Dynamics of Singlet Oxygen Molecule Trapped in Silica Glass, Studied by Luminescence Polarization Anisotropy and Density Functional Theory

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Abstract

The lowest excited electronic state of the O$_2$ molecule, $a^1g$, the "singlet oxygen", is of utmost importance for photochemistry and photobiology. For O$_2$ trapped in silica glass, the lifetime of this state and the associated $a^1g \rightarrow X^3\Sigma_g^-$ photoluminescence (PL) is the longest known for O$_2$ in any condensed medium at room temperature. We studied the temperature dependence, decay kinetics and polarization anisotropy of this PL with 1064 nm excitation to the $a^1g$ ($v=1$) state, as well as with excitation to higher energies. PL at this excitation shows non-zero polarization anisotropy at 295 K, which increases with cooling to 14 K. At variance, excitation to higher energies yields depolarized PL. Polarization data indicate weak electric dipole character of the emission of the spin- and parity-forbidden $a^1g \rightarrow X^3\Sigma_g^-$ transition, enabled by O$_2$ – SiO$_2$ cage interactions. Density functional theory calculations indicate that at low temperatures the rotation of O$_2$ is partially or fully frozen even in large silica voids. As the temperature increases, PL is increasingly depolarized by libration movement of O$_2$ molecules. Analysis of O$_2$ optical absorption in optical fibers allows one to obtain the absorption cross sections of $X\rightarrow a$ and $X\rightarrow b$ transitions of O$_2$ in SiO$_2$ glass and to evaluate both radiative and non-radiative rates of $a\rightarrow X$ luminescence.
Introduction

The two lowest electronic excited states of free or matrix-isolated oxygen molecule O$_2$ are the metastable singlets ($a^1\text{g}$ and $b^1\Sigma^+_g$), located at 0.97 eV and 1.62 eV above the triplet ground state ($X^3\Sigma^+_g$), respectively (Fig. 1). O$_2$ molecules in the lowest excited $a^1\text{g}$ state are often referred as "singlet oxygen" or "$1\text{O}_2"$. They are of immense importance in photobiology $^1$, photodynamic cancer therapy $^1$–$^3$, and photocatalysis $^4$. Many reviews spanning decades of research are available, e.g. refs. $^5$–$^7$. The presence of $1\text{O}_2$ is commonly monitored by the $\sim$1270 nm luminescence band caused by the $a(v=0)\rightarrow X(v=0)$ transition (Fig. 1, $v$ denotes the vibrational quantum number). In free O$_2$ this transition is forbidden by spin and symmetry selection rules. The luminescence is observable only because these selection rules are relaxed by perturbations from the surroundings. The theoretical models of the enhancement of radiative and non-radiative

![Fig.1. Optical absorption and luminescence transitions observed $^8$–$^{10}$ in interstitial O$_2$ molecule embedded in glassy SiO$_2$. The transitions studied in this work are indicated by bold arrows. The transition wavelengths are in nm. Zero-field splittings ($\approx 4$ cm$^{-1}$) $^{11}$ of both the triplet ground state $X(v=0)$ and its first vibrational ($v=1$) sublevel are shown.](image-url)
transitions were recently reviewed\textsuperscript{11,12}. Despite the external perturbations, the absorption transitions (Fig.1) remain extremely weak, therefore in most cases the luminescence is excited indirectly, via energy-transfer from an activator. More recently, a direct photoexcitation via $X \rightarrow a$ and $X \rightarrow b$ transitions has been employed\textsuperscript{13} and the absorption cross sections of these two transitions in different solvents have been evaluated\textsuperscript{14,15}. The option of enhancing $X \rightarrow b$ transition by surface plasmon resonance was recently explored\textsuperscript{16}.

Apart from the fields of photobiology and photocatalysis, singlet and triplet O\textsubscript{2} plays an important role in the physics of glassy SiO\textsubscript{2} (g-SiO\textsubscript{2}, silica glass), the basic material for fiber optical waveguides and ultraviolet (UV) optical components. Interstitial O\textsubscript{2} molecules strongly affect their optical properties and radiation toughness\textsuperscript{17}. They are introduced in g-SiO\textsubscript{2} by manufacturing\textsuperscript{18}, high-T diffusion\textsuperscript{19}, dimerization of O atoms, displaced from SiO\textsubscript{2} network by nuclear irradiation\textsuperscript{8} or by fs laser pulses\textsuperscript{20}, or by electric field applied at high temperatures\textsuperscript{21}. While the interstitial O\textsubscript{2} is detrimental to UV applications of g-SiO\textsubscript{2}\textsuperscript{17,22}, it is found to increase the radiation toughness of optical fibers in the near-infrared range\textsuperscript{23}. Luminescence of singlet O\textsubscript{2} provides means for high-sensitivity monitoring of O\textsubscript{2} concentration in g-SiO\textsubscript{2}\textsuperscript{24,25} and has been used to study O\textsubscript{2} diffusion, isotope exchange with the glass network, or defect creation in bulk g-SiO\textsubscript{2}\textsuperscript{10} and SiO\textsubscript{2} nanoparticles\textsuperscript{9}.

Comparison of the basic properties of interstitial O\textsubscript{2} in g-SiO\textsubscript{2} with the large base of data on $^1$O\textsubscript{2} in solvents and solid matrices reveals an outstanding feature: the lifetime of the $a^1g$ state of O\textsubscript{2} in g-SiO\textsubscript{2} $\tau \approx 0.82$ s,\textsuperscript{26} is the longest observed for O\textsubscript{2} in any condensed medium at room temperature. $^1$O\textsubscript{2} lifetimes in liquids are typically in the microsecond range with an exception of only few halogenated solvents, where they are up to few hundreds of milliseconds: (e.g., $\tau = 128$ ms for CCl\textsubscript{4}, 309 ms for perfluorodecalene C\textsubscript{10}F\textsubscript{18}\textsuperscript{27}). Lifetimes of $^1$O\textsubscript{2} in different liquids are compiled in ref.
and in the supplement of ref.\textsuperscript{11}. \textsuperscript{1}O\textsubscript{2} lifetimes in organic polymer matrices are typically in the range of 5 μs – 100 μs (ref.\textsuperscript{7}, p.34); they are significantly higher in fluorocarbon polymers, e.g., 320 μs in nafion matrix.\textsuperscript{28} In nanoporous aluminosilica and zeolite nanoparticles the \textsuperscript{1}O\textsubscript{2} lifetimes are generally into the same range (3 μs to 64 μs)\textsuperscript{29}. The shortening of \textsuperscript{1}O\textsubscript{2} lifetimes in these solids or liquids is due to a much stronger non-radiative quenching, compared to the case of \textsuperscript{1}O\textsubscript{2} in g-SiO\textsubscript{2}.

