bond acceptor and its interaction with each hydroxyl group involved in the intramolecular hydrogen bonding network is envisaged in Chart IV, though it must be remembered that these molecules in solution are flexible and the hydrogen bonds resulting from time-averaged conformations and interactions are very weak. Support for the concept of three-center hydrogen bonds is given not only by previous solution studies[12] but also by detailed analysis of neutron-scattering results in carbohydrate crystals.[5,6] The major difference between solution- and solid-state studies is that for molecules in the solid state the hydrogen bond networks are intermolecular whereas in solution it has been shown in the present work that hydrogen bond networks are intramolecular.

Conclusions

Hydrogen bonding between hydroxyl groups in carbohydrates is conveniently studied by the SIMPLE ^{1}H NMR method (i.e., observation of Secondary Isotope Multiplet NMR of Partially Labeled Entities). In the present work we have shown that OH3′···O2 intramolecular hydrogen bonds occur for 1′-chloro-1′-deoxysucrose derivatives in Me_2SO-d_6 solution and that this hydrogen bond stabilizes cooperative hydrogen bonding in both the aldose (OH2···OH3···OH4···OH6) and fructose (OH3′···OH4′) residues, the extent of which depends on the substitution patterns in the two sugar residues. Assuming that the magnitudes of the isotope effects reflect the relative strengths of hydrogen bonds, it is shown that the strength of the hydrogen bonds in the aldose residue becomes progressively weaker at distances further from the relatively strong interresidue hydrogen bond. It is also shown that the strength of the interresidue hydrogen bond becomes stronger as the hydrogen bond network becomes more extensive, i.e., the process is cooperative.

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Oxygen-17 NMR Study of Bonding in Silicates: The d-Orbital Controversy

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Abstract: Bonding models for silicates are assessed in relation to the local environment of oxygen, as determined by analysis of the oxygen-17 nuclear quadrupole coupling constants (NQCC), using Townes–Dailey methods. The experimental NQCC of the silica polymorph low cristobalite is indicative of covalent charge transfer from the oxygen lone pairs to silicon and is consistent with Pauling's (d–p) π-bonding model. Bonding models for both hybridized and unhybridized oxygen which exclude lone pair charge transfer give poor agreement with the experimental results. The oxygen-17 NQCC of the bridging oxygen of diopside is shown to be in agreement with McDonald's (d–p) π-bonding hypothesis. Calcium coordination to the diopside bridging oxygen is consistent with calcium acting as a charge acceptor. The structural significance of the (d–p) π-bonding effect is discussed and related to the expected variation in the NQCC as a function of bridging bond angle. Trends in the NQCC of oxygen bonded to other elements are discussed and related to bond ionicities. The use of Pauling ionicities in conjunction with the Townes–Dailey model gives good agreement with the experimental NQCC results for a variety of well-defined oxide and silicate systems and further supports the (d–p) π-bonding hypothesis in silicates.

I. Introduction

The existence of delocalized π-bonding networks throughout silicate frameworks has been a topic of debate for a number of years. The two salient features of silicate silicon–oxygen bonds are (1) the large variability in bond length (1.55–1.80 Å) and (2) the large variability of the bond angle for the oxygen bridging the linked silicate tetrahedra (≈120–180°). In the 1950's Pauling[1,2] and Jaffe[3] used the concept of silicon-d oxygen-p π-bonding to account for bond lengths in TO_4^{n-} (T = Cl, S, P, Si) tetrahedra, which were considerably shorter than the single bond lengths predicted by Schomaker and Stevenson.[4] In 1961 Cruickshank[5] extended the treatment to a broad class of silicon, phosphorus, and sulfur compounds using valence bond formalism. He used group theory arguments to show that only the two E silicon d-orbitals ($3d_{x^2-y^2}$ and $3d_{z^2}$) are of suitable geometry to form strong π-bonds. For illustrative purposes we show in Figure 1 a schematic of the atomic orbitals involved. The large, diffuse, silicon d-orbitals are contracted by the positively charged silicon core, thereby facilitating overlap. Cruickshank attributed the variability in bridging-oxygen bond lengths to increased participation in (d–p) π-bonding of the "lone pair" sp^n orbital (in the Si–O–Si plane) as the bridging angle widens and the orbital gains p-character, thereby increasing the valence bond order and shortening the bond length. Cruickshank attributed the variability of the bridging bond angle to steric and Coulombic effects and not to (d–p) π-bonding. Others, however, have attached structural significance to the (d–p) π-bonding effect in regard to the bridging angle, and thereby rationalize, for instance, the increase in bridging angle from dimethyl ether (111°) to disiloxane (144°), or the planarity of trisilylamine.[6,7]

Over the years the topic has engendered lively debate. The nature of the silicon–oxygen bond has been extensively examined by semiempirical and ab initio methods.[8-37] While there is

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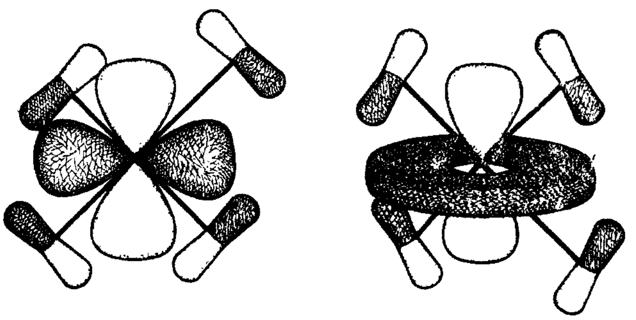

Figure 1. Schematic representation of the atomic E d-orbitals of silicon ($d_{x^2-y^2}$, d_{z^2}) and p-orbitals of oxygen in TO_4^{n-} tetrahedra. In actuality there may be an admixture of s and p character in the d-orbitals, as well as significant overlap with the three T silicon d-orbitals and/or the silicon σ^*-orbitals.

considerable disagreement about the extent of (d–p) π-bonding, which many believe small or absent,[31-36] it is generally found that the basis set need not include silicon d-orbitals in order to reproduce the experimental bridging angle.[8,17,19,28,36,37] On this basis, the structural characteristics of silicates, especially bridging angle, are attributed to the electronegativity of the σ-bonding orbitals (e.g., Bent's rule), as well as steric and Coulombic effects, and oxygen polarization functions. The role of (d–p) π-bonding is generally thought to be either very small or nonexistent, and if present, it is not enough to have much structural significance.

The discovery that Pauling's electroneutrality principle was valid in low quartz, based on an X-ray electron density map,[38] not only settled a long-standing misconception about Pauling's concept of atomic electronegativity, which had led to estimates of formal charge twice as large as the experimental values,[39] but also elicited an exchange between Pauling[40] and Stewart[41] whereby the experimental formal charges were rationalized on the basis of multiple and single Si–O bonds, respectively. The heart of the dispute involved the controversial role of silicon d-orbitals. Stewart was able to account for the formal charges on the basis of orbital electronegativity of the σ-orbitals alone, and consequently he felt no need to resort to (d–p) π-bonding schemes. Pauling, on the other hand, framed his bonding model in terms of atomic electronegativities. The issue, however, only peripherally involves the differing concepts of electronegativity, atomic and orbital. The (d–p) π-bonding model does not preclude use of orbital electronegativities. For instance, Jaffe was instrumental in advancing both ideas.[3,42,43]

An empirical correlation between bridging angle and bond lengths has been reported for the well-defined silica polymorphs, where all oxygens are doubly coordinated bridging oxygens and the O–Si–O bond angle varies little. A good correlation (0.95, $N = 8$) was observed between bond length and degree of orbital hybridization, expressed as $(-\sec(\angle \mathrm{SiO_{br}Si}))$, for the framework silicate coesite, which exhibits a wide range of bridging angles and bond lengths ($R(\mathrm{Si{-}O}) = 0.6712(-\sec(\angle \mathrm{SiOSi})) + 1.529$).[12] The Si–O bond length shortens linearly both with respect to (1) increasing s-hybridization of the oxygen σ-bonding orbitals or alternatively (2) to increasing p-content of the oxygen "nonbonding" sp^n orbital. This behavior is consistent with both models. Considerations of orbital electronegativity are based on the former. As the s-character of the σ-bonding orbital increases, the orbital electronegativity increases so that the bond becomes more ionic, stronger, and shorter.[42,43] Considerations of (d–p) π-bonding are based on the latter idea. As the p-character of the "nonbonding" hybrid orbital increases, the π-bond order increases, causing a shortening of bond length.[5]

A pronounced difference between these two models is reflected in the effective atomic charges as a function of SiOSi angle. Orbital electronegativity considerations postulate increased ionicity at wider bridging angles and enhanced effective silicon and oxygen formal charges, while (d–p) π-bonding considerations postulate increased silicon d-orbital populations at wider bridging angles and smaller effective silicon and oxygen formal charges. Yet, the dependence of the effective atomic charges on bridging angle is, to date, unknown.

A second pronounced difference between the two bonding models concerns the predicted departure of the oxygen electron cloud from spherical symmetry. The Stewart model postulates two bonding orbitals with significant covalence and two lone pairs. This bonding scheme predicts a much larger departure of the electron cloud from spherical symmetry than the Pauling model, wherein all four oxygen valence orbitals are considered bonding orbitals. Departures from spherical electronic distribution about a given nucleus are reflected in the electric field gradient (efg) at that nucleus.

