

Bond Length and Radii Variations in Fluoride and Oxide Molecules and Crystals

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Abstract. Molecular orbital calculations completed on fluoride molecules containing first and second row cations have generated bond lengths, R , that match those observed for coordinated polyhedra in crystals to within ~ 0.04 Å, on average. The calculated bond lengths and those observed for fluoride crystals can be ranked with the expression $R = Kp^{-0.22}$, where $p = s/r$, s is the Pauling strength of the bond, r is the row number of the cation and $K = 1.34$. The exponent -0.22 ($\approx -2/9$) is the same as that observed for oxide, nitride and sulfide molecules and crystals. Bonded radii for the fluoride anion, obtained from theoretical electron density maps, increase nearly with bond length. Those calculated for the cations as well as for the fluoride anion match calculated promolecule radii to within ~ 0.03 Å, on average, suggesting that the electron density distributions in the vicinity of the minima along the bond paths possess a significant atomic component despite bond type.

Bonded radii for Si and O ions provided by experimental electron density maps measured for the oxides coesite, danburite and stishovite match those calculated for a series of monosilicic acid molecules. The resulting radii increase with bond length and coordination number with the radius of the oxide ion increasing at a faster rate than that of the Si cation. The oxide ion within danburite exhibits several distinct radii, ranging between 0.9 and 1.2 Å, rather than a single radius with each exhibiting a different radius along each of the non-equivalent bonds with B, Si and Ca. Promolecule radii calculated for the coordinated polyhedra in danburite match procrystal radii obtained in a structure analysis to within 0.002 Å. The close agreement between these two sets of radii and experimentally determined bonded radii lends credence to Slater's statement that the difference between the electron density distribution observed for a crystal and that calculated for a procrystal (IAM) model of the crystal "would be small and subtle, and very hard to determine by examination of the total charge density."

Introduction

In 1982, Gibbs suggested that a molecule might serve as a useful basis for modeling the bond length and angle variations of a silicate mineral. This suggestion was based on the observation that the separations and angles between the Si and O atoms in the coordinated polyhedra of a number of siloxane molecules are not unlike those in quartz (Gibbs et al. 1972; Tossell and Gibbs 1978; Newton and Gibbs 1980; Gibbs et al. 1981; Gibbs and Boisen 1986; Gibbs et al. 1987). He also suggested that such models might provide important insight into the forces that govern bond length and angle variations and electron density distributions of the silica polymorphs and silicates in general. The development of such models has since yielded a theoretical basis for the correlation first observed by Smith (1953) between SiO bond length and bond strength sum for melilite and later established for a variety of oxide bond lengths by Baur (1970) and a number of correlations established by Brown and Shannon (1973) between bond strength and bond length (Gibbs et al. 1981; Gibbs et al. 1987). They have also provided a basis for a correlation proposed between SiO bond length and SiOSi angle (Cruickshank 1961; Brown et al. 1969; Newton and Gibbs 1980; Boisen et al. 1990; Boisen and Gibbs 1993).

Since that time, molecular orbital (MO) calculations, completed on a variety of molecules with 4- and 6-coordinated first and second row metal atoms, have generated bond lengths and angles that match those observed, to within a few percent, for chemically similar oxide, sulfide and nitride molecules and crystals (Geisinger and Gibbs 1981; Julian and Gibbs 1985, 1988; Gibbs and Boisen 1986; Gibbs et al. 1987b; Bartelmehs et al. 1989; Buterakos et al. 1992). The close correspondence between observed and calculated bond length data for chemically similar molecules and crystals suggests that the force field that governs bond length and angle variations in a wide range of insulating materials is short ranged and, in large part, independent of the forces exerted on the coordinated polyhedra by the other atoms

of a structure. It also indicates that the force constants and minimum energy SiO bond lengths and SiOSi and OSiO angles calculated for a molecule like $H_6Si_2O_7$ can be viewed as being similar to those of a Si_2O_7 group in a silicate crystal and can be used to construct a force field for silica (McMillan and Hess 1990; Lazarev and Mirgorodsky 1991). In fact, a potential energy function based in large part on such a field has been used to generate the structures, the volume compressibilities, the elastic constants and the Poisson ratios for several silica polymorphs (Lasaga and Gibbs 1987, 1988, 1991; Stixrude and Bukowinski 1988; Gibbs et al. 1988; Tsuneyuki et al. 1988; van Beest et al. 1990; Chelikowsky et al. 1990; Purton et al. 1993; Boisen and Gibbs 1993). It has also been used to generate the zero pressure structure of coesite, reproducing both the observed SiO bond lengths to within ~ 0.01 Å and the correlation observed between SiO bond length and SiOSi angle (Boisen and Gibbs 1993). It was also found that when $P1$ symmetry was assumed in the calculations that the resulting structures for the silica polymorphs quartz, cristobalite and coesite possess the observed space group symmetries to within 0.001 Å (Boisen and Gibbs 1993). The success of these calculations not only provides support for the assertion that the nature of the bonding in the Si_2O_7 group in $H_6Si_2O_7$ is similar to that of the group in the silica polymorphs, but it also indicates that the local force field of the group plays an important role in governing the properties and the observed space group symmetries adopted by the silica polymorphs.