The most common non-radiative quenching mechanism of \textsuperscript{1}O\textsubscript{2} is electronic-to-vibrational (e-v) energy transfer to vibrationally-excited electronic ground state of O\textsubscript{2}. The energy difference between the 0-th vibrational level of the excited state (\textsuperscript{1}g, v=0) and vibrationally excited ground state (\textsuperscript{3}Σ\textsubscript{g}−, v=m, m>0) is absorbed by vibrations of some "deactivator species" Y. The energy balance is given by:\textsuperscript{5,27}

\begin{equation}
\text{O}_2 (^{1}\text{g}, v=0) + Y(v'=0) \rightarrow \text{O}_2 (^{3}\Sigma\textsubscript{g}^−, v'=m) + Y(v'=n) + E_{mn}
\end{equation}

where m and n are vibrational quantum numbers of m-th and n-th vibrational excited states of O\textsubscript{2} and Y, and E\textsubscript{mn} is the "off-resonance" difference energy, not absorbed by these vibrational modes. It is provided or absorbed by some low-energy excitations of the surroundings.

A long lifetime of \textsuperscript{1}O\textsubscript{2} is highly desired in photodynamic therapy applications where a photosensitizer is encapsulated in a nanoparticle, protected from reactants by a silica shell, and photogenerated \textsuperscript{1}O\textsubscript{2} must traverse the shell to its target before it is quenched. The lifetime of \textsuperscript{1}O\textsubscript{2}, strongly confined in the interstitial voids in g-SiO\textsubscript{2} glass network, is ~10\textsuperscript{4} times longer than \(\tau=64\ \mu\text{s}\), measured for porous SiO\textsubscript{2}.\textsuperscript{29} The largest source of this difference is evidently the presence of \textendash\Si–O–H groups on the internal surfaces of porous SiO\textsubscript{2}. They are known as very efficient quenchers of \textsuperscript{1}g state with \(m=0, n=2\) in eq.1.

The second cause of the more rapid quenching of \textsuperscript{1}O\textsubscript{2} in porous SiO\textsubscript{2} could be the additional rotational and translational degrees of freedom, available for O\textsubscript{2} in the porous SiO\textsubscript{2} as compared to
O2, tightly confined in g-SiO2 voids, which have an estimated average diameter of ≈5 Å. These degrees of freedom could provide the E_{mn} in eq.1 and thus enhance luminescence quenching.

Another point of interest in interstitial O2 is its ground-state magnetic momentum, which can be optically modulated by excitation to the \( ^1g \) state. O2 has been used as a test magnetic molecule for diamond NV-center based nanoscale magnetometry. For this type of experiments, the dynamic properties of O2 in SiO2 are of interest.

The main aim of the present study is a better understanding of the conditions which provide the outstandingly long lifetime of \(^1\)O2 in silica. We studied the thermal quenching of \(^1\)O2 and luminescence polarization anisotropy. The latter, as well as its temperature behavior, gives information as to whether interstitial O2 can rotate in the voids of g-SiO2. We find that the rotational motion of O2 in silica voids is largely hindered, thus explaining polarization anisotropy and also the long luminescence lifetimes.

**Methods**

**Samples**

Typical g-SiO2 does not contain interstitial O2 in measurable concentration (>10^{14} cm^{-3}). Two special samples, obtained by oxidation of SiCl4 in oxygen-excess conditions were used. They had similar, albeit not entirely equal concentrations (in units of 10^{16} cm^{-3}) of bound hydroxyl =SiOH groups (6 and 5.3), interstitial Cl2 molecules (51 and 79) and interstitial O2 (29 and 43), respectively. The O2 concentrations were determined with ±20% accuracy by the intensities of singlet O2 PL intensities relative to Raman bands, pre-calibrated by comparison to O2 thermal desorption data. Sample dimensions were 5×10×12 mm^3, all 6 faces were optically polished.
Instrumentation and measurement methods

For a direct excitation of $^1$O$_2$ luminescence, CW mode lasers, modulated by electro-mechanich shutter were used: (1) 1064 nm diode-pumped Nd-YAG laser (LSR1064H, max. power 3 W) with Edmund Optics (EO) laser line cleanup filter 68-859, (2) 766 nm diode-laser (Leading Tech ADR1805, spectrum full width at half maximum, FWHM=2 nm, max. 600 mW) with 950 nm shortpass filter EO 64-328. The wavelengths of the laser light, 1064 nm and 766 nm roughly correspond to $X\rightarrow a$ ($v=1$) and $X\rightarrow b$ ($v=0$) transitions (Fig. 1). The laser light was focused on the sample by $F=210$ mm lens.

$^1$O$_2$ PL spectra were recorded using AMKO LTI 200 mm monochromator with 600 l/mm grating blazed at 1200 nm and Hamamatsu R5509-43 liquid N$_2$-cooled photomultiplier tube (PMT). Spectral resolution was 8 to 16 nm. Time-resolved PL spectra or kinetics were obtained in photon counting or analog (photocurrent) modes.

PL polarization anisotropy was obtained in the usual "L" geometry $^{32}$, featuring horizontal and mutually perpendicular excitation and emission beams. The excitation beam was polarized with E-vector in either vertical (V) or horizontal (H) directions. The $^1$O$_2$ PL beam was observed at right angle with polarization filter turned in (v) or (h) directions. The ratio $I_{Vh}/I_{Vv}$ * between the intensities of horizontally ($I_{Vh}$) and vertically ($I_{Vv}$) polarized emission, observed using vertically polarized excitation beam, was measured. To obtain the correction for the polarization-dependent instrument

*The 1st index (capital H or V) denotes the excitation polarization direction, the 2nd one (lower case h or v) – the PL emission polarization direction.
response, the ratio $I_{Hh}/I_{Hv}$ was measured with horizontally polarized excitation light. The PL polarization anisotropy $r^*$ was then calculated\textsuperscript{32}:

$$r^* = \frac{1}{R - 1},$$

where $R = (I_{Vh}/I_{Vv}) (I_{Hv}/I_{Hh})$ is the true intensity ratio, obtained by dividing the measured ratio $I_{Vh}/I_{Vv}$ by the instrument response $I_{Hh}/I_{Hv}$.\textsuperscript{†}

For correct polarization anisotropy measurements of a weak PL emission under high-power excitation, it is of utmost importance to suppress detection of any excitation light scattered from the sample or optical elements, since it is strongly polarized and can distort the results. Therefore, for an accurate measurement of $r$, time-resolved mode was used as an alternative to spectral scans. After exciting the sample for 3 s, the laser beam was blocked by a mechanical shutter and the PL decay signal was collected for 5 s. It was averaged over many cycles by photon counter or analog waveform recorder. To minimize the instrumentation-induced polarization distortions ($I_{Hh}/I_{Hv}$), in

\textsuperscript{*} For historical reasons, polarization degree $P = (1-R)/(1+R)$ is often alternatively used. It is related to $r$ as $P = 3r/(r+2)$. Usage of $r$ is preferred, since it simplifies many polarization-related calculations\textsuperscript{32}.

