# Factors influencing the $^{17}$O quadrupole coupling constant in bridging oxygen environments

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## Abstract

Ab initio calculations were performed on the series of clusters $[(OH)_3M-O-M(OH)_3]^{-2}$ where M = B, Al, and Ga, $(OH)_3M-O-M(OH)_3$ where M = C, Si, and Ge, $(OH)_2OM-O-MO(OH)_2$ where M = P and As, and $(OH)O_2M-O-MO_2(OH)$ where M = S and Se. These clusters were constructed to model the effect of changing the coordinating cation and coordinating cation–oxygen distances on the bridging oxygen $^{17}$O quadrupole coupling constant. For all clusters studied, we observed a general trend that the magnitude of $C_q$ increases linearly with increasing 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. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Oxygen; Ab initio calculations; Quadrupole coupling

## 1. Introduction

Recent advances in solid-state NMR have lead to an significant increase in the number of $^{17}$O quadrupole coupling constants measured for bridging oxygen environments [1–13]. Experimental $C_q$ values for bridging oxygen range from 1.5 to 2.4 MHz when coordinated by aluminum [1] to greater than 10 MHz in organic systems [10]. Included in this spread are values in the 4 to 6 MHz range for silicate systems [10,13] and values in the 6–8 MHz range for germanate systems [7,8]. These variations can be attributed to a number of factors, including variations in bridging oxygen angle [13,14], coordinating cation-bridging oxygen distance [15], coordinating cation electronegativity [10–12], and for bridging oxygen in modified inorganic oxide networks the possibility of additional coordination by network modifier cations [16]. Early in the use of $^{17}$O solid-state NMR a strong correlation was established between $C_q$ and the electronegativity of coordinating cations [10]. Recently, however, we have shown that changes in bridging oxygen $C_q$ with different coordinating cations is not related solely to coordinating cation electronegativity, but rather to a combination of changing coordinating cation–oxygen distance as well as changing electronegativity [15]. In this communication we extend these ab initio calculations and consider model clusters where the coordinating

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cations are varied from Group III to Group VI, while simultaneously varying the coordinating cation-bridging oxygen distance. Based on these calculations we propose a refined model for predicting $^{17}O$ $C_q$ values for bridging oxygen in a variety of coordination environments.

## 2. Theoretical method

Ab initio calculations were performed on a Silicon Graphics Origin 200 workstation using GAUSSIAN 94 [17] at a restricted Hartree–Fock level with a $6-31+G(d)$ basis set for elements in periods 1–3, and a $6-311+G(d)$ basis set for elements in period 4. GAUSSIAN 94 calculates the traceless 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

$$C_q = e^2 Q \langle q_{zz} \rangle / h, \text{ and } \eta_q = \frac{\langle q_{xx} \rangle - \langle q_{yy} \rangle}{\langle q_{zz} \rangle} \quad (1)$$

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 $e^2 Q / h = -6.11$ MHz a.u.$^3$ was used to convert the $q_{zz}$ output from Gaussian into the $^{17}O$ quadrupolar coupling constant.

The theoretical approach of performing calculations at a restricted Hartree–Fock level with $6-31+G(d)$ and $6-311+G(d)$ basis sets involving representative model clusters has been previously utilized to describe trends in the quadrupolar coupling parameters for elements in periods 3 and 4, which are bound to a bridging oxygen atom [15,16]. The pragmatic extension of this approach for calculations involving analogous model clusters is expected to also accurately describe tends in the $^{17}O$ quadrupolar coupling parameter when the oxygen atom is in a bridging oxygen environment. It is less clear, however, that this theoretical approach would also be appropriate in model clusters when the local environment is significantly altered. For example, if modifying cations are in close proximity to the bridging oxygen atom, or if the model cluster is highly distorted, then the trends in the $^{17}O$ quadrupolar coupling parameter may need to be reconsidered.

