

Vibrational spectra and dissociation of aqueous Na_2SiO_3 solutions

Istvan Halasz,* Mukesh Agarwal, Runbo Li, and Neil Miller

R&D Center, PQ Corporation, 280 Cedar Grove Road, Conshohocken, PA 19428, USA

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To facilitate molecular spectroscopic observation of the mysterious transition of dissolved sodium silicate molecules into nanoparticles of desired silica gel and zeolite structures, the IR and Raman spectra of $\text{Na}_2\text{H}_2\text{SiO}_4$ monomers are studied here in details. It is demonstrated that the 3–0.2 mol/L aqueous solutions of Na_2SiO_3 and $\text{Na}_2\text{SiO}_3 \times 9\text{H}_2\text{O}$ contain mostly $\text{Na}_2\text{H}_2\text{SiO}_4$ monomers dissociated about 30%–80%, respectively. In contrast to the common belief the Si–O vibrations of these monomers depend on their dissociation level generating FTIR and Raman bands which are frequently associated with polymer silica structures in the current literature. To stay consistent with the molweight and dissociation measurements, these vibrational assignments are revised in this paper. Some unique and unexpected effects of D_2O used instead of H_2O as solvent are also reported.

KEY WORDS: Raman spectroscopy; FTIR spectra; silicate; sodium silicates; soluble silicates; conductivity.

1. Introduction

Aqueous sodium silicate solutions are frequent ingredients for the synthesis of zeolites and silica gel based catalysts. Despite many decades of commercial production experience and research, there is still much empirical knack in these syntheses since the transition of dissolved silicate molecules into desired solids is poorly understood. Research efforts for better understanding have intensified recently [1–11], but especially the initial assembly of molecules into nanoparticles is still quite an obscure process.

Raman and FTIR spectroscopy are widely used for distinguishing various siloxane bonds in both aqueous and solid phase hence in principle these techniques could be well-suited for in situ investigation of the silica-solidification processes. However, such studies are surprisingly rare in the literature, which is partly due to the far less developed molecular spectroscopic identification of dissolved silicate structures than that of solid silicates. There are several Raman [12–23] and IR [17,21–28] publications which focus specifically on aqueous silicate solutions and one can also find such spectra in some zeolite synthesis related papers [28–41]. However, only a small group from these authors has assigned certain vibrational bands to specific molecular structures like monomers or siloxane chains, rings, etc. [16–20,26,35,38,41] and even these contain much inconsistency [42–46]. One impediment to more reliable structural interpretations is the lack of relevant model

compounds. A particularly important issue is separation of the vibrational bands of monomer silicate ions from those of larger molecules since most theories assume that the formation of crystalline and amorphous silicates starts with the assembly of dissolved monomers into precursor nanostructures [2,47–49].

We report here that 0.2–3 mol/L aqueous solutions of crystalline sodium metasilicate, Na_2SiO_3 , contain almost exclusively monosilicate ions at $\text{pH} > 10$ unlike most other aqueous sodium silicate solutions typically manufactured from amorphous glasses [43]. Thus, these metasilicate solutions are excellent models for studying the IR and Raman spectra of sodium silicate monomers. It will be shown that in contrast to prior assumptions these vibrational spectra depend on the level of sodium ion dissociation, which alternates from about 30% to 80% in this practically important range of silicate concentrations.

2. Experimental

Anhydrous Na_2SiO_3 from PQ Corporation (Metso Beads® 2048) and $\text{Na}_2\text{SiO}_3 \times 9\text{H}_2\text{O}$ from Sigma (>98% purity) were dissolved in deionized water or in 99.9% D_2O from Aldrich. Powder XRD measurements indicated that both crystalline silicates had pure orthorhombic phases [50,51]. Every experiment was carried out at ambient conditions at temperatures alternating between 22 and 23 °C with solutions equilibrated for at least 24 h after making any alteration including further dilutions with water or addition of NaOH. Numerous measurements were also repeated after several weeks of storage in closed (but not sealed) containers. Repeated

*To whom correspondence should be addressed.
E-mail: Istvan.Halasz@pqcorp.com

results deviated with less than $< \pm 5\%$ from each other unless stated differently.

Vapor pressures were measured with a Wescor Type 5500 osmometer calibrated with both NaCl and NaOH standards. Electrical conductivity measurements were carried out in a YSI Model 32 conductometer calibrated with a $1,000 \text{ mS} \times \text{cm}^{-1}$ standard. A Thermo Orion Model 720Aplus pH/Ion Selective Meter equipped with matching ROSS electrodes was used for measuring the pH and Na⁺ concentrations. A Model 86–11 sodium selective electrode was filled with 2 M potassium acetate and calibrated with home made NaOH solutions based on their pH values. The conductivity of Na₂SiO₃ solutions was consistent with data reported by Kohlraush [52] more than a century ago. Applying the Kohlrausch law or Debye–Hückel–Onsager equation [53], $\Lambda_0 = \Lambda_N + A (N^{1/2})$, where Λ_0 is the equivalent conductivity at infinite dilution, Λ_N is the equivalent conductivity at N concentration, A is a constant for a given solute–solvent system, and N is the normality of solutions, we obtained $\Lambda_0 = 163 \text{ mS} \times \text{cm}^{-1} \times \text{mole}^{-1}$ which fits well to that reported by Harman [54,55]. These data were used to calculate the α dissociation level using Ostwald’s dilution function [56]

$$K_d = \frac{\Lambda_N^2 \cdot a}{\Lambda_0(\Lambda_0 - \Lambda_N)} = \frac{\alpha^2 \cdot a}{1 - \alpha}$$

