An $^{17}$O NMR Investigation of Crystalline Sodium Metasilicate: Implications for the Determination of Local Structure in Alkali Silicates

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Crystalline sodium metasilicate, Na$_2$SiO$_3$, has been investigated by $^{29}$Si, $^{23}$Na, and $^{17}$O MAS NMR spectroscopy. The $^{17}$O quadrupolar coupling parameters have been measured for the bridging oxygen (BO) and nonbridging oxygen (NBO) sites. Ab initio calculations have also been performed for clusters modeling these oxygen sites, as well as other sites in crystalline silicates of known structure. On the bases of ab initio calculations, parametrized equations are discussed which describe trends in the BO $^{17}$O quadrupolar coupling parameters. The agreement between these parametrized equations and reported values for a variety of crystalline environments is shown to be quite good. The ab initio calculated NBO $^{17}$O quadrupolar coupling parameters are also in agreement with measured results for Na$_2$SiO$_3$ and analogous crystalline alkali silicates such as $\alpha$-Na$_2$Si$_2$O$_5$ and Li$_2$Si$_2$O$_5$.

1. Introduction

A multinuclear NMR investigation can provide a comprehensive description of local structure around a variety of atoms in a material, even in the absence of long range order. Advances in solid-state NMR$^{1-3}$ during the past decade have greatly improved this approach, placing quadrupolar nuclei such as $^{17}$O, $^{23}$Na, and $^{11}$B nearly on par with more commonly studied spin $\frac{1}{2}$ nuclei such as $^1$H, $^{13}$C, $^{29}$Si, and $^{31}$P. The remaining task, however, is to bring our understanding of the relationships between the NMR parameters of quadrupolar nuclei and local structure to the same level that currently exists for spin $\frac{1}{2}$ nuclei.

Because of the historical difficulties associated with doing $^{17}$O solid-state NMR, relatively little is known of the relationships between $^{17}$O NMR parameters and structure when compared to the more commonly used spin $\frac{1}{2}$ probes. Investigations by Tossell and co-workers$^{4-6}$ were one of the earliest to have shown that ab initio quantum mechanical calculations can be a powerful tool for researchers trying to connect measured $^{17}$O NMR parameters to structural features. Indeed, the ab initio trends predicted in $^{17}$O quadrupolar coupling parameters with Si–O–Si bond angle by Tossell and co-workers have been experimentally verified using $^{17}$O DAS,$^7$ and these theoretically derived trends have been indispensable in quantifying structural distributions in silicate glasses.$^8$

A crucial step in confirming theoretically derived trends between NMR parameters and structure is to compare experimental results obtained for crystalline compounds with those predicted by calculations. At present, the agreement between experimental and theoretical results for relatively simple oxygen environments, such as bridging oxygen sites in SiO$_2$ polymorphs, has been quite good.$^9$ Although ab initio calculations have been performed for more complex oxygen environments which include modifier cations,$^{10}$ it is important to determine how well these calculated trends are in agreement with experimental results.

The experimentally determined $^{17}$O quadrupolar coupling parameters of Na$_2$SiO$_3$, reported here, allow us to consider oxygen sites which are more structurally complex. For example, the bridging oxygen site in Na$_2$SiO$_3$ is coordinated by two sodium cations, each at a distance of 2.40 Å, and two silicon atoms, both at a distances of 1.62 Å, considerably longer than Si–O distances found in SiO$_2$ polymorphs such as quartz, cristobalite, or coesite. The nonbridging oxygen site is also remarkable because it is, to our knowledge, a rare example of a nonbridging oxygen site in an alkali silicate for which a known crystal structure exists and a reliable measurement of the $^{17}$O NMR chemical shift, quadrupolar coupling constant, and asymmetry parameter may be readily obtained since the bridging oxygen and nonbridging oxygen resonances are well resolved. In previous studies$^{11}$ severe overlap of bridging and nonbridging resonances in combination with the inherent low sensitivity of $^{17}$O solid-state NMR made the determination of NMR parameters, particularly the quadrupolar coupling asymmetry parameter somewhat suspicious.

Thus, Na$_2$SiO$_3$ is ideally suited for an investigation which continues the process of joining experimentally determined $^{17}$O quadrupolar coupling parameters, ab initio calculations, and a discussion of local structure at oxygen sites. In the present multinuclear NMR investigation, $^{29}$Si and $^{23}$Na results also serve to confirm the identity of the sample. The $^{17}$O results for the bridging and nonbridging oxygen sites in Na$_2$SiO$_3$ are then
TABLE 1: Experimental NMR Parameters in NaSiO₃ Obtained from Lineshape Analyses

<table>
<thead>
<tr>
<th>nucleus</th>
<th>chemical shift parameters</th>
<th>quadrupole coupling parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δₑ, ppm</td>
<td>Δₑ, ppm</td>
</tr>
<tr>
<td>²³Na</td>
<td>22.1 ± 0.5</td>
<td>-76.7 ± 0.2</td>
</tr>
<tr>
<td>²⁹Si</td>
<td>-76.7 ± 0.2</td>
<td>-76 ± 10</td>
</tr>
<tr>
<td>¹⁷O</td>
<td>63 ± 2</td>
<td>39 ± 2</td>
</tr>
</tbody>
</table>

* The simulations of the experimental spectra were performed using a modified version of the Bruker WinFit software package. Simulation conditions included second-order quadrupolar broadened line shapes under infinite spinning speed conditions. Gaussian distributions in Cₑ with a standard deviation of σ = 0.19 and 0.09 MHz were used for simulating the NBO ¹⁷O and ²³Na resonances, respectively. A Herzfeld–Berger analysis of the spinning sidebands for the ²⁹Si spectrum was performed to obtain the chemical shift anisotropy (CSA) parameters.