Model clusters were constructed so that the influence of the coordinating cation electronegativity and coordinating cation-bridging oxygen distance on the bridging oxygen $C_q$ could be examined. For the Group III elements, the clusters $[(OH)_3M-O-M(OH)_3]^{-2}$ where M = B, Al, and Ga, were investigated in which the coordination number for each cation is four, with oxygen atoms arranged in a tetrahedral geometry. Although such a tetrahedral configuration is not unusual in borates [18], it is typical for Al−O−Al sites and was chosen over a trigonal geometry to avoid variations in the metal coordination number. For the Group IV elements, clusters with the formula $(OH)_3M-O-M(OH)_3$ where M = C, Si, and Ge, were investigated. This configuration, in which the cations are tetrahedrally coordinated to four oxygen atoms, is quite typical in silicates and germanates and such clusters have been used in previous investigations employing ab initio calculations [14,16,19,20]. Tetrahedrally coordinated cations are also present in the clusters constructed for the Group V elements which have the formula $(OH)_2OM-O-MO(OH)_2$ where M = P, As. The $H_4P_2O_7$ cluster is representative of the basic structural unit of phosphate glass in which the hydrogen atoms are used to terminate the dangling bonds of the oxygen atoms [21]. The diarsenate anion, in which the arsenic cations share a bridging oxygen atom and are each coordinated to three other oxygen atoms, is also a common structural feature in a variety of compounds [22]. Clusters with the formula $(OH)O_2M-O-MO_2(OH)$ where M = S and Se, were constructed for the Group VI elements. These are the disulfuric and diselenic acid molecules [23], where the coordination number of the cations is four and they are joined by a bridging oxygen atom.

For each cluster a full geometry optimization was calculated and selected minimum energy structural parameters are given in Table 1. Then a second geometry optimization was performed with the $\angle M-O-M$ held fixed at 180° and these minimum energy structural parameters (given in Table 2) were used while the cation-bridging oxygen distance was systematically varied.

When the $\angle M-O-M$ is fixed at 180°, $\langle q_{xx} \rangle$ and $\langle q_{yy} \rangle$ are approximately equal for the Group III and

Table 1

Ab initio optimized structural parameters and calculated $C_q$ and $\eta_q$ values of model clusters

| Cation | ∠M−O−M (°) | $d$(OH) (Å) | $d$(M−O) (Å) | $d$(M=O) (Å) | $C_q$ | $\eta_q$ |
|--------|-----------|-------------|--------------|--------------|-------|----------|
| B  | 138.3 | 0.947 | 1.481 | –     | − 8.22  | 0.29 |
| Al | 180.0 | 0.950 | 1.785 | –     | − 3.98  | 0.0  |
| Ga | 148.4 | 0.945 | 1.741 | –     | − 6.14  | 0.19 |
| C  | 127.7 | 0.947 | 1.352 | –     | − 13.34 | 0.59 |
| Si | 180.0 | 0.949 | 1.632 | –     | − 6.93  | 0.0  |
| Ge | 140.3 | 0.946 | 1.737 | –     | − 7.59  | 0.29 |
| P  | 141.0 | 0.952 | 1.576 | 1.453 | − 8.77  | 0.44 |
| As | 138.4 | 0.952 | 1.698 | 1.585 | − 9.17  | 0.55 |
| S  | 130.9 | 0.958 | 1.594 | 1.417 | − 11.71 | 0.82 |
| Se | 133.3 | 0.956 | 1.714 | 1.560 | − 11.07 | 0.77 |

Group IV clusters resulting in an $\eta$ value of zero. However, the $\eta$ values are non-zero at 180° for the clusters containing Group V and Group VI cations because these tetrahedrally coordinated sites are asymmetric with the cations being bonded to both single oxygen atoms and hydroxyl groups. The reported trend [16] that $\eta$ increases as the ∠M−O−M is decreased is observed for each cluster (see $\eta$ values in Tables 1 and 2). These findings indicate that $\eta$ is closely correlated with the geometry of the model cluster and indirectly influenced by the cation in as much as the chemistry of the cation affects the number and geometry of anions bonded to it.

For all clusters with the ∠M−O−M fixed at 180° the efg principal axis system (PAS) has its $x$- and $z$-axes lying in the plane of the M−O−M angle, with the $z$-axis perpendicular to the bisector of the ∠M−O−M. At this angle the orientation of the efg PAS is not dependent on the cations coordinated to the bridging oxygen atom and may not be determined based on the magnitude of $C_q$ or $\eta_q$.

