

# Dependence of bridging oxygen $^{17}\text{O}$ quadrupolar coupling parameters on Si–O distance and Si–O–Si angle

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Received 25 April 2003

Published 23 July 2003

Online at [stacks.iop.org/JPhysCM/15/S2387](http://stacks.iop.org/JPhysCM/15/S2387)

## Abstract

*Ab initio* quantum chemistry calculations and comparisons with experimental  $^{17}\text{O}$  solid-state nuclear magnetic resonance (NMR) investigations were used to determine the dependence of the  $^{17}\text{O}$  quadrupolar coupling constant and asymmetry parameter on the first-coordination-sphere structure around bridging oxygen. The quadrupolar asymmetry parameter was found to be dependent on the Si–O–Si angle, in agreement with previous studies, and independent of the Si–O distance. In contrast, the quadrupolar coupling constant was found to have a strong dependence on Si–O distance as well as Si–O–Si angle. Analytical expressions describing these dependences were proposed and used to develop an approach for relating measured  $^{17}\text{O}$  quadrupolar coupling constant and asymmetry parameter values for bridging oxygen to their Si–O–Si angle and average Si–O distance. Examples of this approach were given using  $^{17}\text{O}$  NMR results from the crystalline silica polymorphs, coesite,  $\alpha$ -quartz, cristobalite, and ferrierite.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

As a probe of local structure in network-forming oxide glasses,  $^{17}\text{O}$  nuclear magnetic resonance (NMR) spectroscopy has been an invaluable tool [1–10]. For bridging oxygen there are a number of structural features that play a role in determining the  $^{17}\text{O}$  quadrupolar coupling parameters, with the most significant features occurring in the first coordination sphere of the bridging oxygen. In the mid-1980s Oldfield and co-workers [11–13] clearly established on the basis of their  $^{17}\text{O}$  magic-angle spinning (MAS) NMR measurements that the electronegativity of the cations coordinated to a bridging oxygen atom is a primary factor influencing the magnitude of the  $C_q$ -parameter for the bridging oxygen. In a series of *ab initio* calculations

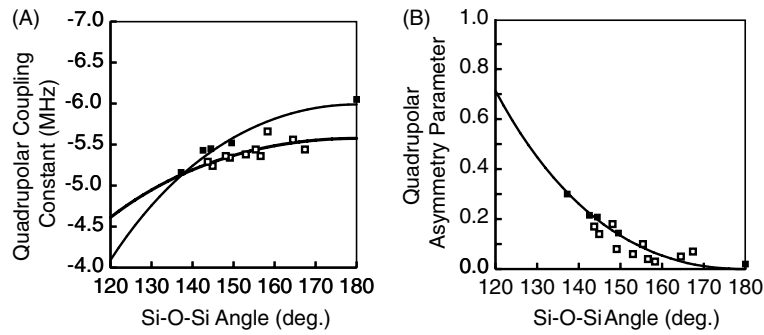
on model clusters focusing on the silicate bridging oxygen linkage Tossell and co-workers [14–16] predicted simple trends for the  $^{17}\text{O}$  quadrupolar coupling parameters with Si–O–Si angle. These trends were later experimentally confirmed by Grandinetti *et al* [17] in  $^{17}\text{O}$  dynamic-angle spinning (DAS) measurements on coesite.

In a more recent paper Clark and Grandinetti [18] used *ab initio* methods to study a number of clusters with the coordinating cations varied from group III to group VI and from periods 2 to 4 while simultaneously varying the network-forming cation–oxygen distance. A general trend was observed that the magnitude of  $C_q$  increases linearly with increasing network-forming cation–oxygen bond distance and cation group number, suggesting that group number and cation–bridging oxygen distance can serve as a better predictor of the bridging oxygen quadrupole coupling constant than electronegativity differences [12, 13].

Vermillion *et al* [19] further refined this understanding by examining the effect of additional coordination of the bridging oxygen by network-modifier alkali cations. They found that the previously established trend in  $^{17}\text{O}$   $C_q$  with Si–O–Si angle is systematically shifted to lower magnitudes with increasing number and field strength of coordinating alkali cations, and is relatively insensitive to variations in the alkali cation–bridging oxygen internuclear vector orientation. They also found that the previously established trend [14–16, 20] in  $^{17}\text{O}$  quadrupolar coupling asymmetry parameter,  $\eta_q$ , with Si–O–Si angle is systematically shifted to higher values by the presence of one coordinating alkali cation, and only slightly shifted to higher values by the presence of two coordinating alkali cations. As with the quadrupolar coupling constant, the magnitude of the shift in asymmetry parameter increases with increasing field strength of the coordinating alkali cation(s).

