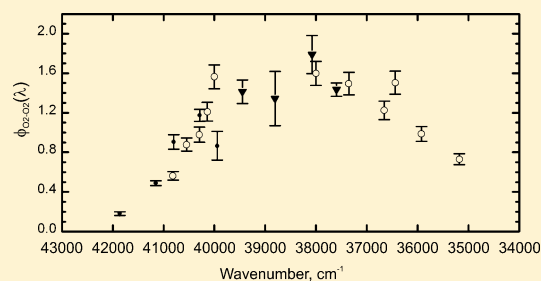


Quantum Yield and Mechanism of Singlet Oxygen Generation via UV Photoexcitation of O_2-O_2 and N_2-O_2 Encounter ComplexesAleksandra P. Trushina,^{†,§} Veniamin G. Goldort,[‡] Sergei A. Kochubei,[‡] and Alexey V. Baklanov^{*,†,§}[†]Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk 630090, Russia[‡]Institute of Semiconductor Physics, Lavrentiev Ave. 13, Novosibirsk 630090, Russia[§]Novosibirsk State University, Pirogova Str. 2, Novosibirsk 630090, Russia

Supporting Information

ABSTRACT: The mechanism and spectral dependence of the quantum yield of singlet oxygen $O_2(a^1\Delta_g)$ photogenerated by UV radiation in gaseous oxygen at elevated pressure (32–130 bar) have been experimentally investigated within the 238–285 nm spectral region overlapping the range of the Wulf bands in the absorption spectrum of oxygen. The dominant channel of singlet oxygen generation with measured quantum yield up to about 2 is attributed to the one-quantum absorption by the encounter complexes O_2-O_2 . This absorption gives rise to oxygen in the Herzberg III state $O_2(A' \ ^3\Delta_u)$, which is assumed to be responsible for singlet oxygen production in the relaxation process $O_2(A' \ ^3\Delta_u, v) + O_2(X \ ^3\Sigma_g^-) \rightarrow O_2(\{a^1\Delta_g\}, \{b^1\Sigma_g^+\}) + O_2(\{a^1\Delta_g, v=0\}, \{b^1\Sigma_g^+, v=0\})$ with further collisional relaxation of b to a state. This mechanism is deduced from the analysis of the avoiding crossing locations on the potential energy surface of colliding O_2-O_2 pair. The observed drop of the $O_2(a^1\Delta_g)$ yield near spectral threshold for O_2 dissociation is explained by the competition between above relaxation and reaction giving rise to $O_3 + O$ ($O + O + O_2$) supposed in literature. The quantum yield of $O_2(a^1\Delta_g)$ formation from encounter complex N_2-O_2 measured at $\lambda = 266$ nm was found to be the same as that for O_2-O_2 .



INTRODUCTION

In a recent paper we have revealed the formation of singlet oxygen $O_2(a^1\Delta_g)$ when oxygen at elevated pressure is excited by UV radiation at the wavelength of 248 nm, which is below threshold of O_2 photodissociation.¹ Two sources were found to contribute to this process. One is absorption of “free” O_2 molecules, which was small at the conditions of the experiment. Another one was contribution of encounter complexes O_2-O_2 , which dominated at the elevated pressure. To estimate the role of this last process in the gas or condensed phase, the quantitative information about absorption spectrum of the encounter complexes and spectral profile of the quantum yield of singlet oxygen are necessary. This last information can also help in understanding of mechanism of singlet oxygen photogeneration by encounter O_2-O_2 complexes.

All electronic transitions of the ground state $O_2(X \ ^3\Sigma_g^-)$ molecule are spin and/or orbital symmetry forbidden within the whole UV–IR spectral region, causing the photoabsorption of individual O_2 molecules to be very weak there. The photochemistry of molecular oxygen within the UV spectral region has been reviewed by Parker.² Within the UV region of 242–290 nm there are three weak discrete band systems in the oxygen absorption spectrum named as Herzberg I, II, and III bands that correspond to forbidden transitions into the so-called Herzberg I ($A \ ^3\Sigma_u^+$), II ($c \ ^1\Sigma_u^-$), and III ($A' \ ^3\Delta_u$) states, respectively. The main contribution into UV absorption is provided by transition into Herzberg I state. The UV

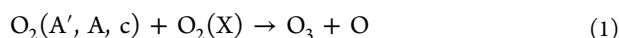
absorption by oxygen is dramatically enhanced when O_2 molecules interact with molecular environment. This drastic effect takes place in collisions of molecules in the gas phase and in the liquid phase when oxygen is dissolved in some solvent or in solid cryogenic matrixes. Wulf³ and then Finkelburg⁴ were first to observe the diffuse bands in UV absorption of gaseous oxygen in the region 240–290 nm, which overlaps with discrete Herzberg absorption. Now these bands are named the “Wulf bands” or “high-pressure bands”. These bands are the diffuse triplets with splitting due to spin–orbit coupling. This structure of the bands is assigned to be governed by the transition into the Herzberg III ($A' \ ^3\Delta_u$) state.^{5,6} 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.⁷ The measurements of the absorption within Wulf bands with high spectral resolution were carried out by Bernath et al.⁸ These authors have revealed that the spectrum of the oxygen Wulf band absorption normalized on the same O_2 concentration did not change qualitatively and semiquantitatively with different collision partners Ar, N_2 , and O_2 . So these authors concluded the collision-induced absorption (CIA) governed by absorption of oxygen encounter complexes $X-O_2$ to be a mechanism responsible for Wulf band appearance. The

Received: February 14, 2012

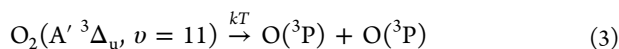
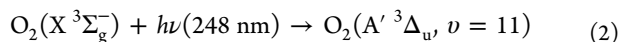
Revised: April 12, 2012

Published: June 4, 2012

Wulf bands of oxygen governed by the $\text{O}_2\text{--O}_2$, $\text{O}_2\text{--N}_2$, and $\text{O}_2\text{--Ar}$ collisions have also been quantitatively studied by Fally et al.⁹ In spite of the name “high-pressure bands” the contribution of CIA governed by absorption of $\text{O}_2\text{--O}_2$ and $\text{O}_2\text{--N}_2$ encounter complexes is comparable with linear absorption of oxygen at atmospheric conditions already¹⁰ and that makes it to be of atmospheric interest. The measurements of CIA in oxygen have been carried out for many various collisional partners, which demonstrate the widespread in efficiency of absorption enhancement.^{11,12} The CIA dramatically affects the photophysics and photochemistry of molecular oxygen as it was established in experiments with van der Waals (vdW) complexes X--O_2 of oxygen.^{13–17} These complexes generated in the molecular beam are the ideal model for the encounter complexes responsible for CIA. The results of excitation of vdW complexes above the dissociation threshold within the Herzberg continuum demonstrate the enhancement of the O atom yield which is in agreement with the enhancement of the UV absorption by O_2 due to CIA. The velocity map imaging (VMI) experiments carried out with vdW complexes X--O_2 revealed a very rich picture of the effect of intermolecular interaction in the complex on its photoabsorption and photodissociation. Up to five channels providing O atoms with different kinetic energies and the angular anisotropy of the recoil direction have been revealed by Baklanov et al. with the use of VMI approach.¹⁷ The new photochemistry is due to enhanced absorption by the encounter complexes of oxygen with excitation below threshold of O_2 molecule dissociation. Slanger et al. revealed the formation of ozone when oxygen at the pressure of 1000 Torr was irradiated by the excimer KrF laser at wavelength of 248 nm.¹⁸ Two mechanisms have been suggested. Shi and Barker suggested the bimolecular reaction between the photoexcited oxygen molecule in one of three Herzberg states $\text{O}_2(\text{A}', \text{A}, \text{c})$ with oxygen molecule in the ground state $\text{O}_2(\text{X})$ to be the source of ozone¹⁹



Discrimination between three excited states was concluded to be impossible because of closeness in energy for these states and supposed high exchange rate between them. Andruhiv et al. observed well pronounced positive effect of temperature on the yield of ozone and concluded that the O_3 formation proceeds via the processes²⁰



It is necessary to take into account that actually the encounter complex $\text{O}_2\text{--O}_2$ participates in process 2 because the collision-induced absorption dominates at this high pressure. Process 3 is also collisional in nature. Sugimoto et al. measured spectral profile for quantum yield of ozone within the region from 232 to 255 nm.²¹ This quantum yield went down to zero only at about 255 nm that is far below the threshold of O_2 molecule dissociation located at 242.3 nm. Detailed analysis of data devoted to the high-pressure absorption by O_2 in the UV region and photochemistry governing the formation of ozone is given in the review by Koda and Sugimoto.²² These authors

concluded that extra experiments are necessary to discriminate between mechanism 1 and mechanisms 3 and 4.

