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On the Issue of Structure-Chemical Features of Silicon Oxides and Thermal Emission of Singlet Oxygen

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Abstract—Special features of the chemical structure of silicon oxides were analyzed by the methods of vibrational and electronic spectroscopy and it was found that cationic (Si–Si) and anionic (O_2 and O_3) sublattices contain isolated individual Si–O oscillators, including electron-excited oscillators, and homoatomic bonds. By means of chromatographic and sorption-calorimetric analyses inverse dependence of singlet oxygen specific thermal emission on specific surface area of samples was found that corresponds to volume generation of excited states.

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The combination of experimental data on the thermal emission of singlet oxygen molecules initiated by oxides of *p*- and *d*-elements [1–3] brings attention to possible reasons of this effect. Processes of formation and interaction of point defects are among the most probable excitation sources. Their presence in the SiO_2 structure [4, 5] caused by the dorientation and destruction of the chemical bonds ($n\mathrm{SiO_2} \rightarrow n\mathrm{SiO} + n/2\mathrm{O_2})^*$ appreciably defines properties of one type of materials most widespread in technology. Such defects are characterized by a great excess of free energy and a high reactivity in accordance with electronic states in a forbidden band [5]. The presence of local structural excitations was revealed earlier in complex oxides and vanadium oxides [6, 7].

The amount of information on the spectral structure-chemical analysis of such states in oxides in general, and in silicon oxides in particular, is rather moderate. For example, the studies of disperse SiO_2 samples by vibrational spectroscopy are concentrated mainly in the region of 3000–4000 $\mathrm{cm^{-1}}$ [8], which is a consequence of practical difficulties in obtaining highly resolved vibrational spectra of solid samples and in assigning characteristic bands.

The experimental data [9] point to the fact that in real structures, including those isoelectronic to $[SiO_4]^{4-}$, *And* orbitals are appreciably populated by electrons, which is caused by a considerable contribution of electron-excited configurations to a real state of complexes of non-transition elements. Thus, the electronic structure of silicon oxides provides a possibility for initiating redox transformations due to native (thermal) loosening of Si–O bonds. Incomparability of energies of quanta of vibrational and electronic excitations, and also the model of the formation of electron excitations within the limits of the band theory [10] suggest that there are conditions for effective accumulation of the vibrational excitation energy. The main barrier to the V–R–T relaxation of vibrational excitations is deficit of rotational freedom degrees that can be caused by increase in the bond order due to domination of bonding and antibonding π orbitals in the electronic structure of tetrahedral polyhedra [9].

Empirical Hilsh and Paul formula: $W = (e^2/na)(2\mu\text{-}1) + E - I$ [11] corresponds to the potential of (*) transformation. It provides an inverse dependence of the energy of Vannier–Mott exciton formed by an electron (>Si) and a “hole” (O) on its size (*na*, *a* are interatomic distances). The numerical estimate of this dependence for SiO_2 shows (Fig. 1) that, starting from *n* 2, negative values corresponding to exoergic stages appear and increase in absolute values. They can provide energy for the evolution of the one-electron transfer process. It is seen from Fig. 1 that the excitation energy for KCl (the absence of directed bonds) is positive within the whole range of *n* values.

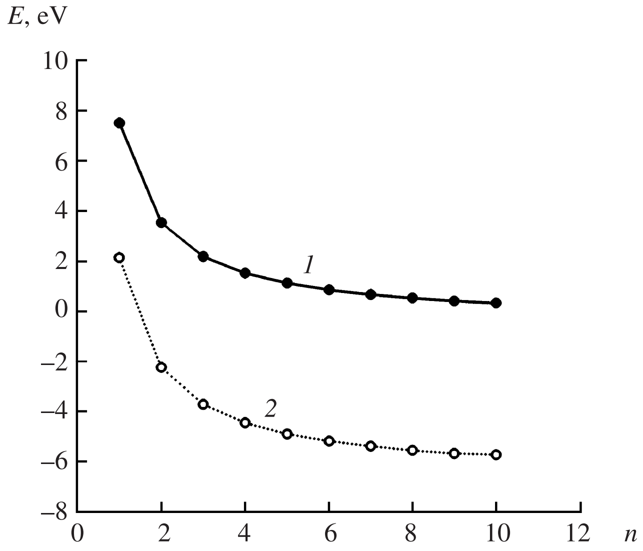

Fig. 1. Dependence of the energy (E) of Vannier–Mott excitons on their size (n). (*1*) KCl, (*2*) SiO_2.