In this paper we use experimental oxygen-17 electric field gradient tensor information to assess the plausibility of the Pauling and Stewart models. The efg at the nucleus is extremely sensitive to the local electronic environment and to the details of bonding. Townes and Dailey[44] ascribed the efg to an imbalance in the valence p- or d-orbital occupations. This model has for many years served as the simplest and most useful framework for discussing the efg's of light nuclei, where Sternheimer effects are believed small.[45,46] Until recently, however, rather little was known about

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the efg at the oxygen-17 nucleus, especially in silica and silicates, due to its low natural abundance (0.037%) and modest gyromagnetic ratio. However, recent advances in high-field nuclear magnetic resonance (NMR) techniques, including "magic-angle" sample spinning (MASS)[47] and "variable-angle" sample spinning (VASS),[48-50] in conjunction with advances in high-field superconducting solenoid technology, have sparked increased interest in the study of oxygen-17 nuclei in solids and the concomitant interpretation of the efg at the nucleus. In addition, the development of the Slusher-Hahn double-resonance technique[51] in NQR has facilitated the investigation of oxygen-17 in compounds containing protons. Recently, the Townes-Dailey (T-D) model has been applied successfully in analyzing oxygen-17 efg's for oxygen bonded to carbon,[52] nitrogen,[53,54] sulfur,[55] and phosphorus,[55] and the method has been confirmed by SCF calculations.[56] On the basis of the success of the Townes-Dailey model in analyzing these polar bonding situations, we have extended use of the model to the study of silicon-oxygen bonding. In particular, we use the orbital occupancies obtained from the Pauling and Stewart bonding models to calculate the experimental efg observables, the nuclear quadrupole coupling constant (NQCC), and asymmetry parameter (η) and compare these calculated values with the experimental ones observed in low cristobalite.

II. Methods

The analysis is presented in two parts. Initially, we restrict our attention to the interpretation of the oxygen-17 NQCC for silicon-oxygen bonds in terms of various models of bonding in silica and silicates. In the latter section, the analysis is extended to include the NQCC of divalent oxygen bonded to other elements in more well-defined systems, thereby supporting the validity of our approach as applied to the more controversial topic of bonding in silicates.

The experimental observables reflect only the local electronic environment of oxygen. Therefore, the characterization of the silicon bonding orbitals is necessarily made by inference. Thus, the term (d-p) π-bonding, unless made with historical reference, is not meant to exclude the possibility of s,p mixing into the silicon d-orbitals, nor does it preclude hyperconjugation to the silicon σ^* orbitals.[57]

Throughout the text we have adopted the σ-π description of the Si-O bond as developed by Pauling,[1] Jaffe,[3] and Cruickshank.[5] In subsequent work, however, Pauling has shown a preference for the bent (or banana) bond description.[2,40] These descriptions are generally regarded as equivalent for most substances.[6]

The Townes-Dailey Model. Following Townes and Dailey[44] the molecular orbitals, ψ_j, are expressed as a linear combination of oxygen atomic orbitals, ϕ_j:

$$\psi_j = \sum a_j\phi_j$$

An sp^n ($2 \geq n \geq 1$) hybrid set can be formed to describe bridging oxygen bond angles from 120 to 180°,[45] where

$$\psi_1 = \phi_{210}$$

$$\psi_2 = s^{1/2}\phi_{200} + (1 - s)^{1/2}\phi_{21-1}$$

$$\psi_3 = 2^{-1/2}((1 - s)^{1/2}\phi_{200} - s^{1/2}\phi_{21-1} + \phi_{211})$$

$$\psi_4 = 2^{-1/2}((1 - s)^{1/2}\phi_{200} - s^{1/2}\phi_{21-1} - \phi_{211})$$

$$s = \cot^2 (\theta/2)$$

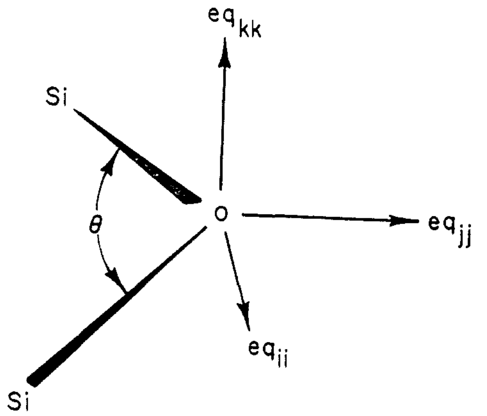

Figure 2. Oxygen-17 efg axis system used in Townes-Dailey model.

Here s is the hybrid orbital s-character and θ is the SiO$_{br}$Si angle. ψ_1 is the nonhybridized p-orbital perpendicular to the SiO$_{br}$Si plane with an orbital occupancy designated p$_\pi$. ψ_2 is the hybridized orbital directed along the SiO$_{br}$Si bisector with an orbital occupancy designated by p$_\sigma$. ψ_3 and ψ_4 are equivalent σ-bonding orbitals with an occupancy designated by σ. The principal axes of the electric field gradient tensor in terms of the axis system shown in Figure 2 are as follows:

$$\begin{aligned} eq_{ii} &= eq_{210}((-1/2)p_\pi + ((2 - s)/2)\sigma + (1/2)(s - 1)p_\sigma) \\ eq_{jj} &= eq_{210}((-1/2)p_\pi + ((2s - 1)/2)\sigma + (1 - s)p_\sigma) \qquad (1) \\ eq_{kk} &= eq_{210}(p_\pi - ((1 + s)/2)\sigma + (1/2)(s - 1)p_\sigma) \end{aligned}$$

where eq_{210} is the electric field gradient produced by one unbalanced p-electron (20.88 MHz).[58] By convention, the principal values are ordered as follows:

$$|e^2Qq_{ZZ}| \geq |e^2Qq_{YY}| \geq |e^2Qq_{XX}| \qquad (2)$$

and the asymmetry parameter, η, defined as

$$\eta = \frac{e^2Qq_{XX} - e^2Qq_{YY}}{e^2Qq_{ZZ}} \qquad (3)$$

Bonding models for sp^n ($n > 2$) oxygens are treated in a similar fashion, but with a different LCAO/MO basis set.[45]

The orbital populations deduced from a Townes-Dailey analysis are roughly equivalent to atomic orbital populations based on a Mulliken-type population analysis of the ground-state molecular wave function.

III. Results and Discussion

The Pauling and Stewart Bonding Models. The orbital occupancies obtained from both Pauling's (d-p) π-bonding and Stewart's orbital electronegativity models are Mulliken-like populations[40,41] which are amenable to a Townes-Dailey approach. Populations deduced from these models are used in eq 1 to obtain values for the principal efg components. The NMR observables NQCC and η are easily obtained by using eq 2 and 3.

The Stewart model[41] is based on Jaffe's orbital electronegativities, orbital electron affinities, and orbital ionization potentials of neutral atoms.[42,43] The deduced ionic character of the σ bonds, however, is obtained by using a relationship introduced by Klopman,[59-61] which differs by a factor of 2 from that proposed by Jaffe.

Since Stewart was able to account for the observed charge in low quartz without resorting to (d-p) π-bonding, we assume that oxygen has two lone pairs, that is p$_\pi$ = p$_\sigma$ = 2.0. The σ-orbital ionicity calculated by Stewart using Jaffe's data in Klopman's expression is 25.36% for the σ-orbitals in low quartz. On this basis the orbital occupation can be expressed as follows: $\sigma = 1.2536$, p$_\pi$ = 2.0, p$_\sigma$ = 2.0. Using eq 1 we find $|eq_{ii}| \geq |eq_{kk}| \geq |eq_{jj}|$ and $e^2Qq/h = -14.71$ MHz, $\eta = 0.18$. A minor calculation error

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changes the ionicity only slightly to 26.40%, yielding the occupancies $\sigma = 1.264$, $p_\pi = 2.0$, $p_\sigma = 2.0$, with the ordering of the principal axes the same, such that $e^2Qq/h = -14.51$ MHz, $\eta = 0.18$. Similar results are obtained for low cristobalite: $i = 26.77\%$, $\sigma = 1.2677$, $p_\pi = 2.0$, $p_\sigma = 2.0$, $e^2Qq/h = -14.61$ MHz, $\eta = 0.14$, with the same ordering of axes.