In this study, MO calculations are completed to see whether the minimum energy bond lengths calculated for a number of fluoride molecules match those observed for the coordinated polyhedra in fluoride crystals. Bonded and promolecule radii are also calculated to see whether the radius of the fluoride anion varies in a regular way with bond length as observed for oxide, nitride and sulfide anions. In addition, bonded and procrystal radii obtained from experimental electron density maps for several oxide crystals are compared with bonded and promolecule radii calculated for chemically similar molecules and coordinated polyhedra (Nicoll 1993).

Molecular Orbital Calculations

The MO calculations were completed on $H_{m-n}X^{n+}F_m$ fluoride molecules with $m = 3-, 4-, 5-,$ and $6-$ coordinated first and second row main group metal atoms, X. In the calculations, (1) 6–31 G* basis sets were used on the metal atoms and the fluorine atom and a 31G basis set was used on H and (2) ideal geometries (trigonal planar, tetrahedral, trigonal bipyramidal and octahedral fluoride coordinated polyhedra) were assumed with all of the XF bond lengths constrained to be equal and with all the HF bond lengths constrained to be equal. The minimum energy $R(XF)$ and $R(HF)$ bond lengths and the XFH angles were obtained using unrestricted Roothaan-Hartree-Fock self consistent field (SCF) strategies, using GAUSSIAN86 (Frisch et al. 1984).

Table 1. Observed and theoretical bond lengths, $R_o(XF)$ and $R_t(XF)$, and crystal (Shannon 1976), bonded, and promolecule radii, $r_c(X)$, $r_b(X)$, and $r_p(X)$, for first and second row atoms

$H_{m-n}X^{n+}F_m$	XF	$R_o(XF)$	$R_t(XF)$	$r_c(X)$	$r_b(X)$	$r_p(X)$
H_3LiF_4	LiF	1.88	1.81	0.73	0.70	0.72
H_5LiF_6	LiF	2.05	1.96	0.90	0.75	0.77
$HBeF_3$	BeF	1.45	1.46	0.30	0.52	0.53
H_2BeF_4	BeF	1.56	1.54	0.41	0.54	0.55
H_4BeF_6	BeF	1.74 ^a	1.73	0.59 ^a	0.60	0.61
BF_3	BF	1.30	1.30	0.15	0.44	0.45
HBF_4	BF	1.40	1.39	0.25	0.46	0.47
H_3BF_6	BF	1.56 ^a	1.59	0.41 ^a	0.52	0.57
CF_4	CF	1.44 ^b	1.30	0.29 ^b	0.42	0.49
H_2CF_6	CF	1.45 ^c	1.52	0.30 ^c	0.56	0.67
HNF_6	NF	1.42 ^c	1.50	0.27 ^c	0.69	0.72
H_3NaF_4	NaF	2.28	2.13	1.13	0.99	1.01
H_4NaF_5	NaF	2.29	2.18	1.14	1.00	1.03
H_5NaF_6	NaF	2.31	2.22	1.16	1.02	1.04
H_2MgF_4	MgF	1.86	1.85	0.71	0.83	0.85
H_3MgF_5	MgF	1.95	1.92	0.80	0.86	0.87
H_4MgF_6	MgF	2.01	1.96	0.86	0.87	0.89
AlF_4	AlF	1.68	1.68	0.53	0.73	0.75
H_2AlF_5	AlF	1.77	1.75	0.62	0.75	0.77
H_3AlF_6	AlF	1.82	1.80	0.675	0.77	0.79
SiF_4	SiF	1.55	1.56	0.40	0.65	0.68
H_2SiF_6	SiF	1.69	1.68	0.54	0.69	0.72
PF_5	PF	1.58	1.55	0.43	0.62	0.65
HPF_6	PF	1.67 ^a	1.61	0.52 ^a	0.64	0.68
SF_6	SF	1.58 ^a	1.55	0.43 ^a	0.60	0.68

