Bond-length and bonded-radii variations in sulfide molecules and crystals containing main-group elements: A comparison with oxides

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Abstract

Molecular orbital calculations on 18 hydrosulfide molecules containing selected main-group X cations yield minimum-energy theoretical bond lengths, $R_t(XS)$, that reproduce those observed in chemically similar sulfide crystals. A linear-regression analysis of these bond lengths shows that $R_t(XS)$ can be estimated by the equation $R = 1.83(p)^{-0.21}$ with $p = s/r$, where s is the Pauling bond strength and r is the row number of the X cation in the periodic table, with 98% of the variation of $R_t(XS)$ being explained in terms of a linear dependence on R with slope 1 and intercept 0. In addition, R serves to rank the observed XS bond lengths, as tabulated by Shannon (1981), for sulfide crystals with main-group X cations for rows 1 through 5 of the periodic table to within 0.12 Å, on average, with R accounting for 96% of the variation in the observed bond lengths. The equation that relates R to p for the sulfides is similar to that found for the oxides (also using theoretical bond lengths), $R = 1.39(p)^{-0.22}$.

Bonded radii obtained from electron-density maps calculated for the hydrosulfide molecules show that these radii for both the X cations and the S anion increase with $R_t(XS)$. A similar trend has been found to hold for bonded-radii and $R_t(XO)$ bond-length data calculated for hydroxyacid molecules. The bonded radius of the S anion is smaller (1.16 Å) when bonded to more electronegative atoms like 4-coordinate As and is larger (1.67 Å) when bonded to less electronegative atoms like 4-coordinate Li, but the bonded radius of S is smaller than Shannon's (1.70 Å) crystal radius and Pauling's ionic radius (1.84 Å) in all of the cases that we considered.

Introduction

Recent advances in our understanding of the bonding in silicate crystals have come from the observation that the bond lengths and angles in these crystals are not very different from those in chemically similar molecules. For example, the SiO bond length (1.634 Å) and the SiOSi angle (144°) of the disiloxy SiOSi group in the gas-phase molecule disilyl ether, H_6Si_2O, are very similar to those calculated for the molecule (1.632 Å and 143.7°; Gibbs et al., 1987a) and those observed on average (1.626 Å and 144°) for the disiloxy group in silicate crystals (see Table 3, Gibbs et al., 1981). Thus, it is not surprising that molecular orbital (MO) calculations on monosilicic, disilicic, and hexoxosilicic acid molecules have generated bond-length and bond-angle variations, bulk moduli, and electron-density distributions that are in reasonable agreement with those observed for the silica polymorphs and related silicates (O'Keeffe et al., 1980; Spackman et al., 1987; Gibbs et al., 1987a, 1987b). In addition, MO calculations on a variety of beryllosilicate, aluminosilicate, borate, phosphate, sulfate, and germanate hydroxyacid molecules have generated geometries and charge-density distributions that compare well with those observed

for chemically similar crystals (Downs and Gibbs, 1981; Geisinger et al., 1987; Zhang et al., 1985; O'Keeffe et al., 1985; Lindsay and Gibbs, 1988; Gibbs et al., 1987a). The success of these calculations may be taken as evidence that the binding forces that govern the local structure, the force constants, and the electron-density distribution of an oxide crystal may not be very different from those that govern such properties in a chemically similar hydroxyacid molecule (Gibbs, 1982).