2. Experimental Methods

2.1. Sample Synthesis. Approximately 40% ¹⁷O-enriched SiO₂ powder was prepared by the hydrolysis of SiCl₄ with H₂O. Crystalline Na₂SiO₃ was prepared by initially decarbonating a mixture of 17 O-enriched SiO₂ with a stoichiometric quantity of Na₂CO₃ and 0.1% cobalt oxide (to decrease T₁) at 1033 K for 15 h. The sample was then reground and recrystallized at the same temperature for 15 h. All heating took place under Ar gas. Due to the hygroscopic nature of the product, care was taken to avoid exposing the sample to the atmosphere and an Ar-gas substituted glovebox was utilized during the handling of the sample, i.e., the rotor packing for the nuclear magnetic resonance (NMR) measurements. This synthesis procedure results in single phase polycrystalline Na₂SiO₃, as confirmed by X-ray diffraction, and the identity and purity of the crystalline sample used in this investigation has been confirmed by X-ray diffraction. ²³Na MAS NMR spectroscopic results.

2.2. NMR Spectroscopy. ²³Na, ²⁹Si, and ¹⁷O magic angle spinning NMR experiments were performed at 9.4 T on a Chemagnetics CMX II spectrometer using a home-built probe. Experiments were done at ambient temperature with sample spinning rates between 12 and 14 kHz, unless otherwise noted. Samples were contained in a silicon nitride rotor with a 4 mm diameter. Recycle times were obtained using a saturation recovery experiment. Chemical shift data references are 1M NaCl for ²³Na, TMS for ²⁹Si and tap water for ¹⁷O. The ²³Na spectrum was acquired using a Bloch decay sequence with a flip angle below ½π (pulse length of 0.5 microseconds), a recycle delay of 1.0 s, and a spectral width of 50 kHz. The ²⁹Si spectrum was also acquired using a Bloch decay sequence with a nonselective pulse length of 0.54 microseconds, a recycle delay of 15.0 s, and a spectral width of 25 kHz. An echo sequence (90°-π-180°-acquire) was used to collect the ¹⁷O spectrum with a ½π and π pulse lengths of 7.0 and 14.0 microseconds, respectively, an echo shift of 9.0 milliseconds, a recycle delay of 660 s, and a spectral width of 20 kHz. The experimental NMR spin coupling parameters obtained from line shape analyses of these three spectra are given in Table 1.

3. Theoretical Methods

Ab initio calculations were performed using GAUSSIAN 94 at a restricted Hartree–Fock level with a 6-31+G(d) basis set used for all atoms. GAUSSIAN 94 calculates the traceless electric field gradient (eFG) tensor and outputs its Cartesian tensor elements. These calculated eFG tensor elements are related to the quadrupolar coupling constant Cₑ and quadrupolar coupling asymmetry parameter ηₑ according to

\[ C_e = e^2 Q(q_{zz})/h, \quad \eta_e = \langle q_{zz} \rangle, \quad \eta_q = \langle q_{zz} \rangle - \langle q_{xy} \rangle/\langle q_{zz} \rangle \] (1)

where \( e(q_{zz}), e(q_{xy}), \) and \( e(q_{zw}) \) are the principal components of the electric field gradient tensor defined such that \( \langle q_{zz} \rangle > \langle q_{xy} \rangle > \langle q_{zw} \rangle \) and \( Q \) is the nuclear electric quadrupole moment. For ¹⁷O, a value of \( e^2Q/h = -6.11 \text{ MHz a.u.}^3 \) was used to convert the \( q_{zz} \) output from Gaussian into the ¹⁷O quadrupolar coupling constant.

As noted by Xue and Kanzaki, the nuclear quadrupole moment cannot be directly measured and is typically derived from the experimental \( C_e \) value and the calculated EFG for the free atom. The \( eQ \) value is therefore dependent on the manner in which the EFG is calculated, i.e., the basis set(s) and method employed, and it has been common in many ab initio studies to treat the \( eQ \) value as an adjustable parameter when calculating the quadrupolar coupling constant. In this work we have chosen to calibrate the absolute \( C_e \) values obtained by ab initio methods with several experimental results, an approach consistent with a previous investigation.