FTIR spectra were obtained on a Nicolet Magna 550 spectrometer using a single bounce diamond attenuated total reflectance (ATR) accessory from ASI. A Kaiser HoloProbe Raman spectrometer (200 mW frequency doubled Nd:YAG; -40°C CCD detector) was used to measure the Raman scattering without polarization. Further details of our spectroscopic equipment and methods have been published elsewhere [57–59].

3. Results and discussion

3.1. Molweight, conductivity, dissociation

We used the osmolality method as reported by Bass *et al.* [27] to determine the average molecular weight (AMW) of silicates in variously diluted solutions. Since this measurement actually gives the number of total ions per unit solution, it is imperative to know how many free Na⁺ ions entered the solution from the silicate, i.e., the degree of dissociation, to calculate AMW. Therefore, we determined the Na⁺ concentrations in every solution both with using a Na⁺ selective electrode and, since the interaction of silicate with the glass electrode made this method unreliable even after appropriate modification of the salt filling [60], also by electrical conductivity or EC measurements. These two differently measured dissociations were found to correlate well but their numerical values are somewhat different from each

other. We could not decide which α is more correct hence use their mathematical average to represent the correct dissociation level of Na₂SiO₃.

The calculation of AMW along with some characteristics of the sodium silicate solutions can be followed in table 1. Monomers have been identified in such solutions by various authors before [12,24,61], but many studies have suggested dimer or polymer silicon units to be present [24,61–64]. Since silicon is always tetrahedrally bonded to the oxygen [24,65], stoichiometry and charge balance dictates that the composition of silicate ions in the solution of Na₂SiO₃ must be Na₂H₂SiO₄ when it is not dissociated and H₂(SiO₄)²⁻ ions must exist in fully dissociated solutions ($< 0.2 \text{ M}$). Based on data in table 1, other structures like Na₂SiO₃, Na₄H₂(Si₂O₇), H₃(SiO₄)⁻, H(SiO₄)³⁻, etc. that have all been assigned to the vibrational spectra of Na₂SiO₃ [17,18,24] can be neglected especially at our major pH, concentration, and temperature ranges. Note that the bulk of the above-described experiments was done by dissolving Na₂SiO₃ \times 9H₂O in water. Several control experiments with anhydrous Na₂SiO₃ showed identical results within experimental error.

3.2. FTIR spectra

Figure 1 compares the FTIR spectra of solid crystalline Na₂SiO₃ \times 9H₂O and Na₂SiO₃ in the Si–O vibrational range. It is known from X-ray structure analysis [51] that the anhydrous sodium metasilicate is built up from chains of $[-\text{O}-(\text{SiO}_2)^{2-}-\text{O}]_n$ tetrahedra, each sharing two oxygen atoms with their neighbors (Q₂ type siloxane bonds according to the widely accepted NMR nomenclature [66]). Sodium ions compensate the negative charges along the chains. The Na₂SiO₃ \times 9H₂O crystals on the other hand contain Na⁺ ions surrounded by edge-shared, distorted octahedra of H₂O molecules. Some vacant coordination positions of these octahedra are occupied by isolated Q₀ type HO–(SiO₂)²⁻–OH tetrahedral that compensate the positive charges of sodium ions [50].

The Na₂SiO₃ spectrum in figure 1 is quite similar to that reported by Gaskell [67], but we found only one, extremely low resolution IR spectrum for the hydrated metasilicate in the literature [17]. In table 2, we assign the observed IR vibrations of these two crystalline metasilicates to various Si–O vibrations based on their molecular geometry and published calculations for sodium silicate glasses [79–81] and gels [14,68,69,82–84]. Pertinent data of certain crystalline silicates like quartz [14,70,71,85,94,95] and siliceous zeolites [72,73,96] are also referred in the table. A vast number of silica related spectroscopic study demonstrates that the stretching Si–O vibrations (ν) appear at higher wavenumbers than the less energetic deformation vibrations (δ) and asymmetric vibrations (ν_{as} , δ_{as}) have usually also higher energies than their symmetric pairs (ν_{s} , δ_{s}). The frequencies (wave

Table 1
Concentration, dissociation, ion size and other parameters of aqueous Na₂SiO₃ solutions

