

Temperature dependence of the OH⁻ absorption in SiO₂ glass and melt to 1975 K

ANDRZEJ GRZECHNIK* AND PAUL F. McMILLAN*†

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, U.S.A

ABSTRACT

FTIR absorbance spectra of SiO₂ glass containing 1200 ppm OH⁻ groups were recorded in situ to 1975 K. There are only minor changes in peak height to 1700 K, indicating that the molar extinction coefficient measured at ambient conditions, at the peak maximum, is applicable for OH⁻ determination at high temperature. However the integrated peak intensity shows a slight decrease with increasing temperature over the entire temperature range, due to changes in the band shape associated with small modifications to the hydrogen bonding environment and loss of hydrous component at the highest temperatures.

INTRODUCTION

By studying the role of H₂O in high silica magmas, its effects on magma rheology and degassing behavior may be understood (e.g., Carroll and Holloway 1994; Hurwitz and Navon 1994). Infrared spectroscopy is an ideal technique for this type of study because it can give quantitative information on the H₂O content, as well as a detailed appreciation of the speciation and structural environment of the OH⁻ groups (Newman et al. 1986; Ihinger et al. 1994). Several in situ high-temperature studies of silicate melts and liquids, using the dispersive infrared spectrometers, have been reported in the literature (Sweet and White 1969; Aines et al. 1983; Gable and Shankland 1984). These experiments were very difficult to perform at temperatures above about 1000 K due to the black body radiation. Recently, the use of Fourier-transform infrared spectrometers and technical developments have permitted investigations of the behavior of OH⁻ (and H₂O) species in silicate glasses and melts in situ at higher temperatures or under combined high *P-T* conditions (Keppler and Bagdassarov 1993; Bassett et al. 1994; Nowak and Behrens 1995; Shen and Keppler 1995; Nowak et al. 1996; Behrens and Nowak 1997). It is now important to evaluate the influence, if any, of pressure and temperature on the infrared absorption coefficients of the principal OH⁻-bearing species to determine the temperature- and pressure-dependence of H₂O speciation (Nowak and Behrens 1995; Shen and Keppler 1995; Holtz et al. 1996). In the present study, we have investigated the O-H stretching vibration in SiO₂ glass and melt containing 1200 ppm OH⁻, dissolved as hydroxyl groups (Stone and Walrafen 1982), by infrared absorption spectroscopy to >1900 K. This method permits the evaluation of the effect of temperature on the molar absorp-

tion coefficient, both measured at the peak maximum and integrated over the entire band. In addition, it is well known that the presence of even trace amounts of dissolved OH has dramatic effects in reducing the relaxation time associated with viscous flow in high silica melts. Analysis of the IR band shapes at high temperature give some insight into how the OH species interact with SiOSi linkages within the melt to facilitate the bond breaking process.

EXPERIMENTAL METHODS

Spectra were collected using a Bio-Rad Digilab FTS-40 FTIR instrument (a Michelson interferometer) coupled with an IR microscope (Cassegrainian objective). A quartz beamsplitter, tungsten source, and MCT detector were used to measure near-infrared spectra, and 64 scans (128 s) were accumulated for each spectrum. The spectral resolution was 8 cm⁻¹.

Experiments were carried out on thin (20–40 μm) plates of Suprasil (commercial SiO₂ glass containing 1200 ppm OH⁻ by weight; Brückner 1970; McMillan and Remmele 1986), pressed into a 400 μm diameter hole in an Ir wire heater (Daniel et al. 1994). The sample thickness was limited to avoid potential problems with temperature gradients. The thin sample was also used to minimize the reabsorption of the black body radiation (see the discussion below). The diameter of the infrared beam at the focal point of the Cassegrainian objective in the Bio-Rad IR microscope used in that study was 200 μm. We found that the use of the 400 μm hole in the wire loop is a good compromise between temperature gradients, increasing with the increased diameter of the hole in the wire loop and lack of the black body radiation from the wire itself, providing that the infrared beam (200 μm) is perfectly focused in the middle of the hole (400 μm) during the entire series of measurements. Temperatures were calibrated from known melting point standards. The heating stage was mounted under the IR microscope with

* Present address: Laboratoire des Sciences de la Terre, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cédex 07, France.

