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Spectral resolution and Raman Q and Q cross sections

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24 A comparative study of Raman and ^{29}Si MAS NMR spectral intensities indicates that Raman Q^2 and Q^3
 25 species cross sections are respectively, 1.07 and 0.97, based on the assumption that they are 1.0 in ^{29}Si MAS NMR
 26 spectra. The Q^2 band of the Raman spectrum is dominantly Lorentzian in shape whereas the Q^3 band is asymmetric.
 27 There are two explanations for the asymmetry, one related to alkali-tetrahedral oxygen interactions and the other
 28 related to $Q^{n,i,j,k,l}$ clustering. The explanations are not mutually exclusive and both may contribute to production of
 29 asymmetric Q^3 bands in Raman and ^{29}Si MAS NMR spectra. The combination of ^{29}Si static NMR and high
 30 resolution Raman spectroscopy now can provide highly accurate estimates of Q^2 , Q^3 and Q^4 species abundances in
 31 glasses containing 35-41 mole % Na_2O . It remains to be determined if similar quantification can be achieved over a
 32 wider compositional range.

33 The Q species abundances derived from ^{29}Si MAS and static NMR have been used to evaluate equilibrium
 34 constants for the speciation reactions $Q^3 \rightarrow Q^4$, $Q^2 \rightarrow Q^3$ and $Q^1 \rightarrow Q^2$. Mass action and mass balance equations
 35 then were solved to obtain concentrations of Q^1 , Q^2 , Q^3 , Q^4 and free oxygen (oxygen not bonded to Si) in glasses
 36 ranging from 0 to 45 mol% Na_2O . The calculated values are consistent with ^{29}Si NMR, Raman, and O 1s X-ray
 37 Photoelectron spectroscopic (XPS) experimental results. Thermodynamic constraints (mass action equations) are
 38 more reliable than traditional stoichiometric constraints in extracting Q and O species abundances from
 39 spectroscopic data and in testing the accuracy of the results.

401. Introduction

41 Insights into the short-range structure and chemical speciation of silicate glasses and melts have been
 42 obtained mainly by four spectroscopies, Raman, ^{29}Si Nuclear Magnetic Resonance (NMR), ^{17}O NMR, and O 1s X-
 43 ray Photoelectron Spectroscopy (XPS) (e.g., Hehlen et al., 2017; Nesbitt et al., 2017a,b,c,d; 2015a,b; Sawyer et al.,
 44 2015; 2012; Stebbins and Xue, 2014; Nesbitt and Bancroft, 2014; Nesbitt et al., 2011; Bancroft et al., 2009; Lee and
 45 Stebbins, 2009; Dalby et al., 2007; Neuville et al., 2014; Neuville, 2006; Xue et al. 1994; Mysen and Frantz, 1993;
 46 Maekawa et al., 1991; Stebbins, 1988; 1987; McMillan, 1984; Matson et al., 1983; Furukawa et al, 1981; Bruckner
 47 et al., 1980; Virgo et al. 1980; Brawer and White, 1975). They have allowed quantification of the five tetrahedrally
 48 coordinated Si species (Q species) in alkali silicate melts and glasses where each species hosts a different number of
 49 'Bridging Oxygen' atoms (BOs, Si-O-Si moieties) and 'Non-Bridging Oxygen' (NBO, Na-O-Si moieties). The Si
 50 tetrahedra are referred to as Q^n species, where the 'n' represents the number of BO's of the tetrahedron. Q^n species
 51 abundances strongly affect chemical and physical properties of melts and glasses (e.g., Le Losq and Neuville,
 52 2017), the mechanisms of melting (e.g., Nesbitt et al. 2017d; 2015a; Mysen and Richet, 2018; Richet et al., 1998;
 53 1996; 1994) and reaction mechanisms, including redox reactions (Nesbitt et al. 2015a; Magnien et al., 2008). There
 54 are, therefore, good reasons to obtain highly accurate Q species abundances in glasses and melts.

55 The main objective of the study is to establish accurate Raman cross sections for Q^3 and Q^2 species in sodic
 56 glasses. A reason for focussing on Raman spectroscopy relates directly to its superior resolution relative to the
 57 resolution of other techniques, and its potential for obtaining highly accurate estimates of Q species in silicate melts.
 58 To emphasize this aspect, quantitative estimates of the Q species abundances obtained from NMR studies are
 59 contentious for Na and K silicate glasses (e.g., Stebbins et al. 2017; Nesbitt et al. 2017c; Sawyer et al. 2015; Malfait,
 60 2015; Nesbitt et al. 2015b; Nesbitt et al. 2011). Raman spectral analysis may help to resolve the ambiguities but to
 61 do so Raman Q species cross sections are required. These can be evaluated following the procedure of Frantz and
 62 Mysen (1995) who argue that Raman cross sections may be determined by comparison of Q species intensities
 63 obtained from Raman spectra with Q species intensities derived from ^{29}Si MAS NMR spectra based on the
 64 assumption that the NMR cross sections of all Q species are 1.0.

65 We here undertake a detailed analysis of Q^2 and Q^3 spectral intensities (peak areas) obtained from a Raman
 66 spectrum of a 40.9 mol% Na_2O glass and compare them with intensities obtained from ^{29}Si NMR spectra of glasses
 67 ranging from ~36 to ~41 mol% Na_2O . We then assess Q and O species abundances over a much broader range of
 68 compositions (i.e., glasses containing 0 to 45 mol% Na_2O) using thermodynamic constraints (mass action equations)
 69 to ensure that Q species abundances obtained for the 40.9% Na_2O glass are consistent with Q and O species
 70 abundances in sodic glasses of other compositions. With Q and O species abundances and spectral intensities known
 71 for the 40.9% Na_2O glass, Q^2 and Q^3 Raman cross sections are then evaluated.