Model clusters were constructed to represent the oxygen environments in Na₂SiO₃ and other silicates. The clusters used to model bridging oxygen environments are similar to those described previously with hydrogen atoms being added to terminate dangling oxygen bonds. A variety of clusters were employed for the study of nonbridging oxygen sites. The justification for the construction of these model clusters is addressed below.

4. Experimental Results and Discussion

4.1. Sodium-23. The ²³Na MAS NMR spectrum obtained in the present investigation is shown in Figure 1. On the bases of diffraction studies, we expect one sodium site in Na₂SiO₃, coordinated by five oxygen atoms with Na–O distances ranging from 2.2 to 2.5 Å. This site has a geometry of a distorted trigonal bipyramidal and four of the oxygen coordinated to the sodium are nonbridging oxygen with the fifth being a bridging oxygen. Fitting the ²³Na spectrum to a single site, however, gives a somewhat unsatisfactory result and suggests a sodium site which is at least partially disordered. A spectrum similar in appearance was reported by Xue and Stebbins and the line shape attributed...
Figure 2. $^{29}$Si MAS NMR spectrum collected for crystalline Na$_2$SiO$_3$ at high and low spinning speeds, approximately 12 and 2.1 kHz, respectively. In (a) a narrow region of the spectrum at high spinning speed is shown which includes the resonance from the silicon site in Na$_2$SiO$_3$. The spectrum (b), at low speed, includes signal from the silicon nitride rotor and the sample. In each plot the experimental data is shown along with a simulation fitting the data. Components of the simulation are shown below the spectrum.

Local Structure in Alkali Silicates

It is evident from the $^{23}$Na electric field gradient can be comparable to contributions from higher coordination sphere structures around sodium to the $^{23}$Na electric field gradient can be comparable to contributions from higher coordination sphere structures, making it difficult to more precisely predict the local structure of sodium sites based solely on the quadrupolar coupling parameters.

4.2. Silicon-29. The only silicon site in Na$_2$SiO$_3$ is a tetrahedrally coordinated Q$^2$ site. A high spinning speed (12 kHz) spectrum showing only the region containing the resonance from the silicon site in Na$_2$SiO$_3$ is shown in Figure 2a. The full spectrum collected at a low spinning speed of 2.1 kHz is shown in Figure 2b and includes an additional peak at approximately $-50$ ppm attributed to the silicon nitride rotor. The $^{29}$Si isotropic chemical shift, chemical shift tensor axiality, and chemical shift tensor asymmetry parameters of $\delta_{iso}$, $\Delta^{si}$ = $-76.7$ ppm, $\Delta^{si}$ = $-76 \pm 10$ ppm, and $\eta^{si} = 0.7 \pm 0.3$, respectively, were measured for the Na$_2$SiO$_3$ sample from the high speed spectrum and by fitting of the sidebands present in the low spinning speed spectrum. The previously reported chemical shift parameters for Na$_2$SiO$_3$, i.e., $\delta_{iso} = -77.6$ ppm, $\Delta^{si} = -78$ ppm, and $\eta^{si} = 0.52 \pm 0.3$, are in good agreement with the values reported here.

In general, silicon tetrahedrally coordinated by oxygen have $\delta_{iso}$ values in the range of $-60$ to $-120$ ppm, and those in a Q$^3$ environment within the range of $-74$ to $-95$ ppm. The axiality and the asymmetry parameters, which are defined elsewhere, are sensitive to the Q-species of the silicon atoms. For example, both Q$^{10}$ and Q$^{15}$ species have low $\Delta^{si}$ values due to their highly symmetric environments. It is also possible to distinguish Q$^3$ species, which have large $\eta$ values, from Q$^1$ or Q$^{15}$ environments which have $\eta$ values near zero. A $\Delta^{si}$ value between $-50$ and $-90$ ppm and the large $\eta$ value reported for the silicon site in Na$_2$SiO$_3$ is typical of Q$^2$ sites in alkali silicates. As expected, all three $^{29}$Si chemical shift parameters in Na$_2$SiO$_3$ are in good agreement with those of other Q$^2$ environments.
Si atoms in a Q (2) environment.

by a broad, lower intensity resonance with a oxygen sites are given in Table 1. The spectrum is characterized from the line shape simulation for the bridging and nonbridging the chemical shift and quadrupolar coupling parameters derived

Figure 4. Plot of $^{17}$O chemical shift versus average metal-ion radius in (a) alkali and (b) alkaline earth silicates. Bridging and nonbridging oxygen are shown as open and filled symbols, respectively, in both plots. The Na$_2$SiO$_3$ results from this investigation are represented as a star. Results for (Na,K$_{1-x}$)$_2$Si$_2$O$_5$ glasses and crystalline alkali disilicates and for crystalline alkaline earth silicates are shown as squares. The nonbridging oxygen site in Li$_2$Si$_2$O$_5$ (an outlier) is shown as an open square. Best fit lines for the BO and NBO are $y = 13.6x + 46.4$ ($r^2 = 0.972$) and $y = 105x - 83.5$ ($r^2 = 0.985$), respectively, for the alkali silicates, and $y = 15.2x + 52.8$ ($r^2 = 0.905$) and $y = 128x - 50.4$ ($r^2 = 0.875$), respectively, for the alkaline earth silicates. Effective ionic radii data are from ref 34.