\textsuperscript{†} Obtaining the "instrument function" as $I_{Hh}/I_{Hv}$ is accurate only for transitions, excited by the electric field component of the excitation beam. For $I_{Hv}$ and $I_{Hh}$ this component is directed along the observation axis and creates axially symmetric ensemble of excited PL centers, for which $I_{Hh}$ must be equal to $I_{Hv}$. Any deviations are due to instrumental effects. This is correct in vast majority of cases. It may be incorrect for magnetic dipole transitions, where $I_{Vv}/I_{Vh}$ should be used instead. We checked that $I_{Hh}/I_{Hv}$, measured with 766 nm excitation at 295 K is within 1.5\% of ratio $I_h/I_v$ measured using depolarized tungsten lamp instead of luminescent sample as a light source.
the case of time-resolved polarization measurements the emission monochromator was removed, and additional filters were used to block any light outside the $^1\text{O}_2$ PL emission region. The emitted light was collimated by BK7 glass aspheric lens, and then sequentially filtered by 4 filters: 1) interference 1100 nm long-pass edge filter (Edmund Optics EO 66-241); 2) interference bandpass filter (1250-1300nm, EO 87-865); 3) silicon wafer of thickness 0.5 mm; 4) wire-grid polarizer (Thorlabs WP25M-UB) to analyze the polarization of the emitted light. The light was then focused on PMT by BK7 glass lens. The polarization of the excitation light was rotated by a half-wave plate (1064 nm) or by rotating the laser case (766 nm).

For room-T to 14 K range measurements the sample was placed in vacuum in closed-cycle He refrigerator; measurements at higher $T$ were performed in air atmosphere. During the low-$T$ measurements, it was verified by changing the laser intensity that sample heating by laser does not significantly affect the results.

**Calculation methods**

To support the experimental findings, we have performed electronic structure calculations based on density functional theory (DFT). The principal task of calculations is to study rotational motion of interstitial O$_2$ in glassy silica. Calculations have been performed using the VASP code$^{33,34}$. We have employed the semi-local GGA (generalized gradient approximation) density functional of Perdew-Burke-Ernzerhof (PBE) to describe the electronic structure$^{35}$. We have used the projector-augmented-wave approach$^{36}$ with a plane-wave energy cutoff of 400 eV to describe electronic wavefunctions. The Brillouin zone was sampled at the $\Gamma$ point. In our calculations the O$_2$ molecule is charge-neutral with a spin $S=1$. Our principal interest is to determine the potential energy surface for the rotation of O$_2$ in silica, and we expect the potential energy surfaces for singlet and triplet oxygen to be rather similar, since they have the same nominal electron configuration and therefore similar electronic structure. This premise is supported by the negligible Stokes shift in the PL 9
spectra and by calculated close polarizabilities in both states. The polarizability in the excited singlet state is estimated as ~93% of that in the ground state of O$_2$ in organic solvents$^{37}$ and ~95% or 96%$^{38}$ for gaseous O$_2$.

It is well documented$^{39–41}$ that the behavior of O$_2$ in various forms of silicon dioxide (e.g., α-quartz, β-cristobalite, and various forms of amorphous SiO$_2$) can be very different. One of the main factors determining this difference is the volume of interstitial voids. These volumes are on average larger in amorphous SiO$_2$ than in crystalline SiO$_2$. Thus, it is important to use representative structures of α-SiO$_2$ in computational studies of O$_2$ in SiO$_2$. In this work we have employed the 144-atom model developed by Bongiorno and Pasquarello$^{39,40}$. The model has been obtained via molecular dynamics simulations by quenching the amorphous structure from the melt by first employing empirical force fields and then using density functional theory to relax the final structure. The model consists of a random network of corner-sharing tetrahedra, and reproduces the most important parameters of experimental amorphous SiO$_2$ structures, most crucially, the density $\rho=2.2 \text{ g/cm}^3$, as well as pair distribution functions between different atom types (Si-Si, O-O, and Si-O). More detailed information is provided in Refs.$^{39,40}$.

**Results**

**Temperature dependence of luminescence kinetics**

The decay kinetics of luminescence, excited at 766 nm, measured in the 15 K-503 K temperature range are shown in Fig. 2. The emission intensity was measured with monochromator set at the maximum of $^{1}$O$_2$ PL band (1272 nm) and spectral resolution 10 nm. Even at the highest measurement temperature (503 K) the emission was only partially quenched (Fig.3, inset). Measurements at higher Ts were hindered by an increasingly strong thermal radiation from sample surroundings swamping the PL signal. The decay kinetics is close to mono-exponential, in accord
with the previous observations. The decay constant $\tau$ was obtained by least-squares fits (Fig. 2) drawn over the dynamic range of $e^2$, corresponding to the decay of $\approx 85\%$ of all excited O$_2$ molecules. The temperature dependences of $\tau$ and of the luminescence intensity are shown in Fig. 3. The low-T limit value of $\tau$, 1115 ms, denoted as $\tau_0$ in Fig. 3, was slightly excitation wavelength-dependent. With the 1064 nm excitation $\tau_0 \approx 1230$ ms. A higher value, $\tau_0 = 1350$ ms was observed in some g-SiO$_2$ samples, where O$_2$ was excited by energy transfer from activator (to be published elsewhere).

Fig. 2. Decay kinetics of $^1$O$_2$ luminescence in dry silica glass in temperature range 15 K-503 K. Exponential fits to the initial parts of kinetics, corresponding to intensity decay $e^2$ times, are shown by solid lines.

The temperature dependence of PL intensity at low T's, while generally following the changes of $\tau$, was additionally affected by the decreasing widths of $X\rightarrow a$ $(v=1)$ and $X\rightarrow b$ excitation bands. This changes the efficiencies of excitation by 1064 nm and 766 nm lasers, whose wavelengths do not exactly match the respective excitation maxima. Therefore, only the more reliable high-T part of the temperature dependence of PL intensity is presented (Fig. 3, inset).
Fig. 3. Arrhenius plot according to eq.(3), showing activation energy of $\approx 1550 \text{ cm}^{-1}$ for the high-temperature non-radiative quenching of $\mathrm{O}_2$ PL. Inset shows the measured temperature dependence of the PL intensity and of the PL decay constant.

Fig. 4. $^1\mathrm{O}_2$ luminescence spectra of vertically (Vv) and horizontally (Vh) polarized components, excited by vertically (V) polarized 766 nm light at $T=16$ K. Inset shows Vv and Vh component intensities, measured in time-resolved mode after cut-off of the excitation light. No measurable polarization is detected.

**Luminescence polarization anisotropy**

When excited by the 766 nm laser, the polarization anisotropy $r$ (eq. 2) of $^1\mathrm{O}_2$ PL is zero within the measurement accuracy (\~0.6\%). $r$ does not increase at low temperature (\~15 K): the intensities
of the vertically (Vv) and horizontally (Vh) polarized components remain equal (Fig. 4), whether measured in the spectrally resolved or time-resolved (Fig. 4, inset) modes.

Fig. 5. Strongly polarized fundamental 440 cm\(^{-1}\) and 800 cm\(^{-1}\) Raman bands and \(^1\)O\(_2\) luminescence spectra of silica glass with embedded O\(_2\) molecules, measured with linearly polarized 1064 nm excitation for Vv, Vh, Hv and Hh polarization components.