Thus, the first-coordination-sphere structural features that appear to be most important in determining the  $^{17}\text{O}$  quadrupolar coupling parameters of the bridging oxygen are the nature of the two coordinating network-forming cations, the T–O–T' linkage angle, the T–O bond distances, and the nature and number of coordinating network-modifier cations. Contributions from beyond the first coordination sphere of the bridging oxygen appear to be secondary in importance. For example, Xue and Kanzaki [21] 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 of the order of a few per cent in the  $^{17}\text{O}$   $C_q$ - and  $\eta_q$ -values.

In a recent article by Bull *et al* [22] a series of multi-field double-rotation (DOR) NMR and multiple-quantum magic-angle spinning (MQ-MAS)  $^{17}\text{O}$  NMR experiments were presented for a high-silica ferrierite sample and the isotropic chemical shift and the second-order isotropic quadrupolar shift for each of the ten crystallographically distinct bridging oxygen sites in ferrierite were extracted. To assist in the spectrum assignment a series of *ab initio* calculations of the  $^{17}\text{O}$  chemical shift and quadrupolar coupling parameters using clusters modelling each of the ten bridging oxygen environments out to four coordination spheres were made. Unfortunately, the sensitivity of the experimental  $^{17}\text{O}$  NMR data was insufficient for an unambiguous determination of the  $C_q$ - and  $\eta_q$ -values of the bridging oxygen sites in ferrierite and on the basis of chemical shift only a partial assignment of the resonances was possible. Nonetheless, on the basis of their *ab initio* calculations Bull *et al* [22] concluded that ‘no simple correlation appears to exist between the zeolite structure, such as the Si–O–Si bond angles or lengths, and the  $^{17}\text{O}$  NMR parameters’. On closer examination of their *ab initio* data, however, we find this is not quite the case. As can be seen in figure 1(A), there is a strong dependence on the calculated  $C_q$ -values in ferrierite on the Si–O–Si angle, although it is somewhat weaker than the dependence of the  $C_q$ -values in coesite on Si–O–Si angle. By fitting, separately, the experimental  $^{17}\text{O}$   $C_q$ -data from coesite and the *ab initio* calculated  $^{17}\text{O}$   $C_q$  from ferrierite to



**Figure 1.** Plots of (A)  $^{17}\text{O}$  quadrupolar coupling constants  $C_q$  versus Si–O–Si angle, and (B)  $^{17}\text{O}$  quadrupolar coupling asymmetry parameters  $\eta_q$  versus Si–O–Si angle that were experimentally measured [17] for the oxygen sites in coesite (filled squares) and calculated with *ab initio* methods [22] for the ten oxygen sites in ferrierite (open squares).

the modified semiempirical correlations [17, 19] given below,

$$C_q(\Omega) = a \left( \frac{1}{2} + \frac{\cos \Omega}{\cos \Omega - 1} \right)^\alpha, \quad (1)$$

$$\eta_q(\Omega) = b \left( \frac{1}{2} - \frac{\cos \Omega}{\cos \Omega - 1} \right)^\beta, \quad (2)$$

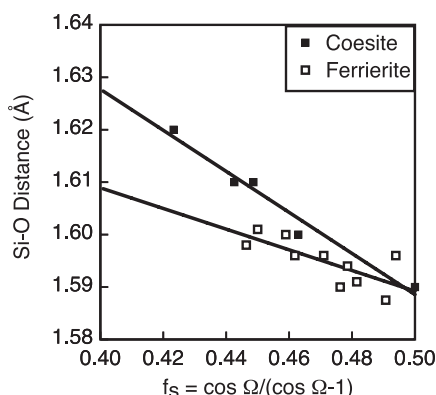
we obtain the correlations shown as the solid curves in figure 1. In figure 1(B) is the plot of calculated  $\eta_q$ -values of Bull *et al* [22] in ferrierite as a function of Si–O–Si angle. In contrast to the case for  $C_q$ , there is good agreement for both the experimental  $\eta_q$ -values for coesite and *ab initio* predicted  $\eta_q$ -values for ferrierite with equation (2).