## 3. Results and discussion

In the mid-1980s Oldfield et al. [10–12] clearly established on the basis of their experimental 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. We have reproduced this trend in Fig. 1A using the optimized structures given in Table 1. Since the work of Oldfield et al., an additional dependence of the bridging oxygen [17]O quadrupole coupling constant on bridging oxygen angle has been established both theoretically [19] and experimentally [13]. In Fig. 1B we have removed this bridging oxygen angle dependence from the data

Table 2

Ab initio optimized structural parameters and calculated $C_q$ and $\eta_q$ values of model clusters with the M−O−M angle held constant at $\Omega = 180°$

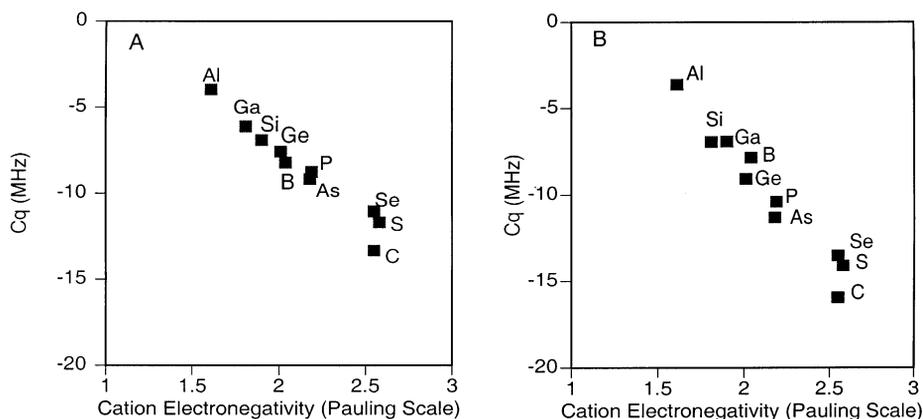| Cation | ∠M−O−M (°) | $d$(OH) (Å) | $d$(M−O) (Å) | $d$(M=O) (Å) | $C_q$ | $\eta_q$ |
|--------|-----------|-------------|--------------|--------------|-------|----------|
| B  | 180 | 0.947 | 1.478 | –     | − 9.38  | 0.0  |
| Al | 180 | 0.950 | 1.785 | –     | − 3.98  | 0.0  |
| Ga | 180 | 0.948 | 1.850 | –     | − 6.99  | 0.0  |
| C  | 180 | 0.947 | 1.366 | –     | − 15.95 | 0.0  |
| Si | 180 | 0.949 | 1.632 | –     | − 6.93  | 0.0  |
| Ge | 180 | 0.946 | 1.632 | –     | − 9.07  | 0.0  |
| P  | 180 | 0.952 | 1.573 | 1.453 | − 10.40 | 0.04 |
| As | 180 | 0.952 | 1.694 | 1.585 | − 11.30 | 0.03 |
| S  | 180 | 0.958 | 1.555 | 1.417 | − 14.10 | 0.12 |
| Se | 180 | 0.956 | 1.684 | 1.560 | − 13.50 | 0.11 |

Fig. 1. The $C_q$-parameters for a bridging oxygen in a variety of M−O−M clusters plotted versus the Pauling electronegativity of the cations. In (A) the cluster geometries were optimized with respect to all angles and distances. In this case the linear correlation coefficient between $C_q$ and EN is $r^2 = 0.950$. In (B) the cluster geometries were optimized with the M−O−M angle held constant at $\Omega = 180°$. In this case the linear correlation coefficient between $C_q$ and EN is $r^2 = 0.957$.

in Fig. 1A by recalculating the optimized cluster geometries with the bridging oxygen angles all held fixed at 180°. Although the correlation with electronegativity improves slightly as the scatter due to varying bridging oxygen angles is eliminated there still remains a considerable degree of scatter in the correlation with electronegativity.