In the present paper we quantitatively study another route of oxygen photochemistry initiated by the oxygen collision-induced UV photoabsorption giving rise to reactive species of oxygen in its first excited singlet state $\text{O}_2(\text{a } ^1\Delta_g)$. In the current paper the spectral dependence of the quantum yield of $\text{O}_2(\text{a } ^1\Delta_g)$ has been measured within the region 238–285 nm overlapping the Wulf bands. The quantum yield of $\text{O}_2(\text{a } ^1\Delta_g)$ resulting from excitation of encounter complex $\text{N}_2\text{--O}_2$ at 266 nm has been also measured. Results obtained are discussed from the point of view of the suggested mechanism governing the formation of singlet oxygen.

■ EXPERIMENTAL METHODS

The used experimental setup is similar to the one described earlier¹ and consists of a laser source of UV radiation, a high-pressure cell, a detector of IR luminescence, UV photodiodes, and a digital oscilloscope.

Gaseous oxygen (99.99%) or the mixture of oxygen with nitrogen (99.9% with oxygen content less than 0.0007%) was let into the cylindrical cell made of stainless steel, which was designed to withstand pressure of more than 150 bar. The pressure was varied in the experiments within the range 18–130 bar. The cell was T-shaped with three quartz windows of 10 mm in thickness and 13.5 mm in diameter. The windows were used with O-rings of Teflon or copper. The length of the optical pass is equal to 5.5 cm.

The gas in the cell was irradiated by the second harmonic of the dye laser generated in the nonlinear BBO crystal. The dye laser radiation has been generated with the use of the dyes Coumarin 102, 307, and 153 in ethanol with pumping by the third harmonic of the nanosecond Nd:YAG laser (LS-2137U, LOTIS TII) or nanosecond XeCl excimer laser. This allowed us to get UV radiation tunable in the spectral range 238–285 nm with up to 1 mJ pulse energy. The second harmonic was separated from the fundamental by a prism and UV light filters. The small part of the UV pulse at the entrance reflected by the thin quartz plate and the radiation passed through the cell were measured by the photodiodes for the control of the incoming and outgoing radiation. In some experiments the fourth harmonic 266 nm of the Nd:YAG laser has been used to directly irradiate the gas in the cell. In these experiments UV pulse energy range was 30 μJ to 3.5 mJ. The spot of laser radiation in the cell was about 0.1 cm^2 .

Singlet oxygen $\text{O}_2(\text{a } ^1\Delta_g)$ has been detected by its IR-luminescence within a-X 0–0 band at 1.27 μm , which was registered transversely to the laser beam direction with an InGaAs photodiode G6126 (Hamamatsu). An interference filter (transmission peak at 1.27 μm ; transmittance maximum, 92.5%; transmission half-bandwidth, 30 nm) and a silicon plate of 0.4 mm in thickness were used to register a narrow spectrum region around 1.27 μm . Luminescence signals have been obtained by averaging a set of shots.

For the measurements of the quantum yield of singlet oxygen generated from $\text{O}_2\text{--O}_2$ complexes several procedures have been used. In one of them the luminescence of $\text{O}_2(\text{a } ^1\Delta_g)$ has been measured simultaneously with the UV radiation absorption for pure oxygen and for oxygen at the same pressure but with small admixture of ozone prepared by extra UV irradiation of mercury lamp light. This extra irradiation during 10–30 min by the mercury line 253.7 nm provided ozone in concentrations at the level of 0.1 Torr. The process of

ozone photogeneration at the elevated pressure of oxygen with the use of radiation with quantum energy below the threshold of the O_2 molecule dissociation is described in the Introduction. The quantum yield of ozone photogeneration at the wavelength 253.7 nm is small but nonzero.²¹ This process of ozone preparation provided longitudinally near uniform distribution of O_3 because of small cross-section of oxygen.⁹ Estimation shows that oxygen in our cell at the pressure of $P = 30$ bar absorbs only about 10% of radiation at 253.7 nm. The zone illuminated by the lamp in the cell was about 1 cm in diameter, bigger by several times than the size of laser beam. The waiting for the time of 30–40 min providing extra averaging of O_3 concentration by diffusion over several millimeters did not effect on the measured absorption of the pumping radiation and luminescence signal. This indicates the absence of any essential radial nonuniformity within the laser beam. In Figure 1 the $O_2(a^1\Delta_g)$ luminescence signals for the

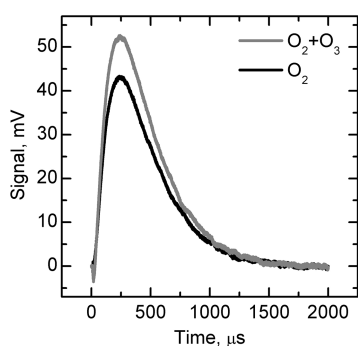


Figure 1. Time profile of $O_2(a^1\Delta_g)$ luminescence signals in pure O_2 and an oxygen–ozone mixture at a pressure of 86.5 bar observed on an oscilloscope. The excitation wavelength was 248.21 nm, and signals were averaged over 64 laser pulses with 1 Hz repetition rate.

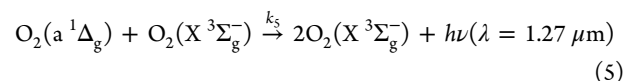
cases of UV irradiation of pure O_2 and of the mixture $O_3 + O_2$ are shown. The distinct change of the luminescence signal due to ozone photodissociation and known from literature value of the quantum yield of $O_2(a^1\Delta_g)$ photogeneration in the process $O_3 + h\nu \rightarrow O_2(a^1\Delta_g) + O$ allows us to determine the quantum yield of the process $O_2-O_2 + h\nu \rightarrow O_2(a^1\Delta_g) + O_2$. In the second approach without ozone generation the quantum yield measured earlier at the wavelength 266 nm or at 263.2 nm was then used as a reference point. In this approach the signal of $O_2(a^1\Delta_g)$ luminescence and pulse energy of UV radiation were measured for the pumping radiation wavelength under study. The absorptions at this wavelength and at 263.2 or 266 nm were calculated with the use of the cross sections measured by Fally et al.⁹ and with concentration value corresponding to the value of pressure used. The values at 263.2 or 266 nm have been used as the reference points for the wavelengths lower than 263.2 or higher than 266 nm, respectively. The use of these two reference points is due to the necessity of the reference wavelength to be accessible with the dye providing wavelength under study.

Because the absorption of N_2-O_2 encounter complexes is much weaker than O_2-O_2 absorption,⁹ high excitation energy was required to investigate singlet oxygen generation from N_2-O_2 complexes. Thus experiments with a nitrogen–oxygen mixture were carried out only at the fourth harmonic of the Nd:YAG laser (266 nm) as the excitation wavelength. To calculate the value of the singlet oxygen quantum yield, the luminescence signals and absorption in pure oxygen have been

compared with those in nitrogen–oxygen mixtures with the same concentration of oxygen and different nitrogen concentrations. The minimal oxygen pressure needed to register singlet oxygen luminescence (about 18–25 bar) was used in these experiments to reduce the contribution of O_2-O_2 complexes.