The Pauling model[1,2,40] is based on a relationship of bond order and bond length which is not strictly applicable to this situation. It was formulated to rationalize bond shortening to TO_4^{n-} tetrahedra and assumes (1) that two oxygen–p π-bonding orbitals are equivalent and (2) that there is an additional resonance shortening of the bond, due to the presence of two, rather than one, π-bonding p-orbitals. The model is also dependent on parametrizations, that is, derived bond orders are sensitive to the lengths chosen for a single, double, and triple bond (D_1, D_2, D_3).[2] When the relationship between bond length and bridging angle obtained for coesite[12] is used, a bond length of 1.663 Å corresponds to a bond angle of 120°. For simplicity, we make the valence bond assumption that at a 120° bridging angle p_σ is a lone pair[5] and the derived bond order is due to bonding from σ and p_π alone. As the bridging angle widens, we assume that p_π remains constant and that the p_σ occupancy will decrease from the lone-pair value of 2.0. We will ignore any hypothetical charge redistribution between the p_π and p_σ orbitals, and we will interpret any hypothetical bond shortening due to resonance stabilization by a second π-bond as indicating increased π overlap. Following Pauling,[40] we choose a single bond length $D_1 = 1.77$ Å and choose values of D_2 and D_3 intermediate to those tabulated on p 241 of his 1960 book[2] ($D_1 - D_2 = 0.21$ Å, $D_2 - D_3 = 0.105$ Å) and an ionicity of 50%. The orbital occupancies are $\sigma = 1.50$, $p_\pi = 1.6848$, and $p_\sigma = 1.7459$ for low cristobalite, yielding $|e^2Qq_{ll}| \geq |e^2Qq_{jj}| \geq |e^2Qq_{kk}|$. $e^2Qq/h = -4.27$ MHz and $\eta = 0.29$. However, if we use the more commonly accepted single bond length 1.76 Å[5] and the latter column in Pauling's table ($D_1 - D_2 = 0.24$ Å, $D_2 - D_3 = 0.12$ Å), then $\sigma = 1.5$, $p_\pi = 1.7618$, and $p_\sigma = 1.8087$, yielding $e^2Qq/h = -5.67$ MHz, $\eta = 0.11$, and the same ordering of axes. These calculations indicate that although the Pauling model is sensitive to parametrization, the coupling constants derived from the Pauling model are qualitatively smaller than the coupling constant derived from the Stewart model.

These results, of course, depend on our characterization of oxygen hybridization. Two other bonding models were advanced wherein oxygen remains unhybridized and bonds according to the bent-bond formalism with (1) two unhybridized, p-orbitals each bonded to a silicon atom[30] and (2) one unhybridized p-orbital each lobe bonding to a silicon atom.[32,33] The unhybridized oxygen is easily treated in Townes–Dailey language as described elsewhere.[45,55] If we assume the absence of (d–p) π-bonding and implicate the bonding σ-orbitals in charge transfer such that the oxygen charge is −0.5 eu, as observed experimentally, the situation can be modeled. In the former case of two bonding unhybridized p-orbitals, we assume that the s-orbital and one p-orbital have populations of two while the bonding p-orbitals have populations of 1.25, and thereby obtain $e^2Qq/h = +15.66$ MHz and $\eta = 0$. In the latter case, all the valence orbitals are full except one very depleted p-orbital of population 0.5, in which case $e^2Qq/h = -31.32$ MHz and $\eta = 0$.

We suggest, therefore, that the quadrupole coupling constants determined from oxygen-17 NMR can be used to assess the role of d–p π-bonding in silicates. In the absence of (d–p) π-bonding, we expect a gross p-orbital imbalance and a large quadrupole coupling constant (−14 MHz or larger), while in the presence of (d–p) π-bonding, we expect a modest p-orbital imbalance, and a modest quadrupole coupling constant (−4 to −6 MHz).

Recent experimental results from this laboratory include the oxygen-17 mass and VASS NMR spectra of low cristobalite.[62] The second-order quadrupolar mass line shape is characterized by $e^2Qq/h = |5.3| \pm 0.2$ MHz and $\eta = 0.0 \pm 0.05$. These results indicate that the p-orbital imbalance is modest, and within the range of couplings expected from Pauling's (d–p) π-bonding treatment. The p-orbital imbalance predicted by the Stewart and the unhybridized oxygen bonding models are not observed.

"Extreme Case" Parametrization of the Stewart Model. In the foregoing discussion, the Pauling and Stewart models were presented directly with use of the most basic Townes–Dailey terminology. While the Townes–Dailey interpretation of quadrupole coupling constants has proven valuable in ascertaining subtle differences in bonding among related compounds, the theory is considerably more approximate when used to distinguish the merits of bonding models based on absolute orbital occupancies. This necessitates a careful assessment of the weaknesses inherent in the Townes–Dailey model, and the construction of "extreme case" orbital occupancies for the Stewart bonding model, in order to fairly assess the sensitivity of the model to parametrization. The weaknesses of the treatment are largely threefold: (1) Implicit in the treatment is the partial atomic charge chosen for oxygen (−0.5 eu). The concept of atomic charge in solids is somewhat arbitrary and subjective, thus reported experimental values must be regarded as estimates. (2) The value chosen for e^2Qq_{210}/h, the efg produced by one unbalanced 2p electron, is that reported for neutral oxygen; the value for anionic oxygen is slightly less. (3) Orbital distortions induced by neighboring charges or crystal lattice polarizations (Sternheimer effects) have been ignored for the light oxygen atom.

The effective charge on an ion in a crystal is somewhat arbitrary since the charge is not formally an observable.[63] Consequently, the electron distributions obtained from X-ray charge density maps are dependent on the chosen atomic volume. It is thus desirable to examine other experimental measurements of charge in order to gauge the magnitude of the uncertainty. Si Kα and Si Kβ spectral shift measurements,[64] and phonon spectral analysis,[65] yield effective atomic charges for oxygen of −0.7 and −0.71 eu, respectively, in quartz. Compton scattering results have been rationalized in terms of a completely ionic quartz;[66] however, the successful application of ionic wave functions does not preclude substantial covalence.[29,67] Thus, experimental atomic charges for oxygen in quartz generally range from −0.5 to −0.7 eu. That these values may be roughly appropriate for all SiO_2 phases (or all bridging angles) is indicated by the coesite X-ray electron density map, which satisfies the electroneutrality principle.[68] In the Stewart model, any increase in the chosen effective oxygen charge is reflected by increased σ-bond ionicities, a lessened p-orbital imbalance, and smaller NQCC. Thus, in the "extreme case" analysis, a value of −0.7 eu will be employed.

The radial characteristics of the oxygen 2p orbital are also dependent on the effective atomic charge. Consequently, the efg produced by one unbalanced p-electron is, in turn, also charge dependent. The following correction has been suggested for oxygen,[45]

$$e^2Qq_{210}^{\text{eff}} = e^2Qq_{210}(1.2)^n$$

where n is the effective atomic charge. This correction is, in general, not large and is seldom used. For oxygen, in particular, its validity has not been well established. Nonetheless, the relationship should provide crude scaling of the effective orbital efg. Use of this term will also scale the Stewart model toward the experimental value.

Implicit in the Townes–Dailey treatment are the neglect of crystal field effects, which induce distortions in the oxygen electron cloud, as well as inner-shell distortions induced by valence bonding

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Table I. Orbital Occupancies for Low Cristobalite

case	e^2Qq/h sign	orientation of Z axis[a]	σ	p_π	p_σ	covalence of silicon	Q_O[b]
1	+	*kk*	1.562	1.815	1.562	6.8	−0.50[c]
2	−	*kk*	1.688	1.434	1.688	9.6	−0.50[c]
3	+	*jj*	1.555	1.555	1.834	6.7	−0.50[c]
4	−	*jj*	1.695	1.695	1.416	9.8	−0.50[c]
5	+	*ii*	1.758	1.504	1.480	12.4	−0.50[c]
6	−	*ii*	1.492	1.746	1.770	5.9	−0.50[c]
Pauling model[d]							
	−	*ii*	1.500	1.685	1.746	6.3	−0.43
	−	*ii*	1.500	1.762	1.809	6.1	−0.57
Stewart model[d]							
	−	*ii*	1.268	2.00	2.00	4	−0.54
	−	*ii*	1.350	2.00	2.00	4	−0.70[c]
B&G model							
3	+	*jj*	1.721	1.721	2.00	6.0	−1.2
6	−	*ii*	1.721	1.975	2.00	4.2	−1.4

[a] With respect to the axis system in Figure 2. [b] Effective atomic charge of oxygen. [c] Charge constrained by model. [d] Parametrization as described in the text.

orbitals.[46,69–75] As a consequence, the T–D treatment is most suitable for light nuclei without large, polarizable inner shells. The effect is at a minimum for the framework silicates but is likely to become increasingly important for silicates with lower degrees of polymerization and aluminosilicates, wherein the crystal lattice becomes increasingly ionic.

Sternheimer effects in metal halides are believed to overstate the halide NQCC expected from consideration of p-orbital imbalance alone and tend to exaggerate the actual σ-orbital depletion.[69,72] Similarly, we expect that the p-orbital imbalance predicted from the experimental NQCC for low cristobalite may also be overstated. On the basis of the antishielding factor from spherical potential ions,[74] however, we expect that oxygen is much less sensitive to field effects than are the halides, and four times less sensitive than chlorine. As a result, Sternheimer effects will tend to favor the large orbital imbalance at the nucleus predicted by the Stewart model. Therefore, in constructing an "extreme case" system, no correction for crystal field effects will be attempted, since such a modification is not likely to favor the smaller p-orbital imbalance observed experimentally. Furthermore, the good success of the T–D method as used for monocoordinate oxygen[52–56] and, as shown later, bicoordinate oxygen in polar bonding situations indicates that lattice effects are of secondary importance.

