

IR absorption spectra of vitreous silica and silicate glasses: The nature of bands in the 1300 to 5000 cm^{-1} region

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Abstract

The transmittance spectra of Types I and III silica glasses in the 1300 to 5000 cm^{-1} region are measured and the absorptivity spectra calculated from data obtained are processed with the dispersion analysis method based on the convolution model for the complex dielectric function. The IR absorption bands with inherent frequencies around 1480, 1630, 1760, 1870, 1980, 2140, 2260, 2370, 2540, 2660, and 2810 cm^{-1} in the spectra of glasses of both types are shown to be due to the combination modes and overtones of the silica matrix; the same is assumed for a weak 3140 cm^{-1} band. A weak band with frequency around 3490 cm^{-1} is assigned tentatively to the symmetric stretching mode of interstitial H_2O molecules present in trace amounts. For Type III glass, nine other water-related bands are found. Of these, three bands with frequencies from 3570 to 3675 cm^{-1} are assigned to the stretching modes of hydroxyl groups in two different structural sites and the remaining six bands with frequencies from ~ 3750 to ~ 4510 cm^{-1} are assigned to unidentified combination modes involving certain stretching vibrations of hydroxyl groups. Data obtained are compared to recent data on the IR band parameters of $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{K}_2\text{O}-\text{CaO}-\text{BaO}-\text{SiO}_2$ and window glasses. Bands around 1540–1610, 1670–1750, 1810–1840, 1900–1930, and 2030–2110 cm^{-1} in the spectra of these glasses are concluded to be envelopes, each of the envelopes covering a hydroxyl-related band and a band or two due to certain combination modes or overtones of glass matrices.

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1. Introduction

Water is not only an important component of natural magmas and many minerals but also an unavoidable impurity in synthetic glassforming liquids and commercial glasses. Among properties influenced by the water-

related species, it is the absorption in the near- and mid-IR that is of principal importance. It is noteworthy that:

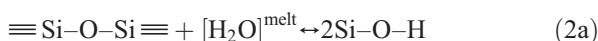
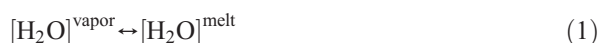
- variations in the number, locations, and intensities of the water-related IR absorption bands depending on temperature, total water content, etc. are the manifestations of changes in the equilibria between different water-related species;
- these bands influence the radiative heat transfer in glasses and glassforming liquids (see, for example, van Nijnatten et al., 1999);

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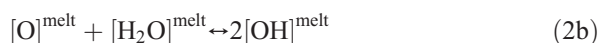
- for optical glasses, the occurrence of such bands is the main factor determining the long-wavelength limit of their transparency range;
- in laser glasses, these bands decrease the quantum yield of luminescence, thus diminishing the efficiency of light generation.

The principal mechanism of interaction of water with silicon–oxygen network is known (see, for example, Scholze, 1966, 1991; Stolen and Walrafen, 1976; Stone and Walrafen, 1982; Stolper, 1982; Bartholomew, 1983; Tomozawa, 1985; Davis and Tomozawa, 1996; Grzechnik and McMillan, 1998; Kohn, 2000) to consist in breaking the Si–O–Si bridges by water molecules dissolved in a melt in accord with reactions as follows:



An increase in the total H₂O content was shown to result in a consecutive increase in the fraction of molecular water, whereas the fraction of water in the form of the hydroxyl group was found to tend to saturation when reaching the total H₂O content of 4–6 wt.% (see, for example, Tomozawa, 1985).

For purely thermodynamic considerations, Eq. (2a) is often (Zhang et al., 2000; Nowak and Behrens, 2001) reduced to



Davis and Tomozawa (1996) presented this mechanism in more detail by assuming (i) the dissolved water molecules to be attached by hydrogen bonding to the bridging oxygens of the matrix and (ii) the silanol Si–O–H groups just formed to be connected first to one another by the hydrogen bonding and then parting through diffusion.

The equilibrium of reaction (2a), (2b) was found to shift to the right-hand side with temperature, which is why this equilibrium was considered to be indicative of cooling rates of magmas (Zhang et al., 2000; Nowak and Behrens, 2001). Naturally, Eq. (2a) is only a general scheme; other equilibria between Si–O–H groups in different structural sites occur as well.

Generally, all the vibrational bands characteristic of H₂O molecule and Si–O–H group are referred to as the water-related ones. In the spectra of silica films and glasses synthesized under reducing conditions, bands due to the stretching modes of ≡Si–H groups were found (see, for example, Wang et al., 2005). Sometimes,

such bands are considered to be water-related as well. The list of possible water-related bands was presented by Davis and Tomozawa (1996) that was compiled using various literature sources and the authors' own data on the high-water-content silica spectrum.

From the viewpoint of the dynamics of crystal lattices and glass networks, it is expedient to distinguish two types of such bands. The ≡Si–O–H group in the right-hand side of Eq. (2a) should be considered to contain two vibrators, namely, the terminal group of the hydrated silicon–oxygen network and the bound hydroxyl group as such. For brevity, the groups are denoted further by Si–O(H) and (Si)O–H, respectively. Due to dynamical and kinematical reasons, these vibrators are practically independent from each other, so that the fundamental modes of these vibrators are separated well at the wavenumber scale. Bands due to the fundamental modes of (Si)O–H group occur at wavenumbers substantially greater than the upper limit for bands due to the first order matrix vibrations.¹ The same is valid also for bands due to the fundamental modes of the coordinated or interstitial water molecule. When studying glasses with small total water content, it is bands of this type alone (and also bands due to the overtone and combination modes involving such fundamental modes) that are often described as “water-related.”

The IR absorption bands due to the fundamental Si–O(H) modes were found in the spectra of crystalline acidic silicates, their hydrates (Ryskin and Stavitskaya, 1960; Ryskin, 1971), and high-water-content glasses (Bartholomew, 1983; Tomozawa, 1985; McMillan and Remmele, 1986; Davis and Tomozawa, 1996). These bands occur in a region practically the same as that for the fundamental bands of water-free matrices (for the lattice vibrations involving the Si–O(H) stretch, this region lying in between 700 and 1000 cm^{−1} – see Ryskin and Stavitskaya, 1960; Ryskin, 1971). In the IR spectra of glasses synthesized under atmospheric pressure whose total water content is much less than 1 wt.%, the corresponding IR bands are, as a rule, too weak to be resolved from the intense multiband IR spectrum of the water-free matrix. In the Raman spectra of such glasses, however, a band around 970 cm^{−1} due to the stretching Si–O(H) mode is observable (Hartwig and Rahn, 1977; McMillan and Remmele, 1986; Davis and Tomozawa, 1996).

The IR band frequencies corresponding to the (R)O–H stretching modes (R being Si, P, B, etc.) were found

¹ This concerns modes of the same type only: the bending modes of H₂O molecules can fall into the region of the stretching matrix modes.

long ago to vary greatly depending on the strength of the hydrogen bonding in which the (R)O–H group is involved (see, for example, Ryskin and Stavitskaya, 1960; Scholze, 1966, 1991; Ryskin, 1971). At the same time, these band frequencies were shown, in accord with their separation from the matrix modes, to be almost insensitive to the kind of a matrix: the locations of the strongest bands due to various (R)O–H modes were found to be similar irrespective of whether R was Si or P. For bands due to the coordinated water molecules in hydrates, such insensitivity to the kind of a matrix was shown as well (Ryskin and Stavitskaya, 1960; Ryskin, 1971).

There is still a substantial controversy about data available on the total number and origin of particular first order water-related bands of the latter type in glass spectra. Initially (see, for example, Scholze, 1966), these bands were considered to occur at wavenumbers no less than 3500 cm^{-1} in silica glasses and no less than 2300 cm^{-1} in binary and multicomponent glasses.

For silica glasses, Scholze took the principal water-related maximum centered at $3650\text{--}3700\text{ cm}^{-1}$ to be a single band due to the stretching mode of the “free” (Si) O–H group, i. e., that in a site lacking hydrogen bonding. Soon, however, bands due to the stretching and bending modes of H_2O molecule around $3450\text{--}3500$ and $1610\text{--}1630\text{ cm}^{-1}$, respectively, were found (Stolen and Walrafen, 1976; Ernsberger, 1977; Stolper, 1982; Bartholomew, 1983; Tomozawa, 1985; Newman et al., 1986; McMillan and Remmele, 1986; Davis and Tomozawa, 1996) in the IR and Raman spectra of silica glasses with increased water content. With an increase in the total water content, the concentration of (Si)O–H groups was found (see, for example, Tomozawa, 1985) to tend to saturation, which is why the predominant species at low and high water content are the (Si)O–H group and interstitial H_2O molecule, respectively. Also, a band around 2800 cm^{-1} was observed in the spectra of water-enriched glasses (Bartholomew, 1983; Tomozawa, 1985; Davis and Tomozawa, 1996), this band being assigned to the stretching mode of the hydrogen-bonded (Si)O–H group.

In many studies, the $3650\text{--}3700\text{ cm}^{-1}$ maximum was found to be an envelope, the assumed number of individual bands under this envelope varying greatly from source to source. Using Gaussian band shapes, Walrafen and Samanta (1978) found this number in the spectrum of Type III silica glass to be four, the band frequencies being 3510 , 3615 , 3665 , and 3690 cm^{-1} . The band assignments were based on an idea of pairing the (Si)O–H groups in the so-called bidentate units of two kinds. Three different sites for (Si)O–H groups in

these units were assumed, the sites corresponding to the strongest hydrogen bonding, hydrogen bonding intermediate in strength, and no such bonding at all. The mode corresponding to two (Si)O–H groups in the symmetric bidentate unit with intermediate hydrogen bonding was assumed to be split into two components. After Walrafen and Samanta (1978), this idea was used, with no or minor changes, by many subsequent authors for interpreting the fundamental (Wakabayashi and Tomozawa, 1989; Bredol et al., 1990; Gerasimov, 1990; Davis and Tomozawa, 1996) and multiphonon (Stone and Walrafen, 1982; Yokomachi et al., 1987; Bredol et al., 1990; Humbach et al., 1996; Davis and Tomozawa, 1996) spectra of silica.

In contrast, McMillan and Remmele (1986) assumed the $3650\text{--}3700\text{ cm}^{-1}$ maximum to be a single band with a substantially asymmetric contour (line shape) that is due to a continuous distribution of hydrogen bond strengths for (Si)O–H groups. Then, Davis and Tomozawa (1996), using an empirical Pearson VII contour for representing the band shapes, found the number of individual bands under this envelope to vary, depending on the conditions of heat/water treatment of a melt, from three to six. Later, Grzechnik and McMillan (1998) assumed, based on the occurrence of the $4450/4520\text{ cm}^{-1}$ doublet in the combination mode region, that the fundamental $3650\text{--}3700\text{ cm}^{-1}$ envelope in the spectrum of Type III silica glass sample consists of two components as well (no deconvolution of the envelope being made). Furthermore, it was shown (Efimov, 2002) with the dispersion analysis based on the convolution model for the complex dielectric function (see below) that only three strong components around 3570 , 3630 , and 3670 cm^{-1} are necessary for representing the $3650\text{--}3700\text{ cm}^{-1}$ envelope quite accurately. The overtone band around 7200 cm^{-1} was also shown (Efimov and Hobert, 2004) to be reproduced, with maximum accuracy, using three spectral components only (the asymmetric band contours being used).