RESULTS AND DATA ANALYSIS

Source of Singlet Oxygen $O_2(a^1\Delta_g)$. The time profile of $O_2(a^1\Delta_g)$ luminescence resulting from photoexcitation of oxygen at the elevated pressure is shown in Figure 1. As established in our earlier work, the rising part of this profile is governed by frequency response characteristic of the photodiode and the falling part is governed by the quenching of the $O_2(a^1\Delta_g)$ state in collisions with ground state oxygen molecules.¹ The experimentally observed pressure (P) dependence of the $O_2(a^1\Delta_g)$ luminescence amplitude (A) was found to be fitted well by the sum of quadratic and cubic terms $A = C \cdot P^2 + D \cdot P^3$. As discussed in the same work, the quadratic term comes from unimolecular excitation process $O_2 \xrightarrow{h\nu} O_2(a^1\Delta_g)$ and the cubic term comes from excitation of encounter complexes of oxygen $O_2-O_2 \xrightarrow{h\nu} O_2(a^1\Delta_g)$ in the process of CIA. One extra unit in the power dependence comes from the collision-induced nature of the $O_2(a^1\Delta_g)$ luminescence



As estimated in the same paper, process 5 dominates over the forbidden spontaneous emission of $O_2(a^1\Delta_g)$ by several orders of magnitude under the pressure conditions of tens of bar used.¹ The pure collision-induced nature of $O_2(a^1\Delta_g)$ luminescence has been also established for the oxygen pressure conditions similar to ours by Furui et al.²³ The cubic and quadratic terms in the upper pressure dependence are comparable in values at the pressure of about 1 bar.¹ This is in agreement with earlier data¹⁰ that linear UV absorption by “free” O_2 molecules and by encounter complexes of oxygen are comparable at atmospheric pressure. This means that at our pressure conditions of tens of bar we can neglect the contribution of the quadratic term and consider only contribution of the cubic term due to excitation of the encounter complexes O_2-O_2 .

The dependence of singlet oxygen signal on the laser pulse energy is linear like that one observed previously¹ for excitation at 248 nm which identifies one-quantum absorption by the encounter complexes O_2-O_2 (see Supporting Information Figure S1).

Here we should also mention other possibility of $O_2(a^1\Delta_g)$ formation due to ozone generation following the photoexcitation of the encounter complexes O_2-O_2 . According to the literature data described in the Introduction the photoexcitation of the encounter complex O_2-O_2 within the blue part of the Wulf bands gives rise to ozone formation via mechanisms 1 or 2–4. This ozone could be dissociated by the same laser pulse giving rise to singlet oxygen in the known process $O_3 + h\nu \rightarrow O_2(a^1\Delta_g) + O(^1D)$.²⁴ As discussed in our previous paper, the results on pulse energy dependence for $O_2(a^1\Delta_g)$ luminescence as well as absence of the rise of singlet oxygen luminescence signal during the irradiation by long sequence of the laser UV pulses allowed us to neglect the contribution of this mechanism in our experimental con-

ditions.¹ So, finally, we can summarize that one-quantum excitation of the encounter complexes O_2-O_2 is the dominating process of singlet oxygen generation in our experiments with oxygen at the elevated pressure.

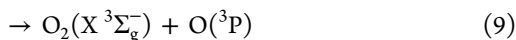
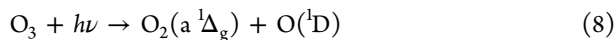
Quantum Yield of $O_2(a^1\Delta_g)$ from O_2-O_2 Encounter Complexes. As stated above, the singlet oxygen quantum yield can be determined from the comparison of luminescence signal and light absorption in pure oxygen with those measured in presence of ozone. The admixture of ozone in oxygen results in the rise of the $O_2(a^1\Delta_g)$ luminescence signal without changing the shape of the time profile, as is seen in Figure 1. The ratio of luminescence amplitudes detected in the absence (A_{O_2}) and in the presence ($A_{O_3+O_2}$) of ozone can be expressed in terms of quantum yields of singlet oxygen generated from ozone ϕ_{O_3} and from O_2-O_2 complexes $\phi_{O_2-O_2}$:

$$\frac{A_{O_3+O_2}}{A_{O_2}} = \frac{N'_{O_3}\phi_{O_3} + N'_{O_2}\phi_{O_2-O_2}}{N_{O_2}\phi_{O_2-O_2}} \quad (6)$$

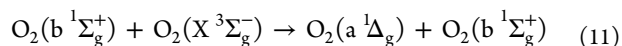
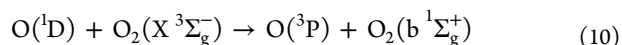
where N'_{O_3} , N'_{O_2} , and N_{O_2} are the numbers proportional to the number of light quanta absorbed in the central part of the cell by ozone and oxygen in the presence and in the absence of ozone, respectively. Equation 6 can be modified to give the ratio between the quantum yields ϕ_{O_3} and $\phi_{O_2-O_2}$:

$$\phi_{O_2-O_2} = \frac{\frac{N'_{O_3}}{N_{O_2}}}{\frac{A_{O_3+O_2}}{A_{O_2}} - \frac{N'_{O_2}}{N_{O_2}}} \cdot \phi_{O_3} \quad (7)$$

The ratio of the quantum yields was determined from eq 7 with the use of experimentally determined ratio of the luminescence amplitudes $A_{O_3+O_2}/A_{O_2}$ and calculated ratios N'_{O_3}/N_{O_2} and N'_{O_2}/N_{O_2} . The last ratios have been calculated with the use of the measured absorbance of UV light in the cell filled by oxygen without or with admixture of ozone as well as with the use of the ratio of the photodiode signals proportional to the UV-radiation pulse energy at the cell entrance in these two cases. Because the quantum yield ϕ_{O_3} is known from the literature, the needed $O_2(a^1\Delta_g)$ quantum yield $\phi_{O_2-O_2}$ can be calculated. The value of ϕ_{O_3} is governed by the processes proceeding after UV photoexcitation of ozone. The O_3 photodissociation within the Hartley band (200–300 nm) proceeds via mechanism



On the basis of the results of the experimental measurements of the quantum yield of $O(^1D)$ by Takahashi et al.²⁵ and by Taniguchi et al.²⁶ Schinke and McBane²⁷ concluded that the quantum yield of the process 8 giving rise to $O_2(a^1\Delta_g)$ is almost constant within the limits $(0.87 \pm 0.02) - (0.93 \pm 0.02)$ for the spectral range 230–305 nm. In the wavelength region 238–266 nm where ozone photodissociation has been used as a reference process in our work the fixed value $\phi_{O_3} = 0.90$ corresponding to the center of the above interval has been utilized. The singlet oxygen atoms $O(^1D)$ arising in the process 8 also contribute to the formation of singlet oxygen via the processes:



According to the data by Green et al.,²⁸ the yield of $O_2(b^1\Sigma_g^+)$ molecules in the relaxation process 10 is equal to $0.95^{+0.05}_{-0.13}$. According to paper by Knickelbein et al.,²⁹ all oxygen molecules in the $^1\Sigma_g^+$ state relax to the $^1\Delta_g$ state via process 11. Interaction of ozone with oxygen atoms arising in the processes 8 and 9 does not give rise to singlet oxygen.³⁰ Thus the quantum yield of singlet oxygen $O_2(a^1\Delta_g)$ formation is equal to $\phi_{O_3} = 0.90 + 0.90 \times 0.95 \times 1 = 1.76$ and this number was used in the whole wavelength region 238–266 nm where the photodissociation of ozone was used as the reference process for $O_2(a^1\Delta_g)$ quantum yield determination. Several independent measurements have been carried out at each wavelength. The average of these results together with the scatter of measured values is presented in Figure 2 and listed in Table S2 (see Supporting Information).