Another factor that can influence the magnitude of the $C_q$ parameter for a bridging oxygen atom but

until recently [15] not considered is the cation–oxygen bond distance, an aspect that is also quite difficult to examine independently with experimental systems but may be considered with ab initio calculations. In Figs. 2 and 3 are the ab initio predicted variations in bridging oxygen $C_q$ for all clusters as a function of cation–bridging oxygen distance with the bridging oxygen angles all held fixed at 180°. For all clusters studied we observed a general trend that *the*
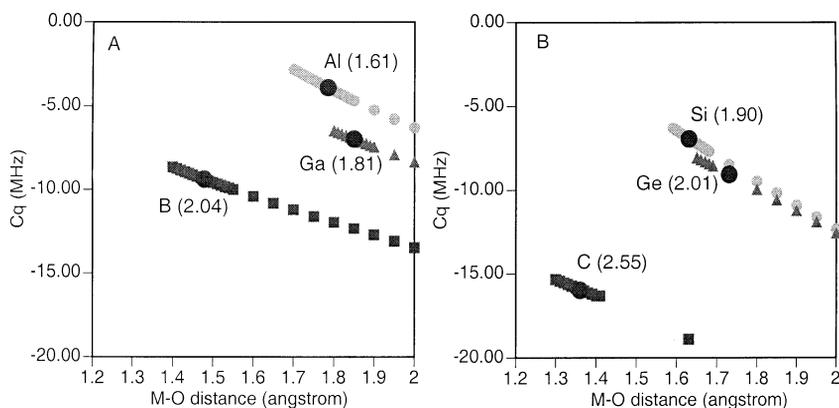


Fig. 2. Dependence of Cq for a bridging oxygen on the distance $d$(M−O) in clusters with the formula (A) $[(OH)_3M−O−M(OH)_3)]^{-2}$ where M = B, Al, and Ga and (B) $(OH)_3M−O−M(OH)_3$ where M = C, Si, and Ge. The values at the optimized $d$(M−O) values are represented by circles. Pauling electronegativities (taken from Huheey [23]) are given in parenthesis next to each element symbol. The rate of change in $C_q$ with distance is 8.0, 11.7, and 9.4 MHz/Å for B, Al, and Ga, and 11.4, 14.7, and 12.8 MHz/Å for C, Si, and Ge, respectively.
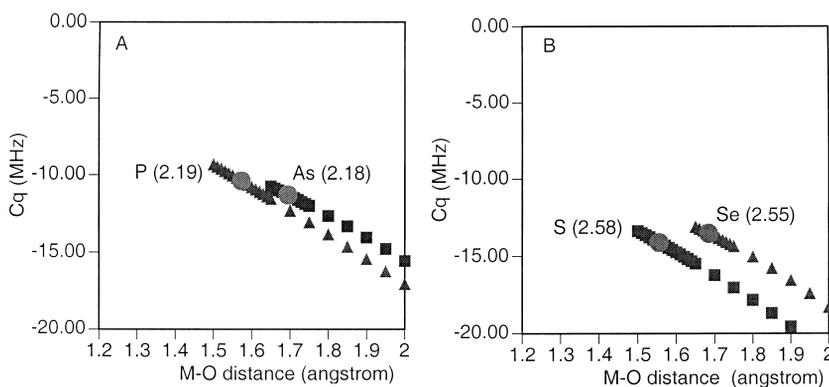
Fig. 3. Dependence of $C_q$ for a bridging oxygen on the distance $d(M-O)$ in clusters with the formula (A) $(OH)_2OM-O-MO(OH)_2$ where M = P and As, and (B) $(OH)O_2M-O-MO_2(OH)$ where M = S and Se. The values at the optimized $d(M-O)$ values are represented by circles. Pauling electronegativities (taken from Huheey [23]) are given in parenthesis next to each element symbol. The rate of change in $C_q$ with distance is 15.3 and 13.6 MHz/Å for P and As, and 15.9 and 14.5 MHz/Å for S and Se, respectively.

*magnitude of $C_q$ increases linearly with increasing cation–oxygen bond distance.* The average change in $C_q$ with cation–oxygen distance is $12.7 \pm 2.6$ MHz/Å for all clusters studied in the range of $d(M-O) = 1.30$ to $2.00$ Å.

The calculated results for the Group III elements in the clusters $[(OH)_3M-O-M(OH)_3]^{-2}$ where M = B, Al, and Ga, are shown in Fig. 2A. Notice the nearly linear increase in the magnitude of $C_q$ for the bridging oxygen. As noted in Fig. 1B, at optimized distances the $C_q$ value is greatest in magnitude for the boron cluster followed by the gallium cluster and the aluminum cluster. This occurs even though the optimized boron–oxygen distance is much shorter than either the Al–O or Ga–O distances. This ordering of $C_q$ values agrees well with those obtained experimentally [1,9,24].

