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Hydroxyl sites in SiO_2 glass: A note on infrared and Raman spectra

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ABSTRACT

There is some interest in the speciation of water in silicate glasses and melts, and the effect of bulk composition on this speciation. We have obtained infrared and Raman spectra for SiO_2-H_2O glasses with low (1200 ppm) and high (6.3 wt%) water contents. The low-water-content glass shows an asymmetric band in the fundamental O–H stretching region, consistent with an SiOH species involved in a range of hydrogen-bonding environments. The high-water-content sample shows features due to both hydroxyl groups, as observed for the low-water-content glass, and molecular H_2O dissolved in the glass. This sample also shows a Raman band at 3598 cm^{-1}, which probably corresponds to a new type of SiOH species. We have also obtained the Raman spectrum for a sodium silicate glass $Na_2O \cdot 4SiO_2$ containing 1 wt% H_2O. Addition of water to this composition causes considerable changes in the silicate band region below 1200 cm^{-1}. The O–H stretching bands are very different to those observed for the SiO_2-H_2O glasses, and a weak band near 2350 cm^{-1} may correspond to SiOH groups involved in intratetrahedral hydrogen bonding, across an edge of the SiO_4 tetrahedron.

INTRODUCTION

There is some interest in the speciation of water in silicate melts and glasses with a view to understanding water solubility and diffusion mechanisms. Vibrational spectroscopy has been used in a number of studies to investigate the number and types of hydrous species present in a range of silicate glasses (e.g., Scholze, 1966; Stolen and Walrafen, 1976; Mysen et al., 1980; Stolper, 1982a, 1982b; McMillan et al., 1983). Stolper (1982a, 1982b) and Stolper et al. (1983) have shown that both undissociated molecular H_2O and hydroxyl groups are solute species in aluminosilicate glasses and melts. These studies found little change in the form of the O–H stretching band near 3500 cm^{-1} (or its associated overtones and combinations) with glass composition over the range of aluminosilicate glasses studied by them. However, other workers have observed considerable changes in the O–H stretching region as a function of composition for many silicate and aluminosilicate glasses, which have been interpreted in terms of several independent types of hydroxyl site (e.g., Scholze, 1966; Walrafen and Samanta, 1978; Stone and Walrafen, 1982). If this is so, then the water-dissociation equilibrium written by Stolper (1982a, 1982b) should contain several component dissociation constants and may depend considerably on composition. As a preliminary investigation into the effect of composition on the speciation of hydroxylated groups in silicate glasses, we have obtained Raman and infrared spectra for SiO_2 glass with low and high water contents and for a hydrous sodium silicate glass.

EXPERIMENTAL METHOD

The low-water-content sample was a block of Suprasil approximately 1 × 0.5 × 0.2 cm (Electro-Quartz Company, France) containing around 1200 ppm OH (quoted by the company, and estimated by infrared absorption). This sample was similar to that studied by Stolen and Walrafen (1976), Walrafen and Samanta (1978), and Stone and Walrafen (1982). The high-water-content SiO_2 glass was prepared at 1.5 kbar and 1190°C in an internally heated argon-gas pressure vessel in the laboratory of J. R. Holloway at Arizona State University. The sample was run for 24 h, then quenched isobarically. The water content of the bubble-free quenched glass was analyzed using a Perkin-Elmer thermogravimetric analysis system and was found to be 6.3 ± 0.05 wt% H_2O. This is close to the water solubility for SiO_2 found by Kennedy et al. (1962) for our run conditions, showing that the liquid was saturated during the run and that this water content was retained on the quench. The dry sodium silicate glass was prepared from a gel mix at 1 atm and 1000°C, and its composition was verified by electron-microprobe analysis. The glass was then hydrated at 1000°C and 10 kbar in a piston-cylinder apparatus (Patera and Holloway, 1978). The water content was estimated at 1 ± 0.1 wt% by the 110°C weight-loss method (e.g., Oxtoby and Hamilton, 1978).