Concentration (mol SiO ₂ /L)	pH	K_{ac}^a	Total Na ⁺ (mol/L)	Dissociation ^b α	Free Na ⁺ (mol/L)	Na ⁺ in silicate ^c (mol/L)	Total ions ^d (mol/L)	Silicate ions ^e (mol/L)	[SiO ₄] ⁴⁻ /Silicate ion ^f	AMW ^g (g/mole)
3.0	13.6	1.87E-13	6.0	0.32	1.89	4.10	4.91	3.02	0.99	125
2.0	13.5	1.92E-13	4.0	0.37	1.48	2.52	3.52	2.04	0.98	121
1.0	13.3	2.01E-13	2.0	0.47	0.95	1.05	1.90	0.95	1.05	123
0.5	13.2	2.11E-13	1.0	0.60	0.60	0.40	1.07	0.47	1.08	119
0.2	13.0	2.24E-13	0.4	0.82	0.33	0.07	0.52	0.19	1.04	106

^aDissociation constant of silicic acid calculated according to the $a^+ = [(K_{ac} \times K_w)/c]^{1/2}$ formula for dissociation of salts formed from weak acid and strong base [106]; a^+ is the activity of protons (from pH), K_w is the ionization constant of water, and c is the concentration of silicate solution.

^bAveraged from electrical conductivity and ion selective electrode measurements as described in the text.

^cNon-dissociated Na⁺ ions remaining in the silicate ions.

^dNumber of ions in the solution from osmolality measurements.

^eNumber of silicate ions in the solution = Total ion - Free Na⁺.

^f[SiO₄]⁴⁻ tetrahedra per silicate ion without referring to the ionicity of chemical bonds; it follows from the stoichiometry that the negative charge of such tetrahedra must be balanced by 2 H⁺ and 2 Na⁺ ions.

^gAverage molecular weight of the dissociated silicate ions.

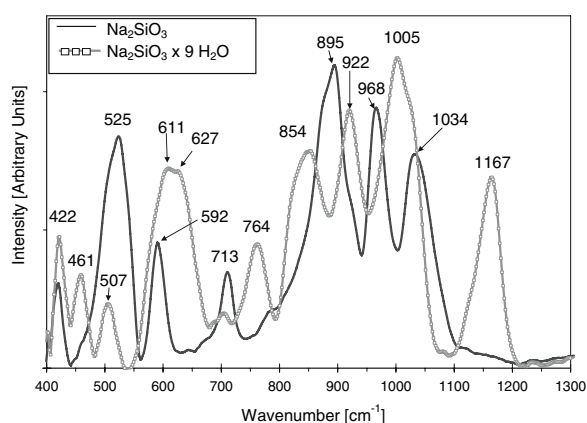


Figure 1. FTIR ATR spectra of crystalline Na₂SiO₃ and Na₂SiO₃ × 9H₂O.

numbers) of oxygen motions are also higher when nothing (Si-O⁻) or only a proton (Si-OH) is attached to the oxygen than the frequencies of oxygens connected to Na⁺ ions (Si-ONa) or that of the bridging oxygens that connect [SiO₄] tetrahedra with each other.

The distinct 1165 cm⁻¹ band of the Q₀ type Na₂SiO₃ × 9H₂O silicate (figure 1) is rather surprising. Many researchers associate this band position with ν_{as} Si-O-Si bridging vibrations in Q₃ or Q₄ type silicates [18,25,36,71]. In contrast, a band near this position has been observed in various zeolites and assigned to “intra-tetrahedral” or “localized” ν_{as} Si-O vibration as opposed to “inter-tetrahedral” (bridging) or “delocalized” Si-O vibration [68,72,73,96,97]. A longitudinal-optic-transverse-optic (LO-TO) frequency splitting of the vibrational modes of Si-O with one component appearing near 1200 cm⁻¹ can also be considered [72,74,98], but one would rather expect this in the spectrum of the Q₂ type dehydrated metasilicate in which such band does not show up (figure 1).

The 1165 cm⁻¹ vibration never appears in the FTIR spectra of the aqueous solutions of Q₀ type silicates (figures 2–4) regardless of Na₂SiO₃ or Na₂SiO₃ × 9H₂O origin. The characteristic changes in figure 2 must be related to changes in the dissociation of dissolved Na₂H₂SiO₄ since there is no other significant molecular difference between the solutions. Specifically the shift of the 989 cm⁻¹ band to 1022 cm⁻¹, the disappearance of 931 cm⁻¹ and the appearance of 883 cm⁻¹ bands, as well as the increase of the 420 cm⁻¹ band should reflect changes in the dissociation level.

Based on these observations and considerations described in connection with the solid silicates, we assigned the major IR bands of dissolved metasilicates as shown in table 3. The $\nu_1 \rightarrow \nu_2$ shift of Si-O(H) vibration near 1000 cm⁻¹ caused by the dissociation of Na₂H₂SiO₄ can be estimated using the $\nu_1/\nu_2 = (\mu_2/\mu_1)^{1/2}$ formula [99] in which μ_1 and μ_2 are the reduced masses of the OH group and the rest of the molecule, respectively. Assuming that 1020 cm⁻¹ corresponds to the totally dissociated H₂SiO₄²⁻, the calculated values for NaH₂SiO₄⁻ and Na₂H₂SiO₄ are shown in table 3. Considering the dissociation results from table 1, these data match nicely the measured values in figure 2. There is no measurable difference if Si-O⁻ group is considered instead of the Si-O(H).