For clarity, we have developed a parametrization skewed against the large orbital imbalance predicted by the Stewart model in order to show that the T–D results are not a consequence of fortuitous parametrization. We employ an effective oxygen charge of −0.7 eu, a reduced value for the efg produced by an unbalanced p-electron, and no correction for Sternheimer effects. The resulting values in terms of the Stewart model are $\sigma = 1.35$, $p_\pi = 2.0$, $p_\sigma = 2.0$, $e^2Qq/h = -11.42$ MHz, $\eta = 0.14$. In spite of this deliberately skewed parametrization, the orbital imbalance predicted by the Stewart model is nonetheless quite large, qualitatively much larger than that observed experimentally. The quadrupole coupling constants predicted by the Pauling and Stewart models are shown graphically in Figure 3 as a function of bridging angle, together with the experimental result for low cristobalite.

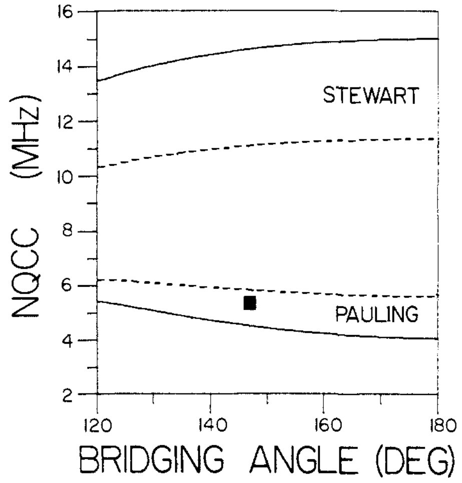

Figure 3. Predictions of the Stewart and Pauling bonding models for SiO_2 as a function of bridging-oxygen bond angle. The upper solid line represents Stewart's original formulation, while the dotted lines represent the extreme parametrizations as described in the text. The Pauling models represent the two bond-length–bond-order correlations described in the text. Due to the approximations involved in Pauling's model, the p_π and p_σ orbital occupancies differ slightly from equality at a linear bridging angle.

Townes–Dailey Results for Low Cristobalite. In the preceding discussion we have used the Mulliken-like orbital occupancies predicted from two different bonding models for bridging oxygens in silicates to calculate quadrupole coupling constants consistent with those models. Traditionally, however, the procedure has been the reverse: the quadrupole coupling constant is analyzed in T–D fashion to determine orbital occupancies. This procedure is more involved and subject to more ambiguity than the previous discussion. There are two main complications inherent when establishing orbital occupancies from the quadrupole coupling constant and asymmetry parameter. First, the NMR data yield the only two observables, NQCC and η, while there are three unknown orbital occupations. As a consequence, either an assumption must be made about one of the orbital occupancies or else experimental data concerning orbital populations must be used. Historically, assumptions have been made about orbital occupancies. For pure sp hybridization the two p-orbital occupancies are assumed identical. For pure sp^2 hybridization, the nonbonding sp^2 orbital is assumed a lone pair. The bridging oxygen hybridization in silicates is intermediate between these two cases, so that neither assumption is particularly useful. As a consequence, we choose to constrain the total oxygen charge to the experimental value, −0.5 eu, obtained from X-ray electron density maps.[38] The second complication is that since both the ordering of the principal axes *and* the sign of the quadrupole coupling are unknown, occupancies must be calculated for all six possible principal axis systems of Figure 2, as well as for both positive and negative NQCC, a total of 12 cases. For the case of low cristobalite, however, $\eta = 0$ and two of the principal axes are equivalent, so that the total number of possible axis systems is reduced to three,

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for a total of six cases. Orbital occupancies for these six cases are shown in Table I. The ordering of the principal axes and the sign of the NQCC predicted by both the Pauling and Stewart models are represented by case 6 in Table I. Clearly, the orbital occupancies are similar to those predicted by Pauling's (d–p) π-bonding model, and rather different from the occupancies predicted by Stewart. Moreover, none of the six cases have orbital occupancies which resemble those predicted by the Stewart model.

In order to assess the "reasonableness" of the other five cases, we will use the covalency concept. Covalency has proven very useful in valence bond formalism[2] and presumes that a single bond is defined by the orbital occupancy of the (oxygen) σ–bonding orbital, which is assumed more directed and stronger than π-bonds. In Cruickshank's valence bond treatment, the covalence of silicon is six, four from the σ-bonding sp^3 hybrid orbitals plus two from the assumed more strongly bonding E silicon d-orbitals. If we consider bonding to the T_2 silicon d-orbitals, the overlap integrals have been estimated as at least 1.73 times less than that of the overlap integral of the E d-orbitals, with one 2p orbital at the same internuclear distance,[5] thus the maximum covalence is 7.7. Pauling determined a covalence of a 6.2 for silicon.[40] To apply covalence to the six cases in Table I, the σ-orbital population is assumed representative of a single bond, a bond order of one. On this basis, bond orders can be calculated for the π-orbitals. We recognize that while the covalency concept has proven very useful over the years, it is inherently based on atomic electronegativities and makes the assumption that the ionicity of a single σ-bond and single π-bond are similar. As we use maximum covalence, the full σ-bond is presumed to have an ionic character roughly less than or equal to a full π-bond, as one would anticipate. Since the occurrence of (d–p) π-bonding in silicates is controversial, we choose a conservative value of nine for the maximum covalence, in recognition of ab initio calculations which show that the overlap of all five silicon 3d atomic orbitals are of comparable significance.[23] In the valence bond formalism a covalence of nine implies that all five silicon d-orbitals are fully bonded, and resonance structures indicate both substantially overbonded silicon and oxygen, with an average Si–O bond order of 2.25, and nine full bonds to silicon. By using the criteria of covalency, three cases, 2, 4, and 5, appear unreasonable, since silicon is clearly overbonded in conventional chemical terms.

We expect, furthermore, that p_π is roughly less than or equal to p_σ, since our model assumes that the orientation and orbital electronegativity of the p_π orbital is more favorable for overlap than the p_σ orbital. Cases 1 and 4 do not fit this expectation.

The two remaining cases, 3 and 6, are both indicative of substantial depletion of p_σ and p_π occupancies from the full orbital value of 2, presumably due to back-bonding to the silicon d-orbitals. The principal axis system, sign of the quadrupole coupling constant, and orbital occupations of case 6 are similar to those predicted by the parametrizations proposed earlier with use of Pauling's model. In particular, the small difference in orbital occupancies of p_π and p_σ observed is similar to that predicted by the Pauling model. The close correspondence of the orbital occupancies obtained from the Pauling model, and those obtained from the case 6 analysis, supports the applicability of the Pauling orbital occupancies used in conjunction with the Townes–Dailey model. In later sections, this point will be reinforced by showing that the Pauling orbital occupancies predicted for a variety of well-defined oxides yield good agreement with the experimental NQCCs.

It is hard to reconcile the large difference between the two π-bonding oxygen orbital populations predicted by case 3. The hybridization character changes rapidly near a bridging angle of 120° so that at the low cristobalite angle, 146.8°, the p_σ orbital has 91% p-character vs. 67% at 120°. Yet the p_σ orbital population is quite large, 1.83, near the full orbital value, while the p_π occupancy is unusually low, 1.56, indicating strong bonding. Unless substantial uncertainty in the orbital occupancies is assumed, this case cannot be treated with use of a model basing orbital occupancies on hybridization index. If, for instance, the π-overlap were governed by changes in silicon d-orbital electronegativity, due to variations in s,p mixing, a simple relationship between orbital occupancy and oxygen hybridization index may not be expected. Yet both the experimental bond lengths and recent theoretical evidence[11,12] indicate that the characteristics of Si–O–Si bonding are dependent on the oxygen hybridization index, but no such model for case 3 can be constructed without considerable speculation. Thus, while we consider the case 3 orbital occupancies much less realistic, given the complexity of the bonding situation we cannot completely dismiss this possibility.

G&B Analysis. Geissberger and Bray (G&B) previously obtained the O–17 NQCC of amorphous silica using continuous wave NMR techniques.[27] The observed NQCC of the less well defined amorphous silica ($|e^2Qq/h| = 5.2$ MHz) is reasonably close to the value obtained for low cristobalite from high-field FT–NMR studies. Their interpretation of the data, however, differs markedly from that presented here, despite our common use of a similar LCAO/MO approach and similar ^{17}O NQCC. Although the same orientation and sign of the efg are considered "reasonable" (cases 3 and 6) in both analyses, different assumptions in the T–D treatment lead to different orbital occupancies for the two cases and, consequently, G&B assign different significance to their results as to the implications for bonding in silicates.

In the present analysis, both cases are interpreted as representative of a π-bonding mechanism in silicates. Case 6 corresponds well to Pauling's predictions for (d–p) π-bonding in silicates and is considered the more reasonable assignment. Case 3 exhibits a degree of p_π orbital depletion unexpected from the degree of hybridization, corresponds to no extant model, and, therefore, is considered a less realistic assignment. Shown in Table I are the orbital occupancies for both cases as calculated by using the G&B approach as applied to low cristobalite, which are quite similar to their original values noted for amorphous silica. The orbital occupancies obtained are uniformly inflated from those of the present analysis. As a result, G&B conclude that case 3 is representative of a π-bonding mechanism, while case 6 is representative of the absence of π-bonding. They further state that while there is considerable ambiguity as to the relative merits of the two cases, the evidence weakly supports a π-bonding mechanism (case 3). Clearly it is important to recognize and assess the merits of the assumptions involved in the two approaches, which lead to different interpretations.

