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Overton-Region IR Registration of $(\equiv\text{Si–O})_2\text{Si=O}$ and $(\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle\text{C=O}$ Groups on the Silica Surface

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Abstract—IR spectroscopy in a range of 2050–4000 cm^{-1} (the range of overtones and composite frequencies) is used to study the groups $(\equiv\text{Si–O})_2\text{Si=O}$ and $(\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle\text{C=O}$ with different isotopic compositions (^{16}O, ^{18}O, ^{12}C, and ^{13}C). Analysis of the experimental data and quantum-chemical calculations of vibrational spectra for the model compounds are used to identify the IR bands. New data are obtained on the vibrational spectra of these groups. Their identification is shown to be possible in the spectral range that is convenient for the study of silica samples.

INTRODUCTION

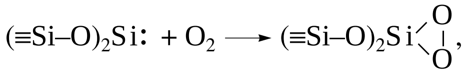
It is known that even fine samples of quartz glass absorb in the range of wave numbers of 750–1300 cm^{-1} with a range of partial transparency between 850 and 1000 cm^{-1} [1]. To register low-intensity bands associated with structural defects and impurities in quartz glass, samples that are at most 100-μm thick have to be used. The range of wave numbers >2050 cm^{-1} becomes free of intense absorption by a silicon-oxygen skeleton. Absorption bands associated with structural defects and impurities in quartz glass belonging to the region of poor transparency can be detected by registering their first overtones or composite frequencies if they fall into the corresponding spectral region (with wave numbers >2050 cm^{-1}). Because their intensities are usually two orders of magnitude lower than the corresponding main bands [2], only rather strong bands can be identified by this method. Note that due to various reasons, the near IR region (1–2.5 μm), to which the first and second overtones of OH, NH, and CH vibrations and some combination frequencies belong, proved to be the most convenient in the first studies on solid surfaces [3].

This paper deals with the results of the IR studies of the $(\equiv\text{Si–O})_2\text{Si=O}$ and $(\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle\text{C=O}$ groups stabilized on the silica surface. These studies were carried out in the overtone region (2050–4000 cm^{-1}; transitions $0 \longrightarrow 2$, $(0, 0) \longrightarrow (1, 1)$). Earlier, separate basic frequencies ($0 \longrightarrow 1$ transitions) were registered for these structures [4, 5]. The band at 1306 cm^{-1} (ν_1) due to the stretching vibrations of the Si=O bond is associated with the $(\equiv\text{Si–O})_2\text{Si=O}$ group. A carbonate structure reveals itself in absorption bands at 1930 (ν_2) and 891 cm^{-1} (ν_3). The first of these bands is associated with the stretching vibrations of the C=O bond, and the second band is associated with the vibrations of a four-membered cycle [5]. All these bands are “strong.” The band intensities at 1930 and 891 cm^{-1} are comparable, but the intensity of the band at 1306 cm^{-1} is 3–5 times lower (at the same concentration of surface groups). Based on these data, it is expectable that overtones and composite frequencies associated with these normal vibrations belong to the region of quartz glass transparency. To interpret experimental findings, including the isotopic substitution effects, we used quantum-chemical calculations of vibrational spectra for the molecular models of these groups.

EXPERIMENTAL

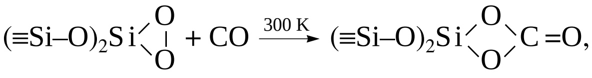
Morterra and Low [6, 7] developed a method for activating the silica surface. The method enables a substantial increase in the chemical activity of this surface and the formation of reactive silica (RS), and it was described in detail in [6–8]. Silylene groups $(\equiv\text{Si–O})_2\text{Si}$ are the main type of defects stabilized on the reactive silica surface responsible for its chemisorption activity [8, 9]. Their concentration is ~10^{13} cm^{-2}.

Silanone groups were prepared from silylene groups in two stages. First silylene groups were transformed into dioxasilirane form [8, 9]:

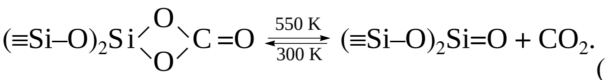


$$(\equiv\text{Si–O})_2\text{Si}\colon + \text{O}_2 \longrightarrow (\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle, \qquad \text{(I)}$$

and then the latter were reduced to form silanone groups using CO:



$$(\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle + \text{CO} \xrightarrow{300\text{ K}} (\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle\text{C=O}, \qquad \text{(II)}$$



$$(\equiv\text{Si–O})_2\text{Si}\langle \text{O}_2\rangle\text{C=O} \underset{300\text{ K}}{\overset{550\text{ K}}{\rightleftarrows}} (\equiv\text{Si–O})_2\text{Si=O} + \text{CO}_2. \qquad \text{(III)}$$

A carbonate group is an intermediate product in this transformation. Reaction (III) is reversible. This

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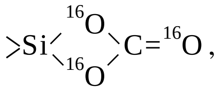
enables the transformation of silanone groups into the carbonate form and backward.