Of interest in this study has been the success with which Gibbs et al. (1987b) have related theoretical bond lengths—$R_t(XO)$, calculated for hydroxyacid molecules containing first-row (Li^+ through N^{5+}) and second-row (Na^+ through S^{6+}) main-group X cations—to a bonding parameter $p = s/r$, where s is the Pauling bond strength of the X cation and r is its row number in the periodic table. With the derivation of an empirical equation relating $R_t(XO)$ to p, they were able to rank the XO bond lengths reported for oxide crystals for main-group cations from Li^+ through Np^{6+} (rows 1 through 6 of the periodic table) with respect to $R_t(XO)$ (Shannon, 1976). In related studies, Finger and Gibbs (1985) and Gibbs and Boisen (1986) showed that bonded radii, obtained from theoretical electron-density maps of the molecules calculated for

TABLE 1. XS bond lengths and bonded radii calculated for the XS$_\nu$ coordination polyhedra in selected hydrosulfide molecules

Molecule	XS	$R_t(X$S$)$	$R_o(X$S$)$	r_c	r_X	r_S
H$_7$LiS$_4$	LiS	2.49	2.44	0.74	0.83	1.66
H$_{11}$LiS$_6$	LiS	2.72	2.70			
H$_6$BeS$_4$	BeS	2.13	2.09	0.39	0.65	1.48
H$_5$BS$_4$	BS	1.94	1.94	0.24	0.59	1.35
H$_3$BS$_3$	BS	1.83	1.81			
H$_2$CS$_3$	CS	1.74	1.71			
H$_4$CS$_4$	CS	1.83*				
H$_7$NaS$_4$	NaS	2.78	2.81	1.11	1.12	1.66
H$_6$MgS$_4$	MgS	2.46	2.42	0.72	0.92	1.54
H$_{10}$MgS$_6$	MgS	2.63	2.60			
H$_5$AlS$_4$	AlS	2.27	2.26	0.56	0.81	1.46
H$_9$AlS$_6$	AlS	2.45	2.39			
H$_4$SiS$_4$	SiS	2.14*	2.13	0.425	0.76	1.38
H$_3$PS$_4$	PS	2.06	2.05	0.35	0.81	1.25
H$_7$KS$_4$	KS	3.16	3.19	1.49	1.49	1.67
H$_5$GaS$_4$	GaS	2.31	2.28	0.58	1.01	1.30
H$_4$GeS$_4$	GeS	2.23*	2.21	0.51	0.91	1.32
H$_3$AsS$_4$	AsS	2.18	2.17	0.465	0.98	1.20
H$_4$SnS$_4$	SnS	2.44*	2.39			

* Gibbs et al. (1987a).

several silicic acid molecules, match those obtained from maps observed for the silica polymorphs to within about 0.5 Å (Spackman et al., 1987; Geisinger et al., 1987). Because oxygen and sulfur belong to the same group in the periodic table, a similar study was undertaken on 18 hydrosulfide molecules to explore the extent to which the bond lengths calculated for these molecules agree with those obtained for sulfide crystals (see Table 1). The extent to which the bonded radii correlate with crystal radii (Shannon, 1981) and the extent to which $R_t(X$S$)$ correlates with p were also examined (Bartelmehs, 1987).

MOLECULAR ORBITAL CALCULATIONS ON HYDROSULFIDE MOLECULES

Hartree-Fock self-consistent-field molecular orbital calculations were completed on hydrosulfide H$_{6-m}X^{m+}$S$_3$, H$_{8-m}X^{m+}$S$_4$, and H$_{12-m}X^{m+}$S$_6$ molecules containing selected main-group 3-, 4-, and 6-coordinate X cations from rows 1 through 4 of the periodic table. A total of 18 minimum-energy XS bond lengths, $R_t(X$S$)$, were calculated using the GAUSSIAN 82 (Binkley et al., 1982) and GAUSSIAN 86 programs (Frisch et al., 1984). A 6-31G* basis set was used on first- and second-row X cations, and a newly published 3-21G* basis set was used on third- and fourth-row X cations (Dobbs and Hehre, 1986). A 6-31G** basis set was used on S when bonded to Si and C, and a 6-31G basis set was used when it was bonded to the remaining first- or second-row cations. This was done because the addition of the costly d-type polarization functions to the basis set of S had little or no effect on the calculated XS bond lengths. When S was bonded to Ge and Sn, a 3-21G* basis set was used, whereas a 6-31G basis set was used on S when it was bonded to the remaining third- or fourth-row cations. In these calculations, the SXS angles in the triangular, tetrahedral, and octahedral molecules were clamped at their ideal values
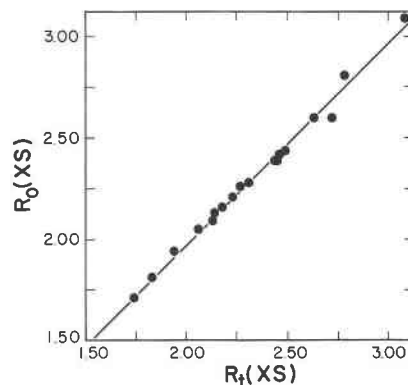