We attempted to fabricate Na₄SiO₄ orthosilicates by adding two mole NaOH to each mole Na₂SiO₃ in the variously diluted sodium metasilicate solutions. This attempt resulted in precipitation of solid silicate within a few hours from the 3 mol/L solution made from dehydrated Na₂SiO₃ and within about 1–2 days from the 3 mol/L solutions made from Na₂SiO₃ × 9H₂O. We believe that this effect is due to the over-saturation of solvent with solutes (salting out effect), which occurs slower in the latter solutions with more H₂O delivered with the crystals. One can reason that about 10–12H₂O

Table 2
Assignments of IR and Raman vibrations of solid, crystalline sodium metasilicates

Frequencies (cm ⁻¹)		Assignments	References
IR	Raman		
Na ₂ SiO ₃ × 9H ₂ O (Q ₀)			
1167	1150	<i>v</i> _{as} Si–O(H)	[18,36,68–78]
1005	–	<i>v</i> _{as} Si–O(Na)	–
922	927	<i>v</i> _s (Na)O–Si–O(H)	[14,36,68–70,72,73,75,79–88]
854	–	<i>v</i> _s (Na)O–Si–O(Na)	[69]
764	771	<i>δ</i> _{as} (H)O–Si–O(H)	[67,69,72,86,88–90]
–	706	<i>δ</i> _{as} (H)O–Si–O(Na)	[86,88]
627	–	<i>δ</i> _{as} (H)O–Si–O(Na)	[68,72]
611	–	<i>δ</i> _{as} (H)O–Si–O(Na)	[69]
595	–	<i>δ</i> _{as} (Na)O–Si–O(Na)	–
507	–	<i>δ</i> _s (H)O–Si–O(H)	[68,72]
461	455	<i>δ</i> _s (H)O–Si–O(Na)	[14,67–69,72,74,83,89]
422	421	<i>δ</i> _s (Na)O–Si–O(Na)	[67–69];
–	350	<i>δ</i> _s (H)O–Si–O(Na)	[86]
–	268	<i>δ</i> _s (H)O–Si–O(Na)	[67,69,72,86,88,89,91,92]
–	185	<i>δ</i> _s (H)O–Si–O(Na)	[86]
–	143	<i>δ</i> _s Si–O–Na	[88,91,92]
Na ₂ SiO ₃ (Q ₂)			
1034	–	<i>v</i> _{as} Si–O(Na)	–
968	972	<i>v</i> _{as} Si–O(Si)	[14,68,69,75–78,80,86–89,91,92]
897	–	<i>v</i> _s Si–O(Na)	[67]
–	756	<i>δ</i> _{as} (H)O–Si–O(H)	[86]
713	712	<i>v</i> _s Si–O(Si)	[71,86]
592	588	<i>δ</i> _{as} as (Na)O–Si–O(Na)	[14,20,31,69,72,76,77,79,86,88,91–93]
525	–	<i>δ</i> _{as} (Si)O–Si–O(Si)	[68]
420	412	<i>δ</i> _s (Na)O–Si–O(Na)	[67–69,86,88,89,92]
–	152	<i>δ</i> _s Si–O–Na	[88,89,91]

Attached to the oxygen atoms the next connecting atoms are shown in parentheses. In Na₂SiO₃ × 9H₂O a hydrate sphere restricts the mobility of Na⁺ ions [50]. Qi denotes the connectedness of [SiO₄] tetrahedral [66]. The last column gives relevant references for models and calculations for the given vibration position. *v* refers to stretching and *δ* to deformation (bending, twisting, and rocking) vibrations and the indexes “s” and “as” refer to symmetric and asymmetric motions, respectively.