The Suprasil and high-water-content samples were polished on three faces for polarized Raman spectroscopy, and the Suprasil sample was doubly polished for infrared absorption study. There was only sufficient high-water-content sample for powder infrared spectroscopy, using a 3-mg ground sample in a KBr disc. The disc was dried overnight in a vacuum oven at 115°C to remove traces of adsorbed surface water. This was verified by running both blank KBr and KBr with dry SiO_2 discs under the same conditions. Raman spectra were obtained with an Instruments S.A. U-1000 Raman system, using the 5145, 4880, or

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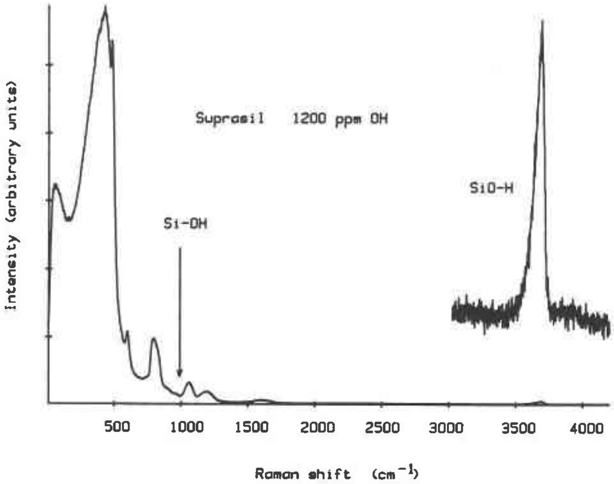

Fig. 1. The unpolarized Raman spectrum of Suprasil: SiO_2 glass containing 1200 ppm water (measured as OH). Laser power 1500 mW; 4800-Å line: spectral slit width, 600 μm (5 cm^{-1}).

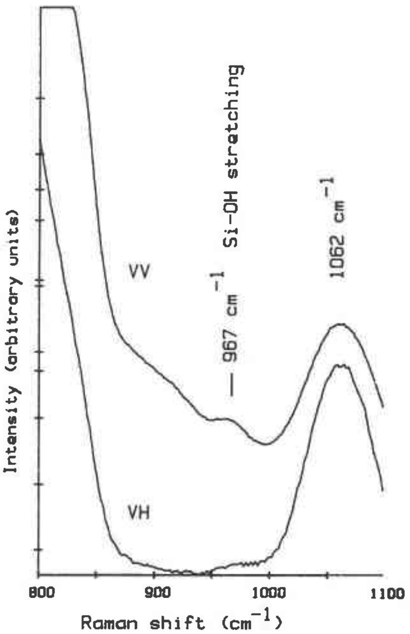

Fig. 2. Parallel-polarized (VV) and perpendicular-polarized (VH) Raman spectra of Suprasil in the 800–1100-cm^{-1} region, showing the Si–OH stretching peak.

4579Å lines of a Coherent Innova 90-4 argon ion laser for sample excitation. Fourier-transform infrared spectra were run on a Nicolet MX-1 interferometer.

LOW-WATER-CONTENT SiO_2 GLASS

The Raman spectrum of Suprasil with 1200 ppm OH is shown in Figure 1. This spectrum is essentially identical to that obtained by Stolen and Walrafen (1976) for a similar sample. The weak asymmetric band near 3670 cm^{-1} is due to the O–H stretching vibration of hydroxyl groups (Stolen and Walrafen, 1976; Walrafen and Samanta, 1978; Stone and Walrafen, 1982). The weak polarized feature at 967 cm^{-1} (Fig. 2) has been shown via isotopic substitution experiments to be due to Si–OH stretching (Hartwig and Rahn, 1977). It is generally accepted that the O–H stretching and Si–OH stretching vibrations arise from the same groups and that the only hydrous species present in Suprasil and other low-water-content silicas are hydroxyls in silanol (SiOH) groups (e.g., Stolen and Walrafen, 1976). This is consistent with the presence of an overtone band near 4500 cm^{-1}, resulting from the combination of the SiO–H and Si–OH stretching vibrations (Stone and Walrafen, 1982), and supports Stolper's (1982b) suggestion that hydroxyl groups should be the only or dominant species at low total water content.