In another approach for $\phi_{O_2-O_2}$ determination the measurements in pure oxygen have been carried out. As the reference notes, the results of measurements of $\phi_{O_2-O_2}$ within the foregoing approach at the wavelengths $\lambda = 266$ and 263.2 nm

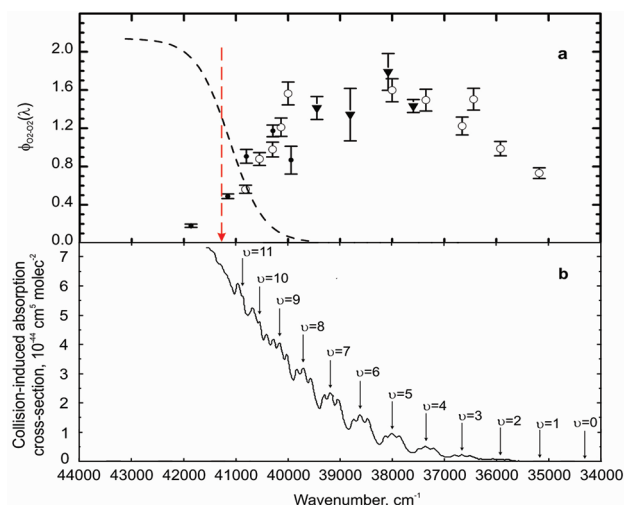


Figure 2. (a) Spectral dependence of the quantum yield of singlet oxygen generated from O_2-O_2 encounter complexes. Different experimental techniques are labeled by different types of symbols. Filled circles: data obtained from comparison of singlet oxygen luminescence signals and absorption in pure oxygen with those in oxygen-ozone mixture. Empty circles: data obtained from comparison of luminescence signals and absorption in pure oxygen at selected wavelengths with those at the fixed reference wavelength (266 nm for the long-wavelength region and 263.2 nm for the short one). Filled triangles: data obtained as a result of averaging of a series of experiments involving both types of quantum yield determination. The scatter of the quantum yield values are shown with error bars. The black dashed line corresponds to the wavelength dependence of the quantum yield of ozone formation obtained by smoothing of the data presented by Sugimoto et al.²¹ The red arrow shows the position of the O_2 photodissociation threshold at 41269 cm^{-1} . (b) O_2-O_2 collision-induced absorption cross section in the Wulf bands. The mean positions of vibrational Wulf bands $v = 0-11$ are shown on the plot also. The chart is plotted on the basis of Figure 2 from the paper by Fally et al.⁹ with permission.

have been used. In this case the singlet oxygen quantum yields measured at λ and Λ are expressed with the equation

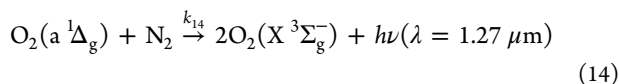
$$\phi_{\text{O}_2-\text{O}_2}(\lambda) = \frac{A_\lambda}{A_\Lambda} \cdot \frac{N_\Lambda}{N_\lambda} \cdot \phi_{\text{O}_2-\text{O}_2}(\Lambda) \quad (12)$$

where A_λ/A_Λ is ratio of the amplitudes of $\text{O}_2(\text{a } ^1\Delta_g)$ luminescence signals resulted from photoexcitation at wavelengths λ and Λ , N_Λ/N_λ is ratio of the numbers of absorbed quanta in the central part of the cell under irradiation at wavelengths λ and Λ , calculated with the use of the literature spectral data on UV absorption of oxygen within the Wulf bands.^{8,9} These data on $\phi_{\text{O}_2-\text{O}_2}$ are also presented in Figure 2 and in Table S2 (see Supporting Information).

Quantum Yield of $\text{O}_2(\text{a } ^1\Delta_g)$ from N_2-O_2 Encounter Complexes. The quantum yield of $\text{O}_2(\text{a } ^1\Delta_g)$ from the encounter complexes N_2-O_2 has been measured for excitation at one wavelength 266 nm. The ratio of the quantum yields for complexes N_2-O_2 and O_2-O_2 is described by

$$\frac{\phi_{\text{N}_2-\text{O}_2}}{\phi_{\text{O}_2-\text{O}_2}} = \frac{\frac{A_{\text{N}_2+\text{O}_2}}{A_{\text{O}_2}} N_{\text{O}_2} - N^*_{\text{O}_2}}{N^*_{\text{N}_2-\text{O}_2}} \quad (13)$$

where $A_{\text{N}_2+\text{O}_2}/A_{\text{O}_2}$ is the ratio of $\text{O}_2(\text{a } ^1\Delta_g)$ luminescence signals measured for excitation at 266 nm of mixture N_2-O_2 and of pure oxygen, $N^*_{\text{N}_2-\text{O}_2}$ and $N^*_{\text{O}_2}$ are the numbers proportional to the number of light quanta absorbed by N_2-O_2 encounter complexes and by oxygen molecules in the center of the cell filled with nitrogen–oxygen mixture respectively, and N_{O_2} is the number of light quanta absorbed by pure oxygen at 266 nm. These parameters were calculated with the use of data for O_2 and N_2-O_2 absorption cross sections presented in paper by Fally et al.⁹ The value of $\phi_{\text{O}_2-\text{O}_2}$ at 266 nm used has been obtained in the experiments with ozone generation. The composition of the N_2-O_2 mixture was varied within the range $P_{\text{N}_2}/P_{\text{O}_2} = 0.45\text{--}3.7$. When the contribution of nitrogen was small, the ratio of $\text{O}_2(\text{a } ^1\Delta_g)$ luminescence signals in pure oxygen and N_2-O_2 mixture with the same O_2 pressure corresponded to the ratio of the quantum yields $\phi_{\text{N}_2-\text{O}_2}/\phi_{\text{O}_2-\text{O}_2} = 1.2 \pm 0.2$. When the ratio $P_{\text{N}_2}/P_{\text{O}_2}$ rose at the constant oxygen pressure the ratio of $\text{O}_2(\text{a } ^1\Delta_g)$ luminescence signals rose somewhat faster than the rise of absorption. To interpret this rise, we should take into account that in our pressure conditions the luminescence of singlet oxygen is the collision induced process 5. Nitrogen molecules also provide collision-induced luminescence

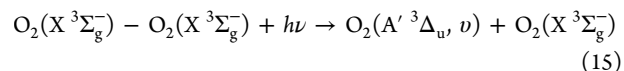


The ratio of rate constants k_5/k_{14} has been determined by Badger et al. to be about 5.4.³¹ This ratio fits well the rise of the $\text{O}_2(\text{a } ^1\Delta_g)$ luminescence signals ratio mentioned above with the rise of $P_{\text{N}_2}/P_{\text{O}_2}$. So we can conclude that the quantum yields of singlet oxygen $\text{O}_2(\text{a } ^1\Delta_g)$ from encounter complexes O_2-O_2 and N_2-O_2 measured at 266 nm coincide in value within the experimental uncertainty.