In the spectra of low-water-content silica glasses at wavenumbers from 3000 down to 1300 cm^{-1} , all bands are commonly assigned (see, for example, Silin' and Trukhin, 1985; Haken et al., 2000) to the multiphonon modes of the water-free SiO_2 matrix.

For binary and multicomponent oxide glasses, three broad water-related absorption maxima were known long ago to occur at 2350 ± 30 , 2800 ± 170 , and $3500\pm 200\text{ cm}^{-1}$. Scholze (1966, 1991) assumed these maxima to be individual bands and assigned them to the stretching modes of hydroxyl groups in three different structural sites. The 2350 ± 30 and $2800\pm 170\text{ cm}^{-1}$ bands were assigned to the sites differing in the strength

of the hydrogen bonding formed with the nonbridging oxygens of Q^0 and Q^3 (or Q^2) tetrahedron species, respectively. The $3500 \pm 200 \text{ cm}^{-1}$ band was assigned, as in the silica glass spectrum, to the stretching mode of “free” hydroxyl group in a site lacking any hydrogen bonding.

Scholze’s assumption that it is the hydroxyl groups alone that are responsible for the absorption in the $2300\text{--}3700 \text{ cm}^{-1}$ region was used recently by Geotti-Bianchini et al. (1999, 2000) for calculating the total water content of glasses. The so-called “single band method” and “two band method” were developed for borosilicate and soda–lime–silica glasses, respectively. The former uses the peak absorption coefficient at 3580 cm^{-1} only. The latter method uses two peak absorption coefficients at 3500 and 2900 cm^{-1} assigned to the “free” hydroxyl group and the group participating in the hydrogen bonding, respectively.

Similar to the case of silica, the pattern of the fundamental water-related spectra of binary and multicomponent oxide glasses was shown soon after Scholze (1966) to be the more complicated than that assumed by Scholze himself and his successors. First, bands due to the stretching and bending modes of the interstitial H_2O molecules were found in the IR spectra of water-enriched glass samples (Ernsberger, 1977; Stolper, 1982; Bartholomew, 1983; Newman et al., 1986; Tomozawa, 1985; McMillan and Remmele, 1986; Kohn, 2000). Further, three unappreciated strong bands were discovered in the IR spectra of sodium zinc pyrophosphate glasses (Efimov et al., 1998), the inherent frequencies of these bands being calculated, with the dispersion analysis, to be 1680 , 1785 , and 2060 cm^{-1} . The peak absorptivities and oscillator strengths of these bands were found, with the dispersion analysis based on the convolution model for the complex dielectric function (see below), to vary substantially depending on the water content and temperature of glass melting,² which indicated these bands to be water-related. It was shown also that variations in the peak absorptivities of these three bands and the known (Scholze, 1966, 1991) hydroxyl-related band at 2330 cm^{-1} are correlated with each other, which indicated that (i) all four bands are due to some stretching (P)O–H mode and (ii) this mode occurs in (P)O–H groups occupying the same structural site. Based on the above and also on the fact that these band frequencies fall into the regions covered by the known broad (P)O–H-related bands in the spectra of various hydrophosphate crystals (Ryskin

and Stavitskaya, 1960; Ryskin, 1971), the 1680 , 1785 , 2060 , and 2330 cm^{-1} bands were assigned to the stretching mode of the (P)O–H group in a site that corresponds to strong hydrogen bonding with certain nonbridging oxygens of a glass matrix, this stretching mode being split into four components.

A broad water-related $2450\text{--}3700 \text{ cm}^{-1}$ envelope in the spectra of the same glasses was deconvoluted into four individual bands with frequencies of 2837 , 2940 , 3180 , and 3410 cm^{-1} . Variations in the peak absorptivities of these bands with the water content of glass and glass melting temperature showed no correlation to variations characteristic of the above hydroxyl-related 1680 , 1785 , 2060 , and 2330 cm^{-1} bands but were correlated with each other. This indicated that (i) these bands are related to the stretching modes of the interstitial H_2O molecule rather than (P)O–H group and that (ii) these modes occur in H_2O molecules occupying the same structural site. Therefore, the 2837 , 2940 , 3180 , and 3410 cm^{-1} bands were assigned by Efimov et al. (1998) to the components of the ν_{as} and ν_{s} modes of the interstitial H_2O molecule, each mode being split into two components. For crystalline hydrophosphates, the frequencies of the ν_{s} modes were found (Ryskin, 1971), unlike the case of liquid water, to be greater than those for the ν_{as} modes. In view of this, the 2837 and 2940 cm^{-1} bands were assigned to the ν_{as} mode and the 3180 and 3410 cm^{-1} bands were assigned to the ν_{s} mode.

In the experimental IR spectra of various silicate glasses (Glebov and Boulos, 2000; Efimov and Pogareva, 2000; Efimov et al., 2003), three distinct strong bands at wavenumbers in between 1500 and 2150 cm^{-1} and the less intense well-known band around 2300 cm^{-1} were found as well. Glebov and Boulos (2000) deconvoluted, from the spectrum of a $\text{Na}_2\text{O}\text{--}\text{CaO}\text{--}\text{SiO}_2$ glass, four Gaussian components with frequencies of 1580 , 1760 , 2070 , and 2300 cm^{-1} , these components being assumed to be due to the multiphonon vibrations of the glass matrix. Efimov (2002) and Efimov et al. (2003) deconvoluted, with the dispersion analysis the same as that used by Efimov et al. (1998), six bands with frequencies of $1539\text{--}1606$, $1670\text{--}1745$, $1807\text{--}1840$, $1903\text{--}1927$, $2030\text{--}2107$, and $2302 \pm 8 \text{ cm}^{-1}$ from the spectra $\text{Na}_2\text{O}\text{--}\text{SiO}_2$, $\text{K}_2\text{O}\text{--}\text{CaO}\text{--}\text{BaO}\text{--}\text{SiO}_2$, and window glasses. The oscillator strengths of all the bands were shown to vary with water content of glasses, which indicated these bands to be water-related. This was confirmed by the fact that these band frequencies fall into the regions covered by the known broad (Si)O–H-related bands in the spectra of various hydrosilicate crystals (Ryskin and Stavitskaya, 1960; Ryskin, 1971). For the

² Similar to the case for silica, the equilibrium of Eq. (2a) type was found to shift, with temperature, to the formation of (P)O–H groups.

water-enriched sample, a weak 1674 cm^{-1} band due to the bending H_2O mode was resolved also. In view of closeness of the frequencies of the $1539\text{--}1606$, $1670\text{--}1745$, $2030\text{--}2107$, and $2302\pm 8\text{ cm}^{-1}$ distinct bands to those of the 1680 , 1785 , 2060 , and 2330 cm^{-1} bands in the pyrophosphate glass spectra, the former bands were acknowledged (Efimov and Pogareva, 2000; Efimov, 2002; Efimov et al., 2003) to be counterparts of the latter. This allowed for extending the band assignments validated for pyrophosphate glasses (Efimov et al., 1998) to silicate glasses, thus assigning the $1539\text{--}1606$, $1670\text{--}1745$, $2030\text{--}2107$, and $2302\pm 8\text{ cm}^{-1}$ bands to four components of the stretching mode of (Si)O–H group in a site that corresponds to strong hydrogen bonding with certain nonbridging oxygens of a glass matrix.

It was shown also (Boulos et al., 1997; Efimov, 2002; Efimov et al., 2003) that, in the spectra of silicate glasses, the well-known water-related $2450\text{--}3700\text{ cm}^{-1}$ envelope with two broad maxima around 2800 and 3500 cm^{-1} covers, in fact, much greater number of individual bands than two. Boulos et al. (1997) deconvoluted, for a $\text{Na}_2\text{O}\text{--}\text{CaO}\text{--}\text{SiO}_2$ glass, five Gaussian components centered at 2800 , 3125 , 3461 , 3557 , and 3615 cm^{-1} (no assignments of the components to particular species being given). Efimov (2002) and Efimov et al. (2003) deconvoluted the envelope in the spectra $\text{Na}_2\text{O}\text{--}\text{SiO}_2$, $\text{K}_2\text{O}\text{--}\text{CaO}\text{--}\text{BaO}\text{--}\text{SiO}_2$, and window glasses into eight bands with frequencies of about 2542 , 2750 , 2910 , 2959 , 3200 , 3393 , 3524 , and 3595 cm^{-1} . The 2910 , 2959 , 3200 , and 3393 cm^{-1} bands were assumed by Efimov et al. (2003) to be counterparts of the above 2837 , 2940 , 3180 , and 3410 cm^{-1} bands in the pyrophosphate glass spectra and, correspondingly, were assigned to the components of the ν_{as} (for the former band pair) and ν_{s} (for the latter band pair) modes of the interstitial H_2O molecule. The 2542 and 2750 cm^{-1} bands, like the above $1807\text{--}1840$ and $1903\text{--}1927\text{ cm}^{-1}$ ones, lack in the pyrophosphate glass spectra. So, all the bands clearly have nothing in common with the above site responsible for the occurrence of the (Si)O–H mode split into four components (the components being observable in not only silicate but also pyrophosphate glass spectra). Among these bands, it is mostly the 2750 cm^{-1} band that forms a broad absorption maximum around 2800 cm^{-1} taken by Scholze (1966, 1991) to be an individual (Si)O–H-related band. Therefore, following Scholze's assignment for this band, the $1807\text{--}1840$, $1903\text{--}1927$, 2542 , and 2750 cm^{-1} bands were assumed to be due to four components of the stretching mode of (Si)O–H group in another site that corresponds to weaker hydrogen bonding with certain nonbridging oxygens of a glass matrix.

The remaining 3524 and 3595 cm^{-1} bands form a maximum around $3500\pm 200\text{ cm}^{-1}$ taken by Scholze (1966, 1991) to be a single band due to the stretching (Si)O–H mode in a site corresponding to the “free” (Si)O–H group. Therefore, the 3524 and 3595 cm^{-1} bands were assigned (Efimov, 2002; Efimov et al., 2003), following Scholze's assignment for the $3500\pm 200\text{ cm}^{-1}$ band, to be the components of the $\nu(\text{Si})\text{O}\text{--}\text{H}$ mode related to a site in which no hydrogen bonding occurs between the (Si)O–H group and nonbridging oxygens of the matrix. The fact that even the highest frequency component of the mode is shifted by $70\pm 20\text{ cm}^{-1}$ to the smaller wavenumbers compared to the envelope maximum in the spectrum of vitreous silica was interpreted in terms of formation, in this site, of weak hydrogen bonding with the oxygen of another (Si)O–H group, thus assuming the groups to occur in pairs.