The parallel- and perpendicular-polarized Raman spectra and the infrared spectrum of Suprasil in the O–H stretching region are shown in Figure 3. The O–H stretching band is obviously quite asymmetric, with a tail to lower frequency. Walrafen and Samanta (1978) deconvoluted the Raman and infrared bands into four Gaussian components at 3690, 3665, 3605, and 3510 cm^{-1}, which they interpreted as due to four different types of hydroxyl site in the glass. These authors observed inflections in their Raman and infrared spectra that lent support to these deconvolutions. However, we see no evidence for the inflections suggested by Walrafen and Samanta (1978) (Fig. 3), and we suggest that the data may be equally well interpreted in terms of a single type of OH site. The effect of hydrogen bonding on O–H stretching vibrations is well known: peaks are broadened and shifted to lower wavenumber with increased hydrogen bonding (e.g., Ryskin, 1974). We suggest that the high-frequency edge of the asymmetric peak at 3690 cm^{-1} corresponds to SiOH groups that are not involved in any hydrogen bonding, or are essentially "free," and that the low-frequency tail in all these spectra reflects SiOH groups involved to an increasing degree in hydrogen bonding. The O–H stretching of the "free" SiOH groups should be more symmetric, so should be more active and more polarized in the Raman spectrum. The stretching of the hydrogen-bonded groups will be perturbed by the hydrogen bonding and hence should be less polarized and weaker in the Raman spectrum, but stronger in the infrared, as well as being shifted to lower frequency. These considerations suggest that the perpendicular (VH) Raman spectrum should resemble the infrared spectrum and that both should have their maximum shifted to lower frequency than the parallel (VV) polarized Raman spectrum. Inspection of Figure 3 shows that this is the case. Both Stone and Walrafen (1982) and Aines et al. (1984) observed a distinct shoulder on the combination band near 4500 cm^{-1}, which Stone and Walrafen (1982) considered as support for the suggestion that several types of OH sites were present. However, the appearance of the shoulder in the overtone and combination spectra associated with OH stretching could simply reflect the differing anharmonicities of hydrogen-bonded versus "free" OH groups. Instead of several distinct types of OH site in this low-water-content SiO_2 sample, we suggest that

