

A note on the Raman spectra of water-bearing albite glasses

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Abstract—The Raman spectra of albite glasses with 4.5 and 6.6 weight percent water have been obtained, and are compared with that of a dry sample. The hydrous glasses show bands near 3600 cm^{-1} due to O-H stretching, and a previously unreported weak band near 1600 cm^{-1} due to bending of molecular H_2O . Other weak spectral features are discussed, and the effect of dissolved water on the aluminosilicate framework vibrations is considered.

INTRODUCTION

THE IMPORTANCE of water as a magmatic volatile has been discussed by a number of authors (*e.g.*, BURNHAM, 1967, 1979; MYSEN, 1977; HOLLOWAY, 1981), and there have been several attempts to model its solubility behaviour in aluminosilicate melts. Thermodynamic relations in the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ have been the subject of a number of experimental studies (*e.g.*, BURNHAM and JAHNS, 1962; ORLOVA, 1962; BURNHAM and DAVIS, 1971, 1974; KADIK and EGGLE, 1974; OXTOPY and HAMILTON, 1978). Such results led to the melt-water mixing model of BURNHAM (1975), which has been reasonably successful in predicting water solubilities in a variety of melts. However, the model is critically dependent on the choice of hydrous species present in the melt, which BURNHAM (*e.g.*, 1975) assumed to be hydroxyl (OH^-). STOLPER (1982a,b) has recently suggested that realistic models should include both dissolved molecular H_2O and hydroxyl species, on the basis of infra-red measurements.

Vibrational spectroscopy, especially infra-red absorption, has been used by workers in the glass sciences for many years to characterize the hydroxylated species present in hydrous silicate glasses (*e.g.*, ADAMS, 1961; SCHOLZE, 1966). These studies have generally been of glasses prepared near atmospheric pressure with relatively low water contents. A few infra-red and Raman studies of more petrologic interest have been carried out on hydrous aluminosilicate glasses quenched from several kilobars pressure in an attempt to understand the dissolution mechanism of H_2O in corresponding melts (*e.g.*, ORLOVA, 1962; MYSEN *et al.*, 1980a; MYSEN and VIRGO, 1980; STOLPER, 1982a). All of the studies on hydrous silicate glasses have shown a band near $3500\text{--}3600\text{ cm}^{-1}$, or some multiple (overtone) of this. This band is characteristic of O-H stretching (NAKAMOTO, 1970, pp. 79, 88-91), but does not distinguish between hydroxyl or H_2O species (*e.g.*, SCHOLZE, 1960). However, a number of studies (*e.g.*, ORLOVA, 1962; ERNSBERGER, 1977) of glasses with a

wide range in water content have also observed a band near 1600 cm^{-1} , due to the ν_2 bending vibration of the H_2O molecule (NAKAMOTO, 1970, pp. 18, 83), and which is characteristic of molecular H_2O dissolved in the glass. This is supported by recent proton nuclear magnetic resonance studies of hydrous glasses (BARTHOLOMEW and SCHREURS, 1980). ORLOVA (1962) also observed a band near 4500 cm^{-1} in hydrous albite glasses, due to the combination of O-H stretching at 3500 cm^{-1} and Si-O stretching near 1000 cm^{-1} , which she assigned to Si-OH groups in the glass. BURNHAM (1975) used this assignment as support for his dissolution model *via* hydroxyl groups, but ignored ORLOVA's (1962) band at 1600 cm^{-1} indicative of molecular H_2O . STOLPER (1982a,b) has re-examined the near-infrared spectra of water-bearing albite glasses. Apart from the fundamental O-H stretching near 3500 cm^{-1} and its overtone near 7000 cm^{-1} , he observed a band near 5200 cm^{-1} which may be assigned to a combination of H-O-H bending near 1600 cm^{-1} with the O-H fundamental (STOLPER, 1982a). A band near 4500 cm^{-1} was attributed to Si-O-H groups, similar to ORLOVA (1962). These assignments then indicated that both hydroxyl and molecular H_2O groups were dissolved in the glasses, and STOLPER (1982b) used the variation of their relative concentration with total water content to construct an alternative quantitative model for melt-water interactions.