Some above findings for silicate glasses can be of interest for band assignments in silica glass spectra. In particular, the locations of the 1540 to 2300 cm^{-1} bands in the spectra of silicate glasses are rather close to those reported for the low-wavenumber bands in the spectra of silica glasses (Silin' and Trukhin, 1985; Haken et al., 2000), thus raising a question whether the latter bands have something in common with not only the multiphonon matrix modes but also the water-related absorption or not.

Thus, the origin of particular water-related absorption bands (especially those in the $1300\text{--}3000\text{ cm}^{-1}$ region) still remains disputable. This hinders understanding (i) the nature of various structural sites occupied by water-related species and (ii) the actual origin of multiphonon water-related bands at wavenumbers greater than 3700 cm^{-1} that greatly influence the radiative heat transfer in glass-forming liquids and glass objects during cooling. Therefore, a further insight into the origin of the water-related absorption bands in the IR spectra of glasses and glassforming liquids is of importance for (i) the better understanding of equilibrium between different water-related species in natural and synthetic silicate materials and (ii) refining the processes of glass melting and annealing in the glass industry. Recent data (Efimov and van Nijnatten, 2002, 2003) have shown temperature changes in these spectra to consist mostly of gradual variations in the band intensities. In view of this, the above insight can be gained through the investigation of the room-temperature glass spectra.

For obtaining reliable information on the number and origin of particular overlapped bands in an experimental spectrum, quantitative processing of the spectral data (including the deconvolution of a multiband

spectrum into individual bands) is necessary. Without quantitative data processing, qualitative judgments are only possible that cannot be tested reliably. When conducting such processing, the problems of (i) which kind of the band contour is the most appropriate for a spectrum and (ii) how to obtain the most accurate fit to the spectrum are of utmost importance. There are various standard empirical methods for deconvoluting a spectrum differing in the kind of the band contour used. In particular, it is the Gaussian band contour that was used by Walrafen and Samanta (1978), Wakabayashi and Tomozawa (1989), Stone and Walrafen (1982), Yokomachi et al. (1987), Humbach et al. (1996) and many others. The most powerful method for spectral data processing is the dispersion analysis (Spitzer and Kleinman, 1961; Pavinich and Belousov, 1978; Berreman and Unterwald, 1968; Brantley et al., 1971; Gervais and Piriou, 1974; Efimov and Makarova, 1983; Efimov, 1995, 1996); various versions of the method are briefly discussed below.

In the research presented here, the parameters of the IR absorption bands in the 1300–5000 cm^{-1} region for Types I and III silica glasses are computed with a version of the dispersion analysis specially intended for the multiband spectra of glasses and results obtained are compared to the corresponding data on $(\text{Me}_2\text{O}/\text{MeO})\text{-SiO}_2$ glasses (Me being Na, K, Ca, Ba).

2. Experimental

The absorption spectra of Type I and III Russian silica glasses KITM (Type I) and KU1TM (Type III) in the 1300–5000 cm^{-1} region were measured. Based on the impurity contents predetermined by the specific features of industrial technology, there are four principal types of commercial silica glasses (see, for example, Hetherington et al., 1965). Silica glasses ascribed to Type I (another example being IR VitreosilTM) are melted in electric furnaces from crystalline quartz of natural origin, their water content being known to be less than 5 ppm. Silica glasses ascribed to Type III (other examples being Corning 7940TM and SuprasilTM) are synthesized by oxidizing SiCl_4 in an oxygen–hydrogen flame, their water content being known to be in between 1000 and 1200 ppm. Glass samples of each type prepared for measurements were 0.15–0.17, 1.0, and 3.6 mm thick. The transmittance spectra were recorded with double-beam dispersive spectrophotometer (Perkin-Elmer 983). The level of noise filtering for a particular slit program and scan speed was supported automatically throughout a spectrum. The best resolution, for each scan mode

used, was about 3 cm^{-1} . For reliably revealing weak spectral features, either averaging over several scans or slower-speed scanning of a region of interest was used. The random error in the transmittance due to the noise of the spectrophotometer was no more than ± 0.0003 .

The spectra of the absorption coefficient, $\alpha(\omega)$, entering into the Lambert–Bouguer law, $\tau = \exp(-\alpha l)$, where τ is the internal transmittance of a sample and l is the sample thickness were calculated as follows:

- for the 1300 to 2100 cm^{-1} region, through the optical density of a sample 0.15 (for KI) or 0.17 (KU1) mm thick and reflection loss;
- for the 2100 to 5000 cm^{-1} region, through the ratio of the optical densities and thicknesses of two samples.

For any transmittance magnitude and sample thickness, the above random error in the transmittance resulted in absorptivity errors that were too small to be shown in the figures presented below.

3. Computational

The formalism of quantitative IR spectroscopy is based on the notion of the complex dielectric function $\hat{\varepsilon}(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ (see, for example, Garbuny, 1965) where ω is the frequency (the latter being expressed usually in wavenumbers). The real and imaginary parts of the function can be expressed through the optical constants such as the refractive index $n(\omega)$ and absorption index $\kappa(\omega)$ that are the real and imaginary parts of the complex refractive index $\hat{n}(\omega) = n(\omega) + i\kappa(\omega)$ as follows:

$$\varepsilon'(\omega) = n^2(\omega) - \kappa^2(\omega);$$

$$\varepsilon''(\omega) = 2n(\omega) \cdot \kappa(\omega).$$

The absorption coefficient $\alpha(\omega)$ is connected to $\kappa(\omega)$ by $\alpha(\omega) = 2\omega \cdot \kappa(\omega) / c$, where c is the light velocity.

Data on the $\alpha(\omega)$ spectra of samples obtained as described above were processed with the so-called dispersion analysis method. The specific features of the dispersion analysis are outlined briefly below.

The procedure of the dispersion analysis consists in the simulation of the experimental spectrum through consecutive variations in the parameters of a certain analytical model for $\hat{\varepsilon}(\omega)$ dispersion that determines the IR band shapes assumed for the material. When the

model chosen is valid for a material under study, the dispersion analysis allows for obtaining simultaneously (i) the numerical values of parameters of the model, (ii) the spectra of the optical constants $n(\omega)$ and $\kappa(\omega)$, and (iii) the pattern of individual absorption bands consisting the $\alpha(\omega)$ spectrum (thus being a method for the reliable deconvolution of the spectrum). Various versions of the dispersion analysis differ in the $\hat{\epsilon}(\omega)$ model used.

Historically, this method was first implemented for the spectra of crystals (see, for example, Spitzer and Kleinman, 1961) using the well-known classical model of the damped harmonic oscillators as follows:

$$\hat{\epsilon}(\omega) = \epsilon_{\infty} + \sum_{j=1}^J \frac{S_j}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega} \quad (3)$$

Here ϵ_{∞} is the dispersionless high-frequency dielectric constant, ω is the current frequency of the incident beam, ω_j and γ_j are the inherent frequency and damping coefficient for the j -th oscillator, respectively, and S_j is the intensity of the corresponding optical transition.

The dispersion analysis based on Model (3) was used successfully for processing the IR spectra of most crystals. Some authors (such as Felty et al., 1967, and Bendow et al., 1981) applied Model (3) to the spectra of glasses. However, the best fits obtained had substantial deviations from experiment that indicated the model bands to have flatter wings than those in the experimental spectra. The reason for this, as stressed, for example, by Gaskell and Johnson (1976), was the fact that Model (3) assumes purely Lorentzian band shapes and therefore describes great bandwidths in glass spectra solely in terms of an increase in the damping coefficient. In fact, however, these great bandwidths are due mainly to the effect of structural disorder, which cannot be taken into account in Model (3).

For a few crystals with the most intense IR bands (such as TiO_2 , BaTiO_3 , Al_2O_3 , and some others), the quality of best fits around the reflection maxima obtainable with Model (3) was insufficient; better results were provided by the so-called factorized model (Berreman and Unterwald, 1968; Gervais and Piriou, 1974). This model represents the band intensities through the magnitudes of splitting the longitudinal and transverse optical modes and, in a general case, assumes different magnitudes of the damping coefficients, γ_{LO} and γ_{TO} , for these modes. For crystals such as α - and β -quartz, γ_{LO} and γ_{TO} were found (Gervais and Piriou, 1975) to be practically equal to each other, thus making the factorized model equivalent to the classical one. The greater flexibility of the model due to the use of four

adjustable parameters per kind of oscillator (instead of three in the classical model) allowed a satisfactory quality of best fits to the IR spectra of some glasses to be obtained (Gervais et al., 1987; Parot-Rajaona et al., 1992). However, the factorized model also assumes Lorentzian band shapes and therefore retains the above shortcoming with respect to glass spectra, namely, the inability to represent the band broadening in any other way except in terms of an increase in the damping coefficient. After 1992, attempts to apply the factorized model to the spectra of glasses ceased.

The convolution model for $\hat{\epsilon}(\omega)$ of glasses first proposed as a basis for the dispersion analysis by Efimov and Makarova (1983) owes its name to the fact that it involves the convolution of a Lorentzian function and a Gaussian probability density. The latter represents the distribution of oscillators over frequency that arises due to disorder in glass structures. As indicated by Efimov (1995, 1998, 1999), this distribution is the natural consequence of the spatial localization of phonons in disordered networks (the localization being proved unambiguously with modeling of the vibrational density of states of a large cluster by Bell et al., 1968, 1970). The convolution model is as follows:

$$\hat{\epsilon}(\omega) = \epsilon_{\infty} + \sum_{j=1}^J \frac{S_j}{\sqrt{2\pi}\sigma_j} \int_{-\infty}^{+\infty} \frac{\exp[-(x-\omega_j)^2/2\sigma_j^2]}{x^2 - \omega^2 - i\gamma_j\omega} dx. \quad (4)$$

Here ω and x are the current frequency for which the dielectric function is being calculated and the variable oscillator frequency, respectively, ω_j is the central frequency for the oscillator distribution inherent in the j -th absorption band, and σ_j is the standard deviation for this distribution. Parameters such as S_j and γ_j retain the same meanings as in Eq. (3). For brevity, the band contour determined by the imaginary part of Eq. (4) is denoted below by the convolution contour.

When developing the procedure of the dispersion analysis based on this model (Efimov and Makarova, 1983; Efimov, 1995), the specific features of the method as a whole were analyzed in detail.