Figure 3. $^{17}$O MAS NMR spectrum for Na$_2$SiO$_3$. The experimental data is shown along with a simulation fitting the data. Components of the simulation are shown below the spectrum. Details of the numerical simulation are given in the caption of Table 1.

4.3. Oxygen-17. There are two oxygen sites in Na$_2$SiO$_3$, a bridging oxygen site and a nonbridging oxygen site, present in the BO/NBO ratio of 33/67. The bridging oxygen links two SiO$_4$ tetrahedra and is also coordinated by two sodium cations that are each 2.4 Å from the bridging oxygen. The nonbridging oxygen is coordinated by four sodium cations and these cations, together with the silicon, form a distorted trigonal bipyramidal structure. The Si=OBO distance is 1.592 Å, a value typical of Si atoms in a Q$^2$ environment.

The $^{17}$O MAS NMR spectrum is presented in Figure 3 and the chemical shift and quadrupolar coupling parameters derived from the line shape simulation for the bridging and nonbridging oxygen sites are given in Table 1. The spectrum is characterized by a broad, lower intensity resonance with a $C_q$ value of 4.20 MHz and a $\delta^{(17)}_{iso}$ value of 63 ppm, and a narrow higher intensity resonance with a $C_q$ value of 2.43 MHz and a $\delta^{(17)}_{iso}$ value of 39 ppm. The ratio of integrated intensities of the two line shapes is approximately 40/60 and are assigned to the bridging and nonbridging oxygen sites, respectively. This assignment is also consistent with the respective quadrupolar coupling constants and chemical shifts for the two resonances. While a good fit to the bridging oxygen line shape was obtained assuming a single site, a less than satisfactory fit to a single site was obtained for the nonbridging oxygen line shape. An improved fit to the nonbridging oxygen line shape, shown in Figure 3, was obtained using a Gaussian distribution in $C_q$ values centered about 2.43 MHz with a standard deviation of 0.15 MHz. This implies that there may be partial disordering of sodium primarily about the nonbridging oxygen, and would also be consistent with the disorder implied by the $^{23}$Na spectrum.

In general, the quadrupolar coupling constant of the non-bridging oxygen is expected to be approximately half of that for the bridging oxygen in silicates. This factor of 2 difference follows from a simple point charge model of the electric field gradient where the nonbridging oxygen is coordinated by one silicon instead of two. Much more subtle structural details around each of these sites, however, can be determined from the quadrupolar coupling parameters, and this will be discussed in the next section.

As with the $^{29}$Si chemical shift, it is expected that the paramagnetic contribution to the $^{17}$O chemical shift will be more sensitive to structural changes around oxygen than the diamagnetic contribution. Thus it is not surprising that, just like $^{29}$Si, strong linear correlations exist between $^{17}$O chemical shift and bond distances in the first coordination sphere. This trend is strongly pronounced for oxygen coordinated by alkaline earth cations in the series BeO, MgO, CaO, SrO, and BaO, or for the group IIB oxides in the series ZnO, CdO, HgO. Timken et al. first observed this trend in a series of alkaline earth metasilicates for both bridging and nonbridging oxygen, although the effect was more pronounced for the nonbridging oxygen. A similar trend appears for oxygen coordinated by alkali cations, although the effect is less pronounced, as demonstrated by Maekawa et al. in a series of crystalline and glassy alkali disilicates. This trend in alkali silicates is most apparent in the $^{17}$O DAS results for a series of mixed alkali (sodium or potassium) disilicate glasses by Vermillion et al. These results, which are summarized in Figure 4 for bridging and nonbridging oxygen sites modified by alkali and alkaline earth cations, clearly demonstrate the strong correlation between the $^{17}$O chemical shift and structural features in the first coordination sphere.

In contrast to $^{17}$O quadrupolar coupling parameters, the use of $^{17}$O isotropic chemical shifts as a probe of more subtle structural features has been elusive as it is becoming apparent that structural variations out to third coordination sphere can...
work on 17O chemical shifts is currently in progress. To obtain the bridging oxygen with hydrogen atoms. These clusters were used, after geometry oxygen sites were constructed by placing atoms in their example, in coesite the experimentally measured 17O isotropic

<table>
<thead>
<tr>
<th>TABLE 2: 17O Experimental and ab Initio Calculated Results for the Bridging Oxygen Sites in Crystalline Silica Polymorphs and Alkali Silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>bridging oxygen environment</strong></td>
</tr>
<tr>
<td><strong>compound</strong></td>
</tr>
<tr>
<td>α-quartz</td>
</tr>
<tr>
<td>cristobalite</td>
</tr>
<tr>
<td>coesite</td>
</tr>
<tr>
<td>14.53</td>
</tr>
<tr>
<td>14.46</td>
</tr>
<tr>
<td>137.22</td>
</tr>
<tr>
<td>Li2SiO4</td>
</tr>
<tr>
<td>Na2SiO3</td>
</tr>
<tr>
<td>α-Na2Si2O5</td>
</tr>
<tr>
<td>K2SiO4</td>
</tr>
<tr>
<td>147.79</td>
</tr>
<tr>
<td>141.79</td>
</tr>
</tbody>
</table>