However, MYSEN *et al.* (1980a) measured Raman spectra of albite glasses with 1.2, 2.5 and 4.2 wt% water, quenched from hydrous liquids held at 20 kbars and 1500°C . They found no evidence for a band near 1600 cm^{-1} , and concluded that molecular H_2O was not present in these glasses. (MYSEN *et al.* (1980a) do suggest (p. 905) that a weak band near 1380 cm^{-1} on their Fig. 2 is due to H-O-H bending. The band in fact appears on their Fig. 1, occurs near 1280 cm^{-1} on that figure and is almost certainly not that due to H-O-H bending, although it could be due to Si-O-H bending (RYSKIN, 1974). The present study was undertaken to resolve the apparent conflict between the above infra-red and Raman studies.

EXPERIMENTAL METHODS

The reference dry albite for Raman work was a bubble-free sample prepared from a gel mix by vacuum melting (sample CG-Ab in MCMILLAN *et al.*, 1982) while that for infra-red was obtained from Corning Glass Works. The hydrous samples were also prepared from a gel mix, using analytical grade reagents. The gel was fired at 1000°C for 24 hours, ground under acetone, dried at 125°C for 6 hours, then loaded into Pt capsules (0.2" OD, 0.2" long) with appropriate amounts of doubly-distilled deionized water. The capsules were run for 4 hours at 1200°C and 10 kbars in a piston cylinder apparatus (BOYD and ENGLAND, 1960; PATERA and HOLLOWAY, 1978) using the piston-out technique. The pressure medium was a 0.5" talc-pyrex-graphite assembly with alumina spacers which was predried at 125°C. In order to deter diffusion of H₂ through the capsule walls, the capsules were embedded in powdered pyrex. Temperatures were measured with a Pt-Pt 90 Rh 10 thermocouple separated from the capsule-pyrex powder assembly by an alumina disc, and are believed accurate to within $\pm 5^\circ\text{C}$ for the temperature at the capsule centre. No corrections have been applied to the pressure readings.

Unpolarized Raman spectra were obtained from small chips (~1–2 mm across) using the 4880 Å line of a Spectra-Physics 171 argon laser, a Spex 1402 double monochromator, and an RCA photomultiplier with photon-counting electronics.

Quantitative infrared transmission spectra were obtained for doubly-polished thin sections of the hydrous samples with Cary 17 and Perkin-Elmer 180 spectrophotometers, following the technique used by STOLPER (1982a). Some powder KBr disc spectra were also run on the Perkin-Elmer instrument. From the molar absorptivities given by STOLPER (1982a) for the bands near 5200 and 4500 cm⁻¹, the amounts of water dissolved as molecular H₂O and hydroxyl species were calculated. These were summed to give total water contents of 4.5 and 6.6 wt% for the hydrous albite samples.

EXPERIMENTAL RESULTS

The Raman spectra of the dry and hydrous albite glass samples are shown in Figs. 1 and 2. A weak feature is present at 1635 cm⁻¹ in both the 4.5 and 6.6 wt% samples, which is more clearly observed in the spectra of Fig. 2, run at higher gain. Overtone and combination bands from aluminosilicate network vibrations might be expected to appear in this region (WALRAFEN and STONE, 1975; GALEENER and LUCOVSKY, 1976), however the reference dry albite sample shows no analogous band (see inset to Fig. 1). The frequency of this band agrees well with that of the ν_2 vibration of molecular H₂O (NAKAMOTO, 1970). Further, the 4000–1500 cm⁻¹ region of the infra-red spectrum of the 4.5 wt% glass (Fig. 3a), shows a sharp peak near 1630 cm⁻¹ along with the O-H stretching fundamental near 3500 cm⁻¹. We suggest that the band appearing near 1630 cm⁻¹ in the Raman and infra-red spectra of these hydrous albite glasses is due to the fundamental bending vibration of H₂O, and is indicative of molecular H₂O dissolved in the glasses. This band is extremely weak in the Raman spectrum of even the 6.6 wt% glass, suggesting why the band may have been overlooked by MYSEN *et al.* (1980a).