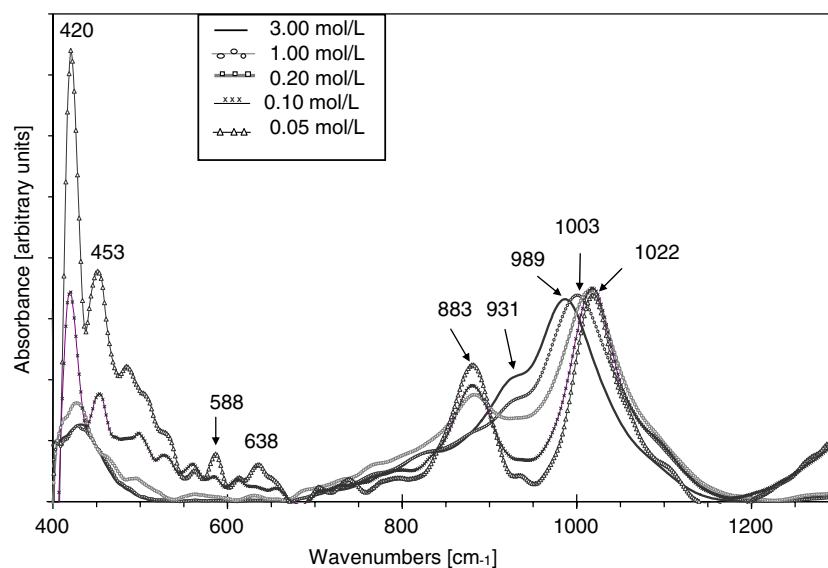


Figure 2. FTIR ATR spectra of aqueous solutions of Na₂SiO₃ normalized to bands near 1000 cm⁻¹. Spectra vary with level of dissociation.

molecules form a hydrate sphere around each Na₂H₂SiO₄ molecule and roughly two spheres are needed to keep the silicate in solution. The amount of water

(~55 moles/L) is “just enough” to do this job in a 3 mol/L solution of Na₂SiO₃ and the extra water from Na₂SiO₃ × 9H₂O helps a lot. Water supply becomes a

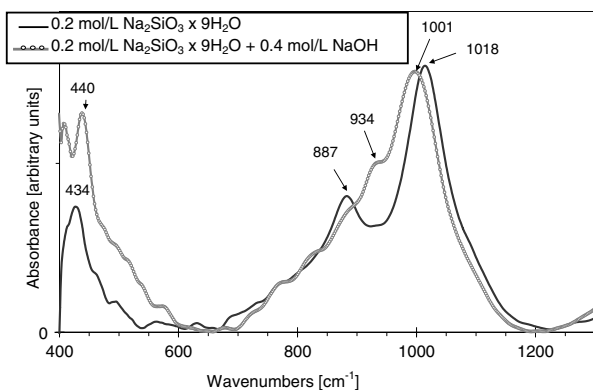


Figure 3. Added NaOH retards the dissociation of $\text{Na}_2\text{H}_2\text{SiO}_4$ monomers thus $\nu_{\text{as}} \sim 1018 \text{ cm}^{-1}$ of $\text{H}_2\text{SiO}_4^{2-}$ shifts to lower wave numbers and $\nu_{\text{as}} \sim 934 \text{ cm}^{-1}$ reappears (see text and Table 3).

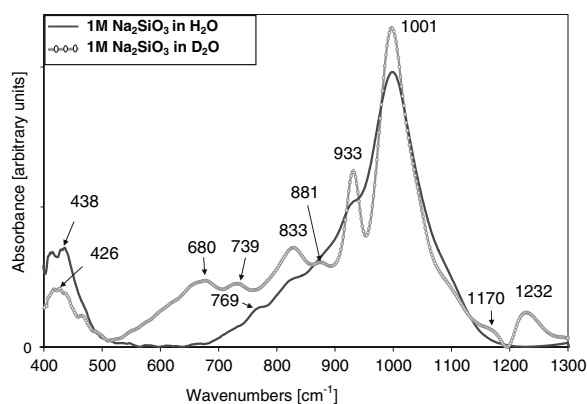


Figure 4. FTIR ATR spectra of Na_2SiO_3 dissolved in H_2O and D_2O . Only 769 and 438 cm^{-1} bands shift in D_2O in which band sharpening and 1170 and 1232 cm^{-1} vibrations hint on possible polymerization.

premium when the ions of added NaOH have to be also hydrated hence the silicate starts to polymerize. There was no NaOH induced precipitation from the 2 mol/L or more diluted solutions.

As figure 3 illustrates, the added NaOH did not generate any new IR bands. The suppression of 887 cm^{-1} band, increase of 934 cm^{-1} band, and red-shift

of the 1018 cm^{-1} band suggest that NaOH shifts the dissociation of $\text{Na}_2\text{H}_2\text{SiO}_4$ backward, from approximately $\text{H}_2\text{SiO}_4^{2-}$ to $\text{NaH}_2\text{SiO}_4^-$ in this case.

To see which IR bands are associated with OH vibrations we replaced H_2O with D_2O as solvent for Na_2SiO_3 . Our attempts to make stable 3 and 2 mol/L solutions in D_2O were not successful but the 1, 0.5, and 0.2 mol/L solutions proved to be stable for at least 8 weeks. Figure 4 compares the FTIR spectra of the 1.0 mol/L Na_2SiO_3 solutions in D_2O and H_2O . The increased number of relatively sharp bands and the appearance of 1170 and 1230 cm^{-1} bands in the optically clear D_2O solution hint on the presence of nano-scale crystalline silicates [72–74]. Only the 438 cm^{-1} band shifted to 426 cm^{-1} (calculated 427 cm^{-1}) and the extremely weak 769 cm^{-1} band to 737 cm^{-1} (calculated 750 cm^{-1}) that might be associated with the OH \rightarrow OD exchange. One would expect for the 1001, 934, and 881 cm^{-1} bands shifts to about 977, 911, and 865 cm^{-1} , respectively, if they were sensitive to the OH \rightarrow OD exchange. The lack of such shifts is probably due to the fact that these stretching vibrations are mostly related to motions of the small Si atom.