† Also Visiting Member, Institut Universitaire de France.

the sample at the focal point of the Cassegrainian objective and paraboloid mirror underneath it.

Gervais (1983) and Keppler (1996) have discussed the methodology of high-temperature FTIR spectroscopy. The signal of interest in transmission spectroscopy is the IR beam emitted by the source, modulated into a time-dependent signal by the interferometer, and passed through the sample to the detector. The resulting time-dependent interferogram, $I(t)$, is then Fourier transformed to obtain a single beam spectrum, $I(\nu)$. During in situ high-temperature measurements, the sample also plays the role of an IR source and emits a signal. One part of the signal is directed immediately toward the detector as a non-modulated signal, which results in a constant voltage offset, easily removed from any spectrum or interferogram. Another part of the emitted signal is directed to the interferometer, where it is modulated into a frequency dependent component that is sent back through the sample to the detector (Gervais 1983). The measured signal is then a sum of the Fourier-transformed interferograms from the instrument IR source passed through the sample and the frequency modulated signal from the heated sample, independent of their shape or size.

During our experiments with the Bio-Rad IR instrument, we found that the corresponding signals from the black body and sample were opposed (the center burst were opposed to each other). The real signal from the sample had a negative value and the black body one was positive. There was no offset of the center bursts. What it means mathematically is that in the complex coordinate system, these two signals differ by π in their imaginary coordinates. After Fourier transforming them, they have opposite signs (no interference fringes). We measured the values of the real and black body signals (the centerbursts of the corresponding interferograms) and found that their difference was constant. The temperature dependence of the two signals, separately, is linear (both had the same positive temperature dependence). Later we temperature calibrated our MCT detector using that method. Our experience with the transmission experiments at high temperatures indicates that the discussion of the black body effect in the IR measurements presented by Gervais (1983) is general.

There are two simple ways to remove this contribution of the black body radiation from the heated sample to the measured infrared signal (Gervais 1983). One involves an intentional misalignment of the light path between the interferometer and the sample (for example, by misaligning the parabolic mirror below the sample stage in our experimental geometry), so that the light paths for the signal from the instrument infrared source and the heated sample are different (Gervais 1983). The second method involves an analytical correction based on measurements of the sample and background spectra at every temperature (Gervais 1983). This method is based on the mathematical rule that the Fourier transform of a sum (or difference) is a sum (or difference) of the Fourier

transforms. The absorbance A is obtained using the following formula:

$$A = \log_{10} \frac{I_{\text{on}}^{\text{b}} + I_{\text{off}}^{\text{b}}}{I_{\text{on}}^{\text{s}} + I_{\text{off}}^{\text{s}}} \quad (1)$$

where the Fourier transformed interferograms I are measured (1) with the sample and with the IR source on (I_{on}^{s}) and off ($I_{\text{off}}^{\text{s}}$) (i.e., the beam was blocked, rather than the source switched off), and (2) without the sample, with the source on and off (I_{on}^{b} and $I_{\text{off}}^{\text{b}}$, respectively). This method then involves measuring two spectra (source on and off) at each temperature, in two series of experiments, one for the sample and the other for an empty sample holder to provide a background. In fact, the values of I_{on}^{s} and $I_{\text{off}}^{\text{s}}$ have the opposite signs from I_{on}^{b} and $I_{\text{off}}^{\text{b}}$, respectively, and the latter should be subtracted from the first ones, respectively. However, the calculated single beam spectra, after Fourier transforming of the interferograms, are given as the absolute values in the software used in IR instruments. As a result, summation is used in the above formula, rather than subtraction.

To measure the spectra without the true infrared source, we blocked the IR source by blinding the smallest aperture (0.5 cm⁻¹) of the set of apertures in the beam path, immediately after the IR source. We used a thick layer of a standard material for thermal isolation, commonly used for high-temperature furnaces. This way of masking assures that no light leaks from the source. We checked the absence of the signal from the true IR source by the absence of the interferogram when the blinded 0.5 cm⁻¹ aperture was in the optical path. The apertures can be automatically changed so that there were no problems with constant switching the source on and off and the stability of the source during a long series of separate experiments. We used the 1 cm⁻¹ aperture for the measurements (with other parameters set up for NEAR-IR region in the Bio-Rad spectrometer) so that the effective spectral resolution was 8 cm⁻¹.