722. Experimental Considerations

73 The Raman spectrum here fit was originally published by Neuville (2006) where details of sample
 74 preparation and of Raman analytical techniques are provided. He analysed the glass using a Cameca SX100 electron
 75 microprobe and obtained a composition of 40.85 ± 0.11 mol% Na_2O and 59.14 ± 0.14 mol% SiO_2 . Although the glass
 76 has 40.9% Na_2O , it and other glasses of similar composition are also referred to as a ~40 mol% Na_2O glass in some
 77 parts of the text, primarily for convenience. The procedures for fitting the Raman spectrum follow those of Bancroft
 78 et al. (2018) where peak shapes include a substantial Lorentzian component and all Q^3 -related peaks are assigned
 79 the same Full Width at Half Maximum (FWHM). The CasaXPS software was used to fit spectra, including the

80 Raman spectrum. To accomplish this, the Raman spectrum was imported into the program as a two-field, tab-
81 delimited ASCII file. Fitting of the asymmetric Lorentzian peak required inversion of Raman shift values to obtain
82 the proper sense of peak asymmetry. As well, ²⁹Si MAS NMR spectra of ~40 mol% Na₂O glasses first reported by
83 Nesbitt et al. (2011) and Stebbins (1987), and an O 1s XPS spectrum from Nesbitt et al. (2011) have been redrawn
84 and illustrated in Fig. 1.

853. Peak Resolution of Spectra

863.1. Measurement of Resolution

87 The comparative resolution of Raman, ²⁹Si MAS NMR, ¹⁷O NMR and O 1s XPS spectroscopic techniques
88 has not been evaluated but is required if uncertainties associated with reported Si and O species abundances are to
89 be established across techniques. We attempt to quantify the resolution of different types of spectra by introducing a
90 non-parametric measure associated with two peaks of any type of spectrum (e.g., the Q² and Q³ signals of Figs. 1a
91 and 1b). It entails comparison of the maximum intensity of the *weaker* peak (e.g., the Q² peak intensity of Fig. 1a)
92 with the intensity at the *minimum* separating the two peaks (i.e., the minimum intensity between the Q² and Q³ peaks
93 of Fig. 1a), and calculating the percentage difference in intensities according to:

$$94 \quad Q^2\text{-}Q^3 \text{ Peak Resolution}(\%) = 100 \times (\text{peak}/(\text{peak} + \text{minimum})) \quad (1)$$

95 A value of 100% indicates complete resolution of the two peaks whereas a value of 50% indicates an absence of a
96 minimum between the peaks. Where a minimum is absent the inflection point between the peaks may be used to
97 obtain an estimate of Peak Resolution but all such values will be less than 50% and spectra will be considered very
98 poorly resolved. The utility of the equation in assessing the resolution of numerous techniques follows.

993.2 ²⁹Si MAS NMR and Raman spectra

100 The ²⁹Si MAS NMR spectra of two ~40 mol% Na₂O glasses are illustrated in Figs. 1a and 1b and both
101 display a Q² and a Q³ band. The spectrum of Fig. 1a was collected from a glass containing a natural ²⁹Si abundance
102 (~4.7%) whereas ²⁹Si was enriched to 57% in the other study (Fig. 1b). The application of Equation 1 to Fig. 1a
103 yields a Q²-Q³ Peak Resolution of ~54%. The spectrum of Fig. 1b has a Q²-Q³ Peak Resolution of ~57%
104 demonstrating that ²⁹Si enrichment improves spectral counting statistics and resolution. The Raman spectrum of a
105 40.9 mol% Na₂O glass (Fig. 1c) has two strong bands similar to the NMR spectra. The two peaks at ~950 cm⁻¹ and
106 1100 cm⁻¹ have been assigned to the Q² and Q³ species as discussed subsequently. Application of Equation 1 yields a
107 Q²-Q³ Peak Resolution of ~73%, indicating high resolution. Ambiguities associated with interpretation of Raman
108 spectra are discussed subsequently.

1093.3 ¹⁷O NMR and O 1s XPS spectra

110 The ¹⁷O static and MAS NMR techniques have not been used to obtain BO and NBO abundances for sodic
111 glasses, although numerous spectra have been published (e.g., Lee and Stebbins, 2009; Stebbins et al., 2001). They
112 yield complex spectra and the six MAS NMR spectra published by Lee and Stebbins (2009) have, by Equation 1,
113 NBO-BO Peak Resolution less than 50%. The techniques require samples to be enriched in ¹⁷O. The expense and
114 poor resolution has rendered the ¹⁷O static and MAS NMR techniques of limited use in quantifying oxygen species
115 in Na₂O-SiO₂ glasses. The O 1s XPS spectrum of a ~40 mol% Na₂O glass shown in Fig. 1d has a BO-(NBO+O²⁻)
116 Peak Resolution of ~67%, indicating good resolution. The third peak in the spectrum is the broad, high binding
117 energy (BE) Na KLL Auger peak (Nesbitt et al., 2011). O 1s XPS line shapes and widths are well established and O
118 species abundances are readily obtained (Sawyer et al., 2015; 2012; Nesbitt and Bancroft, 2014; Nesbitt et al.,
119 2015a; 2015b; 2011; Dalby et al., 2007).