The quality of the best fit in the dispersion analysis is quantitatively characterized by the error function of a type as follows:

$$Q(\{p_m\}_1^M) = \sqrt{\frac{1}{\omega_a - \omega_b} \int_{\omega_a}^{\omega_b} [\alpha_{\text{mod}}(\omega, \{p_m\}_1^M) - \alpha_{\text{exp}}(\omega)]^2 d\omega} \quad (5)$$

where $\{p_m\}_1^M$ is the multitude of the band parameters, ω_a and ω_b are the limits of the frequency range under processing, $\alpha_{\text{mod}}(p_m)_1^M$ is the optical function (in the research presented here, the absorption coefficient) computed with a model chosen, and $\alpha_{\text{exp}}(\omega)$ is the experimental magnitude of the optical function. The best possible quality of spectrum simulation is attained when an inequality $Q(\{p_m\}_1^M) \leq \Delta\alpha_{\text{exp}}$ is reached, $\Delta\alpha_{\text{exp}}$ being the random error of α_{exp} measurements.

The accuracy of calculation of the band parameters is not so high as that of $\alpha(\omega)$ or reflectivity values because, in the course of the dispersion analysis, errors in the parameters of neighboring bands in a spectrum tend to compensate each other (Efimov, 1995). The random errors in ω_j and S_j obtainable with the version of the dispersion analysis based on Model (4) were estimated (Efimov, 1995; Efimov et al., 1998) to be, for strong and distinct absorption bands, no more than 0.3% and 6%, respectively; for weak and/or greatly overlapped bands, these estimates increase by a factor of ~ 2 .

As stressed by Kopilevich and Makarova (1987), the dispersion analysis can provide a unique set of band parameters only if two conditions are obeyed:

- (i) a model chosen for $\hat{\epsilon}(\omega)$ is correct for a material under study,
- (ii) the experimental data are informative, i.e., the amount and accuracy of the data allow for calculating reliably the parameters of all bands assumed to occur in the spectrum.

In view of the second condition, obeying the correctness of dispersion analysis is more difficult with the greater number of adjustable parameters and, hence, spectral bands assumed. Therefore, a criterion for the most appropriate $\hat{\epsilon}(\omega)$ model is, in accord with the principle of ‘‘Occam’s razor,’’ the capability of the model to provide a high accuracy of the best fit with the smallest number of spectral bands.

Apart from the properties of the analytical model for $\hat{\epsilon}(\omega)$ dispersion, the accuracy of $\hat{\epsilon}(\omega)$ function assumed for a material under consideration is determined by a set of spectral bands for the material. There is no way of estimating beforehand the total number, J , of bands in a spectrum to be processed, which results in the problem of how to choose this number in the most reasonable way. This problem is inherent in any method for deconvoluting a complicated multiband spectrum into individual bands including the dispersion analysis. In general, it is impractical to equate J to the minimum number of distinct spectral features (resolved maxima or shoulders) because some weak bands can be

concealed by the wings of the stronger neighbouring bands. On the other hand, choosing J only from considerations of minimizing the error of the best fit (as was made by Mysen et al., 1982, for the Raman spectra) is dangerous as well because weak false ‘‘bands’’ can thus be added for neutralizing some local discrepancies that, in fact, can be due to the inaccuracy of the $\hat{\epsilon}(\omega)$ model chosen.

In accord with Efimov (1995, 1996), a reasonable compromise between the above extremes is to add, into the model, an extra band over the total number of distinct spectral features on condition that two criteria are obeyed simultaneously:

- (i) adding such extra band improves substantially the fit in the corresponding frequency range with no measurable worsening the fit in other ranges;
- (ii) there is independent information (such as data on the spectra of other glasses or crystals close in composition) that indicates the occurrence of an unappreciated band in this range.

The validity of these conditions was justified by further studies.

Another problem is how to process the regions of low absorption in between the bands occurring in the region under study. The idea of subtracting a linear background used in some studies (see a review by Kohn, 2000) is impractical because, in fact, this background is formed by the absorption tails due to the wings of strong bands located outside the range under consideration and therefore cannot be linear (see, for example, Bredol et al., 1990). Hence there is a substantial sensitivity of the results of spectrum deconvolution to the way of estimating the background mentioned by Kohn (2000). In terms of the dispersion analysis, the natural way of representing such absorption tails is to fit them through the incorporation of effective oscillators with frequencies corresponding to the expected locations of strong bands falling outside the limits of a spectrum measured. It is this way that was used in studies by Efimov and van Nijnatten (2002, 2003), Efimov and Hobert (2004), and Efimov et al. (1998, 2003, 2005).

Because the Gaussian function appearing in Eq. (4) is symmetric, Model (4) retains the approximate symmetry of the $\epsilon''(\omega)$ maxima inherited from the classical model. A high quality of best fits calculated with this model in many studies by the author of the research presented here and his co-authors (Efimov and Makarova, 1983; Efimov, 1995, 1996; Efimov and Pogareva, 2000; Efimov and van Nijnatten, 2002, 2003; Efimov et al.,

1998, 2003, 2005), and also a good agreement of the optical constants thus obtained with those found with the Kramers–Kronig transform (Efimov, 1995), indicated the symmetric $\varepsilon''(\omega)$ maxima to be valid for the IR spectra of the glasses studied. Furthermore, Model (4) was used independently for processing, with good accuracy, the reflection and absorption spectra of glasses and glassy films on various substrates by Naiman et al. (1984), Brendel and Bormann (1992), Kucirkova and Navratil (1994), Hobert and Dunken (1996), and others.

Thus, the dispersion analysis based on Model (4) was shown to be a quite accurate tool for processing most mid-IR spectra of glasses. Rare exceptions are discussed by Efimov and Hobert (2004) for which the assumption of asymmetric $\varepsilon''(\omega)$ contours was justi-

fied. This was the reason for choosing the dispersion analysis based on Model (4) for data processing in the research presented here. The computational procedure of the method adapted by Efimov et al. (1998) to processing the spectra of the absorption coefficient $\alpha(\omega)$ (rather than the reflection spectra processed in most studies) was used.

In the tables and figures to follow, the band intensities are expressed in terms of the oscillator strengths $\Delta\varepsilon_{0j} = S_j / \omega_j^2$.

When indicating different types of vibrations, the standard abbreviations are used as follows:

Stretching mode (symmetry being not specified): ν
 Asymmetric stretching mode: ν_{as}
 Symmetric stretching mode: ν_s

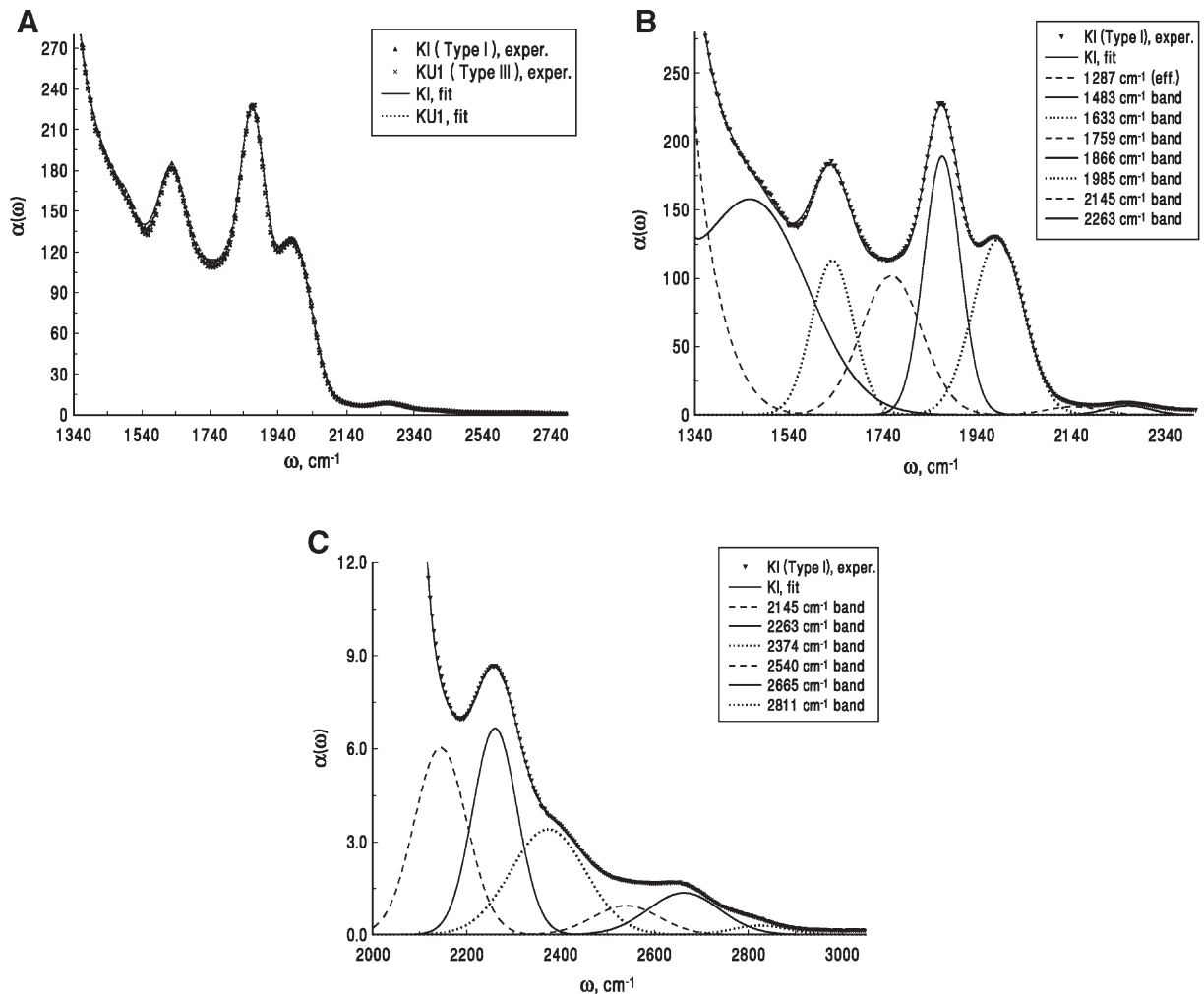


Fig. 1. Absorption spectra of silica glass samples in the low-wavenumber (1300 to 2800 cm^{-1}) region. (A) Best fits to the spectra of Type I and III samples. (B) Individual bands deconvoluted from the spectrum of Type I sample at wavenumbers from 1300 to 2400 cm^{-1} . (C) Enlarged view of individual bands deconvoluted from the spectrum of Type I sample at wavenumbers from 2000 to 3000 cm^{-1} .

4. Results

The IR absorption spectra obtained for Types I and III silica glass samples, best fits to these spectra obtained with the dispersion analysis, and individual bands deconvoluted are shown in Figs. 1–5. For representing the contributions of the tails of the fundamental and low-wavenumber 2nd order matrix modes to the absorption in the region under study, two effective oscillators with frequencies of 1053 and 1287 cm^{-1} were used. The total number of bands deconvoluted with the dispersion analysis in the entire 1300 to 5000 cm^{-1} region was thirteen for the Type I glass sample and twenty two for the Type III glass sample. As seen from Tables 1 and 2, the band frequencies were found to be 1483, 1633, 1759, 1866, 1985, 2145, 2263, 2374, 2540, 2665, 2811, 3140, 3486, 3571, 3635, 3675, 3748, 3842, 3920, 4075, 4447, and 4512 cm^{-1} . Figs. 1–5 show the quality of best fits to be high (the deviations of the simulated spectra from experiment falling within the experimental error). This guarantees the reliability of data obtained on the IR band frequencies and oscillator strengths for the samples that are presented in Tables 1 and 2.