The results shown in Fig. 2B for the Group IV elements in the clusters $(OH)_3M-O-M(OH)_3$ where M = C, Si, and Ge, also display a strong distance dependence of $C_q$ on the cation–oxygen distance. Similar to the finding observed for boron, the high electronegativity of carbon insures that the $C_q$ parameter for this cluster is much higher than that for the analogous Si or Ge clusters even though a shorter carbon–oxygen bond distance serves to somewhat reduce the magnitude of the $C_q$ parameter for the carbon cluster. When comparing the $C_q$ parameter for the silicon and germanium clusters it is apparent that both the slightly greater electronegativity of

germanium and a larger cation–oxygen distance combine to result in a larger $C_q$ value for the germanium cluster. Again, this is in agreement with recent $^{17}O$ results by Dupree et al. on germanate systems [7,8].

The Group V elements investigated in clusters with the formula $(OH)_2OM-O-MO(OH)_2$ where M = P and As, are shown in Fig. 3A. As was shown in Fig. 1B, at optimized distances the arsenic cluster has a larger $C_q$ than does the phosphorus cluster, despite the fact the electronegativity of arsenic is slightly smaller. This discrepancy may be explained by considering the differences in cation–oxygen distances. The optimized $d(M-O)$ value is greater in the arsenic cluster than in the phosphorus cluster and this difference serves to increase the $C_q$ parameter slightly above that calculated for phosphorus.

For the Group VI elements shown in Fig. 3B, the $C_q$ for the sulfur cluster is slightly greater than that for the selenium cluster at their optimized distances. In this instance, the smaller $d(M-O)$ value for the sulfur cluster reduces the magnitude of $C_q$ in comparison to that of the selenium cluster, but once again the larger electronegativity of the sulfur overcomes this factor and the net result is that the $C_q$ value is slightly larger for the sulfur cluster than for the selenium cluster.

Of particular interest are the plots of $C_q$ versus $d(M-O)$ across periods shown in Fig. 4. Notice the nearly equally spaced and parallel data for the Al, Si,
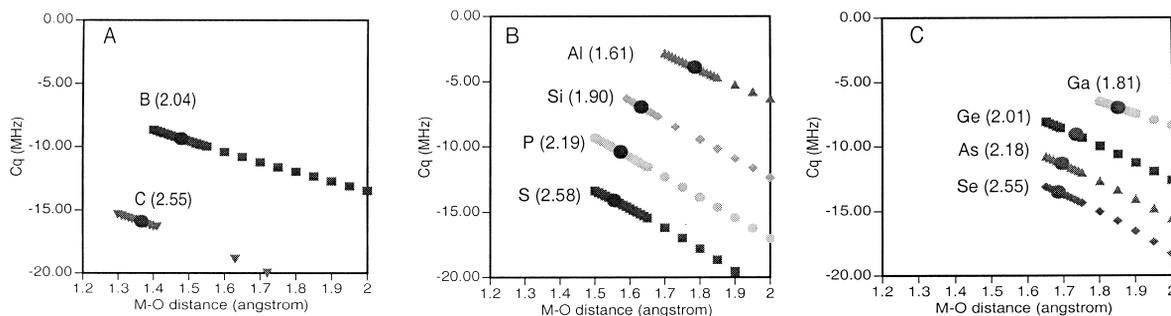
Fig. 4. Dependence of $C_q$ for bridging oxygen on the distance $d(M-O)$ in cluster for (A) period 2, (B) period 3, and (C) period four elements. The values at the optimized $d(M-O)$ values are represented by circles. Pauling electronegativities (taken from Huheey [23]) are given in parentheses next to each element symbol.

P, and S clusters as a function of cation-bridging oxygen distance shown in Fig. 4B. Such a plot suggests a better correlation of $C_q$ to group number (Fig. 5) than to electronegativity. Indeed, at constant distance ($d(M-O) = 1.85$ Å) and constant bridging oxygen angle ($\Omega = 180°$) the correlation of $C_q$ to group number for period 3 elements is $r^2 = 0.995$, whereas to electronegativity we obtain $r^2 = 0.835$. Similar improvements in the correlation coefficient using group number instead of electronegativity are also obtained for the period 4 elements; the correlation of $C_q$ to group number for period 4 elements is $r^2 = 0.991$, whereas to electronegativity we obtain $r^2 = 0.852$. Such a linear dependence on the group
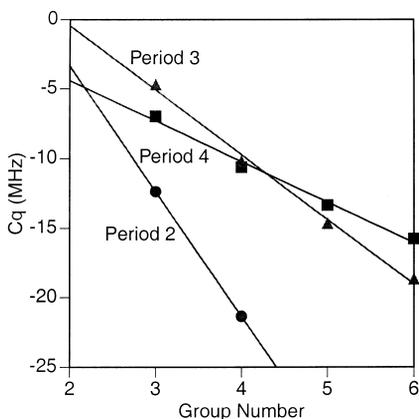