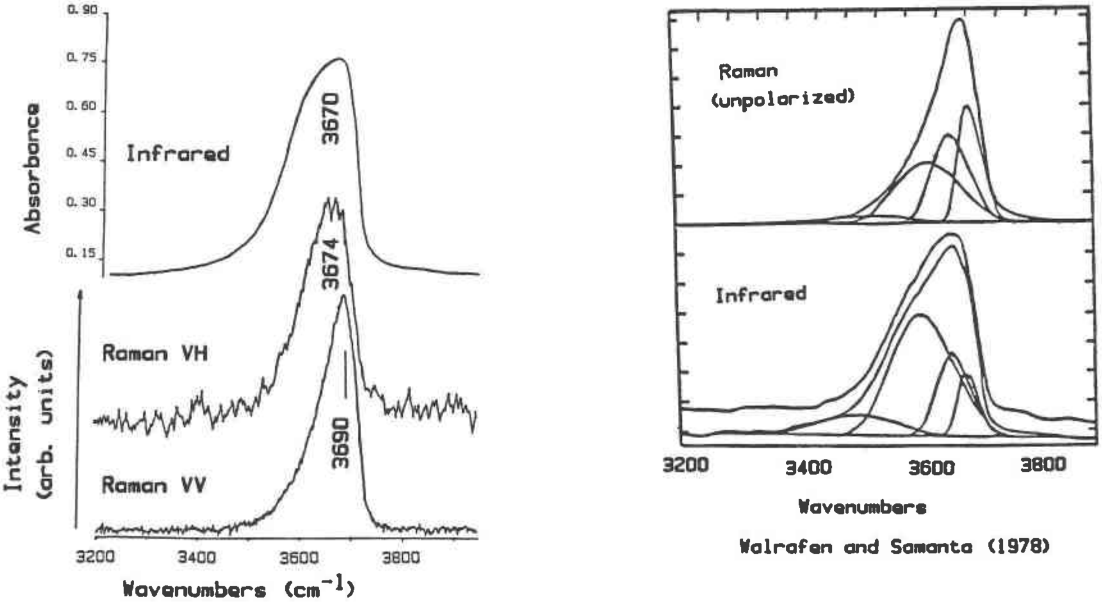

Fig. 3. Infrared absorption and parallel-polarized (VV) and perpendicular-polarized (VH) Raman spectra of Suprasil in the O–H stretching region. The deconvoluted spectra of Walrafen and Samanta (1978) are shown for comparison.

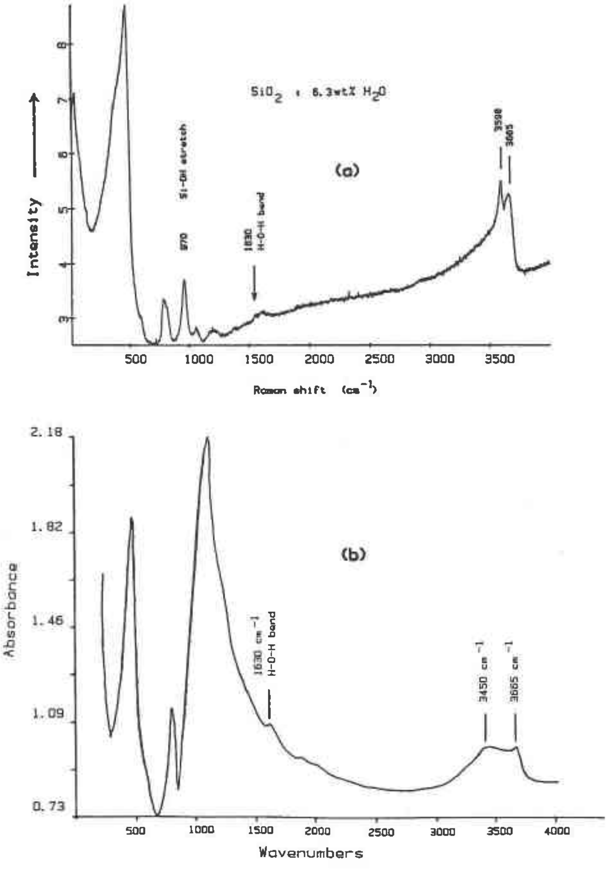

Fig. 4. Unpolarized Raman spectrum for SiO_2 glass containing 6.3 wt% H_2O. Laser power 200 mW, 4579-Å line. (b) Powder infrared spectrum for the same glass.

the Raman and infrared data are consistent with a single type of SiOH group involved in hydrogen bonding of varying degree. The low-frequency tail of the O–H stretching band does not extend below 3500 cm^{-1}, suggesting that the hydrogen bond lengths O–H···O are no shorter than around 2.9 Å (Nakamoto et al., 1955).