DISCUSSION

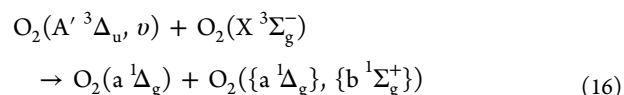
Mechanism of Singlet Oxygen Generation from UV Excitation of O_2-O_2 Encounter Complexes. As we

discussed in Introduction the spectrum of collision-induced absorption responsible for Wulf bands indicates the excitation of one of the molecules of the encounter complex O_2-O_2 into Herzberg III state according to the following process:

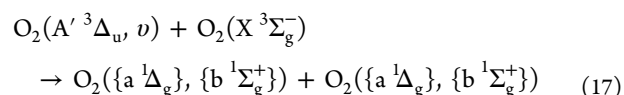


In the investigated spectral region ($v = 0$) transitions from the ground $\text{O}_2(\text{X } ^3\Sigma_g^-, 0)$ to Herzberg III state $\text{O}_2(\text{A } ^3\Delta_u, v)$ with $v = 1$ to $v = 11$ have been investigated. We did not succeed in observing the (0, 0) transition at 291.3 nm because of extremely low O_2-O_2 absorption cross section.

In our previous work¹ the further relaxation involving simultaneous annihilation of spin of two collision partners is assumed to be the principal channel of singlet oxygen $\text{O}_2(\text{a } ^1\Delta_g)$ formation:



where the excited $\text{O}_2(\text{A } ^3\Delta_u, v)$ molecule is a triplet sensitizer. We can further assume that both singlet oxygen molecules can appear in the a or b state. So we can rewrite process 16:



The high value of the quantum yield of $\text{O}_2(\text{a } ^1\Delta_g)$ generated from encounter complex O_2-O_2 (Figure 2a) as well as from N_2-O_2 complex being close to 2 can be explained with a process like 17. Process 17 can proceed via a spin-allowed path. Triplet states on the left side can provide states of the whole system with spin $S = 2, 1, 0$. The singlet state with $S = 0$ correlates with the overall singlet state of the right side system of two singlet O_2 molecules. The energy of initial excitation ($h\nu \approx 4.35\text{--}5.2$ eV) is sufficient for all four variants of singlet oxygen generation 17 to occur because the $v = 0$ energy of singlet a and b states is equal to 0.98 and 1.63 eV, respectively. In our experiments we cannot exclude singlet oxygen in b state $\text{O}_2(\text{b } ^1\Sigma_g^+)$ as a precursor of observed $\text{O}_2(\text{a } ^1\Delta_g)$ molecules because the conversion $\text{O}_2(\text{b } ^1\Sigma_g^+) + \text{O}_2(\text{X } ^3\Sigma_g^-) \rightarrow \text{O}_2(\text{a } ^1\Delta_g) + \text{O}_2(\text{X } ^3\Sigma_g^-)$ in collisions with ground state oxygen molecules proceeds with unit probability.²⁹ The rate constant of this relaxation is high enough (the value $4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ is recommended by Wayne³²) to make this relaxation time shorter than the response characteristic of the photodiode used ($\sim 10^{-4}$ s) at the oxygen pressure of tens of bar. The process of singlet oxygen generation via process 17 can be considered as the transition in the region of the avoided crossing between diabatic states corresponding to pair $\text{O}_2(\text{A } ^3\Delta_u, v) + \text{O}_2(\text{X } ^3\Sigma_g^-)$ and to pair $\text{O}_2(\{\text{a } ^1\Delta_g\}, \{\text{b } ^1\Sigma_g^+\}) + \text{O}_2(\{\text{a } ^1\Delta_g\}, \{\text{b } ^1\Sigma_g^+\})$. To find the position of accessible avoided crossing, we should build the potential energy curves for the involved states. The potential energy profile of the initial state of $\text{O}_2(\text{A } ^3\Delta_u, v) + \text{O}_2(\text{X } ^3\Sigma_g^-)$ can be derived as a sum of fixed zero-point energy of $\text{O}_2(\text{X } ^3\Sigma_g^-)$ and potential energy profile of the $\text{O}_2(\text{A } ^3\Delta_u)$ state. The intramolecular distance in the last molecule changes during the vibrational motion. The initial excitation energy is governed by the initial excitation wavelength of the encounter O_2-O_2 complex (Figure 2b). To build the potential energy profile for the $\text{O}_2(\{\text{a } ^1\Delta_g\}, \{\text{b } ^1\Sigma_g^+\}) + \text{O}_2(\{\text{a } ^1\Delta_g\}, \{\text{b } ^1\Sigma_g^+\})$ pair, we should take into account that the transition between

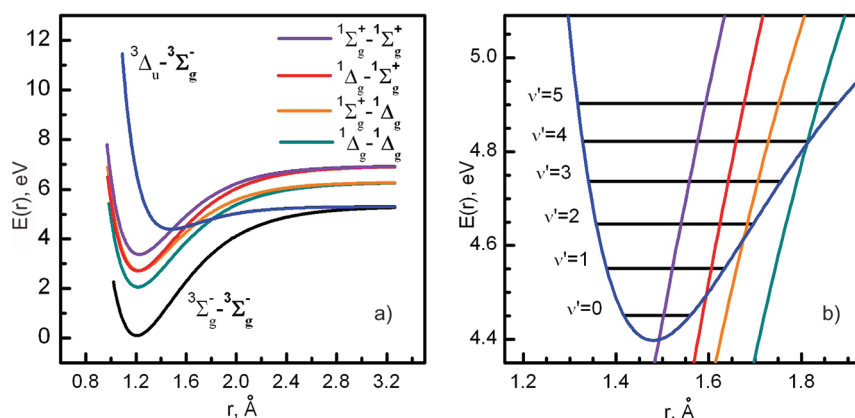
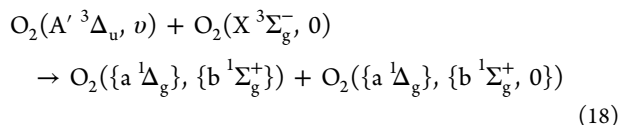


Figure 3. (a) Dependence of the potential energy profiles for the excited states of the colliding $\text{O}_2\text{--O}_2$ pair on the internuclear distance of one of the oxygen molecules, which is indicated first in the pair. The states in bold (second in the pair) represent molecules with fixed internuclear distance (see text). (b) Expanded region of the curves crossing with the vibrational levels of oxygen molecule in Herzberg III state $\text{O}_2(\text{A}'^3\Delta_u, v)$. To calculate the Morse curves and energy of vibrational levels of oxygen molecule, the data from NIST³⁴ have been used. Zero energy corresponds to the potential minima for both O_2 molecules of the encounter complex in the ground $\text{X}^3\Sigma_g^-$ state.

diabatic states corresponding to the process 17 must proceed without the change of geometry. In the initial state $\text{O}_2(\text{X}^3\Sigma_g^-)$ molecule has fixed geometry. This means that one O_2 molecule becomes the singlet one in the process 17 at the geometry of the ground $\text{O}_2(\text{X}^3\Sigma_g^-)$ state. At this geometry the O_2 molecule will appear in the ground vibrational state of the a or b singlet state with near unit probability. We conclude this on the basis of values of the Franck–Condon factors being of about 0.99 for the transition $\text{O}_2(\text{a}^1\Delta_g, 0) \leftarrow \text{O}_2(\text{X}^3\Sigma_g^-, 0)$ and of about 0.98 for the transition $\text{O}_2(\text{b}^1\Sigma_g^+, 0) \leftarrow \text{O}_2(\text{X}^3\Sigma_g^-, 0)$ calculated by Nicholls.³³ Thus at least one singlet oxygen molecule generated in process 17 will be in the ground vibrational state $\text{O}_2(\text{a}^1\Delta_g, 0)$ or $\text{O}_2(\text{b}^1\Sigma_g^+, 0)$:

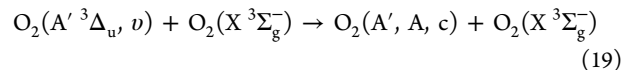


So we can consider the O–O distance in $\text{O}_2(\text{a}^1\Delta_g, 0)$ or $\text{O}_2(\text{b}^1\Sigma_g^+, 0)$ to be fixed and calculate the potential energy of the diabatic state corresponding to the right-side pair $\text{O}_2(\{\text{a}^1\Delta_g\}, \{\text{b}^1\Sigma_g^+\})\text{--O}_2(\text{a}^1\Delta_g, 0)$ or $\text{O}_2(\{\text{a}^1\Delta_g\}, \{\text{b}^1\Sigma_g^+\})\text{--O}_2(\text{b}^1\Sigma_g^+, 0)$ as a sum of the fixed energy of $\text{O}_2(\text{a}^1\Delta_g, 0)$ or $\text{O}_2(\text{b}^1\Sigma_g^+, 0)$ state with the potential energy profile of $\text{O}_2(\text{a}^1\Delta_g)$ or $\text{O}_2(\text{b}^1\Sigma_g^+)$ state.