The nominal temperature is reproduced by applying the same voltage in the wire loop heating experiments described here. The black body characteristics of the cavity in the empty wire and one filled with sample are slightly different, but the mismatch is not severe in the infrared region, particularly at high temperatures (Hadni 1967). Thick samples may strongly reabsorb black body radiation. Ideally, the thickness of the sample should be infinitely small. However, during the real experiments, the thickness of the sample is always finite. The proper balance between the sample thickness and the black body mismatch between the empty and filled wire loop is necessary to carry out the correct quantitative analysis through the use of the above formula. In addition, the intensity of the black body radiation and its reabsorption by a sample can be minimized by the intentional misalignment of the optical system between the sample and interferometer (as discussed earlier). Any deviation in temperature between the sample and background series results in a change in baseline to the absorbance spec-

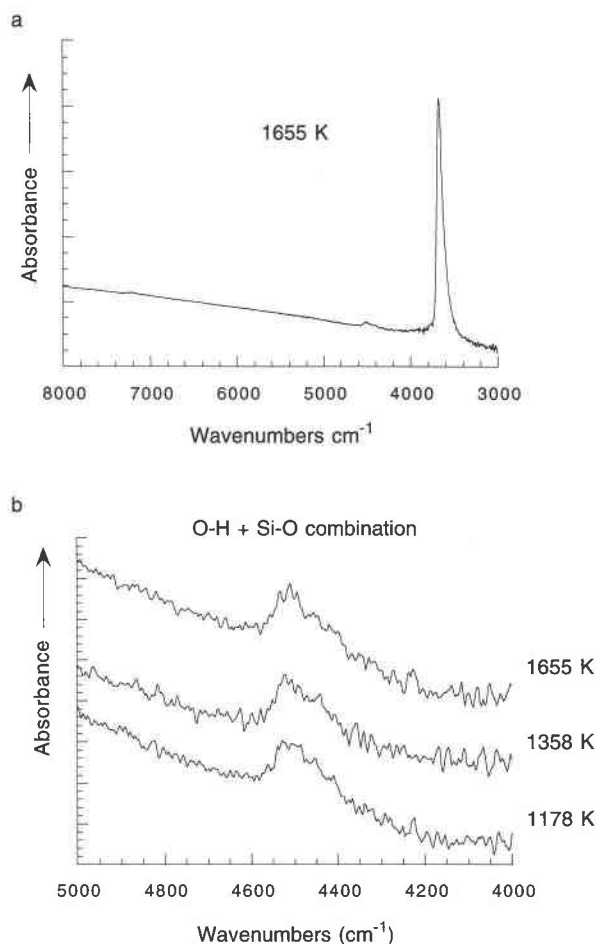


FIGURE 1. (a) Representative high-temperature (1655 K) FTIR spectrum of SiO₂ glass containing 1200 ppm OH⁻ in the region of the O-H fundamental and overtone vibrations. (b) Representative high-temperature spectra in the region of the Si-O + O-H combination band.

trum, which is evaluated by comparing with low-temperature spectra.

RESULTS

A spectrum of Suprasil in the 3000–8000 cm⁻¹ region at 1655 K is shown in Figure 1a. A slightly rising background with variable slope is commonly observed in the high-temperature spectra partly due to the procedure used to eliminate the black body emission from the sample. However a similar background is also present for the room temperature sample due to reflectance effects at the sample surfaces and also to the tail of absorption due to defects absorbing in the UV region (Brückner 1970). The OH⁻ fundamental band at 3680 cm⁻¹ is asymmetric due to OH sites present in a range of O-H...O bonding environments (Walrafen and Samanta 1978; McMillan and Remmele 1986). The first overtone appears at 7200 cm⁻¹, and there is a combination band between the O-H fun-

damental and Si-O stretching at 4500 cm⁻¹ (Stolen and Walrafen 1976; Stone and Walrafen 1982) (Fig. 1b).