Room-temperature excitation at 1064 nm (Fig. 5) gives rise to strongly polarized (Vv) g-SiO\(_2\) fundamental Raman bands and to a weaker \(^1\)O\(_2\) PL band with Vv polarized component having slightly higher intensity as compared to Vh, Hv and Hh-polarized spectra. However, the intensity difference between Vv and other 3 polarizations only marginally exceeded the measurement error. Therefore, the polarization anisotropy and its temperature dependence were further measured, using the more accurate time-resolved mode (Fig. 6). At each temperature, 4 identical sets of decay kinetics were measured, each set comprising measurements at 4 polarization configurations (Vv, Vh, Hv, and Hh), and the respective r values were calculated from them by eq. (2). The temperature dependence of their average \(r=r(T)\) and its dispersion are shown in Fig. 6. Insets to Fig. 6 show the intensities of PL decay at 4 polarization configurations at 295 K and 14.6 K. It is most evident in the 14.6 K measurement that the Vv-polarized component is more intense, while Vh, Hv and Hh components have smaller and mutually equal intensities.
Fig. 6. Temperature dependence of polarization anisotropy of $^1\text{O}_2$ luminescence measured by recording the luminescence decay intensities, integrated over 20 to 1840 ms interval after cutoff of the polarized 1064 nm excitation light. Insets show luminescence transients at $T=14.6$ and 295 K. Vh, Hv and Hh-polarized components have equal intensities, lower than the Vv component intensity.

The polarization anisotropy $r$ is clearly non-zero (+1.6%) at room temperature and reaches +4.5% at 14.6 K (Fig. 6). We checked that $r$ does not change significantly during the PL decay (Fig. 7). Both Vv and Vh component decay similarly at least within the first 5 seconds. The slight difference between the fitted decay constants is within the error limits.
Fig. 7. Comparison of decay kinetics of vertically (Vv) and horizontally (Vh) polarized components of $^1\text{O}_2$ luminescence under vertically polarized excitation at 1064 nm. The emission was collected in 1250 nm-1300 nm spectral range. Solid lines are fits to semilog scale data in 0 ms - 2480 ms range.

**Calculation of interstitial O$_2$ rotation**

$g$-$\text{SiO}_2$, as an amorphous material, is characterized by a wide distribution of interstitial voids$^{30}$. Volumes of the voids extend from approximately 25 Å$^3$ (radius 1.8 Å) to more than 250 Å$^3$, (radius $\sim$4Å)$^{39-41}$, with the average volume being about 65 Å$^3$ (radius 2.5 Å)$^{30}$. In contrast to $g$-$\text{SiO}_2$, the distribution of voids in $\alpha$-$\text{quartz}$ is very narrow, with an average volume of $\approx$33 Å$^3$$^{39,40}$. The volume of interstitial voids has direct consequences on the energy of the interstitial O$_2$ molecule. It has been shown that there is a clear inverse correlation between the volume of the void and the energy of O$_2$ incorporation$^{39,40}$. In particular, this energy is $\sim$3.5 eV for O$_2$ in $\alpha$-quartz (volume 33 Å$^3$), and reaches nearly zero when the volume becomes larger than about 125 Å$^3$$^{40}$. Thus, under thermal equilibrium conditions O$_2$ in $g$-$\text{SiO}_2$ will reside in voids having the largest volumes. High
incorporation energy of O\(_2\) in \(\alpha\)-quartz is probably one of the reasons why, to the best of our knowledge, interstitial O\(_2\) has never been observed in undamaged lattice of \(\alpha\)-quartz.

![Fig. 8. Contour plots describing the rotation barriers for an O\(_2\) molecule in voids with radii of 2.8, 3.1 and 3.3 Å. The energy values are in meV.](image)

Instead of trying to perform an extensive statistical analysis, our main goal is to answer the following qualitative question: is the rotation of O\(_2\) molecules in large voids, where they are likely to be under thermal equilibrium, frozen, hindered, or nearly free? In order to answer it, we have chosen three large voids with volumes 92 Å\(^3\) (radius 2.8 Å), 125 Å\(^3\) (radius 3.1 Å), and 150 Å\(^3\) (radius 3.3 Å), all of which are larger than the average void in silica. To investigate the rotational motion of O\(_2\) in these voids, we calculated the potential energy surface of the O\(_2\) molecule as a function of the spherical angles \(\vartheta, \varphi\). As the first step, the potential energy surface was calculated by keeping the lattice frozen, and only the molecule was allowed to rotate. The resulting contour plots of the potential energy surfaces \((\vartheta, \varphi)\) for the three voids are shown in Fig. 8. Due to the inversion symmetry of the molecule, the potential has the property \((\vartheta, \varphi) = (-\vartheta, +\varphi)\), and thus it is sufficient to take the range of \(\varphi\) from 0 to 180 degrees. In the plot the value \(\vartheta=0\) corresponds to the lowest-energy orientation of the molecule. Allowing the lattice to relax for each
orientation of the molecule lowers the energies by at most 15%, and therefore we discuss the
results of a frozen lattice here.

The calculated potential energy surface helps understanding the behavior of the rotational motion of the molecule at
different temperatures. Let us first discuss the behavior of the molecule in the void with radius 3.1 Å (Fig. 8(b)). At
cryogenic temperatures $\ll 10$ meV, and the orientation of the O$_2$ molecule is essentially frozen. At room temperature $\approx 25$
meV, and now the
orientation of the molecule can exhibit vibrational motion in the solid angle of $\leq 1$, corresponding to $\leq 30$ degrees. The barrier for the molecule
to change from 0 to 180 degrees is $\approx 80$ meV. However, the total rotational motion of the molecule is partially hindered up to $\approx 200$ meV (the
highest barrier in Fig. 8(b)), that means, under essentially all experimental conditions.

If we consider a smaller void (Fig. 8(a), radius 2.8 Å), the barriers are yet higher: the rotational
motion of the molecule is frozen at low temperatures, and only some wobbling around the
equilibrium orientation is allowed at room temperature. As the volume of the voids increases, the
rotational barriers tend to decrease. E.g., for voids with radius 3.3 Å (Fig. 8(c)), those barriers can
become as small as 20 meV. This means that the rotational motion is still frozen at low
temperatures, but as the temperature approaches room temperature, molecules experience
substantial libration motion.

While, as discussed above, an exhaustive statistical analysis is not the aim of the present paper,
the analysis of the behavior of O$_2$ molecules in a few representative voids suggests that rotational
movement of O$_2$ molecules in voids, in which they are likely to reside, is frozen at low
temperatures, and partially allowed at room temperature.

To make sure that our computational setup is reliable regarding the rotational motion of
molecules in g-SiO$_2$, we have performed identical calculations for the H$_2$ molecule. There are
strong indications from Raman scattering studies that H$_2$ rotates nearly freely in g-SiO$_2$ at room temperature $^{42}$. Indeed, we find that, e.g., the highest barrier of rotation of H$_2$ inside the 3.1 Å radius void in g-SiO$_2$ is ~5 meV, compared to ~200 meV for the O$_2$ molecule. This means that the H$_2$ molecule indeed rotates nearly freely at room temperature, in agreement with the experiment (Ref. $^{42}$ and Supplement B).