3.3. Raman spectra

Numerous papers report Raman spectra of anhydrous crystalline, amorphous, or melted Na_2SiO_3 [67,75,86,89,91–93,100]. These spectra are quite similar to each other and strongly resemble the spectrum of Metso Beads® 2048 in figure 5 indicating that these materials contain the same major structural units (silica chains, charge compensated with Na^+ ions) regardless of their crystallinity. We have not found Raman spectrum for hydrated metasilicate in the literature. Its broadened Raman bands hint on the vibration-retarding and bond-distorting effect of hydrogen bonded H_2O molecules, similar to the line broadening effect of silanol defects on zeolites [59].

Proposed chemical bond assignments of the Raman vibrations of these solid silicates are shown in table 2. Most Raman study in the literature is directed toward

Table 3
Assignments of IR and Raman vibrations of dissolved Na_2SiO_3

Frequencies (cm^{-1})		Assignments
IR	Raman	
1020	1032	$\nu_{\text{as}}(\text{X})\text{O}-\text{Si}-\text{O}(\text{X})$ [X = H or – charge; in $\text{H}_2\text{SiO}_4^{2-}$]
1006	1018	$\nu_{\text{as}}(\text{X})\text{O}-\text{Si}-\text{O}(\text{X})$ [X = Na, H, or – charge; in $\text{NaH}_2\text{SiO}_4^-$]
985	997	$\nu_{\text{as}}(\text{X})\text{O}-\text{Si}-\text{O}(\text{X})$ [X = H or Na; in $\text{Na}_2\text{H}_2\text{SiO}_4$]
934	931	$\nu_{\text{as}}(\text{X})\text{O}-\text{Si}-\text{O}(\text{X})$ [X = H or Na; in $\text{Na}_2\text{H}_2\text{SiO}_4$]
887	–	$\delta_{\text{as}}^- \text{O}-\text{Si}-\text{O}^-$
–	782	$\delta_{\text{as}}(\text{H})\text{O}-\text{Si}-\text{O}(\text{H})$
–	606	$\delta_{\text{as}}(\text{Na})\text{O}-\text{Si}-\text{O}(\text{Na})$
420–450	450	$\delta_{\text{as}}(\text{X})\text{O}-\text{Si}-\text{O}(\text{X})$ [X = Na, H, or – charge]

Symbols as at Table 2.

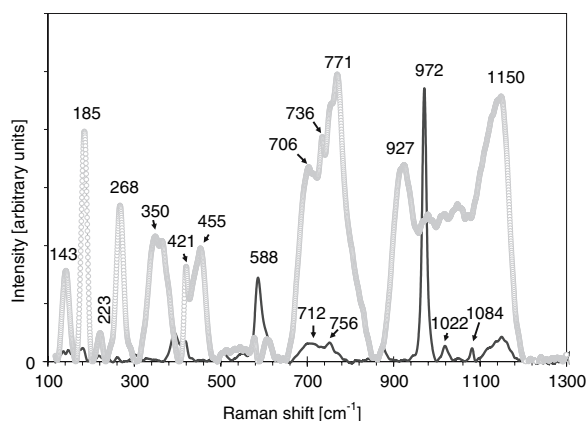


Figure 5. Raman spectra of crystalline Na₂SiO₃ and Na₂SiO₃ × 9H₂O.

the understanding of three dimensional (3D) silicate networks with Q₃ and Q₄ type [SiO₄] tetrahedra and the published band assignments vary even more widely than the assignments of IR bands. For example vibrations near 1145 cm⁻¹ are typically associated with 3D silica networks [18,36,69,72,74–78,93] which cannot be the case in our metasilicates. In contrast, most investigators identify a Raman band near 975 cm⁻¹ with a chain like Q₂ silicate structure [14,69,75–78,86–89,91,92] like that of Na₂SiO₃ (figure 5, table 2). Likewise, bands near 764 and 706 cm⁻¹ have been associated with Si–O stretching [88] though a δ Si–O–Si vibration has also been assigned to 769 cm⁻¹ Raman shift in certain aluminosilicates [90]. A band in the 910–940 cm⁻¹ region that also appears in various calculations of spectra of a fully dissociated, Q₀ type orthogonal [SiO₄]⁴⁻ monomer ion [14,64] has been assigned to ν_{as} Si–O [14,64,88], δ O–Si–O [88], and Q₃ type ν Si–O–Si [75,79,87] vibrations. A Raman band near 600 cm⁻¹ has been associated with ν_s Si–O–Si vibrations [14,20,29,32,72,79,88,101] and it is a known benchmark of planar 3-fold Si–O rings [14,72,77,102–105] in various silicates. This band was also assigned to O–Si–O bending in defect sites of molten and glassy alkaline silicates [77,93] and Si–O stretching vibrations in solid sodium metasilicate [88]. Raman shifts at around 460 and 270 cm⁻¹ are also characteristic calculation results for δO–Si–O vibrations in [SiO₄]⁴⁻; [14,72,89] but only the latter one has been reported in the experimental Raman spectra of solid or molten Na₂SiO₃ [77,88,92]. Except for the 347 cm⁻¹ band, the other low wavelength vibrations in table 2 appear in various sodium silicate related papers and have been assigned to different deformation motions of the O–Si–O bonds [86,88].