The asymmetry of the O-H fundamental in Raman and IR spectra of OH-containing silica samples has been previously discussed (Walrafen 1975; Walrafen and Samanta 1978; Stolen and Walrafen 1976; Stone and Walrafen 1982; McMillan and Remmele 1986). Walrafen and Samanta (1978) deconvoluted the band into four separate Gaussian components but, based on a detailed comparison of IR and Raman spectra, McMillan and Remmele (1986) considered that there was only evidence for a single asymmetric distribution of O-H stretching vibrations. However, examination of the first overtone region (principal maximum at 4520 cm⁻¹) shows a distinct shoulder developed at 4450 cm⁻¹ (Stone and Walrafen 1982), which indicates that at least two distinct O-H stretching bands contribute to the O-H band profile. In the present high-temperature experiments using the wire loop heating technique (Daniel et al. 1994), the sample thickness was limited to approximately 40 μm within the hot part of the flattened Ir wire, so that our spectra in the overtone region have considerably poorer signal-to-noise ratio than the high quality data of Stone and Walrafen (1982), obtained using a very long absorbing path length. However, the combination band in our spectra shows a distinct asymmetry, even at high temperature (Fig. 1b).

Although the actual number of components contributing to the O-H fundamental is debated (e.g., Walrafen and Samanta 1978; McMillan and Remmele 1986), the band can be represented most simply by two major components, at 3685 and 3635 cm⁻¹, consistent with the two features observed in the overtone region (Stone and Walrafen 1982). The higher frequency component corresponds to the principal maximum observed in the Raman spectrum (McMillan and Remmele 1986), and the lower frequency component corresponds to the principal Gaussian component deconvoluted by Walrafen and Samanta (1978). The higher frequency component is involved in little or no hydrogen bonding (Site I), as discussed by McMillan and Remmele (1986), whereas the lower frequency band component represents OH groups (Site II) involved in a range of hydrogen bonds. Because the lower limit of this band lies near 3500 cm⁻¹, even the most strongly hydrogen bonded sites correspond to only very weak hydrogen bonding, with minimum O...O distances on the order of 2.9–3.0 Å and OH...O bond energies on the order of 10 kJ/mol (Lippincott and Schroeder 1955; Novak 1974). The higher frequency, essentially non-hydrogen bonded (NHB) component of Site I OH groups is more strongly active in the Raman spectrum (and is more strongly polarized) (McMillan and Remmele 1986). The lower frequency, hydrogen bonded (HB) component gives rise to a stronger IR absorption, as expected because the charge transfer associated with the hydrogen bonding causes a greater dipole moment change during the vibration (Lippincott and Schroeder 1955; Umeyama and Morokuma 1977; Paterson 1982). A large distribution of site geometries is expected in glass, so that the pres-

ence of two major components in the vibrational spectra of Suprasil glass could indicate two major diffused distributions (two types of sites), rather than two specific sites.

Two components in the infrared and Raman spectra in Suprasil glass (1200 ppm of OH) could also be interpreted as due to the transverse (TO) and longitudinal (LO) optical components of one band. This implies that the glass structure has a non-centrosymmetric character and that the mode in question is polar due to dipole moment changes both in infrared and Raman spectra. In that case, the observed TO-LO splitting would arise from the long-range interactions in the silica glass network. Galeneer and Lucovsky (1976), Galeneer et al. (1983), and Gervais et al. (1987, 1989) indeed observed close correspondence of the Raman modes to the poles in the imaginary part of the dielectric constant (TO) and the energy loss function (LO), both inferred from the infrared reflectivity spectra of OH/H₂O-free silica glass. However, Denisov et al. (1984) found that the Raman bands did not exhibit the polariton behavior (i.e., their frequencies did not depend on the scattering angle). Instead, the polariton behavior was observed by hyper-Raman spectroscopy, which has the selection rules close to infrared spectroscopy. The conclusion of the study by Denisov et al. (1984) is that the Raman spectrum of OH/H₂O-free silica glass is not polar and infrared, and Raman spectroscopies, through their distinct selection rules, probe different sets of vibrational modes. The OH⁻ groups present in Suprasil glass at the level of 1200 ppm should be considered as local defects in a glass-forming network, not influences on the character of the vibrational density of states. The spectral changes as a function of temperature (a different temperature dependence of the two components), described below, can be well explained by two types of sites, at which the OH⁻ groups reside, without invoking the TO-LO arguments. However, the case of silica glasses with high OH⁻/H₂O contents should be carefully addressed in further studies that use infrared reflectivity spectroscopy (Grzechnik et al. 1994; McAloon and Hofmeister 1995).