The two treatments differ with respect to the two main complications noted earlier: (1) the assignment of three unknown orbital occupancies from two NMR observables and (2) the choice of the proper efg orientation and sign. G&B adopted a traditional approach to these complications by reducing the unknown orbital occupancies from three to two by characterizing oxygen as a modified sp^2 hybrid, thereby assigning the p_σ orbital the lone-pair occupancy of two. The proper efg orientation and sign are then determined from considerations of effective atomic charge.

The characterization of the SiO_2 oxygen as a modified sp^2 system, despite an average bridging angle of 144° (very similar to that of low cristobalite), ignores, we believe, the "intermediate" nature of oxygen hybridization. Thus, while the bridging angle may be closer to the sp^2 angle of 120°, the hybridization index more closely resembles the sp case of 180°. Furthermore, the characterization differs from Cruickshank's valence bond treatment, in which such bridging angles are believed to facilitate π-bonding of the p_σ orbital.[5]

In the present discussion, no assumption about individual orbital occupancies is made, except to constrain the collective orbital occupancies to fit the experimental atomic charge obtained from other techniques. In this manner, we bypass the usual T–D assumptions for sp^2 ($p_\sigma = 2$) and sp ($p_\sigma = p_\pi$) hybridization schemes, which we believe have little relevance for most silicates, due to the intermediate nature of oxygen hybridization in these compounds.

The consequence of the G&B characterization of oxygen as a modified sp^2 system is uniformly inflated orbital occupancies that are characteristic of effective atomic charges for silicon and oxygen that greatly exceed electroneutrality and imply effective silicon charges greater than two for all possible orientations and signs of efg axes. Their reasonable axis systems, however, were chosen on the basis of equally inflated oxygen effective charges similar to the 50/50 description of the SiO bond (Si = +2, O = −1) propagated by the misinterpretation of Pauling's electronegativities. In particular, G&B cite effective oxygen charges of −1.2 and −1.14 eu. The former estimate was obtained from an LCAO/MO treatment of quartz-like clusters.[33] Not only does this treatment explicitly neglect d-orbital participation in the basis set, but it assumes unhybridized oxygen bonding orbitals, which may have little relevance for comparison with the G&B modified sp^2 scheme. Previously we showed that such a bonding model cannot satisfy both the NQCC and electroneutrality considerations. Indeed, even for an effective oxygen charge of −1.2 eu, this model predicts an NQCC of −16.7 MHz ($\sigma = 1.2$, p_x, $p_y = 2.0$), far from the observed value. The latter estimate is based on modified Phillips' ionicities obtained from the experimental optic dielectric constant of quartz.[34] The calculated ionicity is 57% and in rough agreement with Pauling's ionicity. The effective oxygen charge is calculated for both 8 and 16 bonding valence electrons per SiO_2 fragment, representing the absence and presence of π-bonding, respectively. In the absence of π-bonding, a charge of −1.14 eu on oxygen is obtained, and it is this value that is cited in the G&B treatment. In the presence of (d–p) π-bonding, however, the calculated oxygen effective charge is much less, −0.28 eu. Using these effective oxygen charge estimates G&B interpret the data as favoring case 3, since the T–D charge for case 3 (−1.2 eu) was in better agreement than case 6 (−1.4 eu) with the cited value (−1.2 eu).

The present alternative analysis, however, makes very conservative use of covalence arguments in the choice of reasonable efg axis system and sign. Although the present interpretation also depends on the chosen effective atomic charge of oxygen, we have employed the most modern and widely accepted value.

Note that although we find the p_σ and p_π orbital occupancies are not too different (as would be expected in a model that precludes (d–p) π-bonding and where oxygen has two lone pairs), this does not mean that a (d–p) π-bonding model is incompatible with similar orbital depletion of the p_σ and p_π orbitals for typical bridging angles in silicates. For case 6 to represent the absence of π-bonding, a gross systematic error must be assumed in the T–D model. Later, we show that for oxygen bonded to other elements in well-defined oxide systems, this is certainly not the case.

Diopside Bridging Oxygen. The diopside bridging oxygen is characterized by $|e^2Qq/h| = 4.4$ MHz and $\eta = 0.3$.[50] The $Si-O_{br}$ bond lengths are significantly longer than those for the framework bridging oxygens and slightly asymmetric, 1.664 and 1.687 Å, while the bridging oxygen angle is rather narrow 135.9°.[76] The narrow bridging angle permits further coordination to oxygen without undue steric hindrance, and the bridging oxygen is coordinated to two calcium sites. Within the (d–p) π-bonding scheme the slight asymmetry in the $Si-O_{br}$ bond length is ascribed to differing π-bond orders, and it can be described exactly in the T–D formalism with the same value for the σ-orbital occupancy, σ, for each bond. The calcium sites, however, are located in an asymmetric manner to the plane which bisects the SiOSi angle and are inclined toward the longer $Si-O_{br}$ bond ($Si^{I}-O-Ca^{I,II}$ = 101°, 118°; $Si^{II}-O-Ca^{I,II}$ = 91°, 95°). As a result, a slight mismatch must be assumed between the p_σ, p_π orbitals and the O–Ca internuclear vector. In lieu of an experimental value for the bridging oxygen effective charge, we choose to examine differences in orbital occupancies rather than absolute values, and in recognition of the approximate treatment of calcium coordination we shall not place undue emphasis on exact values.

The p-orbital imbalance for the diopside bridging oxygen using the case 6 T–D analysis described previously is $p_\pi - \sigma = 0.232$, 0.190; $p_\sigma - \sigma = 0.227$, 0.277, for both possible orientations of the minor efg axes. In comparison, a significantly larger p-orbital imbalance was observed for the bridging oxygen of low cristobalite $p_\pi - \sigma = 0.254$, $p_\sigma - \sigma = 0.278$.

Within the context of the Townes–Dailey model, the reduced p-orbital imbalance cannot be explained without considering the coordination to calcium. Only small changes in NQCC are likely due to the narrower bridging angle. Orbital electronegativity considerations postulate a longer, more covalent bond at narrower angle and a slightly increased p-orbital imbalance, while the hybridization dependence of the T–D model tends to slightly decrease the NQCC. These two effects are small and opposite and largely cancel. Changes in silicon electronegativity due to the decreased degree of polymerization are expected to affect both the σ and π system and are not likely to be able to explain the lowered NQCC.

Is calcium an electron donor or electron acceptor in the bridging oxygen–calcium coordination? Calcium is widely believed to be an electron donor with respect to the *non*bridging oxygens and the silicate tetrahedra.[1–3,5,7,22,23,31] Yet, if calcium were an electron donor to the bridging oxygen as well, the increased p_σ, p_π orbital occupancies would tend to increase the p-orbital imbalance and NQCC. Instead, to account for the smaller p-orbital imbalance in diopside (0.9 MHz smaller than that for low cristobalite), the calcium must be considered an electron acceptor with respect to the bridging oxygen. That is, calcium accepts charge density from the bridging oxygen p_σ and p_π orbitals. In this way the bridging oxygen–calcium coordination can be viewed in much the same manner as for oxygen involved in hydrogen bonding, which causes depletion of the coordinated orbital.[52,53]

In restating Baur's extended electrostatic valence rule[77] in molecular orbital terms, Burdett described the effect of coordination as follows:[78]

"An advantage of the orbital approach over a purely ionic model is that it alloys an extremely simple explanation for Baur's extended electrostatic valence rule. At the simplest level, this rule amounts to the remark that increasing the coordination number of an anion or the electronegativity of its metal neighbors ties up more and more of its electron density in these bonds and leaves less density available for bonding with another fixed neighboring atom."

McDonald[79] extended the (d–p) π-bonding formalism to coordinated bridging oxygens and postulated partial covalent charge transfer from the bridging oxygen to the coordinated cations. In this manner charge density involved in the (d–p) π-bond is transferred to the coordinated cation away from the $Si-O_{br}$ π-bond. As a result, the π-bond order of the $Si-O_{br}$ bond decreases and in turn causes an increase in the $Si-O_{br}$ bond length greater than that expected from the bond-length–bond-angle correlation described previously for the framework oxygens, in agreement with the crystal structure results.[76]

The most straightforward explanation of the lower p-orbital imbalance observed for bridging oxygen upon coordination is consistent with covalent charge transfer from the bridging oxygen to the cation, in agreement with Burdett's molecular orbital treatment of the Pauling/Baur electrostatic bond strength sum rule and McDonald's (d–p) π-bonding treatment. This result highlights the similarities between these two approaches (both originally proposed by Pauling[2]) and is evidence for their mutual compatibility. We have, of course, ignored the Sternheimer effects which may become increasingly important in describing the influence of the calcium ions on NQCC. Moreover, while the results are consistent with (d–p) π-bonding, they are not necessarily exclusive of other interpretations.