**Discussion**

**Lifetime and quantum yield of singlet O$_2$ in glassy SiO$_2$**

The decay constant $\tau_{\text{meas}}$ of $^1$O$_2$ PL in g-SiO$_2$, measured at 766 nm excitation, increases from ~860 ms at 295 K to the "saturation value" 1115 ms, observed at temperatures below 80 K (Fig. 3). The saturation value, obtained with 1064 nm excitation is slightly different ($\tau_{\text{meas}} \approx 1230$ ms). This difference is most likely explained by static site-to-site variations of O$_2$ sites in glassy matrix in conjunction with site-selective excitation: the ensembles, excited by 766nm and by 1064nm are evidently different. It gives a rough estimate of the disorder-induced spread of $\tau_{\text{meas}}$ values. The low-T saturation of $\tau_{\text{meas}}$ values is typical for most luminescence centers, where T-dependent non-radiative process with rate $1/\tau_{\text{nr}}$ competes with (usually less T-sensitive) radiative transitions, having rate $1/\tau_{\text{rad}}$:

$$1/\tau_{\text{nr}} = 1/\tau_{\text{rad}} + \text{loose terms}$$

(3)

Our measured lifetimes are ≈1.6 times longer than those reported for $^1$O$_2$ in O$_2$-saturated Aerosil nanoparticles (460 ms and 700 ms at 295 K and 10 K, respectively)$^{43}$. Assuming that the temperature-dependent non-radiative rate is described by the Arrhenius-type expression $1/\tau_{\text{nr}} \sim \exp(-E/k_B T)$, the activation energy $E$ can be obtained as the slope of the plot of
\[ \ln\left(\frac{1}{\tau_{\text{meas}}}-\frac{1}{\tau_0}\right) \text{ vs. } 1/T, \] where \( \tau_0 \) is the measured decay constant in the low-temperature limit.

Assuming \( \tau_0=1115 \) ms (Fig. 3, inset), the activation energy of \( \approx 1550 \text{ cm}^{-1} \) is obtained for the high-temperature thermal quenching (Fig. 3). This energy is well above the highest fundamental vibration mode of \( \text{g-SiO}_2(\approx 1200 \text{ cm}^{-1}) \) and close to the vibration energy of O\(_2\) molecule embedded in SiO\(_2\): 1549 cm\(^{-1}\) in the \( X^3\Sigma_g^- \) (ground state)\(^8\) and 1493\(\pm\)20 cm\(^{-1}\) in the \( a^1\Sigma_g^+ \) excited state\(^9\).

That might indicate that the mechanism of high-temperature quenching of \( ^1\text{O}_2 \) PL involves the activation of O\(_2\) vibration modes.

As Fig. 3 demonstrates, the effective activation energy changes in the low-temperature region. However, the estimate of the PL quenching activation energy in this region, \( E=380 \text{ cm}^{-1} \) (Fig. 3), is only tentative at best: it is based on just 2 data points and it is very sensitive to the choice of \( \tau_0 \), which shows slight excitation wavelength dependence (see the Results part). Presently it can be only noted that: (i) similar value of low-T activation energy, \( E=340\pm40 \text{ cm}^{-1} \) was obtained for O\(_2\) in Aerosil particles\(^{43}\); (ii) this energy is close to the energy of the main Raman-band in \( \text{g-SiO}_2 \) (200...500 cm\(^{-1}\), see, \textit{e.g.}, ref.\(^{24}\)); (iii) coupling to SiO\(_2\) vibration modes is demonstrated by phonon sidebands in high-resolution \( ^1\text{O}_2 \) PL spectra\(^8\), showing that the involvement of the SiO\(_2\) phonons in non-radiative decay is plausible.

It has been shown that the radiative rate of \( ^1\text{O}_2 \) PL can also be temperature-dependent\(^{44}\). In the present case, however, the PL T-dependence in the high-T region is dominated by the change in non-radiative rate, since the intensity is proportional to the measured decay constant \( \tau_{\text{meas}} \) (Fig. 3, inset) as predicted by eq. 3. This proportionality can not be proved in the low-T region, because reliable data on intensity T-dependence are not available.

The measured low-temperature decay constant \( \tau_0 \) (1115 ms, Fig. 3) is significantly smaller than the decay constant \( \tau_{\text{meas}} \approx 2150 \text{ ms} \), measured at \textit{room} temperature for isotope-enriched \( ^{18}\text{O}^{18}\text{O} \)}
molecules in g-SiO$_2$\textsuperscript{45}. Evidently, the radiative lifetime $\tau_{\text{rad}}$ of $^1$O$_2$ in g-SiO$_2$ must be at least 2150 ms. Assuringly, this lifetime is calculated to be around 3000 ms in the next section of the present paper; and it is estimated between 0.7 and 5 s for O$_2$ dissolved in different liquids (Table 2).

The difference between $\tau_0$ and $\tau_{\text{rad}}$ ($\tau_{\text{rad}}/\tau_0 \geq 2$) indicates that a significant thermally non-activated quenching persists even at 15 K, and the PL quantum yield $\eta=\tau_0/\tau_{\text{rad}}$ is lower than $\approx 0.5$ at T=15 K. Adopting the estimate of $\tau_{\text{rad}} \approx 3000$ ms would yield $\eta=0.37$ at T=15 K and $\eta=860/3000=0.29$ at room temperature. It is unlikely that the radiative rate $1/\tau_{\text{rad}}$ for $^1$O$_2$ in SiO$_2$ could be much lower than the values listed in Table 2, therefore the luminescence quantum yield $\tau_0/\tau_{\text{rad}}$ of $^1$O$_2$ in g-SiO$_2$ should be surely larger than 0.1. To the best of our knowledge, it is then the largest reported quantum yield for $^1$O$_2$ PL in solids at room temperature.

**O$_2$ absorption cross sections and $^1$O$_2$ radiative lifetime in glassy SiO$_2$**

Absorption cross sections $\sigma$ of O$_2$ $b\rightarrow X$ and $a \rightarrow X$ transitions are extremely low, and for O$_2$ in various solutions it has been possible to measure them only indirectly, by quantifying the photochemical effects of singlet oxygen, created by direct $X\rightarrow a$ or $X\rightarrow b$ photoexcitation. Using this technique, $\sigma$ for O$_2$ in different solvents were recently re-examined in Ref. \textsuperscript{14}.