The obvious question here is why the  $^{17}\text{O}$  quadrupolar coupling constant of the bridging oxygen in two pure silica compounds exhibit different trends as a function of  $\angle\text{Si–O–Si}$ . We show below that these differences arise from the strong dependence of the bridging oxygen  $C_q$  on the Si–O distance. As we have demonstrated elsewhere [18] the quadrupolar coupling constant has a strong linear dependence on the Si–O distance, of the order of  $13 \text{ MHz } \text{\AA}^{-1}$ . This dependence is not explicitly indicated in equations (1) and (2), but rather is included implicitly by assuming that the Si–O distance is energetically constrained by the Si–O–Si angle. This did not seem to be an unreasonable assumption, as correlations between Si–O distance and  $\angle\text{Si–O–Si}$  were well established [23, 24] in the literature. In this paper, we present the results of a series of *ab initio* quantum chemistry calculations of  $^{17}\text{O}$  quadrupolar coupling parameters for the Si–O–Si linkage where we eliminate this assumption and demonstrate how simultaneous measurements of the  $^{17}\text{O}$  quadrupolar coupling constant and asymmetry parameter of a bridging oxygen can be used to determine both the Si–O–Si angle and average Si–O distance.

## 2. Methods

*Ab initio* calculations were performed using Gaussian 94 [25] 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,  $C_q$ , and quadrupolar coupling asymmetry parameter,  $\eta_q$ , according to

$$C_q = e^2 Q \langle q_{zz} \rangle / h, \quad \text{and} \quad \eta_q = \frac{\langle q_{xx} \rangle - \langle q_{yy} \rangle}{\langle q_{zz} \rangle} \quad (3)$$



**Figure 2.** A plot of the average Si–O bond length for each bridging oxygen as a function of the fractional s character of the bridging oxygen,  $f_s$ .  $d_{\text{Si-O}}^{\text{coes}} = -0.3914388f_s + 1.784295$  and  $d_{\text{Si-O}}^{\text{fer}} = -0.1970883f_s + 1.687759$ .

where  $e\langle q_{xx} \rangle$ ,  $e\langle q_{yy} \rangle$ , and  $e\langle q_{zz} \rangle$  are the principal components of the efg tensor defined such that  $|\langle q_{zz} \rangle| > |\langle q_{yy} \rangle| > |\langle q_{xx} \rangle|$ , and  $Q$  is the nuclear electric quadrupole moment. For  $^{17}\text{O}$  a value of  $e^2Q/h = -6.11 \text{ MHz au}^3$  was used to convert the  $q_{zz}$ -output from a Gaussian to the  $^{17}\text{O}$  quadrupolar coupling constant. An additional scaling of 0.92 was employed to bring the coupling constant into agreement with experimental measurements [26].