Model clusters used in the ab initio calculations are denoted in column 6, and the ratio value in last column refers to C_q (experimental)/C_q (calculated).

also have a significant influence on the chemical shift. For example, in coesite the experimentally measured 17O isotropic chemical shifts for the bridging oxygen appear to be entirely uncorrelated to Si–O–Si angle and Si–O distance. Xue and Kanzaki performed ab initio calculations employing clusters expanded out to four coordination spheres to model each of the silicate bridging oxygen linkages in coesite and found that while the 17O C_q and η values converged within the first coordination sphere of each oxygen, it was necessary to extend the cluster calculations out to higher coordination spheres to obtain qualitative agreement with the 17O isotropic chemical shifts. In work by Bull et al. complete coordination spheres around each oxygen site were needed in an ab initio calculations to obtain reasonable agreement with experimentally observed 17O chemical shifts in siliceous zeolite faujasite. As a result of this strong dependence of 17O chemical shifts on structural variations beyond the first coordination sphere, we have limited our theoretical investigations in the next section to the 17O quadrupolar coupling parameters. Further theoretical work on 17O chemical shifts is currently in progress.

5. Theoretical Results and Discussion

We employed ab initio calculations on model clusters depicting the bridging oxygen and the nonbridging oxygen sites and compared these to 17O quadrupolar coupling parameters measured in crystalline compounds of known structure. Thus, in addition to Na2SiO3 results presented here, we have used the specific oxygen geometries found in the crystalline compounds α-quartz, cristobalite, coesite, α-Na2Si2O5, Li2SiO4, and K2SiO4, whose crystal structures are known and the NMR parameters for the oxygen sites have been experimentally determined.

5.1. Bridging Oxygen. Clusters modeling the bridging oxygen sites were constructed by placing atoms in their crystallographic lattice positions and capping dangling oxygen with hydrogen atoms. These clusters were used, after geometry optimization of hydrogen positions only, in ab initio calculations to obtain the bridging oxygen C_q and η values. Selected structural parameters for the bridging oxygen sites are given in Table 2.

As expected, the calculated C_q values need to be scaled to bring them into agreement with the experiments. All scalings, shown in Table 2, fall into a narrow range centered around 0.89, indicating that the clusters used in these calculations are reasonable models for the different oxygen sites. With a few notable exceptions there is generally good agreement between the experimental and ab initio predicted quadrupolar coupling parameters for each site. There is good agreement between calculated η values and experiment for all the crystalline silica polymorphs, and again with a few notable exceptions, there is also good agreement between calculated and experimental η values for all alkali silicates. The exceptions occur in cases where severe overlap of bridging and nonbridging resonances in combination with the inherent low sensitivity of 17O solid-state NMR made the experimental determination of η problematic.

5.1.1. General Trends. In general, there are a number of structural features that play a role in determining the 17O quadrupolar coupling parameters of the bridging oxygen, with the most significant features occurring in the first coordination sphere of the bridging oxygen. The relevant features are the nature of the two coordinating network forming cations, and the nature and number of coordinating network modifier cations. For the quadrupolar coupling parameters contributions from beyond the first coordination sphere of the bridging oxygen appear to be secondary in importance. For example, Xue and Kanzaki performed ab initio calculations employing clusters expanded out to four coordination spheres to model each of the silicate bridging oxygen linkages in coesite and obtained a slightly improved agreement with the experimental trends, with corrections on the order of a few percent in the 17O C_q and η values.

Taking these first coordination sphere structural features into account, we employ the following general expression for the 17O quadrupolar coupling parameters of a bridging oxygen in an alkali silicate:

\[ C_q(\Omega, n_M) = a \left( \frac{1}{2} - \frac{\cos\Omega}{\cos\Omega - 1} \right)^\alpha + n_M \Delta C_q^M \] (2)

\[ \eta_q(\Omega, n_M) = b \left( \frac{1}{2} - \frac{\cos\Omega}{\cos\Omega - 1} \right)^\beta + \Delta \eta_q^M(n_M) \] (3)

Here \( \Omega \) is the Si–O–Si angle, \( n_M \) is the number of coordinating alkali metal cations, and \( \Delta C_q^M \) and \( \Delta \eta_q^M \) are the shifts in C_q and η_q.
with increasing modifier field strength and coordination. Two expressions. This implies, however, that the 17 O quadrupolar coupling constant is also linearly dependent on the Si-O-Si angle.