1204. Raman Spectrum of 40.9 mol% Na₂O Glass

1214.1. Establishing Line Shape and Width

122 Ambiguities concerning interpretation of Raman spectra have limited use of the technique to obtain
123 accurate Q species abundances (Bancroft et al., 2018; Neuville et al., 2014; Neuville, 2006; Mysen and Frantz,
124 1992; 1993; McMillan et al., 1992; Furukawa et al., 1981; Brawer and White, 1975). We address the ambiguities by
125 analyzing a 40.9 mol% Na₂O glass spectrum. The Raman spectrum of Fig. 2a is composed of two well resolved
126 bands centered at ~950 cm⁻¹ and ~1100 cm⁻¹. To initiate fitting of the spectrum, two peaks were introduced with one
127 optimized to fit the low frequency side of the 950 cm⁻¹ band and the other to fit the high frequency side of the 1100
128 cm⁻¹ band. Raman band shapes should contain a Lorentzian component (Bancroft et al., 2018; Haken and Wolf,
129 1991; Kamitsos and Risen, 1984) and the introduced peaks were adjusted for line shape and FWHM using a pseudo-
130 Voigt sum function (Hesse et al., 2007). The derived peak parameters are listed in Table 1. Peak #1 yields an 80:20
131 Lorentzian:Gaussian line shape whereas Peak #2 is 50:50, and their FWHM are respectively 45.5 cm⁻¹ and 58.2 cm⁻¹
132. These are consistent with shapes and widths obtained from spectral fits to other alkali silicate glasses (Nesbitt et
133 al., 2019; Bancroft et al., 2018). The line shapes are used subsequently to complete the fit. FWHM are not
134 constrained in subsequent fits but any fit which yields values substantially different from these is considered a poor
135 or inappropriate fit.

1364.2. Peak Assignments and Intensities

1374.2.1. Preliminary Fit

138 To complete the fit, a third peak was introduced to the spectrum with its shape set to 50% Lorentzian (as
139 for Pk#2 of Fig. 2b). A least squares best fit then was obtained as shown in Fig. 2b. Fit parameters are listed in Table
140 1. The fit is similar to a previous fit to the same glass (Neuville, 2006, his Fig. 6c) although he used 100% Gaussian
141 peak shapes. The fit shown in Fig. 2b is reasonable from a statistical perspective but the FWHM of the third peak is
142 14295 cm^{-1} and too broad to represent a single peak, as noted by Bancroft et al. (2018). This aspect is addressed in the
143 refinements to the fit (section 4.4.2).

144 The ^{29}Si MAS NMR spectrum of Fig. 1b demonstrates that the Q^2 and Q^3 species represent the only two
145 major signals of $\sim 40\text{ mol}\%$ Na_2O glasses (Nesbitt et al., 2011; Zhang et al., 1996; Maekawa et al., 1991; Stebbins,
146 1987). Based on Raman shifts, Pk#1 is interpreted as a Q^2 signal and Pk#2 as a Q^3 signal. The assignments are
147 consistent with both NMR and other Raman studies (Neuville et al., 2014; Richet et al., 1996; 1994; Stebbins, 1987;
148 McMillan, 1984; Furukawa et al., 1981; Brawer and White, 1975). The intensity of the Raman Q^2 peak represents
149 $\sim 31.5\%$ of the total Raman intensity (Fig. 2b, Pk#1, Table 1). Q^2 intensity averages 29.3% in ^{29}Si NMR spectra for
150 $\sim 40\text{ mol}\%$ Na_2O glasses (Table 2), confirming the assignment of Pk#1 (Fig. 2b) to the Q^2 species. The remaining
151 intensity of the Raman spectrum is 68.5% ($100\% - 31.5\%$) but the average Q^3 species abundance is $\sim 68.3\%$ from
152 ^{29}Si MAS NMR results (Table 2, see Average values). With Pk#1 of Fig. 2b assigned to Q^2 , *all remaining intensity*
153 of the Raman spectrum represents mostly Q^3 species; that is, both Pk#2 and Pk#3 of Fig. 2b represent Q^3
154 contributions. The interpretation does not imply that there are two distinct Q^3 bands because the Q^3 band may be
155 asymmetric (McMillan et al., 1992; Bancroft et al., 2018; Nesbitt et al., 2019).

1564.2.2. Refinements to Fit

157 Three ambiguities of Fig. 2b stand out: (1) there is an inflection at $\sim 860\text{ cm}^{-1}$ and the residuals (Fig. 2c)
158 indicate a weak band at this frequency; (2) Peak #3 is exceedingly broad at $\sim 95\text{ cm}^{-1}$ and requires explanation; (3)
159 there is no evidence of a Q^4 band, although ^{29}Si static NMR results indicate $\sim 2\text{ mol}\%$ Q^4 species (Stebbins, 1987).

160 An unconstrained peak was introduced to account for the inflection at $\sim 860\text{ cm}^{-1}$ (Fig. 2d). Its Raman shift
161 is consistent with, and is interpreted as, a Q^1 peak (Neuville et al., 2014; McMillan, 1984). The second concern was
162 addressed using the technique employed by Bancroft et al. (2018) and Nesbitt et al. (2019) where two peaks were
163 introduced to replace the one broad Pk#3 of Fig. 2b, where the two peaks constrained to the same FWHM and line
164 shape as Pk #2. With these changes, the least squares best fit shown in Fig. 2d is obtained. Peak fit parameters are
165 listed in Table 1. These modifications decreased the Root Mean Square (RMS) by $\sim 14\%$. Pk#2 of Fig. 2b has been
166 labelled Q^3 -1 and the added peaks were labelled Q^3 -2 and Q^3 -3, indicating that they contribute to the Q^3 intensity.