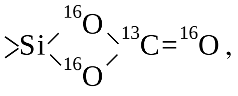
When synthesizing carbonate and silanone groups (reactions (I)–(III)), we used isotope-labeled molecules $^{18}O_2$ (with ~30% $^{16}O^{18}O$ admixtures) and/or $^{13}C^{16}O$ (with ~15% $^{12}C^{16}O$ admixtures), which provided information on the values of IR-band isotopic shifts. These values were used for band assignment to certain types of normal vibration of surface structures. We synthesized groups with the following isotopic compositions ($^{16,\,18}O$ indicates the presence of groups of different isotopic compositions):

$(\equiv Si–O)_2Si=^{16}O$, $(\equiv Si–O)_2Si=^{16,\,18}O$,

I **II**



III



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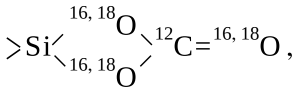

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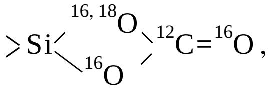
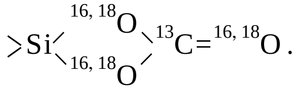


VI



VII

When preparing samples **IV** and **VII**, we used ^{13}CO molecules. When obtaining samples **II**, **V**, and **VII**, molecular oxygen enriched in the ^{18}O isotope was used. The presence of the ^{18}O atom in the carbonyl group (structure **V**) was associated with exchange reactions occurring during reaction (**II**) (see [5]). The preparation of sample **VI** will be discussed below.

Silanone groups were obtained by the thermal decomposition of carbonate structures (see reaction (III)). Compounds **V** and **VII** can be a source of the mixture of silanones with different isotopic compositions: $>Si=^{16}O + >Si=^{18}O$ (sample **II**). In the course of the chemisorption of the $^{12}C^{16}O_2$ molecules (reaction (III)), this sample was used to form groups **VI**. Unlike the reaction of CO addition to a dioxasilirane group (see above), the addition of CO_2 to a silanone group at 300 K is not accompanied by an isotopic exchange between oxygen atoms involved in the carbonate structure [5].

Experiments were carried out with a sample of highly disperse Aerosil A-300 with an initial specific surface area of ~300 m^2/g. The samples were semitransparent plates, which were 50–250-μm thick and had an area of 14 × 8.5 mm^2. They were prepared by pressing the initial powder [10]. After high-temperature treatments, the value of the specific surface area of this material decreased to 100–150 m^2/g. At a concentration of silylene centers on the surface of activated sample of ~10^{13} cm^{-2}, a table with a volume of 1 cm^3 contained ~10^{19} surface defects. The use of such "filmed" samples enabled quantitative spectral measurements in the IR range. To record IR spectra, the sample was placed into a special cell with windows made of IR-transparent silicon plates. All procedures for recording spectra were carried out under a high vacuum or under the conditions of a controlled atmosphere.

IR spectra were recorded at room temperature using a Digilab Fourier-transform spectrometer with 256–1024 scans and a resolution of 4 or 8 cm^{-1}. To record the IR spectra of the sample at wave numbers higher than 1300 cm^{-1} and in the transparency range 850–950 cm^{-1}, we used plates with a thickness of ~50 μm. For the range of wave numbers above 2050 cm^{-1}, the samples were ~6 times thicker. They contained more surface groups of interest.

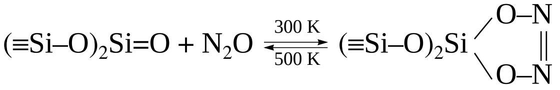
Quantum-chemical calculations were carried out using Gaussian 94 [11]. The structure optimization was performed using density functional theory (DFT) within the gradient approximation (B3LYP/6-311G**) [12, 13]. For all optimized structures, including those with different isotopic compositions, we calculated their vibrational spectra.

RESULTS AND DISCUSSION

1. Group *(≡Si–O)$_2$Si=O*

The presence of silanone groups on the surface of reactive silica can be identified by an IR band at 1306 cm^{-1} and by an optical absorption, the maximum of which is located near 5.6 eV [4]. Figure 1 shows the IR spectrum, which is the difference between the IR spectra for the sample containing the silanone groups $>Si=^{16}O$ before and after their interaction with CO_2 molecules at room temperature (see reaction (III)). In addition to the measurements that were known from [4] (the disappearance of a band at 1306 cm^{-1} and the appearance of two bands of the carbonate group at 1930 and 891 cm^{-1}), the disappearance of low-intensity bands at (2602 ± 1) and (2113 ± 1) cm^{-1} (arrows in Fig. 1) and the appearance of three new bands at (3839 ± 1), (2820 ± 2), and (2207 ± 2) cm^{-1} (stars in Fig. 1) were detected in the range 2050–4000 cm^{-1}. The thermal decomposition of carbonates resulting in the reduction of silanone groups (reaction (III)) is accompanied by the disappearance of new bands and restoration of bands that previously disappeared.

N_2O molecules also react with silanone groups [4, 5]:



$$(\equiv Si–O)_2Si=O + N_2O \underset{500\,K}{\overset{300\,K}{\rightleftarrows}} (\equiv Si–O)_2Si\begin{matrix}/O–N\\ \quad\;\|\\ \backslash O–N\end{matrix}$$

The disappearance of low-intensity bands at (2602 ± 1) and (2113 ± 1) cm^{-1} was observed. These bands were restored in the course of the thermal decomposition of the complex.