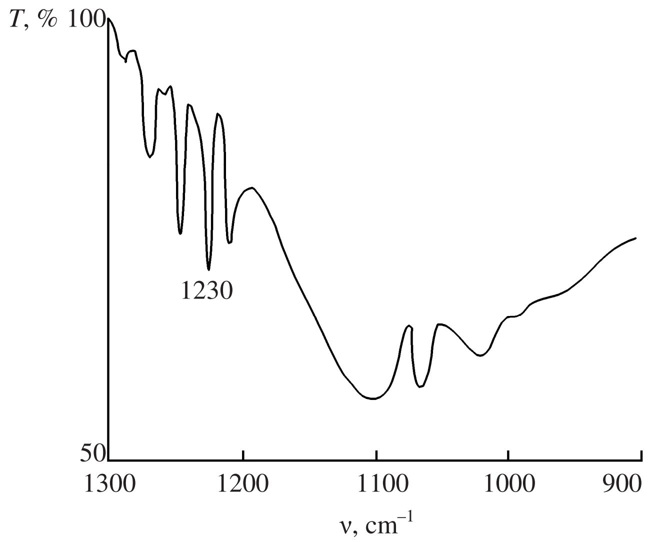

Fig. 2. High-frequency abnormality and fundamental absorption in the quartz glass spectrum (T is transmittance).

The barycentre of the wide fundamental ν_{as}(Si–O–Si) band, which is characteristic for all polysiloxanes and silicon earths, is recorded in the IR spectra near 1100 cm^{-1} [12].

The absorption maximum at 1110 cm^{-1} corresponds to quartz glass (Fig. 2). Short- and long-wave branches of the absorption curve contain characteristic series of clearly resolved fine structure. In the field of adjacent frequencies, but above the frequency of this maximum, a series of bands with a local absorption maximum at 1230 cm^{-1} is observed (Fig. 2). In [13] treating the oxides of *d*-elements such high-frequency absorption bands were assigned to the vibrations of cation-oxygen surface bonds. It is assumed that the high-frequency shift is caused by strengthening cation-oxygen bonds due to the interaction of the surface O^{-2} ion only with one of cations in the lattice, that results in a decrease in the metal atom coordination number. This approach can be considered as valid only if metal-oxygen vibrations are assumed to be isolated, i.e. they appear as local vibrations. Quantum-mechanical calculations fulfilled with regard to this condition [13] and their good agreement with the isotope shifts found for the absorption bands of M–O bonds make sufficiently conclusive the assignment of the observed maxima to local vibrations (weakly depending on neighbors). The logic of the presented reasoning, and also a principle of electroneutrality conservation require an additional conclusion that in this case the cation should be in a lower oxidation state. The fact of existence of such vibrational and electronic states and their nature point to a possibility of their localization not only on an exterior boundary, but also, with equal probability, in the bulk structure. In the latter case microheterogeneous structural irregularities and crystal defects are implied. This assumption was supported by the fact that for some oxide systems, such as NiO and CuO, it was not possible to prove reliably that the characteristic absorption bands belong to surface vibrations of cation-oxygen bonds [13].

The upper frequency limit of intrinsic vibrations of Si–O bond is limited by the frequency of the basic transition in the isolated molecular electronic state X $^1\Sigma^+$ at 1229 cm^{-1} [14]. Therefore the series of bands recorded in the range 1263–1205 cm^{-1} (Fig. 2) can be assigned to vibrational transitions in the quantum system of the Si–O isolated state.

