

Quantum Mechanical Studies of Si–O and Si–F Bonds in Molecules and Minerals*

J.A. Tossell

Department of Chemistry, University of Maryland, College Park, MD 20742, USA

Abstract. The capability of quantum mechanical computation for the description of the geometric and electronic structure of molecules containing Si–F and Si–O bonds is assessed. For gas phase analogues of silicates, such as SiF₄, geometric and energetic quantities can be calculated very accurately and many spectral properties, e.g. photoemission, x-ray absorption near edge and NMR spectra, can be evaluated with reasonable accuracy. Extension of such methods to molecular models for Si–O bond in solids yields accurate average Si–O bond properties and reproduces experimental trends but detailed values of such properties in particular solids are difficult to reproduce. The present status of band theoretical and ionic lattice techniques applied to SiO₂ is also briefly discussed.

Since the most common minerals are silicates the nature of the Si–O bond is of great importance to mineralogists. The proper formalism for a fundamental understanding of any chemical bond is quantum mechanics and substantial advances have recently been made in the application of both quantum mechanical computations and qualitative concepts within mineralogy. Before discussing recent studies of the Si–O bond (and related bonds such as Si–F and P–O) I will list some properties of the Si–O bond which have been studied and discuss the levels of specificity and interpretability of these properties. I will then briefly distinguish the various quantum computational methods and then consider some applications. Most of my time will be spent upon the results of molecular cluster approaches but I will also describe some highlights of recent band theoretical and ionic lattice simulation studies.

Properties studied by quantum mechanics may be usefully divided into those relating to the ground state of the unperturbed material, such as the equilibrium bond distances and angles, the enthalpies of reactions or the electron density distributions and those which involve excited states, such as the cations created in photoemission, the bound or continuum excited states arising in x-ray absorption or the perturbed molecule within a magnetic field created in NMR. Much progress has been made in the computation of ground state properties for molecules containing 3rd row (Na–Cl) and even heavier elements, but excited state properties represent a current challenge.

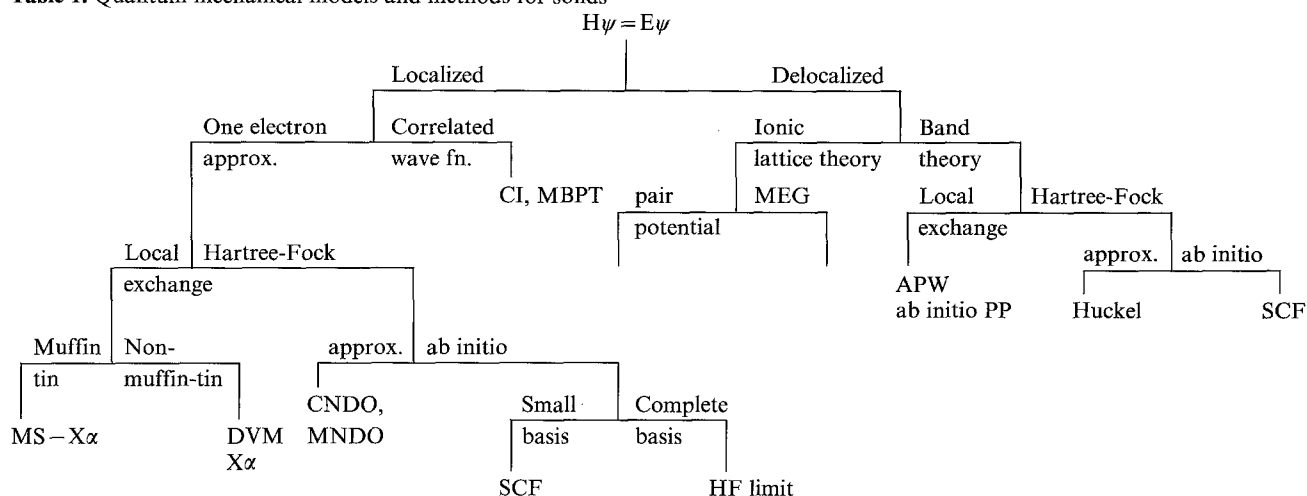
It is also important to designate the level of specificity desired in the description of the property. Are we interested in the average absolute value of a property, e.g. the average Si–O bond distance, in trends in a property as a function of chemical environment, e.g. Si–O distance as a function of Si or O coordination number, or in particular values of Si–O distance in a specific structure, e.g. the inequivalent Si–O distances in quartz or stishovite. Replication of particular distances is clearly most difficult and trends are often easier to obtain than accurate absolute values.

There are also a number of levels at which we can interpret the computational results. We can simply accept the computed number as it stands as the result of a computer experiment and not attempt further explanation. We can relate the calculated value for one quantity to computed or experimental values of other quantities using the quantum mechanical calculation as the framework for developing a unified picture of the electronic structure of the material. In some cases we may be able to abstract qualitative principles directly from the results of accurate calculations. Finally, we can examine the ability of simple, qualitative and easily interpretable theories to explain the experimental values. For example, in understanding the average value and range of values for <Si–O–Si> accurate calculations can be of value first because they can accurately reproduce experimental values. We can also extract from them effective “charges”, valence electron density distributions and hybridizations which allow us to interpret more qualitatively the value of the angle. Simple qualitative MO theories of angle bending and ionic model theories incorporating anion polarization can also be used to interpret this quantity.

In categorizing the application of quantum computational techniques to solids I find it informative to use a flow chart approach (Table 1), in which the first branch involves the choice of localized or delocalized approaches, both of which are now extensively applied to solids. Without going through the flow chart in detail, I should indicate that one branch characteristically leads to more accurate approaches and one to less accurate approaches, e.g. correlated wave functions vs. one electron approximation wave functions. Of course, the more accurate calculations are characteristically more difficult and time consuming.

A good example of a state-of-the-art ab initio Hartree-Fock calculation on a molecule containing an Si–O bond is that of Snyder and Raghavachari (1984) on SiO and Si₂O₂ (Table 2). Using reasonably large polarized basis sets,

* Paper from Conference on Quantum Theory and Experiment, July 1986

Table 1. Quantum mechanical models and methods for solids**Table 2.** Calculated^a and experimental properties of SiO and Si₂O₂

Si-O				
	R(Si-O) (Å)		$\nu(\text{cm}^{-1})$	
STO-3G	1.475		1349	
6-31G*	1.487		1407 (scaled to 1252)	
Exp.	1.51		1242	

	R(Si-O)	R(Si-Si)	$\angle \text{O-Si-O}$	$\Delta E_{\text{dimer}}(\text{Kcal/mol})$
STO-3G	1.684	2.530	82.6	
6-31G*	1.683	2.469	85.7	-59.8(HF), -38.9(MP4)
Exp.				-44.6 ± 3.0
Vib. freq.	$\nu_{B_{2u}}$	$\nu_{B_{3u}}$	ν_{1u}	
Scaled 6-31G*	789	758	247	
Exp.	804	766	252	

^a From Snyder and Raghavachari, 1984

such as those designed by Francl et al. (1982) they were able to definitively determine the geometry of Si₂O₂, calculate accurate geometries for both monomer and dimer and assign and accurately match the vibrational energies. Since the HF method gives bond distances which are systematically too short and vibrational frequencies which are systematically too large, standard scale factors were employed to obtain the best match with experiment. The calculated dimerization energy was also in good agreement with experiment after correlation corrections were made using many body perturbation theory.

Similar methods have recently been applied to SiF₄ and Si(OH)₄ by Hess et al. (1986) (Tables 3 and 4). For SiF₄ the calculated vibrational frequencies are slightly higher than experiment before correction and the bond distance slightly smaller. For Si(OH)₄ in *D*_{2d} symmetry the calculated bond distance matches well against average values

in monosilicates and the calculated vibrational energies are somewhat larger than those obtained in aqueous silicate solutions, presumably for the species SiO₂(OH)₂⁻². Vibrational frequencies in silicate glasses, e.g. CaMgSiO₄ are somewhat higher. Of course, Si(OH)₄ must be considered only a crude first approximation to the silicate species existing in condensed phases. Nonetheless, agreement of calculation and experiment for the condensed phase SiO₄ species is only slightly poorer than for gas phase SiF₄.

In general, bond distances in solids can be reproduced reasonably well using small basis set *ab initio* HF techniques (and carefully parameterized approximate MO methods). For example, Downs et al. (1982) demonstrated that minimal basis STO-3G calculations could accurately reproduce the change in equilibrium Si-O distance with Si coordination number. Gibbs et al. (1987) have demonstrated excellent agreement of calculated equilibrium bond distances in

Table 3. Calculated^a and experimental properties of SiF₄

	R(Si–F) (Å)
STO-3G	1.585
6-31G	1.625
6-31G*	1.557
TZ+TD	1.54
Exp.	1.552

	Vibrational frequencies (cm ⁻¹)			
	E	T ₂	A ₁	T ₂
STO-3G	263	370	761	1,099
6-31G	233	356	757	1,037
6-31G*	274	406	849	1,108
Exp.	267	390	807	1,044
	264	388	801	1,031

^a From Hess, McMillan and O’Keeffe, in press, 1986

Table 4. Calculated^a and experimental properties of Si(OH)₄ (D_{2d})

	R(Si–O) (Å)	
STO-3G	1.655	
6-31G	1.662	
6-31G*	1.629	
Exp. av.	1.635	Si–O in monosilicates

	Vibrational frequencies (cm ⁻¹)		
	A ₁	E	B ₂
STO-3G	770	1,271	1,272
6-31G	604	1,059	985
6-31G*	816	1,042	1,047
Exp.	854	850–1,000	CaMgSiO ₄
	777	935?	SiO ₂ (OH) ₂ ²⁻

^a From Hess, McMillan and O’Keeffe, 1986

tetrahedral hydroxyacid molecules with average experimental bond distances for tetrahedrally coordinated cations. For the third row elements, addition of d polarization functions is necessary to closely match experiment, a point we will return to. The experimental or calculated bond distances also scale smoothly with the number of valence electrons divided by the product of the coordination number and the row number, i.e. Pauling bond strength over principal quantum number of the valence shell. The origin of such a relationship is not obvious and might be a good topic for discussion at this meeting.

Another structural parameter of great interest in mineralogy is the Si–O–Si bond angle, which has a typical value around 140–150 degrees. STO-3G *ab initio* SCF calculations give a bent minimum energy <Si–O–Si but only at the level of double zeta plus Si and O 3d polarization functions are Si–O distance and <Si–O–Si adequately reproduced in disiloxane, (SiH₃)₂O (Table 5). Indeed, disiloxane appears to be a very flexible molecule, with a very small barrier to linearity. A molecular species more relevant to mineralogy, although more computationally demanding, is probably (OH)₃SiO–Si(OH)₃, which seems to have a

Table 5. Calculation of <Si–O–Si

	H ₃ SiOSiH ₃ ^a	(OH) ₃ SiOSi(OH) ₃ ^b
STO-3G	128(R(Si–O)=1.63)	137(R(Si–O)=1.62)
DZ	180	
DZ+Sid	180	
DZ+Od	145	
DZ+Si, Od	154(143)	139
Exp.	144	144 α-quartz

^a From Ernst et al. 1981 and references therein

^b From Gibbs, 1982

deeper minimum as a function of <Si–O–Si. The <Si–O–Si has been used to define the importance of Si3d participation, the conclusion being that Si3d participation is no more important than O3d, i.e. that the Si3d are polarization functions (Oberhammer and Boggs 1980). Similar SCF–MO methods applied to a number of <T–O–T containing molecules, where T is tetrahedral cation, show minimum energy angles and variations of energy with angle which are consistent with average values and ranges of bridging angles observed in solids (Geisinger et al. 1985). Trends in bridging angle may be explained using simple qualitative MO approaches (Tossell 1984) which focus upon the difference in energy of the pi-nonbonding HOMO and the sigma-antibonding LUMO in the linear geometry. The smaller this difference the more strongly the angle is bent. However, given the strong basis set dependence of some of the calculated bridging angles, this approach must be considered an interpretation rather than a complete and fundamental explanation of the property. A more fundamental explanation may be possible through study of the electron density distribution. It is now possible to obtain theoretical electron density deformation maps which are in good agreement with experimental results. Such maps for coesite show bonds which are “bent” in the sense that the deformation density maxima do not lie exactly along the bonds for the Si–O–Si linkage (Gibbs 1982).

Further information on electronic structure may be obtained through studies of the spectral properties of materials. Within the past decade photoemission spectroscopy has been a valuable spectroscopic tool. It is again instructive before studying the PES of condensed phase silicates to examine the capacity of present day quantum techniques to reproduce the PES of molecular analogues, such as SiF₄. Both local density and Hartree-Fock calculations correctly reproduce the order of orbital IP’s in SiF₄ and give accurate separations in the upper valence region (*Fp* and Si–*Fp* sigma) (Fig. 1). If proper HF calculations are done at a Δ SCF or many body perturbation theory (MBPT) level agreement is even better. However, substantial discrepancies appear for the F2s levels, for which relaxation and correlation effects are much larger, so that local density approaches underestimate the F2s IP’s and Koopmans’ theory HF results overestimate them. The detailed assignment of such a spectrum is difficult and it is very useful to consult studies of PES intensity as a function of incident photon energy (Yates et al. 1985) or electron momentum spectra (Fantoni et al. 1986), giving individual orbital momentum distributions, to help in assignment. Similar discrepancies appear in modeling the PES of SiO₂, using either a MS–X α SiO₄⁴⁻ cluster model (Tossell 1985) or an ab

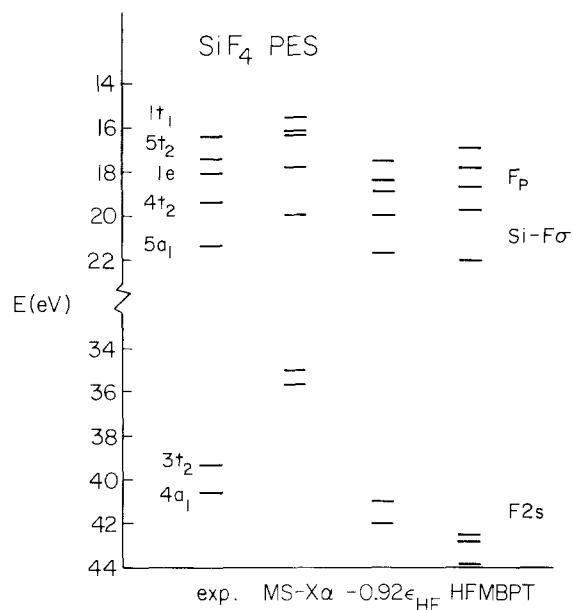


Fig. 1. SiF_4 photoemission spectrum: experimental (Perry and Jolly 1974), MS-X α (DeAlti 1978), Hartree-Fock (Tossell and Lazzarotti 1986 and present results), HFMBPT (Fantoni et al., 1986)

initio self-consistent pseudopotential model (Chelikowsky and Schluter 1977). This suggests that relaxation and correlation may cause significant discrepancies in this inner valence region, as has been observed for numerous gas phase molecules, e.g. CO_2 , as shown by Nakatsuji (1983).

X-ray emission spectra have also been extensively studied for SiO_2 . Although several band theoretic calculations have given a good overall description of these spectra, one substantial discrepancy has been in the intensity of the high energy feature of the $\text{SiL}_{2,3}$ spectra, corresponding within the SiO_4^{4-} model to $\text{Si}2p$ to $1e, 5t_2$ MO transitions. The high intensity of this transition was early attributed to $\text{Si}3d$ participation. It is now apparent that to correctly describe the energy and intensity of this spectral feature one must include d functions which have great radial flexibility. Although the d functions may not make a large overall contribution to the wavefunction, their contracted components can strongly contribute to the spectral intensity. I showed this for the PO_4^{3-} and ClO_4^- anions (Tossell 1980a) isoelectronic to SiO_4^{4-} , and it has been confirmed by Dietz (1983). Such contracted components of the 3d functions can also strongly influence the optimum geometry, as shown by Stromberg et al. (1984) among others for S-O bonds. It is worth noting that the same group (Stromberg et al. 1982) found that modeling S-O distances in solids, even presumably ionic ones such as Na_2SO_3 , was not an easy task. Inclusion of the counterions of the SO_3^{2-} anion gave a S-O bond distance apparently in worse agreement with experiment than for free SO_3^{2-} . This indicates that careful consideration of correlation effects and vibrational effects, in addition to counterion inclusion, will be necessary for accurate reproduction of particular bond distances in solids. By contrast, O'Keeffe and McMillan (1986) were able, using the $\text{H}_6\text{Si}_2\text{O}_7$ model, to reproduce the inequivalence of Si-O bond distances in α -quartz (1.615 and 1.623 Å calculated vs. 1.605 and 1.614 Å observed).

In the past five years two new and important spectroscopies have emerged in solid state science and specifically

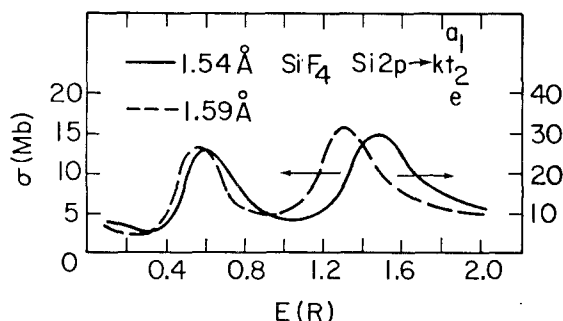


Fig. 2. Calculated $\text{Si}2p \rightarrow$ continuum x-ray absorption cross sections for Si-F distances of 1.54 and 1.59 Å in SiF_4 (cross sections in megabarns, electron energy in Rydbergs, $1-R = 13.6$ eV)

in mineralogy. One is *x-ray absorption near-edge spectroscopy* (XANES), in which a core electron is excited to a bound or continuum level, and the other is NMR, in which the response of the system to an applied magnetic field is probed. Both spectroscopies are difficult to describe theoretically, XANES because it generally involves both bound and continuum or "resonant" states and demands calculated intensities as well as energies for proper understanding and NMR because quantum mechanical perturbation theory utilizing large expansion basis sets is necessary for an accurate theoretical description. Even for small molecules like N_2 such calculations are by no means routine. Nonetheless, useful results may be obtained for mineralogically interesting molecules.

The XANES for the $\text{Si}2p$ shell of SiF_4 shows four features, two lying below the $\text{Si}2p$ and two above. Bond state MS-X α calculations assign the bound state features to a_1 and t_2 Si-F σ^* orbitals and suggest that the first continuum feature arises from an e orbital. More formally correct scattering calculations within the MS-X α model identify the continuum peaks with e and t_2 continuum "resonances" (Tossell, Brown and Waychunas 1985), although these results appear to change somewhat depending upon the details of the calculations. An important feature of the XANES is its dependence upon geometric parameters. Plotting MS-X α calculated absorption cross section vs. emerging electron energy for two different Si-F distances shows that the t_2 peak is dramatically lowered as $R(\text{Si-F})$ is increased (Fig. 2). Such a dependence of peak energy upon distance has been observed for many other gas phase and chemisorbed molecules (Sette et al. 1984) and may be value in determining structural parameters in solids. The same features appear in the XANES of compounds with Si-O bonds, e.g. quartz and albite, and analogous features may be observed in the K XANES of other materials containing tetrahedral oxyanions, e.g. the $\text{ClO}_4^- - \text{AlO}_4^{3-}$ series. Caution must be exercised in applying selection rules since some states occur even when apparently forbidden, due to configuration interaction.

For calculation of NMR chemical shielding we can now employ coupled Hartree-Fock perturbation theory in its ab initio form (Tossell and Lazzarotti 1986) yielding good agreement between calculated chemical shieldings, σ , and experimental chemical shifts, δ , as shown in Figure 3. Note that this figure does not show a correlation of some simple quantity like gross charge or orbital population imbalance with δ - it represents direct ab initio calculations. We can reproduce trends as a function of identity and number of

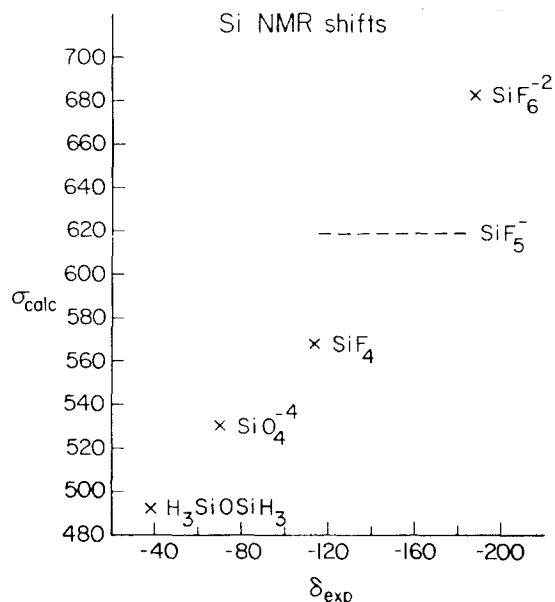


Fig. 3. Comparison of calculated ^{29}Si NMR shielding constants and experimental ^{29}Si chemical shifts (Marsmann 1981)

nearest neighbors and can readily predict σ values for exotic species like Si_2O_2 . Calculations of $(\text{SiH}_3)_2\text{O}$ as a function of $\langle \text{Si}-\text{O}-\text{Si} \rangle$ ($R(\text{Si}-\text{O})$ held constant) give small variations of σ^{Si} and σ^{O} , in the direction consistent with experiment for Si (Fig. 4). For the case of ^{17}O another quantity of interest in the NMR experiment is the electric field gradient tensor. We have calculated this tensor as a function of $\langle \text{Si}-\text{O}-\text{Si} \rangle$ and show its anisotropy and its largest principal value (expressed as the nuclear quadrupole coupling constant e^2qQ/h) as a function of angle in Figure 4. The values of e^2qQ/h for $\langle \text{Si}-\text{O}-\text{Si} \rangle = 140\text{--}150^\circ$ are in the range observed for silica glass (Geissberger and Bray 1983) and the magnitude of the dependence suggests that such NMR studies may be able to accurately define $\langle \text{Si}-\text{O}-\text{Si} \rangle$. Finally, ^{17}O NMR parameters may also be calculated for distorted SiO_4^{-4} groups. For example, in an idealized C_{3v} symmetry SiO_4^{-4} anion with one short and three long $R(\text{Si}-\text{O})$ we obtain e^2qQ/h and σ_{av} values qualitatively consistent with values observed in forsterite (Schramm and Oldfield 1984). Note, however, the large anisotropy of NMR shielding, $\Delta\sigma$, which complicates the analysis of the NMR data.

Finally, it is interesting to consider recent progress in describing the electronic and structural properties of the SiO_2 polymorphs. Non-selfconsistent LCAO bond calculations on a range of SiO_2 polymorphs yield densities of states which are observably different. For example, from α -quartz to β -tridymite the intensity of the $\text{Si}-\text{O}$ π bonding vs. $\text{Si}-\text{O}p\pi$ bonding feature increases (Li and Ching 1985). This is consistent with the increased intensity of the high energy SiK XES shoulder in β -tridymite observed by Wiech and Kurmaev (1985). Extended Huckel bond theory has been used to interpret the structure of β -quartz by Burdett and Caneva (1985), who found that $\text{O}-\text{O}$ interactions are the primary structure determinant. Bond theoretical studies and MS-X α cluster calculations have both been done on stishovite, containing octahedrally coordinated Si. The cluster calculations (Tossell 1975), even after consideration of the difference of cluster and bond approaches, seem to give

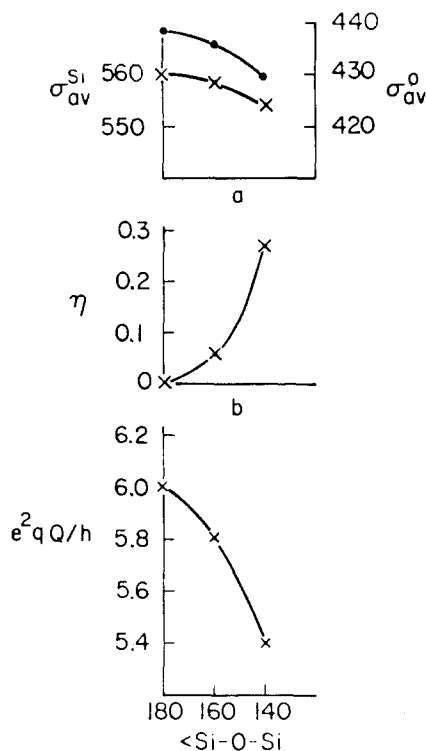


Fig. 4. (a) ^{29}Si and ^{17}O NMR chemical shieldings as a function of $\langle \text{Si}-\text{O}-\text{Si} \rangle$ in $(\text{H}_3\text{Si})_2\text{O}$, (b) anisotropy in electric field gradient at O as function of $\langle \text{Si}-\text{O}-\text{Si} \rangle$, (c) quadrupole coupling constant at O as function of $\langle \text{Si}-\text{O}-\text{Si} \rangle$

Table 6. Electric field gradients, nuclear quadrupole coupling constants, isotropic NMR shieldings and shielding anisotropies (in ppm) at ^{17}O in apical and equatorial sites of C_{3v} symmetry SiO_4^{-4} , $R(\text{Si}-\text{O})_{\text{ap}} = 1.56 \text{ \AA}$, $R(\text{Si}-\text{O})_{\text{eq}} = 1.631 \text{ \AA}$

$ q (\text{au})$	0.3983	0.3606
$e^2qQ/h(\text{MHz})^a$	2.08	1.89
σ_{av}^d	458.3	457.1
σ_{av}^p	-174.3	-180.0
σ_{av}	284.0	277.1
$\Delta\sigma$	225	266

^a Using $eQ = 2.233 \times 10^{-2}$ barns

a considerably narrow upper valence band than do the band calculations (Li and Ching 1985; Rudra and Fowler 1983). Experimental XES show SiL and OK spectra much like those in α -quartz but a SiK spectrum more like the AlK of Al_2O_3 (Brytov et al. 1977). Further consideration of those valence band features awaits calculation of the spectral intensities.

The structural features of stishovite have also proven difficult to reproduce. Earlier Modified Electron Gas (Kim and Gordon 1974) calculations gave an atmospheric pressure volume which was considerably too large and the wrong sense of distortion within the SiO_6 polyhedron (Tossell 1980b). Extended Huckel calculations (Burdett 1985) and empirical ionic model calculations give the same results. Much more accurate MEG calculations have recently been performed but the difficulty in describing the anisotropy of the SiO_6 polyhedron remains. There has been speculation

that incorporation of O anion polarization may be necessary to overcome this problem.

For the fluorite phase of SiO₂ the situation is more clear cut. It is clear from band theoretical and MEG studies (Carlsson et al. 1984; Bukowinski and Wolf 1986) that the transformation pressure of SiO₂ stishovite→fluorite will be far outside the range of mantle pressures and that even after transformation the fluorite and stishovite densities will be very similar. Also the SiO₂ fluorite band gap initially increases with applied pressure and metallization occurs only at very high P.

Finally, let me briefly mention some recent simulations of SiO₂ systems. Woodcock et al. (1975) obtained quite good agreement with radial density distribution functions of SiO₂ glass using a simple SiO₂ pair potential employing formal charges on all the atoms using molecular dynamics simulation. Later studies by Mitra et al. (1981) obtained similarly good results. Static lattice studies using MEG methods (Tossell 1980) or empirical potentials, however, yielded <Si—O—Si which were too large. This problem has recently been overcome by the inclusion of three-body anglebonding forces either empirically (Catlow et al. 1985) or from quantum mechanical calculation (Lasaga and Gibbs 1987). The empirical simulations reproduce a number of properties of SiO₂, including the dependence of <Si—O—Si upon pressure. A central topic of this conference will be the assessment of the strengths and weakness of the different computer simulation approaches.

The SiO₂ fluorite, Si₂O₂ and SiF₄ results indicate that we are close to reaching "third age of quantum mineralogy" — the point at which calculated values become more accurate than experiment for certain simple materials which are hard to study due to the extreme conditions needed for their stability, whether inert gas matrices or high pressure (cf. the third age of quantum chemistry as described by Richards (1979)).

However, although we possess the ability to accurately calculate properties for some medium size molecules there are many systems which are still very difficult to treat, both perfect crystals and defect structures whether local or infinite, e.g. surfaces. Only by proper use of qualitative theory and simulation and by careful experimental design will we be able to understand the principles that govern the average and particular properties of silicon oxides and other solids.

Acknowledgements. This work was supported by NSF grant no. EAR-82-13115.

References

- Brytov IA, Romashchenko YN, Shchegolev BF (1979) Electronic structure of the octahedral oxyanions for aluminum and silicon. *J Struct Chem* 20:190–196
- Burdett JK (1985) Electronic control of the geometry of rutile and relative structure. *Inorg Chem* 24:2244–2253
- Burdett JK, Caneva DC (1985) Energetic description of solids in terms of small fragments. *Inorg Chem* 24:3866–3873
- Carlsson AE, Ashcroft NW, Williams AR (1984) Properties of SiO₂ in a high-pressure fluorite structure phase. *Geophys Res Lett* 11:617–619
- Catlow CRA, Freeman CM, Royle RL (1985) Recent studies using static simulation techniques. *Physica* 131B:1–12
- Chelikowsky JR, Schluter M (1977) Electron states in α -quartz in self-consistent pseudopotential calculation. *Phys Rev B* 15:4020–4029
- DeAlti G, Decleva P, Sgamellotti A (1978) An MS—X α study of the photoelectron spectra and bonding in the fluorosilanes. *Chem Phys* 35:283–292
- Dietz ER (1983) Scattered-wave calculations of the PL x-ray emission spectrum of ligand substituted phosphorous oxyanions. *J Phys B At Mol Phys* 16:4593–4599
- Downs JW, Hill RJ, Newton MD, Tossell JA, Gibbs GV (1982) Theoretical and experimental charge distributions in euclase and stishovite. In: *Electron Distribution and the Chemical Bond*. Coppons P, Hall MB (ed). Plenum Press, New York, NY pp 173–179
- Ernst CA, Allred AL, Ratner MA, Newton MD, Gibbs GV, Moskowitz JW, Topid S (1981) Bond angles in disiloxane: a pseudo-potential electronic structure study. *Chem Phys Lett* 81:424–429
- Fantoni R, Giardini-Guidoni A, Tiribelli R, Cambi R, Rosi M (1986) Ionization potentials and electron momentum distributions for SiF₄ valence-shell orbitals: an (e,2e) spectroscopic investigation and Green's function study. *Chem Phys Lett* 128:67–75
- Francl MM, Pietro W, Hehre WJ, Binkley JS, Gordon MS, DeFrees DJ, Pople JA (1982) Self-consistent molecular orbital methods. XXIII. A polarizationtype basis set for second-row elements. *J Chem Phys* 77:3654–3666
- Geisinger KL, Gibbs GV, Navrotsky A (1985) A molecular orbital study of bond length and angle variations in framework structures. *Phys Chem Minerals* 11:266–283
- Geissberger AE, Bray PJ (1983) Determination of structure and bonding in amorphous SiO₂ using ¹⁷O NMR. *J Non-crystallogr Solids* 54:121–137
- Gibbs BV (1982) Molecules as models for bonding in silicates. *Am Mineral* 67:421–450
- Gibbs GV, Finger LW, Boisen MB Jr (1987) Molecular mimicry of the bond length — bond strength variations in oxide crystals. *Phys Chem Minerals* 14:327–331
- Hess AC, McMillan PF, O'Keeffe M (1986) Force fields for SiF₄ and H₄SiO₄: ab initio molecular orbital calculations. *J Phys Chem* 90:5661–5665
- Lasaga AC, Gibbs GV (1987) Applications of quantum mechanical potential surfaces to mineral physics calculations. *Phys Chem Minerals* 14:107–117
- Li YP, Ching WY (1985) Band structures of all polycrystalline forms of silicon dioxide. *Phys Rev B* 31:2172–2179
- Marsmann H (1981) ²⁹Si-NMR spectroscopic results. In: *NMR Basic Principles and Progress*. Diehl P, Fluck E, Kosfeld R (ed). Springer-Verlag, Berlin Heidelberg New York, pp 65–235
- Mitra SK, Amini M, Fincham D, Hockney RW (1981) Molecular dynamics simulation of silicon dioxide glass. *Philos Mag B* 43:365–372
- Nakatsuji H (1983) Cluster expansion of the wavefunction. Valence and Rydberg excitations, ionizations and inner-valence ionizations of CO₂ and N₂O studied by the SAC and SAC CI theories. *Chem Phys* 75:425–441
- Oberhammer H, Boggs JE (1980) Importance and (p-d) π bonding in the siloxane bond. *J Am Chem Soc* 107:7241–7244
- O'Keeffe M, McMillan PF (1986) The Si—O—Si force field: ab initio MO calculations. *J Phys Chem* 90:541–542
- Perry WB, Jolly WL (1974) Valence electron binding energies of some silicon compounds, from x-ray photoelectron spectroscopy. *J Electron Spectrosc Relat Phenom* 4:219–232
- Richards G (1979) The third age of quantum chemistry. *Nature* 78:507
- Rudra JK, Fowler WB (1983) Electronic band structure of stishovite (tetragonal SiO₂). *Phys Rev B* 28:1061–1067
- Schluter M, Chelikowsky JR (1977) Electron states in α -quartz (SiO₂). *Solid State Commun* 21:381–384
- Schramm S, Oldfield E (1984) High resolution Oxygen-17 NMR of solids. *J Am Chem Soc* 106:2502–2506
- Sette F, Stohr J, Hitchcock AP (1984) Correlation between intramolecular bond lengths and K-shell σ -shape resonances in gas-phase molecules. *Chem Phys Lett* 110:517–520

- Snyder LC, Raghavachari K (1984) Ab initio quantum chemical study of the dimerization of silicon monoxide. *J Chem Phys* 80:5076–5079
- Stromberg A, Gropen O, Wahlyren U, Lindquist O (1983) Ab initio calculations of the sulfite ion, SO_3^{2-} , and hydrogen sulfite ion, HSO_3^- or SO_2OH . *Inorg Chem* 22:1129–1133
- Stromberg A, Wahlgren U, Petterson L, Siegbahn PEM (1984) On the role of 3d orbitals in sulfur. *Chem Phys* 89:323–328
- Tossell JA (1975) The electronic structures of Mg, Al and Si in octahedral coordination with oxygen from SCF–X α MO calculations. *J Phys Chem Solids* 36:1273–1280
- Tossell JA (1980a) Calculation of L x-ray emission energies and intensities in PO_4^{3-} and ClO_4^- . *Inorg Chem* 19:3328–3330
- Tossell JA (1980b) Theoretical studies of structures, stabilities and phase transitions in some metal dihalide, and dioxide polymorphs. *J Geophys Res* 85:6456–6460
- Tossell JA (1985) Quantum mechanical models and methods in mineralogy, in *Chemical Bonding and Spectroscopy in Mineral Chemistry* Berry FJ, Vaughan DJ (ed). Chapman and Hall, London, pp 1–30
- Tossell JA, Brown GE Jr, Waychunas GA (1985) Studies of the unoccupied molecular orbitals of tetrahedral molecular orbitals of tetrahedral oxyanions, TO_4^{n-} , and related molecules by x-ray absorption near edge spectroscopy (XANES) and multiple scattering (MS) X α molecular orbital calculations, 1985 GSA abstr
- Tossell JA, Lazzeretti P (1986) Ab initio calculations of ^{29}Si NMR chemical shifts for some gas phase and solid state silicon fluorides and oxides. *J Chem Phys* 84:369–374
- Wiech G, Kurmaev EZ (1985) X-ray emission bands and electronic structure of crystalline and vitreous silica (SiO_2). *J Phys C Solid State Phys* 18:4393–4402
- Woodcock LV, Angell CA, Cheeseman P (1976) Molecular dynamics studies of the vitreous state: simple ionic systems and silica. *J Chem Phys* 65:1565–1577
- Yates BW, Tan KH, Bancroft GM, Coasworth LL, Tse J (1985) Photoelectron study of the valence levels of CF_4 and SiF_4 from 20 to 100 eV. *J Chem Phys* 83:4906–4916

Received September 26, 1986