167 The residuals plot of Fig. 2f reveals a 'sinusoidal' pattern between ~ 1050 and $\sim 900\text{ cm}^{-1}$ indicating that an
168 additional peak should improve the fit. Another peak was introduced (i.e., peak Q^3 -4) with line width and shape
169 constrained to those of the Q^3 -1 peak. The resulting fit decreased the RMS by 5% (Fig. 2e). Fit parameters are listed
170 in Table 1. Addition of still another peak had no appreciable effect on RMS values and the fit of Fig. 2e is taken as
171 the best fit to the spectrum (residuals in Fig. 2g). The Q^2 and Q^3 peak intensities derived from the three fits to the
172 Raman spectrum (Figs. 2b, 2d, 2e) differ by less than 1.5% (Table 1) indicating that the number of peaks used to fit
173 the spectrum, does not alter Q^2 and Q^3 intensities appreciably.

174 The ^{29}Si static NMR spectrum of Stebbins (1987) indicates $2.0 (\pm 1)\text{ mol}\%$ Q^4 in his $41.1\text{ mol}\%$ Na_2O glass
175 and we estimate that Q^4 is $\sim 2.1\%$ Q^4 in our $40.9\text{ mol}\%$ Na_2O glass (as shown subsequently). The Q^4 peak should
176 reside between ~ 1140 - 1200 cm^{-1} , hence beneath the Q^3 -1 peak of Fig. 2e (Nesbitt et al., 2019; Bancroft et al., 2018).
177 With the Q^4 intensity set to 2.1%, the total Q^3 peak intensity has been decreased by the same amount, from 67.2% to
178 65.1 mol% (Table 1). Thus Q^2 and Q^3 intensities derived from fitting the Raman spectrum of the $40.9\text{ mol}\%$ Na_2O
179 glass are 32.2% and 65.1%, which are similar to averages obtained from ^{29}Si MAS NMR spectra (Table 2).

1805. Q^n Species in 40.9 mol% Na_2O Glass

181 The Q^n species abundances derived from the three ^{29}Si MAS NMR studies of Table 2 apply to compositions
182 slightly different from the $40.9\text{ mol}\%$ Na_2O glass (Fig. 2) and accurate estimates of the Q^n species abundances for
183 this glass are required to obtain accurate Raman cross sections. The abundances and their uncertainties are evaluated
184 in this section.

1855.1. Q^4 species Uncertainties

186 Accurate Q^4 values can be obtained using the ^{29}Si static NMR technique (Stebbins, 1987; Sen and
187 Youngman, 2003). Stebbins (1987) reported 7.2, 4.0 and 2.0 mol% ($\pm 1\%$ absolute) Q^4 species for glasses containing
188 34.2, 37.0 and 41.1 mol% Na_2O and Maekawa et al. (1991) obtained 5 mol% Q^4 species in a glass containing 36.4
189 mol% Na_2O using the same technique. These Q^4 abundances are plotted on Fig. 3a (solid symbols). They were fit to
190 a power law ($y = ax^n$) and an exponential equation ($y = ae^{nx}$) where, for both equations, $y = \text{mol}\% Q^4$ and $x = \text{mol}\%$
191 Na_2O . They yield similar results for glasses ranging from ~ 32 to $50\text{ mol}\%$ Na_2O . At $40.9\text{ mol}\%$ Na_2O the Q^4 species
192 abundance is $\sim 2.1\%$. Stebbins indicates an uncertainty of $\pm 1\%$ (absolute) but the fit is derived from four

193 independent measurements, and the systematics of the data with respect to composition (Fig. 3a) indicate a
194 somewhat smaller uncertainty.

195 5.2. Q^2 and Q^3 Uncertainties

196 Experimentally derived Q species abundances for a wide compositional range of sodic glasses are listed in
197 Table 3. Most data are derived from fits to ^{29}Si MAS NMR spectra and subject to appreciable uncertainties because
198 Q^4 - Q^3 Peak Resolution is near or less than 50% (Nesbitt et al., 2011; Olivier et al., 2001; Maekawa et al., 1991;
199 Stebbins, 1987). Of these, the three ^{29}Si MAS NMR spectra of Stebbins (1987) are the best resolved. Stebbins
200 (1987) reported Q^4 abundances for these glasses did not report Q^2 and Q^3 species abundances. They can be
201 evaluated, however, using his reported disproportionation constant for the reaction whereby two Q^3 species react to
202 produce a Q^2 and a Q^4 species:

$$203 \quad K_3 = (X_{Q2})(X_{Q4})/(X_{Q3})^2 \quad (3)$$

204 K_3 is the equilibrium (disproportionation) constant. Replacement of activities by mole fractions makes K_3 a
205 conditional equilibrium constant. Stebbins quotes $K_3 = 0.011 \pm 0.005$. Using this value, the mass action equation
206 (Eq. 3), the mass balance equation ($Q^2+Q^3+Q^4 = 100\%$) and the Q^4 values listed by Stebbins (1987), the mass action
207 and mass balance equations were solved to obtain mole fractions (and mol%) of Q^2 and Q^3 for his three glasses
208 (Table 3, Stebbins, 1987, where $K_3 = 0.011$). The results are plotted on Fig. 3b (open circles).