TABLE 3: Best Fit Parameters for Equations 2 and 3, and the Linear Fit to the C_q and η_q ab Initio Data (C_q Scaled by 0.88) for Clusters with Zero, One, or Two Coordinating Alkali Cations  

<table>
<thead>
<tr>
<th>Cation(s)</th>
<th>C_q dependence</th>
<th>η_q dependence</th>
<th>C_q, η_q correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>a = -5.85 MHz</td>
<td>α = 1.18 MHz</td>
<td>ΔC_q^M = 0.00 MHz</td>
</tr>
<tr>
<td>Li^+ (d_{LiO} = 2.0 Å)</td>
<td>-5.85 MHz</td>
<td>1.70 MHz</td>
<td>-0.66 MHz</td>
</tr>
<tr>
<td>Na^+ (d_{NaO} = 2.5 Å)</td>
<td>-5.85 MHz</td>
<td>1.69 MHz</td>
<td>-0.43 MHz</td>
</tr>
<tr>
<td>K^+ (d_{KO} = 2.8 Å)</td>
<td>-5.85 MHz</td>
<td>1.70 MHz</td>
<td>-0.21 MHz</td>
</tr>
</tbody>
</table>

η_q due to the presence of these alkali cations coordinated at their equilibrium distances. The parameters a, α, b, and β are additional adjustable parameters that have been calibrated using both experiment and ab initio calculations. Of course, these expressions are by no means unique in their ability to describe these relationships, and other expressions have been used previously.38,40 On the bases of these relationships, a plot of C_q versus η_q is also expected to be nearly linear for bridging oxygen clusters, with the C_q-intercept decreasing in magnitude with increasing modifier field strength and coordination.

As discussed by Clark and Grandinetti,28 the quadrupolar coupling constant is also linearly dependent on the Si-O distance. This dependence, however, is not explicitly indicated in equations 2 and 3, but rather is included implicitly by assuming that the Si-O distance is energetically constrained by the Si-O-Si angle as described by Newton and Gibbs.50 Thus its effect is included in the adjustable parameters of the two expressions. This implies, however, that the 17 O quadrupolar coupling constant of bridging oxygen linking highly “strained” tetrahedra with Si-O distances deviating from the local energy minimum associated with a given bridging oxygen angle may not be well described by these equations. In such cases, the quadrupolar asymmetry parameter would serve as a better probe of the Si-O-Si angle.

These relationships were calibrated by performing ab initio calculations for the model clusters (OH)_3Si-O-Si(OH)_3, M(OH)_3Si-O-Si(OH)_3, and M_2(OH)_5Si-O-Si(OH)_3, where M = Na, Li, or K. A graphical representation of these various clusters is shown in Figure 5. Although previous results were obtained for clusters containing Li- and Na-cations10 we have extended these calculations to include the effects of coordination by K-cations. In each case, the Si-O-Si angle was varied between 120° and 180°. Modifying cations were placed at a distance typically observed in crystalline alkali silicates, i.e., 2.0 Å for the Li-cluster, 2.5 Å for the Na-cluster, and 2.8 Å for the K-cluster. The best fit of the ab initio data to eqs 2 and 3 yields the parameters in Table 3, and the associated best fit curves are shown as solid lines in Figure 6. Experimental and calculated results are also included for bridging oxygen sites in alkali silicate compounds. For comparison, results are also provided for silicate samples which do not have modifiers present, i.e., coesite7 and cristobalite.31

With the exception of the O2 site in K_2Si_3O_8 (which is structurally unique, joining tetrahedrally and octahedrally coordinated Si-atoms), there is excellent agreement between the experimental C_q values and the predicted general trends. As shown in Figure 6, the experimental values are in agreement with the predicted trend in C_q, i.e., the experimental points are near the solid line which incorporates the best fit parameters listed in Table 3. For a variety of bridging oxygen sites the C_q parameter is systematically reduced in magnitude when modifying alkali cations are present, with this decrease being related to the cation’s field-strength.

Given that the general trends, which calculated using highly symmetric model clusters (shown in Figure 5), still apply to the wide range of structures found in crystalline compounds suggests that the C_q parameter is primarily dependent on the Si-O-Si angle, and the type and number of modifier cations present. Within the range of geometries characteristic of crystalline alkali silicates, other structural features, such as cation orientation, appear to have a relatively minor influence on C_q.10 Thus these results confirm that the C_q parameter can serve as a reliable probe of the Si-O-Si angle and the number of coordinating modifiers for the bridging oxygen in alkali silicates over a wide range of geometries.

In general, the experimental results for the asymmetry parameter follow the general trends with the magnitude of η_q increasing for a given Si-O-Si bond angle when alkali modifiers are present. There are, however, a few notable exceptions. Both of the η_q values for bridging oxygen sites in Li_2Si_3O_8 are far from the expected values; the experimental value for the bridging oxygen site with a single Li modifier is much too low (Figure 6b) and the second site, which does not include a modifying cation, has an experimental value much too high (Figure 6b). The experimental results for these particular sites also diverge significantly from the predicted trends when plotting η_q versus C_q (Figure 6b). Not surprisingly, the ab initio calculated η_q values for bridging oxygen in clusters
designed to match the exact geometries of the bridging oxygen in each crystal structure are in excellent agreement with the general trends in every example considered, including the sites whose experimental $\eta_q$ values are in poor agreement with the general trends. This supports our argument that the experimental values for the outliers may be suspect. In general it is more difficult to extract precise $C_q$ values than $\eta_q$ values, suggesting that while the $C_q$ parameters for these sites may be correct, many $\eta_q$ values may require reconsideration. Indeed, inspection of the published experimental MAS spectrum for the Li$_2$Si$_2$O$_5$ sample reveals that the bridging oxygen site resonances are broadened, overlapping, and display marginal signal/noise, and thus are difficult to completely resolve. By combining recent advances such as RAPT or dynamic-angle spinning or FASTER with multiple-quantum magic-angle spinning these compounds should be revisited for a more accurate $\eta_q$ measurement.