Figure 6 indicates dramatic changes in the normalized Raman spectra of variously dissociated Na₂H₂SiO₄. The 606, 931, and 1010 cm⁻¹ bands must reflect sodium related vibrations in the 3 M solution. Published SiO₄⁴⁻ related calculations [14,72] predict a ν_s Si–O band at 775 cm⁻¹ and a ν O–Si–O band at 460 cm⁻¹. The

935 cm⁻¹ disappears from spectra of highly dissociated Na₂H₂SiO₄ hence can be assigned to ν_{as} (H)O–Si–O(Na) vibration [we will show later why not (Na)O–Si–O(Na)]. The ν_{as} (X)O–Si–O(X) vibrations (X can be negative charge or hydrogen atom) in the 1000–1030 cm⁻¹ range are less intense than those in the FTIR spectra which is a well-known common phenomenon in silicate spectroscopy. Assuming that 1032 cm⁻¹ corresponds the fully dissociated H₂SiO₄²⁻, we calculated the expected shifts in a similar manner as described in the previous chapter and show in table 3. Agreement with the experimental data in figure 6 is quite good.

Although Alvarez and Sparks [11] assign the 1068 cm⁻¹ band to Si–O–Si stretching vibration, we found similar to Twu *et al.* [28] that this band coincides with a Raman scattering of Na₂CO₃ that can be present as contamination in these solutions. Therefore, we ignore the assignment of this band.

As mentioned before the 1236 cm⁻¹ band might indicate some crystallites in the 1 and 0.2 M solutions, but its intensity is surprising because more than 90% of the dissolved silicate is monomer (table 1) and the relative intensity of this band is usually low even in fully crystalline silicates [59]. Another anomaly is the split of ν_s ~ 780 cm⁻¹ band in the 1 and 0.5 mol/L solutions of Na₂SiO₃ × 9H₂O (figure 6) which might also be related to LO–TO splitting as Galeener's [113,119] and van Santen's [53] calculations for vitreous silica predict. However, such splits never appeared in solutions made from the dehydrated Na₂SiO₃ and the Raman spectra of the two types of solutes were virtually identical with each other at other concentrations. The spectrum of 0.05 M solution of fully dissociated H₂SiO₄²⁻ starts to resemble the spectrum of crystalline Na₂SiO₃ × 9H₂O (figure 5), a possible indication for ordering as a prelude to solidification. Note however that the 1226 cm⁻¹ band is broad and relatively small in this spectrum.

Most authors assign the 606 cm⁻¹ band to Q₂ type linear or 3-fold ring structures in aqueous silicate solutions [14,18,22,36,72], but it cannot be the case with our monomer solutions. This band tends to disappear in more diluted solutions hence must be associated with the dissociation of Na⁺ ions. An example in figure 7 illustrates that, unlike the 930 cm⁻¹ band, the 606 cm⁻¹ band could not be recovered by adding NaOH to the dilute solutions. Therefore we assign this latter Raman shift to (Na)O–Si–O(Na) and the former one to (Na)O–Si–O(H) vibrations. This assignment agrees well with the fact that a band near 600 cm⁻¹ appears only in the Raman spectrum of dehydrated crystalline Na₂SiO₃ in which direct Si–O(Na) connections exist while a band near 930 cm⁻¹ appears only in the spectrum of the hydrated crystalline Na₂SiO₃ × 9H₂O in which Si–OH also exists.

Figure 8 shows that D₂O also had some unexpected effects on the Raman scattering of these solutions. The increased 606 and 936 cm⁻¹ bands hint on restricted