In the work [15] on the application of reflection-absorption spectroscopy it was shown for the first time by the example of polycrystalline LiF that the maximum of the fundamental absorption band corresponds to the frequency of longitudinal vibrations (ν_l) that is considerably shifted to the high-frequency region (Berreman’s effect). However later this effect was not taken into consideration [16], and the high-frequency position of bands in experimental spectra was related to the presence of nonexistent compounds

Table 1. Comparison of wave numbers (cm-$^{-1}$) of basic vibrational transitions in the system of electronic states of isolated Si–O oscillators and spectral lines of SiO_2 samples

Term/*E*, eV	SiO [14]	Quartz glass	Quartz single crystal	A-300	Silica gel
$x\ ^1\Sigma^+$/0	1230	1230	1230	1230	1230
$a\ ^3\Sigma^+$/4.20	782	800–780	800–780	800–780	800–740
$b\ ^3\Pi_{0-2}$/4.25	998	–	998	–	998
$d\ ^3\Delta_r$/4.56	759	–	–	–	–
$e\ ^3\Sigma^-$/4.79	740	–	–	–	–
$C\ ^1\Sigma^-$/4.82	732	–	–	–	–
$D\ ^1\Delta$/4.85	722	720	–	–	720
$A\ ^1\Pi$/5.35	840	840	–	898–760	846
$E\ ^1\Sigma^+$/6.61	667	670	669	669	669
$C\ ^3\Sigma^+$/7.20	935	–	–	940	945
$f\ ^3\Pi_i$/7.41	482	480	–	485	485
$f\ ^1\Sigma^+$/8.56	1115	1115	–	1115	1115
$G\ ^1\Pi$/8.71	863	863	–	898–760	860
$I\ ^1\Pi$/8.81	879	870–879	–	898–760	890–870
$M\ ^1\Pi$/10.1	833	833	–	898–760	830

on the surface. When studying SiO_2 nanolayers on a silicon surface by the method of frustrated total internal reflection [16], simultaneous appearance of vibrational activity of longitudinal and transverse vibrations was convincingly proved. In this case absorption bands ν_t at 1100 and ν_l at 1240 cm^{-1} were recorded. At frequencies between longitudinal and transverse vibrations several less intensive bands corresponding to the absorption of each of monolayers in the total poly-layer structure were observed. The term "exciton" [12], which is understood as elementary excitation in crystals submitting to Bose statistics, is applied to the explanation of the nature of the present effect. The model in use corresponds to concept of the stabilization of excitons in a two-dimensional quantum "well." According to the model, the existence of Coulomb excitons under conditions of dimensional limitations should manifest itself in the form of new strong absorption bands, and their position should weakly depend on the chemical nature of structural oscillators.

Considering the high-frequency abnormality in the region of framework vibrations as a manifestation of chemical structure defects in the form of quasi-molecules of silicon monooxide in the ground electronic state, which weakly interact with environmental atoms, we can suggest that the appearance of vibrational activity of a series of electron-excited states accompanies them. The frequency of the basic vibrational transition at 790 cm^{-1} corresponds to the first electron-excited state of the Si–O bond ($^3\Sigma^+$, E ~4 eV) [14]. The experiment (Table 1) shows a series of absorptions with maxima at 800, 795, 792, 790, and 785 cm^{-1}, and the maximum at 720 cm^{-1} ($^1\Delta$) in the range of states with energy from 4 up to 5 eV is prominent. States with a high excitation energy (5–10 eV) are exhibited in the form of a characteristic set of bands at 480 and 1115 cm^{-1} and a progression at 833, 840, 862, at 878 cm^{-1} ($^1\Pi$) with positions which agree well with the reference data [14] for individual SiO oscillators.

The spectrum of single-crystal quartz contains a high-frequency abnormality in the form of well-resolved set of bands in the range 1233–1215 cm^{-1} (Table 1). The vibrational activity of electron-excited states of the localized Si–O bond is detected as the doublet of bands at 800 and 998 cm^{-1} widened into the low-frequency region up to 720 and 900 cm^{-1}, respectively. This result agrees well with the idea that a thermodynamically stable crystal structure is characterized by a lower concentration of deformed structural bonds and a lower level of the excitation of intrinsic defects compared to a metastable glass-like structure.