Several representative spectra taken at high temperatures of the O-H fundamental are shown in Figure 2. A best linear baseline has been subtracted from the raw data. The height and width of the bands has been measured off the baseline corrected spectra. The position of the peak maximum or the barycenter of the band does not shift with temperature below 1500 K (Fig. 3a). The O-H stretching frequency is expected to be little affected by anharmonicity, because of its large wavenumber value compared with thermal energies at these temperatures. Small shifts (on the order of a few wavenumbers) are observed above this temperature, associated with slight changes in band shape (Fig. 3b, also see below). Above approximately 1700 K, the band height obviously decreases (Fig. 3c) because the 1 atm solubility limit is exceeded at these temperatures (Moulson and Roberts 1961).

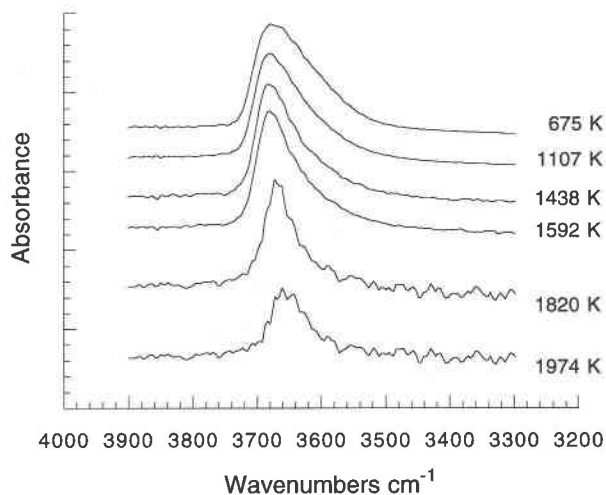


FIGURE 2. Representative high-temperature spectra in the region of the O-H fundamental. A best fit linear baseline has been subtracted from the raw data.

Between room temperature and 1300 K, there is a slight decrease (~15%) in band width (Fig. 3b). The width decreases rapidly between 1300–1600 K, then remains approximately constant on further heating. Below 1600 K, essentially all of the decrease in band width is due to loss of intensity from the low frequency tail of the fundamental band (Figs. 2 and 3a), indicating a decrease in hydrogen bonding of the strongest HB sites. We suggest that this is due to excitation of SiOH bending or hindered rotations of the silanol groups that constitute the hydrogen-bonded Site II. If this were the case, we should expect an increased intensity at the highest frequency band edge, because both Site I and Site II OH groups contribute to the non-HB signal at high temperature. There does appear to be a slight increase in band height measured at the peak maximum, between 1300–1600 K (Fig. 3c). Also consistent with this suggestion is the observation that the integrated band intensity decreases over this entire temperature range (Fig. 3d). Because the NHB groups have a lower infrared activity, we expect a decrease in integrated molar absorptivity as hydrogen bonds are broken with increasing temperature. These changes in the OH spectrum occur over a temperature regime where the molar volume of SiO₂ glass and supercooled liquid is essentially constant (Brückner 1970), although average O...O distances may actually decrease due to thermal excitation of SiOSi bending vibrations (McMillan et al. 1994).

At temperatures above 1600 K, the high-frequency edge of the OH fundamental begins to move to lower frequency, resulting in the high-temperature frequency decrease in the peak maximum (Fig. 3a). The band remains narrow (FWHM = 70 cm⁻¹, compared with 126 cm⁻¹ for the room temperature spectrum), and the peak height begins to decrease rapidly due to loss of hydrous component from the sample (sharp peaks due to the ro-

