

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

Linards Skuja^{†}, Krisjanis Smits[†], Anatoly Trukhin[†], Florian Gahbauer[‡], Ruvin Ferber[‡], Marcis
Auzinsh[‡], Laima Busaite[‡], Lukas Razinkovas[§], Mažena Mackoit-Sinkevičienė[§], and
Audrius Alkauskas[§]*

[†]Institute of Solid State Physics, Kengaraga 8, University of Latvia, Riga LV-1063, Latvia

[‡]Laser Centre, University of Latvia, 19 Raina Blvd., Riga LV-1586, Latvia

[§]Center for Physical Sciences and Technology (FTMC), Vilnius LT-10257, Lithuania

*email of the corresponding author: skuja@latnet.lv

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56

Abstract

The lowest excited electronic state of the O₂ molecule, a^1_g , the "singlet oxygen", is of utmost importance for photochemistry and photobiology. For O₂ trapped in silica glass, the lifetime of this state and the associated $a^1_g \rightarrow X^3\Sigma_g^-$ photoluminescence (PL) is the longest known for O₂ 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^1_g ($v=1$) 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 $a^1_g \rightarrow X^3\Sigma_g^-$ transition, enabled by O₂ – SiO₂ cage interactions. Density functional theory calculations indicate that at low temperatures the rotation of O₂ is partially or fully frozen even in large silica voids. As the temperature increases, PL is increasingly depolarized by libration movement of O₂ molecules. Analysis of O₂ optical absorption in optical fibers allows one to obtain the absorption cross sections of $X \rightarrow a$ and $X \rightarrow b$ transitions of O₂ in SiO₂ 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_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_g state are often referred as "singlet oxygen" or " 1O_2 ". They are of immense importance in photobiology¹, photodynamic cancer therapy¹⁻³, and photocatalysis⁴. Many reviews spanning decades of research are available, *e.g.* refs.⁵⁻⁷. The presence of 1O_2 is commonly monitored by the ~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

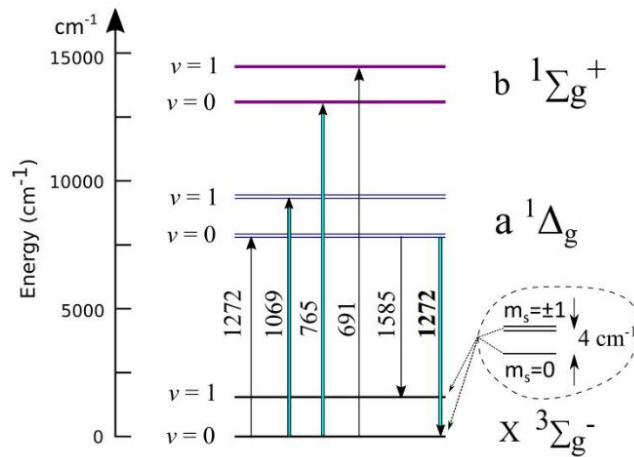


Fig.1. Optical absorption and luminescence transitions observed⁸⁻¹⁰ in interstitial O_2 molecule embedded in glassy SiO_2 . The transitions studied in this work are indicated by bold arrows. The transition wavelengths are in nm. Zero-field splittings ($\approx 4\text{ cm}^{-1}$)¹¹ of both the triplet ground state X ($v=0$) and its first vibrational ($v=1$) sublevel are shown.

1 transitions were recently reviewed ^{11,12}. Despite the external perturbations, the absorption transitions
2 (Fig.1) remain extremely weak, therefore in most cases the luminescence is excited indirectly, via energy-
3 transfer from an activator. More recently, a direct photoexcitation via $X \rightarrow a$ and $X \rightarrow b$ transitions has been
4 employed ¹³ and the absorption cross sections of these two transitions in different solvents have been
5 evaluated ^{14,15}. The option of enhancing $X \rightarrow b$ transition by surface plasmon resonance was recently
6 explored ¹⁶.
7
8

9 Apart from the fields of photobiology and photocatalysis, singlet and triplet O₂ plays an important
10 role in the physics of glassy SiO₂ (g-SiO₂, silica glass), the basic material for fiber optical
11 waveguides and ultraviolet (UV) optical components. Interstitial O₂ molecules strongly affect their
12 optical properties and radiation toughness ¹⁷. They are introduced in g-SiO₂ by manufacturing ¹⁸,
13 high-T diffusion ¹⁹, dimerization of O atoms, displaced from SiO₂ network by nuclear irradiation ⁸ or
14 by fs laser pulses ²⁰, or by electric field applied at high temperatures ²¹. While the interstitial O₂ is
15 detrimental to UV applications of g-SiO₂ ^{17,22}, it is found to increase the radiation toughness of
16 optical fibers in the near-infrared range ²³. Luminescence of singlet O₂ provides means for high-
17 sensitivity monitoring of O₂ concentration in g-SiO₂ ^{24,25} and has been used to study O₂ diffusion,
18 isotope exchange with the glass network, or defect creation in bulk g-SiO₂ ¹⁰ and SiO₂ nanoparticles
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Comparison of the basic properties of interstitial O₂ in g-SiO₂ with the large base of data on ¹O₂ in
solvents and solid matrices reveals an outstanding feature: the lifetime of the a^1_g state of O₂ in g-
SiO₂ $\tau \approx 0.82$ s, ²⁶ is the longest observed for O₂ in any condensed medium at room temperature.
¹O₂ 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 CCl₄,
309 ms for perfluorodecalene C₁₀F₁₈ ²⁷). Lifetimes of ¹O₂ in different liquids are compiled in ref.

7 (p.31) and in the supplement of ref.¹¹. ¹O₂ lifetimes in organic polymer matrices are typically in the range of 5 μs – 100 μs (ref.⁷, p.34); they are significantly higher in fluorocarbon polymers, e.g., 320 μs in nafion matrix²⁸ In nanoporous aluminosilica and zeolite nanoparticles the ¹O₂ lifetimes are generally into the same range (3 μs to 64 μs)²⁹. The shortening of ¹O₂ lifetimes in these solids or liquids is due to a much stronger non-radiative quenching, compared to the case of ¹O₂ in g-SiO₂.

The most common non-radiative quenching mechanism of ¹O₂ is electronic-to-vibrational (e-v) energy transfer to vibrationally-excited electronic ground state of O₂. The energy difference between the 0-th vibrational level of the excited state (¹_g, v=0) and vibrationally excited ground state (³Σ_g⁻, v=m, m>0) is absorbed by vibrations of some "deactivator species" Y. The energy balance is given by:^{5,27}



where m and n are vibrational quantum numbers of m-th and n-th vibrational excited states of O₂ and Y, and E_{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 ¹O₂ is highly desired in photodynamic therapy applications where a photosensitizer is encapsulated in a nanoparticle, protected from reactants by a silica shell, and photogenerated ¹O₂ must traverse the shell to its target before it is quenched. The lifetime of ¹O₂, strongly confined in the interstitial voids in g-SiO₂ glass network, is ~10⁴ times longer than τ=64 μs, measured for porous SiO₂²⁹. The largest source of this difference is evidently the presence of ≡Si–O–H groups on the internal surfaces of porous SiO₂. They are known as very efficient quenchers of ¹_g state with m=0, n=2 in eq.1.