For the 1300 to 2800 cm^{-1} region, Fig. 1A shows $\alpha(\omega)$ spectra of Types I and III silica glasses to coincide practically. Slight differences between the spectra at wavenumbers less than 2100 cm^{-1} seen in Fig. 1A are due to an error caused by ± 0.01 mm spread of sample thickness over the diameter of a sample 0.15–0.17 mm thick. With the dispersion analysis, eleven bands are deconvoluted in this region (Fig. 1B and C and also Table 1). In accord with the similarity of $\alpha(\omega)$ spectra of Types I and III glasses in this region, ω_j values obtained for the bands (Table 1) coincide for both glass types,

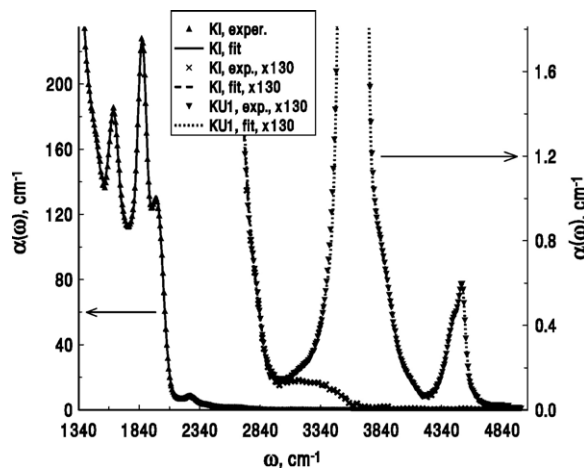


Fig. 2. Absorption spectra of silica glass samples in the entire 1300 to 5000 cm^{-1} region and best fits to the spectra.

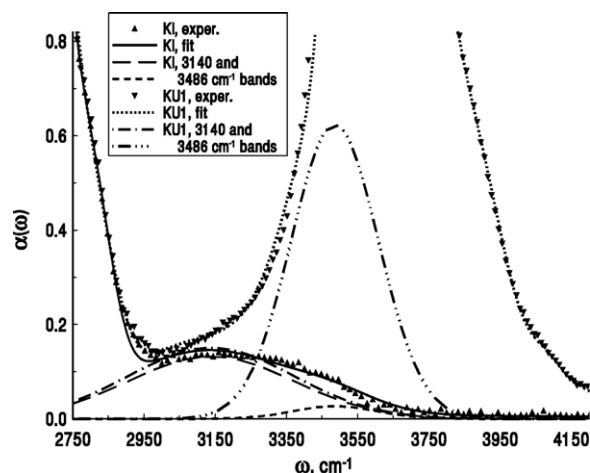


Fig. 3. Best fits and individual bands in the 2750–3500 cm^{-1} sections of $\alpha(\omega)$ spectra of silica glass samples.

$\Delta\epsilon_{0j}$ values being similar as well within the calculation error. Fig. 2 shows the complete coincidence of the Types I and III glass spectra to extend up to ~ 3000 cm^{-1} .

In the 3000 to 5000 cm^{-1} region, the spectra of these glass types differ greatly (Figs. 2–5). The only feature that is observed here for the Type I glass spectrum is a broad shoulder at wavenumbers from 3000 to 3500 cm^{-1} . This shoulder is formed, as seen from the dispersion analysis data presented in Fig. 3 and Table 2, by two weak bands that occur in the Type III glass spectrum as well. In the latter spectrum, however, these bands are practically hidden under the low-wavenumber wing of the well-known water-related envelope centered at approximately 3670 cm^{-1} . At wavenumbers from 3500 to 5000 cm^{-1} , the Type I glass spectrum is characterized by negligibly small

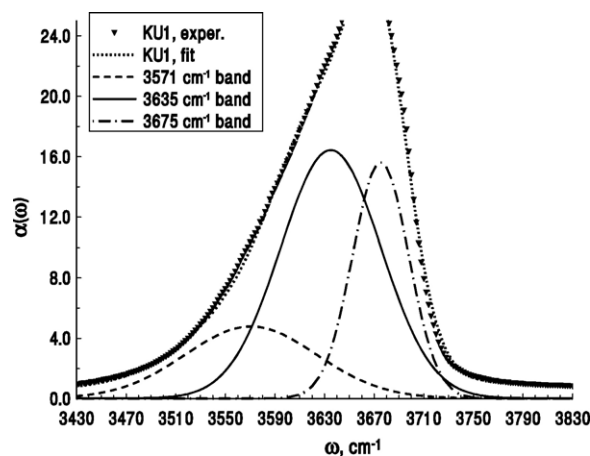


Fig. 4. Individual bands forming the 3430–3700 cm^{-1} envelope in the $\alpha(\omega)$ spectrum of Type III silica glass sample.

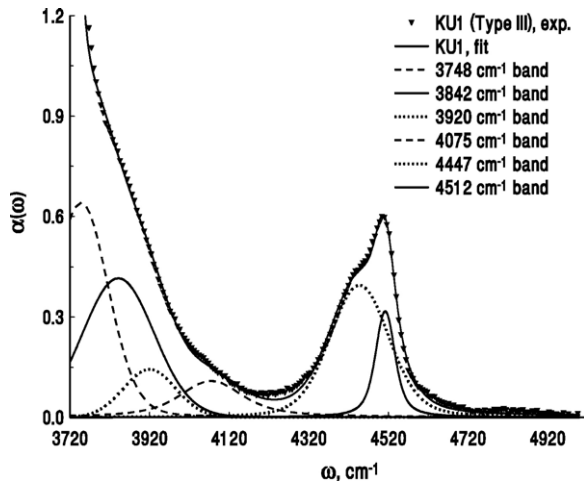


Fig. 5. Absorption spectrum of Type III silica glass sample in the 3720 to 5000 cm^{-1} region, best fit to the spectrum, and individual bands deconvoluted.

absorption, which, as indicated in Table 2, is due to the lack of any bands with measurable intensities. On the contrary, the Type III glass spectrum not only contains the 3670 cm^{-1} envelope (Fig. 4) but also reveals an appreciable absorption at wavenumbers up to 4700 cm^{-1} (Figs. 2 and 5). Data obtained with the dispersion analysis show the Type III glass spectrum in the 3500 to 5000 cm^{-1} region to consist of as many as nine bands (Table 2). As shown in Figs. 4 and 5, three of the bands form the above 3670 cm^{-1} envelope, three bands are responsible for the formation of a broad shoulder in between 3750 and 4000 cm^{-1} , a band around 4075 cm^{-1} manifests itself in the form of another quite weak shoulder adjacent to the above one, and two highest frequency bands form the well-known water-related envelope centered at approximately 4500 cm^{-1} .

5. Discussion

5.1. Silica glass, the 1300 to 3000 cm^{-1} region

The inherent band frequencies and oscillator strengths of all bands in the 1300 to 3000 cm^{-1} region coincide quantitatively (Table 1) for Types I and III glass samples that differ in the water content by more than two orders of magnitude. This indicates that these bands have nothing in common with the low-frequency vibrations of water-related species known, for example, for water-containing silicate crystals (Ryskin and Stavitskaya, 1960; Ryskin, 1971). Thus, the earlier assignment (Silin' and Trukhin, 1985; Haken et al., 2000) of bands in this region to the multiphonon vibrations (combination modes and overtones) of the silica glass matrix is confirmed for Types I and III silica glass samples (and, hence, other samples with water content no more than 1200 ppm).

The overtone frequencies can be estimated with a simple formula used, for example, by Humbach et al. (1996):

$$\omega_{jn} = n\omega_{jf}[1 - x_a(n + 1)], \quad (6)$$

where n is the overtone number, ω_{jf} and ω_{jn} are the frequencies of the j -th fundamental mode and of the n -th overtone of this mode, respectively, and x_a is the anharmonicity constant.

It seems possible to rewrite this formula for the combination modes as well; in this case, the formula should take the form as follows:

$$\omega_{c(jk)} = (n_j\omega_{jf} + n_k\omega_{kf})[1 - x_a(n_j + n_k)]. \quad (7)$$

Here n_j and n_k are factors for the ω_{jf} and ω_{kf} fundamental modes, respectively, $\omega_{c(jk)}$ is the corresponding

Table 1
Oscillator frequencies and oscillator strengths computed for the 1300 to 2900 cm^{-1} region of silica glass spectra

Band locations in the $\alpha(\omega)$ spectrum (cm^{-1})	Dispersion analysis data		Band assignments	
	ω_j (cm^{-1})	Δe_{0j} for glass samples		
		KI (Type I)		KU1 (Type III)
1470, shoulder	1483	$1.9 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	Combination modes and overtones of SiO_2 glass matrix
1630	1633	$5.3 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	
–	1759	$6.4 \cdot 10^{-4}$	$6.2 \cdot 10^{-4}$	
1860	1866	$6.6 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$	
1980	1985	$5.7 \cdot 10^{-4}$	$5.6 \cdot 10^{-4}$	
–	2145	$2.4 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$	
2260	2263	$2.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$	
2400, shoulder	2374	$1.6 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	
–	2540	$3.6 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	
2650	2665	$4.7 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$	
2800, shoulder	2811	$8.2 \cdot 10^{-7}$	$8.1 \cdot 10^{-7}$	

Table 2
Oscillator frequencies and oscillator strengths computed for the 3000 to 5000 cm^{-1} region of silica glass spectra

KI (Type I)			KU1 (Type III)		
Feature in the $\alpha(\omega)$ spectrum	Dispersion analysis data		Feature in the $\alpha(\omega)$ spectrum	Dispersion analysis data	
	ω_j (cm^{-1})	$\Delta\epsilon_{0j}$		ω_j (cm^{-1})	$\Delta\epsilon_{0j}$
2900–3500, shoulder	3140	$1.1 \cdot 10^{-6}$	Hidden under an envelope centered at 3670 cm^{-1}	3140	$1.3 \cdot 10^{-6}$
	3486	$9.2 \cdot 10^{-8}$		3486	$2.2 \cdot 10^{-6}$
Lack	–		3665	3571	$7.2 \cdot 10^{-6}$
				3635	$1.8 \cdot 10^{-5}$
				3675	$9.4 \cdot 10^{-6}$
				3748	$1.2 \cdot 10^{-6}$
				3842	$9.2 \cdot 10^{-7}$
				3920	$2.2 \cdot 10^{-7}$
				4075	$2.5 \cdot 10^{-7}$
				4447	$5.9 \cdot 10^{-7}$
				4512	$1.8 \cdot 10^{-7}$

combination mode frequency, and x_a remains to be the anharmonicity constant.