Highly dispersed non-porous silica (aerosil A-300 and silica gel KSK-2.5) has the spectrum (Table 1) which contains additional bands of surface states of the $\equiv$Si–O bonds (898–860 cm^{-1}) as compared to the

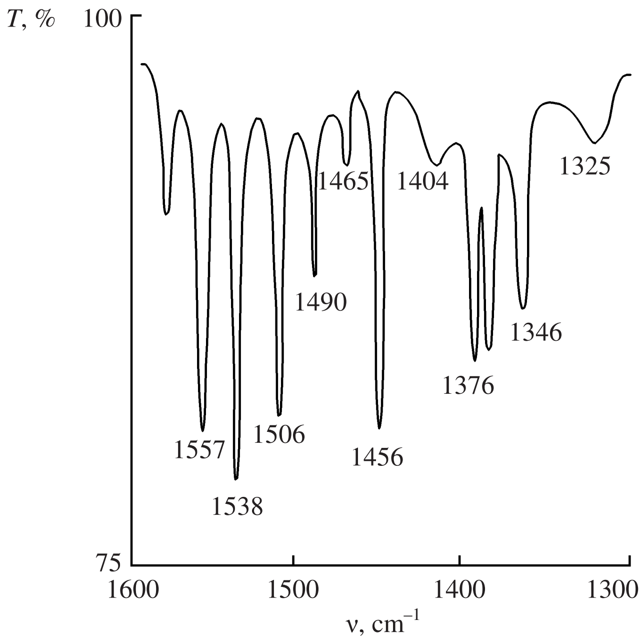

Fig. 3. Vibrational transitions involving triplet and singlet states of O_2 in the quartz glass spectrum (*T* is transmitance).

spectrum of quartz glass [17]. The radical increase in the specific surface area of samples slightly changes the concentration of local Si–O states at the lower singlet level $^1\Sigma^+$. The integral absorption intensity in the range 1230–1215 cm^{-1} remains practically unchanged.

The presence of molecular forms of oxygen in the structure of oxides is traditionally considered as a result of sorption binding. It is commonly to assumed [13] that the appearance of stretching vibrations of uncharged molecular forms of adsorbed oxygen in the spectral range of 1500–1700 cm^{-1} is caused by the polarizing action of the solid surface. This circumstance allows us to expand possibilities of IR spectophotometry to recording vibrational activity which is forbidden by symmetry and by dipole moment.

Vibrational activity of ionic species and peroxide and superoxide compounds is usually observed in the range of 800–1200 cm^{-1} [13].

In the spectrum of glass-like quartz a series of vibrational transitions is recorded: ν_{1-0} 1557, ν_{2-1} 1538, ν_{3-2} 1506, ν_{4-3} 1490, and ν_{5-4} 1465 cm^{-1} (Fig. 3). They are attributed to the quantum system of the ground electronic state of molecular oxygen $^3\Sigma_g$ [14]. The presence of the intensive absorption peak at 1457 cm^{-1}, which precisely corresponds in frequency to the basic transition in the first electronically excited singlet state $^1\Delta_g$ [14], and also of the less intensive series of higher transitions (ν_{2-1} 1431, ν_{3-2} 1415, ν_{4-3} 1380, and ν_{5-4} 1354 cm^{-1}) confirms the validity of such assignment. The second singlet state of molecular oxygen $^1\Sigma_g^+$ appears as well-resolved absorption bands of various intensity: ν_{1-0}1 1404, ν_{2-1} 1376, ν_{3-2} 1346, and ν_{4-3} 1325 cm^{-1} (Fig. 3). Low-intensity absorption bands at 770 cm^{-1} ($^1\Sigma_u$ 4.2 eV), 810 cm^{-1} ($^3\Delta_u$ 4.3 eV), and 775 cm^{-1} ($^3\Sigma_u^+$ 4.5 eV) point to the presence of highly excited states. The appearance of vibrational activity of isolated molecular states of oxygen can be attributed to the components of similar structural defects which are responsible for the localized vibrations of quasi-molecular Si–O bond.