Fig. 1. Average observed crystal XS bond lengths (Shannon, 1981), $R_o(X$S$)$, vs. theoretical XS bond lengths, $R_t(X$S$)$, calculated for the hydrosulfide molecules. $R_o(X$S$)$ and $R_t(X$S$)$ are given in Table 1.

(120.0°, 109.47°, and 90.0°, respectively) and the molecules were optimized assuming that all of the XS and all of the HS bond lengths were equal, resulting in a single optimized bond length for each. These XS bond lengths, $R_t(X$S$)$, are reported in Table 1 together with bond-length data for H$_4X$S$_4$, with X = C, Si, Ge, and Sn obtained in a previous study by Gibbs et al. (1987a).

Using the basis sets discussed above, Mulliken population analyses showed reasonable charges on the cations and anions for all of the molecules examined in this study with the exception of H$_5$BS$_4$ and H$_3$PS$_4$, where negative charges were calculated on both B and P and positive charges were calculated on S. Calculations were repeated for these two molecules using a more robust 6-31G* basis set on S and a 31G** basis on H. The calculations on H$_3$PS$_4$ resulted in realistic charges, but those on H$_5$BS$_4$ remained virtually unchanged for reasons that are unclear to us.

A COMPARISON OF BOND-LENGTH–BOND-STRENGTH PARAMETER VARIATIONS FOR OXIDES AND SULFIDES

Figure 1 shows a plot of $R_o(X$S$)$ versus $R_t(X$S$)$, where $R_o(X$S$)$ is the average XS bond length recorded for a variety of sulfide crystals (Shannon, 1981). The $R_t(X$S$)$ values match the $R_o(X$S$)$ values to within 0.03 Å, on average. A linear-regression analysis of these two data sets yields a slope and intercept that are statistically identical with 1.0 and 0.0, respectively, and a coefficient of determination, R^2, of 0.99. This well-developed linear correlation indicates, as observed for oxides, that the forces that govern bond-length variations in hydrosulfide molecules may not be very different from those that govern bond-length variations in sulfide crystals containing main-group cations.

A linear-regression analysis by Gibbs et al. (1987b) of the theoretical bond-length data calculated for hydroxy-acid molecules versus the bonding parameter p was found to yield the equation
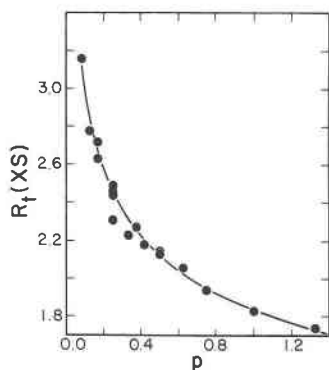
$$R(X\mathrm{O}) = 1.39p^{-0.22}, \qquad (1)$$

Fig. 2. Theoretical XS bond lengths, $R_t(XS)$, calculated for hydrosulfide molecules vs. the bonding parameter, $p = s/r$, where s is the Pauling bond strength of the X cation and r is its row number in the periodic table.