209 Maekawa et al. (1991) fit their ^{29}Si MAS NMR spectrum of a glass containing 36.4 mol% Na_2O to obtain
210 77% Q^4 , 76% Q^3 and 17% Q^2 (Table 3). Their ^{29}Si static NMR spectrum of the same glass yielded, however, a value
211 of 5% for Q^4 , which should be more accurate than the MAS NMR value. The Q^4 and Q^3 bands overlap so that
212 decreasing Q^4 from 7 mol% to 5% requires increasing Q^3 from 76 to 78 mol%, with Q^2 remaining at 17 mol%.
213 These abundances yield $K_3 = 0.014$, which is within the uncertainty in K_3 (± 0.005) quoted by Stebbins (1987).

214 The Q species abundances for the Stebbins' glasses then were recalculated using $K_3 = 0.014$. The results
215 are listed in Table 3 (Stebbins, 1987 where $K_3 = 0.014$) and plotted on Fig. 3b (solid circles). An indication of the
216 uncertainties in Q^2 and Q^3 species abundances derived from the ^{29}Si MAS NMR spectra of Stebbins (1987) and
217 Maekawa et al. (1991) can be obtained using $K_3 = 0.011$ in one calculation and $K_3 = 0.014$ in another. As example,
218 with $K_3 = 0.011$, $Q^2 = 27.4\%$ and $Q^3 = 70.6\%$, and with $K_3 = 0.014$, $Q^2 = 31.2\%$ and $Q^3 = 66.8\%$, a difference in Q^2
219 of 4% absolute (13% relative). Speciation modelling is performed in an attempt to establish the most reasonable Q^2
220 and Q^3 abundances.

221 6. Speciation Reactions

222 The speciation reaction whereby Q^3 is converted to Q^4 may be written as:



224 where Na_2O_m represents 'free oxygen' (i.e., all oxygen *not bonded to Si*; alternatively, oxygen *not* associated with Si
225 tetrahedra). It is here denoted as Na_2O but commonly is referred to as O^{2-} (Nesbitt et al., 2017; 2015; 2011) and Na^+
226 and O^{2-} can be used in place of Na_2O_m in Equation 4. Na_2O_m is used here to be consistent with the treatment of
227 Maekawa et al. (1991). The mass action equation for Reaction (4) is:

$$228 \quad K_4 = [(X_{Q4})(X_{\text{Na}_2\text{O}_m})^{1/2}]/(X_{\text{Na-Q}^3}) \quad (5)$$

229 K_4 is the equilibrium constant. Where mole fractions are used in place of activities, K_4 becomes a conditional
230 equilibrium constant. Reaction of Q^2 to produce Q^3 may be written as:



232 The associated mass action equation is:

$$233 \quad K_6 = [(X_{\text{Na-Q}^3})(X_{\text{Na}_2\text{O}_m})^{1/2}]/(X_{\text{Na}_2\text{-Q}^2}) \quad (7)$$

234 Conversion of Q^1 to Q^2 and its associated mass action equation are:



236 and

$$237 \quad K_8 = [(X_{\text{Na}_2\text{-Q}^2})(X_{\text{Na}_2\text{O}_m})^{1/2}]/(X_{\text{Na}_3\text{-Q}^1}) \quad (9)$$

238 6.1. Evaluation of Equilibrium Constants

239 Two sets of Q and O species have been obtained from the results of Stebbins (1987) as discussed
240 previously, and they are listed in Table 3 for $K_3 = 0.011$ and for $K_3 = 0.014$. The Q species mol% were converted to
241 mole fractions and substituted into the above mass action equations to obtain 'conditional' equilibrium constants.
242 The set consistent with $K_3 = 0.011$ yields $K_4 = 0.0425$ and $K_6 = 0.385$ and the set consistent with $K_3 = 0.014$ gives
243 $K_4 = 0.0400$ and $K_6 = 0.285$. There are insufficient data to accurately evaluate K_8 and an *estimate* of 5.0 has been
244 adopted for both sets. As a test of these constants, note that the disproportionation reaction where two Q^3 species
245 react to form Q^2 and Q^4 can be obtained by subtracting Reaction (6) from Reaction (4) so that $K_3 = K_4/K_6$. For the
246 first set $K_3 = 0.00425/0.385 = 0.011$ and for the second set, $K_3 = 0.0040/0.285 = 0.014$, demonstrating consistency
247 of constants.

248 6.2. Modelled Q species Abundances

249 With the conditional equilibrium constants evaluated, the equilibrium distribution of Q^4 , Q^3 , Q^2 , Q^1 and
 250 Na_2O_m (free oxygen) in glasses from 0 to 45 mol% Na_2O were calculated by solving the three mass action Equations
 251 15, 7 and 9, and the two mass balance equations involving Si and O (i.e., 5 eqns. in 5 unknowns). The dashed curves
 252 of Fig. 3b represent the Q species abundances consistent with $K_3 = 0.011$ and the solid curves represent Q species
 253 abundances consistent with $K_3 = 0.014$. In evaluating the conditional equilibrium constants, the greatest weight has
 254 been placed on the four experiments where Q^4 mol% was measured by ^{29}Si static NMR. The calculations with $K_3 =$
 255 0.014 (Fig. 3b, solid curves) are consistent with the static NMR experimental results of both Stebbins (1987) and
 256 Maekawa et al. (1991), as shown by the solid and open diamonds of Fig. 3b. They are also consistent with most of
 257 the other experimental data (Fig. 3b, shaded symbols) and the results obtained with $K_3 = 0.014$ are adopted as the
 258 best estimates of Q species abundances for the 40.9 mol% Na_2O glass. These are: $Q^1=0.6\%$; $Q^2=30.2\%$; $Q^3=67.1\%$
 259 and $Q^4=2.1\%$ (Table 2, 'Modelled Values'). The calculations cannot be applied to glasses more sodic than ~45 mol%
 260 Na_2O for two reasons: (1) K_3 is an estimate only; (2) the speciation reaction involving Q^0 is not included for lack of
 261 data.