HIGH-WATER-CONTENT SiO_2 GLASS

The Raman spectrum of SiO_2 glass containing 6.3 wt% H_2O is shown in Figure 4a. The Si–OH stretching mode at 970 cm^{-1} is much more prominent relative to other bands in the spectrum, showing that considerably more silanol groups are present than in Suprasil. The O–H stretching region is much broader than for Suprasil, extending from below 3000 cm^{-1} to near 3700 cm^{-1}. This is mainly due to the presence of molecular H_2O in this high-water-content glass (Stolper, 1982a, 1982b). The powder infrared spectrum of the high-water-content glass is shown in Figure 4b. This clearly shows the SiO–H stretching band at 3665 cm^{-1} and the O–H stretching of molecular H_2O maximized near 3450 cm^{-1} (Fig. 5; Walrafen, 1964). The H_2O bending mode is present in the infrared spectrum at 1630 cm^{-1}. This band is very weak in the Raman spectrum (McMillan et al., 1983), but may be observed in Figure 4a as an extra weak feature on the second-order bands of dry SiO_2 (Galeener and Lucovsky, 1976a). Aines et al. (1984) observed a band near 5200 cm^{-1} in the near-infrared spectrum of a similar hydrous SiO_2 glass (8 wt% H_2O), due to the OH stretch plus HOH bend of molecular water (Stolper, 1982a, 1982b).

The SiO–H stretching feature occurs at 3665 cm^{-1} in both polarizations of the Raman and in the infrared spec-