Fig. 3. Average crystal XS bond lengths compiled by Shannon (1981), $R_o(XS)$, vs. XS bond lengths, $R(XS)$, estimated with the equation $R(XS) = 1.83p^{-0.21}$.

where $R(XO)$ is an estimator of $R_t(XO)$. With this equation, all the Shannon (1976) $R_o(XO)$ bond-length values for main-group X cations in oxide crystals were reproduced to within 0.05 Å, on average. This analysis included X cations from rows 1 through 6 of the periodic table. Because of the success of Equation 1 in estimating XO bond lengths, we determined a similar equation for the sulfides based on the theoretical bond lengths $R_t(XS)$ presented in Table 1 and plotted against p in Figure 2. A regression analysis of these data yields the equation

$$R(XS) = 1.83p^{-0.21}, \qquad (2)$$

where $R(XS)$ is an estimator of $R_t(XS)$ with an R^2 value of 0.98. Furthermore, the line of regression of $R(XS)$ versus $R_t(XS)$ passes through the origin and has a slope statistically identical to 1.0. Equation 2 is strikingly similar to that derived for the oxides (Eq. 1). We extended Equation 2 by using $R(XS)$ as an estimator of $R_o(XS)$ values presented by Shannon (1981) for the main-group X cations from rows 1 to 5 of the periodic table (see Fig. 3). A linear-regression analysis of these data indicates that 96% of the variation in $R_o(XS)$ can be explained in terms of a linear dependence on $R(XS)$. Furthermore, Equation 2 reproduces all of the $R_o(XS)$ values involving the main-group X cations reported by Shannon (1981) to within 0.12 Å, on average.

Writing the right-hand side of Equations 1 and 2 in the form ap^b, several observations can be made about the constants a and b. The most obvious one is that the b values are essentially the same. Since the relative change for the function

$$f(p) = ap^b$$

is b/p and since b is the same for the oxides and sulfides studied, we may conclude that the relative change of bond length as a function of p, for any given p, is the same for both of these anions. Hence, when one cation is replaced by another, the relative change in bond length is the same regardless of whether the cation is bonded to O^{2-} or S^{2-}.
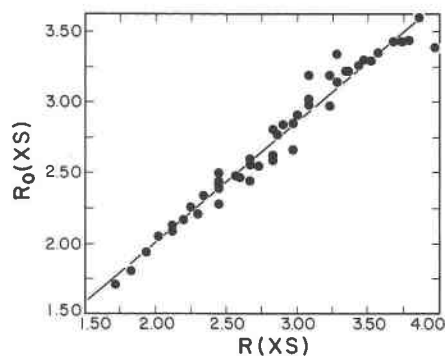
One interpretation of the constant a is that, since $f(1.0) = a$, it equals the estimation of any bond length involving a cation with a p value of 1.0. Since $p = 1.0$ for 3-coordinate B and for 4-coordinate C, $a = R(XY)$ for $X = B^{3+}$, C^{4+} and $Y = O^{2-}$, S^{2-}. Moreover, since the ionic radius of 3-coordinate B is essentially zero (Shannon and Prewitt, 1969; Shannon 1976), a values are approximately equal to the ionic radii of O^{2-} (1.40 Å) and S^{2-} (1.84 Å), respectively. The ionic radii of O^{2-} and S^{2-} are also in close agreement with $R_t(CY)$ calculated for the molecules H_4CO_4 (1.37 Å) and H_4CS_4 (1.83 Å) (Gibbs et al., 1987a).

BONDED RADII FOR OXIDES AND SULFIDES

Since the advent of the computer and the automated single-crystal diffractometer, the structures of a large number of oxides and sulfides have been determined, providing a wealth of precise bond-length data. Shannon and Prewitt (1969) and Shannon (1976, 1981) have used these data to derive sets of radii for oxides and sulfides. In their derivations, they assumed that the radii of the oxide and sulfide ions were constant for a given coordination number and that cation radii can be derived by subtracting the anion radii from sets of average bond lengths. The cation radii that result are corrected for coordination number, oxidation state, and spin state, but they are not corrected for the ionicity of the bond. For example, the radius of an oxide or a sulfide anion with a given coordination number was assumed to be fixed regardless of whether it is bonded to a highly electronegative cation like P^{5+} or to a less electronegative one like Na^+. Nonetheless, the sum of the crystal radii of two bonded ions reproduces bond lengths for oxide and sulfide crystals to within about 0.01 Å. Although these radii do a good job of reproducing bond lengths, they do not seem to be directly related to such physical properties as the electron-density distribution in a crystal.