262 3. Oxygen Species

263 BO, NBO and free oxygen (Na_2O_m or O^{2-}) abundances predicted from the modelling exercise are plotted on
 264 Fig. 3c. Oxygen species abundances determined by O 1s XPS spectroscopy (Nesbitt et al., 2015a) are plotted on
 265 Fig. 3c as solid circles. Error bars ($\pm 2\%$ absolute) are shown for O 1s XPS-derived BO values but they also apply to
 266 $NBO+O^{2-}$. Oxygen species abundances listed in Table 3 are plotted as open symbols and crosses. NBO and O^{2-} are
 267 combined because O 1s XPS experiments cannot distinguish between them (Nesbitt et al., 2011).

268 7. Raman Cross Sections of Q^2 and Q^3 Species

269 The spectral intensity of a Q^n species (I_Q^n) is the product of its cross-section (σ_Q^n) and mole fraction (X_Q^n):
 270
$$I_Q^n = \sigma_Q^n X_Q^n \quad (2)$$

271 The Q^3 and Q^2 Raman spectral intensities are respectively 65.1 and 32.2 mol% for the 40.9 mol% Na_2O glass (Table
 272, Raman Intensities) whereas the best estimates of Q^3 and Q^2 abundances evaluated from the above modelling
 273 exercise are respectively 67.1 and 30.2 mol% (Table 2, 2nd last row). The Q^3 cross section consequently is 0.97
 274 (65.1/67.1) and the Q^2 cross section is 1.07 (32.2/30.2).

275 There is experimental and theoretical support for these values. Q^3 and Q^2 cross sections of 1.04 and 1.02
 276 respectively have been obtained for Li silicate glasses (Umesaki et al., 1993). Furukawa et al. (1981) calculated Q
 277 species cross sections from theoretical considerations (their Fig. 9) obtaining absolute cross sectional values of ~3.0
 278 for Q^2 and ~2.3 for Q^3 . Only relative cross sectional values are important in evaluating peak areas of a spectrum, and
 279 normalizing their Q^3 cross sectional value to 1.0, a Q^2 cross section of ~1.27 is obtained, whereas our normalized
 280 ratio is 1.10:1.0. The agreement is remarkable considering the simplicity of their theory. Koroleva et al. (2013)
 281 estimated Q^3 and Q^2 cross sections obtaining a $Q^2:Q^3$ ratio of 1.26:1.0 based on the Q species abundances reported
 282 by Maekawa et al. (1991). The cross sections reported here require additional testing and refinement but Raman Q^2
 283 and Q^3 species cross sections are not appreciably different from unity for the sodic glass.

284 8. Discussion and Conclusions

285 8.1. Raman Resolution and Cross Sections

286 Raman spectral resolution is superior to ^{29}Si MAS NMR resolution for ~40 mol% Na_2O glass. The Raman
 287 spectrum consists of two major bands assigned to Q^2 and Q^3 species and its high resolution reveals an asymmetric
 288 Q^3 band. The Q^2 and Q^3 spectral intensities, without correction for cross sections, are within 10% of those obtained
 289 from ^{29}Si MAS NMR spectra, indicating that both Raman cross sections are close to 1.0. This detailed analysis
 290 indicates that the Q^2 cross section is 1.07 and the Q^3 cross section is 0.97. Additional Raman spectra must be
 291 analysed to determine if these conclusions apply to other compositions and to Raman spectra of other alkali silicate
 292 glasses.

293 8.2. Raman and ^{29}Si MAS NMR Line Shapes

294 Olivier et al. (2001) and Sen and Youngman (2003) note that Q^3 or Q^4 peaks of siliceous Na and K glasses
 295 are non-Gaussian and asymmetric in ^{29}Si MAS NMR spectra. The 2D ^{29}Si NMR study of Duer et al. (1995)
 296 demonstrates that the Q^3 band of $Na_2Si_2O_5$ glass includes two distinct Q^3 signals which cannot be discerned in ^{29}Si
 297 MAS NMR spectra. Although the maxima of the two Q^3 signals are almost coincident, their sum seems to yield a Q^3
 298 peak asymmetric toward its low frequency side (their Fig. 5). The Q^3 band of the Raman spectrum (Fig. 2) is also
 299 asymmetric toward its low frequency side and how best to fit such spectra is an obvious question. The Raman
 300 spectrum of Fig. 2e has been fit using four symmetric Gaussian-Lorentzian peaks (Fig. 2e) but it can also be fit
 301 using one asymmetric peak as shown in Fig. 4. To accomplish the latter fit, the CasaXPS program was used to fit an
 302 asymmetric Lorentzian peak to the Q^3 band of the 40.9 mol% Raman spectrum. The resulting Q^2 and Q^3 intensities

303 are reasonable and the simplicity of the fit is appealing but the root mean square measure indicates a somewhat
304 poorer fit than obtained in Fig. 2e. Additional study is required to determine the best fitting procedures.

