appearance of $O_2({}^1\Delta_g, v = 0)$ with REMPI. These authors suggested some relaxation of excited state $O_2(A^3\Sigma_u^+, v')$ as a source of singlet oxygen. We can suggest the same mechanism of singlet oxygen formation responsible for the quadratic term in the pressure dependence of $O_2(a^1\Delta_g)$ luminescence signal we observe.

As we discussed in the Introduction the spectrum of the collision-induced absorption responsible for the Wulf-bands indicates excitation of one of the molecules of the encounter complex O_{2^-} O_2 into Herzberg III state which can be presented with the equation

$$O_2(X^3\Sigma_g^-) - O_2(X^3\Sigma_g^-) + h\nu \to O_2(A'^3\Delta_u) + O_2(X^3\Sigma_g^-). \tag{4}$$

According to the assignment of the high-pressure bands of oxygen [5,10] the used excitation wavelengths coincide with the overlap of the subbands ($\Omega = 1,2$) of the band corresponding to the excitation of one O₂ molecule of the complex O₂–O₂ into the vibrational level v' = 9 of Herzberg III state. This assignment allows us to expect the appearance of vibrationally excited O₂($A'^3 \Delta_u$, v' = 9) in the process (4). We can postulate that the further relaxation can be a source of singlet oxygen O₂($a^1 \Delta_g$) formation. But we should definitely favor the schemes of relaxation involving simultaneous annihilation of spin of two collision partners

$$O_2(A'^3\Delta_u) + O_2(X^3\Sigma_g^-) \rightarrow O_2(a^1\Delta_g) + O_2(a^1\Delta_g, b^1\Sigma_g^+), \tag{5}$$

where the excited oxygen molecule in $A'^3\Delta_u$ state is the triplet sensitizer. The energy of the initial excitation ($hv \approx 5$ eV) is sufficient for the process (5) to occur, because the energy of singlet *a* and *b* states are equal to 0.98 and 1.63 eV, respectively. The similar processes can govern the formation of $O_2(a^1\Delta_g)$ proceeding after excitation of O_2 molecules into Herzberg I state

$$O_2(X^3\Sigma_{\sigma}^-) + h\nu \to O_2(A^3\Sigma_{\mu}^+), \tag{6}$$

with the excited $O_2(A^3\Sigma_u^+)$ being the triplet sensitizer in the process

$$O_2(A^{\mathsf{s}}\Sigma_{\mathfrak{u}}^+) + O_2(X^{\mathsf{s}}\Sigma_{\mathfrak{g}}^-) \to O_2(a^{\mathsf{s}}\Delta_{\mathfrak{g}}) + O_2(a^{\mathsf{s}}\Delta_{\mathfrak{g}}, b^{\mathsf{s}}\Sigma_{\mathfrak{g}}^+)$$
(7)

The importance of oxygen as the principal collision partner for generation of $O_2(a^1\Delta_g)$ from $O_2(A^3\Sigma_u^+)$ was established in papers by Ali et al. [21] and Ogryzlo et al. [22] who studied effect of principal col-

A.P. Trushina et al. / Chemical Physics Letters 485 (2010) 11-15

lision partner on the yield of singlet oxygen after recombination of O atoms. After termolecular recombination of O atoms the O₂ molecule in one of the Herzberg states was generated and singlet oxygen appeared then due to the relaxation of this excited O₂. Pejaković et al. [20] point out the significance of spin-allowed character of $O_2(A^3\Sigma_u^+)$ relaxation with $O_2(X^3\Sigma_g^-)$ as a collision partner.

Here we should also consider the possibility of another process of $O_2(a^1\Delta_g)$ formation due to ozone photodissociation. As it was mentioned in the Introduction the production of ozone was observed in the number of papers (see review [13]) when high-pressure oxygen was excited by laser UV-radiation even below O_2 dissociation threshold involving the wavelength region used in this work. In turn ozone has absorption band in UV-region which is named Hartley band (200–320 nm). Absorption within this band results in the photodissociation giving rise to singlet oxygen [23]

$$O_3 + h\nu \to O_2(a^1\Delta_g) + O(^1D). \tag{8}$$

So the formation of ozone could provide another source of singlet oxygen. But our results allow us to neglect this contribution in our experiments. First, the concentration of ozone generated by photoexcitation at 248 nm was found to be rising in time (number of pulses) via linear dependence at the pressure conditions similar to ours [24]. This rise should result in growth of singlet oxygen production if accumulated ozone is its precursor. But in our case the amplitude of $O_2(a^1 \Delta_g)$ luminescence signal did not depend on the number of pulses used for accumulation. Second, the rate of ozone formation was found to be of the first order at the pressure conditions similar to ours [24]. Absorption of extra quantum in the process (8) should make the pulse energy dependence of singlet oxygen production via this mechanism to be of the second order. The laser pulse energy dependence of $O_2(a^1 \Delta_g)$ signal in our experiments has not the second but the first order (see Fig. 4). In our experiments on laser energy dependence the energy fluence of laser pulse was varied within the limits 6×10^{15} – 8×10^{16} guantum/cm². In these mild conditions no one excitation step can be saturated to reduce the order of pulse energy dependence from 2 to 1. So we can neglect the formation of singlet oxygen via mechanism involving ozone formation in our experiments.