One problem in defining the radius of an ion in terms of its electron-density distribution is to decide upon a feature of that distribution that, in some sense, determines the outer "surface" of the ion. As the distribution of the electron density of an ion extends to infinity, the

outermost excursions of its electrons is not a useful feature. One useful feature of an isolated atom is the maximum radial charge density of its outermost shell of electrons. In fact, the atomic radii determined by Bragg (1920) and extended by Slater (1964) have been found to correlate with this feature. One advantage of these radii is that they can be used to generate bond lengths equally well for covalent, metallic, and ionic bonds for both crystals and molecules. However, since coordination number and other factors affecting bond lengths were not considered, these radii do not reproduce bond lengths as accurately as do crystal radii.

Within the context of a bond, one feature that may be used to define the radius of an ion is the point of "contact" between a pair of bonded ions, which is assumed to be the point along the bond at which the total electron density is a minimum (Gourary and Adrian, 1960). Such radii are called bonded radii by Bader et al. (1971). Unlike the definition of the crystal or the atomic radius, the bonded radius of an ion is dependent upon its environment. For example, the bonded radius of an oxide ion in an XO bond may vary when bonded to different X cations. Such a variable radius is consistent with arguments that the oxide-ion radius should vary with the field strength of the X cation (Johnson, 1973). Note that because the bonded radius only describes the "size" of an ion in the direction of the bond, the term *bonded radius* should not be taken to imply that the ion is spherical with the same radius in all directions.

One drawback of the bonded-radius model is the paucity of accurate experimentally determined electron-density maps for crystals that may be used to determine a set of bonded radii. As deformation maps calculated for borate, silicate, and sulfate molecules reproduce experimental maps recorded for crystals reasonably well, Finger and Gibbs (1985) undertook a derivation of a set of bonded radii for a variety of hydroxyacid molecules. They found, in the case of the monosilicic acid molecule, H_4SiO_4, which has 4-coordinate Si, that the bonded radius of the oxide ion agrees to within 0.01 Å with that reported for coesite (Geisinger et al., 1987). Finger and Gibbs (1985) also found that the bonded radius of the oxide ion calculated for the hexoxosilicic acid molecule, H_8SiO_6, which has 6-coordinate Si, is only 0.04 Å larger than that measured for stishovite (Spackman et al., 1987). These results suggest that bonded radii obtained for molecules may provide a reasonable estimate of these radii obtained for the same bonds in chemically similar crystals. Figure 4a shows a plot of the bonded radii determined by Finger and Gibbs (1985) from total electron-density maps for optimized $H_{8-m}X^{m+}O_4$ hydroxyacid molecules with first- and second-row 4-coordinate X cations versus the minimum-energy XO bond lengths. An examination of Figure 4a shows that the bonded radius of the oxide ion, r_O, increases linearly with $R_t(XO)$ according to the equation
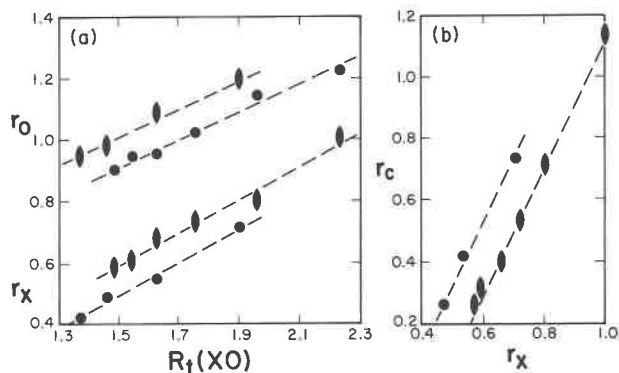
$$r_O = (0.35 - 0.1r) + R_t(XO)/2, \qquad (3)$$