It was found earlier [13] that the position of bands in the vibrational spectra of molecular forms of adsorbed oxygen with strongly loosened bonds correlates with the ESR spectra of O_2^- radicals. Weakly perturbed states are characterized by a doublet 1140–1180 cm^{-1}, which we recorded clearly only in the spectrum of A-300. We have concluded that ion-radical forms of adsorbed molecular oxygen are observed only on reduced surfaces of oxides and are unstable against temperature action [13]. The stabilization of a superoxide oscillator is caused first of all by a fundamental decrease of the energy level of this system (~0.5 eV) compared to the uncharged oxygen molecule [18].

When considering the manifestation of vibrational activity of oxygen peroxiadducts on a silicon surface we observed the absorption band in the region of 660 cm^{-1}, which appeared at a reversible sorption of molecular oxygen by silicon earths containing hemin [19]. To detect experimentally and assign absorption bands which are authentically connected with the presence of peroxide groups on the surface of silicate structures, we have taken spectra of aqueous solutions of hydrogen peroxide spread on the surface of thin mica films. In this case the characteristic intensive absorption at 670–663 (doublet), 628, 1262 and 1388 cm^{-1} appears and grows with increasing concentration. In the spectrum of quartz glass we recorded a medium-intensity doublet at 670–665 cm^{-1} and a series of narrow bands in the region of 630, 1262, and 1388 cm^{-1}.

Ozone, as the most stable of oxygen oligomers, is one of probable products of the association of oxygen atoms in the structure of silicon oxide. We used the IR spectra [20] of neutral and isotope-substituted forms of

Table 2. Absorption bands (IR spectrum) of quartz glass and ozone sorbed on a silica gel surface

Frequency, cm^{-1}	Quartz	$^{16}O_3$	$^{16}O^{16}O^{18}O$	$^{18}O^{16}O^{18}O$	$^{16}O^{18}O^{16}O$	$^{16}O^{18}O^{18}O$	$^{18}O_3$
ν_2	705	703					664
ν_3	1040–1032	1037	1021	1014	1003.2	988.8	978.8
ν_1	1107	1104	1093	1074	1076	1060.9	1044.7
$\nu_2 + \nu_3$	1716	1717					
$\nu_1 + \nu_2$	1760–1740	1799.5					
$2\nu_3$	2047–2000	2045				1949.8	1935
$\nu_1 + \nu_3$	2107, 2104	2106.4	2085.9	2055	2046.3	2022	1992

ozone sorbed on the silica gel surface as a basis for a reliable spectral identification of weakly-bound molecules. The symmetry of the ozone molecule defines three fundamental vibrational transitions, $\nu_1[\nu_s(O_3)$, $A_1,]$, $\nu_2[\delta(O_3)$, $A_1,]$, and $\nu_3[\nu_a(O_3)$, B], which appear as weak bands at 1103 and 700.9 cm^{-1} and also a strong band at 1042.1 cm^{-1}, respectively [21]. The spectra (Table 2) contain 18 bands of $^{16O}{}_3$ and 15 bands of $^{18O}O_3$, which include double and triple frequencies, and also transitions to various combinative levels.

The decrease in the intensity of absorption bands of O–H stretching vibrations at 3750 and 3670 cm^{-1} and the shift of the absorption maximum to 3640 cm^{-1} [21] are characteristic manifestations of the adsorption interaction of ozone with a silicagel surface due to the formation of hydrogen bonds with hydroxy groups. Such effect is not recorded in the quartz glass spectrum that is obviously connected with a small specific surface area of a sample or points to the localization of ozone molecules in the bulk structure.