The processes (5) and (7) are similar to the widely used spin-allowed process of triplet sensitization which has very broad literature (see reviews [25–27])



Fig. 4. Plot shows the dependence of the $O_2(a^1\Delta_g)$ quenching (vanishing) rate constant on O_2 pressure. The excitation wavelength is 248.3 nm.

$$T_1 + {}^3O_2({}^3\Sigma_g^-) \to {}^1S_0 + {}^1O_2({}^1\Delta_g, {}^1\Sigma_g^+). \eqno(9)$$

In the processes (5) and (7) the triplet $O_2(A'^3 \Delta_u)$, $O_2(A^3 \Sigma_u^+)$ and singlet $O_2(a^1 \Delta_g)$ states of oxygen play the same role as triplet T_1 and ground singlet ${}^{1}S_0$ states of usually used organic sensitizers do in the process (9). The processes (4) and (5) of $O_2(a^1 \Delta_g)$ production via oxygen self-photosensitization definitely take place in atmosphere as well as the processes (6) and (7). Further quantitative study is necessary to estimate the relative role of these two contributions in atmosphere as compared with the mechanism of $O_2(a^1 \Delta_g)$ photogeneration in the photodissociation of ozone within the Hartley band.

3.3. Singlet oxygen quenching

The descending part of the temporal profile (1) of IR-luminescence is governed by parameter k_2 . This parameter defines the rate of the quenching of $O_2({}^1\Delta_g)$ and depends on oxygen pressure linearly as it is shown in Fig. 4. This indicates that the parameter k_2 is a pseudo-first-order rate constant of bimolecular process of quenching. This quenching proceeds via two channels. One of them is bimolecular collision-induced luminescence (3) with rate constant k_{bl} . Another channel is radiationless collisional relaxation on oxygen with quenching rate constant k_q

$$O_2(a^1\Delta_g) + O_2(X^3\Sigma_g^-) \xrightarrow{\kappa_q} 2O_2(X^3\Sigma_g^-)$$
(10)

The sum of the rate constants $(k_{bl} + k_q)$ defines the parameter $k_2 = (k_{bl} + k_q) \cdot [O_2]$. The linear fit to the experimental dependence of k_2 on oxygen pressure in Fig. 4 provides the value of this sum $(k_{bl} + k_q) = (1.93 \pm 0.02) \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$. Taking into account that the rate constant of the process (3) $k_{bl} = 3.4 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$ [18] is by about four orders of magnitude lower than this sum we can neglect its contribution. So finally we get the rate constant for radiationless quenching (10) $k_q = (1.93 \pm 0.02) \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$. This value can be compared with the data of earlier measurements summarized in the book [25] and being scattered within the interval $(1.5-2.4) \times 10^{-18}$ cm³ s⁻¹ and with the most recent data for this rate constant $(1.6\pm0.2)\times10^{-18}~cm^3~s^{-1}~~[28]$ and $(1.7\pm0.2)\times10^{-18}~cm^3~s^{-1}$ [19]. The last value has been measured by Furui et al. also at the high-pressure conditions. In our experiments even at the smallest pressure value of 10 atm used for k_2 measurements (Fig. 4) the diffusion of singlet oxygen out of detection zone proceeds with the estimated rate constant of about 0.5 s^{-1} which is much less than the measured rate constant $k_2 \approx 500 \text{ s}^{-1}$. The diffusion to the walls of the cell proceeds even slower. So our value together with that one measured by Furui et al. are free from the influence of diffusion and wall effects on the rate constant which were observed in the earlier low-pressure experiments. The advantage of our measurements is also rather low uncertainty of the value obtained due to the high statistics used.