Fortunately, g-SiO$_2$ is peculiar not only as the matrix providing the longest $^1$O$_2$ lifetime, but also as a material for fiber optical waveguides, which due to their typically long optical paths are sensitive to weak absorptions. Surprisingly, our analysis of literature data shows that $\sigma$ for $X\rightarrow a$ and $X\rightarrow b$ transitions can be obtained directly, by supplementing the data on absorption of O$_2$ in optical fibers, published more than two decades ago \textsuperscript{18,46} with later spectroscopic work \textsuperscript{24,25}, which allows to determine in hindsight the concentration of O$_2$ in these fibers (see supplement S1 for spectra and for details of their processing).
In optical fibers, produced in oxygen-rich conditions, two sharp optical absorption lines have been observed: one at 1273 nm and the other at 765 nm (see Supplement, figure S1). Their amplitudes and full widths at half maximum (FWHM) are listed in Table 1 (denoted as "Experiment A"). The origin of these two lines was initially unidentified, however, their positions and small FWHM's clearly show that they are due to $X \rightarrow a$ and $X \rightarrow b$ transitions of O$_2$ in silica. They yield the ratio between the $X \rightarrow a$ and $X \rightarrow b$ absorption intensities (integrals $I$ of absorption bands): $I_{1272\text{nm}}/I_{765\text{nm}} = 2.7 \pm 0.3$. Note that due to an extremely low absorption cross-section, requiring km-long samples, direct measurements are only possible in optical fibers, making such experiments unique.

The 765nm band in optical fiber was subsequently assigned to O$_2^{18}$. This assignment was proved by observing the sharp Raman line of interstitial O$_2$ at 1549 cm$^{-1}$ and the 765 nm optical absorption band (Figs. S4 and S5 in Supplement) in the same optical fiber (Table 1, Experiment "B"). However, the concentration of O$_2$ in that optical fiber was not known. Our later work allows to determine the absolute concentration of O$_2$ in g-SiO$_2$, using the intensity of the O$_2$ Raman band relative to the intensities of fundamental g-SiO$_2$ Raman bands. Hence, the concentration of O$_2$ in the fiber, studied in experiment "B"$^{18}$ can be determined in hindsight ($2.4 \times 10^{17}$ O$_2$/cm$^3$, Table 1). Further, by comparing the 765 nm absorption band integrals, the concentration of O$_2$ in the fiber used in Experiment "A"$^{46}$ is calculated (Table 1). Since O$_2$ $X \rightarrow a$ and $X \rightarrow b$ absorption bands are clearly visible in this fiber and their intensities $\alpha$ can be measured, their peak absorption cross sections $\sigma = \alpha/[O_2]$ can now be finally obtained after a slight correction for lower spectral resolution in Experiment B (see Supplement and footnote (c) under Table 1). Table 2 provides a comparison between the obtained $\sigma$ values for O$_2$ in g-SiO$_2$ and O$_2$ in different organic solvents. They are reasonably similar. The accuracy of the cross sections for g-SiO$_2$ calculated in this paper (Tables 1, 2) is limited by the accuracy, with which numerical values can be extracted from the published
absorption and Raman spectra of the optical fibers. Repeating these experiments with dedicated O₂-loaded optical fibers would provide a way of accurate direct measurement of O₂ X→a and X→b absorption cross sections in g-SiO₂.

If the integral of absorption spectrum α( ) and concentration N of absorbing/emitting species is known, then for narrow, not Stokes-shifted absorption/emission spectra the radiative transition (emission) rate 1/τ rad can be calculated by Perrin’s formula (e.g., refs.11,32)

\[
\frac{1}{\tau_{\text{rad}}} = \int_{\omega_0}^{\infty} n \alpha(\omega) \, d\omega
\]

where \( n \) is the refractive index of the medium; \( \omega_0 \) is the central wavenumber (cm⁻¹) and \( g_{em} \) and \( g_{abs} \) are the relative weights of all statistically equivalent emission and absorption transitions at this wavenumber. These weights increase from 1 to 2 or 3, if the destination state is 2- or 3-fold degenerate, and they decrease below 1, if the effective population of the initial state is <1. Given the complex nature of the X→a transition, and the fact that transitions become allowed only by perturbations from the surrounding host, the choice of \( g_{em}/g_{abs} \) is nontrivial, as already noted in Ref. 11. Theoretical considerations indicate that X→a transition in perturbed O₂ occurs mostly from the \( m_s=0 \) spin sub-level of the X ground state (Fig.1, see supplement of Ref. 11). Transitions X→a from the other two spin sub-levels (\( m_s=±1 \)) are not enhanced by the interaction with the host matrix, and their contribution to absorption is negligible. Therefore, the effective occupancy of the ground level for the X→a absorption transition is ~1/3 at the room temperature, when all three spin sublevels are almost equally populated (zero-field splitting is 4 cm⁻¹, much smaller than \( kT \)). On the other hand, the X→a absorption intensity is enhanced by factor 2 because the upper (spin singlet) level \( a^1_g \) is orbitally two-fold degenerate. Together this yields \( g_{abs}= 2/3 \) for the X→a transition. Conversely, for the reverse a→X transition the statistical weight \( g_{em}= 1 \), since the only allowed
transition is to \( m_S = 0 \) sublevel. Hence the ratio \( g_{em}/g_{abs} = 3/2 \) can be used for eq. (4). Substituting this value, the absorption integral from Table I and the refractive index \( n = 1.447 \) at 1272 nm in eq.(4) yields \( 1/\tau_{rad} = 0.336 \text{ s}^{-1} \) or \( \tau_{rad} \approx 3.0 \text{ s} \). The longest room-temperature lifetime of \(^1\text{O}_2\) in g-SiO\(_2\), reported in literature, is 2.1 s, measured for \(^{18}\text{O}^{18}\text{O}\) molecules \(^{45}\). Therefore the calculated \( \tau_{rad} \) value, which is the upper limit for the experimentally observed lifetimes, is not unreasonable. The estimates of \( \tau_{rad} \) of \(^1\text{O}_2\) in solvents range from 0.3 to 5 seconds \(^{5}\) (and see Table 2). In the present paper, the main sources of error are the uncertainties related to eq.(4) and the accuracy of the concentration estimates, which mainly depends on the accuracy of the published relatively weak 765 nm absorption band \(^{18}\). In any case, these data demonstrate that \( X \rightarrow a \) and \( X \rightarrow b \) transitions of \(^1\text{O}_2\) can be directly studied with relatively high accuracy using \( \text{O}_2 \)–containing optical fibers. Such fibers are presently being developed for near-infrared applications in radiation environments \(^{23}\) and for luminescent dosimetry applications \(^{47}\).

**Character of the 1272 nm radiative transition**

Quantum mechanical considerations, regarding the character of the lower optical transitions in a free and perturbed \( \text{O}_2 \) have been recently summarized by Bregnhøj et. al. \(^{11}\). Their analysis indicates that in a free \( \text{O}_2 \) molecule the strongest contribution to \( a \rightarrow X \) transition is given by magnetic dipole transition, while the additional contribution of electric quadrupole component is much weaker \(^{11}\). The forbidden electric dipole transition is, however, more sensitive to perturbations from the environment. When \( \text{O}_2 \) is perturbed by an external potential, the transition can acquire electric-dipole character and can become up to \( \sim 1000 \) more intense than the magnetic dipole component of \( a \rightarrow X \) transition in the same perturbed \( \text{O}_2 \) molecule \(^{11}\).
The relation between the intensities of differently polarized PL components (Fig. 6, left inset), with a more intense Vv component and less intense and mutually equal Vh, Hv and Hh components, is consistent with an electric-dipole character of the \( a^1_g \rightarrow X^3\Sigma_g^- \) transition suggested in ref. 11.