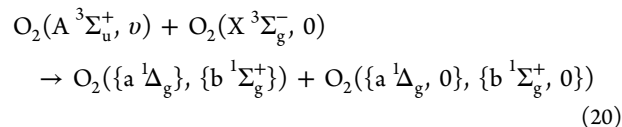
So the obtained curves of overall potential energy of the pair states $(\text{A}'^3\Delta_u, \text{X}^3\Sigma_g^-)$, $(\text{a}^1\Delta_g, \text{a}^1\Delta_g)$, $(\text{a}^1\Delta_g, \text{b}^1\Sigma_g^+)$, $(\text{b}^1\Sigma_g^+, \text{a}^1\Delta_g)$, and $(\text{b}^1\Sigma_g^+, \text{b}^1\Sigma_g^+)$ are shown in Figure 3 where internuclear distance in first molecule in the pair is variable and in the second one it is fixed. As follows from Figure 3, the curve corresponding to the excited oxygen pair $(\text{A}'^3\Delta_u, \text{X}^3\Sigma_g^-)$ intersects all curves corresponding to the pairs of oxygen singlet states $(\text{a}^1\Delta_g, \text{a}^1\Delta_g)$, $(\text{b}^1\Sigma_g^+, \text{a}^1\Delta_g)$, $(\text{a}^1\Delta_g, \text{b}^1\Sigma_g^+)$, and $(\text{b}^1\Sigma_g^+, \text{b}^1\Sigma_g^+)$ in ascending order of the intersection energy. Within the intersection region the conversion of oxygen molecule from the curve of the Herzberg III state to the vibrationally excited one of the singlet states can occur. Thus all four possible channels of process 18 can proceed when the vibronic states $\text{O}_2(\text{A}'^3\Delta_u, v \geq 4)$ are excited. For the excitation with lower v values the accessible channels involve formation of at least one oxygen molecule in the $(\text{b}^1\Sigma_g^+)$ singlet state. Considering that we have observed the formation of singlet oxygen via excitation

of $\text{O}_2(\text{A}'^3\Delta_u, v)$ vibronic states with $11 \geq v \geq 1$, we can conclude that the channels with formation of $\text{O}_2(\text{b}^1\Sigma_g^+)$ contribute to the photogeneration of singlet oxygen in our experiments. As we have discussed above, the collisional relaxation $\text{O}_2(\text{b}^1\Sigma_g^+) \rightarrow \text{O}_2(\text{a}^1\Delta_g)$ is fast enough to make the processes of formation of $\text{O}_2(\text{b}^1\Sigma_g^+)$ and $\text{O}_2(\text{a}^1\Delta_g)$ states indistinguishable from the point of their contribution to the observed $\text{O}_2(\text{a}^1\Delta_g)$ luminescence.

Here it is also necessary to note that three near energetic Herzberg states I ($\text{A}^3\Sigma_u^+$), II ($\text{c}^1\Sigma_u^-$), and III ($\text{A}'^3\Delta_u$) equilibrate fast^{35,36} in a process:



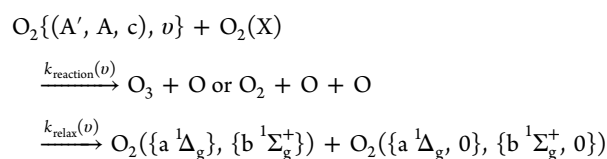
The other triplet state $\text{O}_2(\text{A}^3\Sigma_u^+, v)$ may further give singlet oxygen in the process similar to 18, providing quantum yield equal to 2 for singlet oxygen



This $\text{O}_2(\text{A}^3\Sigma_u^+)$ state lies a little bit higher in minimum energy than $\text{O}_2(\text{A}'^3\Delta_u)$ by only 0.09 eV. So the crossings analogous to those shown in Figure 3 but with the curve of the excited oxygen pair $(\text{A}^3\Sigma_u^+, \text{X}^3\Sigma_g^-)$ instead of $(\text{A}'^3\Delta_u, \text{X}^3\Sigma_g^-)$ look very similar. This means that the process 20 as well as process 18 should result in the formation of the vibrationally unexcited $\text{O}_2(\text{a}^1\Delta_g, 0)$ and $\text{O}_2(\text{b}^1\Sigma_g^+, 0)$ simultaneously with highly vibrationally excited singlet oxygen in the a and b states. The relaxation processes of oxygen in Herzberg I state $\text{O}_2(\text{A}^3\Sigma_u^+, v)$ with formation of singlet oxygen in the a and b states have been studied by many authors at low pressure in relevance to the processes proceeding in the upper atmosphere and the results are considered in the review by Slinger and Copeland³⁶ and later in the paper by Pejaković et al.³⁷ It is shown that the relaxation of $\text{O}_2(\text{A}^3\Sigma_u^+, v)$ on $\text{O}_2(\text{X}^3\Sigma_g^-, 0)$ proceeds with the rate constant $k \approx 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and is followed by the prompt formation of vibrationally unexcited singlet oxygen $\text{O}_2(\text{a}^1\Delta_g, 0)$ and $\text{O}_2(\text{b}^1\Sigma_g^+, 0)$ as well as of highly vibrationally excited singlet oxygen in the a and b states.³⁶ These results are in very good agreement with the expectations based on the

suggested mechanism of relaxation 20 with its energy diagram similar to that one shown in Figure 3. In spite of the energetic closeness of the ($c\ ^1\Sigma_u^-$) state to states ($A\ ^3\Sigma_u^+$) and ($A'\ ^3\Delta_u$), the relaxation process of $O_2(c\ ^1\Sigma_u^-, \nu)$ similar to 18 and 20 is not expected to contribute because it is spin-forbidden. The experimental attempts to detect formation of highly vibrationally excited $O_2(b\ ^1\Sigma_g^+)$ in the relaxation of $O_2(c\ ^1\Sigma_u^-, \nu)$ did not reveal this process in contrast with the relaxation of $O_2(A\ ^3\Sigma_u^+, \nu)$.³⁶ But formation of singlet oxygen $O_2(a\ ^1\Delta_g)$ may be expected to result from cascade relaxation of $O_2(c\ ^1\Sigma_u^-, \nu)$, giving rise only to one singlet oxygen molecule providing some reduction of the effective quantum yield of $O_2(a\ ^1\Delta_g)$ in our experiments as compared with the maximum value of 2.