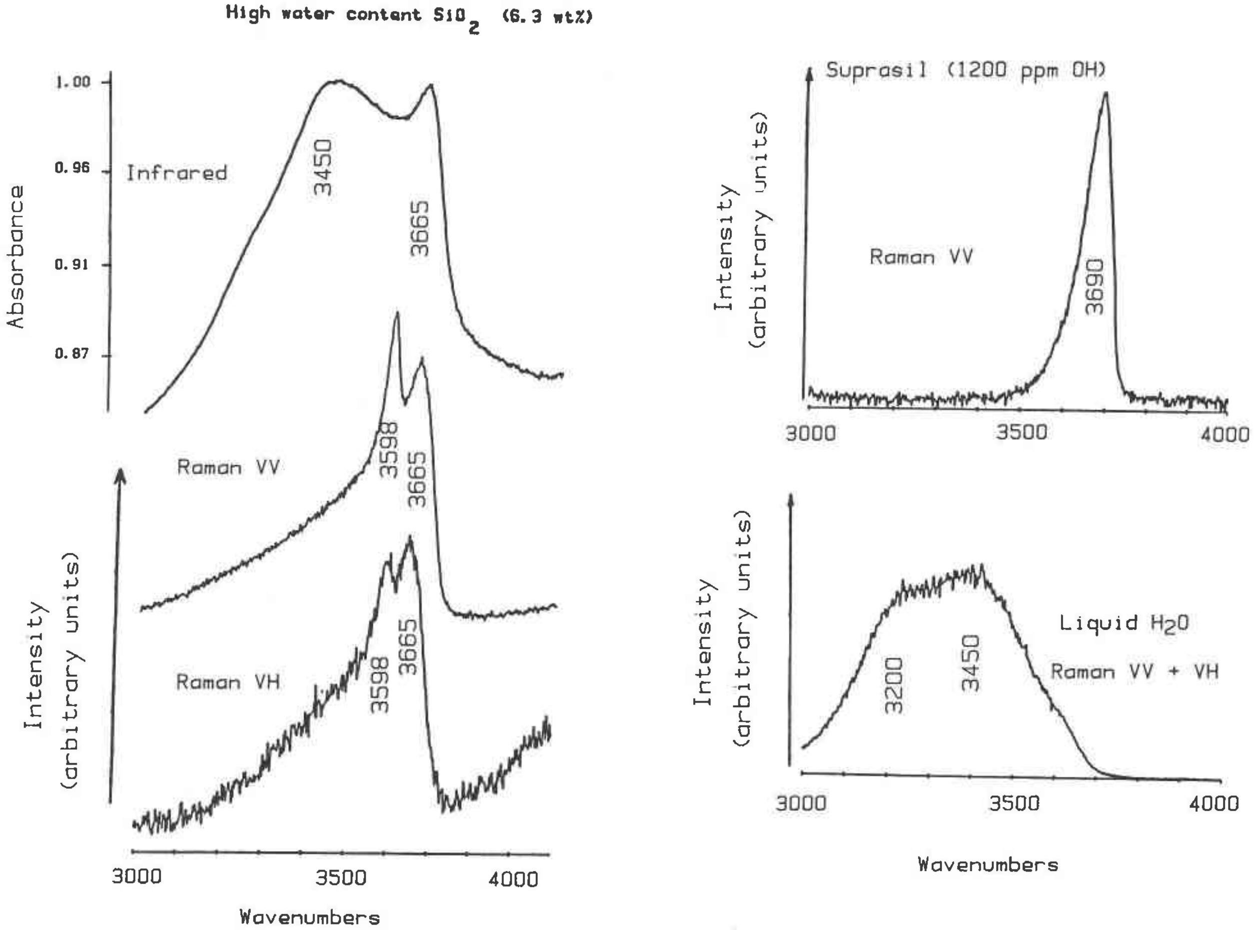

Fig. 5. Infrared transmission and parallel- and perpendicular-polarized Raman spectra in the O–H stretching region for the high-water-content SiO_2 glass. Also shown for comparison at right are the spectra for liquid water and the low-water-content Suprasil in the same region.

tra. This is slightly but significantly lower in frequency than the corresponding peaks for low-water-content SiO_2 in the infrared and VH Raman spectra (3670 and 3674 cm^{-1}, respectively; Figs. 3, 5), whereas the VV Raman peak of Suprasil at 3690 cm^{-1} is no longer present, the VV peak for the 6.3 wt% glass coinciding with the VH peak at 3665 cm^{-1}. This suggests that all the SiOH groups in the high-water-content sample are involved in hydrogen bonding, probably correlated with a smaller molar volume due to structural collapse in the glass prepared at high pressure (Seifert et al., 1983; McMillan et al., 1984).

Finally, we also observe a new band in the O–H stretching region, at 3598 cm^{-1} (Figs. 4, 5). This band is only present in the Raman spectra and is polarized (Fig. 5), which suggests a highly symmetric mode. At present, we have no intuitive structural interpretation for this peak, but we consider that this peak indicates the presence of some new type of OH group present in hydrous SiO_2 at high water content, which should presumably be taken into account in any thermodynamic or structural modeling of the SiO_2-H_2O system.

SiO_2 FRAMEWORK BANDS

The Raman bands near 430, 800, 1060, and 1200 cm^{-1} are well known as fundamental vibrations of the dry SiO_2 glass framework (Fig. 1). The sharp peaks at 490 and 600 cm^{-1} are commonly known as the "defect bands" and have had various structural interpretations (e.g., Stolen and Walrafen, 1976; Galeener and Lucovsky, 1976b; Galeener, 1982; Sharma et al., 1982; Phillips, 1982). Our results shed no light on the nature of the defect modes, but it is of interest that the 600-cm^{-1} peak has all but disappeared in the spectrum of the high-water-content glass, whereas the 490-cm^{-1} peak remains prominent (Fig. 4). The framework band at 430 cm^{-1} appears narrower and at higher frequency than for the low-water-content sample. This has been correlated with a narrower average Si–O–Si angle in densified silica samples, but noticeable effects did not occur until much higher pressures than for the present hydrous sample (Seifert et al., 1983; McMillan et al., 1984). The form of the bands in the 400–600-cm^{-1} region is reminiscent of silica gels annealed at 200–400°C