In the spectrum of the single-crystal quartz there are low-intensity bands of free and bound hydroxy groups, respectively, at 3750–3720 and 3670–3680 cm^{-1}, a high-intensity triplet 3648, 3645, 3640 cm^{-1} which appears due to a disturbing action of ozone molecules. Taking into account the crystal-chemical perfection of single crystals, we suggest that the most probable sites of localization of functional groups are non-equilibrium displacement structures where dislocations provide a diffusion transport of defects and their concentrating.

The integral intensity of the absorption band of molecular oxygen in the ground state (1557 cm^{-1}, Fig. 3) exceeds the intensity of the same band in quartz glass almost by an order of magnitude. The intensity of the band of molecular oxygen in the first singlet state ($^1\Delta_g$) is almost twice higher. Therewith the intensity of the basic absorption band of ozone (1040–1020 cm^{-1}) is rather low. Superoxide groups are weakly expressed as low-intensity absorptions at 1060 cm^{-1}. A medium-intensity series of bands in the range of 700–600 cm^{-1} points to the presence of peroxide groups.

The spectrum of Aerosil-300, despite of its large specific surface area, contains absorption bands of the ground and electron-excited states of oxygen, close in intensity to those of quartz glass. A considerable increase in the integral intensity of the absorption bands of superoxide groups in the form of structured doublet at 1180 and 1140 cm^{-1} correlates with the increase in the specific surface area. The intensive absorption band of a regular shape at 669 cm^{-1} corresponds to peroxide groups.

The presence of ozone is proved by a characteristic set of intensive bands in the ranges 1030–1075 and 1760–1740 cm^{-1} and of medium- and low-intensity bands at 1110, 1990, 2045, and 2110 cm^{-1}. Intensive maxima at 3655, 3645, 3638, and 3630 cm^{-1} show, at least, a partial localization of these states on a surface.

The series of four absorption bands of ozone connected with electronic transitions is located in a wide range from near infrared region up to deep ultraviolet [21]. The weak diffuse system of Woolf's bands caused by the $1^1A_2 \leftarrow 1^1A_2$ transition [21] stretches from ~1000 up to ~750 nm. Chappue's bands, which are assigned to the $1^1B_1 \leftarrow 1^1A_1$ transition, are located in the visible region at 430–470 nm, being adjacent to Woolf's bands. The long wavelength boundary of the following Higgins absorption band in fact begins in the region of ~350 nm. The range of 430–350 nm is transparent for ozone. The diffuse system of Higgins bands converts at $\lambda \sim 300$ nm to the most intensive Hartley's band ($200 \leq \lambda \geq 300$ nm) with a maximum at 255.5 nm [21]. Both bands are considered to have a common upper state 1^1B_2. Ozone

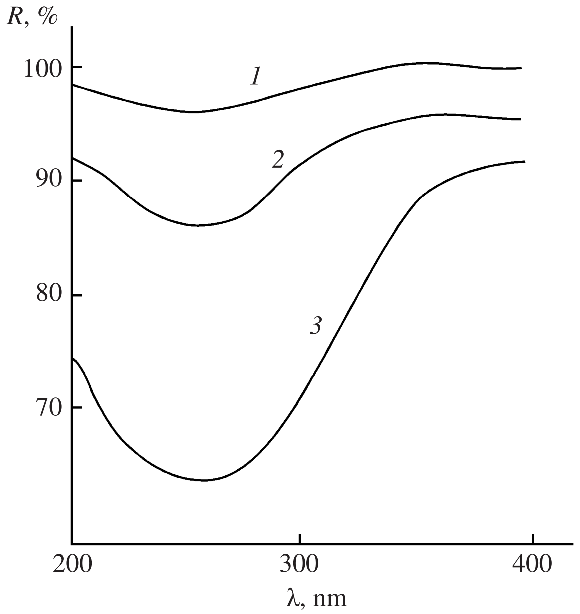

Fig. 4. Diffuse-reflection spectra of aerosils. (*1*) A-120, (*2*) A-175, (*3*) A-300.