Figure 3b shows the near infra-red spectra of the

4.5 and 6.6 wt% samples, which show the bands near 5200 and 4500 cm⁻¹ respectively assigned by previous workers to combination vibrations of molecular H₂O and SiOH (and/or AlOH) groups (see STOLPER, 1982a). Following STOLPER (1982a), their intensities were used to calculate the amounts of water dissolved as hydroxyl and molecular H₂O in the glasses. Figure 4 shows the H₂O/OH ratios for the present albite glasses *versus* total water content, compared with values obtained by STOLPER (1982a, Fig. 12) for other hydrous albite, rhyolitic and basaltic glasses.

It may be argued that the molecular H₂O observed in these glasses is present as fluid inclusions, perhaps exsolved from the melt during quenching. This question has been addressed in some detail by STOLPER (1982a,b), who presents a reasonable case for molecular H₂O as a dissolving species in the melt. No bubbles were observed optically ($\times 1000$) or by scanning electron microscopy ($\times 50000$) in the present samples. Further, STOLPER *et al.* (1983) have shown that molecular H₂O persists in hydrous glasses to at least 500°C at atmospheric pressure. However, it remains possible that other hydroxylated species are present in hydrous aluminosilicate melts at high pressure and temperature, which may react to give molecular water or hydroxyl during even the fastest quench currently attainable.

Two weak peaks are observed in the Raman spectra of the hydrous albite glasses at 2327 and 1554 cm⁻¹ (Figs. 1 and 2). These correspond to the stretching vibrations of molecular N₂ and O₂ (NAKAMOTO, 1970, p. 78; MYSEN *et al.*, 1980a). These may have been incorporated as air in the gel mix during capsule loading or could be due to nitrate compounds incompletely removed during firing, and may be physically dissolved in the glasses. A peak near 2175 cm⁻¹ was assigned by MYSEN *et al.* (1980a) to N₂⁺ species. The peak observed here at 2177 cm⁻¹ (Figs. 1 and 2) is quite intense for the spectra of the dry and 4.5 wt% H₂O samples, collected when the fluorescent lights in the room adjoining the Raman laboratory were on. This peak is practically absent from the spectrum of the 6.6 wt% sample when these lights were switched off. The frequency 2177 cm⁻¹ relative to the 4880 Å laser line corresponds to 5461 Å, which agrees well with an intense emission line of Hg vapour (CRC Handbook of Chemistry and Physics, 60th edition 1980, p. E-277; 5460.74 Å). It is likely that the observed 2177 cm⁻¹ peak is due to emission from mercury vapour in the laboratory fluorescent lights. A weak peak remains in the spectrum of the 6.6 wt% sample (Fig. 2), which may arise from the corridor lighting adjacent to the laboratory. A final weak peak is observed in this region at 1378 cm⁻¹ for the 4.5 wt% sample, which is not present for the dry or 6.6 wt% samples (Figs. 1 and 2). No such band is observed in the powder infrared spectrum of the 4.5 wt% sample (Fig. 3c). Its frequency could correspond to the deformation vibration of strongly hydrogen-bonded silanol groups (RYSKIN, 1974), but such a