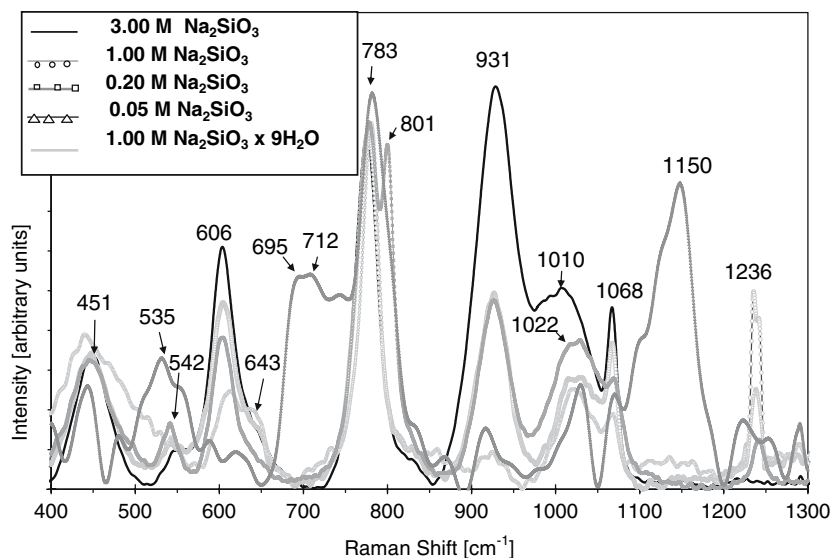


Figure 6. Raman spectra of aqueous solutions of Na_2SiO_3 and $\text{Na}_2\text{SiO}_3 \times 9\text{H}_2\text{O}$ normalized to their 780 cm^{-1} band which splits in 1.0 and 0.5 M solutions of the hydrated silicate.

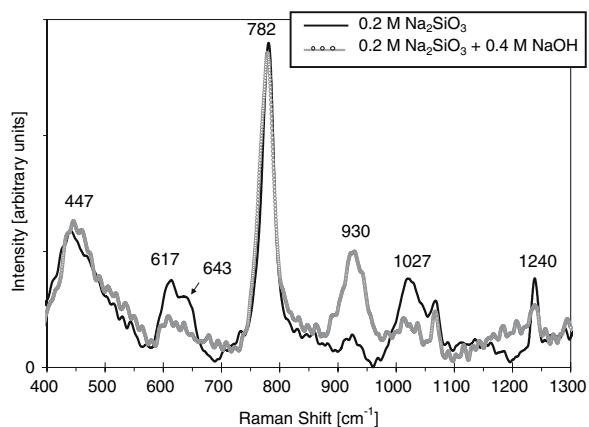


Figure 7. Added NaOH retards the dissociation of $\text{Na}_2\text{H}_2\text{SiO}_4$ monomers thus the $\nu_s \sim 930\text{ cm}^{-1}$ (H)O-Si-O(Na) Raman band reappears but the $\delta_s \sim 606\text{ cm}^{-1}$ (Na)O-Si-O(Na) band does not.

dissociation of $\text{Na}_2\text{H}_2\text{SiO}_4$. Only the 780 cm^{-1} band shows the expected shift to 761 cm^{-1} . Freund [16] reported similar result with $\text{H}_2\text{SiO}_4^{2-}$ solutions. The most unusual, but repeatable result is the extreme large 1210 cm^{-1} band in the 1 M solution. We do not have an explanation for this phenomenon. D_2O itself does not give any Raman signal in the $400\text{--}1400\text{ cm}^{-1}$ spectral range.

4. Conclusions

- (1) Aqueous solutions of Na_2SiO_3 and $\text{Na}_2\text{SiO}_3 \times 9\text{H}_2\text{O}$ contain mostly $\text{Na}_2\text{H}_2\text{SiO}_4$ monomers at concentrations from 0.2 to 3 mol/L. The dissociation of these monomers changes from about 30% to 80% with dilution in this concentration range.

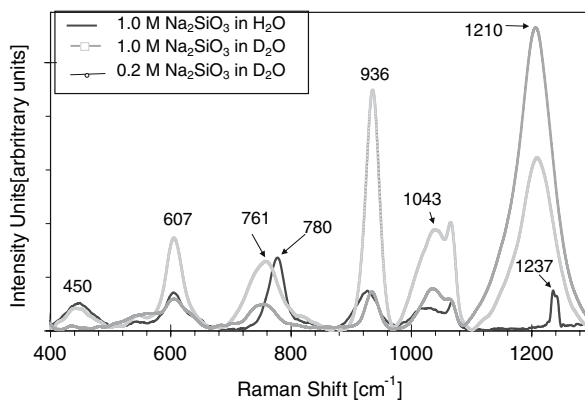


Figure 8. Raman spectra of Na_2SiO_3 dissolved in H_2O and D_2O . Large 607 and 936 cm^{-1} bands indicate retarded dissociation in D_2O which promotes extreme 1209 cm^{-1} band with dilution.

- (2) The Si–O vibrations in the FTIR and Raman spectra of these silicate solutions depend strongly on the dissociation level of Na₂H₂SiO₄. Thus the common practice of neglecting dissociation can lead to serious misinterpretation of the spectra of silicate solutions.
- (3) Based on known structural data and studies on the effect of dilution, NaOH addition, and substitution of H₂O for D₂O as solvent, we propose consistent assignments for the observed IR and Raman vibrations of the above-mentioned two crystalline sodium metasilicates and their solutions as summarized in tables 2 and 3.
- (4) D₂O is a significantly worse solvent for these metasilicates than H₂O and retards the dissociation of Na₂H₂SiO₄. Some unique and unexpected effects were observed in the Raman spectra of solutions made with D₂O.

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