305 Asymmetric peak shapes can be justified using the argument of Olivier et al. (2001) and Sen and
306 Youngman (2003) where charge density on a central tetrahedron is partly determined by the types of Q species to
307 which it is bonded. A central Q³ species will have greater charge density if bonded to three other Q³ species than if
308 bonded to three Q⁴ species (Sen and Youngman, 2003) because charge density is transferred via BOs to the central
309 tetrahedron. Another explanation for peak asymmetry relates to Na₂O abundance (Nesbitt et al., 2019; 2017a). Its
310 addition to a melt increases the electron density over all tetrahedra of the glass through transfer of Na 3s electrons to
311 apical O atoms, both NBOs and BOs (Nesbitt et al., 2017a, 2017b; 2015a). As evidence, Na atoms are in close
312 proximity to both NBO and BO atoms in glasses (note Na-BO and Na-NBO distances in Na silicate glasses of Du
313 and Cormack, 2004). The acquired charge, whether transferred via BO or NBO, is preferentially redistributed to Si
314 of the tetrahedron (Demiralp et al., 1999), thus diminishing the Si-O Coulombic interaction and weakening the Si-O
315 force constant (Nesbitt et al., 2017a). The weaker force constant results in decreased vibrational frequency of the
316 tetrahedral symmetric stretch resulting in tetrahedra with the greatest electron density having lowest Raman shifts.
317 The result is an asymmetric band (Nesbitt et al., 2019; 2017; Bancroft et al., 2018).

318 The effect of Na₂O and the Q^{n_ijkl} cluster effect are not mutually exclusive in that both explanations appeal
319 to modification of charge density on central tetrahedra. The Q^{n_ijkl} cluster explanation assumes that all charge derived
320 from Na 3s electrons is transferred to NBO of a tetrahedron and that some of the charge is then transferred to the
321 central tetrahedron via the bridging BO. The second explanation emphasizes that charge transfer occurs through
322 both Na-NBO and Na-BO to affect charge density on the central tetrahedron. Both explanations modify the electron
323 density over central tetrahedra (Nesbitt et al., 2019; 2017a; 2017d; Sen and Youngman, 2003; Olivier et al., 2001)
324 and both should lead to asymmetric bands in both Raman and ²⁹Si MAS NMR spectra, as elegantly shown by Sen
325 and Youngman (2003) for K silicate glasses, and by Olivier et al. (2001) for 25 mol% Na₂O silicate glass. The above
326 two studies provide strong evidence for Q³ and Q⁴ peak asymmetry in ²⁹Si MAS NMR and Raman spectra.

327 8.3. Implications Concerning Fitting Procedures

328 The dashed curve of Fig. 2e represents the sum of the four Q³ peak intensities. It is terminated at ~940 cm⁻¹
329 whereas the asymmetric fit (Fig. 4) extends to lower frequency (~850 cm⁻¹). With respect to peak intensities, the 4
330 peak fit yields a less intense Q³ band and a more intense Q² band (Fig. 2e, Q³ = 67.2%, Q² = 32.2%) than is obtained
331 using an asymmetric peak (Fig. 4, Q³ = 71% and Q² = 29%). The use of four distinct peaks (Fig. 2e) may
332 underestimate Q³ and overestimate Q² abundances whereas the opposite may be true for the asymmetric fit.
333 Moreover, use 100% Gaussian peaks, with each Gaussian peak intended to represent the contribution of one Q
334 species underestimates the abundance of any Q species with an appreciably asymmetric band because it does not
335 include the intensity of the tail. The intensity of the 'tail' will be incorporated into another Gaussian peak thereby
336 complicating the fit and the interpretation of the spectrum.

337 8.4. Oxygen Speciation

338 The BO, NBO and free oxygen (O²⁻ or Na₂O_m) abundances of Table 3 are plotted on Fig. 3c. Agreement
339 among the modelling results (solid curves) and experimental O 1s XPS and ²⁹Si MAS NMR data (symbols) is for
340 the most part within experimental uncertainty. As apparent from Table 3, ~0.2-2.6 mol% free oxygen (O²⁻ or Na₂O_m)
341 is present in glasses containing 15-41 mol% Na₂O. About 1.6 mol% free oxygen is present in the 40.9 mol% Na₂O
342 glass, increasing to 3.9% at 45 mol% Na₂O. These values are consistent with previous experimental studies (Sawyer
343 et al., 2015; 2012; Nesbitt et al., 2017a; 2017b; 2015a; 2015b; 2011). The relationship between free oxygen and Q
344 species abundances is quantitatively addressed in Appendix A. In Table A1 the mol% of Q⁴ species is kept constant
345 and the Q² mol% is incremented by 1 mol% beginning at 28% (and Q³ decremented by 1 mol% beginning at
346 69.8%). The mol% of free oxygen has been calculated and listed for each increment (Table A1, last column). With
347 increased Q² abundance free oxygen decreases but Q² must reach 40.5 mol% for free oxygen to be absent from the
348 glass. Q² species abundances are appreciably lower than this value in all experimental measurements listed in Table
349, thus requiring free oxygen to be present in all the glasses. As apparent from Table 2, ~40 mol% Na₂O glass,
350 averages 29.4% Q² species (1σ = 1.2%), and contains ~2.0 mol% free oxygen.

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472
473
474

475Fig. Captions

476Fig. 1: Illustrates NMR, Raman and O 1s XPS spectra of ~40 mol% Na₂O glasses collected at ambient temperature
477 and pressure. (a) A ²⁹Si MAS NMR spectrum of 40 mol% Na₂O glass of natural ²⁹Si isotopic concentration
478 (~4.7%) redrawn after Nesbitt et al. (2011). (b) A ²⁹Si MAS NMR spectrum of 41.1 mol% Na₂O glass
479 redrawn after Stebbins (1987). The ²⁹Si isotopic concentration has been enriched to 57%. (c) Raman
480 spectrum of a 40.9 mol% Na₂O glass redrawn after Neuville (2006). These results are the original
481 experimental data first published by Neuville (2006). (d) An O 1s XPS spectrum of 40 mol% Na₂O glass
482 redrawn after Nesbitt et al. (2011).