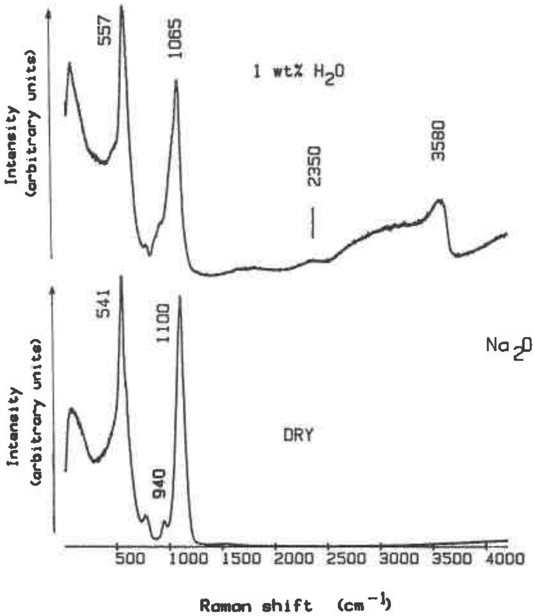

Fig. 6. Unpolarized Raman spectra for a sodium silicate glass $Na_2O \cdot 4SiO_2$ containing 1 wt% H_2O. Also shown for comparison is the spectrum of the dry glass.

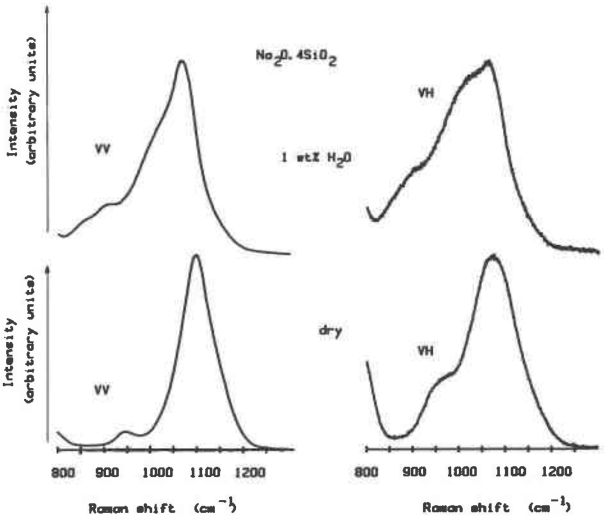

Fig. 7. Comparison of the polarized Raman spectra of the wet (top) and dry (bottom) sodium silicate glasses in the 800–1200-cm^{-1} region. Parallel-polarized spectra (VV) at left and perpendicular-polarized spectra (VH) at right.

(Bertoluzza et al., 1982; Gottardi et al., 1984). These authors noted that the 600-cm^{-1} peak first increased, then decreased in intensity with decreasing water content in these gels, whereas the 490-cm^{-1} peak decreased smoothly. A different result was found by Stolen and Walrafen (1976), who observed a decrease in relative intensity of both the 490- and the 600-cm^{-1} peaks with increasing hydroxyl content of low-water-content silicas. Finally, for SiO_2 samples prepared via chemical vapor deposition (Huffman and McMillan, 1985), the 600-cm^{-1} peak is very intense just after preparation when the water content is high and decreases in relative intensity with decreasing water content. We conclude that an interpretation of these "defect" bands is needed, not only for a description of the structure of SiO_2 glass and melt, but for an understanding of the dissolution and precipitation processes of SiO_2 in aqueous systems.