Fig. 4. (a) A plot of the bonded radii for the oxide anion, r_O, and the bonded radii, r_X vs. the theoretical bond lengths, $R_t(XO)$ for first- and second-row X cations as determined by Finger and Gibbs (1985). (b) A plot of the crystal radii, r_c, determined by Shannon (1976) vs. the bonded radii r_X for first- and second-row X cations for oxides determined by Finger and Gibbs (1985).

where r is the row number of a main-group X cation (Gibbs and Boisen, 1986). The term $R_t(XO)/2$ in Equation 3 implies that the change in $R_t(XO)$ is shared equally rather than proportionally by the bonded radius of the cation and the oxide ion as one X cation is replace by another from its same row. Equation 3 also indicates that if the crystal radii for cations in a given row were plotted as a function of their corresponding bonded radii, then the resulting graph should be linear with a slope of 2.0. Figure 4b bears out this assertion. We also note that the bonded radii of the oxide ion decrease with increasing covalent character of the bond. Lindsay and Gibbs (1988) made a similar observation in a theoretical study of the SO bond where they found that the bonded radii of both S^{6+} and O^{2-} increase at the same rate with SO bond length as the s character of the SO bond decreases. Consequently, unlike the crystal and ionic radii, the bonded radii of the oxide ion appears to be responsive to the bonding characteristics of the cation to which it is bonded.

In the previous section, it was found that the bond-length–bond-strength parameter relationships in the sulfides were similar to those in the oxides. To see whether this similarity may be carried over to the bonded radii, the electron-density maps were calculated for 12 tetrahedral $H_{8-m}X^{m+}S_4$ molecules. These maps are displayed in Figure 5. The bonded radii, r_X, were calculated by fitting a quartic function to the electron-density function along the bond and taking the minimum of the quartic as the point at which the electron density is a minimum. The resulting bonded radii are plotted in Figure 6a against $R_t(XS)$. The resulting trends in Figure 6a are similar to those observed in Figure 4a for the oxides. The corresponding equation relating the bonded radii, r_S, of the sulfide ion to $R_t(XS)$ is