4. Conclusions

The formation of singlet oxygen $O_2(a^1\Delta_g)$ has been observed as a result of excitation of gaseous oxygen at elevated pressure by laser radiation at 248 nm. Singlet oxygen has been monitored by its IR-luminescence at 1.27 µm. The pressure dependence of this luminescence has been investigated within the pressure range of 3–80 atm. The signal was found to be the sum of processes of the second- and third-order in dependence on the pressure of oxygen. These two processes are identified to be due to the absorption of individual O_2 molecules and encounter complexes O_2 – O_2 , respectively. The extra unit in the power of pressure dependence is due to the predominance of collision-induced mechanism of luminescence under conditions used. The laser pulse energy dependence indicates the one-quantum absorption as a source of singlet oxygen. The bimolecular collisional process with excited triplet state of molecular oxygen $O_2({}^3\Delta_u)$ as a sensitizer is supposed to be responsible for singlet oxygen $O_2(a^1\Delta_g)$ production. In turn the excited triplet oxygen $O_2(^3\Delta_u)$ appears as a result of UV-photon absorption by encounter complexes O_2-O_2 (collision-induced absorption of O_2).

Acknowledgement

The financial support of this work by Russian Foundation for Basic Research (Grant No. 09-03-00310-a) is gratefully acknowledged.

References

- [1] D.H. Parker, Acc. Chem. Res. 33 (2000) 563.
- [2] O.R. Wulf, Proc. Natl. Acad. Sci. (USA) 14 (1928) 609.
- [3] W. Finkelnburg, Z. Phys. 90 (1934) 1.
- [4] G. Herzberg, Can. J. Phys. 31 (1953) 657.
- [5] B. Coquart, D.A. Ramsay, Can. J. Phys. 64 (1986) 726.
- [6] A.J. Blake, D.G. McCoy, J. Quant. Spectrosc. Radiat. Transfer 38 (1987) 113.
- [7] G.Y. Zelikina, V.V. Bertsev, M.B. Kiseleva, Opt. Spectrosc. 81 (1996) 685.
- [8] B.F. Minaev, K.V. Mikkelsen, H. Agren, Chem. Phys. 220 (1997) 79.
- [9] P. Bernath et al., Chem. Phys. Lett. 297 (1998) 293.

- [10] S. Fally et al., J. Mol. Spectrosc. 204 (2000) 10.
- [11] Y. Oshima, Y. Okamoto, S. Koda, J. Phys. Chem. 99 (1995) 11830.
 [12] A.V. Baklanov, G.A. Bogdanchikov, K.V. Vidma, D.A. Chestakov, D.H. Parker, J.
- Chem. Phys. 126 (2007) 124316.
- [13] S. Koda, K. Sugimoto, J. Photochem. Photobiol., C 4 (2003) 215.
- [14] T.G. Slanger, L.E. Jusinski, G. Black, G.E. Gadd, Science 241 (1988) 945.
- [15] V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, V.A. Tsymarnyi, Thermodynamic Properties of Oxygen, Hemisphere Publishing Corp., Washington, DC, 1987 (National Standard Reference Data Service of the USSR. Volume 5).
- [16] Shardanand, J. Quant. Spectrosc. Radiat. Transfer 18 (1977) 525. [17] S.M. Newman, A.J. Orr-Ewing, D.A. Newnharn, J. Ballard, J. Phys. Chem. A 104
- (2000) 9467.
- [18] J. Wildt, E.H. Fink, P. Biggs, R.P. Wayne, Chem. Phys. 159 (1992) 127.
 [19] E. Furui, N. Akai, A. Ida, A. Kawai, K. Shibuya, Chem. Phys. Lett. 471 (2009)
- 45. [20] D.A. Pejaković, R.A. Copeland, P.T. Cosby, T.G. Slanger, J. Geophys. Res. 112 (2007) A10307.
- A.A. Ali, E.A. Ogryzlo, Y.Q. Shen, P.T. Wassell, Can. J. Phys. 64 (1986) 1614. [21]
- [22] E.A. Ogryzlo, Y.Q. Shen, P.T. Wassell, J. Photochem. 25 (1984) 389.
- [23] H. Okabe, Photochemistry of Small Molecules, Wiley-Interscience, New York, 1978.
- [24] V.I. Andrukhiv, V.V. Bertsev, M.O. Bulanin, A.A. Pastor, P.Y. Serdobintsev, Optika i Spectroskopiya 76 (1994) 165.
- [25] A.A. Frimer (Ed.), Singlet O2, CRC Press, Boca Raton, FL, 1985.
- [26] R. Schmidt, Photochem. Photobiol. 82 (2006) 1161.
- [27] A.A. Krasnovsky Jr., J. Phochem. Photobiol. A: Chem. 196 (2008) 210.
 [28] K.S. Klopovskiy, D.V. Lopaev, N.A. Popov, A.T. Rakhimov, T.V. Rakhimova, J. Phys. D: Appl. Phys. 32 (1999) 3004.