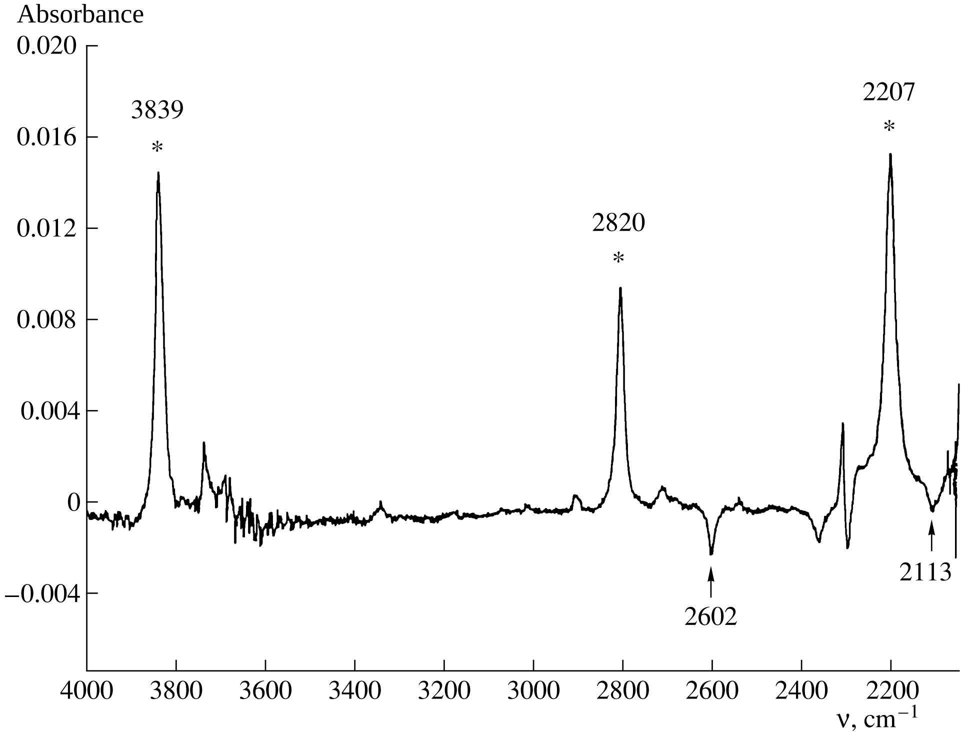


Fig. 1. Difference IR spectrum that characterizes the transformation $(\equiv\text{Si–O})_2\text{Si=O} + \text{CO}_2 \longrightarrow (\equiv\text{Si–O})_2\text{Si}\langle\text{O}_2\rangle\text{C=O}$ on the surface of reactive silica.

The band at 2602 cm^{-1} disappears after the sample treatment with molecular hydrogen at as low temperature as 300 K. As this takes place the absorption bands assigned to the Si–H and SiO–H groups were registered by IR spectroscopy. It was shown in [14, 15] that the silanone group reacts with hydrogen under these conditions:

$$(\equiv\text{Si–O})_2\text{Si=O} + \text{H}_2 \longrightarrow (\equiv\text{Si–O})_2\text{Si(H)(OH)}.$$

Experimental data point to the fact that the low-intensity band with a maximum at (2602 ± 1) cm^{-1} (Fig. 2, spectrum *1*) appears and disappears together with a band at 1306 cm^{-1}. The ratio between the integral intensities $\left(\int D(\nu)\mathrm{d}\nu\right)$ of these bands is approximately 1/(450 ± 100).

Figure 2 (spectrum *2*) shows the IR spectrum of sample **II** which was expected to have silanone groups with different isotopic compositions $>\text{Si}={}^{16}\text{O}$ + $>\text{Si}={}^{18}\text{O}$ judging from the preparation procedure (see above). In this case, we registered two bands at 2602 and 2542 cm^{-1}.

In one of the runs, sample **I** containing silanone groups of one type ($>\text{Si}={}^{16}\text{O}$) (Fig. 2, spectrum *1*) was treated by the ${}^{13}\text{C}^{16,\,18}\text{O}_2$ molecules enriched in ${}^{18}\text{O}$ at 300 K. The fragment of the IR spectrum of this sample in the region of the stretching vibrations of the C=O bond of a carbonate group is shown in Fig. 3 (spectrum *1*). The main bands belong to the groups with the isotopic composition $>{}^{13}\text{C}={}^{16}\text{O}$ (1881 cm^{-1}) and $>{}^{13}\text{C}={}^{18}\text{O}$ (1846 cm^{-1}). After the thermal decomposition of carbonates formed, two bands were registered in the IR spectrum of silanone groups: 2602 and 2542 cm^{-1} (Fig. 2, spectrum *3*). That is, during the process, silanone groups with different isotopic compositions were formed. Isotopic exchange resulted in a decrease in the concentration of the ${}^{18}\text{O}$ atoms in CO_2 molecules, which are the products of carbonate group decomposition. Figure 3 (spectrum *2*) shows the fragment of the IR spectrum of carbonate groups obtained using these CO_2 molecules ($>\text{Si}={}^{16}\text{O}$ + ${}^{13}\text{C}^{16,\,18}\text{O}_2$). A relative decrease in the intensity of the $>{}^{13}\text{C}={}^{18}\text{O}$ band (1846 cm^{-1}) and an increase in the intensity of the $>{}^{13}\text{C}={}^{16}\text{O}$ band (1881 cm^{-1}) in the carbonate structure are seen. This indicates that the concentration of ${}^{18}\text{O}$ atoms in the CO_2 molecules decreased and the concentration of ${}^{16}\text{O}$ atoms increased.

The possible isotopic exchange of an oxygen atom in the silanone group via a carbonate group suggests that the latter has a structure in which both oxygen atoms associated with the surface silicon atom are chemically equivalent. Quantum-chemical calculations also point to the symmetric structure of bidentate carbonate [5, 16] (see also Fig. 4b).