Fig. 5. Bridging oxygen $C_q$ dependence on the group number of coordinating cations for each period. The rate of change in $C_q$ with increasing group number is $-9.00$, $-4.64$, $-2.90$ MHz for periods 2, 3 and 4, respectively.

number or atomic number makes sense in the context of the Townes–Dailey model [25] for the electric field gradient of the bridging oxygen [13]. In this simple approximation the magnitude of the bridging oxygen quadrupole coupling constant is proportional to the population difference between the bonding and non-bonding valence orbitals of oxygen. With the non-bonding orbital populations remaining constant then the population of the bonding orbital will decrease linearly with the increasing nuclear charge, $Z$, of the coordinating cations. The change in bonding orbital population with each coordinating cation nuclear charge increase is nearly identical within a given period since the screening by inner shell electrons is nearly constant. Amongst periods, however, there will be an increased screening with increasing period and hence the slope $\partial C_q / \partial Z$ decreases with period.

On the basis of these results we would suggest a relationship between $C_q$ and bridging oxygen environment to be of the general form [16]

$$C_q(\Omega, d(M-O), Z)$$

$$\approx a(d(M-O), Z) \cdot \left( \frac{1}{2} + \frac{\cos \Omega}{\cos \Omega - 1} \right)^{\alpha} \qquad (2)$$

where to a good approximation $a(d(M-O), Z)$ is linearly dependent on both $d(M-O)$ and $Z$. The caveats being, of course, that $\partial C_q / \partial Z$ is approximately constant over the subset of coordinating cations considered within a given period, and that

$\partial C_q/\partial d(\text{M}-\text{O})$ is defined over a small enough range of distances that it is also constant. In general, however, the slope $\partial C_q/\partial d(\text{M}-\text{O})$ is not expected to be constant over the full range of distances in a given period (i.e., from alkali to halogen). In addition, Eq. (2) only holds for bridging oxygen angles in the range of 120° to 180°. Eq. (2) can be additionally modified if one included the effects of coordinating network modifier cations as described elsewhere [16].

A limitation of Eq. (2) is that only a small number of bridging oxygen sites have experimentally determined quadrupole coupling parameters. As a result, although some of constants noted in Eq. (2) may be confirmed with experimental results [16], it is generally not possible to calibrate each of the calculated constants without further experimental results. Nonetheless, it is reasonable to propose that the trends established in this investigation are valid for a wide range of compounds which contain bridging oxygen environments similar to those examined in this work.

## 4. Summary

We have examined a number of clusters using ab initio methods to model changes in the bridging oxygen $^{17}\text{O}$ quadrupole coupling constant with changing coordinating cations. Although previous studies have shown that the magnitude of the $^{17}\text{O}$ quadrupole coupling constant is related to the ionic strength (i.e., electronegativity difference) of the cation–oxygen bond, we have found that a combination of coordinating cation–oxygen distance, coordinating cation group number, and bridging oxygen angle can serve as a better predictor of $C_q$. Specifically, with the bridging oxygen angle held constant our ab initio calculations predicted linear relationships between $C_q$ and coordination cation distance, and between $C_q$ and coordination cation group number.

It is reasonable to expect that these results can be somewhat generalized to bridging oxygen connecting unlike cations (i.e., the effect of changing cation and coordination distance has an additive effect on $C_q$), although, in general, unlike coordinating cations will result in the $z$-axis of the bridging oxygen principal

axis system moving away from the axis perpendicular to the bisector of the M–O–M axis [13]. Thus, the relationship between $C_q$ (and $\eta_q$) and bridging oxygen angle will need to be modified slightly depending on the electronegativity difference of the two coordinating cations. Investigations along these lines are currently in progress.

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