The angular dependence of PL polarization anisotropy, expected in the case of electric quadrupole excitation and emission transitions is different from the one, observed in our work. Such transitions should yield \( r = -2/7 \approx -0.286 \) when the polarization of the excitation beam is horizontal, and yield \( r = 0 \), when the excitation beam is polarized vertically. This difference further confirms the electric-dipole character of \(^1\text{O}_2\) PL in silica.

In the case of 766 nm excitation the situation is more complicated: the \( X \rightarrow b \) excitation is predicted to have magnetic-dipole character, and after \( b \rightarrow a \) relaxation, \( a \rightarrow X \) luminescence transition occurs, which, as discussed above, has electric-dipole character. The present data indicate that the polarization anisotropy is strongly decreased in this case, and is close to zero within our current level of accuracy (\( r \approx 0.6\% \)).

**Rotation of O\(_2\) in silica glass**

\( \text{O}_2 \) molecules are tightly confined in interstitial voids. An extrapolation of the temperature-dependence of the \( \text{O}_2 \) diffusion coefficient to room temperature yields diffusion length \( L = (6Dt)^{1/2} \) of only \( \approx 0.02 \) Å in 1 second, indicating that \(^1\text{O}_2\) does not hop to neighboring void during its \( \approx 1 \) s lifetime. However, in principle this does not exclude its rotation within the containing void. In contrast to the case of interstitial H\(_2\) molecules in g-SiO\(_2\), rotation-vibrational Raman bands of O\(_2\) in g-SiO\(_2\) have not been found. The non-zero PL polarization anisotropy (Fig. 6) indicates a definite correlation between the orientations of O\(_2\) molecule during the photo-excitation and during the emission, which occurs on average \( \approx 1 \) second later. The molecule either stays in a single, fixed
orientation, or, at least, has one preferred orientation, where it spends the largest fraction of time. In any case, it does not leave the void. The observed behavior is evidently an average over the distribution of void sizes in SiO₂ glass.

The polarization anisotropy is given by:

\[
\frac{\alpha}{\cos^2 \alpha} \approx \frac{\alpha}{2} = (\alpha - \frac{\alpha}{2}) = \frac{\alpha}{2}
\]

(5)

where \( \alpha \) is the angle between the directions of absorbing and emitting dipoles and \( \langle \cos^2 \alpha \rangle \) denotes average of \( \cos^2 \alpha \) over all possible \( \alpha \) values. If these directions coincide (\( \alpha=0 \)), then \( r=0.4 \).

If the luminescent excited state is orbitally doubly degenerate, as is the case for \( \alpha^1_g \) state of O₂, PL is additionally depolarized even if the molecular axis direction is fixed. Due to the axial symmetry of the molecule, the absorption and emission dipole transitions from non-degenerate to degenerate state (\( X \rightarrow a \)) and back must be polarized in plane, normal to molecular axis. Since all directions in this plane are equivalent, the absorbing and emitting dipoles in this case can assume any mutual angle \( \alpha \) within this plane. The value of \( \langle \cos^2 \alpha \rangle \) in this case is 0.5 and, according to eq.(5), \( r \) is reduced to 1/10. If, in addition, the direction of the O₂ molecular axis can change during the excited state lifetime, and therefore, the emission plane is tilted from the absorption plane by an angle \( \theta_0 \), then \( \langle \cos^2 \alpha \rangle = (1+\cos^2 \theta_0)/4 \) and, according to eq.(5), the resulting anisotropy is further decreased:

\[
\frac{\alpha}{\cos^2 \alpha} \approx \frac{\alpha}{2} = (\alpha - \frac{\alpha}{2}) = \frac{\alpha}{2}
\]

(6)

For \( r = 4.5\% \) at 14.6 K and 1.6\% at 295 K (Fig. 6), eq.(6) yields "average" angles (\( \text{arc} \cos(\langle \cos^2 \theta_0 \rangle) \)) of O₂ axis deviation between absorption and emission events \( \theta_0 \approx 37^\circ \) and \( \theta_0 \approx 48^\circ \), respectively. Note that the "baseline value", a completely chaotic tumbling of O₂ corresponds to \( \theta_0 = \text{arc} \cos (3^{1/2}) \approx 55^\circ \). While this result should be regarded as a merely qualitative one, it may
give the idea of the magnitude of the fluctuation of O$_2$ molecular axis directions in interstitial voids of g-SiO$_2$.

**Conclusion**

The temperature-dependent polarization anisotropy of $^1$O$_2$ luminescence in g-SiO$_2$ and DFT calculations demonstrate that O$_2$ molecule does not rotate freely in interstitial voids and maintain a correlation between the absorption and emission polarization directions. The transitions between the ground state (X) and the lowest singlet state (a) have weakly allowed electric dipole character, in accord with the theoretical predictions $^{11}$.

The temperature dependence of $^1$O$_2$ PL kinetics and its comparison to the radiative lifetime of $\sim 3$ seconds, deduced by an analysis of the O$_2$ optical absorption in fiber optical waveguides, allows to estimate that the $^1$O$_2$ PL quantum yield is above 0.1. To our knowledge, this is the highest quantum yield for $^1$O$_2$ luminescence at room temperature in any condensed matrix. The PL is still not completely quenched at temperatures as high as 200°C and O-O molecular vibration probably participates in the thermal quenching process.

It is evident that the tight confinement of O$_2$ in g-SiO$_2$ interstitial voids helps to avoid the collisional quenching of excited $^1$O$_2$ and contributes to the record-long lifetime of $^1$O$_2$ at room temperature in g-SiO$_2$. However, it also slows down the diffusion of O$_2$. For applications in photobiology $^7$, where both long lifetimes and long diffusion paths of $^1$O$_2$ are desired, an optimization of the confinement degree may be useful and could be a subject for further studies.
Supporting Information Description

Analysis of the literature data on optical fiber waveguides, which yields optical absorption cross sections of the $X \rightarrow a$ and $X \rightarrow b$ transitions of $\text{O}_2$ molecule trapped in silica glass.

Raman spectra of gaseous $\text{H}_2$ and $\text{H}_2$ in silica glass, illustrating the rotation of $\text{H}_2$.

Acknowledgements

The support from M-ERANET project "MyND" is acknowledged. A. A., M. M-S., and L. R. were supported by the Research Council of Lithuania (grant M-ERA.NET-1/2015). Authors thank A. Pasquarello for providing the structures of the amorphous SiO$_2$ matrix for our computational work and K. Kajihara (Tokyo Metropolitan University) for valuable advice in PL kinetics measurements.