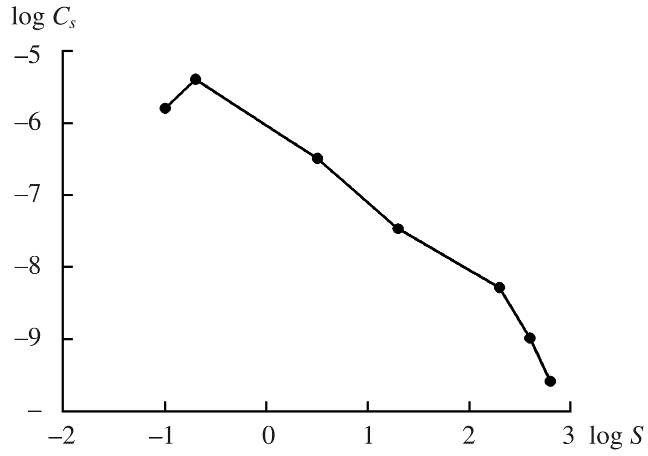

Fig. 5. Specific emission of singlet oxygen (C_s, mol m^{-2}) vs. specific surface area of SiO_2 samples (*S*, m^2 g^{-1}) at 300°C.

absorbs also in the visible and deep ultraviolet regions, the spectrum represents a continuous background with wide maxima [21]. The ion O_3^- absorbs in the visible and ultraviolet regions and has orange color, $\lambda_{max} \leq$ 257 and λ ~440 nm.

The electron spectrum of O_O^- contains an intensive absorption band in the UV region (ε 1060 l mol^{-1} cm^{-1}) with a maximum at λ~240 nm [21]. Its characteristic feature consists in the fact that the position of the maximum varies only slightly on changing the chemical nature of a medium. The maximum in the region of 462 nm [22] was also detected. The O_2^{2-} ion does not absorb in the visible and near-ultraviolet regions.

The comparison of electron transmission spectra of quartz glass and of single-crystal quartz showed that in both cases the absorption maximum at 250 nm, which was detected earlier [4], is recorded was the spectrum, the intensity of the band of single-crystal quartz being much higher. It can be caused by a greater concentration of superoxide groups.

The diffuse-reflection spectra of aerosil samples with specific surface area varied over the range of 75–300 m^2 g^{-1} show (Fig. 4) that, as the surface increases, the intensity of the absorption maximum (λ 250 nm) increases, the absorption band becomes diffuse, and the intensity in the region of the short-wave shoulder at 220–240 nm increases. All this corresponds to an increase in the concentration of surface superoxide groups.

The concentration of trimeric associates of oxygen and superoxide groups calculated using published values of molar absorption coefficients [18, 21] is of the order of 10^{17}–10^{18} cm^{-3}. This result agrees with the data on the optical transmission of quartz glass and with the chemical analysis of nonstoichiometry [4] and diffuse-reflection spectra of dispersed silicon earth [22].

The examination of the dependence of specific (per a surface area unit) thermal desorption (emission) of singlet oxygen ($^1\Delta_g$ + $^1\Sigma_g^+$) on the specific surface area of samples has shown (Fig. 5) the presence of a negative linear correlation, which points to the volume localization of the main source of labile oxygen states.

The fact that oxygen is prone to the formation of associates in single-crystal quartz seems to be similar to the association of admixture atoms on dislocations, which corresponds to the mechanism of associating point defects in crystals [23]. Owing to the presence of free bonds the dislocation acts as a multiply ionizing acceptor and tends to capture electrons which are delivered by donor atoms. If we neglect multipoint interactions, then we can find after Kroger [23] that the association energy (H_p) is equal to the sum of the energy gain on the electron transition from a donor to a dislocation (the energy gap width E_i) and the electrostatic energy of the pair formation $H_e = -q^2/\varepsilon r$.

Taking r to be equal to half the Si–O distance (~1.6 Å) and E_i = 5 eV, we obtain $H_p = H_e + E_i$ ~7 eV. Accounting for the mutual influence of various ionized donors, the interaction of the electrons situated on a dislocation, and the interaction between the ionized donors and various charges on the dislocation a correction to the transfer energy E_i and H_e appeares opposite in sign to the association energy. Therefore it is most likely that the real value of the association energy is much less. However its order of magnitude points to the association process on the dislocations as one of possible energy sources for the formation and stabilization of electron-excited states.