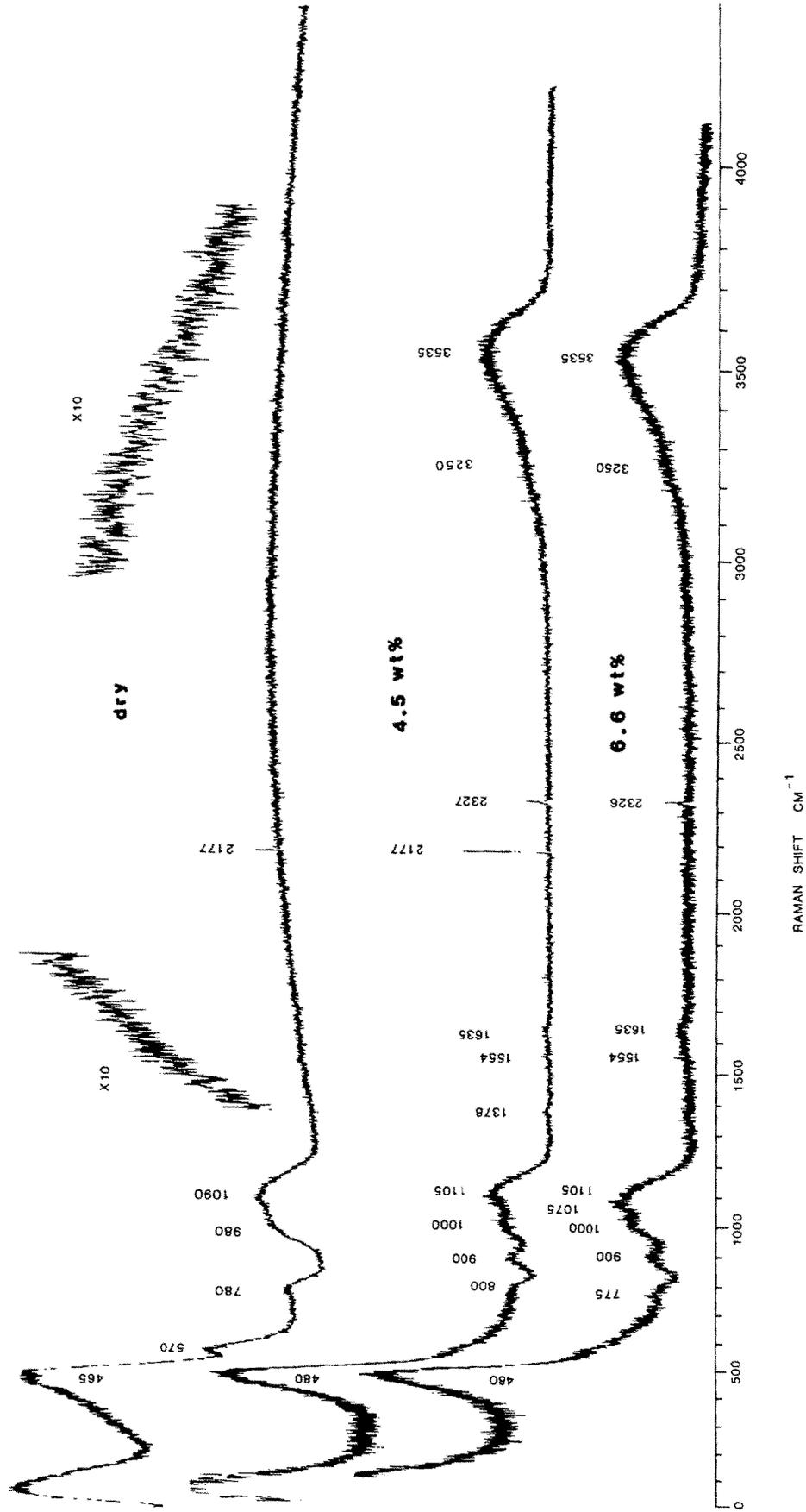


FIG. 1. Unpolarized Raman spectra of dry, (1 atm) albite glass (CG-Ab) and 4.5 wt% and 6.6 wt% water-bearing (10 kbar) albite glasses. The two insets above the dry glass spectrum show the regions near 1600 cm^{-1} and 3500 cm^{-1} amplified $\times 10$. Slit width $150 \mu \approx 4 \text{ cm}^{-1}$.