The second cause of the more rapid quenching of ¹O₂ in porous SiO₂ could be the additional rotational and translational degrees of freedom, available for O₂ in the porous SiO₂ as compared to

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

O₂, tightly confined in g-SiO₂ voids, which have an estimated average diameter of $\approx 5 \text{ \AA}$ ³⁰. These degrees of freedom could provide the E_{mm} 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 1_g state. O₂ has been used as a test magnetic molecule for diamond NV-center based nanoscale magnetometry³¹. 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 $^1\text{O}_2$ in silica. We studied the thermal quenching of $^1\text{O}_2$ 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 ($>10^{14} \text{ cm}^{-3}$). 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 $\equiv\text{SiOH}$ groups (6 and 5.3), interstitial Cl₂ molecules (51 and 79) and interstitial O₂ (29 and 43), respectively. The O₂ concentrations were determined with $\pm 20\%$ accuracy by the intensities of singlet O₂ PL intensities relative to Raman bands, pre-calibrated²⁵ by comparison to O₂ thermal desorption data. Sample dimensions were $5 \times 10 \times 12 \text{ mm}^3$, all 6 faces were optically polished.

Instrumentation and measurement methods

For a direct excitation of $^1\text{O}_2$ luminescence, CW mode lasers, modulated by electro-mechanic 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.

$^1\text{O}_2$ 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" geometry³², 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 $^1\text{O}_2$ 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 calculated³²:

$$r = \frac{1-R}{1+2R}, \quad (2)$$

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} .[†]

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

* 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 calculations³².

† 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.

1 the case of time-resolved polarization measurements the emission monochromator was removed,
2 and additional filters were used to block any light outside the $^1\text{O}_2$ PL emission region. The
3
4 emitted light was collimated by BK7 glass aspheric lens, and then sequentially filtered by 4
5
6 filters: 1) interference 1100 nm long-pass edge filter (Edmund Optics EO 66-241); 2) interference
7
8 bandpass filter (1250-1300nm, EO 87-865); 3) silicon wafer of thickness 0.5 mm; 4) wire-grid
9
10 polarizer (Thorlabs WP25M-UB) to analyze the polarization of the emitted light. The light was
11
12 then focused on PMT by BK7 glass lens. The polarization of the excitation light was rotated by a
13
14 half-wave plate (1064 nm) or by rotating the laser case (766 nm).
15
16

17 For room-T to 14 K range measurements the sample was placed in vacuum in closed-cycle
18
19 He refrigerator; measurements at higher T were performed in air atmosphere. During the low- T
20
21 measurements, it was verified by changing the laser intensity that sample heating by laser does
22
23 not significantly affect the results.
24
25
26

27 Calculation methods

28 To support the experimental findings, we have performed electronic structure calculations based on
29
30 density functional theory (DFT). The principal task of calculations is to study rotational motion of
31
32 interstitial O_2 in glassy silica. Calculations have been performed using the VASP code^{33,34}. We have
33
34 employed the semi-local GGA (generalized gradient approximation) density functional of Perdew-
35
36 Burke-Ernzerhof (PBE) to describe the electronic structure³⁵. We have used the projector-
37
38 augmented-wave approach³⁶ with a plane-wave energy cutoff of 400 eV to describe electronic
39
40 wavefunctions. The Brillouin zone was sampled at the Γ point. In our calculations the O_2 molecule is
41
42 charge-neutral with a spin $S=1$. Our principal interest is to determine the potential energy surface for
43
44 the rotation of O_2 in silica, and we expect the potential energy surfaces for singlet and triplet oxygen
45
46 to be rather similar, since they have the same nominal electron configuration and therefore
47
48
49
50 similar electronic structure. This premise is supported by the negligible Stokes shift in the PL 9
51
52
53
54
55
56
57
58
59
60

1 spectra and by calculated close polarizabilities in both states. The polarizability in the excited singlet
2
3 *a* state is estimated as ~93% of that in the ground state of O₂ in organic solvents³⁷ and ~95%
4
5
6 ³⁷ or 96%³⁸ for gaseous O₂.

7
8 It is well documented³⁹⁻⁴¹ that the behavior of O₂ in various forms of silicon dioxide (e.g., α -
9
10 quartz, β -cristobalite, and various forms of amorphous SiO₂) can be very different. One of the
11
12 main factors determining this difference is the volume of interstitial voids. These volumes are on
13
14 average larger in amorphous SiO₂ than in crystalline SiO₂. Thus, it is important to use
15
16 representative structures of *a*-SiO₂ in computational studies of O₂ in SiO₂. In this work we have
17
18 employed the 144-atom model developed by Bongiorno and Pasquarello^{39,40}. The model has
19
20 been obtained via molecular dynamics simulations by quenching the amorphous structure from
21
22 the melt by first employing empirical force fields and then using density functional theory to
23
24 relax the final structure. The model consists of a random network of corner-sharing tetrahedra,
25
26 and reproduces the most important parameters of experimental amorphous SiO₂ structures, most
27
28 crucially, the density $\rho=2.2$ g/cm³, as well as pair distribution functions between different atom
29
30 types (Si-Si, O-O, and Si-O). More detailed information is provided in Refs.^{39,40}.

31 32 33 34 35 36 37 38 **Results**

39 40 **Temperature dependence of luminescence kinetics**

41 The decay kinetics of luminescence, excited at 766 nm, measured in the 15 K-503 K temperature
42
43 range are shown in Fig. 2. The emission intensity was measured with monochromator set at the
44
45 maximum of ¹O₂ PL band (1272 nm) and spectral resolution 10 nm. Even at the highest measurement
46
47 temperature (503 K) the emission was only partially quenched (Fig.3, inset). Measurements at higher
48
49 T's were hindered by an increasingly strong thermal radiation from sample surroundings swamping
50
51 the PL signal. The decay kinetics is close to mono-exponential, in accord
52
53
54
55
56
57
58
59
60

with the previous observations²⁶. The decay constant τ 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 τ and of the luminescence intensity are shown in Fig.3. The low-T limit value of τ , 1115 ms, denoted as τ_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-SiO₂ samples, where O_2 was excited by energy transfer from activator (to be published elsewhere).

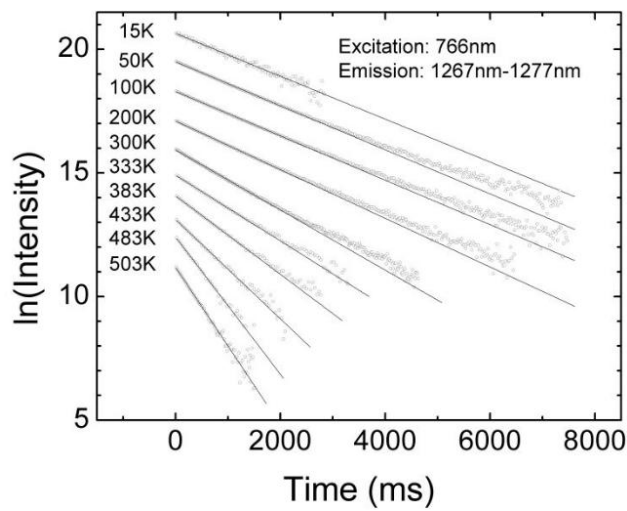


Fig. 2. Decay kinetics of 1O_2 luminescence in dry silica glass in temperature range 15 K-503 K. Exponential fits to the initial parts of kinetics, corresponding to intensity decay e^2 times, are shown by solid lines.

The temperature dependence of PL intensity at low T's, while generally following the changes of τ , 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 O_2 PL. Inset shows the measured temperature dependence of the PL intensity and of the PL decay constant.

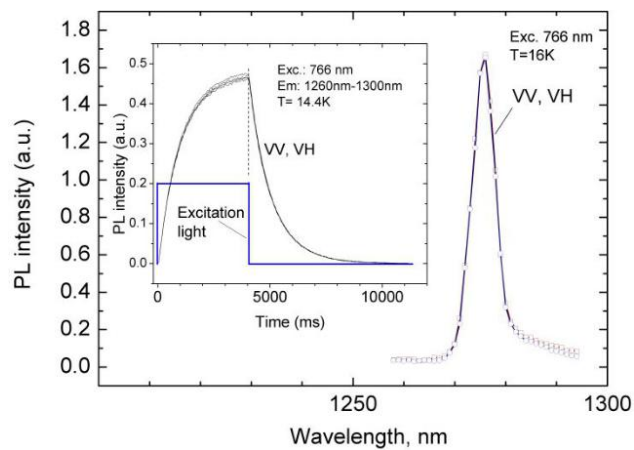
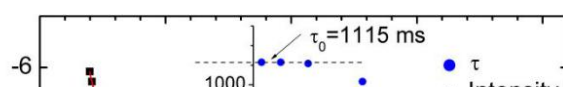


Fig.4. $^1\text{O}_2$ luminescence spectra of vertically (Vv) and horizontally (Vh) polarized components, excited by vertically (V) polarized 766 nm light at $T=16 \text{ K}$. Inset shows Vv and Vh component intensities, measured in time-resolved mode after cut-off of the excitation light. No measurable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

Luminescence polarization anisotropy

When excited by the 766 nm laser, the polarization anisotropy r (eq. 2) of $^1\text{O}_2$ PL is zero within the measurement accuracy ($\sim 0.6\%$). r does not increase at low temperature ($\sim 15 \text{ K}$): 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.

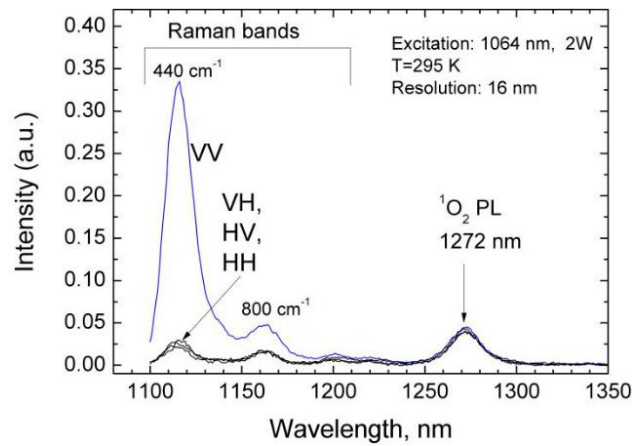


Fig.5. Strongly polarized fundamental 440 cm^{-1} and 800 cm^{-1} Raman bands and $^1\text{O}_2$ luminescence spectra of silica glass with embedded O_2 molecules, measured with linearly polarized 1064 nm excitation for Vv , Vh , Hv and Hh polarization components.

Room-temperature excitation at 1064 nm (Fig. 5) gives rise to strongly polarized (Vv) g-SiO₂ fundamental Raman bands and to a weaker $^1\text{O}_2$ 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.

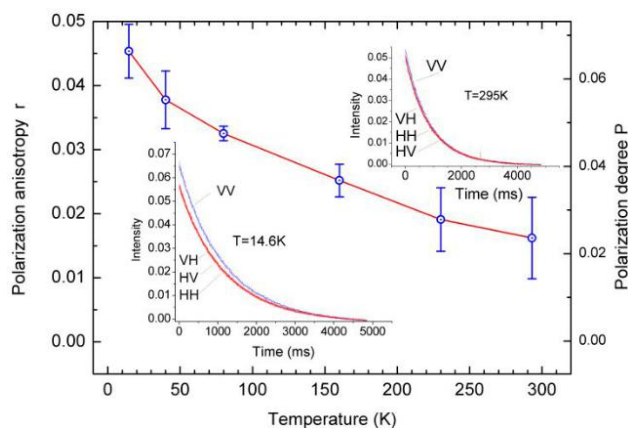


Fig.6. Temperature dependence of polarization anisotropy of $^1\text{O}_2$ luminescence measured by recording the luminescence decay intensities, integrated over 20 to 1840 ms interval after cut-off of the polarized 1064 nm excitation light. Insets show luminescence transients at $T=14.6$ and 295 K.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

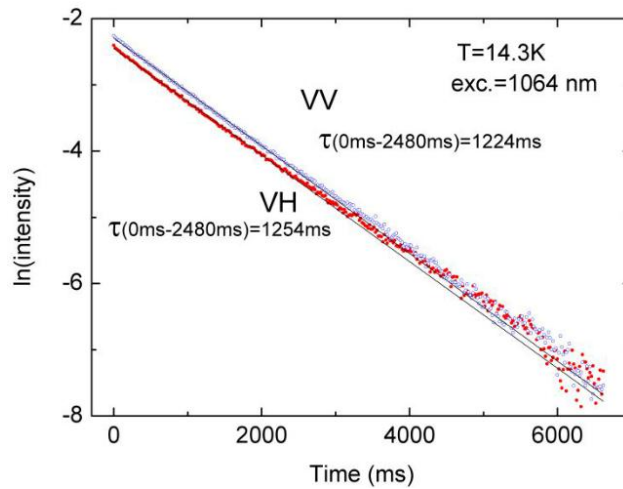


Fig.7. Comparison of decay kinetics of vertically (Vv) and horizontally (Vh) polarized components of $^1\text{O}_2$ luminescence under vertically polarized excitation at 1064 nm. The emission was collected in 1250 nm-1300 nm spectral range. Solid lines are fits to semilog scale data in 0 ms - 2480 ms range.

Calculation of interstitial O₂ rotation

g-SiO₂, as an amorphous material, is characterized by a wide distribution of interstitial voids³⁰. Volumes of the voids extend from approximately 25 Å³ (radius 1.8 Å) to more than 250 Å³, (radius ~4Å)³⁹⁻⁴¹, with the average volume being about 65 Å³ (radius 2.5 Å)³⁰. In contrast to *g*-SiO₂, the distribution of voids in α -quartz is very narrow, with an average volume of ≈ 33 Å³^{39,40}. The volume of interstitial voids has direct consequences on the energy of the interstitial O₂ molecule. It has been shown that there is a clear inverse correlation between the volume of the void and the energy of O₂ incorporation^{39,40}. In particular, this energy is ~3.5 eV for O₂ in α -quartz (volume 33 Å³), and reaches nearly zero when the volume becomes larger than about 125 Å³⁴⁰. Thus, under thermal equilibrium conditions O₂ in *g*-SiO₂ will reside in voids having the largest volumes. High

incorporation energy of O₂ in α-quartz is probably one of the reasons why, to the best of our knowledge, interstitial O₂ has never been observed in undamaged lattice of α-quartz.

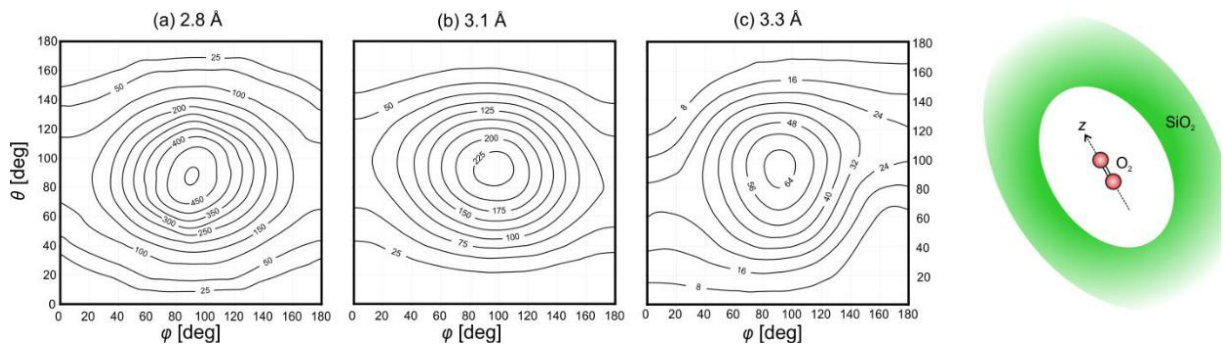


Fig. 8 . Contour plots describing the rotation barriers for an O₂ molecule in voids with radii of 2.8, 3.1 and 3.3 Å. The energy values are in meV.

Instead of trying to perform an extensive statistical analysis, our main goal is to answer the following qualitative question: is the rotation of O₂ 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 Å³ (radius 2.8 Å), 125 Å³ (radius 3.1 Å), and 150 Å³ (radius 3.3 Å), all of which are larger than the average void in silica. To investigate the rotational motion of O₂ in these voids, we calculated the potential energy surface of the O₂ molecule as a function of the spherical angles ϑ , φ . 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 (,) for the three voids are shown in Fig. 8. Due to the inversion symmetry of the molecule, the potential has the property (,) = (- , +), and thus it is sufficient to take the range of φ 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

1 orientation of the molecule lowers the energies by at most 15%, and therefore we discuss the
2 results of a frozen lattice here.

3 The calculated potential energy surface helps understanding the behavior of the rotational motion of the molecule at
4 different temperatures. Let us first discuss the behavior of the molecule in the void with radius 3.1 Å (Fig. 8(b)). At
5 cryogenic temperatures $\ll 10$ meV, and the orientation of the O₂ molecule is essentially frozen. At room temperature ≈ 25
6 meV, and now the
7 orientation of the molecule can exhibit vibrational motion in the solid angle of $\lesssim 1$, corresponding to $\lesssim 30$ degrees. The barrier for the molecule
8 to change from 0 to 180 degrees is ~ 80 meV. However, the total rotational motion of the molecule is partially hindered up to ≈ 200 meV (the
9 highest barrier in Fig. 8(b)), that means, under essentially all experimental conditions.

10 If we consider a smaller void (Fig. 8(a), radius 2.8 Å), the barriers are yet higher: the rotational
11 motion of the molecule is frozen at low temperatures, and only some wobbling around the
12 equilibrium orientation is allowed at room temperature. As the volume of the voids increases, the
13 rotational barriers tend to decrease. *E.g.*, for voids with radius 3.3 Å (Fig. 8(c)), those barriers can
14 become as small as 20 meV. This means that the rotational motion is still frozen at low
15 temperatures, but as the temperature approaches room temperature, molecules experience
16 substantial libration motion.
17
18
19
20
21
22
23
24
25
26
27

28 While, as discussed above, an exhaustive statistical analysis is not the aim of the present paper,
29 the analysis of the behavior of O₂ molecules in a few representative voids suggests that rotational
30 movement of O₂ molecules in voids, in which they are likely to reside, is frozen at low
31 temperatures, and partially allowed at room temperature.
32
33
34
35
36

37 To make sure that our computational setup is reliable regarding the rotational motion of
38 molecules in g-SiO₂, we have performed identical calculations for the H₂ molecule. There are
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

strong indications from Raman scattering studies that H₂ rotates nearly freely in g-SiO₂ at room temperature⁴². Indeed, we find that, *e.g.*, the highest barrier of rotation of H₂ inside the 3.1 Å radius void in g-SiO₂ is ~5 meV, compared to ~200 meV for the O₂ molecule. This means that the H₂ 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 O₂ in glassy SiO₂

The decay constant τ_{meas} of ¹O₂ PL in g-SiO₂, 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 O₂ 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 τ_{meas} values. The low-T saturation of τ_{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 $1/\tau_{\text{rad}}$:

$$\frac{1}{\tau_{\text{meas}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nr}}} \quad (3)$$

Our measured lifetimes are ≈ 1.6 times longer than those reported for ¹O₂ in O₂-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(1/τ_{meas}-1/τ₀) vs. 1/T, where τ₀ is the measured decay constant in the low-temperature limit.

Assuming τ₀=1115 ms (Fig. 3, inset), the activation energy of ≈1550 cm⁻¹ is obtained for the high-temperature thermal quenching (Fig.3). This energy is well above the highest fundamental vibration mode of g-SiO₂(~1200 cm⁻¹) and close to the vibration energy of O₂ molecule embedded in SiO₂: 1549 cm⁻¹ in the X ³Σ_g⁻ (ground) state ⁸ and 1493±20 cm⁻¹ in the a ¹_g excited state ⁹. That might indicate that the mechanism of high-temperature quenching of ¹O₂ PL involves the activation of O₂ 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 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 τ₀, 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±40 cm⁻¹ was obtained for O₂ in Aerosil particles ⁴³; (ii) this energy is close to the energy of the main Raman-band in g-SiO₂ (200...500 cm⁻¹, see, e.g., ref. ²⁴); (iii) coupling to SiO₂ vibration modes is demonstrated by phonon sidebands in high-resolution ¹O₂ PL spectra ⁸, showing that the involvement of the SiO₂ phonons in non-radiative decay is plausible.

It has been shown that the radiative rate of ¹O₂ PL can also be temperature-dependent⁴⁴. 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 τ_{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 τ₀ (1115 ms, Fig.3) is significantly smaller than the decay constant τ_{meas} ≈2150 ms, measured at *room* temperature for isotope-enriched ¹⁸O-¹⁸O

1 molecules in g-SiO₂⁴⁵. Evidently, the radiative lifetime τ_{rad} of ¹O₂ in g-SiO₂ must be at least 2150
2 ms. Assuringly, this lifetime is calculated to be around 3000 ms in the next section of the present
3 paper; and it is estimated between 0.7 and 5 s for O₂ dissolved in different liquids (Table 2).
4

5 The difference between τ_0 and τ_{rad} ($\tau_{\text{rad}}/\tau_0 > 2$) indicates that a significant thermally non-activated
6 quenching persists even at 15 K, and the PL quantum yield $\eta = \tau_0/\tau_{\text{rad}}$ is lower than ≈ 0.5 at T=15 K.
7

8 Adopting the estimate of $\tau_{\text{rad}} \approx 3000$ ms would yield $\eta = 0.37$ at T=15 K and $\eta = 860/3000 \approx 0.29$ at
9 room temperature. It is unlikely that the radiative rate $1/\tau_{\text{rad}}$ for ¹O₂ in SiO₂ could be much lower
10 than the values listed in Table 2, therefore the luminescence quantum yield τ_0/τ_{rad} of ¹O₂ in g-
11 SiO₂ should be surely larger than 0.1. To the best of our knowledge, it is then the largest reported
12 quantum yield for ¹O₂ PL in solids at room temperature.
13
14
15
16
17
18
19
20
21

22 **O₂ absorption cross sections and ¹O₂ radiative lifetime in glassy SiO₂**

23 Absorption cross sections σ of O₂ $b \rightarrow X$ and $a \rightarrow X$ transitions are extremely low, and for O₂ in various
24 solutions it has been possible to measure them only indirectly, by quantifying the photochemical effects of
25 singlet oxygen, created by direct $X \rightarrow a$ or $X \rightarrow b$ photoexcitation. Using this technique, σ for O₂ in different
26 solvents were recently re-examined in Ref. ¹⁴.
27

28 Fortunately, g-SiO₂ is peculiar not only as the matrix providing the longest ¹O₂ lifetime, but
29 also as a material for fiber optical waveguides, which due to their typically long optical paths are
30 sensitive to weak absorptions. Surprisingly, our analysis of literature data shows that σ for $X-a$
31 and $X-b$ transitions can be obtained *directly*, by supplementing the data on absorption of O₂ in
32 optical fibers, published more than two decades ago ^{18,46} with later spectroscopic work ^{24,25},
33 which allows to determine in hindsight the concentration of O₂ in these fibers (see supplement S1
34 for spectra and for details of their processing).
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 In optical fibers, produced in oxygen-rich conditions, two sharp optical absorption lines have
2 been observed⁴⁶: one at 1273 nm and the other at 765 nm (see Supplement, figure S1). Their
3 amplitudes and full widths at half maximum (FWHM) are listed in Table 1 (denoted as
4 "Experiment A"). The origin of these two lines was initially unidentified, however, their positions
5 and small FWHM's clearly show that they are due to $X \rightarrow a$ and $X \rightarrow b$ transitions of O₂ in silica.
6 They yield the ratio between the $X \rightarrow a$ and $X \rightarrow b$ absorption intensities (integrals I of absorption
7 bands): $I_{1272\text{nm}}/I_{765\text{nm}}=2.7 \pm 0.3$. Note that due to an extremely low absorption cross-section,
8 requiring km-long samples, direct measurements are only possible in optical fibers, making such
9 experiments unique.

10
11 The 765nm band in optical fiber was subsequently assigned to O₂¹⁸. This assignment was proved
12 by observing the sharp Raman line of interstitial O₂ at 1549 cm⁻¹ and the 765 nm optical absorption
13 band (Figs. S4 and S5 in Supplement) in *the same* optical fiber (Table 1, Experiment "B"). However,
14 the concentration of O₂ in that optical fiber was not known. Our later work^{24,25} allows to determine
15 the absolute concentration of O₂ in g-SiO₂, using the intensity of the O₂ Raman band relative to the
16 intensities of fundamental g-SiO₂ Raman bands. Hence, the concentration of O₂ in the fiber, studied
17 in experiment "B"¹⁸ can be determined in hindsight (2.4×10^{17} O₂/cm³, Table 1). Further, by
18 comparing the 765 nm absorption band integrals, the concentration of O₂ in the fiber used in
19 Experiment "A"⁴⁶ is calculated (Table 1). Since O₂ $X \rightarrow a$ and $X \rightarrow b$ absorption bands are clearly
20 visible in this fiber and their intensities α can be measured, their peak absorption cross sections
21 $\sigma = \alpha/[O_2]$ can now be finally obtained after a slight correction for lower spectral resolution in
22 Experiment B (see Supplement and footnote (c) under Table 1). Table 2 provides a comparison
23 between the obtained σ values for O₂ in g-SiO₂ and O₂ in different organic solvents. They are
24 reasonably similar. The accuracy of the cross sections for g-SiO₂ calculated in this paper (Tables 1, 2)
25 is limited by the accuracy, with which numerical values can be extracted from the published
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

absorption and Raman spectra of the optical fibers^{18,46}. 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 $\alpha(\nu)$ and concentration N of absorbing/emitting species is known, then for narrow, not Stokes-shifted absorption/emission spectra the radiative transition (emission) rate $1/\tau_{\text{rad}}$ can be calculated by Perrin's formula (e.g., refs.^{11,32})

$$\frac{1}{\tau_{\text{rad}}} = \frac{2\pi^2 N_A}{15} \frac{f_0}{n^2} \sum_i g_{\text{em}}^i \alpha(\nu_i) \quad (4)$$

where n is the refractive index of the medium; ν_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 $g_{\text{em}}/g_{\text{abs}}$ 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 ($m_s= \pm 1$) 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 $g_{\text{abs}}= 2/3$ for the X→a transition. Conversely, for the reverse a→X transition the statistical weight $g_{\text{em}}= 1$, since the only allowed

1 transition is to $m_S=0$ sublevel. Hence the ratio $g_{em}/g_{abs} = 3/2$ can be used for eq. (4). Substituting this
2 value, the absorption integral from Table I and the refractive index $n=1.447$ at 1272 nm in eq.(4) yields
3 $1/\tau_{rad} = 0.336 \text{ s}^{-1}$ or $\tau_{rad} \approx 3.0 \text{ s}$. The longest room-temperature lifetime of $^1\text{O}_2$ in g-
4 SiO_2 , reported in literature, is 2.1 s, measured for ^{18}O - ^{18}O molecules ⁴⁵. Therefore the
5 calculated τ_{rad} value, which is the upper limit for the experimentally observed lifetimes, is not
6 unreasonable. The estimates of τ_{rad} of $^1\text{O}_2$ in solvents range from 0.3 to 5 seconds ⁵ (and see
7 Table 2). In the present paper, the main sources of error are the uncertainties related to eq.(4) and
8 the accuracy of the concentration estimates, which mainly depends on the accuracy of the
9 published relatively weak 765 nm absorption band ¹⁸. In any case, these data demonstrate that
10 $X \rightarrow a$ and $X \rightarrow b$ transitions of $^1\text{O}_2$ can be directly studied with relatively high accuracy using O_2
11 -containing optical fibers. Such fibers are presently being developed for near-infrared
12 applications in radiation environments ²³ and for luminescent dosimetry applications ⁴⁷.
13
14
15
16
17
18

19 Character of the 1272 nm radiative transition

20
21
22
23 Quantum mechanical considerations, regarding the character of the lower optical transitions in
24 a free and perturbed O_2 have been recently summarized by Bregnhøj *et. al.* ¹¹ Their analysis
25 indicates that in a free O_2 molecule the strongest contribution to $a \rightarrow X$ transition is given by
26 magnetic dipole transition, while the additional contribution of electric quadrupole component is
27 much weaker ¹¹. The forbidden electric dipole transition is, however, more sensitive to
28 perturbations from the environment. When O_2 is perturbed by an external potential, the transition
29 can acquire electric-dipole character and can become up to ~1000 more intense than the magnetic
30 dipole component of $a \rightarrow X$ transition in the same perturbed O_2 molecule ¹¹.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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 ⁴⁸ 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 1O_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 ¹¹, 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 ($r=0.6\%$).

Rotation of O₂ in silica glass

O₂ molecules are tightly confined in interstitial voids. An extrapolation of the temperature-dependence of the O₂ diffusion coefficient ¹⁹ to room temperature yields diffusion length $L=(6Dt)^{1/2}$ of only ≈ 0.02 Å in 1 second, indicating that 1O_2 does not hop to neighboring void during its ~ 1 s lifetime. However, in principle this does not exclude its rotation within the containing void. In contrast to the case of interstitial H₂ molecules in g-SiO₂ ⁴², rotation-vibrational Raman bands of O₂ in g-SiO₂ have not been found ²⁴. The non-zero PL polarization anisotropy (Fig. 6) indicates a definite correlation between the orientations of O₂ molecule during the photo-excitation and during the emission, which occurs on average ≈ 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:³²

$$r = \frac{\langle \cos^2 \alpha \rangle - 1/3}{2/3} \quad (5)$$

where α 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 α 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 a^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 α 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 ϑ_0 , then $\langle \cos^2 \alpha \rangle = (1 + \cos^2 \vartheta_0)/4$ and, according to eq.(5), the resulting anisotropy is further decreased:

$$r = \frac{\langle \cos^2 \alpha \rangle - 1/3}{2/3} = \frac{(1 + \cos^2 \vartheta_0)/4 - 1/3}{2/3} \quad (6)$$

For $r = 4.5\%$ at 14.6 K and 1.6% at 295 K (Fig. 6), eq.(6) yields "average" angles ($\arccos(\langle \cos^2 \vartheta_0 \rangle)$) of O₂ axis deviation between absorption and emission events $\vartheta_0 \approx 37^\circ$ and $\vartheta_0 \approx 48^\circ$,

respectively. Note that the "baseline value", a completely chaotic tumbling of O₂ corresponds to

$\vartheta_0 = \arccos(3^{-1/2}) \approx 55^\circ$. While this result should be regarded as a merely qualitative one, it

may

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

give the idea of the magnitude of the fluctuation of O₂ molecular axis directions in interstitial voids of g-SiO₂.

Conclusion

The temperature-dependent polarization anisotropy of ¹O₂ luminescence in g-SiO₂ and DFT calculations demonstrate that O₂ 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 predictions¹¹.

The temperature dependence of ¹O₂ PL kinetics and its comparison to the radiative lifetime of ~ 3 seconds, deduced by an analysis of the O₂ optical absorption in fiber optical waveguides, allows to estimate that the ¹O₂ PL quantum yield is above 0.1. To our knowledge, this is the highest quantum yield for ¹O₂ 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 O₂ in g-SiO₂ interstitial voids helps to avoid the collisional quenching of excited ¹O₂ and contributes to the record-long lifetime of ¹O₂ at room temperature in g-SiO₂. However, it also slows down the diffusion of O₂. For applications in photobiology⁷, where both long lifetimes and long diffusion paths of ¹O₂ are desired, an optimization of the confinement degree may be useful and could be a subject for further studies.

Supporting Information Description

1
2
3 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
4 O_2 molecule trapped in silica glass.

5
6 Raman spectra of gaseous H_2 and H_2 in silica glass, illustrating the rotation of H_2 .
7
8

Acknowledgements

9
10
11 The support from M-ERANET project "MyND" is acknowledged. A. A., M. M-S., and L. R.
12 were supported by the Research Council of Lithuania (grant M-ERA.NET-1/2015). Authors
13 thank A. Pasquarello for providing the structures of the amorphous SiO_2 matrix for our
14 computational work and K. Kajihara (Tokyo Metropolitan University) for valuable advice in PL
15 kinetics measurements.
16
17
18
19
20
21
22
23
24
25

Figure Captions

26
27 Fig.1. Optical absorption and luminescence transitions observed $^{8-10}$ in interstitial O_2 molecule
28 embedded in glassy SiO_2 . The transitions studied in this work are indicated by bold arrows. The
29 transition wavelengths are in nm. Zero-field splittings ($\approx 4 \text{ cm}^{-1}$) 11 of both the triplet ground
30 state X ($v=0$) and its vibrational ($v=1$) sublevels are shown.
31
32
33
34
35
36
37
38

39
40 Fig. 2. Decay kinetics of 1O_2 luminescence in dry silica glass in temperature range 15 K-503 K.
41 Exponential fits to the initial parts of kinetics, corresponding to intensity decay e^2 times, are
42 shown by solid lines.
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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 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 $T=16 \text{ K}$. 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 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 O₂ 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 O₂ in Silica Glass Optical Fibers, Obtained from Analysis of Published Data ^{18,24,25,46}.

Experiment	1272 nm ($X \rightarrow a$) band			765 nm ($X \rightarrow b$) band			[O ₂] (O ₂ /cm ³)
	amplitude (db/km)	fwhm (cm ⁻¹)	integral db/km*cm ⁻¹	amplitude (db/km)	fwhm (cm ⁻¹)	integral db/km*cm ⁻¹	
A: ⁴⁶	15.11	105	1587	5.82	103	597	1.6×10^{18} ^{a)}
B: ¹⁸				0.45	180	89	2.4×10^{17} ^{b)}
C ⁹		93 (PL)			103 (PLE)		
D: ²⁴		86 (PL)					
peak σ ^{c)}	2.7×10^{-23} cm ²			0.84×10^{-23} cm ²			

^{a)} O₂ concentration obtained relative to the experiment B by scaling the $X \rightarrow b$ absorption band integrals

^{b)} O₂ concentration obtained by comparing the intensity ratio of the O₂ Raman line relative to the fundamental g-SiO₂ Raman band around 1600 cm⁻¹ (Experiment B) with a similar ratio, measured in Experiment D in a sample with known O₂ concentration.

^{c)} Peak absorption cross sections σ_{X-a} and σ_{X-b} were obtained using absorption band amplitudes from experiment A ⁴⁶ and the calculated O₂ concentrations. σ_{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 CrossSections σ of $X \rightarrow a$ (1272 nm) and $X \rightarrow b$ (765 nm) Transitions, and Radiative Decay Rates for $a \rightarrow X$ Transition.

Medium	$\sigma(1272 \text{ nm})$, (10^{-24} cm^2)	$\sigma(765\text{nm})$ (10^{-24} cm^2)	$k_r^{a-X} (\text{s}^{-1})$
silica glass	27 ^{a)}	8.4 ^{a)}	0.34 ^{a)}
water	6 ^{b)}	4.5 ^{b)} 5.1 ^{d)}	0.209 ^{e)}
toluene	27 ^{b)} 34.8 ^{c)}	6.7 ^{d)}	1.44 ^{d,e)}
benzene	25 ^{b)}		1.5 ^{d,e)}
CCl ₄	20 ^{b)}	2.7 ^{b)}	1.06 ^{d)} 1.17 ^{e)}
ethanol	10 ^{b)} , 17.7 ^{c)}	4.0 ^{b)}	0.55 ^{d,e)}
acetone	11.5 ^{b)} , 11.5 ^{c)}	3.7 ^{b)}	0.56 ^{d)} 0.543 ^{e)}

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

- (1) Jarvi, M. T.; Niedre, M. J.; Patterson, M. S.; Wilson, B. C. Singlet Oxygen Luminescence Dosimetry (SOLD) for Photodynamic Therapy: Current Status, Challenges and Future Prospects. *Photochem. Photobiol.* **2006**, 82 (5), 1198. <https://doi.org/10.1562/2006-05-03-IR-891>.
- (2) Li, B.; Lin, L.; Lin, H.; Wilson, B. C. Photosensitized Singlet Oxygen Generation and Detection: Recent Advances and Future Perspectives in Cancer Photodynamic Therapy. *J. Biophotonics* **2016**, 9 (11–12), 1314–1325. <https://doi.org/10.1002/jbio.201600055>.
- (3) van Straten, D.; Mashayekhi, V.; de Bruijn, H.; Oliveira, S.; Robinson, D.; van Straten, D.; Mashayekhi, V.; de Bruijn, H. S.; Oliveira, S.; Robinson, D. J. Oncologic Photodynamic Therapy: Basic Principles, Current Clinical Status and Future Directions. *Cancers* **2017**, 9 (2), 19. <https://doi.org/10.3390/cancers9020019>.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (4) Nosaka, Y.; Nosaka, A. Y. Generation and Detection of Reactive Oxygen Species in Photocatalysis. *Chem. Rev.* **2017**, *117* (17), 11302–11336. <https://doi.org/10.1021/acs.chemrev.7b00161>.
 - (5) Schweitzer, C.; Schmidt, R. Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chem. Rev.* **2003**, *103* (5), 1685–1758. <https://doi.org/10.1021/cr010371d>.
 - (6) Krasnovsky Jr., A. A. Luminescence and Photochemical Studies of Singlet Oxygen Photonics. *J. Photochem. Photobiol. Chem.* **2008**, *196* (2–3), 210–218. <https://doi.org/10.1016/j.jphotochem.2007.12.015>.
 - (7) *Singlet Oxygen: Applications in Biosciences and Nanosciences, Volume 1*, 1 edition.; Nonell, S., Flors, C., Eds.; Comprehensive Series in Photochemical & Photobiological Sciences; Royal Society of Chemistry: Cambridge, 2016.
 - (8) Skuja, L.; Güttler, B.; Schiel, D.; Silin, A. R. Infrared Photoluminescence of Preexisting or Irradiation-Induced Interstitial Oxygen Molecules in Glassy SiO₂ and α -Quartz. *Phys. Rev. B* **1998**, *58* (21), 14296–14304. <https://doi.org/10.1103/PhysRevB.58.14296>.
 - (9) Agnello, S.; Cannas, M.; Vaccaro, L.; Vaccaro, G.; Gelardi, F. M.; Leone, M.; Militello, V.; Boscaino, R. Near-Infrared Emission of O₂ Embedded in Amorphous SiO₂ Nanoparticles. *J. Phys. Chem. C* **2011**, *115* (26), 12831–12835. <https://doi.org/10.1021/jp2035554>.
 - (10) Kajihara, K.; Skuja, L.; Hosono, H. Diffusion and Reactions of Photoinduced Interstitial Oxygen Atoms in Amorphous SiO₂ Impregnated with ¹⁸O-Labeled Interstitial Oxygen Molecules. *J. Phys. Chem. C* **2014**, *118* (8), 4282–4286. <https://doi.org/10.1021/jp412606a>.
 - (11) Bregnhøj, M.; Westberg, M.; Minaev, B. F.; Ogilby, P. R. Singlet Oxygen Photophysics in Liquid Solvents: Converging on a Unified Picture. *Acc. Chem. Res.* **2017**, *50* (8), 1920–1927. <https://doi.org/10.1021/acs.accounts.7b00169>.
 - (12) Minaev, B. F. Spin-Orbit Coupling Mechanism of Singlet Oxygen a¹_g Quenching by Solvent Vibrations. *Chem. Phys.* **2017**, *483–484*, 84–95. <https://doi.org/10.1016/j.chemphys.2016.11.012>.
 - (13) Jockusch, S.; Turro, N. J.; Thompson, E. K.; Gouterman, M.; Callis, J. B.; Khalil, G. E. Singlet Molecular Oxygen by Direct Excitation. *Photochem Photobiol Sci* **2008**, *7* (2), 235–239. <https://doi.org/10.1039/B714286B>.
 - (14) Krasnovsky, A. A.; Kozlov, A. S. Photonics of Dissolved Oxygen Molecules. Comparison of the Rates of Direct and Photosensitized Excitation of Oxygen and Reevaluation of the Oxygen Absorption Coefficients. *J. Photochem. Photobiol. Chem.* **2016**, *329*, 167–174. <https://doi.org/10.1016/j.jphotochem.2016.06.026>.
 - (15) Bregnhøj, M.; Krægpøth, M. V.; Sørensen, R. J.; Westberg, M.; Ogilby, P. R. Solvent and Heavy-Atom Effects on the O₂(X³ Σ_g^-) \rightarrow O₂(b¹ Σ_g^+) Absorption Transition. *J. Phys. Chem. A* **2016**, *120* (42), 8285–8296. <https://doi.org/10.1021/acs.jpca.6b08035>.
 - (16) Bregnhøj, M.; Rodal-Cedeira, S.; Pastoriza-Santos, I.; Ogilby, P. R. Light Scattering versus Plasmon Effects: Optical Transitions in Molecular Oxygen near a Metal Nanoparticle. *J. Phys. Chem. C* **2018**, *122* (27), 15625–15634. <https://doi.org/10.1021/acs.jpcc.8b03387>.
 - (17) Skuja, L.; Kajihara, K.; Hirano, M.; Hosono, H. Oxygen-Excess-Related Point Defects in Glassy/Amorphous SiO₂ and Related Materials. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2012**, *286*, 159–168. <https://doi.org/10.1016/j.nimb.2012.02.038>.
 - (18) Carvalho, W.; Dumas, P.; Corset, J.; Neuman, V. Raman Spectra and Oxygen-Related Absorption Bands in Pure Silica Core Fibres. *J. Raman Spectrosc.* **1985**, *16* (5), 330–331. <https://doi.org/10.1002/jrs.1250160510>.
 - (19) Kajihara, K.; Kamioka, H.; Hirano, M.; Miura, T.; Skuja, L.; Hosono, H. Interstitial Oxygen Molecules in Amorphous SiO₂. III. Measurements of Dissolution Kinetics, Diffusion