5.2. Nonbridging Oxygen. A limited number of $^{17}$O experimental results are found in the literature for nonbridging oxygen sites in silicates, borosilicates, and aluminosilicates. If one considers only nonbridging oxygen sites in alkali silicates, the number of experimental results becomes even smaller. For this reason it is more difficult to establish trends between structure and NMR parameters in the same manner as was done for bridging oxygen sites, although a few general trends are apparent. As discussed above, the chemical shift values for nonbridging oxygen atoms in silicates are sensitive to the type of metal cation modifying the network. Also, the $C_q$ value for nonbridging oxygen sites is approximately one-half the magnitude (near 2.3 MHz) of that for bridging oxygen sites.

The NMR parameters are given in Table 4 for the nonbridging oxygen site in Na$_2$SiO$_3$. Parameters are also given for nonbridging oxygen sites in $\alpha$-Na$_2$Si$_2$O$_5$, Li$_2$Si$_2$O$_5$, and the number of experimental results becomes even smaller.

Figure 6. Comparison of general trends (solid lines), experimental (filled symbols), and calculated ab initio results (open symbols: $C_q$ scaled by 0.88). Experimental and ab initio predicted quadrupolar coupling parameters for specific bridging oxygen sites coordinated to no alkali cations are represented as squares, to one alkali cation as circles, and to two alkali cations as diamonds. In (a) are plots of quadrupolar coupling parameters of the silica polymorphs, in (b) are plots for the lithium silicate Li$_2$Si$_2$O$_5$, in (c) sodium silicates Na$_2$SiO$_3$, $\alpha$-Na$_2$Si$_2$O$_5$, and (d) potassium silicate O$_2$ site in K$_2$Si$_4$O$_9$. 
A simple point charge calculation one finds that the
the coordinating alkali cations as classical point charges. In such
efg principal axis system lies along the Si
principal axis system lies along the Si

The resulting geometry of cations about the nonbridging oxygen


and Li₂Si₂O₅ is not unexpected since the NBO sites in these
structures are comparable, i.e., they each have four modifier
cations.

In crystalline alkali silicates, nonbridging oxygen atoms are
typically coordinated to three, four, or five modifier cations. 33

The resulting geometry of cations about the nonbridging oxygen
is commonly trigonal bipyramidal or octahedral. In rare
instances, a distorted trigonal bipyramidal structure is observed
such that only three modifier cations are closely coordinated to
the nonbridging oxygen. These geometries are the result of
several constraints, including the need of the cations to
compensate the charge of the anion and also steric factors. To
understand the qualitative differences in quadrupolar coupling
parameters when NBO are coordinated by three, four, or five
alkali cations, we can assume that the z component for the NBO
efg principal axis system lies along the Si−O bond and treat
the coordinating alkali cations as classical point charges. In such
a simple point charge calculation one finds that the C₄ value is
largest for an octahedral geometry with five Na modifiers,
decreases for a tetrahedral geometry with three Na modifiers,
and is smallest for clusters with four modifiers. Differences in
the asymmetry parameter are also present, with η being near
zero for all of these geometries except the trigonal bipyramidal
structure with four modifiers. Deviations from these regular
coordination geometries and differences in the charges of the
cations will affect both quadrupolar coupling parameters.

To explore these effects in a more quantitative fashion one
needs to adopt a more rigorous theoretical approach. For example,
using periodic Hartree−Fock ab initio theoretical
methods Winkler et al. 56 calculated the electric field gradient
tensors for the three nonbridging oxygen sites in crystalline
forsterite, Mg₂SiO₄, and obtained excellent agreement with experiment. 54 As an alternative, we have taken the approach
employed for the bridging oxygen in the previous section,
namely, the nonbridging oxygen environment in Na₂SiO₃ was
modeled by examining the clusters shown in Figure 7. Using the
cluster [(OH)Si−O−Na₄] 3+ (Figure 7a) we examined the
effect of the first coordination sphere of the nonbridging oxygen
on its electric field gradient. The cluster [(OH)Si−O−(Na−
O−H)₂] 2− (Figure 7b) is larger and includes oxygen in the
second coordination sphere which are approximately 3.5 Å from
the nonbridging oxygen and also interstitial to the sodium.

The calculated quadrupolar coupling parameters are shown in Table
4. Hydrogen atoms were also added to this structure to terminate
dangling oxygen bonds and bring the charge of the cluster close
to neutral. In a similar manner, clusters representing the
nonbridging oxygen sites in α-Na₂Si₂O₅ and Li₂Si₂O₅ were
constructed. For each of these clusters four alkali cations are
located near the nonbridging oxygen and these cations, along
with the silicon, form a distorted trigonal bipyramidal geometry.