483Fig. 2: Raman spectrum of the 40.9 mol% Na₂O glass illustrating different aspects of the fits to the spectrum first
484 published by Neuville (2006). (a) A two peak fit to the spectrum where one peak is constrained to fit the
485 low frequency side of the spectrum (Pk#1) and the other was constrained to fit the high frequency side
486 (Pk#2). (b) A least squares three peak fit to the spectrum where the Q² and Q³ peaks were constrained as in
487 Fig. 2a. (c) A least squares, 5 peak fit to the spectrum where the peak at ~860 cm⁻¹ is attributed to Q¹
488 species, the Q² and Q³⁻¹ peaks are constrained as in Fig. 2a and the Q³⁻² and Q³⁻³ peaks are constrained
489 to the same line shape and FWHM as the Q³⁻¹ peak. (d) The same as Fig. 2d except for the addition of
490 peak Q³⁻⁴. Its line shape and FWHM were constrained to those of the Q³⁻¹ peak.

491Fig. 3: Illustrates the distribution of Q species as a function of composition. (a) the Q⁴ species abundances versus
492 composition where the solid circles and diamonds represent Q⁴ mol% measured using the ²⁹Si static NMR
493 technique. The other symbols were obtained using ²⁹Si MAS NMR. The dashed and solid curves are
494 respectively power law ($y = ax^n$) and exponential ($y = ae^{nx}$) fits to the solid symbols. The power law fit
495 yielded $a = 4.59 \times 10^{11}$ and $n = -7.04$. For the exponential fit, $a = 4.23 \times 10^3$ and $n = -0.187$. R² for both fits is
496 0.993. (b) Illustrates experimental and calculated Q species abundances. Experimental data are from Table
497 3. All Open and solid symbols are from Stebbins (1987) with K₃ = 0.011 and 0.014 respectively. Shaded
498 symbols are from other sources (see Table 3). Dashed and solid curves are Q species abundances calculated
499 with K₃ = 0.011 or 0.014. Solid and dashed curves represent calculated Q species abundances. (c)
500 Illustrates experimental oxygen species abundances from Nesbitt et al. (2015). The solid and dashed curves
501 are calculated oxygen species abundances obtained with two sets of equilibrium constants, once consistent
502 with K₃ = 0.011 and one with K₃ = 0.014.

503Fig. 4: Raman spectrum of the 40.9 mol% Na₂O glass illustrating a two peak fit where the Q³ band is asymmetric.
504 The Q² peak intensity is 29.1%. The Q³ asymmetric peak intensity is 70.1% but the Q⁴ peak resides under it
505 and represents ~2.1% of the total intensity so that Q³ intensity = 68.9% and Q⁴ = 2.1%. Note that Q¹ peak
506 has not been included in the fit.

507 **Appendix A**

508 **Oxygen species concentrations**

509 Sawyer et al. (2015, their Appendix A) developed equations to calculate mole fractions of all oxygen
 510 species in melts or glasses based on Q species abundances but note that Equation (A3) of Sawyer et al. (2015,
 511 Appendix A) should read:

512
$$N_{BO}/N_{NBO} = [(4Q^4 + 3Q^3 + 2Q^2 + 1Q^1 + 0Q^0)/2]/(1Q^3 + 2Q^2 + 3Q^1 + 4Q^0) \quad (A1)$$

513 **Sensitivity of O²⁻ to Q species abundances in 40.9% Na₂O glass**

514 Table A1: O²⁻ content from Q species

| Q ² % ^(a) | Q ³ % ^(a) | Q ⁴ % ^(a) | O ²⁻ % ^(b) |
|---------------------------------|---------------------------------|---------------------------------|----------------------------------|
| 28.0 | 69.9 | 2.1 | 2.3 |
| 29.0 | 68.9 | 2.1 | 2.1 |
| 30.0 | 67.9 | 2.1 | 2.0 |
| 31.0 | 66.9 | 2.1 | 1.8 |
| 32.0 | 65.9 | 2.1 | 1.6 |
| 33.0 | 64.9 | 2.1 | 1.4 |
| 40.5 | 57.4 | 2.1 | 0.0 |

515 (a) mol% of Q species.

516 (b) mol% of free oxygen = 100•X_{O2}. where X
 517 is the mole fraction of O²⁻ per mole of O.

518
 519 There is a quick calculation for the mole fraction of free oxygen: X_{O2} = 1 - (N_{Qtotal}/N_{Ototal}) where:

520 X_{O2} is the mole fraction of O²⁻ (or equivalently, Na₂O_m) in a glass.

521 N_{Qtotal} = 3.0X_{Q2} + 2.5X_{Q3} + 2.0X_{Q4}. The numerical coefficients are the number of moles of O per mole of Si in each
 522 Q species and X is the mole fraction of the Q species.

523 N_{Ototal} is the total moles of O per mole of Si in the glass. For a 40.9% Na₂O glass, expressed as Na_{1.38}SiO_{2.69}, N_{Ototal}
 524 = 2.69.

525 EXAMPLE: For the first row in the above Table and after conversion of Q species mol% to mole fractions: X_{O2} =
 526 1 - [3.0(0.28) + 2.5(0.699) + 2.0 (0.021)]/2.69 = 0.023.

527