### 3. Results and discussion

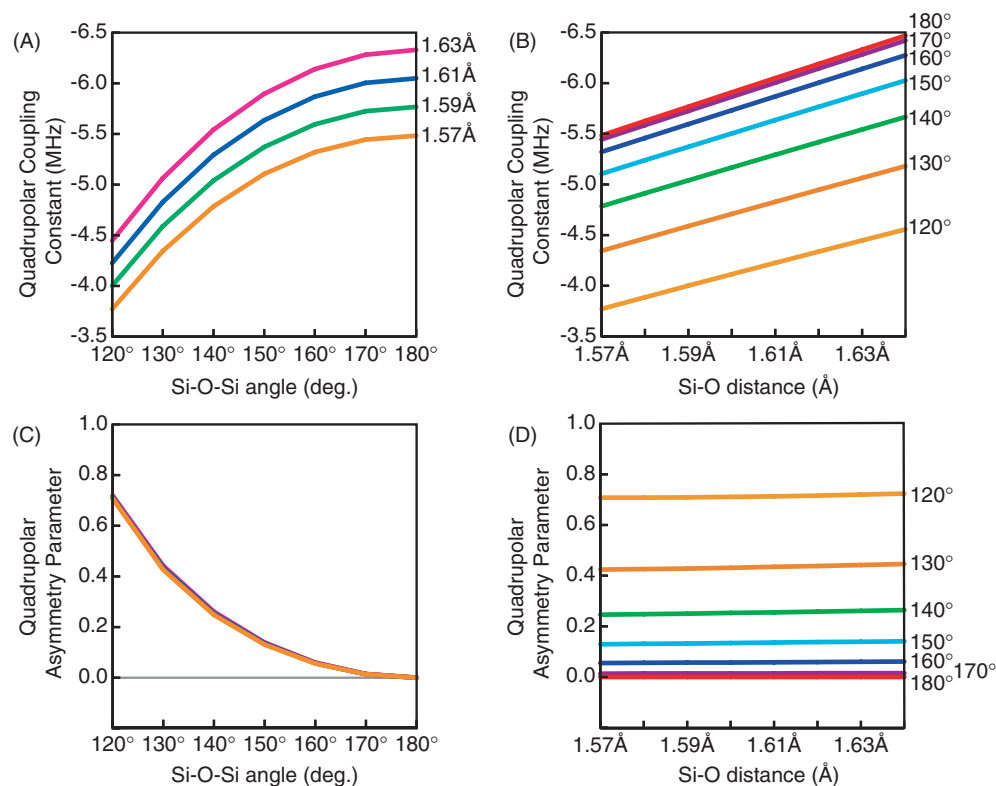
In a series of quantum chemistry calculations on the clusters modelling the bridging oxygen linkage Gibbs and co-workers [27, 28] showed that a two-dimensional energy surface as a function of Si–O distance and  $\angle\text{Si–O–Si}$  has minima that lead to a strong distance–angle correlation. They further showed that the silicon bridging oxygen distance in silicates follows a linear dependence on the s character of the bridging oxygen bonding orbital,  $f_s$ , which in turn varies as a function of the Si–O–Si angle according to

$$f_s(\Omega) = \frac{\cos \Omega}{\cos \Omega - 1}. \quad (4)$$

In figure 2 is a plot of the average Si–O bond length for each bridging oxygen as a function of the fractional s character of the bridging oxygen for each of the bridging oxygen sites in coesite and ferrierite. It is this difference in the distance–angle correlation of coesite and ferrierite coupled with the strong dependence of  $C_q$  on Si–O distance that is responsible for their different  $C_q$ -correlations shown in figure 1(A).

Generally, there are a number of factors to which the Si–O distances can be correlated [23, 24]. In the case of clathrasils, which form in the presence of inorganic and organic molecules directing the network towards less dense framework structures, one also needs to be aware of a strong correlation with static and/or dynamic disorder. Liebau [23, 24] found that the apparent Si–O bond lengths are significantly shorter (1.56 Å) and the Si–O–Si angles are significantly wider (175°), on average, in clathrasils than those observed (1.608 Å, 144°) for the silica polymorphs.

To investigate this matter, the Si–O distance dependence implicit in equation (2) has been removed by performing *ab initio* calculations for  $[(\text{OH})_3\text{O–Si–O–}(\text{OH})_3]$  clusters with the Si–O distance held constant in a manner consistent with previous calculations [26]. In figure 3(A)