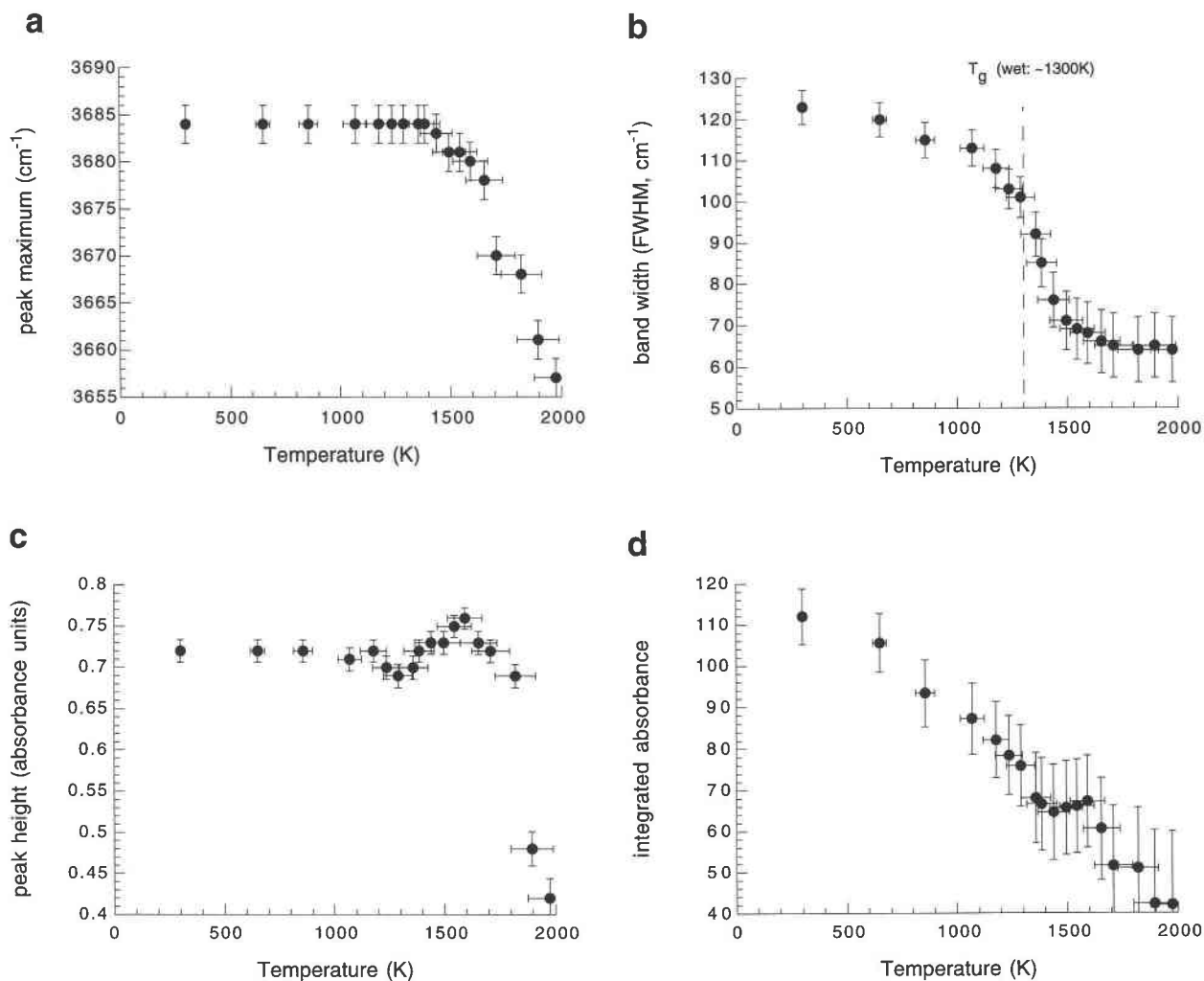


FIGURE 3. (a) Frequency at the peak maximum for the OH⁻ fundamental as a function of temperature. (b) Full width at half maximum of the OH⁻ fundamental as a function of temperature. The glass transition temperature for the wet glass is indicated, estimated from the viscosity-temperature relations in Brückner

(1970). (c) Peak height at the position of maximum intensity for the OH⁻ fundamental as a function of temperature. (d) Integrated absorbance for the OH⁻ fundamental (integration between 3200 and 3900 cm⁻¹) as a function of temperature.

tational-vibrational spectrum of evolved gaseous H₂O were observed in some spectra taken above 1700 K. These temperatures are well into the glass transition range for laboratory time scales (Brückner 1970). Rapid structural relaxation apparently now exposes even the Site I OH groups to hydrogen bonding, because the frequency at the peak maximum (which is now narrow and symmetric) decreases with increasing temperature. This effect should result in an increase in the integrated OH absorbance. However, simultaneous OH loss at high temperature causes the net integrated absorbance to further decrease (Fig. 3d).