Figure Captions

Fig. 1. Optical absorption and luminescence transitions observed $^8$–$^{10}$ in interstitial $\text{O}_2$ molecule embedded in glassy SiO$_2$. The transitions studied in this work are indicated by bold arrows. The transition wavelengths are in nm. Zero-field splittings ($\approx 4 \text{ cm}^{-1}$) $^{11}$ of both the triplet ground state $X (v=0)$ and its vibrational ($v=1$) sublevels are shown.

Fig. 2. Decay kinetics of $^1\text{O}_2$ luminescence in dry silica glass in temperature range 15 K-503 K. Exponential fits to the initial parts of kinetics, corresponding to intensity decay $e^2$ times, are shown by solid lines.
Fig. 3. Arrhenius plot according to eq. (3), showing activation energy of $\approx 1550 \text{ cm}^{-1}$ for the high-temperature non-radiative quenching of $\text{O}_2$ PL. Inset shows the measured temperature dependence of the PL intensity and of the PL decay constant.

Fig. 4. $^1\text{O}_2$ luminescence spectra of vertically (Vv) and horizontally (Vh) polarized components, excited by vertically (V) polarized 766 nm light at $T=16$ K. Inset shows Vv and Vh component intensities, measured in time-resolved mode after cut-off of the excitation light. No measurable polarization is detected.

Fig. 5. Strongly polarized fundamental 440 cm$^{-1}$ and 800 cm$^{-1}$ Raman bands and $^1\text{O}_2$ luminescence spectra of silica glass with embedded $\text{O}_2$ molecules, measured with linearly polarized 1064 nm excitation for Vv, Vh, Hv and Hh polarization components.

Fig. 6. Temperature dependence of polarization anisotropy of $^1\text{O}_2$ luminescence measured by recording the luminescence decay intensities, integrated over 20 to 1840 ms interval after cut-off of the polarized 1064 nm excitation light. Insets show luminescence transients at $T=14.6$ and 295 K. Vh, Hv and Hh-polarized components have equal intensities, which are lower than the Vv component intensity.

Fig. 7. Comparison of decay kinetics of vertically (Vv) and horizontally (Vh) polarized components of $^1\text{O}_2$ luminescence under vertically polarized excitation at 1064 nm. The emission was collected in 1250 nm-1300 nm spectral range. Solid lines are fits to semilog scale data in 0 ms - 2480 ms range.
Fig. 8. Contour plots describing the rotation barriers for an O$_2$ molecule in voids with radii of 2.8, 3.1 and 3.3 Å. The energy values are in meV.

### Tables

**Table 1.** Absorption Cross Sections of $X\rightarrow a$ and $X\rightarrow b$ Transitions of O$_2$ in Silica Glass Optical Fibers, Obtained from Analysis of Published Data $^{18,24,25,46}$.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>amplitude (db/km)</th>
<th>fwhm (cm$^{-1}$)</th>
<th>integral (db/km*$cm^{-1}$)</th>
<th>amplitude (db/km)</th>
<th>fwhm (cm$^{-1}$)</th>
<th>integral (db/km*$cm^{-1}$)</th>
<th>[O2] (O2/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: $^{46}$</td>
<td>15.11</td>
<td>105</td>
<td>1587</td>
<td>5.82</td>
<td>103</td>
<td>597</td>
<td>$1.6\times10^{18}$ $^{a)}$</td>
</tr>
<tr>
<td>B: $^{18}$</td>
<td></td>
<td>0.45</td>
<td>180</td>
<td>89</td>
<td>2.4$\times10^{17}$ $^{b)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C $^{9}$</td>
<td></td>
<td>93 (PL)</td>
<td></td>
<td>103 (PLE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D: $^{24}$</td>
<td></td>
<td>86 (PL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>peak $\sigma$ $^{c)}$</td>
<td>$2.7\times10^{-23}$ cm$^2$</td>
<td></td>
<td>$0.84 \times 10^{-23}$ cm$^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a)}$ O$_2$ concentration obtained relative to the experiment B by scaling the $X\rightarrow b$ absorption band integrals.

$^{b)}$ O$_2$ concentration obtained by comparing the intensity ratio of the O$_2$ Raman line relative to the fundamental g-SiO$_2$ Raman band around 1600 cm$^{-1}$ (Experiment B) with a similar ratio, measured in Experiment D in a sample with known O$_2$ concentration.

$^{c)}$ Peak absorption cross sections $\sigma_{X-a}$ and $\sigma_{X-b}$ were obtained using absorption band amplitudes from experiment A $^{46}$ and the calculated O$_2$ concentrations. $\sigma_{X-a}$ was additionally corrected for insufficient spectral resolution in A. It is upscaled by fwhm ratio 105/86, using luminescence $a\rightarrow X$ transition fwhm data from the high-resolution experiment D.
Table 2. Spectral Parameters of O₂ in SiO₂ Glass and in Different Solvents: Peak Absorption Cross Sections σ of X→a (1272 nm) and X→b (765 nm) Transitions, and Radiative Decay Rates for a →X Transition.

<table>
<thead>
<tr>
<th>Medium</th>
<th>σ(1272 nm) , (10⁻²⁴ cm²)</th>
<th>σ(765nm) , (10⁻²⁴ cm²)</th>
<th>k_r a-X ( s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica glass</td>
<td>27ᵃ)</td>
<td>8.4ᵃ)</td>
<td>0.34ᵃ)</td>
</tr>
<tr>
<td>water</td>
<td>6ᵇ)</td>
<td>4.5ᵇ) 5.1ᵈ)</td>
<td>0.209ᵉ)</td>
</tr>
<tr>
<td>toluene</td>
<td>27ᵇ) 34.8ᶜ)</td>
<td>6.7ᵈ)</td>
<td>1.44ᵈ,e)</td>
</tr>
<tr>
<td>benzene</td>
<td>25ᵇ)</td>
<td></td>
<td>1.5ᵈ,e)</td>
</tr>
<tr>
<td>CCl₄</td>
<td>20ᵇ)</td>
<td>2.7ᵇ)</td>
<td>1.06ᵈ 1.17ᵉ)</td>
</tr>
<tr>
<td>ethanol</td>
<td>10ᵇ), 17.7ᶜ)</td>
<td>4.0ᵇ)</td>
<td>0.55ᵈ,e)</td>
</tr>
<tr>
<td>acetone</td>
<td>11.5ᵇ), 11.5ᶜ)</td>
<td>3.7ᵇ)</td>
<td>0.56ᵈ 0.543ᵉ)</td>
</tr>
</tbody>
</table>

a) This work, based on analysis of data in Refs. 18,24,25,46
b) Ref. 14
c) Ref. 49
d) Ref. 11
e) Ref. 5

References


(49) Sivéry, A.; Anquez, F.; Pierlot, C.; Aubry, J. M.; Courtade, E. Singlet Oxygen (1O2) Generation upon 1270nm Laser Irradiation of Ground State Oxygen (3O2) Dissolved in Organic Solvents: Simultaneous and Independent Determination of 1O2 Production Rate and
Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union’s Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART²