Optical Absorption of Excimer Laser-Induced Dichlorine Monoxide in Silica Glass and Excitation of Singlet Oxygen Luminescence by Energy Transfer from Chlorine Molecules

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An optical absorption (OA) band of interstitial dichlorine monoxide molecules with peak at 4.7 eV and halfwidth 0.94 eV is identified in F₂ laser-irradiated (ℏω = 7.9 eV) synthetic silica glass bearing both interstitial O₂ and Cl₂ molecules. Alongside with intrinsic defects, this OA band can contribute to solarization of silica glasses produced from SiCl₄. Although only the formation of ClCIO is confirmed by its Raman signature, its structural isomer ClOCl may also contribute to this induced OA band. Thermal destruction of this band between 300 °C and 400 °C almost completely restores the preirradiation concentration of interstitial Cl₂. An additional weak OA band at 3.5 eV is tentatively assigned to ClO₂ molecules. The strongly forbidden 1272 nm infrared luminescence band of radiation-induced interstitial molecules located in neighboring nanosized interstitial voids in the structure of SiO₂ glass network.

1. Introduction

Synthetic SiO₂ glass is the dominant optical material for ultraviolet (UV) applications. The decrease in its transparency due to UV-irradiation (“solarization”) is caused by generation of point defects. The separate components of the typically broad UV optical absorption (OA) spectrum in the 4–7 eV range are still not completely identified. The main UV-absorbing intrinsic defects are oxygen dangling bonds (“nonbridging oxygen hole centers,” NBOHCs) with broad OA bands at 4.8 eV and higher energies[6] and different variants of silicon dangling bonds (E-centers) with OA bands at 5.8 eV ± 0.1 eV.[6] At higher energies, additional absorption is caused by bound hydroxyl (silanol, ≡Si–O–H) or chloride groups (≡Si–Cl), which are typically present in (often referred as “high-purity”) synthetic silica due to the manufacturing from SiCl₄ precursor and optional use of H₂–O₂ flame pyrolysis. This OA is unproblematic for many UV applications, since its onset is at photon energies in vacuum UV range: ℏω > 7.3 eV for SiOH groups[3–5] and ≥6.7 eV for ≡Si–Cl groups.[6] However, in “dry” (low OH concentration) silicas, part of chlorine impurities form interstitial Cl₂ molecules, which give rise to a weak near-UV OA band at 3.8 eV[6] and to an associated structured Cl₂ photoluminescence (PL) band at 1.23 eV.[7]

The peak absorption cross section σ of the 3.8 eV OA band is relatively small (2.6 × 10⁻¹⁷ cm² for free Cl₂ molecules). Therefore, this band is of practical importance mostly in fiber optics geometry, where it severely limits the UV transparency of commercial dry silica multimode optical fiber waveguides for visible-to-infrared applications.[8] Another weak chlorine-related OA band appears at 3.26 eV in irradiated optical fibers, which is tentatively assigned[9,10] to radiation-induced interstitial chlorine atoms Cl⁰, previously identified by electron paramagnetic resonance (EPR).[11]

However, chlorine-related species with possibly much stronger OA can form in silica. In the copresence of interstitial Cl₂ and O₂ molecules, creation of dichlorine monoxide ClCIO molecules by 157 nm irradiation was detected in Raman spectra.[7] OA band of ClCIO isolated in Ar matrix at T = 17 K is located at λ = 260 nm (4.77 eV) with a large peak absorption cross section σ = 1.3 × 10⁻¹⁷ cm².[12] It is ~50 times higher than σ of 3.8 eV OA band of Cl₂, and therefore, ClCIO creation in principle can significantly contribute to the UV solarization of silica. Although there is no direct Raman evidence for the other structural isomer of dichlorine monoxide, ClOCl in silica glass, its formation, and possible contribution to solarization should be considered too.
The purpose of this work was to elucidate the UV absorption band of ClClO, ClOCl, or other chlorine oxide molecules in silica glass, and to investigate the conditions under which they can form.

2. Experimental Section

2.1. Samples and Irradiation.

Oxygen-excess “dry” silica glasses, synthesized by oxidizing SiCl₄ in oxygen plasma, were used. They contained relatively large concentrations of interstitial O₂ and Cl₂ molecules and traces of silanol groups (see Table 1, Samples “A”, “B”... “F”). The concentration estimates of Cl₂ were based on Raman/PL spectra, as described in the study by Kajihara et al. [13]; an approximate estimate of Cl₂ was obtained from the amplitude of the 3.8 eV OA band, using peak absorption cross section σ = 2.58 x 10⁻¹⁹ cm² for Cl₂ in gas phase. [14] The possible (≈20%) increase in σ due to effective field in SiO₂ matrix was neglected. Samples A–E were experimental ones [15]; sample F was of commercial “Suprasil W1” type. Historically, glass of this type had served for numerous past studies as a “benchmark” type of dry synthetic silica glass. Concentration of Cl₂ in this sample was below our detection limit. Samples were optically polished, thickness 5 mm (A–E) and 2.54 mm (F).

Sample “A” was irradiated in a vacuum chamber, kept at vacuum ≈0.2 mPa by oil-free turbomolecular pump. Irradiation was performed using F₂ excimer laser (Lambda Physik LPF-210) emitting 7.9 eV (157 nm) photon pulses with length ≈20 ns and power density 19.6 mJ cm⁻² at repetition rate 50 pulses s⁻¹. The irradiation duration was 120 s, resulting in a cumulative fluence of 117.6 J cm⁻² or 9.3 x 10¹⁵ photons cm⁻². The sample was etched in diluted (1%) HF for 30 s to remove the slight surface contamination caused by photolysis of residual vapors in the vacuum chamber. All subsequent measurements were performed in air.

2.2. Instrumentation

Luminescence excitation sources were 3rd harmonic (355 nm, 3.49 eV) of Q-switched Nd-YAG laser (Spectra Physics Quanta Ray/Indi), pulse length 10 ns, energy in the range 1.5, 4.4 mJ; 385 nm UV light-emitting diode (LED) (Nichia U385) with 800 mW flux, 766 nm continuous wave (CW) diode laser (Leading Tech ADR1805, maximum power 600 mW).

Singlet O₂ singlet luminescence band at 1270 nm was measured using 355 nm excitation and Andor SR193 spectrograph with DU490 InGaAs diode array camera (spectral resolution 8 nm). In the cases of 385 nm and 766 nm excitation, PL spectra and PL decay curves were measured by a scanning 200 nm monochromator (spectral resolution 5 nm) and Hamamatsu R5509-43 liquid N₂-cooled near-infrared photomultiplier tube (PMT) or cooled photodiode (G12180-220 A). The slow (seconds-range) PL decay was measured by pulsed excitation and signal integration by multichannel photon counter (Fast ComTec 7822) or by analog waveform recorder (Agilent 34410 A). Pulsed excitation was provided by mechanical shutter (766 nm excitation) or by driving the LED current (385 nm excitation).

OA spectra were obtained using Hamamatsu 10082CAH charge-coupled device (CCD) spectrograph with spectral resolution 1.5 nm and deuterium lamp (Ocean Optics). All measurements were performed at room temperature.

Raman spectra were taken with an aim to detect small irradiation-induced changes on the background of the fundamental Raman spectrum of silica glass. This required particularly high temporal stability and high signal/noise ratio. The spectra were taken in backscattering geometry using 532 nm laser and CCD spectrograph (Andor Newton DU971N/ Shamrock SR303i). Details of the hardware and the measurement procedure are described in our previous study. [7]

3. Results

3.1. Optical Absorption

OA spectra of pristine and F₂ laser-irradiated sample (“A” in Table 1) are shown in Figure 1. Nonirradiated sample (trace 1) shows only the well-known Gaussian-shaped OA band of interstitial Cl₂ molecules at 3.78 eV with full width at half maximum (fwhm) 0.70 eV [14,16,17] and a shoulder of OA bands deeper in vacuum-UV. F₂ laser irradiation gives rise to a distinct band at ≈4.8 eV and to a slight decrease at 3.8 eV (trace 2). In the induced (difference) OA spectrum (trace 3), this decrease is more distinct, causing a negative-going peak at 3.8 eV. It can be compensated for by adding an appropriately scaled (amplitude 0.06 cm⁻¹) Gaussian band with peak energy (3.78 eV) and fwhm (0.70 eV), corresponding to OA of Cl₂ molecules (trace 4). The low-energy wing of the resulting sum spectrum (trace 5) can be approximated by a Gaussian (trace 6) with peak at 4.72 eV, fwhm 0.83 eV.

Table 1. Concentrations of interstitial O₂, Cl₂ molecules, and bound hydroxyl groups SiOH in as-received synthetic SiO₂ glass samples used in this article. Concentrations are given in 10⁻¹⁷ cm⁻³ units. The right-hand column gives relative intensities of singlet O₂ infrared PL (1272 nm, 0.974 eV), excited at 385 nm.

| Sample | O₂    | Cl₂   | SiOH  | PL  | O₂  |
|--------|-------|-------|-------|-----|-----|
| A      | 4.3   | 10.4  | 0.5   | 41.9|     |
| B      | 4.2   | 6.4   | 0.5   | 16.9|     |
| C      | 2.9   | 6.6   | 0.5   | 21.15|     |
| D      | 4.5   | 1.3   | 0.5   | 4.91|     |
| E      | 2.8   | 0.7   | 0.5   | 1.95|     |
| F      | 3.2   | <0.2  | <0.5  | 1.07|     |
300 °C brings relatively small changes in OA spectrum (Figure 3, trace 3), there is a negative dip at \( \approx 3.5 \) eV meaning that some absorbing species are created by annealing. Figure 4, trace 1, shows the strong OA component, annealed out between 300 and 400 °C. It is nearly Gaussian and, at the first glance, similar to the main OA component annealed at 200 °C (Figure 3, trace 1). However, it is slightly redshifted (peak at 4.7 eV) and broader (fwhm 0.94 eV). A more distinctive difference from the OA component annealed at 200 °C is the negative peak at 3.8 eV, which shows that OA band with a peak close to this energy is restored by annealing.

3.2. Raman Scattering Spectra

Alongside with OA measurements, Raman spectra of sample “A” were taken after each isochronal thermal annealing step. Since the purpose was to identify the minor signatures of the decaying species, an utmost care was taken to ensure repeatability and low noise (see the study by Skuja et al.\[7\] for details). The bottom trace in Figure 5 shows a typical Raman spectrum, which, viewed at this magnification scale, remained the same during the entire isochronal annealing series. However, the fine differences between spectra taken before and after each annealing step, plotted at \( \approx 50 \times \) magnification, show a number of bands (Figure 5, right side). Some of them, in particular the “peak derivative”-shaped bands are evidently related to slight spectral shifts of the fundamental Raman bands. The largest ones, which occur into the 300–600 cm\(^{-1}\) range, are not shown here. The exact
spectral positions of these bands are very sensitive to the accuracy of intensity normalization before performing the subtraction of the spectra. In contrast, the difference spectra can be calculated reliably in the flat spectral regions of low fundamental scattering intensity. Two narrow lines can be identified in the difference spectra: at 1550 and at 955 cm\(^{-1}\) (Figure 5). Their intensities are very weak. For example, the integral intensity of the 955 cm\(^{-1}\) line (marked by red circle in Figure 5) is \(\approx 2 \times 10^{-5}\) from the integral intensity of the entire Raman spectrum.

3.3. Infrared PL

During the Raman experiments with samples A–F, it was unexpectedly observed that under 3rd harmonic pulsed Nd-YAG laser excitation (355 nm, 3.49 eV) they emit infrared PL at 1272 nm (0.97 eV) (Figure 6, trace 1). This PL band is a fingerprint of widely studied species, an excited metastable singlet state \(\text{O}_2\) molecule (see, e.g., the article by Bregnhøj et al.\cite{18} for overview and references). It is much studied in silica as well (e.g., the article by Skuja et al.\cite{19}). Its excitation in 300–400 nm spectral region was unexpected, since \(\text{O}_2\) molecule has no electronic states there.\cite{20} By varying the pulse intensities, it was verified that the dependence of PL intensity on pulse energy is slightly sublinear, ruling out the 2-photon excitation. This PL was observed in pristine samples, not exposed to vacuum ultraviolet photons. The PL intensity was stable in time, its photobleaching or enhancement under 355 nm laser irradiation was not observed. Furthermore, this PL band was observed also with 385 nm (3.22 eV) CW LED excitation (trace 3) and—as expected—with the previously reported (e.g., the studies by Bregnhøj et al. and Skuja et al.\cite{18,19}) “direct” 766 nm (1.618 eV) laser excitation of \(\text{O}_2\) (trace 2). The slight differences in the PL band FWHM and peak positions evident in Figure 6 are not meaningful at the present accuracy level. The larger measured halfwidth (FWHM) of PL excited at 355 nm (trace 1) is probably due to lower spectral resolution in this case.

The intensities of the 1272 nm PL band in different samples (A–F) were checked using the 385 nm excitation, and the results were plotted in correlation with the respective concentrations of \(\text{Cl}_2\) and \(\text{O}_2\) in the samples (Figure 7, panels 1 and 2).

Decay of the 1272 nm PL intensity was compared using either 385 or 766 nm excitation in “high \(\text{Cl}_2\)” sample “A” (Figure 8, traces 1,2), and between sample “A” and the “low-\(\text{Cl}_2\)” sample “E”, using 766 nm excitation (traces 2 and 3). The kinetics only

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**Figure 4.** OA in “high-\(\text{Cl}_2\)” sample “A” destroyed by thermal annealing between 300 and 400 °C. Difference spectrum (trace 1), the putative Gaussian component due to the recovery of interstitial \(\text{Cl}_2\) (trace 2, see text), difference spectrum, compensated for the recovery of \(\text{Cl}_2\) (trace 3 = (trace 1) − (trace 2)), Gaussian fit to the main peak of trace 3 (trace 4, peak: 4.686 eV, FWHM: 0.935 eV, height = 0.552 cm\(^{-1}\)).

**Figure 5.** Effects of 15 min isochronal annealing steps on Raman spectrum of \(\text{F}_2\)-laser-irradiated silica glass (‘sample A’). The bottom trace represents the fundamental Raman spectrum, which remains almost unchanged by the annealing. The subtle differences introduced by the annealing are shown magnified (×54.4) above at right. The lowest difference spectrum (“20C–low-\(\text{Cl}_2\)” ) is obtained by subtracting the Raman spectrum of a similarly sized sample with a lower \(\text{Cl}_2\) concentration (sample “D” in Table 1).

**Figure 6.** Infrared PL spectra of unirradiated sample B, measured at room temperature with excitation by: (1) pulsed laser at 355 nm, (2) CW laser at 766 nm, and (3) unfiltered light of CW LED (peak at 385 nm, FWHM = 11 nm). Spectral resolution: 8, 5, 5 nm, respectively. Inset shows the absorption spectrum of this sample with \(\text{Cl}_2\) absorption band; arrows indicate the excitation wavelengths.
slightly deviate from exponential ones. To enable comparison between them, the decay constants $\tau$ are calculated by linear fit to semilog plots over the dynamic range of $e^{-3}$ ($\approx 20$ times), they are indicated in Figure 8.

4. Discussion

4.1. Optical Absorption of Dichlorine Monoxide(s) and Chlorine Dioxide

The main effect of $F_2$ laser-irradiation on OA spectrum is a distinct band at 4.7 eV with fwhm 0.83 eV (Figure 1). The 4.5–5.5 eV spectral range is very complex in silica, with many OA peaks located there. For example, OA peaks of interstitial ozone ($O_3$) molecules and of oxygen dangling bonds (NBOHCs) are both located at 4.8 eV, distinguished only by different fwhm (0.83 and 1.07 eV, respectively$^{[21]}$). The induced OA peak in Figure 1 is thus very similar to $O_3$ OA peak; however, it is redshifted by 0.1 eV. As shown by isochronal annealing data (Figure 2), the induced OA consists of two major components in this spectral region, one of which is stable up to 200 °C and another up to 400 °C.

The negative-going “dip” in the difference spectrum (trace 3 in Figure 1) at the position of $Cl_2$ OA band, 3.78 eV can be compensated by adding $Cl_2$ OA peak with an amplitude of 0.06 cm$^{-1}$ (traces 4 and 5). Using peak absorption cross section of $Cl_2$ molecules$^{[14]}$ $\sigma = 2.6 \times 10^{-19}$ cm$^2$, it can be estimated that $2.3 \times 10^{17}$ $Cl_2$ cm$^{-2}$ have been destroyed by irradiation.

The component of the induced OA, which is destroyed by annealing at 200 °C, has a position and fwhm almost coinciding with those of the ozone band (Figure 3). The half-life of gaseous $O_3$ molecules is 1.5 h at 120 °C and 1.5 s at 250 °C$^{[22]}$. Interstitial $O_3$ in silica glass has been shown to be destroyed in 10 min at 200 °C$^{[23]}$. Creation of $O_3$ in excimer laser-irradiated oxygen-rich silica has been observed in many studies$^{[16,21,23]}$. Therefore, the 4.8 eV OA component in Figure 3 can be reasonably assigned to $O_3$. Using the $O_3$ peak absorption cross section $\sigma = 1.2 \times 10^{-17}$ cm$^2$,$^{[21]}$ it can be estimated that $2.5 \times 10^{16}$ $O_3$ molecules were present. This means that less than 10% of the initially present $O_2$ molecules ($4.3 \times 10^{17}$ cm$^{-4}$) have been converted to $O_3$ by laser irradiation.

Figure 7. Relations between the intensities of UV-excited singlet $O_2$ PL measured in different samples (A–F, see Table 1) and the respective concentrations of interstitial Cl$_2$ (top panel), of interstitial O$_2$ (middle panel), and the product of their concentrations [O$_2$] [Cl$_2$] (bottom panel). Lines are least-squares linear fits; the outlier data point C in the bottom panel was not included in the fit. The inset in the middle panel shows the data of Table 1, indicating an absence of correlation between the concentrations of $O_2$ and $Cl_2$ in the sample set. Excitation: by 385 nm (3.22 eV) CW LED.

Figure 8. Comparison between singlet $O_2$ PL decay kinetics in cases of energy-transfer excitation (1) and direct excitation (2), and between samples with different concentrations of interstitial $Cl_2$ molecules (traces 2 and 3). The solid lines indicate linear fits to semilog scale kinetics plots. The plots are vertically offset for visibility.
Although the changes in OA, introduced by the 300 °C annealing step, are relatively small (Figure 2), noteworthy is the increase in OA in the 3–4 eV range, which indicates a creation, instead of destruction, of some absorbing species. At the first glance, the best candidate can be the interstitial Cl₂ molecule with its 3.8 eV OA band. However, a closer examination of the corresponding negative peak in difference spectrum (Figure 3, trace 3) shows that it cannot be matched by the Cl₂ OA band (3.78 eV/0.70 eV fwhm) and a wider component at lower peak energy (≈3.5 eV) is necessary.

Paramagnetic chlorine dioxide molecule (radical) ClOCl in gas phase has UV absorption, which can be approximated by a Gaussian band at 3.53 eV, fwhm 0.79 eV. This band is drawn in Figure 3 (trace 4), with amplitude scaled to match the negative dip in the difference spectrum (trace 3). Within the limitations of the relatively poor signal/noise ratio of the experimental data (trace 3), the match can be regarded as satisfactory. Presently, there are no OA bands known in silica at this position and with this fwhm. Therefore, the weak ≈3.5 eV OA band, enhanced by the thermal treatment at 300 °C, can be tentatively assigned to creation of interstitial ClOCl molecules in Cl-containing oxygen-rich silica. By using the amplitude of the band 0.032 cm⁻¹ (trace 4 in Figure 3) and peak absorption cross section of ClOCl ², 1.2 × 10⁻¹⁵ cm², their concentration can be estimated as ≈3 × 10¹⁵ molecules cm⁻³.

This assignment is further supported by previous EPR study of Cl-containing F₂-laser irradiated silica, where the creation of interstitial OClO (ground state spin S = 1/2) molecules was unambiguously proved. OA spectra and their correlation with EPR signal intensities were not studied in that work. However, the isochronal annealing pattern of the EPR signal of OClO (Figure 7 in the study by Nishikawa et al.) is in accord with the behavior of the 3.5 eV OA band, assigned in the present work to ClOCl: both signals increase significantly on heating between 200 and 300 °C, have maximum intensities at 300 °C, and decay on heating to 400 °C (See Figure 4, trace 3 in the following section).

The second major induced OA component is destroyed between 300 and 400 °C (Figure 2), compared to the interstitial ozone OA band (Figure 3, trace 1) it is slightly (0.1 eV) redshifted and wider (peak at 4.69 eV, fwhm 0.94 eV, Figure 4). Although this is per se only a marginal difference from the ozone OA band in Figure 3, there are two additional and more distinct features.

First, Raman spectra show that species giving rise to a line at 955 cm⁻¹ are destroyed between 300 and 400 °C. (Figure 5, the red circle). Resonance Raman peak at 954 cm⁻¹ has been assigned to Cl–Cl–O molecules in solid argon, similar Raman peak at 953.5 cm⁻¹ has served as a proof of their presence in F₂-laser irradiated silica.⁷

Second, the OA spectrum of the component destroyed at 300–400 °C (Figure 4, trace 1) clearly shows a restoration of 3.8 eV OA band due to Cl₂ molecules. An assumption that the amplitude of the restored Cl₂ OA is equal to that of the irradiation-destroyed absorption (Figure 1, trace 4, 0.06 cm⁻¹) seems to be reasonable: an addition of an OA band of this magnitude to the difference spectrum (subtracting trace 2 from trace 1 in Figure 4) gives just the right amount to eliminate the dip at 3.78 eV (trace 3). This clearly indicates that some Cl-containing species are destroyed and Cl₂ molecules are restored at the 400 °C annealing step.

In addition, the remaining broad shoulder in the 3 to 4 eV region of trace 3 indicates that the broad OA band at these energies, assigned above to OClO is destroyed at 400 °C.

The thermal destruction of both the OA component 4 in Figure 4 and the Raman signal of ClClO (Figure 5) at 400 °C step provides a seemingly strong evidence that interstitial ClClO molecules are responsible for the induced absorption at 4.7 eV and fwhm ≈0.94 eV, and that the laser-assisted destruction of Cl₂ molecules proceeds by photolysis of O₂ and reaction of O atom with Cl₂

\[
O₂ + Cl₂ + h\omega(7.9 eV) \rightarrow O + O + Cl₂ \rightarrow ClClO + O
\]  

where the remaining atomic oxygen can form peroxy linkage (Si–O–O–Si bond) in silica network or, alternatively, can enter in some other photolytic reaction.

Figure 9 shows the comparison between the OA in silica (trace 1) and OA band of ClClO in argon (trace 2) with peak at 4.8 eV. The ≈0.1 eV peak shift (4.7 vs 4.8 eV) can be explained by the effect of the polarizability of the embedding medium (bathochromic shift), which is larger in SiO₂ as compared to Ar crystal.

There is, however, a discrepancy in this otherwise consistent picture. The published OA band of ClClO (1.3 × 10⁻¹⁷ cm²) is 50.4 times higher than \(σ = 3.78 eV\) Cl₂ OA band (2.58 × 10⁻¹⁹ cm²). Therefore, the laser-induced destruction of 0.06 cm⁻¹ of Cl₂ OA band by converting Cl₂ to ClClO should introduce a ClClO OA band of 3.0 cm⁻¹, ≈5× larger than the actually created OA band (Figure 9, trace 1). There exists a structural isomer of ClClO, the symmetric ClOCl molecule, which is thermodynamically more stable and has lower \(σ = 1.94 \times 10⁻¹⁸\) cm² for OA peak at 4.86 eV, only four times larger than that of Cl₂. The shape of ClOCl OA is shown by trace 3 in Figure 9. If all destroyed Cl₂ molecules would form ClOCl, then the amplitude of the induced OA band would be only ≈0.24 cm⁻¹, much smaller than the amplitude (0.55 cm⁻¹) of the actually induced OA band. Therefore, we suggest that the induced OA band in Figure 9 originates from a mixture of both structural isomers, Cl–Cl–O and Cl–O–Cl. Only one of them,

![Figure 9. Comparison of the OA component, destroyed between 300 and 400°C (trace 1, the same as trace 3 in Figure 4) with the reported absorption spectra of dichlorine monoxide structural isomers: Cl–Cl–O in Ar matrix (trace 2) and Cl–O–Cl in gas phase (trace 3).](image-url)
ClClO is detected in Raman spectra (Figure 5) because the Raman band of Cl–O–Cl is weaker and lays in the “nonflat” spectral region (bands at 634 and 672 cm\(^{-1}\)) where an accurate measurement of low-intensity difference spectra is unreliable. The difference in spectral shapes of traces 1 and a linear combination of traces 2 and 3 (Figure 9) can be attributed to bathochromic shifts and inhomogeneous broadening (typically of \(\approx 0.1\) eV) in silica glass matrix.

4.2. Cl\(_2\)–O\(_2\) Energy Transfer

The luminescence of singlet state O\(_2\) molecules (\(^{1}S_{0}\)) is notoriously difficult to photoexcite directly because the transitions from the ground state to its two lowest electronic excited states are strongly forbidden, both by spin and by parity rules,[130] and reasonably strongly allowed transitions (\(\sigma > 10^{-26}\) cm\(^3\)) start only at photon energies in the vacuum UV range (\(h\nu > 6.5\) eV).[205] Therefore, the vast majority of Cl\(_2\) molecules employ activators (“photosensitizers”) to transfer the absorbed photon energy to a nearby O\(_2\) molecule. Studies of direct excitation to the two lowest electronic excited states (optical transitions at 0.97V and 1.62 eV) are less numerous (see review[285]). In the case of interstitial O\(_2\) in silica the situation is reverse: in numerous past studies of bulk glass (see the article by Skuja et al.[19] for references) or nanoparticles,[29] only the direct photoexcitation of O\(_2\) has been reported for photon energies below 6.4 eV. However, \(^{3}\)O\(_2\) PL in silica is excited also in processes involving excitons or electron–hole recombination, caused by electron.[30] or X-ray[31] irradiation, and in photolysis of interstitial O\(_2\) molecules.[21]

Therefore, the observation of PL band of \(^{3}\)O\(_2\) under 355 nm (3.49 eV) pulsed Nd:YAG laser excitation (Figure 6, trace 1), which falls into photon energy range, void of O\(_2\) excited states,[29] led one to suspect two-photon excitation. However, the sublinear excitation power dependence (Section 3.3) and the excitation of \(^{3}\)O\(_2\) PL by CW light at 385 nm (Figure 6, trace 2) clearly indicates that an energy transfer to O\(_2\) molecule from some “activator” species absorbing in the 3–4 eV range takes place. The low-energy wing of the OA band of interstitial Cl\(_2\) molecules (Figure 1, trace 1) covers this range. Multiple different silica glass samples, apart from those listed in Table 1, having different stoichiometries and irradiation histories were tested, and it was found that the most intense UV-excited PL of \(^{3}\)O\(_2\) is observed in samples containing both O\(_2\) and Cl\(_2\). That strongly hints that energy transfer from Cl\(_2\) to O\(_2\) takes place.

Absorption of photon of 3–4 eV energy by Cl\(_2\) molecule transfers it to \(^{3}\)I\(_{u}\) excited state, which is repulsive,[32] however, the 3.8 eV OA band is not photobleached as both Cl atoms are held together due to the “cage effect” of silica glass.[7] The lower-lying \(^{3}\)I\(_{u}\) triplet state of Cl\(_2\) has a shallow minimum[32] and at low temperatures gives rise to a structured “comb-shaped” near-infrared luminescence of Cl\(_2\) in silica.[5] Its nonstructured part can be approximated by a Gaussian with peak at 1.215 eV and fwhm 0.39 eV,[38] which means that Cl\(_2\) PL spectrum has a significant intensity (35% from the peak value) at the wavelength of the strongest absorption of the O\(_2\) molecule, \(\approx 1270\) nm (0.976 eV), corresponding to the excitation to the \(1\Delta_8^g\) singlet state. In addition, 5% of the Cl\(_2\) PL intensity overlaps with the next higher-energy O\(_2\) absorption band at 765 nm (1.62 eV), providing a possibility of energy transfer to another singlet (\(^{1}\Sigma^+_g\)) state of O\(_2\). Therefore, the lowest triplet (\(^{3}\)I\(_{u}\)) excited state of Cl\(_2\) is a reasonable candidate for the energy-donor state. The energy transfer to the O\(_2\) molecule is most probably described as