SODIUM SILICATE GLASS

Raman spectra of the dry and wet sodium silicate glasses $Na_2O \cdot 4SiO_2$ are shown in Figures 6 and 7. The dry glass has two major bands at 541 and 1100 cm^{-1}. The 1100-cm^{-1} band is indicative of $\equiv$SiO units (Q_3 species: SiO_4 units with one nonbridging oxygen), whereas the 541-cm^{-1} band is associated with vibrations of the bridging oxygen in the Si–O–Si linkages (e.g., Brawer and White, 1975; Mysen et al., 1982; Matson et al., 1983; McMillan, 1984). On hydration, the bands in this region change considerably (Fig. 7). The 541-cm^{-1} band increases in frequency to 557 cm^{-1}. This type of change is usually interpreted for dry silicate glasses in terms of a decrease in average Si–O–Si angle often accompanied by a decrease in average polymerization of the silicate unit (Mysen et al., 1982; Matson et al., 1983; McMillan, 1984). The high-frequency maximum decreases to 1065 cm^{-1}, again often generally associated with depolymerization in dry systems. However, the high-frequency band of the present hydrous sodium silicate glass is considerably more complex than that of corresponding dry glasses. There are obvious shoulders near 850, 960, and 1000 cm^{-1}, suggesting at least four components in the high-frequency envelope (Fig. 7). Mysen et al. (1980) deconvoluted four components near 970, 1060, 1100, and 1150 cm^{-1} from the high-frequency contours of similar hydrous sodium silicate glasses. We have not attempted to deconvolute the high-frequency envelope for the present hydrous sample since there are too many possible plausible components for realistic modeling. Dry sodium silicate glasses are known to have several strong Raman bands in this region, whose relative intensities change with glass polymerization (Brawer and White, 1975; Mysen et al., 1982; Matson et al., 1983; McMillan, 1984), whereas both Si–OH stretching and deformation vibrations are known to occur in this range (Hartwig and Rahn, 1977; Ryskin, 1974). Since any band deconvolution scheme is not unique, it is not yet possible to decide on the actual number of component bands in this high-frequency envelope, nor give them structural interpretations in terms of dry and hydrous species.

The O–H stretching region of the hydrous sodium silicate glass is very different to that observed for either low- or high-water-content SiO_2 (Fig. 6). The major band occurs at 3580 cm^{-1}, at much lower wavenumber than the O–H stretching vibrations for the hydrous silica glasses. This is quite different to the infrared spectra of similar hydrous sodium silicate glasses, which show bands near 2.90, 3.70, and 4.27 μm (3450, 2700, and 2350 cm^{-1}: Adams, 1961; Scholze, 1966; Shelby and McVay, 1976). There is an obvious broad shoulder maximized near 2700

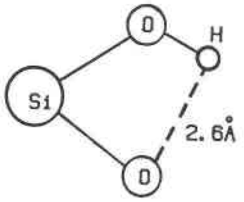

Fig. 8. A possible model for the intratetrahedral hydrogen bond giving rise to the 2350-cm^{-1} band in Figure 6.

cm^{-1} in the Raman spectrum, extending down to around 2500 cm^{-1} (Fig. 6). This probably indicates a higher degree of hydrogen bonding than for the silica glasses, with a minimum OH···O distance near 2.65 Å. Molecular H_2O may be present since an extra weak feature appears near 1630 cm^{-1} in the spectrum of the hydrous glass and may contribute to the broad shoulder in the O–H stretching region. Since we cannot yet interpret the bands near 1000 cm^{-1}, it is not yet possible to enumerate the hydroxyl species present, and it is not even certain that all hydroxyl groups are bound to silicon. Finally, the weak band near 2350 cm^{-1} would correspond well with hydrogen-bonded O–H with a hydrogen bond distance OH···O of 2.6 Å (Nakamoto et al., 1955). This short distance could be interpreted as being due to intratetrahedral hydrogen bonding (Fig. 8), since the O···O distance within the SiO_4 tetrahedron is around 2.7 Å. This would be consistent with the observation that the 2350-cm^{-1} band appears distinct, not as part of the general hydrogen-bonding tail that extends down to about 2500 cm^{-1} (Fig. 6). Scholze (1966) calculated the same hydrogen bond distance from his infrared measurements on hydrous sodium silicate glasses, but did not consider the possibility of *intra*tetrahedral interactions. It is of interest that no similar feature is observed in the spectra for hydrous SiO_2, suggesting that intramolecular hydrogen bonding does not occur in this case. This leads to the suggestion that the intramolecular hydrogen bond in sodium silicate glass is to a nonbridging oxygen, and that perhaps the more extensive hydrogen bonding observed in the sodium silicate glass in general reflects the presence of nonbridging oxygens. It is possible that the energy gained from this hydrogen bonding lends an extra stability to hydrous sodium silicate glasses and helps the understanding of the high-water solubility observed for these systems compared with SiO_2 (Oxtoby and Hamilton, 1978).

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