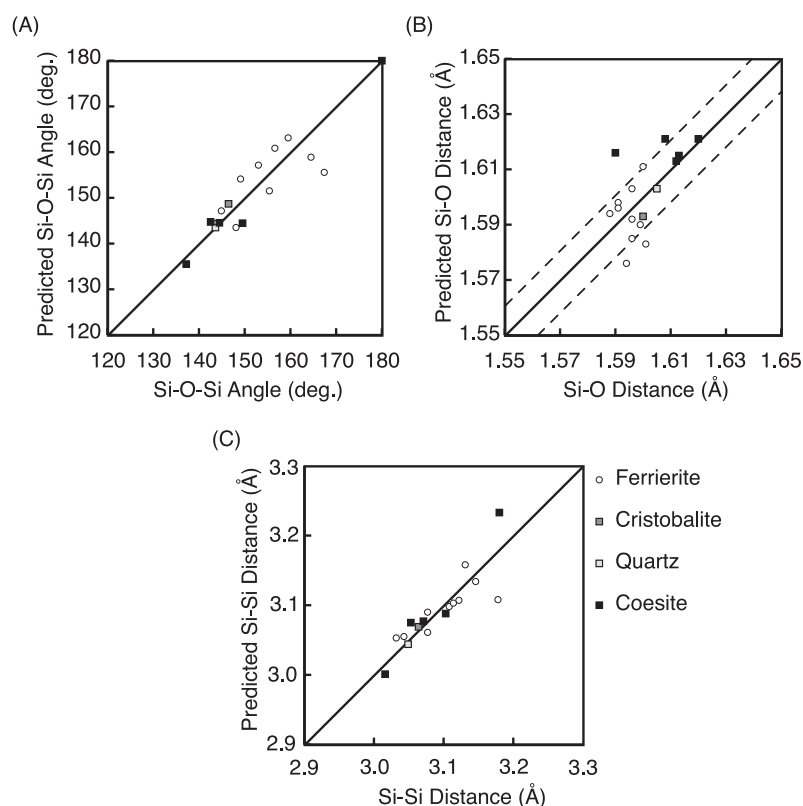


**Figure 3.** *Ab initio* predicted trends in (A)  $C_q$  as a function of Si–O–Si angle with Si–O distance held constant, (B)  $C_q$  as a function of Si–O distance with Si–O–Si angle held constant, (C)  $\eta_q$  as a function of Si–O–Si angle with Si–O distance held constant, (D)  $C_q$  as a function of Si–O distance with Si–O–Si angle held constant.

are the predicted trends in  $C_q$  as a function of Si–O–Si angle with the Si–O distance held constant at different values. The general trend as a function of Si–O–Si angle remains mostly unchanged other than an increase in the magnitude of  $C_q$  with increasing Si–O distance. The same  $C_q$ -data are presented in figure 3(B) as a function of Si–O distance with Si–O–Si angle held constant. Over the relevant range of Si–O distances the  $C_q$ -value follows a simple linear relationship [18]. The dependence of the quadrupolar asymmetry parameter on Si–O–Si angle and Si–O distance is shown in figures 3(C) and (D). Most importantly, the asymmetry parameter is independent of Si–O distance, and its behaviour is dominated by its dependence on Si–O–Si angle. This is also consistent with the findings of recent theoretical  $^{17}\text{O}$  NMR calculations in silicates [29]. Thus, for the asymmetry parameter,  $\eta_q$ , the correlation of equation (2) can still be generally applied. Therefore, given the dependence of  $C_q$  on average Si–O distance, we propose the following relation between  $C_q$  and Si–O–Si angle and Si–O distance:

$$C_q(d_{TO}, \Omega) = a' \left( \frac{1}{2} + \frac{\cos \Omega}{\cos \Omega - 1} \right)^{\alpha'} + m_d(d_{TO} - d_{TO}^\circ), \quad (5)$$

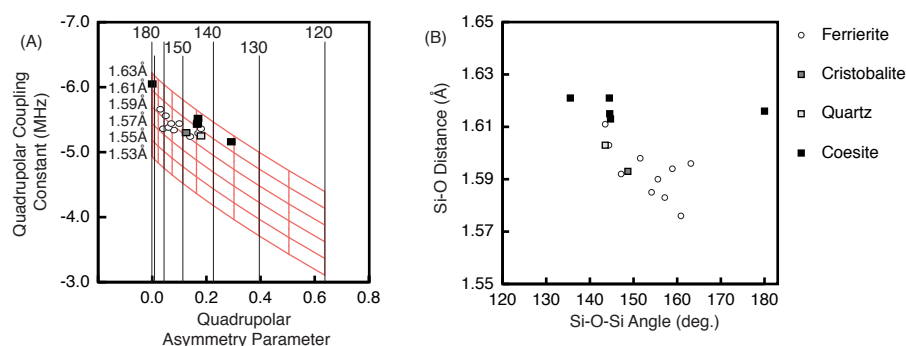
where  $d_{TO}$  is the average silicon–oxygen bond distance. A least-squares fit of equations (2) and (5) to the experimental values for coesite [17], cristobalite [30], and  $\alpha$ -quartz [31] as well as the *ab initio* predicted values for ferrierite [22] yields the parameter values  $a' = -6.53$  MHz,  $\alpha' = 1.80$ ,  $m_d = -12.86$  MHz  $\text{\AA}^{-1}$ ,  $d_{TO}^\circ = 1.654$   $\text{\AA}$ ,  $b = 4.73$ , and  $\beta = 1.12$ .