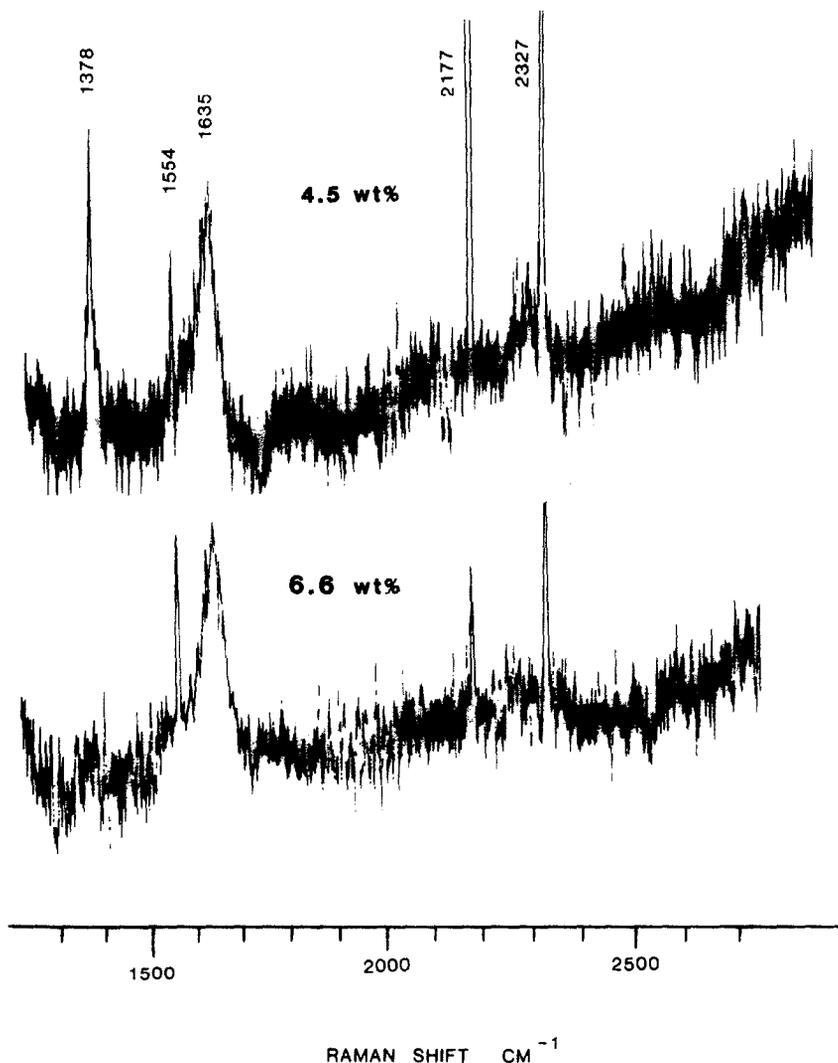


FIG. 2. The 1400–2400 cm^{-1} region of the Raman spectra of 4.5 wt% and 6.6 wt% water-bearing albite glasses, run at higher gain ($\approx \times 10$).

band would likely be broader, occur also for the 6.6 wt% sample, and appear in the infra-red spectrum. The 1378 cm^{-1} peak observed here could also correspond to a vibration of a small molecular species accidentally incorporated in the glass. MYSEN *et al.* (1980a) observed weak peaks near 1280 cm^{-1} (or 1380 cm^{-1} ?; see above) for both H_2O - and D_2O -bearing albite glasses which are likewise difficult to interpret.

A band occurs near 900 cm^{-1} in the Raman spectra of H_2O -bearing albite glass (Fig. 1). A similar band was observed at 870–883 cm^{-1} by MYSEN *et al.* (1980a), which increased in intensity with increasing water content. The same band appeared at 886 cm^{-1} for a D_2O -bearing albite glass (MYSEN *et al.*, 1980a). Based on the apparent absence of an isotope shift for this band, (but see FREUND, 1982; MYSEN and VIRGO, 1982), these authors concluded that the band did not involve Si-OH or Al-OH groups, and assigned it to a vibration of the aluminosilicate network. They

attributed the Si-OH stretching vibration to a component near 980 cm^{-1} deconvoluted from their high-frequency band group.