Structural Implications. There are two main aspects to the d-orbital controversy. On the one hand, the existence of (d–p) π-bonding is disputed. On the other hand, given the existence of (d–p) π-bonding, to what extent is the effect of structural significance? Does the correlation between the Si–O bond length and Si–O–Si bridging angle originate, at least in part, from

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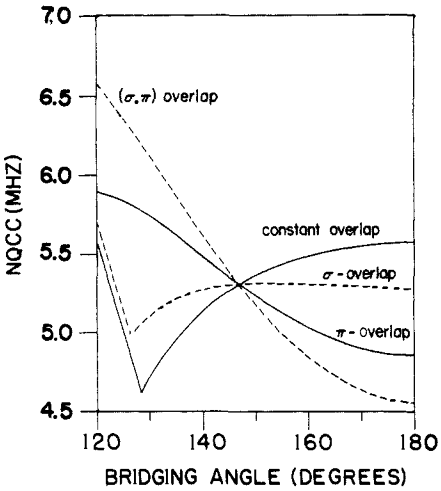

Figure 4. Predicted dependence of the oxygen NQCC on SiOSi angle for bonding models in SiO_2 polymorphs. The solid line labeled "π-overlap" represents the valence bond hypothesis that strong correlation exists between π-bond order and SiOSi angle, which implies that the (d–p) π-bonding is of structural significance. The solid line labeled "constant overlap" represents (d–p) π-bond order that is invariant to changes in SiOSi angle and thus implies a structurally insignificant π-effect. The dotted lines incorporate changes in the σ-bond ionicities using considerations of orbital electronegativity advocated by Stewart/Klopman and discussed in the text. The discontinuity at narrow bridging angles is due to a change in the principal efg axis system.

changes in (d–p) π-bonding? Several recent molecular orbital calculations admit the possibility of (d–p) π-bonding, but they imply only a minor structural significance.[28,36,37] That is, the (d–p) π-bonding effect facilitates charge transfer, but it is found insensitive to variations in bridging angle and/or bond length. For instance, a recent ab initio/MO study of H_4SiO_4 found that a slight *increase* in SiO bond length accompanied inclusion of silicon d-orbitals in the basis set.[37]

Cruickshank's (d–p) π-bonding model was based on the belief that the E d-orbitals in Figure 1 are strongly bonding and that π-overlap is highly correlated with bridging bond-angle. Subsequently, Collins, Cruickshank, and Breeze[23] performed ab initio calculations on orthosilicic acid (H_4SiO_4, ∠SiOH = 109.5°) and noted that all five silicon d-orbitals contain substantial and roughly equivalent orbital occupancies. More recently, Newton and Gibbs[10] reported ab initio results for linear pyrosilicic acid ($H_6Si_2O_7$, ∠SiOH = 109.5, ∠SiOSi = 180°), which indicate that the π-overlap of the E d-orbitals exceeds that of the T_2 d-orbitals by a factor of 2.6, similar to the difference, 1.7 or greater, originally anticipated by Cruickshank. Nonetheless, the observed T_2 overlap was eight times as large as the very small changes in total (d–p) π-overlap which accompanied variation of the bridging bond-angle from 140° to 180° (using clamped bond lengths), leading these authors to suggest that it is inappropriate "to ascribe the Si–O bond length variations in silicates and siloxanes to changes in the π-bond order of the E-type MO's induced by variations in the SiOSi angle" as is customary in Cruickshank's valence bond description, in which the π-overlap is strongly correlated with the bridging angle.

As noted previously, SiO bond length variations which accompany variations in the SiOSi angle are generally ascribed either to changes in the π-bond order or to changes in the σ-bond ionicity. Efforts to assess these effects by reference to changes in the effective atomic charges with bridging bond angle, to date, have been inconclusive. An X-ray electron density map of coesite, which exhibits a variety of bridging oxygen sites, showed no clear trend.[68] MO calculations yield differing results.[10,12]

We believe that it may be possible to assess the origins of the bond-length–bond-angle correlation with reference to variations of the ^{17}O NQCC as a function of SiOSi angle for bonding models which incorporate combinations of σ- and π-effects. We propose the following four bonding models, illustrated in Figure 4, based on the case 6 orbital occupancies of low cristobalite. (1) The solid line labeled "π-overlap" represents a linear correlation between π-bond order (or p_σ orbital depletion) and hybridization index, assuming constant σ-bond ionicity. This model represents Cruickshank's valence bond characterization and implies that the π-bond order largely determines the Si–O bond length. (2) The solid line labeled "constant overlap" represents total σ- and π-orbital occupancies which are invariant to changes in the SiOSi angle, thus variations of the NQCC are determined largely by the hybridization dependence of the T–D model. Charge redistribution between the p_σ and p_π orbitals is postulated to satisfy the necessary equivalence of these orbitals at a linear bridging angle. This model attributes bond-length variations to crystal packing/cation repulsion effects and/or resonance stabilization effects postulated by Pauling due to the varying degree of participation of the p_σ orbital in the π-system.[3,4] The dashed lines labeled "(σ,π)-overlap" and "σ-overlap" incorporate variations in the σ-bond ionicities within the two preceding models, based on the considerations of orbital electronegativity with use of trends from the Klopman/Stewart model discussed previously. The former model presumes that the SiO bond length is determined by both the Pauling/Cruickshank π-bond order and the Klopman/Stewart σ-orbital overlap. The latter model assumes that bond-length variations are due largely to changes in the σ-orbital overlap.

On the basis of the trends in Figure 4, we expect that if the π-bond order determines, at least in part, the SiO bond length, a decrease in NQCC will accompany widened bridging angles. If, however, the π-bond order remains constant, we expect an increasing or constant NQCC to accompany widened bridging angles (with possible change of principal efg axis system at narrow bridging angles). Due to the uncertainties involved, the actual numbers are less significant than the trends in NQCC variation with bridging angle, which indicates, we believe, that this question may be resolved by ^{17}O solid state NMR studies of other SiO_2 phases.

Ionicity and NQCC. In the preceding discussion, the analysis was restricted to oxygen bonded to silicon. In this section, the NQCC of oxygen bonded to other elements is analyzed, and this demonstrates that (1) the orbital occupancies obtained from Pauling's ionicities are in good agreement with the experimental oxygen NQCC in selected, well-defined oxide systems, where assumptions about effective atomic charge need *not* be employed, (2) evidence for a π-bonding mechanism in silicates is discerned from the trends of the NQCC in these selected systems, using electronegativity arguments, and (3) similarities between the oxygen results and earlier halide NQCC results further reinforce our belief of π-bonding in silicates.

Recently, Schramm et al.[62] noted an empirical correlation between multicoordinate oxygen NQCC and the average Pauling bond ionicities of the two strongest interactions. This correlation (with supplemental data), shown in Figure 5, provides a convenient framework for the discussion of trends in oxygen NQCC for a wide range of compounds. The original correlation (solid line) was as follows

$$|e^2Qq/h|(\text{MHz}) = -0.203I(\%) + 14.8$$

Of particular interest are the bicoordinate oxygen compounds with approximate C_{2v} symmetry (such as low cristobalite), but in which π-bonding effects can be dismissed. That is, oxygen has two equally occupied bonding orbitals and two nonbonding lone pairs. This well-defined bonding situation is readily treated in the LCAO/MO approach and permits broad generalizations relating bond ionicities and bridging angle to the oxygen NQCC. The bonding scheme also represents a maximum predicted p-orbital imbalance (or NQCC) for a particular ionicity and bridging angle. If the bridging angle is greater than the tetrahedral angle (109.5°), the major principal efg axis is in the molecular plane perpendicular to the bridging angle bisector, and the NQCC is negative (case 6 in the earlier discussion). At the tetrahedral angle, $\eta = 1$, and the efg axis perpendicular to the molecular plane is of equal magnitude, but opposite sign, to that along the axis perpendicular to the bisector. Below the tetrahedral angle, the major principal

Table II. Predicted Oxygen-17 Nuclear Quadrupole Coupling Constants (MHz) Calculated from Bond Ionicities Assuming No Back-Bonding

	THP[a]	water vapor	low cristobalite	mercuric oxide
exptl	±11.2 ± 0.5[b]	+10.175 ± 0.067[c]	±5.3 ± 0.5[d]	±7.0 ± 0.5[e]
Pauling	−12.4	+10.2	−9.8[f]	+8.5[g] (7.8)[h]
Stewart	−13.5	+14.2	−14.6	[i]
Gordy (0% s)	−8.0	+5.0	−3.0	+3.2[g] (2.4)[h]
Gordy (25% s)	−10.6	+6.7	−4.0	+4.3[g] (3.2)[h]

[a] Tetrahydropyran, $C_5H_{10}O$. [b] Solution-state NMR, ref 83. [c] Microwave, ref 84. [d] Solid-state FT–NMR, ref 62. [e] Solid-state FT–NMR, ref 85. [f] On the basis of Pauling's ionicity with bond order of one. Does not satisfy electroneutrality. [g] Calculated from Pauling's electronegativities, χ_{Hg} = 1.9, ref 2. [h] Calculated from "selected" electronegativity, χ_{Hg} = 1.8, ref 87. [i] Orbital electronegativities for sp-hybridized mercury not available.