Coefficient, and Solubility by Infrared Photoluminescence. *J. Appl. Phys.* **2005**, *98* (1), 013529. <https://doi.org/10.1063/1.1943506>.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (20) Lancry, M.; Poumellec, B.; Canning, J.; Cook, K.; Poulin, J.-C.; Brisset, F. Ultrafast Nanoporous Silica Formation Driven by Femtosecond Laser Irradiation: In the Heart of Nanogratings. *Laser Photonics Rev.* **2013**, *7* (6), 953–962. <https://doi.org/10.1002/lpor.201300043>.
- (21) Redkov, A. V.; Melehin, V. G.; Lipovskii, A. A. How Does Thermal Poling Produce Interstitial Molecular Oxygen in Silicate Glasses? *J. Phys. Chem. C* **2015**, *119* (30), 17298–17307. <https://doi.org/10.1021/acs.jpcc.5b04513>.
- (22) Skuja, L.; Kajihara, K.; Hirano, M.; Hosono, H. Crucial Dependence of Excimer Laser Toughness of “Wet” Silica on Excess Oxygen. *J. Non-Cryst. Solids* **2011**, *357* (8–9), 1875–1878. <https://doi.org/10.1016/j.jnoncrsol.2010.12.047>.
- (23) Kashaykin, P. F.; Tomashuk, A. L.; Salgansky, M. Y.; Abramov, A. N.; Iskhakova, L. D.; Lobanov, N. S.; Nishchev, K. N.; Guryanov, A. N.; Dianov, E. M. Silica Optical Fibers with High Oxygen Excess in the Core: A New Type of Radiation-Resistant Fiber. *Proc. SPIE* **2015**, *9507*, 950705(1-9). <https://doi.org/10.1117/12.2087317>.
- (24) Skuja, L.; Güttler, B.; Schiel, D.; Silin, A. R. Quantitative Analysis of the Concentration of Interstitial O₂ Molecules in SiO₂ Glass Using Luminescence and Raman Spectrometry. *J. Appl. Phys.* **1998**, *83* (11), 6106–6110. <https://doi.org/10.1063/1.367480>.
- (25) Kajihara, K.; Hirano, M.; Uramoto, M.; Morimoto, Y.; Skuja, L.; Hosono, H. Interstitial Oxygen Molecules in Amorphous SiO₂. I. Quantitative Concentration Analysis by Thermal Desorption, Infrared Photoluminescence, and Vacuum-Ultraviolet Optical Absorption. *J. Appl. Phys.* **2005**, *98* (1), 013527(1-6). <https://doi.org/10.1063/1.1943504>.
- (26) Kajihara, K.; Kamioka, H.; Hirano, M.; Miura, T.; Skuja, L.; Hosono, H. Interstitial Oxygen Molecules in Amorphous SiO₂. II. The Influence of Common Dopants (SiOH, SiF, and SiCl Groups) and Fictive Temperature on the Decay of Singlet Photoluminescence. *J. Appl. Phys.* **2005**, *98* (1), 013528. <https://doi.org/10.1063/1.1943505>.
- (27) Schmidt, R.; Afshari, E. Collisional Deactivation of O₂(¹g) by Solvent Molecules. Comparative Experiments with ¹⁶O₂ and ¹⁸O₂. *Berichte Bunsenges. Für Phys. Chem.* **1992**, *96* (6), 788–794. <https://doi.org/10.1002/bbpc.19920960610>.
- (28) Lee, P. C.; Rodgers, M. A. J. Kinetic Properties of Singlet Oxygen in a Polymeric Microheterogeneous System. *J. Phys. Chem.* **1984**, *88* (19), 4385–4389. <https://doi.org/10.1021/j150663a040>.
- (29) Jockusch, S.; Sivaguru, J.; Turro, N. J.; Ramamurthy, V. Direct Measurement of the Singlet Oxygen Lifetime in Zeolites by Near-IR Phosphorescence. *Photochem. Photobiol. Sci.* **2005**, *4* (5), 403–405. <https://doi.org/10.1039/b501701g>.
- (30) Zanatta, M.; Baldi, G.; Brusa, R. S.; Egger, W.; Fontana, A.; Gilioli, E.; Mariazzi, S.; Monaco, G.; Ravelli, L.; Sacchetti, F. Structural Evolution and Medium Range Order in Permanently Densified Vitreous SiO₂. *Phys. Rev. Lett.* **2014**, *112* (4). <https://doi.org/10.1103/PhysRevLett.112.045501>.
- (31) Steinert, S.; Ziem, F.; Hall, L. T.; Zappe, A.; Schweikert, M.; Götz, N.; Aird, A.; Balasubramanian, G.; Hollenberg, L.; Wrachtrup, J. Magnetic Spin Imaging under Ambient Conditions with Sub-Cellular Resolution. *Nat. Commun.* **2013**, *4* (1). <https://doi.org/10.1038/ncomms2588>.
- (32) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, Third edition.; Springer New York, 2006.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (33) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59* (3), 1758–1775. <https://doi.org/10.1103/PhysRevB.59.1758>.
- (34) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561. <https://doi.org/10.1103/PhysRevB.47.558>.
- (35) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (36) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953–17979. <https://doi.org/10.1103/PhysRevB.50.17953>.
- (37) Poulsen, T. D.; Ogilby, P. R.; Mikkelsen, K. V. Polarizabilities of the First Excited ($A\Delta_g$) and Ground ($X^3\Sigma_g^-$) States of Molecular Oxygen. *J. Phys. Chem. A* **1998**, *102* (45), 8970–8973. <https://doi.org/10.1021/jp981925s>.
- (38) Sharipov, A. S.; Loukhovitski, B. I.; Pelevkin, A. V.; Kobtsev, V. D.; Kozlov, D. N. Polarizability of Electronically Excited Molecular Oxygen: Theory and Experiment. *J. Phys. B At. Mol. Opt. Phys.* **2019**, *52* (4), 045101. <https://doi.org/10.1088/1361-6455/aaf9d9>.
- (39) Bongiorno, A.; Pasquarello, A. Oxygen Diffusion through the Disordered Oxide Network during Silicon Oxidation. *Phys. Rev. Lett.* **2002**, *88* (12), 125901. <https://doi.org/10.1103/PhysRevLett.88.125901>.
- (40) Bongiorno, A.; Pasquarello, A. Multiscale Modeling of Oxygen Diffusion through the Oxide during Silicon Oxidation. *Phys. Rev. B* **2004**, *70* (19), 195312(1-14). <https://doi.org/10.1103/PhysRevB.70.195312>.
- (41) Alkauskas, A.; Broqvist, P.; Pasquarello, A. Charge State of the O_2 Molecule during Silicon Oxidation through Hybrid Functional Calculations. *Phys. Rev. B* **2008**, *78* (16), 161305. <https://doi.org/10.1103/PhysRevB.78.161305>.
- (42) Hartwig, C. M.; Vitko, J. Raman Spectroscopy of Molecular Hydrogen and Deuterium Dissolved in Vitreous Silica. *Phys. Rev. B* **1978**, *18* (7), 3006–3014. <https://doi.org/10.1103/PhysRevB.18.3006>.
- (43) Agnello, S.; Vaccaro, L.; Cannas, M.; Kajihara, K. Temperature Dependence of O_2 Singlet Photoluminescence in Silica Nanoparticles. *J. Non-Cryst. Solids* **2013**, *379*, 220–223. <https://doi.org/10.1016/j.jnoncrysol.2013.08.016>.
- (44) Jensen, R. L.; Holmegaard, L.; Ogilby, P. R. Temperature Effect on Radiative Lifetimes: The Case of Singlet Oxygen in Liquid Solvents. *J. Phys. Chem. B* **2013**, *117* (50), 16227–16235. <https://doi.org/10.1021/jp410185n>.
- (45) Kajihara, K.; Miura, T.; Kamioka, H.; Hirano, M.; Skuja, L.; Hosono, H. Isotope Effect on the Infrared Photoluminescence Decay of Interstitial Oxygen Molecules in Amorphous SiO_2 . *Appl. Phys. Express* **2009**, *2*, 056502. <https://doi.org/10.1143/APEX.2.056502>.
- (46) Heitmann, W.; Bonewitz, H. U.; Mühlich, A. New Absorption Bands in Pure and F-Doped Silica Optical Fibres. *Electron. Lett.* **1983**, *19* (16), 616–617. <https://doi.org/10.1049/el:19830420>.
- (47) Di Francesca, D.; Girard, S.; Agnello, S.; Marcandella, C.; Paillet, P.; Boukenter, A.; Gelardi, F. M.; Ouerdane, Y. Near Infrared Radio-Luminescence of O_2 Loaded Radiation Hardened Silica Optical Fibers: A Candidate Dosimeter for Harsh Environments. *Appl. Phys. Lett.* **2014**, *105* (18), 183508. <https://doi.org/10.1063/1.4901340>.
- (48) Feofilov, P. P. *The Physical Basis of Polarized Emission*; Consultants Bureau: New York, 1961.
- (49) Sivéry, A.; Anquez, F.; Pierlot, C.; Aubry, J. M.; Courtade, E. Singlet Oxygen (1O_2) Generation upon 1270nm Laser Irradiation of Ground State Oxygen (3O_2) Dissolved in Organic Solvents: Simultaneous and Independent Determination of 1O_2 Production Rate and

Reactivity with Chemical Traps. *Chem. Phys. Lett.* **2013**, *555*, 252–257.
<https://doi.org/10.1016/j.cplett.2012.10.063>.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table of Contents Image