**Figure 4.** Comparison between the  $^{17}\text{O}$  quadrupolar coupling predicted (A) Si–O–Si angle, (B) Si–O distance, and (C) Si–Si distance with corresponding quantities reported from x-ray crystallography [32–34]. Solid diagonal lines represent perfect agreement. The best-fit parameters for equations (2) and (5) are  $a' = -6.53$  MHz,  $\alpha' = 1.80$ ,  $m_d = -12.86$  MHz  $\text{\AA}^{-1}$ ,  $d_{\text{O}}^{\circ} = 1.654$   $\text{\AA}$ ,  $b = 4.73$ ,  $\beta = 1.12$ .

A comparison of the Si–O–Si angles and Si–O distances predicted by these expressions with actual values is shown in figure 4. It is significant that these results demonstrate close agreement between predicted and reported values, even though only two structural variables are considered, i.e., average bond distance and bond angle. The Si–O–Si angles in figure 4(A) are predicted from  $\eta_q$  alone. The uncertainty in measuring the Si–O–Si angle from the quadrupolar asymmetry parameter will increase as  $\eta_q$  tends to zero, since the derivative of  $\angle\text{Si–O–Si}$  with respect to  $\eta_q$  diverges at  $180^\circ$  (see figure 3(C)). Over the range of values considered, however,  $\eta_q$  appears to be an excellent probe of Si–O–Si angle, as expected. With the Si–O–Si angle determined by  $\eta_q$ , equation (5) is used to predict the Si–O distance from  $C_q$ , as shown in figure 4(B). The predicted Si–O distances are in good agreement with the actual distances, with the majority being within 0.01  $\text{\AA}$  of the predicted value. Having determined the Si–O distance for a given angle, it is also possible to determine the Si–Si distance. These values are shown in figure 4(C), and are in excellent agreement with reported Si–Si distances. Finally, we note that not only can the coupling constant and asymmetry parameter be used to measure the Si–O–Si angle and Si–O distance, but, as shown in figure 5, the simultaneous measurement of  $C_q$  and  $\eta_q$  for each bridging oxygen site can be used to obtain the correlation between Si–O–Si angle and Si–O distance. We note that the adoption of this approach for measuring Si–O–Si angle and Si–O distance requires a good measurement of the quadrupolar asymmetry

Note: This figure had an error in the original journal reprint. This figure has been corrected in this pdf file.



**Figure 5.** Simultaneous measurement of the  $^{17}\text{O}$  quadrupolar coupling constant and asymmetry parameters can be used to measure the correlation between Si-O-Si angle and Si-O distance.

parameter, which has historically been more difficult to measure than the quadrupolar coupling constant. This situation has been improved, however, with the development of techniques such as rotor-assisted population transfer-enhanced [35-38] MAS-DAS [17, 39, 40] which allows overlapping anisotropic  $^{17}\text{O}$  central transition lineshapes to be separated and measured with high sensitivity and minimal lineshape distortions.

#### 4. Conclusions

Difficulties [22] in interpreting  $^{17}\text{O}$  quadrupolar coupling constants for bridging oxygen in different crystalline silica polymorphs, such as coesite,  $\beta$ -quartz, cristobalite, and ferrierite, have been found to arise from (1) differences in structural correlations between Si-O-Si angle and Si-O distance, and (2) a strong linear dependence of the quadrupolar coupling constant on Si-O distance. Using *ab initio* quantum chemistry calculations the quadrupolar asymmetry parameter was found to be determined almost entirely by the Si-O-Si angle, while the quadrupolar coupling constant is nearly equally affected by Si-O-Si angle and Si-O distance. Since the bridging oxygen bond lengths in ferrierite do not increase as dramatically as a function of bridging oxygen angle as in coesite, the quadrupolar coupling constants in ferrierite exhibit a weaker dependence on Si-O-Si angle.

On the basis of these results, we have proposed analytical expressions for describing these dependences. Overall, we have found that  $^{17}\text{O}$  is a richer probe of structure around the first coordinate sphere of bridging oxygen, and that the relationships described here can be generally used for relating measured  $^{17}\text{O}$  quadrupolar coupling constant and asymmetry parameter values for bridging oxygen to their Si-O-Si angle and average Si-O distance. This approach could also be extended to other bridging oxygen environments, such as the Ge-O-Ge linkage [41]. Such an approach will be valuable for obtaining structural details in materials not easily treated with scattering methods of measurement, such as microcrystalline and amorphous network-forming oxides.

#### Acknowledgments

We thank Subramanian Prasad for helpful discussions. This material is based upon work supported by the National Science Foundation under Grant No CHE 0111109. Any opinions,

findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation (NSF).

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