The calculated C₄ values for the nonbridging oxygen clusters
expanded to include oxygen atoms coordinated to the modifying
cations are in reasonable agreement, after scaling, with the
experimental data. All scalings, shown in Table 4, fall into a
narrow range, again indicating that the clusters used in these
calculations are reasonable models for the different oxygen sites.

When examining the calculated η values for the Na₂SiO₃-
clusters it becomes apparent that the ab initio results are
dependent on the cluster used to model the nonbridging oxygen
site. For the cluster [(OH)Si−O−Na₄] 3+ a nonzero η value of
0.42 is obtained, in agreement with the point charge model,
but much larger than the experimentally determined value of
0.17. With an increase of cluster size to [(OH)Si−O−(Na−
O−H)₂] 2−, η decreases to a value of 0.17 and is in closer
agreement with the experimental result. Calculations for even
larger model clusters, such as [(OH)Si−O−(Na−O−H)₄−
(H₂O)] 1−, also produced results within the standard error of
the experimental data and significantly increased the
computational cost. These findings were also noted for the disilicate
clusters, with calculated η values being difficult to reconcile
with experimental results for the clusters which do not include
oxygen atoms coordinated to the modifying cations.

It is not surprising that ab initio calculated η values for clusters which are extended to include the second nearest
neighbors about the nonbridging oxygen are in better agreement
with the experimental results than those which ignore the larger
coordination sphere. The need for larger clusters around
nonbridging compared to bridging oxygen is reasonable since the
first coordination sphere’s contribution to the nonbridging
oxygen efg is approximately half that of the bridging oxygen.

That is, higher coordination sphere structures have a greater
perturbative effect on the nonbridging oxygen efg than on the
bridging oxygen efg. Thus a larger cluster is required to properly
model the nonbridging oxygen efg. This is also a likely
explanation for the need to use slightly different scaling factors
to obtain agreement with experimental C₄ values for the
nonbridging oxygen compared to the bridging oxygen sites. In
general, the clusters used to model the nonbridging oxygen sites
in this investigation are comparable in size to those employed
in other investigations. 23 Although additional experimental data
for alkali silicates are required to more fully understand
the influence of modifying cations on 17O quadrupolar coupling
parameters, it is clear that quadrupolar coupling parameters
are calculable for both bridging and nonbridging oxygen sites
if the model cluster is of sufficient size.

### Table 4: Experimental and ab Initio Calculated Results for the Nonbridging Oxygen Sites in Alkali Silicates

<table>
<thead>
<tr>
<th>compound</th>
<th>experimental NMR parameters</th>
<th>ab initio predicted</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>δ Comet (ppm)</td>
<td>C₄ (MHz)</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>39 ± 2</td>
<td>2.43 ± 0.1</td>
</tr>
<tr>
<td>α-Na₂Si₂O₅</td>
<td>36 ± 2</td>
<td>2.40 ± 0.1</td>
</tr>
<tr>
<td>Li₂Si₂O₅</td>
<td>38 ± 2</td>
<td>2.45 ± 0.01</td>
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*a* Experimental results for α-Na₂Si₂O₅ and Li₂Si₂O₅ are from ref 11. Model clusters used in the ab initio calculations are denoted in column 5, and the ratio value in the last column refers to C₄ (experimental)/C₄ (calculated).
Conclusions

Using $^{23}$Na, $^{29}$Si, and $^{17}$O NMR the local environments of sodium, silicon and oxygen sites have been probed and the results discussed in relation to the reported crystal structure. By joining experimental and ab initio calculated results, we have described the relationship between structure and NMR parameters for bridging oxygen sites in alkali silicates. As suggested in an earlier investigation\(^{10}\), the magnitude of the $^{17}$O quadrupolar coupling constant and asymmetry parameter for bridging oxygen sites in alkali silicates is primarily influenced by the Si–O–Si bond angle. Alkali cations systematically shift the $C_q$ value for a given Si–O–Si bond angle lower in magnitude. This shift increases in magnitude as the field strength of the cation increases, or when the number of modifying increases from one to two. For a given Si–O–Si bond angle, $\eta_q$ is increased in magnitude by the presence of modifier cations. This increase is more pronounced when a single modifier cation (rather than two cations) is coordinated to the bridging oxygen. Parametrized equations for $C_q$ and $\eta_q$ calibrated using ab initio calculations on simple model clusters, have been confirmed by examining a variety of bridging oxygen environments in crystalline alkali silicates, including Na$_2$SiO$_3$, $\alpha$-Na$_2$Si$_2$O$_5$, and Li$_2$Si$_2$O$_5$. We have also demonstrated that clusters, expanded out to the second coordination sphere of a nonbridging oxygen, can also serve as effective models in ab initio calculations of $^{17}$O quadrupolar coupling parameters for nonbridging oxygen in solids.

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References and Notes