

Calculation of bridging oxygen ^{17}O quadrupolar coupling parameters in alkali silicates: A combined ab initio investigation

Ted M. Clark, Philip J. Grandinetti*

Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, OH 43210-1173, USA

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Abstract

Ab initio band-structure calculations based on the density functional theory have been performed for several crystalline Li, Na, and K-silicates to obtain electric-field gradients (efg) for oxygen atoms. The efg for bridging oxygen environments in these compounds were also investigated by performing ab initio self-consistent field Hartree–Fock molecular orbital calculations on silicate clusters, and there is good agreement between these two approaches. By performing additional ab initio quantum chemistry calculations on model silicate clusters the factors influencing the ^{17}O quadrupole coupling parameters for bridging oxygen environments in alkali silicates have been examined. The quadrupolar asymmetry parameter was found to be dependent on the Si–O–Si angle and the nature of the modifier cation, in agreement with previous studies. In contrast, the quadrupolar coupling constant was found to have a strong dependence on Si–O distance, as well as Si–O–Si angle and the nature of the modifier cation. Analytical expressions describing these dependencies are proposed, which should assist in describing the local environments of bridging oxygen in crystalline and amorphous materials.

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1. Introduction

With the continued improvement of computational resources it has become increasingly common to use ab initio quantum methods for predicting the electronic structure in crystalline materials [1–13]. These methods are also extremely useful for interpreting experimental results, such as the NMR spectra of solids, particularly for materials or nuclei where it is difficult to obtain experimental results and establish clear relationships between structural parameters and measurable NMR parameters. Oxygen-17 is one such nuclei which, despite its potential for helping to elucidate the structure of both crystalline and disordered materials, has been hampered by a low natural abundance and large quadrupole interactions which make otherwise

routine solid-state NMR experiments, such as MAS, challenging.

Recently, we have reported relationships for obtaining the Si–O–Si bond angle and Si–O distance from the ^{17}O quadrupolar coupling parameters of a bridging oxygen atom, i.e., the quadrupolar coupling constant, C_q , and the quadrupolar asymmetry parameter, η_q . These relationships were revealed through systematic ab initio calculations on model clusters and calibrated with experimental ^{17}O data for extended networks [14]. We have recently used these relationships to interpret the two-dimensional DAS spectrum of silica glass [15]. This approach resulted in the experimental determination of the two-dimensional correlated distributions in Si–O distance and Si–O–Si angle, as well as the determination of the distribution of Si–O–Si bond angles in this archetypical glass former.

To extend this approach to network-modified silicate glasses requires an understanding of how the

*Corresponding author. Fax: +1 614 292 1685.

E-mail address: grandinetti.1@osu.edu (P.J. Grandinetti).

electric-field gradient (efg) for a bridging oxygen is affected by changes in structural parameters, including the presence of modifier cations. In an earlier investigation of alkali silicates, obtained using ab initio methods on model clusters representing typical bridging oxygen environments in lithium, sodium, and potassium silicates we began this task and demonstrated that several structural variables influence the bridging oxygen O-17 efg [16,17]. A more recent computational investigation of molecular dynamic simulated sodium silicate glasses supported many (but not all) of these general trends [13].

Thus, to investigate network-modified silicate glasses in a manner comparable to that performed for silica requires analytical expressions for bridging oxygen efg parameters that account for the relevant structural parameters. These parameters include the Si–O distances [13,18,19,14], Si–O–Si angles [20–22], and the field strength and number of network-modifier cations coordinated to the bridging oxygen atom [16,17]. Thus, suitable expression for the ^{17}O quadrupolar coupling parameters are

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

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

where Ω is the Si–O–Si bond angle, d_{TO} is the average silicon–oxygen bond distance, m_d is a term (in MHz/Å) accounting for the distance dependence of C_q , with $n_M \Delta C_q^M$ and $\Delta \eta_q^M(n_M)$ accounting for contributions from n_M modifier cations coordinated to the bridging oxygen [14,17,15].

We will show here that the general trends described by these expressions are confirmed by ab initio calculations on model clusters. Additionally, in order to calibrate these expression, we will employ periodic density functional theory (DFT) calculations to determine the efg for bridging oxygen atoms in a variety of crystalline alkali silicates, since insufficient experimental ^{17}O data exists to do so otherwise.

2. Methods

2.1. MO-cluster calculations

The electric-field gradients for bridging oxygen environments in these compounds were investigated by performing ab initio self-consistent field molecular orbital calculations on silicate clusters (MO-cluster calculations) using GAUSSIAN98 [23]. These calculations were performed at a restricted Hartree–Fock level with a $6-31+G(d)$ basis set for all atoms.

Calculated efg tensor elements are related to the quadrupolar coupling constant, C_q , and quadrupolar coupling asymmetry parameter, η_q , according to

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

where $e\langle q_{xx} \rangle$, $e\langle q_{yy} \rangle$, and $e\langle q_{zz} \rangle$ are the principal components of the electric-field gradient 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}O a value of $e^2 Q / h = -6.11 \text{ MHz a.u.}^3$ was used to convert the q_{zz} output from Gaussian into the ^{17}O quadrupolar coupling constant.

2.2. LAPW calculations

These calculations were based on the density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange and correlation potentials [24,25]. The full-potential, linearized, augmented plane-wave (LAPW) package WIEN97 [26] was used. In the LAPW method, the unit cell is divided into spheres centered at the atomic positions and an interstitial region. For the interstitial region, the basis set consists of plane waves which are augmented by atomic-like solutions inside the spheres. Sphere radii of 1.45, 1.50, 1.65, 1.45, 1.35 a.u. were used for Li, Na, K, Si, and O atoms, respectively. The cutoff for the plane wave basis set was chosen as $R_{\text{mt}} K_{\text{max}} = 6.75$, where R_{mt} corresponds to the smallest atomic sphere radii and K_{max} is the plane wave cutoff. These parameters typically resulted in more than 7000 LAPWs being used in our basis sets. Additional calculations confirmed that these results were well converged for these cutoff values. To treat the semicore states for silicon and oxygen additional local orbitals were employed. The number of k points in the irreducible Brillouin zone (IBZ) for the calculations ranged from 12 to 16. Nonspin-polarized calculations were studied in all cases. The LAPW calculations were computationally expensive, typically requiring more than a week to reach convergence when run on a SGI[®] Origin[®] 200 computer. These time constraints precluded the use of additional DFT supercell calculations for the investigation of possible crystalline distortions. The conversion factor for the full-crystal calculations of the quadrupolar coupling constant is given in Ref. [4].

3. Results and discussion

The ^{17}O quadrupolar coupling parameters were calculated using the LAPW approach for several alkali silicates with reported crystal structures. The results are shown in Table 1. For two of the compounds, i.e., Li_2SiO_3 and $\text{Li}_2\text{Si}_2\text{O}_5$, several crystal structures have

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