^a Denotes radii calculated from bond length – bond strength curves

^b Denotes radii from Pauling

^c Denotes radii from Ahrens

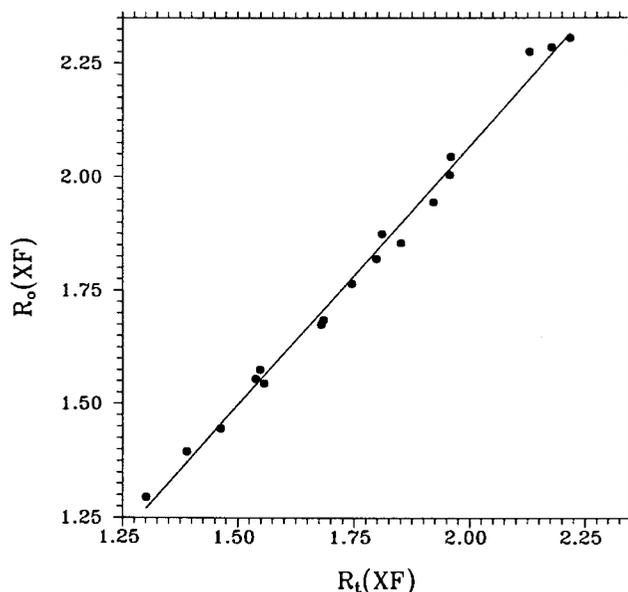


Fig. 1. A scatter diagram of observed $R_o(XF)$ vs. theoretical $R_t(XF)$ bond length data for the molecules given in Table 1. The $R_o(XF)$ data were generated using Shannon's (1976) radii

Bond Length Variations for Fluoride Molecules and Crystals

The theoretical minimum energy bond lengths, $R_t(XF)$, calculated for the fluoride molecules (Table 1) are com-

pared in Fig. 1 with observed bond lengths, $R_o(XF)$, generated from the crystal radii derived by Shannon (1976). A linear regression analysis of this data set yields a slope of 1.13 and intercept of -0.20 . An r^2 value of 0.991 indicates that more than 99% of the variation in $R_o(XF)$ can be explained in terms of a linear dependence on $R_i(XF)$. The calculated bond lengths agree with those observed for fluoride crystals to within ~ 0.04 Å, on average. However, bond length data calculated for some of the more ionic bonds like NaF and LiF are 0.04 to 0.15 Å shorter than observed.

Calculations on oxide, sulfide, and nitride molecules by Gibbs et al. (1987b), Bartelmehs et al. (1989) and Buterakos et al. (1992), respectively, have established correlations between bond length, R , and the bond strength, $p=s/r$, where s is the Pauling bond strength and r is the row number of the X cation. These studies also establish similar correlations between p and R calculated for chemically similar molecules. In an examination of how p relates to $R_o(XF)$, $\ln[R_o(XF)]$ was plotted against $\ln(p)$ (Fig. 2a). A linear regression analysis of the data set shows that more than 98% of the variation of $\ln[R_o(X)]$ can be explained in terms of a linear dependence on $\ln(p)$. Using the estimates of the slope and intercept of this linear correlation, the expression $R(XF)=1.34 p^{-0.22}$ can be derived which reproduces the observed bond lengths to within ~ 0.06 Å, on average. Similarly, p correlates with the bond length data, $R_i(XF)$, obtained in MO calculations on fluoride molecules containing first and second row cations. A scatter diagram of $\ln[R_i(XF)]$ vs. $\ln(p)$ is displayed in Fig. 2b. A linear regression of the data yields an r^2 value of 0.99 and the expression $R(XF)=1.33 p^{-0.22}$ which also reproduces the theoretical bond lengths to within ~ 0.06 Å, on average. These two expressions relating observed and theoretical bond length data for crystals and molecules, respectively, are statistically identical, indi-

cating that the forces that govern bond length variations in fluoride molecules and crystals can be viewed as similar. Furthermore, the exponent derived for the fluorides (-0.22) is statistically identical with those derived for oxides (-0.22), sulfides (-0.21), and nitrides (-0.22). As these values are statistically identical, an exponent of -0.22 ($\approx -2/9$) is accepted for each of these materials. Since the relative change for the function $f(p)=ap^{-2/9}$ is equal to $-2/(9p)$ and since the exponent $-2/9$ is the same for nitrides, oxides, fluorides and sulfides, it can be concluded that the relative change in bond length as a function of bond strength is the same for bonds involving all four anions for any given value of p . That is, when a cation with a given bond strength p is replaced for another, the relative change in bond length is the same, regardless of whether the cation is bonded to the nitride, oxide, fluoride or the sulfide ion (Bartelmehs et al. 1989).

A Comparison of Bonded and Promolecule Radii for Fluoride, Oxide, Nitride and Sulfide Molecules

Ever since Bragg (1920) first proposed that the bond lengths of crystals can be estimated by summing the radii of the two atoms comprising a bond, successively more elaborate sets of radii have been derived and used (1) to generate bond lengths, (2) to infer whether one atom in a crystal can be replaced by another, (3) to rationalize structural types in terms of structural field maps and (4) to serve as a basis for correlating and rationalizing structural and physical properties. (For a good history of radii, see Pauling (1960), Fumi and Tosi (1964), Slater (1965), Shannon and Prewitt (1969), Shannon (1976).) Despite the considerable success that modern crystal (and ionic) radii have had in reproducing the average bond length for a given coordinated polyhedron, such radii may not in general be realistic indicators of the true sizes of ions, particularly as radii relate to the electron density distribution of the bonded atoms in either a molecule or a crystal (Shannon and Prewitt 1969; Gibbs et al. 1992). Gourary and Adrian (1960) and Slater (1965) have argued that a more realistic radius of an atom referred to as bonded radius by Bader et al. (1971) can be derived from the electron density distribution of either a molecule or crystal by measuring the distance from the atom to a minimum along the bond path toward a bonded atom. As the electrons and nuclei of the atoms of a bonded system strive to adopt an arrangement wherein the total energy of the resulting configuration is minimized, the bonded radius, r_b , of an atom in the direction of a given bond can be regarded as a minimum energy feature. Another set of radii obtained for a promolecule is the promolecule radius, r_p , of an atom. A promolecule is a model of a molecule where the electron density distributions of each of its atoms is spherically averaged and placed at its observed position in the molecule (Coppens and Hall 1982). Like the bonded radius of an atom in a molecule, the promolecule radius of an atom is defined to be the distance between the nucleus of the atom and the point of mini-

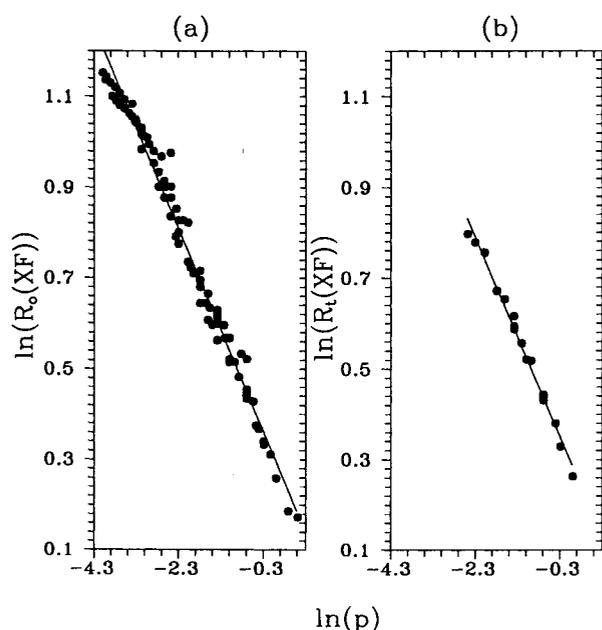


Fig. 2. a Scatter diagrams of $\ln[R_o(XF)]$ vs. $\ln(p)$ and b $\ln[R_i(XF)]$ vs. $\ln(p)$ for nontransition metal X-cations

imum electron density between the atom and nearest neighbor ones in the promolecule.

As observed in this study and elsewhere (Gibbs et al. 1992), bonded radii differ from crystal (and ionic) radii in several important ways: (1) each cation and anion has a single crystal radius for a given set of conditions while they each can have several different bonded radii, a different one in the direction of each of its nonequivalent bonds and (2) cations and anions each have a given crystal radius for a given coordination number, all other things being equal (such as valence, spin state, etc.), whereas for a given coordination number, bonded radii increase in a regular way with bond length.

In accordance with the second observation, the bonded radius of the 6-coordinate chloride ion in rock salt is observed to increase from 1.65 Å for a bond length $R(\text{NaCl})=2.82$ Å to 1.70 Å in sylvite with $R(\text{KCl})=3.15$ Å while the ionic radius of the chloride ion is assumed to be constant (1.81 Å) and independent of bond length (Slater 1965). Similarly, the bonded radius of the 2-coordinate oxide ion in coesite is observed to increase from 0.92 Å to 0.97 Å for SiO bond lengths of 1.595 Å and 1.621 Å, respectively, while the crystal radius of the oxide ion is assumed to be constant (1.21 Å) and independent of bond length (Gibbs et al. 1992). In addition, sets of bonded radii calculated from electron density distributions for a large number of minimum energy oxide, sulfide and nitride molecules show that the bonded radii of the anions in these molecules increase in a regular way with bond length. In these calculations, sets of bonded radii for first and second row main group cations were obtained (Gibbs and Boisen 1986; Bartelmehs et al. 1989; Buterakos et al. 1992). In all cases, it was observed that the bonded radii of the anions, $r_b(Y)$, where Y is O, S, or N increase in a regular manner with increasing bond length, $R_i(XY)$. It was also observed that the radii of the anions decrease with the row number, r , of the main group cation, X, to which it is bonded.

In an examination of whether the bonded radius of the fluoride ion varies in a similar way, electron density maps (Nicoll 1993) were calculated for 25 $\text{H}_{m-n}\text{X}^{n+}\text{F}_m$ fluoride molecules containing 3-, 4-, 5-, and 6- coordinated first and second row main group cations, X. The calculations were completed using a FORTRAN77 program entitled EDEN and the density matrices provided by GAUSSIAN86 Roothaan-Hartree-Fock SCF single-point calculations at the minimum energy molecular geometries. In a determination of the bonded radii, it is assumed that the radius of the atom in the direction of a bonded atom is the distance from the center of the atom to the point of minimum electron density along the line connecting the two atoms. The minimum was located analytically using a strategy based on the quasi-Newton method (Gibbs et al. 1992) in which a quartic polynomial was fit to the data. The resulting radii for the fluoride ion, $r_b(\text{F})$ (Table 1), are plotted against $R_i(\text{XF})$ in Fig. 3 where they increase linearly with bond length.

Gibbs et al. (1992) has observed that promolecule radii calculated for the oxide, nitride and sulfide molecules

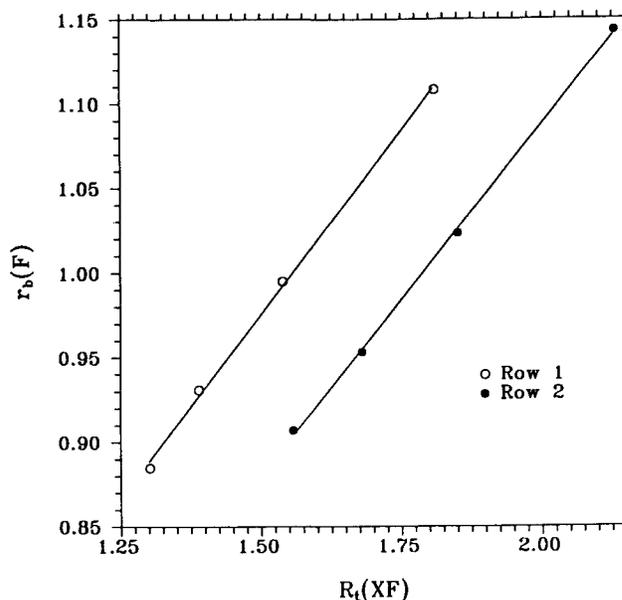


Fig. 3. Scatter diagram of the bonded radii of the fluoride ion, $r_b(\text{F})$ vs. $R_i(\text{XF})$. The open circles are for XF bond lengths involving first row cations and the closed circles are for bond lengths involving second row cations

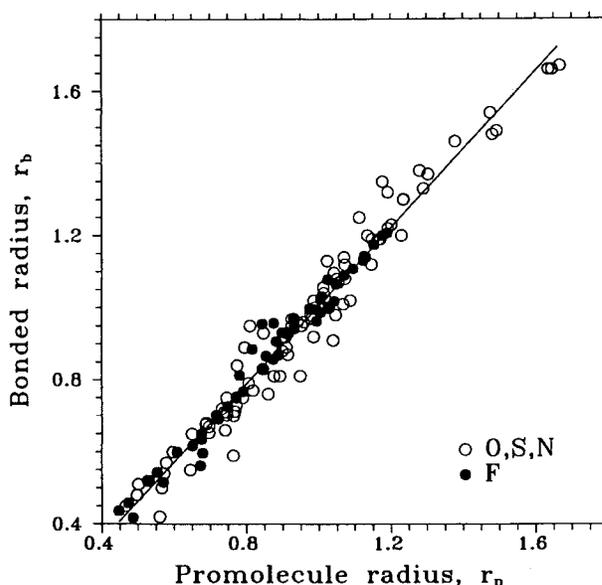


Fig. 4. A scatter diagram of the bonded radii, r_b , vs. promolecule radii, r_p , calculated for oxide, sulfide, nitride and fluoride molecules. Data for the fluorides are plotted as solid circles while the remaining three data sets are plotted as open circles

optimized by Gibbs et al. (1987b), Buterakos et al. (1992) and Bartelmehs et al. (1989), respectively, are highly correlated with the bonded radii calculated for the atoms in these same molecules (data plotted as open circles in Fig. 4). To see whether the bonded radii calculated for the fluoride molecules show a similar correlation, promolecule radii were calculated for the X-cations comprising the fluoride molecules (Table 1). The resulting promolecule radii, $r_p(\text{X})$, are plotted as solid circles in Fig. 4 against the bonded radii of the X-cations, $r_b(\text{X})$, calculated for the fluoride molecules. The resulting radii match those obtained for the oxide, nitride and sulfide

molecules reasonably well. It is noteworthy that the fluoride data fall closer, on average, to the line than the remaining data, a result that probably reflects the fact that the radii for the fluorides were determined analytically whereas those obtained for the oxides, sulfides and nitrides were obtained using graphical methods.

A comparison of the bonded radii for the oxide, fluoride, nitride and sulfide molecules shows that the radius for a given X-cation in a sulfide molecule is, on average, ~ 0.1 Å larger than it is in either an oxide or a fluoride molecule and ~ 0.05 Å larger than it is in a nitride molecule. An examination of the minimum energy bond lengths for these molecules shows, for a given X-cation, that $R(XS)$ is longer than $R(XN)$ which in turn is longer than $R(XO)$ and $R(XF)$. In other words, an X-cation is larger when it is bonded to sulfur (longer bond), it has an intermediate value when bonded to nitrogen and it is smallest when bonded to either oxygen or fluorine (shorter bonds).

Crystal, Procrystal, Bonded and Promolecule Radii for Oxide Crystals

Modern crystal radii such as those derived for the oxides and fluorides reproduce average bond lengths for coordinated polyhedra with a precision of ~ 0.01 Å when coordination number, spin state, and oxidation state are taken into account (Shannon and Prewitt 1969; Shannon 1976). Despite the fact that these radii are relative rather than absolute, they correlate well with the bonded radii for the cations calculated for oxide molecules (Gibbs and Boisen 1986) and for the fluoride molecules studied here. Similarly, the crystal radii derived for sulfide crystals correlate equally well with the bonded radii calculated for sulfide molecules (Bartelmehs et al. 1989). In addition, Cahen (1988) has found that average bonded radii derived from plots of total valence electron densities also correlate with sulfide crystal radii. He also made the important observation that a model based on such bonded radii provides a better understanding of the ease with which Cu can be leached from the enargite Cu_3AsS_4 structure than can be provided by a model based on either ionic or crystal radii. It has also been suggested that such models will provide insight into the occurrence of ferro-electricity, piezoelectricity and magnetic properties in mixed oxides and related materials (Johnson 1975).

Not only do crystal radii correlate well with bonded radii obtained for molecules, but Feth et al. (1993) have also found that they correlate equally well with promolecule radii. In their study, promolecule electron density distributions were calculated for ideal triangular, tetrahedral and octahedral coordinated polyhedra containing main group and non-main group cations from the first four rows of the periodic table with each bond length set equal to the crystal radius sum of the cation and anion. The high correlations that obtain between the resulting promolecule radii and the crystal radii for oxides and sulfides and the ionic radii for nitrides show that Shannon and Prewitt (1969), Shannon (1976) and

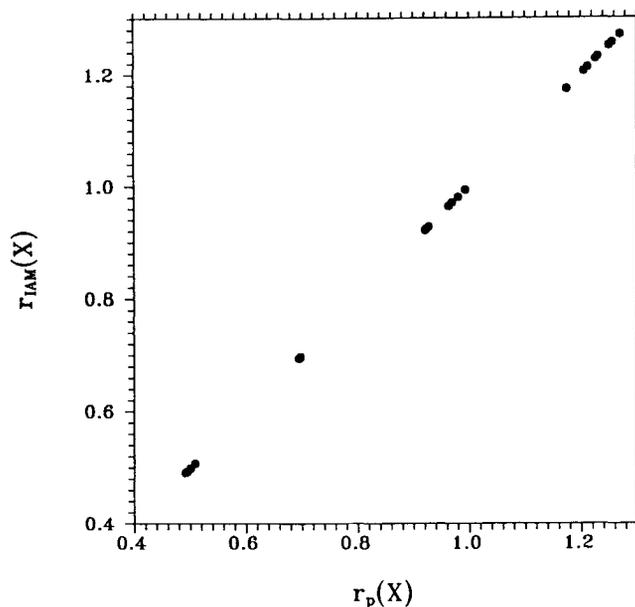


Fig. 5. Scatter diagram procrystal IAM radii, $r_{IAM}(X)$, vs. promolecule radii, $r_p(X)$, for the atoms in danburite, bromellite and stishovite. The procrystal radii for danburite and bromellite were kindly provided by J.W. Downs

Shannon (1981) did an excellent job ordering their radii one relative to another as did Baur (1987) in ordering his nitride ionic radii.

Promolecule electron density maps calculated for the BeO_4 , SiO_4 , CaO_7 , SiO_6 coordinated polyhedra observed for bromellite, danburite and stishovite (Downs 1991; Downs and Swope 1992; Spackman et al. 1987) yield promolecule radii for Be, Si, Ca and O that match the bonded radii obtained from experimental electron density maps to within ~ 0.02 Å, on average (Feth et al. 1993). In addition, procrystal radii obtained for the atoms in the same minerals agree to within 0.002 Å with promolecule radii calculated for the atoms comprising the coordinated polyhedra (Fig. 5). A procrystal is a model of a crystal whose electron density distribution, like that of a promolecule, consists of a superposition of spherically averaged electron density distribution of atoms, each located at its observed position in the crystal (Coppens and Hall 1982). Procrystal radii are obtained in the same way that promolecule radii are determined for such a distribution. Collectively, when considered with the agreement that obtains between the bonded and promolecule radii for rock salt (Gibbs et al. 1992), these results support arguments by Slater (1965) that the electron density distributions in such crystals can be viewed as having a relatively large atomic component, regardless of bond type. It also indicates that promolecule radii calculated for the atoms of a coordinated polyhedron isolated from a crystal closely match procrystal radii calculated for the crystal.

A similar study of experimental electron density distributions indicates that the bonded radii of Si and O in several silicates increase with SiO bond length as observed for the cations in the rock salt structure. In this study, the bonded radii for ^{IV}Si and ^{II}O were calculated for the monosilicic acid molecule, H_4SiO_4 , for a range of SiO bond lengths from 1.50 Å to 1.90 Å and com-

pared with those obtained from experimental electron density maps determined for two silicate crystals (coesite and danburite) that have 4-coordinate Si and 2-coordinate O and one (stishovite) that has 6-coordinate Si and 3-coordinate O.

For the calculation, the geometry of H_4SiO_4 was optimized assuming S_4 point symmetry and a 6-31 G** basis set (Gibbs et al. 1981; Boisen and Gibbs 1988). Additional SCF calculations were completed for the molecule with the SiO bond length set at a range of values that include those reported for the three silicate crystals. Using the density matrices provided by each calculation and the software EDEN, bonded radii for both Si and O were calculated for each molecule. The resulting radii vary linearly with $R(SiO)$ as evinced by Fig. 6 with $r_b(O)$ increasing with $R(SiO)$ about three times more rapidly than $r_b(Si)$. The bonded radii provided by the structural analyses for the three silicate crystals are plotted in Fig. 6 as open symbols. Those determined by the mapping of the experimental electron density distribution of stishovite fall on the curve while those determined for the silicate tetrahedra in coesite and danburite depart from the curve by $\sim 0.02 \text{ \AA}$, at most. The close agreement that obtains between the observed and calculated radii indicates that the position of the minima in the electron density distribution along the SiO bond is governed in large part by the separation between the two atoms.

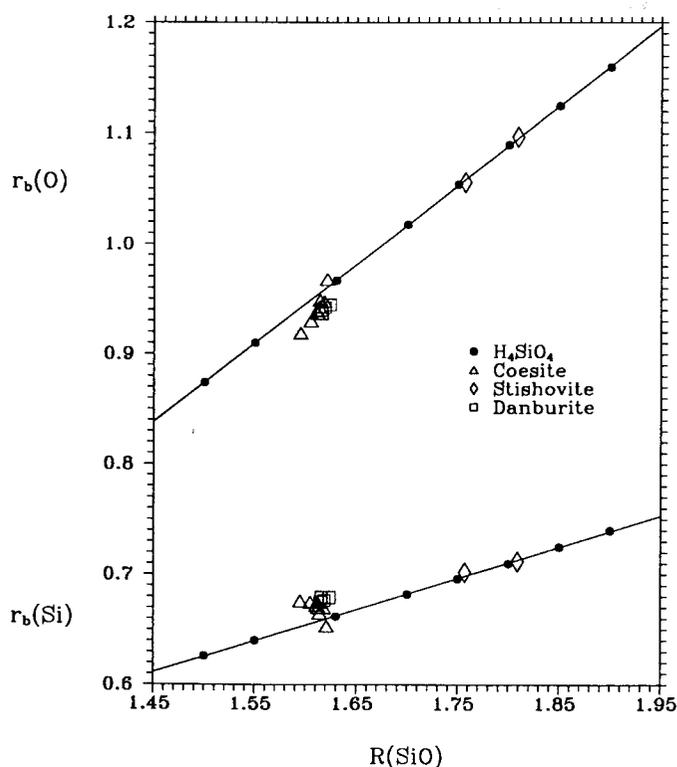


Fig. 6. Scatter plots of the bonded radii, $r_b(O)$ and $r_b(Si)$, for O (upper curve) and Si (lower curve), respectively, calculated for the monosilicic acid molecule vs. SiO bond length, $R(SiO)$ (plotted as solid circles). Superimposed on the plot are experimentally determined bonded radii measured for coesite (open triangles), stishovite (open diamonds) and danburite (open squares). Data for coesite taken from Buterakos (1990)

Discussion

Molecular orbital calculations, completed on molecular models extracted from a variety of insulating crystals, can be taken as evidence that the forces that govern the average bond lengths adopted within coordinated polyhedra in such crystals are largely short ranged. Corroborative evidence is provided by the observation that the bond lengths in a large variety of chemically similar crystals and molecules agree to within 0.04 \AA , on average (Nicol 1993). Also, the observation that crystal and ionic radii serve to generate average bond lengths for the coordinated polyhedra in oxide, nitride, fluoride and sulfide crystals to within $\sim 0.02 \text{ \AA}$ is additional evidence that the average separation among the bonded atoms in a coordinated polyhedron can be viewed as largely independent of any other forces exerted on the polyhedron by the other parts of the structure. Because of the apparent short ranged nature of these forces, a knowledge of the wave functions and the charge density distribution of a molecule, provided by molecular orbital calculations, can improve our understanding of such properties for representative parts of a chemically similar crystal. By completing such calculations, the results can be transferred to the crystal and used to improve our understanding of its crystal chemistry.

As observed by O'Keeffe and Hyde (1985) at The Castle Hot Springs Conference on Structure and Bonding, the divorce between crystal chemistry and molecular chemistry in the early thirties was a mistake in that it left both sciences the poorer. The insights into bond length, angle and force constant variations and charge density distributions calculated for molecules with molecular orbital methods and the successful transference of the results to crystals provides support for the statement that the structures of molecules, their properties and their similarities with crystals should be included as a chapter in any course on crystal chemistry. In addition, in studies using molecules as models for bonding in silicates, molecular orbital methods have been used to probe and clarify the similarities of the binding forces in molecules and chemically similar coordination polyhedra in silicate crystals. There is no doubt that the results of these studies have improved our understanding of silicate crystal chemistry. As discussed in the introduction, the methods have not only generated the bond length and angle variations exhibited by crystals, but they have also provided a theoretical underpinning for a number of empirically established correlations. The methods also show that calculations for a large number of oxide, nitride and sulfide molecules yield bond lengths that match those observed in chemically similar crystals. In addition, the calculations undertaken in this study show that the bond lengths in fluoride molecules match those in crystals as well. They also show that the bonded radii of the cations and the fluoride ion in these molecules increase in a regular way with bond length. It is also observed that bonded radii can be easily derived from electron density distributions calculated for molecules. However, unlike ionic and crystal radii, bonded radii seem to depend both on the atom to which they

are bonded and the length of the bond. Also, individual atoms are observed to exhibit several different radii, depending on their chemical environments, rather than a single radius.

For example, the oxide ions in danburite each exhibit several different bonded radii that range between ~ 0.94 and ~ 1.23 Å (Downs and Swope 1992). Three of the oxide ions are bonded to three different cations, ^{IV}B , ^{IV}Si and ^{VII}Ca at ~ 1.47 , ~ 1.62 and ~ 2.44 Å, respectively. In the direction of the BO bonds, the oxide ions exhibits a radius of ~ 1.00 Å, in the direction of the SiO bonds, a radius of ~ 0.94 Å while in the direction of the CaO bonds, a radius 1.23 Å. Of the two remaining nonequivalent oxide ions, one is bonded to two equivalent ^{IV}B atoms and a ^{VII}Ca atom and has a radius of 1.18 Å in the direction of the CaO bond and a radius of 0.97 Å in the direction of the two BO bonds. The remaining oxide ion is bonded to two equivalent ^{IV}Si atoms and exhibits a single radius of 0.94 Å. The cations in danburite also show variable radii but the variability is much smaller. In the derivation of ionic and crystal radii, it is assumed that such radii are spherical. However, the results presented here show that electron density distributions measured for an atom in the directions of its nonequivalent bonds are aspherical and yield several different radii rather than a single one. This result and those presented above confirm proposals made by Johnson (1973, 1975), O'Keeffe (1981), Cahen (1988) and Gibbs et al. (1992) that cations and anions in molecules and crystals have variable radii rather than a single radius for a given chemical environment.

Finally, an examination of the total electron density distribution observed for danburite indicates that its CaO bonds have a large component of ionic structure which is consistent with bonds involving Ca^{2+} cations (Downs and Swope 1992). If, as is generally believed, the Ca^{2+} cations are indeed smaller than Ca atoms, then the promolecule radii calculated for the Ca atom of a CaO_7 coordinated polyhedra should be larger than the observed bonded radii. But, as noted above, the bonded and the promolecule radii for the Ca atom in danburite agree with one another to within ~ 0.01 Å, a result that indicates that the radius of the atom changes little upon a losing its valence electrons in forming a cation. The close agreement between bonded and promolecule radii is not restricted to the Ca atom in danburite, but it also obtains for the atoms in a wide variety of molecules and crystals with a wide range of bond types. On the basis of these results, it is evident that the bonded radius of an atom remains unchanged, for the most part, with a loss of its electrons for a given bond length.

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