We assign low-intensity bands at 2602 and 2542 cm^{-1} to the first overtone of the stretching vibra-

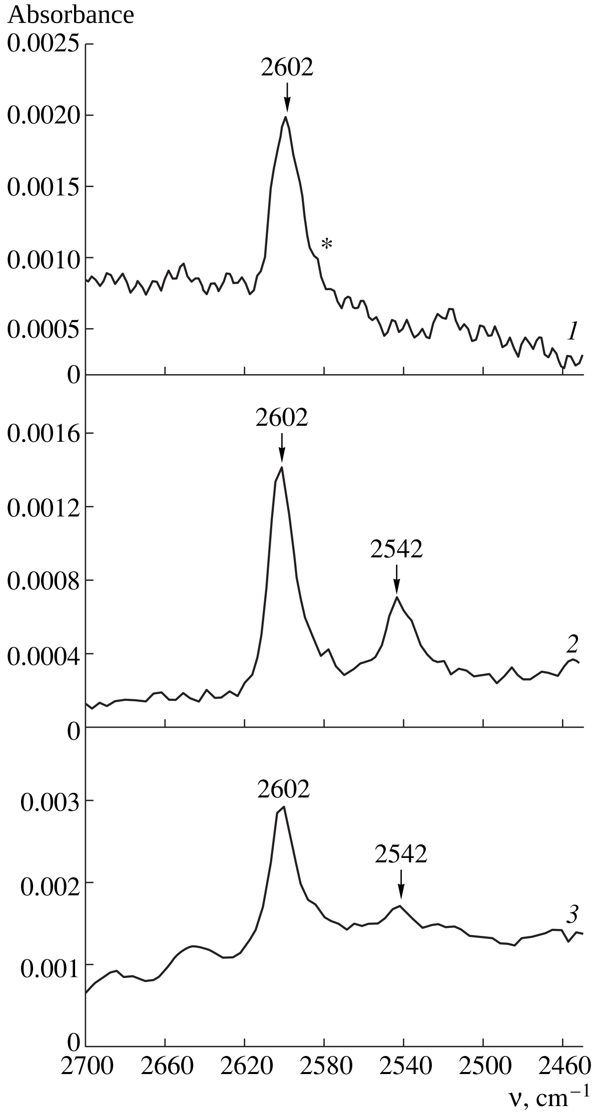


Fig. 2. Absorption band of the first overtone of the Si=O bond stretching vibration in the $(\equiv Si{-}O)_2Si{=}O$ group with different isotopic compositions on the silica surface: (*1*) $(\equiv Si{-}O)_2{}^{28}Si{=}^{16}O$ (sample **I**), (*2*) $(\equiv Si{-}O)_2{}^{28}Si{=}^{16}O$ + $(\equiv Si{-}O)_2{}^{28}Si{=}^{18}O$ (sample **II**), (*3*) after the treatment of sample **I** with $^{13}C^{16,\,18}O_2$ at 300 K and further thermal decomposition of carbonates formed. The star shows the position of the absorption band of the silanone group $^{29}Si{=}^{16}O$.

tions of the $^{28}Si{=}^{16,\,18}O$ bond in the silanone group. The following data are supportive of this assignment: (1) the frequency of the observed transition is close to the doubled frequency of the Si=O stretching vibration band, (2) the bands at 1306 and 2602 cm^{-1} appear and disappear synchronously, (3) the value of the isotopic effect $^{16}O \rightleftarrows {}^{18}O$ is characteristic of a silanone group [17, 18] and equal to (30 ± 1) cm^{-1} (≅1/2(2602–2542) cm^{-1}).

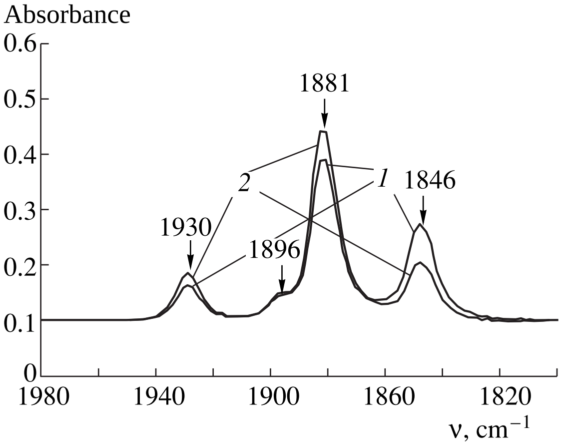


Fig. 3. IR spectrum in the region of the C=O bond stretching vibration in the carbonate $(\equiv Si{-}O)_2Si\langle O_2\rangle C{=}O$ groups with different isotopic compositions (^{12}C, ^{13}C, ^{16}O, and ^{18}O) obtained after the treatment of sample **I** ($>Si{=}^{16}O$) by the molecules $^{13}C^{16,\,18}O_2$ (*1*) enriched in ^{18}O and (*2*) with a low concentration of ^{18}O.

Based on our data, the estimated frequency of Si=O stretches for the silanone group $>{}^{28}Si{=}^{18}O$ on the silica surface is (1276 ± 2) cm^{-1}. The band at 1306 cm^{-1} is located at a wing of the intensive band of the fundamental absorption of silica. Upon a shift by 30 cm^{-1}, the band of $>Si{=}^{18}O$ stretches fall into the region where its registration is difficult for the sample that we used. This prevented us from the experimental registration of the absorption of the isotope-substituted silanone group $>Si{=}^{18}O$ [5].

Figure 4a shows the optimized structure of the $(F_3Si{-}O)_2Si{=}O$ compound (**VIII**), which is a molecular model of the surface silanone group. For this compound and for the molecules $H_2Si{=}O$ (**IX**), $F_2Si{=}O$ (**X**), and $(H_3Si{-}O)_2Si{=}O$ (**XI**), we calculated vibrational spectra. For the $H_2Si{=}O$ and $F_2Si{=}O$ molecules, the frequency of the Si=O stretch was experimentally determined ($H_2Si{=}^{16}O$, 1202; $H_2Si{=}^{18}O$, 1162 [19]; $F_2Si{=}^{16}O$, 1309; $F_2Si{=}^{18}O$, 1276 cm^{-1} [18]; IR registration in an argon matrix at low temperatures). For other molecules, experimental data are unavailable. The calculated frequencies of $Si{=}^{16,\,18}O$ stretching vibrations are as follows: **VIII**, 1300 (1272.5); **IX**, 1216.5 (1175.5); **X**, 1330 (1294); **XI**, 1330 (1306) cm^{-1}. For molecules **VIII** and **XI**, the frequencies of $^{29}Si{=}^{16}O$ fragment vibrations were equal to 1321 and 1290 cm^{-1}, respectively.

To correct the calculated values of frequencies, scaling factors are usually used [20]. If we set the scaling factor equal to the ratio of some experimental and calculated frequencies in the $F_2Si{=}O$ molecule (1309/1330), then we obtain the following values for the frequency of the Si=O stretch in the $(H_3Si{-}O)_2Si{=}O$ and $(F_3Si{-}O)_2Si{=}O$ molecules and their isotopes ($>{}^{28}Si{=}^{18}O$): 1279 (1252.5) and 1309 (1285) cm^{-1}, respectively.

Thus, the calculations agree with the experimental data and show that the frequency of the Si=O bond stretching vibration in the $F_2Si{=}O$, $(F_3Si{-}O)_2Si{=}O$ and $(\equiv Si{-}O)_2Si{=}O$ molecules and in the surface silanone group are close to each other. This probably points to the fact that the silanone group $(\equiv Si{-}O)_2Si{=}O$ has a spatial structure similar to that of the $(F_3Si{-}O)_2Si{=}O$ molecule (in its equilibrium configuration, see Fig. 4a). For the $(H_3Si{-}O)_2Si{=}O$ molecule, the calculated frequency of the Si=O bond stretching is substantially lower. On the one hand, these data suggest that the chemical nature of relatively distant substituents (the replacement of a hydrogen atom by fluorine) substantially affects the spectral characteristics of a group. On the other hand, this is further evidence for a conclusion drawn in [21] that the fluorine atom and the ≡Si–O– group, which are the substituents, have a similar effect on the physicochemical properties of the silicon atom.

In silica samples, the natural concentration of the ^{29}Si isotope is 4.7%. The replacement of $>^{28}Si{=}^{16}O$ by $>^{29}Si{=}^{16}O$ leads to a decrease in the frequency of the stretching vibration of this bond by 9–10 cm^{-1} (according to calculations) and the contribution of silanone groups with this isotopic composition must reveal itself in the appearance of long-wave wings of absorption bands at 1306 and 2602 cm^{-1} (as shown by a star in Fig. 2, spectrum *1*).

The experimental data allow us to estimate the degree of anharmonicity of the Si=O bond stretching vibration. Taking into account the anharmonicity of vibrations in a molecule with many atoms, the energy of its vibrational levels can approximately be described as follows [2]:

$$E(n_1, \ldots, n_i, \ldots) = \Sigma\nu_j(n_i + 1/2) + \Sigma d_{ii}(n_j + 1/2)^2 + \Sigma d_{ij}(n_i + 1/2)(n_j + 1/2), \qquad (1)$$

where ν_j are zero (harmonic) frequencies of the corresponding normal vibrations, d_{ii} is the coefficient that characterizes the anharmonicity of a given normal vibration, and d_{ij} is the relation between different normal vibrations stipulated by anharmonicity. For the first overtone of vibration with the frequency ν_j, the difference in the energies is $E(2\nu_j) - 2E(\nu_j) = 2d_{ii}$. In our case, $E(2\nu_1) - 2E(\nu_1) = (10 \pm 1)$ cm^{-1} and $d_{11} = (5 \pm 1)$ cm^{-1}. This is a typical value for the anharmonicity of vibrations in molecules [2].

It was found in [21] that, on the surface of reactive silica, two fractions of silylene centers are stabilized in comparable amounts. They differ slightly in their characteristics, specifically in their optical and chemical properties. The fraction associated with a short-wave band of optical absorption is characterized by smaller differences inside the group (i.e., it is more homogeneous). Silanone groups are the product of the chemical modification (oxidation) of silylene centers, and they must also differ in their characteristics. The corresponding effects can reveal themselves in the IR spectra of these groups in the form of band broadening or splitting. The silanone group is associated with a line near 1306 cm^{-1}. However, if IR absorption is registered in a region of smaller wave numbers, some technical difficulties appear (see above). There are no such problems in the region of overtone transition where only one slightly asymmetric singlet absorption band was registered for the Si=O bond stretching (Fig. 2, spectrum *1*).

Table 1. Frequencies of stretching vibration of the C=O bond in the $>Si\langle O_2\rangle C{=}O$ group (ν_2) and its first overtone

Isotopic composition	ν, cm^{-1}		$E(2\nu) - 2E(\nu)$, cm^{-1}
	Transition 0 ⟶ 1 ($E(\nu)$)	Transition 0 ⟶ 2 ($E(2\nu)$)	
$>Si\langle {}^{16}O_2\rangle {}^{12}C{=}^{16}O$	1930 ± 1	3839 ± 1	21 ± 2
$>Si\langle {}^{18}O_2\rangle {}^{12}C{=}^{16}O$ + $>Si\langle {}^{16,18}O_2\rangle {}^{12}C{=}^{16}O$	1928 ± 1*	3834 ± 1*	22 ± 2
$>Si\langle {}^{16}O_2\rangle {}^{12}C{=}^{18}O$ + $>Si\langle {}^{16,18}O_2\rangle {}^{12}C{=}^{18}O$	1896 ± 1*	3770 ± 2*	22 ± 3
$>Si\langle {}^{16}O_2\rangle {}^{13}C{=}^{16}O$	1881 ± 1	3742 ± 1	20 ± 2
$>Si\langle {}^{16}O_2\rangle {}^{13}C{=}^{18}O$ + $>Si\langle {}^{16,18}O_2\rangle {}^{13}C{=}^{18}O$	1846 ± 1*	3673 ± 2*	19 ± 3

* Experimental spectrum is a superposition of the signals from the structures of the isotopic composition.

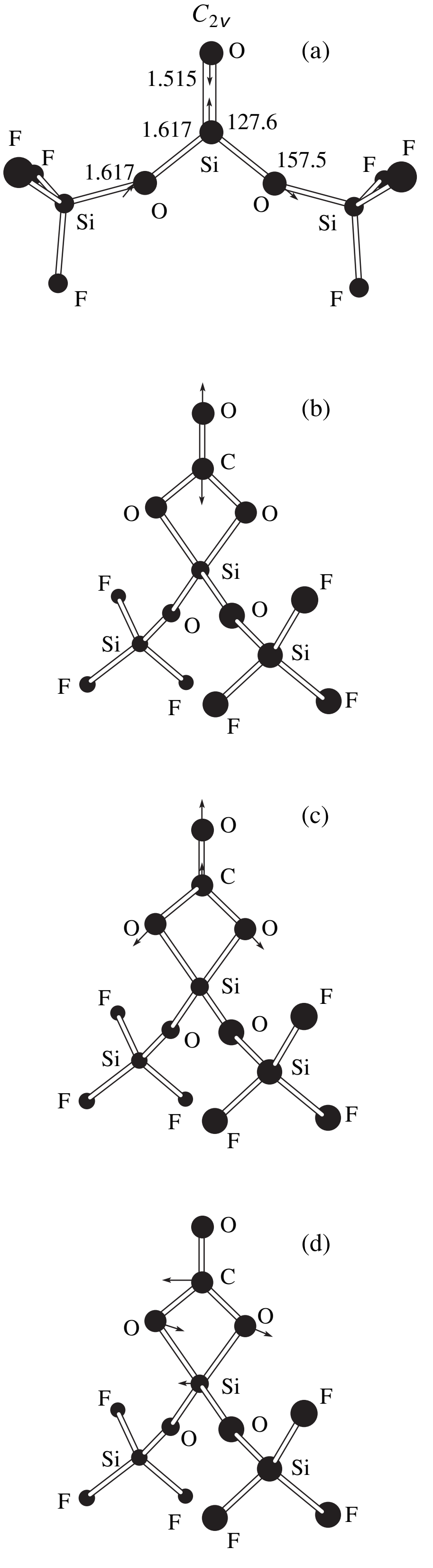


Fig. 4. The equilibrium structure and form of normal vibrations of molecules (a) $(F_3Si–O)_2Si = O$ (ν_1) and (b, c, d) $(F_3Si–O)_2Si\langle O_2\rangle C=O$ (ν_2, ν_3, and ν_4, respectively).

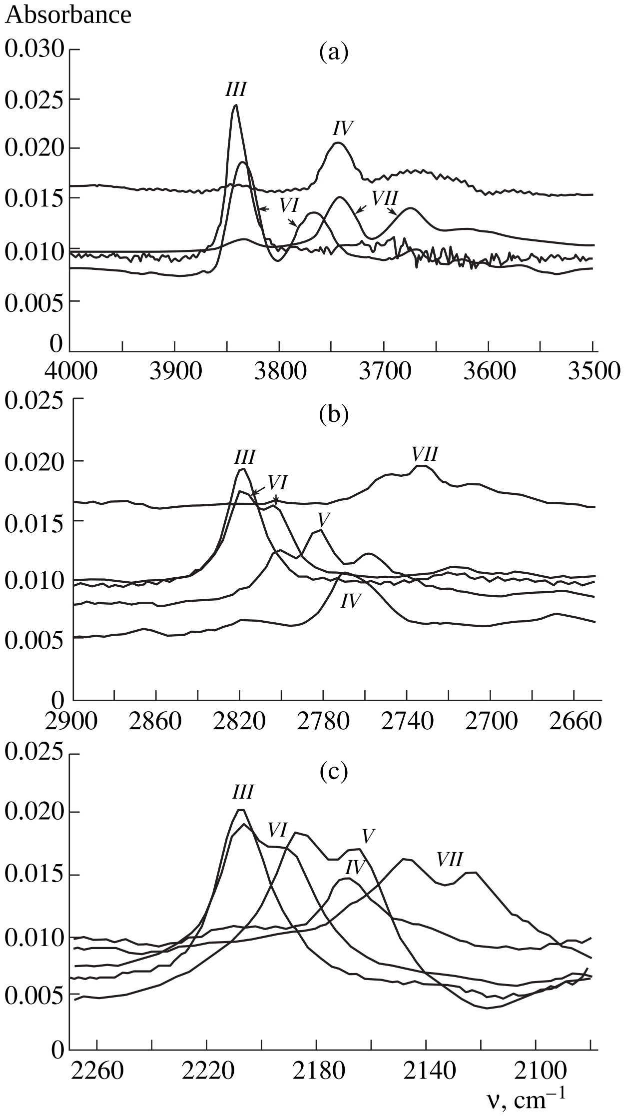


Fig. 5. Isotopic shifts in the IR spectrum of the group $(\equiv Si–O)_2Si\langle O_2\rangle C=O$ for the bands at (a) 3839, (b) 2840, and (c) 2207 cm^{-1}. The numbers of curves correspond to the sample number in the text.

This fact allows us to assert that the region of the main frequencies of Si=O bond stretching has only one singlet absorption band as well. Therefore, possible differences in the vibrational frequencies of silanone groups belonging to different fractions are smaller than the line width (i.e., smaller than 10 cm^{-1}). The asymmetry of the absorption band reveals itself in the region of smaller wave numbers. This suggests (see above), that silanone groups are located here, which were formed from a less homogeneous fraction of silylene centers with an optical absorption band shifted to a long-wave region.

In the beginning of this section we noted that samples containing silanone groups showed another low-intensity band near (2113 ± 2) cm^{-1} (see Fig. 1), but we failed to identify the origin of this band.

2. Group $(\equiv\text{Si–O})_2\text{Si}\langle\text{O}_2\rangle\text{C=O}$

Figure 5a shows the IR spectra of carbonate groups with different isotopic compositions in the region of ~3800 cm^{-1}. The positions of separate bands for different isotopic compositions are listed in Table 1. As follows from these data, the isotopic shift of the main frequency near 1900 cm^{-1} (ν_2) is accompanied by a shift near 3800 cm^{-1} (approximately twice as large). Based on the experimental data, we associate the latter band with the first overtone of the C=O bond stretching in the carbonate group. The intensity $\left(\int D(\nu)\mathrm{d}\nu\right)$ of overtone transition is ~1/(250 ± 75) of the intensity of the main transition. The value d_{22} estimated from formula (1) and characterizing the anharmonicity of this normal vibration is 10.5 ± 2 cm^{-1}.

The second low-intensity band associated with the carbonate group was registered near 2800 cm^{-1}. In this region, the appearance of the main frequency was expected that corresponded to the $(0, 0) \longrightarrow (1, 1)$ transition because the overall frequency of two vibrations in the carbonate group $\nu_2 + \nu_3 = (1930 + 891)$ cm^{-1} falls into this region. The intensity of this band is close to the intensity of the C=O bond stretching overtone and changes synchronously with the intensities of bands related to the carbonate group (1930 and 891 cm^{-1}). The proof of the fact that the apparent band is indeed a composite frequency of the above-mentioned vibrations was obtained in the study of the isotopic shift of these bands. The corresponding experimental data are illustrated by Fig. 5b and Table 2.

According to data reported in Table 2, the frequency of this transition differs only slightly from the sum of the main frequencies. According to formula (1), this means that the value of d_{23}, which characterizes the relation between these two normal vibrations due to anharmonicity, is noticeably higher than in the case of the overtones considered above. On the other hand, the intensity of this band is comparable with overtone intensities. This means that the intensity of the composite band is mainly due to mechanical rather than electrooptical anharmonism, which is associated with the redistribution of the charge densities during the corresponding normal vibrations [2]. For an efficient relation between two normal components, they must have the same symmetry and a common group of atoms. In [5], frequency ν_3 (890 cm^{-1}) was assigned to the normal vibration with symmetry A_1 whose form is shown in Fig. 4c. Figure 4b shows the shifts of atoms for the normal vibration with frequency ν_2. A carbon atom and a terminal oxygen atom are the main participants of this vibration and move in antiphase. The same atoms also participate in normal vibration ν_3, but they synchronously move in the same phase in this case. Both of these normal vibrations have the same symmetry (A_1). Thus, there are favorable conditions in the molecule for the interaction of these two vibrations and for the appearance of the composite frequency ($\nu_2 + \nu_3$) in the spectrum.

The third band associated with the carbonate group (with the isotopic composition $>\text{Si}\langle{}^{16}\text{O}_2\rangle{}^{12}\text{C}={}^{16}\text{O}$) is at 2207 ± 1 cm^{-1} (Fig. 1). Its intensity is comparable with

Table 2. Main experimental frequencies (ν_2 and ν_3) and the corresponding composite frequency of the vibration of the $>\text{Si}\langle\text{O}_2\rangle\text{C=O}$ group with different isotopic compositions*

Isotopic composition	Composite frequency	ν_2	ν_3	$\nu_2 + \nu_3$
$>\text{Si}\langle{}^{16}\text{O}_2\rangle{}^{12}\text{C}={}^{16}\text{O}$	2819 ± 2	1930 ± 1	891 ± 1	2821 ± 2
$>\text{Si}\langle{}^{16}\text{O}{}^{18}\text{O}\rangle{}^{12}\text{C}={}^{16}\text{O}$	2802 ± 2	1928 ± 1	874 ± 1	2802 ± 2
$>\text{Si}\langle{}^{18}\text{O}_2\rangle{}^{12}\text{C}={}^{16}\text{O}$	2783 ± 2	1928 ± 1	864 ± 2	2792 ± 3
$>\text{Si}\langle{}^{16}\text{O}_2\rangle{}^{13}\text{C}={}^{16}\text{O}$	2767 ± 2	1881 ± 1	889 ± 1	2770 ± 2
$>\text{Si}\langle{}^{16}\text{O}{}^{18}\text{O}\rangle{}^{12}\text{C}={}^{18}\text{O}$	2758 ± 2	1896 ± 1	874 ± 2	2770 ± 3
$>\text{Si}\langle{}^{16}\text{O}{}^{18}\text{O}\rangle{}^{13}\text{C}={}^{16}\text{O}$	2749 ± 3	1879 ± 2	874 ± 2	2753 ± 2
$>\text{Si}\langle{}^{18}\text{O}_2\rangle{}^{13}\text{C}={}^{16}\text{O}$	2733 ± 2	1879 ± 1	864 ± 2	2743 ± 3
$>\text{Si}\langle{}^{16}\text{O}{}^{18}\text{O}\rangle{}^{13}\text{C}={}^{18}\text{O}$	2708 ± 3	1846 ± 2	874 ± 2	2720 ± 2

* Energies of transitions are in cm^{-1}.

Table 3. Experimental positions of the band near 2210 cm^{-1} and the calculated vibration frequencies ν_4 for the $>Si\langle O_2\rangle C{=}O$ group with different isotopic compositions*

Isotopic composition	Experiment	ν_4	$2\nu_4$	$(2\nu_4)_{corr}$**
$>Si\langle {}^{16}O_2\rangle {}^{12}C{=}{}^{16}O$	2207 ± 2	1109	2218	2207
$>Si\langle {}^{16}O{}^{18}O\rangle {}^{12}C{=}{}^{16}O$	2192 ± 2	1100	2200	2189
$>Si\langle {}^{18}O_2\rangle {}^{12}C{=}{}^{16}O$	2165 ± 2	1087	2174	2163
$>Si\langle {}^{16}O_2\rangle {}^{12}C{=}{}^{18}O$	2207 ± 2	1107	2214	2203
$>Si\langle {}^{16}O{}^{18}O\rangle {}^{12}C{=}{}^{18}O$	2186 ± 2	–	–	–
$>Si\langle {}^{16}O_2\rangle {}^{13}C{=}{}^{16}O$	2168 ± 2	1087	2174	2163
$>Si\langle {}^{16}O{}^{18}O\rangle {}^{13}C{=}{}^{16}O$	2147 ± 2	–	–	–
$>Si\langle {}^{18}O_2\rangle {}^{13}C{=}{}^{18}O$	2124 ± 2	–	–	–

* Energies of transitions are in cm^{-1}.

** For the convenience of comparison of experimental and theoretical isotopic shifts, the latter are scaled ($(2\nu_4)_{corr}$) with a coefficient of 2207/2218.

the intensities of bands at 3840 and 2840 cm^{-1}. A carbonate group with an ordinary isotopic composition has no other intense bands than the band at 1930 cm^{-1} up to 1280 cm^{-1} (the boundary of sample transparency). The next intensive absorption band is at 891 cm^{-1}. This means that the band at 2207 cm^{-1} is associated with other main frequencies in the vibrational spectrum of a carbonate group. These main frequencies were not identified in the IR spectrum. The origin of this band was determined by analyzing experimental data on the effect of isotopic substitution on its position. This analysis was performed with the aid of the quantum-chemical calculations of the vibrational spectrum of the carbonate group in the molecule $(F_3Si–O)_2Si\langle O_2\rangle C{=}O$. The experimental and theoretical findings are summarized in Table 3. According to quantum-chemical calculations, in the region 900–1300 cm^{-1}, an intensive absorption band $\nu_4 = 1109$ cm^{-1} (450 km/mol) belongs to the carbonate group. Shifts corresponding to this normal vibration are shown in Fig. 4d. They are in the plane of a ring. Oxygen atoms and silicon or carbon atoms shift in different directions. Table 3 shows the frequencies of this vibration calculated for the groups with different isotopic compositions. We see acceptable agreement between the experimental and calculated isotopic shifts. Therefore, our findings suggest that the band at 2207 cm^{-1} should be assigned to the first overtone of carbonate group vibration (Fig. 4d shows its form). Assuming that the value of anharmonicity for this normal vibration is the same as for two other vibrations (1306 and 1930 cm^{-1}), we estimate its frequency: $\nu_4 = 1108 \pm 2$ cm^{-1}. This band belongs to the region of intensive absorption by the silica silicon–oxygen skeleton. The registration of the overtone is a convenient method for its experimental detection by IR spectroscopy.

CONCLUSIONS

(1) We showed that silanone $(\equiv Si–O)_2Si{=}O$ and carbonate $(\equiv Si–O)_2Si\langle O_2\rangle C{=}O$ groups on the silica surface can be registered by IR spectroscopy in a spectral range that is convenient for observations (2100–4000 cm^{-1}).

(2) The first overtone of the Si=O bond stretching in the $(\equiv Si–O)_2Si{=}O$ group was registered. The value of the isotopic shift ${}^{16}O \longrightarrow {}^{18}O$ of the frequency was determined (60 ± 2 cm^{-1}) for this vibration. This supports the correctness of its assignment to the cited vibration.

(3) Several low-intensity bands were found in the IR spectrum of the carbonate group $(\equiv Si–O)_2Si\langle O_2\rangle C{=}O$. Data on the isotopic shifts together with the results of quantum chemical calculations of the model compounds enabled their identification as overtones and composite frequencies of the normal vibrations of a certain type in a carbonate group. A new band assigned to the carbonate group was found at 1108 ± 2 cm^{-1}.

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