The detection of homoatomic associates in the cationic SiO_2 sublattice giving rise to the bands of vibrational transitions in a quantum system of Si–Si oscillators can serve as an additional evidence of redox transformations and also of the association of defects.

The region of the manifestation of vibrational activity of free Si–Si bonds in quartz glass and single-crystal quartz covers the range of 550–400 cm^{-1} (Table 3). The clearly resolved medium-intensity triplet (507, 503, and 500 cm^{-1}) in the spectrum almost exactly corresponds to the ground electron state of the bond (X $^3\Sigma_g^+$). The prolongation of this absorption in the long-wave region is the broade structured band at 500–400 cm^{-1} with a barycentre at 460–470 cm^{-1}. It seems obvious to assign this band to the vibrational series of excited states of the Si–Si bond, K $^3\Sigma_u^-$ (~3.7 eV) and L $^3\Pi_g$ (~4 eV) [14]. The second excited state ($^3\Pi_{u,\mathrm{I}}$) is recorded as a series of medium-intensity peaks in the range of 543-510 cm^{-1}. Bands of the third excited state H $^3\Sigma_u^-$ are in the range of 275–267 cm^{-1} (Table 3).

In the spectra of aerosil and silica gel the same set of Si–Si oscillator states was found. However the intensity of the A-300 bands noticeably exceeds (~5 times) the intensity of the bands of glasses, single crystal, and silica gel.

The totality of the spectral information allows us to connect the thermal emission effect of electron-excited molecules of oxygen with the dark generation of exciton-type excitations due to structural distortions of silicon oxides. The presence of a spectrum of states of isolated Si–O oscillators, to which a high-frequency abnormality corresponds, makes clear the initiating and final stages of this process. The detection of specific electronic and vibrational activity of silicon and oxygen associates confirms in detail the redox transformations. The nature of defects assumes that the associates are accumulated on the external and internal boundaries of microheterogeneous areas. It obviously makes easier their mass transfer, however the linear decreasing of specific thermal emission of singlet oxygen with increasing specific surface area of samples points to the preferential volume origin of the electron-excited states.

Table 3. Frequencies of vibrational transitions in the system of electronic states of isolated Si–Si bond

Si–Si Term	Energy, cm^{-1}	Experimental data, cm^{-1}	Data of [14], cm^{-1}
X $^3\Sigma_g^+$	0	507, 503, 500	507
D $^3\Pi_{u,i}$	–	545–543	543
$\underline{\mathrm{H}}$ $^3\Sigma_u^-$	24429.1	276	271.3
K $^3\Sigma_u^-$	30794.0	470–415	461
L $^3\Pi_{g,i}$	32629.0	500–470	494

EXPERIMENTAL

In the work we used highly sensitive electron-spectroscopy instruments (SF-56), including a diffuse-reflection instrument (SF-26 with a diffuse-reflection attachment PDO-5), traditional high-resolution (~0.01 cm^{-1}) IR spectophotometry (IKS-25M), Fourier spectroscopy (FTIR) (Chromex USA, Shimadzu-8400S), and Raman spectroscopy (Chromex USA, Wisard-1200) instruments, and also devices for chromatographic [2] and adsorption-calorimetric [3] methods of analysis of thermally desorbed oxygen forms.

As subjects of studying we used samples of high-purity dispersed SiO_2 A-300, 175, 120, and 75 aerosils; KSK-2.5 silica gel; plates of quartz glass and synthetic single-crystal quartz. To obtain vibrational spectra, disperse samples were deposited on a thin polymeric film [poly(ethylene terephthalate) and cellulose, l ~5 μm]. The controlled surface density was 1–2 mg cm^{-2}. The spectra of the samples were obtained with a digital compensation of a background signal. The samples passed a preliminary thermal treatment (200°C, 90 min) in a dry atmosphere of purified air. The spectra were measured at 2°C in an argon (special-purity grade) atmosphere.

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