Based on the frequencies of the IR fundamentals for vitreous silica (Table 3) and Eq. (7) with x_a taken to be 0.021 (the same as that used by Humbach et al., 1996), we estimated crudely the frequencies of particular combination modes and overtones of silica matrix that fall into the region of interest. The frequency estimates thus obtained are close to the frequencies of the absorption bands resolved in the experimental spectrum, examples for the 2nd order modes being given in Table 4. This closeness additionally validates the above assignment of bands in the entire 1300 to 3000 cm^{-1} region to certain multiphonon vibrations of the silica glass matrix. Because there are at least two close 2nd order modes per band in Table 4 for the 1300–2000 cm^{-1} region (and three or more 3rd order modes per band in the 2000 to 3000 cm^{-1} region as well), it is difficult to put each absorption band into a strict correspondence with a particular multiphonon vibration.

Table 3
IR fundamental modes of vitreous SiO_2 according to Efimov (1995)

Kind of modes	Mode notation	Inherent band frequency (cm^{-1})	Oscillator strength, $\Delta\epsilon_{0j} = S_j / \omega_j^2$
Asymmetric stretching modes	$\nu_{\text{as}}^{\text{I}} \text{SiOSi}$	1178	0.051
	$\nu_{\text{as}}^{\text{II}} \text{SiOSi}$	1088	0.286
	$\nu_{\text{as}}^{\text{III}} \text{SiOSi}$	1057	0.206
Symmetric stretching modes	$\nu_{\text{s}}^{\text{I}} \text{SiOSi}$	805	0.051
	$\nu_{\text{s}}^{\text{II}} \text{SiOSi}$	635	0.023
Bending modes	$\delta' \text{OSiO}$	460	0.248
	$\delta'' \text{OSiO}$	445	0.114
	$\delta''' \text{OSiO}$	424	0.641

5.2. Silica glass, the 3000 to 5000 cm^{-1} region

As shown in Fig. 3 and Table 2, bands with frequencies of 3140 and 3486 cm^{-1} occur in the spectra of both Type I and Type III silica glasses. These bands are quite weak; however, it is impossible to obtain satisfactory fits to the spectra in the 3000 to 3500 cm^{-1} region without these bands. So, the first of the two above criteria for the addition of the 3140 and 3486 cm^{-1} bands is fulfilled, thus providing grounds for considering such bands in the spectra of Types I and III silica glasses to be real.

There are water-related bands close in locations to the 3140 cm^{-1} one such as (i) the 3208 cm^{-1} band found by Davis and Tomozawa (1996) to be due to the 1st overtone of H_2O bending mode in the high-water-content silica spectrum and (ii) the 3175 to 3209 cm^{-1}

Table 4
Tentative frequency estimates for the second-order combination modes and overtones for silica glasses made based on data of Efimov (1995)

ω_j (cm^{-1}) (dispersion analysis data)	Estimates	
	2nd-order mode frequency (cm^{-1})	Kind of the mode
1483	1453	$\nu_{\text{as}}^{\text{III}} \text{SiOSi} + \delta' \text{OSiO}$
	1469	$\nu_{\text{as}}^{\text{II}} \text{SiOSi} + \delta'' \text{OSiO}$
	1483	$\nu_{\text{as}}^{\text{I}} \text{SiOSi} + \delta' \text{OSiO}$
1633	1621	$\nu_{\text{as}}^{\text{III}} \text{SiOSi} + \nu_{\text{s}}^{\text{I}} \text{SiOSi}$
	1651	$\nu_{\text{as}}^{\text{II}} \text{SiOSi} + \nu_{\text{s}}^{\text{II}} \text{SiOSi}$
	1737	$\nu_{\text{as}}^{\text{I}} \text{SiOSi} + \nu_{\text{s}}^{\text{III}} \text{SiOSi}$
1759	1784	$\nu_{\text{as}}^{\text{III}} \text{SiOSi} + \nu_{\text{s}}^{\text{I}} \text{SiOSi}$
	1813	$\nu_{\text{as}}^{\text{II}} \text{SiOSi} + \nu_{\text{s}}^{\text{II}} \text{SiOSi}$
1866	1900	$\nu_{\text{as}}^{\text{I}} \text{SiOSi} + \nu_{\text{s}}^{\text{III}} \text{SiOSi}$
	1900	$\nu_{\text{as}}^{\text{I}} \text{SiOSi} + \nu_{\text{s}}^{\text{I}} \text{SiOSi}$
1984	2025	$2\nu_{\text{as}}^{\text{III}} \text{SiOSi}$

band due to a component of ν_s H₂O mode in phosphate and silicate glass spectra (Efimov et al., 1998, 2003). However, the oscillator strengths of the 3140 cm⁻¹ band in the spectra of Types I and III glasses with substantially unlike water content are close to one another (Table 2), their difference falling within the calculation error. This is poorly compatible with the water-related nature of this band and can indicate the band to be due to some multiphonon (no less than the third order) band of the silica matrix. If this is the case, the similarity of the 3140 cm⁻¹ band frequency to those of the above bands is merely a coincidence. So, the problem seems to deserve further investigation.

Bands similar in locations to the 3486 cm⁻¹ one were reported earlier for high-water-content silica and for phosphate and silicate glasses. Commonly, a band around 3450–3500 cm⁻¹ in the spectrum of high-water-content silica (Ernsberger, 1977; Stolper, 1982; Bartholomew, 1983; Tomozawa, 1985; Newman et al., 1986; McMillan and Remmele, 1986) was assigned to a certain stretching mode of H₂O molecule. Davis and Tomozawa (1996) estimated the frequency of this band to be 3426±10 cm⁻¹ and assumed the band to result from overlapping two bands due to the ν_{as} and ν_s modes of H₂O molecule in different structural positions. In the spectra of pyrophosphate and silicate glasses, there is an intense band with frequency around 3400–3417 and 3393±3 cm⁻¹, respectively (Efimov et al., 1998, 2003), this band being assigned to another component of the ν_s mode of H₂O molecule. As seen from Fig. 3 and Table 2, the oscillator strength of the 3486 cm⁻¹ band for Type III silica glass (the water content being 1000–1200 ppm) is more than an order of magnitude greater than that for Type I silica glass with substantially lower water content. This fact confirms this band to be water-related, which (i) leads to a conclusion that silica glasses of Type III and even Type I contain traces of molecular water and (ii) indicates the 3486 cm⁻¹ band to be due, in accord with the above assignments of bands similar in location in the spectra of other glasses, to the ν_s mode of interstitial H₂O molecule (Table 5).

At wavenumbers from 3500 to 5000 cm⁻¹, the intensities of the water-related bands in the Type I silica glass spectrum are negligibly small, thus indicating the practical lack of (Si)O–H groups in this sample. For the Type III silica glass spectrum (Figs. 4 and 5), this region needs special discussion.

As mentioned above, Walrafen and Samanta (1978) and most their successors used, for processing the 3500–3700 cm⁻¹ region of the spectrum, Gaussian band shapes and deconvoluted four bands with frequencies of 3510, 3615, 3665, and 3690 cm⁻¹.

However, as indicated by Efimov (1995, 1999), the Gaussian contour has steeper wings than those of the actual bands in the IR spectra of glasses, which is due to the fact that the Lorentzian contribution to the shapes of the latter bands is neglected. This was confirmed by the results of a numerical experiment presented by Efimov (1999). In the experiment, in which a model IR band practically coinciding with that in the experimental spectrum of 8Na₂O·92B₂O₃ glass was fitted with a single and with three Gaussian functions, a poor quality of best fit obtained with a single Gaussian function was shown. The quality of the Gaussian fit could be substantially improved by adding two more side contours with frequencies differing from that of the central contour by ~21 cm⁻¹. Because the band being fitted was single, the side contours had no physical meaning. So, as seen from this numerical experiment, the number of bands in a spectrum can easily be overestimated when using Gaussian band shapes. Therefore, the results of deconvolution by Walrafen and Samanta (1978) and their successors are by no means unambiguous.

The Pearson VII contour used by Davis and Tomozawa (1996) can vary, like the convolution contour given by the imaginary part of Eq. (4), from nearly Lorentzian to nearly Gaussian depending on parameters, thus being the more appropriate tool for processing band shapes in the IR glass spectra. The variable number of bands (from three to six) deconvoluted by Davis and Tomozawa seems to be due to a variety of heat/water treatment conditions of their samples that predetermined a wide range of concentrations of different water-related species.

From general considerations, the assumption of the occurrence, for the 3500–3700 cm⁻¹ region, of a single band with a substantially asymmetric contour formed due to the continuous distribution of (Si)O–H groups over the strength of the hydrogen bonding made by McMillan and Remmele (1986) might be possible. The assumption of the occurrence of two bands made by analogy with the 4450/4520 cm⁻¹ doublet in the combination mode region (Grzechnik and McMillan, 1998) might also be possible from general considerations. However, these assumptions did not allow for quantitative testing because no analytical models for the assumed contours were proposed and, correspondingly, no fits were obtained. It should be noted also that the TO–LO splitting discussed by Grzechnik and McMillan (1998) as a possible reason for the appearance of two spectral components under the 3500–3700 cm⁻¹ envelope cannot produce such an effect because bands due to the LO modes are observable in the Raman

Table 5

Comparison of the IR band frequencies found in the 3000 to 3700 cm^{-1} region and the band assignments proposed with those available for Type III silica glasses in literature

Walrafen and Samanta, 1978		Davis and Tomozawa, 1996		This research	
ω_j (cm^{-1})	Assignments	ω_j (cm^{-1})	Assignments	ω_j (cm^{-1})	Assignments
No bands deconvoluted at wavenumbers less than 3500 cm^{-1}		Not observed		3140	Tentatively, the 3rd-order multiphonon mode of silica matrix
		3208	1st overtone of H_2O bend	Not observed	
		3426	$\nu_{\text{as}}\text{H}_2\text{O}$ and $\nu_{\text{s}}\text{H}_2\text{O}$ modes for various positions of the molecule in glass	3486	$\nu_{\text{s}}\text{H}_2\text{O}$ mode
3510	The asymmetric bidentate unit: $\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}(\text{Si})$ mode	3551	$\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}(\text{Si})$ mode	3571	Components of $\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}(\text{Si})$ mode
3615	The symmetric bidentate unit: components of $\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}(\text{Si})$ mode	3612	The symmetric bidentate unit: $\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}(\text{Si})$ mode; also, the contribution of $\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}_2$ mode	3635	
3665		3661	The symmetric bidentate unit: another component of $\nu(\text{Si})\text{O}-\text{H}\cdots\text{OH}(\text{Si})$ mode	3675	$\nu(\text{Si})\text{O}-\text{H}$ mode unaffected by HB
Not found		3672	$\nu(\text{Si})\text{O}-\text{H}\cdots\text{O}<$ mode		
3690	The asymmetric bidentate unit: $\nu(\text{Si})\text{O}-\text{H}$ mode unaffected by HB	3691	The asymmetric bidentate unit: $\nu(\text{Si})\text{O}-\text{H}$ mode unaffected by HB	Lacks in the deconvolution obtained	

spectra but not in the IR spectra. In particular, Galeener et al. (1983) and some other were forced to assume the IR activity of the longitudinal modes because of inability of the so-called central force model, in its initial crude version, to explain the occurrence of two transverse IR active ν_{as} modes of the Ge–O–Ge bridge. Later, such explanations were proposed (see a review of the situation by Efimov, 1999).