\[
\text{Cl}_2^+(\text{}^{3}\text{I}_u) + \text{O}_2(\text{}^{1}\text{\Sigma}_g^-) \rightarrow \text{Cl}_2(\text{}^{1}\text{\Sigma}_g^+) + \text{O}_2^+(\Delta_8^g)
\]

where the remaining excess energy of excited Cl\(_2\) is absorbed by vibrations of Cl\(_2\) or O\(_2\).

Two basic energy transfer mechanisms are generally considered: the dipole–dipole (Förster) mechanism and the direct electron exchange (Dexter) mechanism.[133] The Förster mechanism works over larger distances up to \(r = 10\) nm, the energy transfer rate decreases with distance as \(\approx 1/r^6\). This energy-transfer mechanism is used in organic macromolecules to measure the distance between the energy donor and acceptor sites.[144] However, it is efficient only for dipole-allowed electronic transitions, but the transition to the excited singlet state of O\(_2\) from its ground state is strictly forbidden. Therefore, the excitation of ground-state O\(_2\) to singlet state must occur by Dexter mechanism,[133] which has much shorter transfer range and requires some overlap of the energy donor and acceptor wavefunctions.

The process of energy transfer from energy donor D to ground-state O\(_2\) molecule must obey the spin conservation rule: the total spin of the system (D + O\(_2\)) must remain unchanged by the energy-transfer process. This is possible by the “triplet annihilation” mechanism, where triplet state excited sensitizer transfers its energy selectively to those ground-state triplet O\(_2\) molecules, which have opposite orientations of their \(S = 1\) total spin. Other spin-allowed mechanism (“triplet exchange”) is also known, which involves a partial energy transfer from the excited singlet state of the donor to triplet O\(_2\), and results in a lower-energy excited triplet state donor and excited singlet O\(_2\). However, this mechanism requires relatively large (at least 1 eV) singlet–triplet splitting in the donor species and is relatively rare; the “triplet annihilation” is by far the most common singlet O\(_2\) activation mechanism.[133] The energy transfer to O\(_2\) from the triplet state of Cl\(_2\) most likely occurs by this mechanism, as suggested by Equation (2). Therefore, it follows that O\(_2\) and Cl\(_2\) molecules giving activated UV-excited PL of \(^{3}\)O\(_2\) are direct or next-closest neighbors.

4.3. Distribution of O\(_2\) and Cl\(_2\) in Silica Network

Figure 7 (panel 1) shows that there is a reasonably strong correlation between the UV-excited \(^{3}\)O\(_2\) PL intensity and concentration of Cl\(_2\) in different samples, where Cl\(_2\) concentration varies over ten times. In contrast, the correlation with the O\(_2\) content is less clear (panel 2). However, this discrepancy may simply reflect the circumstance that the range of the available O\(_2\) concentrations was much smaller (change of only 1.6 times) compared to the range of Cl\(_2\) concentrations. The best, almost linear correlation, apart from 1 outlier point, is found between the singlet O\(_2\) PL intensity and the product of Cl\(_2\) and O\(_2\) concentrations (panel 3). This finding is compatible with a random distribution of Cl\(_2\) and O\(_2\) in glass matrix, since at low concentrations (\(10^{-7} \times 10^{18}\) molecules cm\(^{-2}\)) the probability of forming close pair is proportional to the product of concentrations. A larger range of O\(_2\) and Cl\(_2\) concentrations should be studied to
The number of large (diameter > 0.5 nm) interstices, capable of accommodating O₂ or Cl₂ molecules in silica glass can be roughly estimated as ≈10²⁻²⁵ cm⁻³, using the data of molecular dynamics studies,[36] which give the total volume, occupied by such voids as 32%. With 10¹⁸ molecules cm⁻³ distributed in these voids, the probability of having two neighboring voids occupied is >10⁻⁵. This number (≈10¹⁴–10¹⁵ pairs cm⁻³) is large enough to be detected by luminescence and thus consistent with the current observations. In contrast the OA data (Figure 1) show that a much larger number, of Cl₂ molecules (2 × 10¹⁷ cm⁻³) react with oxygen atoms in F₂ laser-induced reaction. This is possible, either if O₂ and Cl₂ are paired (e.g., in very large interstitial voids), contrary to the random-distribution discussed earlier, or if the laser photolysis-generated O atoms are mobile enough to travel longer paths to distant Cl₂ molecules. It is generally agreed[37] that thermalized O atom diffuses by exchange with network O atoms, and forms a peroxo linkage Si—O—O—Si. This diffusion is very slow at the room temperature. However, it has been demonstrated with isotopically ¹⁸O₂-enriched samples that part of photolysis-generated ¹⁸O atoms while traveling long distances to form O₂ molecules, do not undergo exchange with network oxygens.[21] By analogy, similar process can be involved in SiO₂ formation.