Spectral Dependence of Singlet Oxygen Quantum Yield. The spectral dependence of singlet oxygen quantum yield shown in Figure 2a presents the profile with a not well-pronounced maximum at $38\ 000\ \text{cm}^{-1}$ (263 nm, $\nu = 5$). In the high-energy (blue) part of spectrum the well-defined rise of the quantum yield is observed when the excitation wavenumber drops to about $40\ 000$ – $39\ 500\ \text{cm}^{-1}$ (250–253 nm) corresponding to excitation into the vibronic state $O_2(A\ ^3\Sigma_u^+, \nu = 8)$. In the low-energy part (red) with wavelength longer than 263 nm the reduction of quantum yield is observed. We explain the rise of $O_2(a\ ^1\Delta_g)$ quantum yield in the blue part of the spectrum as a result of competition of above discussed relaxation of $O_2(A', A, c)$ with its reaction $O_2(A', A, c) + O_2(X) \rightarrow O_3 + O$ or $O_2(A', A, c) + O_2(X) \rightarrow O_2 + O + O$ discussed in the Introduction. Both these reactions finally give rise to ozone. Spectral dependence of the quantum yield of ozone formation resulting from the photoexcitation of encounter complexes O_2-O_2 measured by Sugimoto et al.²¹ demonstrates the drop of ozone quantum yield from the values close to 2 at the O_2 photodissociation threshold down to zero at 255 nm ($39\ 200\ \text{cm}^{-1}$), as shown in Figure 2a as well. This behavior is just the opposite of the rise in $O_2(a\ ^1\Delta_g)$ quantum yield we observe in this spectral region. So we interpret the variation of the quantum yields of singlet oxygen and ozone resulted from the photoexcitation of the encounter complex O_2-O_2 to be due to competition between the processes



The variation of k_{relax} resulted from the change of vibrational excitation is known for $O_2(A\ ^3\Sigma_u^+, \nu)$.³⁶ According to these data, the magnitude of k_{relax} goes down with the decrease of ν . The quantum yield of ozone according to this scheme should depend on the ratio $r = k_{\text{relax}}/k_{\text{reaction}}$ of these rate constants via the expression

$$\begin{aligned} \varphi_{O_3}(\nu) &= 2 \times \frac{k_{\text{reaction}}(\nu)}{k_{\text{relax}}(\nu) + k_{\text{reaction}}(\nu)} \\ &= 2 \times \frac{1}{\frac{k_{\text{relax}}(\nu)}{k_{\text{reaction}}(\nu)} + 1} \\ &= 2 \times \frac{1}{r(\nu) + 1} \end{aligned}$$

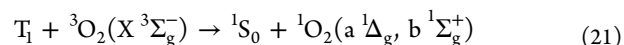
The experimentally observed drop in ozone quantum yield from about 2 to 0 within the exciting radiation wavelength

change from 242.3 to 255 nm ($\Delta h\nu \approx 2100\ \text{cm}^{-1} \approx 6\ \text{kcal/mol}$) indicates the rise of ratio r with a decrease of excitation quantum energy. Taking into account the drop³⁶ in k_{relax} with a decrease of ν , we can deduce an even faster (“drastic”) drop in the value of k_{reaction} within this small energy gap.

Decreasing the $O_2(a\ ^1\Delta_g)$ quantum yield within the long-wavelength region $\lambda > 263\ \text{nm}$ indicates existence of other quenching channels without formation of singlet oxygen on the way. We assume that relaxation without change of spin of the colliding oxygen molecules $O_2(A', A, \nu < 5) + O_2(X\ ^3\Sigma_g^-) \rightarrow 2O_2(X\ ^3\Sigma_g^-)$ contributes essentially to provide the reduction of $O_2(a\ ^1\Delta_g)$ quantum yield in the red wing of spectral dependence in Figure 2a. Examples of relaxation of triplet states of molecules by ground state oxygen without its conversion to the singlet states are known and described in the review by Minaev.³⁸

The small yield of $O_2(a\ ^1\Delta_g)$ $\phi_{O_2-O_2} \approx 0.2$ has been observed for excitation at 238 nm, which is above the threshold of O_2 photodissociation. In this region nearby the threshold it is difficult to attribute this number to any particular process. The matter is that in the encounter complex O_2-O_2 the internal degrees of freedom corresponding to the relative motion of O_2 molecules can also get the part of the excitation energy. So when the quantum energy is only slightly above the threshold the excitation still can provide O_2 molecules with internal excitation below threshold. But we can not identify this part quantitatively.

General Case of X– O_2 Encounter Complexes with Arbitrary X Partner. The processes 18 and 20 are similar to the well-known spin-allowed process of triplet sensitization³⁹

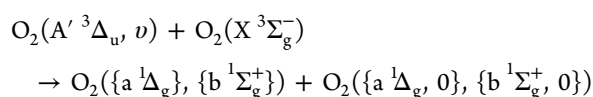


In processes 18 and 20 the triplet oxygen molecules $O_2(A'\ ^3\Delta_u)$ and $O_2(A\ ^3\Sigma_u^+)$ play the same role as a triplet T_1 in process 21. As discussed in the Introduction, the enhancement of the oxygen UV absorption was observed in the encounter complexes of oxygen O_2 with various molecules X , and this effect is attributed to the enhancement of transition into the Herzberg III state ($A'\ ^3\Delta_u$). Hence we assume processes 18 and 20 give rise to singlet oxygen in $O_2(a\ ^1\Delta_g)$ and $O_2(b\ ^1\Sigma_g^+)$ states to follow the excitation of any encounter complexes $X-O_2$ in the media (gas or condensed) containing oxygen. We assume the singlet oxygen generated in the discussed processes started by the excitation of the encounter complexes O_2-O_2 and CO_2-O_2 to be the active agent in the laser-induced oxidation of hydrocarbons in the hydrocarbon/ O_2 /supercritical CO_2 mixtures at 248 nm described in the review.²² We also assume that the singlet oxygen arising in the photoexcitation of the encounter complexes O_2-O_2 and $X-O_2$ provides contribution to the photooxidation of hydrocarbons in cryogenic oxygen matrixes when initiated by UV radiation with quantum energy below threshold of O_2 photodissociation.⁴⁰

CONCLUSIONS

The quantum yield of singlet oxygen arising from UV photoexcitation of O_2-O_2 encounter complexes ($\phi_{O_2-O_2}$) has been measured within the spectral interval 238–285 nm, which corresponds to excitation within the Wulf bands, providing transition of molecular oxygen into the Herzberg III state $O_2(A\ ^3\Delta_u, \nu)$ with vibrational excitation varied in the interval $\nu = 1$ –11. The spectral dependence of singlet oxygen quantum yield

$\phi_{\text{O}_2-\text{O}_2}$ presents the profile with maximum $\phi_{\text{O}_2-\text{O}_2}$ close to 2 at about $38\,000\text{ cm}^{-1}$ (263 nm , $\nu = 5$). In the high-energy (blue) part of spectrum at $238\text{--}253\text{ nm}$ the well-defined rise of the quantum yield is observed. In the low-energy part (red) after 263 nm the reduction of the quantum yield is observed. The closeness of the quantum yield maximum value to 2 allows us to conclude that the bimolecular relaxation of excited oxygen in the Herzberg excited state on the ground O_2 molecule provides formation of two singlet O_2 molecules. This relaxation has been considered as the transition from the potential energy surface (PES) of the colliding pair of the triplet excited and ground state oxygen molecules $\text{O}_2(\text{A}^3\Delta_u, \nu) - \text{O}_2(\text{X}^3\Sigma_g^-)$ onto PES of the pair of O_2 molecules in the first and second singlet states $\text{O}_2(\text{a}^1\Delta_g)$ and $\text{O}_2(\text{b}^1\Sigma_g^+)$. The analysis of the positions of the avoiding crossings accessible at ν levels allowed us to conclude that the relaxation giving rise to singlet oxygen proceeds as a process



A similar process is predicted for relaxation of the other triplet Herzberg state $\text{O}_2(\text{A}^3\Sigma_u^+, \nu)$, which is supposed to be collisionally coupled with the $\text{O}_2(\text{A}^3\Delta_u, \nu)$. The predicted simultaneous formation of both vibrationally unexcited and highly excited singlet O_2 in the process of relaxation is in agreement with experimental data known from the literature for relaxation of $\text{O}_2(\text{A}^3\Sigma_u^+, \nu)$ on $\text{O}_2(\text{X}^3\Sigma_g^-)$.