In the research presented here, the 3500–3700 cm^{-1} region of the KU1 (Type III) silica spectrum was deconvoluted into three bands with the convolution contours and inherent frequencies of 3571, 3635, and 3675 cm^{-1} (Table 2), which is in accord with earlier data by Efimov (2002). These three bands allow for simulating the shape of the 3500–3700 cm^{-1} envelope with high accuracy (Fig. 4), which makes it unnecessary to assume the occurrence of the fourth band at 3690 cm^{-1} as was made by Walrafen and Samanta (1978) and their successors who studied the untreated silica glass samples with water content no more than 1000–1200 ppm as well (Wakabayashi and Tomozawa, 1989; Bredol et al., 1990; Gerasimov, 1990). Following the principle of “Occam’s razor,” it is unreasonable to assume four bands for a situation in which three bands are sufficient for simulating the spectrum with accuracy within the experimental error. Thus, the occurrence of 3690 cm^{-1} band in deconvolutions by Walrafen and Samanta (1978) and the above successors is dubious. In these cases, the 3690 cm^{-1} band

can be a nonexistent spectral feature incorporated for eliminating an error that originated from the use of the more narrow purely Gaussian band shapes compared to the actual ones. The deconvolution, in the research presented here, of the 3500–3700 cm^{-1} envelope in the spectrum of KU1 (Type III) glass sample into three bands is in accord with the fact that the overtone envelope around 7200 cm^{-1} could also be deconvoluted, with maximum accuracy, from the spectrum of Type III glass sample (Efimov and Hobert, 2004) using three spectral bands only. The occurrence of three bands under the overtone envelope implies the same number of bands under the fundamental 3500–3700 cm^{-1} envelope. Notably, Efimov and Hobert used asymmetric band contours, so that possibilities for minimizing the number of individual bands for simulating the envelope at the expense of varying the band shapes were practically exhausted. Thus, no mathematical possibility was found to simulate the 3500–3700 cm^{-1} maximum with two bands or, the more so, a single band, which indicates the corresponding assumptions made by Grzechnik and McMillan (1998) and McMillan and Remmele (1986), respectively, to be dubious. In terms of the occurrence of three bands under the 3500–3700 cm^{-1} envelope, the effect of narrowing the maximum with temperature observed by Grzechnik and McMillan (1998) and then mentioned also by Efimov (2002) is easily explained by the redistribution of the band intensities. Naturally, the

above considerations cannot be extended to the spectra of high-water-content samples containing a variety of (Si) O–H sites practically lacking in the low-water-content samples. In particular, the occurrence of the fourth band around 3690 cm^{-1} in the spectra of high-water-content samples studied by Davis and Tomozawa (1996) should be considered to be possible.

A decrease in the number of bands under the $3500\text{--}3700\text{ cm}^{-1}$ envelope in the spectra of untreated silica glass samples with relatively low water down to three that was validated above is incompatible with the idea of formation of two different kinds of bidentate units proposed by Walrafen and Samanta (1978) and then cited widely. Correspondingly, this leads to a conclusion that band assignments given by Walrafen and Samanta (1978) and their successors for untreated silica glass samples are unfounded. So, assumptions about the simpler (Si)O–H sites than those based on two different bidentate units turn out to be expedient for such samples.

In the research presented here, the 3571 , 3635 , and 3675 cm^{-1} bands deconvoluted from the $3500\text{--}3700\text{ cm}^{-1}$ envelope in the spectrum of KU1 (Type III) glass sample (Table 2) are assigned to the stretching vibrations of (Si)O–H groups in two different structural sites (Table 5). One of the sites is assumed to correspond to the (Si)O–H group that forms the hydrogen bond with another such group (unlike the model by Walrafen and Samanta, 1978, the symmetry of mutual arrangement of the groups being unspecified); hence the splitting of the mode into two components with frequencies of 3571 and 3635 cm^{-1} . When comparing different band assignments in Table 5, such (Si)O–H groups are denoted by (Si)O–H \cdots OH(Si). The second site is assumed to correspond to the (Si)O–H group unaffected by hydrogen bonding (i. e., in a notation according to Scholze, 1966, 1991, to the “free” hydroxyl group), the corresponding mode frequency being 3675 cm^{-1} .

Notably, Davis and Tomozawa (1996) and then Zarubin (2001) rejected the idea of completely free (Si) O–H groups in the glass bulk. Based on a difference between the latter frequency and the position of the stretching mode for the surface (Si)O–H groups ($\sim 3750\text{ cm}^{-1}$), they assumed the (Si)O–H groups in the glass bulk responsible for the 3673 cm^{-1} band to form the hydrogen bonds with the bridging oxygens of the silica matrix. From our viewpoint, it is not possible to formulate a definite opinion about such a scenario because the surface (Si)O–H groups are not subject to the full-scale effect of the force field of the glass bulk and therefore can have somewhat different vibrational

frequencies. When comparing different band assignments in Table 5, (Si)O–H groups matching the above assumption are denoted by (Si)O–H \cdots O \leftarrow .

The structure of the IR absorption spectra at wavenumbers above 3700 cm^{-1} is of importance because a method for calculating the relative concentrations of (Si)O–H groups and H_2O molecules in glasses is known (Kohn, 2000; Nowak and Behrens, 2001; Bykov and Anfilogov, 2001) to use the intensities of the 4500 and 5220 cm^{-1} bands assigned to the multiphonon modes involving the fundamentals of the above species, respectively. Until now, most investigators (see, for example, Stone and Walrafen, 1982 and Davis and Tomozawa, 1996) considered the $3750\text{--}3950\text{ cm}^{-1}$ shoulder in the Type III silica glass spectrum (Fig. 5) to be formed by a single band, thus taking the number of bands in the 3700 to 5000 cm^{-1} region to be four. Data obtained with the dispersion analysis (Table 2) show the $3750\text{--}3950\text{ cm}^{-1}$ shoulder to be formed by three bands (see Fig. 3), no possibility for simulating accurately this shoulder with a single band or two bands being found. This increases the total number of bands in the 3700 to 5000 cm^{-1} region to six (Table 6). These bands can be assigned (like the known bands forming a weak shoulder around 4100 cm^{-1} and the $4400\text{--}4500\text{ cm}^{-1}$ envelope) to the combination modes involving the (Si)O–H vibrations. However, in contrast to the opinion of Stone and Walrafen (1982) and Davis and Tomozawa (1996), we consider the amount of information available to be insufficient for indicating a particular multiphonon vibration responsible for each absorption band in the 3700 to 5000 cm^{-1} region. This opinion is confirmed by disagreement between some combination band assignments forwarded by Stone and Walrafen (1982) and Davis and Tomozawa (1996) (see Table 6) and also by the appearance of band assignments as specific as that by Zarubin (2001) for the $4400\text{--}4500\text{ cm}^{-1}$ envelope. In particular, it yet to be clarified which particular (Si) O–H fundamentals participate in the combination modes forming the $4400\text{--}4500\text{ cm}^{-1}$ envelope, why other (Si)O–H fundamentals do not participate in the modes, and whether some matrix modes participate in the modes or not. Therefore, we assign all six band in the 3700 to 5000 cm^{-1} region to certain multiphonon vibrations for which the constituent modes are yet unidentified.

5.3. Silicate glasses, the 1300 to 2200 cm^{-1} region

As mentioned above, it was concluded earlier (Efimov and Pogareva, 2000; Efimov, 2002; Efimov et

Table 6

Comparison of the IR band frequencies found in the 3700 to 5000 cm^{-1} region with those available for Type III silica glasses in literature

Stone and Walrafen, 1982		Davis and Tomozawa, 1996		This research	
Band locations (cm^{-1})	Assignments	Band locations (cm^{-1})	Assignments	ω_j (cm^{-1})	Assignments
3850, shoulder	$\nu(\text{Si})\text{O}-\text{H}(3)+\text{SiOSi}$ bend	3820, shoulder	$\nu(\text{Si})\text{O}-\text{H}+(\text{Si})\text{O}-\text{H}$ torsion vibration	3748 3842 3920	Unidentified combination modes that involve certain stretching (Si)–OH vibrations
4100, shoulder	$\nu(\text{Si})\text{O}-\text{H}(1)+\text{OSiO}$ bend	4174, shoulder	Unidentified combination mode	4075	
4450, shoulder	$\nu(\text{Si})\text{O}-\text{H}(1)+\nu_{\text{as}}\text{SiOSi}$	4450, shoulder	Combination modes involving	4447	
4520	$\nu(\text{Si})\text{O}-\text{H}(4)+\nu_{\text{as}}\text{SiOSi}$	4522	$\nu(\text{Si})\text{O}-\text{H}$ and (Si)O–H bend	4512	

al., 2003) that six bands found in the 1500 to 2400 cm^{-1} region of binary and multicomponent glass spectra are due to the (Si)O–H vibrational modes. This conclusion was validated based on facts as follows:

- (i) the frequencies of the 1539–1606, 1670–1745, 2030–2107, and $2302 \pm 8 \text{ cm}^{-1}$ bands are close to those for bands in the spectra of pyrophosphate glasses found (Efimov et al., 1998) to be (Si)O–H-related;
- (ii) the frequencies of all bands in this region fall into the regions covered by the known broad (Si)O–H-related bands in the spectra of hydrosilicate crystals (Ryskin and Stavitskaya, 1960; Ryskin, 1971) – see Table 7;
- (iii) the oscillator strengths of these bands vary depending on the water content (Efimov et al., 2003).

A large number of these (Si)O–H-related bands indicated the stretching vibrations of (Si)O–H groups in two different hydrogen-bonded structural sites assumed earlier by Scholze (1966, 1991) to be split, like the case for the hydrogen-bonded site in pyrophosphate glasses (Efimov et al., 1998), into four spectral components each (Efimov, 2002; Efimov et al., 2003). In contrast to Scholze's views, no grounds were shown to exist for relating the hydrogen bonding in these sites to particular kinds of Q^n tetrahedron species. For brevity, the notations of the sites introduced by Efimov et al. (2003) are used below. A site in which the (Si)O–H group forms a hydrogen bond intermediate in strength with the nonbridging oxygen of a glass matrix is denoted by (Si)O–H \cdots O $^{1-}(\text{Si})$ {I}, and a site in which the (Si)O–H group forms the strongest hydrogen bond with the nonbridging oxygen of a glass matrix is denoted by (Si)O–H \cdots O $^{1-}(\text{Si})$ {II}.