A weak Raman band has been observed at 970 cm^{-1} in vitreous SiO_2 containing trace quantities of water, which was assigned to an Si-OH stretching vibration (*e.g.*, STOLEN and WALRAFEN, 1976). VAN DER STEEN and VAN DEN BOOM (1977) diffused H_2 and D_2 into vitreous silica and observed the appearance of bands at 2254 (1629) and 3685 (2720) cm^{-1} , respectively assigned to Si-H (Si-D) and Si-O-H (Si-O-D) stretching vibrations. The same experiment was carried out by HARTWIG and RAHN (1977), who observed a band at 969 (941) cm^{-1} which they assigned to Si-OH (Si-OD) stretching, giving an isotope effect $\nu_{\text{SiOH}}/\nu_{\text{SiOD}} = 1.030$. It is of interest that the reduced mass ratio of the silanol group with motion of both Si and OH (OD) relative to their centre of mass is $\mu_{\text{SiOD}}/\mu_{\text{SiOH}} = 1.018$ (FREUND, 1982), while the assumption of motion of OH(OD) against a silicate

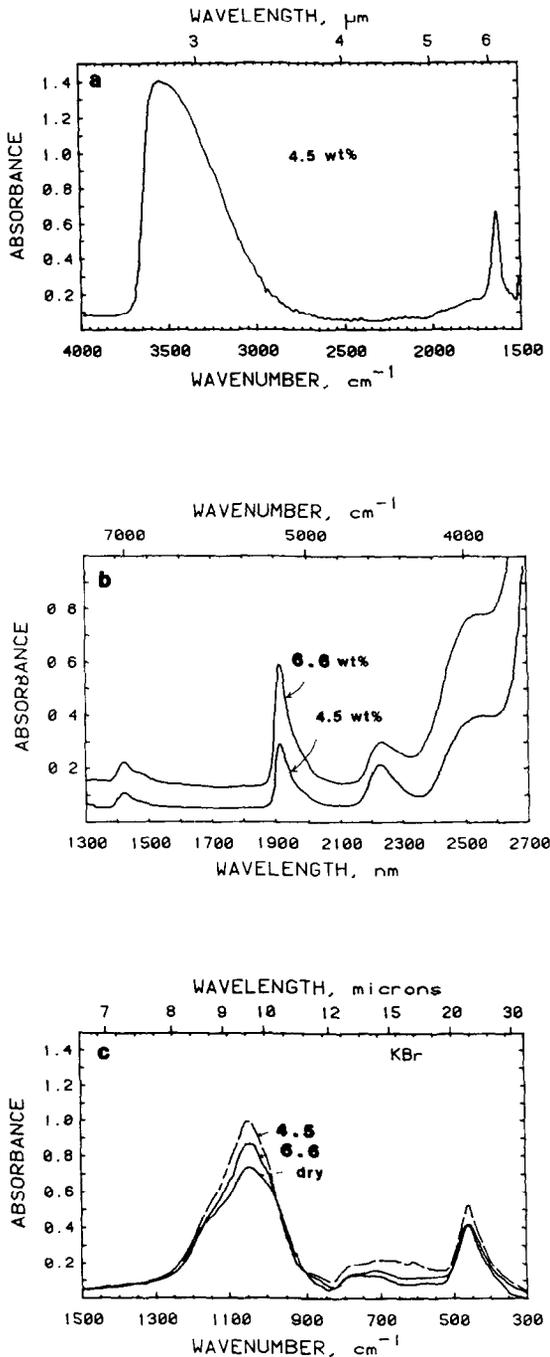


FIG. 3. (a) Infrared absorption spectrum from 4000–1500 cm^{-1} of a doubly-polished thin section of 4.5 wt% albite glass. A background spectrum due to epoxy used for mounting sample has been subtracted.

(b) Infrared absorption spectra in 7700–3700 cm^{-1} region of thin sections of 4.5 and 6.6 wt% albite glasses.

(c) Powder infrared absorption spectra in 1500–300 cm^{-1} region of dry (Corning), 4.5 wt% and 6.6 wt% albite samples run in KBr discs. Spectra are scaled to 0.5 mg glass in disc.

network of infinite mass gives $\sqrt{m_{\text{OD}}/m_{\text{OH}}} = 1.029$, close to the experimental value. This may suggest that the 969 cm^{-1} band in fused silica containing silanol groups corresponds to movement of a hy-

droxyl group against stationary silicon held in a semi-rigid framework. This would be consistent with the isotope shift of near 1.35 ($\nu_{\text{SiOH}}/\nu_{\text{SiOD}}$) observed by VAN DER STEEN and VAN DEN BOOM (1977) for the O-H (O-D) stretching vibration, near the value of 1.37 expected for free hydroxyl.

MYSEN *et al.* (1980a) also observed a band near 860–870 cm^{-1} appearing for hydrous $\text{NaAlSi}_2\text{O}_6$ glasses, and perhaps a weak shoulder near 900 cm^{-1} for $\text{Na}_2\text{Si}_3\text{O}_7$ glass with high water contents. MYSEN and VIRGO (1980) also observed a shoulder appearing near 850–870 cm^{-1} for hydrous $\text{NaCaAlSi}_2\text{O}_7$ glass. We suggest that the Raman band in the 850–900 cm^{-1} region which appears on addition of H_2O to these various silicate and aluminosilicate glasses may be an Si-OH and/or Al-OH stretching vibration, possibly analogous to that observed in hydroxylated vitreous silica. It is likely that Al-OH stretching vibrations also occur in the region 700–900 cm^{-1} (*e.g.*, KOLESOVA and RYSKIN, 1959; RYSKIN, 1974). Such vibrations could contribute to the band near 900 cm^{-1} in the present glasses. However changes are also observed in the profile of the unresolved band group near 800 cm^{-1} with increasing water content (Fig. 1), which could be due to bands associated with Al-OH vibrations. Deformation vibrations of Al-O-H and Si-O-H groups are commonly found near 1000–1100 cm^{-1} (KOLESOVA and RYSKIN, 1959; RYSKIN, 1974), which overlaps with the stretching vibrations of the aluminosilicate network (MYSEN *et al.*, 1980a,b; McMILLAN *et al.*, 1982). Some modifications are

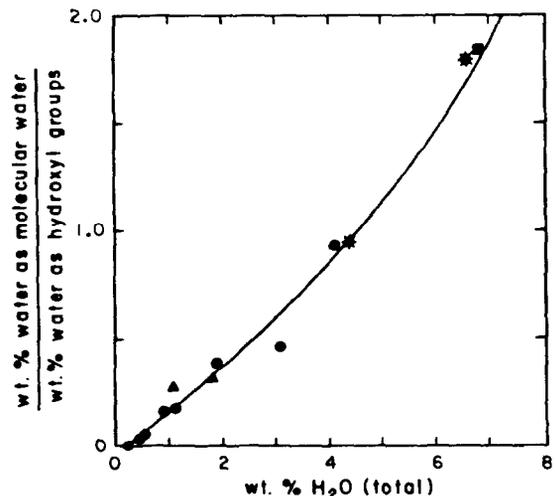


FIG. 4. Ratio of wt% water as molecular H_2O to wt% water as hydroxyl *versus* total water content calculated from intensities of infrared bands in Fig. 3 and molar absorptivities of STOLPER (1982a): ϵ (5200 cm^{-1}) = 1.78; ϵ (4500 cm^{-1}) = 0.98. The 4.5 wt% sample had density = 2.371 g cm^{-3} , thickness = 0.047 cm and absorbances of 0.241 (5200 cm^{-1}) and 0.136 (4500 cm^{-1}). The 6.6 wt% sample had density \sim 2.300 g cm^{-3} , thickness = 0.0142 cm and absorbances of 0.137 (5200 cm^{-1}) and 0.42 (4500 cm^{-1}). *, Albite glasses: this study. Other symbols are from Fig. 12 of STOLPER (1982a). ●, rhyolitic glasses; ▲, basaltic glasses; ■, albite glass

observed in the unresolved 1000–1100 cm^{-1} band group of hydrous albite samples, with the possible appearance of a band near 1075 cm^{-1} (Fig. 1). These could be related to the presence of bands associated with Al-O-H and/or Si-O-H deformation in the hydrous glasses. It is of interest that MYSEN *et al.* (1980a) observed a shoulder appearing near 1060–1080 cm^{-1} for hydrous $\text{Na}_2\text{Si}_2\text{O}_7$ glasses, which could correspond to Si-O-H deformations. The powder infra-red spectra of the present hydrous albite samples (Fig. 3c) do show some changes in this region, but are not easily described or interpreted. However, the presence of the combination band near 4500 cm^{-1} (Fig. 3b) reflects the presence of Si-O-H and/or Al-O-H deformation and/or stretching modes near 1000 (± 100) cm^{-1} , coupling with the O-H stretch. We conclude that detailed interpretation of bands in this region must await more systematic studies of hydrous silicate glasses.

Finally, dry albite glass has a major Raman band near 465 cm^{-1} with a pronounced shoulder at lower frequency, and a weak band resolved at 570 cm^{-1} (Fig. 1). MCMILLAN *et al.* (1982) have assigned the 570 cm^{-1} band to a vibration associated with Al-O-Al linkages within the glass, and the low-frequency shoulder to modes predominantly characteristic of Si-O-Si linkages. These assignments are retained here, although other interpretations have been proposed (*e.g.*, MYSEN *et al.*, 1980a,b; 1982). Both the 570 cm^{-1} band and the low-frequency shoulder are markedly reduced in relative intensity on addition of water to the glass (Fig. 1; MYSEN *et al.*, 1980a). The major band maximum apparently increases to 480 cm^{-1} , but this is probably in part due to removal of the lower frequency component from its shoulder. This may suggest that Al-O-Al and Si-O-Si linkages are suppressed relative to Al-O-Si (responsible for the 480 cm^{-1} band) by preferential reaction with H_2O in the hydrous glasses. It is known that the 400–500 cm^{-1} Raman bands of dry albite glass do show similar changes with increasing pressure due to intertetrahedral angle changes (*e.g.*, MYSEN *et al.*, 1980b; MCMILLAN and GRAHAM, 1981). However, effects analogous to the present 10 kbar hydrous glasses are not observed at pressures below 20 kbar in dry albite glass.

SUMMARY

We conclude that the Raman spectroscopic experiments on hydrous albite glasses are in accord with the infra-red measurements (and with nuclear magnetic resonance spectra for other hydrous glasses), and that molecular H_2O is present in these glasses. Previous Raman studies may have overlooked its characteristic band near 1630 cm^{-1} due to its low intensity. Due to this low Raman cross section, and the weakness or absence of higher order Raman transitions (*e.g.*, STONE and WALRAFEN, 1982), Raman spectroscopy is probably a less useful tool for quan-

titative studies of water speciation in silicate glasses than is infra-red spectroscopy. In contrast, Raman studies have been much more powerful than infra-red spectroscopy in structural studies of the aluminosilicate glass network, with vibrations below 1200 cm^{-1} , and are sensitive to changes introduced by dissolution of water. It remains only to re-state one of the principles of vibrational spectroscopy, that infra-red and Raman experiments are necessary and complementary ingredients in a given vibrational study.

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