The observed rise of $\text{O}_2(\text{a}^1\Delta_g)$ quantum yield in the blue part of the Wulf bands spectrum ($238\text{--}253\text{ nm}$) is explained to be the result of competition between the relaxation of oxygen in Herzberg states $\text{O}_2(\text{A}^3\Delta_u, \nu)$ and the reaction $\text{O}_2\{\text{A}^3\Delta_u, \nu\} + \text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{O}_3 + \text{O}$ or $\text{O} + \text{O} + \text{O}_2$ giving rise to ozone, which was earlier assumed in literature.

The quantum yield of $\text{O}_2(\text{a}^1\Delta_g)$ arising in the photoexcitation of encounter complexes N_2-O_2 at 266 nm has been also measured and found to be the same as that for O_2-O_2 complexes.

We assume that the processes giving rise to singlet oxygen in $\text{O}_2(\text{a}^1\Delta_g)$ and $\text{O}_2(\text{b}^1\Sigma_g^+)$ states to follow the UV excitation within the Wulf bands of any encounter complexes $\text{X}-\text{O}_2$ in the media (gas or condensed) containing oxygen and to contribute to the processes of the photooxidation in these conditions.

■ ASSOCIATED CONTENT

Supporting Information

Figure S1 with laser pulse energy dependence of singlet oxygen luminescence. Table S2 with listed spectral dependence of singlet oxygen quantum yield. This information is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The financial support of this work by Russian Foundation for Basic Research (09-03-00310-a) is gratefully acknowledged. APT thanks also "OPTEC" company for the financial support.

■ REFERENCES

- (1) Trushina, A. P.; Goldort, V. G.; Kochubei, S. A.; Baklanov, A. V. *Chem. Phys. Lett.* **2010**, *485*, 11.
- (2) Parker, D. H. *Acc. Chem. Res.* **2000**, *33*, 563.
- (3) Wulf, O. R. *Proc. Natl. Acad. Sci. U. S. A.* **1928**, *14*, 609.
- (4) Finkelburg, W. Z. *Phys.* **1934**, *90*, 1.
- (5) Herzberg, G. *Can. J. Phys.* **1953**, *31*, 657.
- (6) Coquart, B.; Ramsay, D. A. *Can. J. Phys.* **1986**, *64*, 726.
- (7) Minaev, B. F.; Mikkelsen, K. V.; Agren, H. *Chem. Phys.* **1997**, *220*, 79.
- (8) Bernath, P.; Carleer, M.; Fally, S.; Jenouvrier, A.; Vandaele, A. C.; Hermans, C.; Merienne, M. F.; Colin, R. *Chem. Phys. Lett.* **1998**, *297*, 293.
- (9) Fally, S.; Vandaele, A. C.; Carleer, M.; Hermans, C.; Jenouvrier, A.; Merienne, M.-F.; Coquart, B.; Colin, R. *J. Mol. Spectrosc.* **2000**, *204*, 10.
- (10) Blake, A. J.; McCoy, D. G. *J. Quant. Spectrosc. Radiat. Transfer* **1987**, *38*, 113.
- (11) (a) Zelikina, G. Y.; Bertsev, V. V.; Kiseleva, M. B. *Opt. Spectrosc.* **1994**, *77*, S79. (b) Zelikina, G. Y.; Bertsev, V. V.; Kiseleva, M. B. *Opt. Spectrosc.* **1996**, *81*, 68. (c) Zelikina, G. Y.; Kiseleva, M. B.; Burtsev, A. P.; Bertsev, V. V. *Opt. Spectrosc.* **1998**, *85*, S20.
- (12) Oshima, Y.; Okamoto, Y.; Koda, S. *J. Phys. Chem.* **1995**, *99*, 11830.
- (13) DeBoer, G.; Young, M. A. *J. Chem. Phys.* **1997**, *106*, 5468.
- (14) DeBoer, G.; Prince, A. P.; Young, M. A. *J. Chem. Phys.* **2001**, *115*, 3112.
- (15) Giardini Guidoni, A.; Paladini, A.; Veneziani, M.; Naaman, R.; Di Palma, T. M. *Appl. Surf. Sci.* **2000**, *154*–*155*, 186.
- (16) Parsons, B. F.; Chandler, D. W. *J. Phys. Chem. A* **2003**, *107*, 10544.
- (17) Baklanov, A. V.; Bogdanchikov, G. A.; Vidma, K. V.; Chestakov, D. A.; Parker, D. H. *J. Chem. Phys.* **2007**, *126*, 124316.
- (18) Slinger, T. G.; Jusinski, L. E.; Black, G.; Gadd, G. E. *Science* **1988**, *241*, 945.
- (19) Shi, J.; Barker, J. R. *J. Geophys. Res.* **1992**, *97*, 13039.
- (20) Andruhiv, V. I.; Bertsev, V. V.; Bulanin, M. O.; Pastor, A. A.; Serdobintsev, P. Y. *Opt. Spectrosc.* **1994**, *76*, 165.
- (21) Sugimoto, K.; Otomo, J.; Koda, S. *J. Phys. Chem. A* **2003**, *107*, 1010.
- (22) Koda, S.; Sugimoto, K. *J. Photochem. Photobiol. C* **2003**, *4*, 215.
- (23) Furui, E.; Akai, N.; Ida, A.; Kawai, A.; Shibuya, K. *Chem. Phys. Lett.* **2009**, *471*, 45.
- (24) Okabe, H. *Photochemistry of Small Molecules*; Wiley-Interscience: New York, 1978.
- (25) Takahashi, K.; Hayashi, S.; Matsumi, Y.; Taniguchi, N.; Hayashida, S. *J. Geophys. Res.* **2002**, *107*, 4440.
- (26) Taniguchi, N.; Takahashi, K.; Matsumi, Y. *J. Phys. Chem. A* **2000**, *104*, 8936.
- (27) Schinke, R.; McBane, G. C. *J. Chem. Phys.* **2010**, *132*, 044305.
- (28) Green, J. G.; Shi, J.; Barker, J. R. *J. Phys. Chem. A* **2000**, *104*, 6218.
- (29) Knickelbein, M. B.; Marsh, K. L.; Ulrich, O. E.; Busch, G. E. *J. Chem. Phys.* **1987**, *87*, 2392.
- (30) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1329.
- (31) Badger, R. M.; Wright, A. C.; Whitlock, R. F. *J. Chem. Phys.* **1965**, *43*, 4345.
- (32) Wayne, R. P. In *Singlet O₂*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985.
- (33) Nicholls, R. W. *J. Res. Natl. Bur. Stand., Sect. A* **1965**, *69A*, 369.
- (34) NIST Chemistry WebBook. NIST Standard Reference Database Number 69; <http://webbook.nist.gov/chemistry/>.
- (35) Wildt, J.; Bednarek, G.; Fink, E. H.; Wayne, R. P. *Chem. Phys.* **1991**, *156*, 497.
- (36) Slinger, T. G.; Copeland, R. A. *Chem. Rev.* **2003**, *103*, 4731.
- (37) Pejaković, D. A.; Copeland, R. A.; Cosby, P. T.; Slinger, T. G. *J. Geophys. Res.* **2007**, *112*, A10307.

- (38) Minaev, B. F. *Russ. Chem. Rev.* **2007**, 76, 1059.
- (39) (a) Khan, A. U. In *Singlet O₂*; Frimer, A. A., Ed., CRC Press: Boca Raton, FL, 1985. (b) Schmidt, R. *Photochem. Photobiol.* **2006**, 82, 1161. (c) Krasnovsky, A. A., Jr. *J. Photochem. Photobiol. A: Chem.* **2008**, 196, 210.
- (40) Onodera, K.; Furusawa, G.; Kojima, M.; Tsuchiya, M.; Aihara, S.; Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron* **1985**, 41, 2215 and references therein.