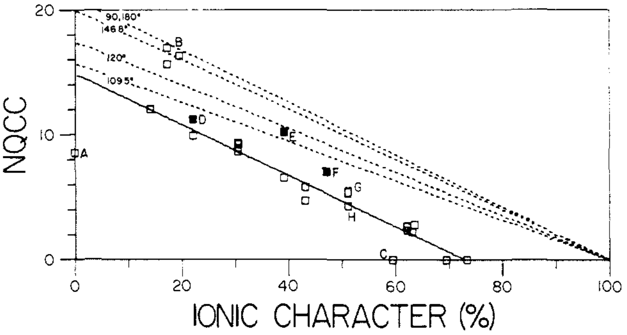

Figure 5. Plot of ^{17}O NQCC (absolute value of e^2Qq/h, MHz) for multicoordinate oxygen vs. average percent ionic character as deduced from Pauling's electronegativities and ionicities, without correction for π-bonding. Adapted from ref 62, with supplemental data. The solid line is the best fit to the data used in the original plot. The dashed lines represent the maximum p-orbital imbalance (or NQCC) predicted for compounds with local C_{2v} symmetry about the bridging bicoordinate oxygen, for a given bridging-angle, as indicated, and calculated according to the considerations given in the text. Solid squares indicate the well-defined systems discussed in the text. Lettered compounds are as follows: (A) ozone, (B) hydrogen peroxide and both oxygens coordinated to iridium in Vaska's dioxygen adduct, (C) zinc oxide, (D) tetrahydropyran, (E) water vapor, (F) mercuric oxide, (G) low cristobalite, (H) diopside bridging oxygen.

axis is fixed perpendicular to the molecular plane, and the NQCC is positive (case 1 in the earlier discussion).

The quadrupole coupling constant is directly related to the bonding orbital occupancies in terms of the sp^n ($1 \leq n \leq 2$) LCAO/MO approach by solving for the field gradient along the major principal axis

$$e^2Qq/h = 0.5(\sigma(2 - s) - p_\sigma(1 - s) - p_\pi)e^2Qq_{210}/h$$

For sp^2 hybridization ($s = {}^1/_3$, $p_\sigma = p_\pi = 2.0$) the relation reduces to the following predicted maximum p-orbital imbalance for compounds with C_{2v} local symmetry

$$e^2Qq/h\ (\text{MHz}) = 0.174I(\%) - 17.4$$

Similar considerations for the low cristobalite bridging-angle (146.8°) yields

$$e^2Qq/h\ (\text{MHz}) = 0.200I(\%) - 20.0$$

Treatment of bridging angles less than 120° necessitates use of a different LCAO/MO basis set,[45] and similar results are obtained for the tetrahedral bridging-angle

$$e^2Qq/h\ (\text{MHz}) = \pm 0.157I(\%) \mp 15.7$$

For still narrower angles, there is a change in the orientation and sign of the major principal axis, represented in the extreme for a 90° bridging angle as follows:

$$e^2Qq/h\ (\text{MHz}) = -0.209I(\%) + 20.9$$

Thus, for constant ionicities, the maximum predicted p-orbital imbalance is least at the tetrahedral angle and increases in absolute magnitude for both narrower and wider bridging angles, such that the predictions for 90° and 180° bond angles are equal in magnitude but opposite in sign. These relations are represented by the dotted lines in Figure 5.

The large majority of the compounds represented in Figure 5, not surprisingly, do not satisfy the simple picture of oxygen with two equivalent bonding orbitals and two nonbonding lone pairs. Instead, the majority exhibit depletion of the lone pair orbital occupancies due to (1) π-bonding effects or (2) hydrogen bonding or other additional coordination. The former effect is well represented by the central oxygen resonance of ozone (e^2Qq/h = −8.52; $I(\%)$ = 0.0).[80] Extensive π-delocalization is reflected by an unusually small NQCC for such a covalent compound (A in Figure 5), and yet the result conforms well to Townes–Dailey expectations for sp^2 oxygen where four electrons are delocalized among the three ozone π-bonding orbitals.[80] In some of the organic compounds, hydrogen bonding could lower the p-orbital imbalance, and in the more ionic materials, additional coordination for oxygen yields the same result. These effects both tend to decrease the p-orbital imbalance from the predicted maximum. Representative of the second effect (multiple coordination) is the negligible NQCC observed for zincite (ZnO, $I(\%)$ = 59.4), in which the oxygen coordination is nearly perfectly tetrahedral (C in Figure 5).[81] Anomalously large NQCC will occur if the bond ionicities of the elements bonded to oxygen differ greatly. In the extreme case of one covalent and one ionic bond, a p-orbital imbalance of one electron (20.88 MHz) is expected. Hydrogen peroxide (e^2Qq/h = 16.3 MHz, $I(\%)$ = 19.5) and Vaska's compound (Ir–O–O: e^2Qq/h = 15.6, 16.9 MHz; $I(\%)$ = 17) are typical examples[82] which approach this limit (B in Figure 5).

The compounds which more closely satisfy the criteria of two equivalent bonding orbitals and two nonbonding lone pairs, represented by the solid squares in Figure 5, are the saturated heterocycle tetrahydropyran ($C_5H_{10}O$),[83] water vapor,[84] and mercuric oxide[85] (D, E, and F, respectively, in Figure 5). The latter compound forms HgO chains in the solid state, with linear and near-tetrahedral bridging angles for mercury and oxygen, respectively, with an HgO bond length as expected for sp-hybridized mercury.[86] Back-bonding into the mercury d-orbitals is proscribed by the full d-shell of mercury. While charge transfer from oxygen into the two empty mercury p-orbitals of a neighboring chain is possible, the relatively large interatomic distance suggests that this effect is probably small, but perhaps not negligible. Thus, mercuric oxide approximately fits the criteria above, and at the very least it represents the minimum ^{17}O NQCC for an isolated HgO chain within the T–D approximation.

The predictions of the Pauling and Stewart models for these three compounds are listed in Table II, and support our earlier claim of π-back-bonding in silicates. The predictions of the Pauling model are quite good, *except* for the low cristobalite model that *precludes* π-back-bonding. The Stewart model is in much better (though quite qualitative) agreement with the experimental data except for low cristobalite. Rationalization of the silicate NQCC *without* π-back-bonding thus requires presumption of unexpectedly ionic SiO bonds, which in Paulings' terms would be characteristic of a silicon electronegativity of 1.2, far from the observed value of 1.8. Allowance for π-bonding in the silicate,

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however, explains the anomaly.

The Pauling orbital occupancies used, in conjunction with the Townes–Dailey LCAO/MO approach, exhibit good agreement with the experimental oxygen NQCC in simple systems where the nature of bonding is uncontroversial. This observation not only substantiates the conclusions of the earlier discussion on silicates but demonstrates, we believe, the predictive and analytic power of the method in interpreting oxygen NQCC, at the very least for compounds of intermediate electronegativity difference.

The acceptance of Pauling's orbital occupancies implies rejection of a similar method of relating electronegativity differences to orbital occupancies, proposed by Gordy,[87-89] as illustrated in Table II. Although both methods were based on experimental data for diatomic halides, Pauling's formulation ($i = 1 - \exp(-{}^1/_4(\Delta\chi)^2)$) was derived from dipole moments,[2] whereas Gordy's formulation ($i = {}^1/_2\Delta\chi$) was derived from halide NQCC. The latter model suffers from uncertainties in the degree of hybridization of the halide bonding orbital, which Gordy characterized as an unhybridized p-orbital. The degree of hybridization of monocoordinate atoms cannot be determined through directed valence arguments based on molecular geometry, as used in this work. Subsequent investigators suggested that the s-hybridization of the halide bonding orbital is neither necessarily zero nor constant[45,90,91] and may overestimate the actual ionicities.[92] The inclusion of s-character in Gordy's relation favors the more covalent predictions of the Pauling model and can be formulated as follows:

$$i = 1 - [(1 - \Delta\chi/2)/(1 - s)]$$

The Gordy predictions for 0% and 25% ($s = 0.25$) s-character are shown in Table II. The inclusion of 25% s-character gives better, but not completely satisfactory, agreement, especially at large electronegativity differences. Similarly, early efforts to reconcile the Pauling and Gordy ionicities through hybridization arguments were abandoned.[87,91] Regardless of hybridization, Gordy considered electronegativity differences greater than two as completely ionic. The implication that aluminum–oxygen bonds are completely ionic is in contradiction to recent analysis of the phonon spectrum of Al_2O_3 (corundum)[93] which indicate that the effective atomic changes of aluminum and oxygen are half the pure ionic value (+1.5, −1.0 eu, respectively) and that the bond ionicities are approximately 70%, in qualitative agreement with Pauling's value of 63.2%. While a detailed investigation of the Gordy model(s) is beyond the scope of the present discussion, it should not be construed that the NQCC results for the halides are in contradiction to those for oxygen. On the contrary, preliminary results indicate that they are complementary, as illustrated in the following.