The possibility that both Cl₂ and O₂ molecules can initially reside in a single large void, can be additionally examined by PL decay measurements (Figure 8). The decay of singlet O₂ PL in “dry” silica (decay constant τ ≈850 ms) at room temperature is the slowest among observations of O₂ PL in any condensed matter matrix[19] because the rate of ¹O₂ nonradiative relaxation in SiO₂ matrix is record-low. All other matrices cause higher nonradiative rates. Therefore, an additional perturbation by a closely contacting activator is generally expected to shorten the decay kinetics. However, Figure 8 shows that ¹O₂ PL kinetics is practically the same in the cases of energy-transfer excitation (385 nm, trace 1) and direct photoexcitation of O₂ (766 nm, trace 2). This finding is supportive of Cl₂ and O₂ having little interaction and is in accord with the assumption that both molecules are located in separate voids in silica glass network. However, it must be kept in mind that Cl₂ can be a relatively low efficiency quencher of ¹O₂ PL in silica compared to, e.g., silanol group ≡Si—O—H, and therefore, the presence of closely located Cl₂ does not necessarily mean strong quenching. The quenching of ¹O₂ PL is often dominated by electronic-to-vibrational energy transfer, which in case of Cl₂ may have low rate because the vibrational frequency of Cl₂ in silica (546 cm⁻¹[17,38]) is significantly lower than that of silanol (≈3700 cm⁻¹). A previous study[19] has shown that chlorine impurities in the form of ≡Si—Cl groups (up to 5 × 10¹⁷ cm⁻³) have no measurable effect on quenching of ¹O₂ PL in silica.

5. Conclusion

The main result of this study is the identification of radiation-induced OA band in the 4.7 eV region due to the formation of dichlorine monoxide Cl₂O molecule in reactions molecular chlorine with oxygen atoms. Although only one of the two structural isomers of dichlorine monoxide, a ClClO molecule was identified by Raman spectrum, the contribution of the other isomer, ClOCl to the 4.7 eV OA band can be significant. These data may help to decipher the often very complex OA spectrum of irradiated silica glass in the “difficult” 4.5–5.5 eV spectral range, where a number of closely spaced OA bands due to intrinsic defects (NBOHC, peroxy radical, silicon oxygen deficiency centers SiODC(II), and interstitial ozone) overlap.

An additional finding is the weak OA band centered at 3.5 eV with fwhm 0.8 eV. Its position and width are similar to those of chlorine dioxide, OCIO molecule. Its tentative assignment to interstitial OCIO in silica is additionally supported by similar intensity changes of this OA band and of the previously published EPR signal of OCIO[25] during isochronal annealing series. This band can contribute to the nonstructured absorption losses in irradiated optical fibers, generally increasing with photon energy in blue and UV regions. It is well established that these losses in optical fibers are related to chlorine impurities[18], the idea that chlorine dioxide can be the responsible species has been proposed long ago.[19] Our present data support this proposal.

For chlorine oxides in silica glass to form, both Cl₂ and O₂ interstittials must be copresent. Chlorine impurities are nearly omnipresent in all silica glasses produced from SiCl₄ or dried by Cl₂ in the porous “soot” preform phase. In contrast, excess O₂ is normally not present in commercial glasses. However, it is a typical product of radiolysis of oxide glasses (e.g., the study by Ollier et al.[40]). Excess O₂ may be added deliberately because it is found to increase the radiation toughness of optical fibers in the near-infrared spectral region by suppressing the generation of self-trapped holes (STH₂).[41] And most commonly, it is inadvertently loaded in subsurface layer of silica by high-temperature processing under atmospheric conditions.[42] The defect generation in the subsurface layer of silica optics is a crucial factor in high-power laser applications.

The present data are consistent with the model of random distribution of Cl₂ and O₂ molecules in silica glass network and of absence of both pair formation and of significant clustering of these molecules in large voids. However, a study over larger ranges of O₂ and Cl₂ concentrations would be useful to finally verify this model. The energy transfer between Cl₂ and O₂ found in the present study may serve as an additional tool to indicate the proximity of both molecules.

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Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

Research data are not shared.

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