As a cautionary note, we also found that the precise dependence of the integrated band intensity on temperature was highly sensitive to details of the baseline subtraction procedure and on the limits chosen for the inte-

gration. The plot in Figure 3d was constructed using the integration limits 3200–3900 cm⁻¹, after subtraction of a best-fit linear baseline in the region of the band. The corresponding data points for the integrated absorbance with the same integration limits, obtained without baseline subtraction, are within the error bars marked in Figure 3d.

DISCUSSION

It is interesting to speculate on the nature of the interaction between the SiOH groups and the glass framework in the vicinity of the glass transition. It is well known that addition of even trace quantities (several parts per million) of OH significantly reduces the temperature of the glass transition, T_g , and also the activation energy for viscous flow. For example, dry SiO₂ has a calorimetric T_g

measured near 1470 K, whereas SiO₂ containing 1200 ppm OH has T_g near 1250 K (Brückner 1970; Richet and Bottinga 1984). A general consensus is that OH dissolution is described by the general reaction



and that breaking the intertetrahedral SiOSi linkage weakens the tetrahedrally bonded framework, resulting in the lowered viscosity (Brückner 1970). The activation energy for viscous flow in dry silica is large and is mainly determined by the energy to break a single Si-O bond (Brückner 1970; McMillan et al. 1994). The presence of SiOH rather than an SiOSi linkage might weaken the neighboring SiOSi links and cause these to break more easily, the SiOH group could serve as an already broken SiOSi linkage permitting easier O²⁻ exchange between neighboring silicate tetrahedra and lowering the activation barrier to structural relaxation (McMillan et al. 1994). Our high- T IR data do not give any additional direct information on the nature of the interaction between OH and the SiO₂ framework, responsible for the reduction in structural relaxation time (lowered T_g). However, they do place some constraints on the mechanism.

In their study of OH⁻ groups in rhyolite at high temperature, Keppler and Bagdassarov (1993) suggested that the O-H fundamental became extremely broad in their highest temperature spectrum (1300 °C), because of the onset of proton hopping between HB sites at the vibrational time scale (10^{-14} s). However, at lower temperatures, they observed a decrease in band width due to a reduction in degree of hydrogen bonding, analogous to that observed here for OH groups in SiO₂. In our study, the OH band width remains narrow to the highest temperatures observed. If any proton hopping (between adjacent O) were to occur, it might be expected that this would result from an increase in hydrogen bonding (decrease in OH...O distances), which is the opposite of what is observed in SiO₂ (and rhyolite) with increasing temperature.

Figure 4 shows an approximate relaxation map based on available data for SiO₂ (Brückner 1970). The OH and H₂ diffusion time scales are many orders of magnitude faster than the structural relaxation time scale in the vicinity of T_g . Probably the existence of rapid relaxation channels, which involve both the protons and some subset of the network-forming anions, interact with the primary structural relaxation process to reduce the viscosity in the hydrated glass. However, any proton hopping mechanism remains much slower than the O-H vibrational time scale and has no signature in the IR spectrum at the O-H stretching frequency (Fig. 2). The reduction in viscosity can also be rationalized through energy and entropy considerations. The presence of broken SiOSi bonds (i.e., SiOH groups) likely causes a static weakening of the glass network, either through weakening of critical SiOSi bonds or a reduction in the average activation barrier for viscous flow. Also, the presence of silanol groups could increase the local configurational possibilities for struc-