Early workers noted that the halide NQCC of the silicon halides was characteristic of an ionicity far greater than expected on electronegativity grounds.[45,87-91] The apparent orbital occupancies for the group 4 halides, assuming no back-bonding, are shown in Figure 6A, as adapted from ref 45. The large apparent ionicity of the silicon tetrahalides was seemingly inconsistent with the nearly equal electronegativities of Si, Ge, Sn, Pb, and Hg (1.8 to 1.9), and this observation has been rationalized in terms of π-back-bonding for the silicon compounds. Additional studies also demonstrated that the silicon halides were much less sensitive to substituent changes than their carbon analogues[45,94] and that perturbations of the halide NQCC caused by the application of an external dc field were less for the silicon halides than for other compounds.[95] These observations were interpreted as resulting from mesomeric π-bonding interactions for silicon. More recently, Jolly[96] has compared the halide lone pair ionization potentials (with corrections from core binding energies) among group 4 halides and concluded that π-bonding effects are present for silicon. Thus, the NQCC of the silicon halides are anomalously small in comparison with other compounds of similar electronegativity. Rather than postulate an anomalously high ionicity for the silicon halides, the results were interpreted as due to π-bonding effects.

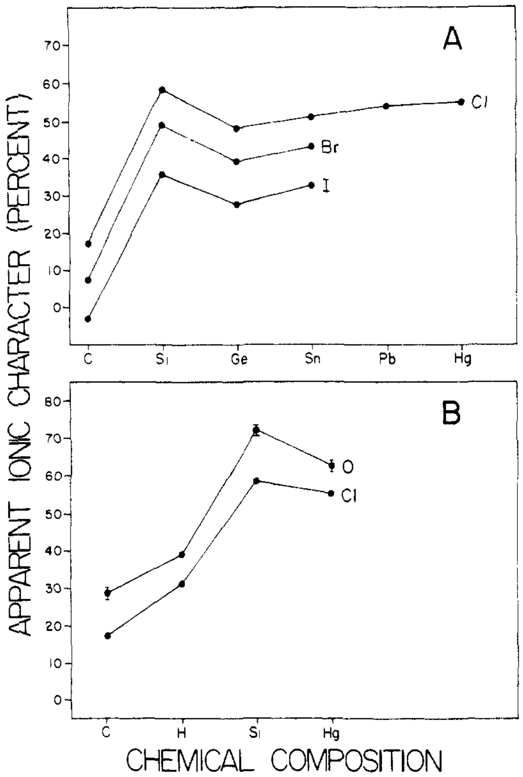

Figure 6. (A) Apparent ionic character of the group 4 (and mercury) halides as determined from the halide NQCC, assuming no π-bonding and 10% s-character in the halide bonding orbitals, as adapted from ref 45. (B) Comparison between the apparent ionic character of various oxides and chlorides, assuming no π-bonding.

The similarities in trends of orbital ionicities determined from chlorine and oxygen NQCC, assuming no π-back-bonding, are shown in Figure 6B. While the number of compounds is limited because of the small oxygen database, there are clear similarities between the two trends. The oxygen NQCC of SiO_2 is significantly smaller than that of HgO (in which π-back-bonding is unlikely), despite the near tetrahedral bonding angle in HgO, which favors a smaller NQCC for a given ionicity. As for the halides, if π-bonding effects are ruled out, this observation implies an anomalously ionic silicon–oxygen bond, which would be surprising given the similar electronegativities of Hg and Si, both 1.8 using the selected values from ref 87, or 1.8 and 1.9, respectively, from Pauling's tabulation.[2] Stewart, on the other hand, rationalized the experimental results concerning the effective oxygen charge in terms not of an anomalously ionic but of an unusually covalent silicon oxygen bond. It is our opinion, however, that the silicon–oxygen bond is neither unusually ionic nor unusually covalent but as expected, based on Pauling's ionicities. Furthermore, we believe that the results concerning the effective oxygen charge and NQCC can be rationalized by considering π-back-bonding to the silicon d-orbitals (or σ^*-antibonding orbitals).

Summary. We conclude the following:

(1) All four valence orbitals of the bridging oxygen of low cristobalite participate in bonding. (2) Our results are consistent with Pauling's (d-p) π-bonding model for silicates. (3) Our results

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are in poor agreement with bonding schemes which consider only two of the four valence orbitals as bonding orbitals. In particular, the hybridized bonding scheme proposed by Stewart, as well as two unhybridized bonding schemes, yields poor agreement with the experimental NQCC unless (d–p) π-bonding (or hyperconjugation) is postulated. (4) Calcium coordination to the diopside bridging oxygen is consistent with calcium in a charge acceptor role. The results are consistent with McDonald's (d–p) π-bonding model. (5) Analysis of the NQCC of bridging oxygen bonded to elements other than silicon in well-defined systems further evidences the usefulness of the Pauling orbital occupancies in tandem with the Townes–Dailey treatment as a predictive tool for oxygen NQCC. (6) The dependence of the ^{17}O NQCC in the SiO_2 polymorphs as a function of bridging angle may yield insight concerning the structural significance of the (d–p) π-bonding effect. (7) Orbital occupancies obtained from Gordy's method yield poor agreement with experiment. (8) The oxygen NQCC are shown consistent with the halide NQCC of analogous systems. (9) Trends in the oxygen and halide NQCC, of compounds with analogous chemical composition, support the conclusions of (d–p) π-bonding or hyperconjugation in silicates, on electronegativity grounds. (10) Considerable potential exists for use of the NQCC in conjunction with more sophisticated molecular orbital calculations, as well as X-ray electron density maps.[97] Furthermore, as we have previously noted, the (d–p) π-bonding effect may influence the silicon-29 NMR isotropic chemical shift.[98]

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Registry No. Si, 7440-21-3; O_2, 7782-44-7; ^{17}O, 13968-48-4.

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Demonstration and Characterization of Two Complexes of Cobalt(II) to Mononucleotides by ^{31}P and ^{1}H NMR

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Abstract: Direct observation, under slow-exchange conditions, of the ^{31}P and ^{1}H spectra of 5′-AMP in solutions containing Co^{2+} demonstrates the existence of at least two different complexes in a temperature-dependent equilibrium. The majority species at low temperature (80% of −10 °C) has a small phosphorus paramagnetic shift, −48 ppm, and a large H8 paramagnetic shift, −203 ppm. This indicates indirect coordination to phosphate and direct coordination to N7. This is the same coordination as in the crystals of 5′-monophosphates of purines complexed with transition-metal ions of the first series. The second complex, a 20% minority at −10 °C, has a large phosphorus shift, −2530 ppm, and a small but significant shift of H8, −37 ppm. This indicates direct coordination to phosphate and suggests indirect coordination to N7. The properties of this complex are in agreement with those of the high-temperature complex, long known from studies in the fast-exchange regime. As a function of temperature, slow and fast exchange regimes are encountered. At some temperatures, one complex is responsible for most of the paramagnetic shift, whereas transverse relaxation is due to the other. The two-complex model fits the ^{31}P data over the entire temperature range. Thermodynamic and kinetic parameters of the complexes are derived. At 22 °C, their concentrations are equal and the lifetimes are 15 μs for the first and 10 μs for the second. The complexation of 5′-CMP with cobalt presents similar properties. The two complexes are octahedral, in contrast to the tetrahedral structure observed in crystals. At least five complexes of Co-5′-ATP are observed on the ^{31}P spectrum at −10 °C. Together with prior work on the association of manganese to polynucleotides, the present results suggest that the temperature-dependent equilibrium between indirect and direct metal-to-phosphate ligation could be a rather general feature among transition metals of the first series.

The interaction of divalent ions with nucleotides has been extensively studied. The nitrogen and oxygen donor groups of the bases, the phosphate group, and the ribose hydroxyls are potential binding sites for metal ions. Metal binding is further complicated by the alternative possibilities of direct or indirect (i.e., through a water molecule) ligation and by possible intermolecular metal bonds leading to dimerisation or macrochelate formation.[1,2]

Transition-metal ions such as Ni, Mn, and Co have been widely used as substitutes for the natural Mg ions in kinetic and structural studies by NMR, X-ray diffraction, temperature-jump, and IR spectroscopy techniques.

A survey of metal–nucleotide crystal structures is given by Swaminathan and Sundaralingam.[3] Despite the large variety of cases, this survey reveals some systematic features:

(a) All crystal structures of purine 5′-monophosphate complexes with the transition ions of the first series (Co–IMP, Co–GMP, Mn–IMP, Mn–GMP, Ni–AMP, Ni–IMP, Ni–AMP, Ni–GMP) share the following properties: (i) the formula is $[M^{2+}\text{-}(NMP)(H_2O)_5]$; (ii) the structure is octahedral; and (iii) the metal ion is coordinated directly to N7 and binds through water to phosphate.

(b) The crystal structures of three pyrimidine-5′-monophosphate complexes of cobalt and manganese ($Co_2(5'\text{-UMP})_2(H_2O)_4$, $Co(5'\text{-CMP})(H_2O)$, and $Mn(5'\text{-CMP})(H_2O)$) are known. They are polymeric and the metal ion is coordinated to the oxygens of two different phosphate groups. In Co–5′-CMP, Co^{2+} coordinates in addition to the nitrogen N3 of a third CMP molecule,[4] a feature

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