Table 7

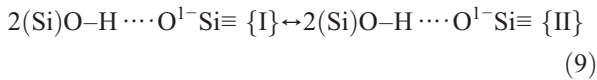
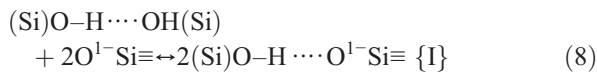
Comparison of band frequencies and assignments for silicate and phosphate glasses to those for $\text{Me}^{+}_{4-x}\text{H}_x\text{SiO}_4$, $\text{Me}^{2+}_2\text{H}_2\text{SiO}_4$, $\text{Me}^{+}_{3-x}\text{H}_x\text{PO}_4$, $\text{Me}^{2+}\text{HPO}_4$ crystals, 1500 to 3000 cm^{-1} region

Scholze, 1966, 1991, glasses		Ryskin and Stavitskaya, 1960; Ryskin, 1971, crystals		Efimov, 2002; Efimov et al., 2003, glasses	
Band locations (cm^{-1})	Assignments	Band locations (cm^{-1})	Assignments	ω_j (cm^{-1})	Assignments
No data for wavenumbers less than 2300 cm^{-1}		1500–1950 (band C)	Stretching modes of (Si,P)O–H groups forming HB	1540–1680	Components of stretching modes of (Si,P)O–H groups in two sites differing in the strength of HB formed by the group ^a (four components of a mode per site)
				1670–1780	
				1805–1840	
				1900–1930	
2330–2380	Stretching modes of (Si,P)O–H groups in two sites differing in the strength of HB formed by the group ^b (single mode per site)	2200–2460 (band B)		2030–2110	
2630–2940		2600–2950 (band A)		2300–2340	
				2525–2560	
				2740–2760	

Note: HB stands for the hydrogen bonding.

^a The kind of matrix Q^n species participating in the HB formation is unspecified (Efimov et al., 1998, 2003).^b The sites are assumed to differ in the kind of matrix Q^n species participating in the HB formation (Scholze, 1966, 1991).

The occurrence of such sites implies that there are equilibria in glass melts between these sites and the above (Si)O–H⋯OH(Si) site as follows:



where $\text{O}^{1-}\text{Si}\equiv$ is the matrix tetrahedron with the nonbridging oxygen.

Early band assignments by Scholze (1966, 1991) were based on an idea such as “one structural site–one spectral band”. This idea was somewhat extended by Walrafen and Samanta (1978) and their successors by assuming the occurrence of two similar sites in the symmetric bidentate unit. In both cases, the underlying reason was the fact that the authors considered the (Si) O–H vibrations to be the local impurity vibrations rather than the phonon modes. In terms of such an approach it is difficult to explain the above splitting a mode into four components: otherwise, a too complicated fixed construction of four (Si)O–H groups in similar positions should be imagined. There is no need, however, to seek some special structural arrangement for explaining the occurrence of several spectral components for each mode in glass spectra. As shown by Bell et al. (1968, 1970), vibrations in disordered networks are the phonon-like modes localized in the microscopic spatial regions. In accord with the approach of the phonon localization regions developed by Efimov (1999), the symmetry conditions within the localization regions determine the regularities of spectrum formation. As a result, the number of bands due to the stretching modes of a structural fragment is influenced by not only the number of the fragments in the phonon localization regions but also differences in the site symmetries of the fragments in the regions. Thus, no upper limit is imposed on the possible total number of bands due to a stretching mode. Therefore, the above occurrence of four components for the stretching modes of hydrogen-bonded (Si)O–H groups (Efimov, 2002; Efimov et al., 2003) is easily explained in terms of the phonon-like nature of these modes in glass spectra.

However, an increase in the oscillator strengths of bands in the 1500–2200 cm^{-1} region with the water content of a $(\text{Me}_2\text{O}/\text{MeO})\text{–SiO}_2$ glass estimated based

on data by Efimov et al. (2003) turned out to be several times less than that for the known water-related bands in the 2300–3700 cm^{-1} region (see Table 8, 4th column). In Table 8, r is given by

$$r = \frac{\Delta\varepsilon_{0 \text{ sat}}}{\Delta\varepsilon_{0 \text{ ini}}}, \quad (10)$$

where $\Delta\varepsilon_{0 \text{ sat}}$ and $\Delta\varepsilon_{0 \text{ ini}}$ are the oscillator strengths for the water-saturated sample and sample not subjected to such saturation, respectively.

In part, such difference in r can be due to a slow rate of reaching equilibria given by Eqs. (8) and (9), which was stressed by Efimov et al. (1998). Moreover, this effect can indicate bands in the 1500–2200 cm^{-1} region to be in fact envelopes formed by overlapped spectral components that are due to not only the stretching (Si) O–H vibrations but also the multiphonon matrix modes. There is a certain similarity between the band locations in the 1300 to 2500 cm^{-1} region for $(\text{Me}_2\text{O}/\text{MeO})\text{–SiO}_2$ and silica glasses (Fig. 6) that is in accord with this assumption. In terms of such an assumption,

- (i) it is the oscillator strengths of the water-related components alone that increase with the water content; hence the smaller rate of increase in the total oscillator strengths of the envelopes compared to the case of water-related bands lacking the multiphonon contributions;
- (ii) the frequency shift of the 1540–1610, 1670–1745 and 1800–1840 cm^{-1} envelopes with the silica content of glasses (Fig. 6) can be assigned

Table 8

Increase in the oscillator strengths due to the water saturation of 41 (K_2O , CaO , BaO)·59 SiO_2 sample (Efimov et al., 2003) and estimates for the matrix mode contributions to the oscillator strengths made based on the assumption of reaching equilibria between all water-related species

Band no.	Data for the water-saturated sample (Efimov et al., 2003)			Matrix mode contributions, no more than
	ω_j (cm^{-1})	$\Delta\varepsilon_{0 \text{ sat}}$	Increase due to H_2O saturation, r	
1	1582	$3.34 \cdot 10^{-4}$	1.29	0.75
2	1708	$6.23 \cdot 10^{-4}$	1.24	0.79
3	1824	$2.20 \cdot 10^{-4}$	1.32	0.73
4	1927	$1.97 \cdot 10^{-4}$	1.36	0.71
5	2047	$3.07 \cdot 10^{-4}$	1.71	0.54
6	2326	$9.60 \cdot 10^{-5}$	5.45	0.10
7	2527	$4.79 \cdot 10^{-5}$	10.3	–
8	2760	$1.27 \cdot 10^{-4}$	10.9	–
9	2908	$9.23 \cdot 10^{-6}$	4.66	0.13
10	2965	$3.29 \cdot 10^{-5}$	11.1	–
11	3193	$5.80 \cdot 10^{-5}$	11.2	–
12	3388	$1.74 \cdot 10^{-5}$	10.6	–

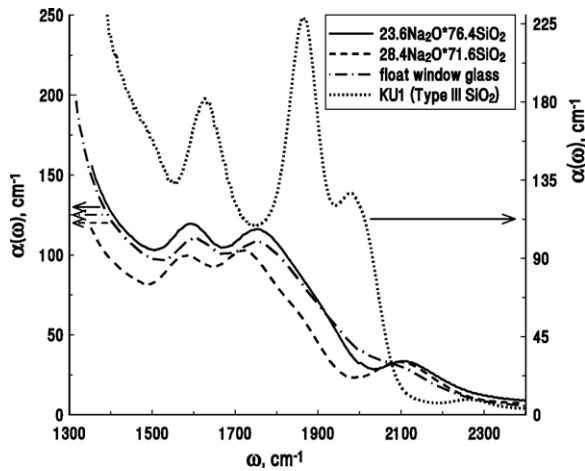


Fig. 6. Comparison of $\alpha(\omega)$ spectra of silica glass and some silicate glasses in the 1300 to 2500 cm^{-1} region.

tentatively to the effect of multiphonon components involving the asymmetric Si–O–Si stretch whose frequency is known (Lazarev et al., 1975) to be composition-dependent.

The contribution of the combination modes of glass matrix, $\Delta\epsilon_{0 \text{ comb}}$, to the total oscillator strength of an envelope might be estimated as follows:

$$\Delta\epsilon_{0 \text{ comb}} = \Delta\epsilon_{0 \text{ sat}} \frac{r_{\text{max}}^{-r}}{(r_{\text{max}} - 1) \cdot r}, \quad (11)$$

where r_{max} is the maximum r magnitude that occurs for purely water-related bands in the equilibrium conditions. Because, as mentioned above, equilibria given by Eqs. (8) and (9) are not reached for the period of glass melting in laboratory conditions, $\Delta\epsilon_{0 \text{ comb}}/\Delta\epsilon_{0 \text{ sat}}$ values obtainable based on Eq. (11) (see Table 8, last column³) are in fact greatly overestimated.

In view of the above, further investigations are necessary for validating a tentative assumption about the contribution of the combination modes of silicate glass matrices to the total oscillator strengths of the IR absorption bands with inherent frequencies around 1540–1610, 1670–1750, 1810–1840, 1900–1930, and 2030–2110 cm^{-1} .

6. Conclusions

1. For Types I and III silica glass, twelve IR absorption bands located in the 1300 to 3200 cm^{-1} wavenumber

region are due to the combination modes and overtones inherent in the silica matrix.

2. Silica glasses of not only Type III but also Type I contain traces of molecular water that manifest themselves in a quite weak band around 3490 cm^{-1} due to the symmetric stretching modes of H_2O molecule. At wavenumbers from 3500 to 5000 cm^{-1} , the intensities of the water-related bands in Type I silica glass spectrum are negligibly small.
3. The 3500–3700 cm^{-1} envelope in Type III silica glass spectrum is formed by three bands due to the stretching vibrations of (Si)O–H groups in two different structural sites. The 3750–3950 cm^{-1} shoulder in this spectrum is formed by three bands that, together with three known bands in the 4000–4550 cm^{-1} region, are considered to be due to certain combination modes involving the (Si)O–H vibrations.
4. For silicate glasses, five IR absorption bands in the 1500–2200 cm^{-1} region are envelopes that cover overlapping spectral components due to (i) the stretching modes of (Si)O–H groups forming hydrogen bonds in two different structural sites and (ii) the multiphonon modes of the glass matrices. This is the reason for the smaller rate of increase in the oscillator strengths of these bands with the water content compared to that observed for the purely water-related bands (such as those known to occur in the 2500–3700 cm^{-1} region).

Acknowledgement

[RR] [JS]

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³ r_{max} value used in the calculations (10.8) was taken to be an average for bands nos. 7, 8, 10, 11, and 12.

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