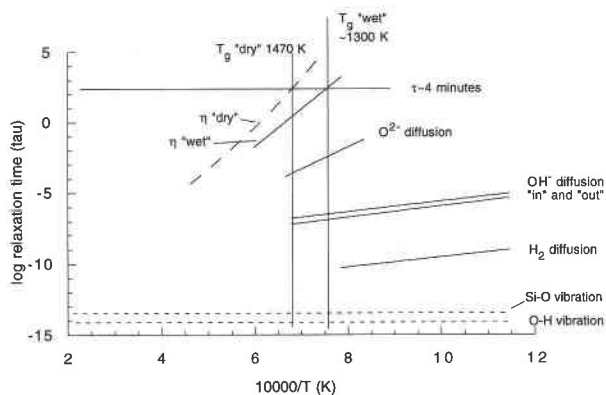


FIGURE 4. Qualitative relaxation map (log time scale vs. inverse temperature) for structural relaxation (viscosity: both dry and wet data are shown), O²⁻, OH (both into and out of glass samples) and H₂ diffusion, and the O-H stretching vibrational time scale for SiO₂-OH (data from Brückner 1970). The data for O²⁻ diffusion are only indicative, because of the relative contributions from different mechanisms, such as those involving molecular O₂ (Brückner 1970; Kalen et al. 1991; Lamkin et al. 1992). The time scale for viscous relaxation is estimated from the Maxwell relation, assuming an infinite frequency shear modulus of ~10 GPa. The time scales associated with diffusional motions are estimated from the Eyring relation, assuming a jump distance of ~2.5 Å (O...O distance). The time scales associated with diffusion of chemical species in vitreous SiO₂ are strongly affected by impurity content, sample preparation history, and so forth, and can vary by several orders of magnitude. They are shown here to indicate their ranges relative to the vibrational time scale and the time scales associated with structural relaxation in dry and wet (i.e., containing ~1200 ppm OH) SiO₂.

tural relaxation (i.e., augments the configurational entropy, ΔS_{conf} , with a corresponding reduction in viscosity) (Richet 1984; Richet and Neuville 1992). Note that the most rapid change in OH line width occurs in the vicinity of T_g for the wet glass. Our preferred interpretation is that this results from increased hydrogen bonding within Type I OH sites, which were previously not exposed to hydrogen bonding in the glass.

From this study, we conclude that the molar absorptivity values determined for the OH fundamental of SiOH groups in SiO₂ glass at low temperature are applicable to high-temperature studies (at least for samples with low OH content), well into the supercooled liquid regime and probably also the stable liquid, if the molar absorptivity is measured at the peak maximum. However, some temperature dependence to the extinction coefficients should be expected when integrated molar absorptivities are used, although our experiences suggest that these should be used with caution for quantitative determinations of OH content at high temperature.

The observation that the infrared absorption coefficient measured at a single frequency is essentially independent of temperature is in agreement with theory for a harmonic oscillator, when all the processes contributing to the population and depopulation of vibrational states are taken

into account (Steele 1971). This is no longer necessarily the case for an anharmonic oscillator but here the O-H stretching frequency is so large that the anharmonic shifts associated with upper vibrational states are hardly sampled. This argument cannot be applied to overtone and combination vibrations, such as those commonly used to determine the OH/H₂O ratio for hydrous species dissolved in glasses (Ihinger et al. 1994), because the intensities of these transitions now have an intrinsic temperature dependence (Sherwood 1972). This has been discussed for liquid H₂O by Buback et al. (1987). We tried to test this for the overtone and combination bands of the SiOH species in the present study. However, within the uncertainty of our measurements, we could detect no change in either the peak height or the integrated absorbance below the point at which volatile loss began to occur.

From analysis of the OH band width at high temperature and consideration of diffusion, vibrational, and structural relaxation time scales, it is unlikely that proton hopping associated with O-H...O sites occurs at the vibrational time scale over the temperature range investigated here. Instead, the observed decrease in structural relaxation time occurs as the network anions are entrained by OH diffusive processes on the 10⁻⁶–10⁻⁷ s time scale, or is due to energetic or entropic effects associated with the presence of dissolved OH groups in the glass. It is not clear that this conclusion can be extended to the rhyolite sample studied by Keppler and Bagdassarov (1993), because the initial degree of hydrogen bonding in the aluminosilicate composition is much greater than in pure SiO₂, with the asymmetric tail of the O-H fundamental absorption extending down to ~3000 cm⁻¹. This could contribute to a difference in behavior of the OH⁻ groups at high temperature in the two melt compositions.

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