$$r_S = (0.59 - 0.13r) + R_t(XS)/2, \qquad (4)$$

where ½ is taken to be the coefficient of $R_t(XS)$ since that determined by a regression analysis (0.48, $\hat{\sigma} = 0.04$) is
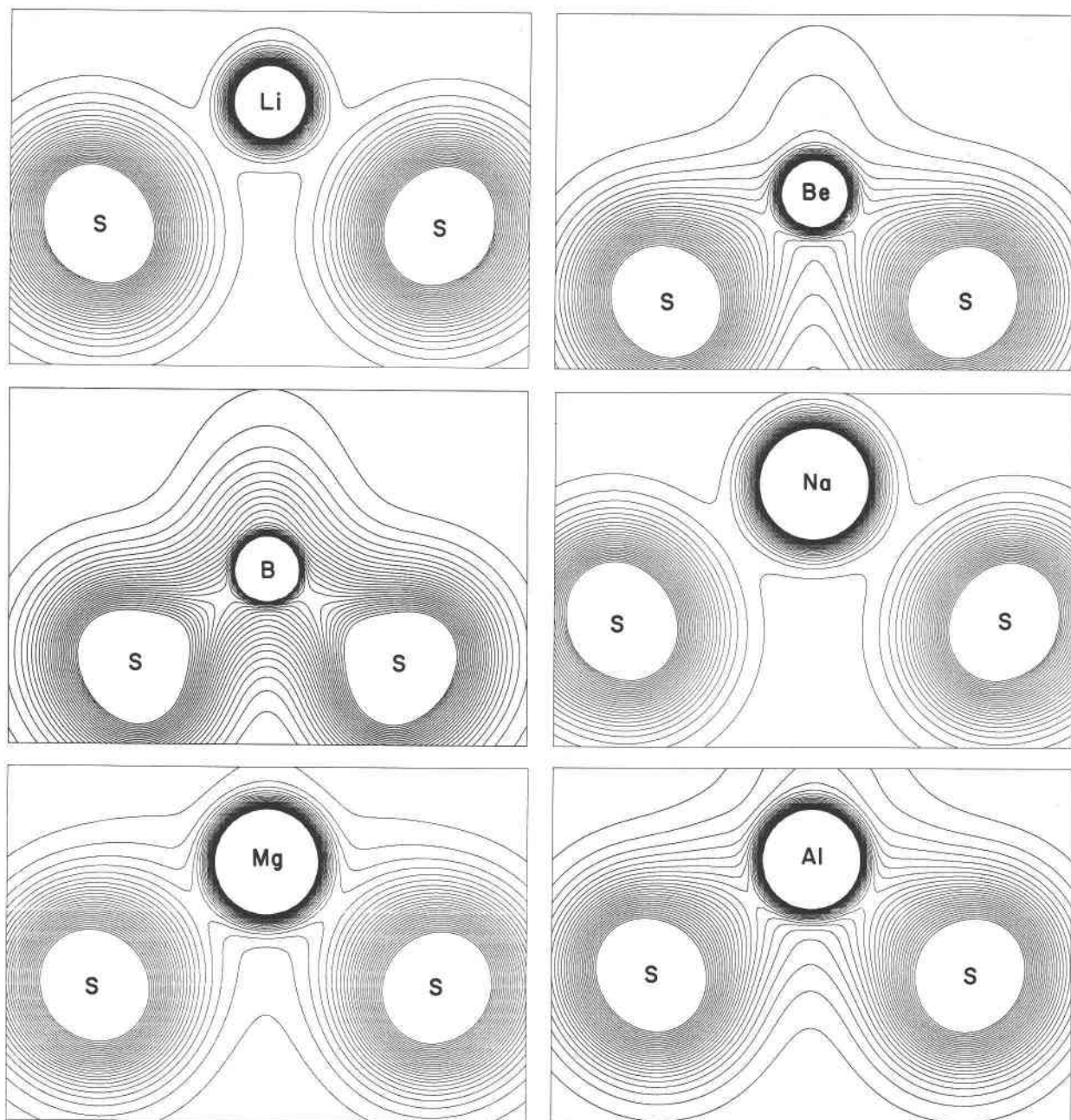
Fig. 5. Total electron-density maps calculated through the SXS bonds of $H_{8-m}X^{m+}S_4$ hydrosulfide molecules using the wave functions calculated for minimum-energy geometries. A contour interval of 0.05 e Å^{-3} was used.

not significantly different from ½. Again the presence of the $R_i(XS)/2$ term indicates that, for a given row, the change in $R_i(XS)$ is shared about equally between the bonded radius of the cation and the sulfide ion as one X cation is replaced by another. Shannon's (1981) crystal radius of the sulfide ion was assumed to be the constant 1.70 Å. The crystal radii of the cations in sulfides, r_c, were derived by subtracting 1.70 Å from the average observed XS bond lengths, and so these average bond lengths are

linearly related with r_c with a slope of 1.0. Assuming that $r_X + r_s$ provides a reasonable estimate of an XS bond length and substituting R_s from Equation 4 into this expression and setting it equal to the linear expression for the XS bond length in terms of r_c, we obtain r_c as a linear function of r_X with a slope of 2.0 as displayed in Figure 6b. The strategies used by Shannon and Prewitt (1969) and earlier workers of obtaining radii by subtracting a fixed anion radius from observed bond lengths must, by
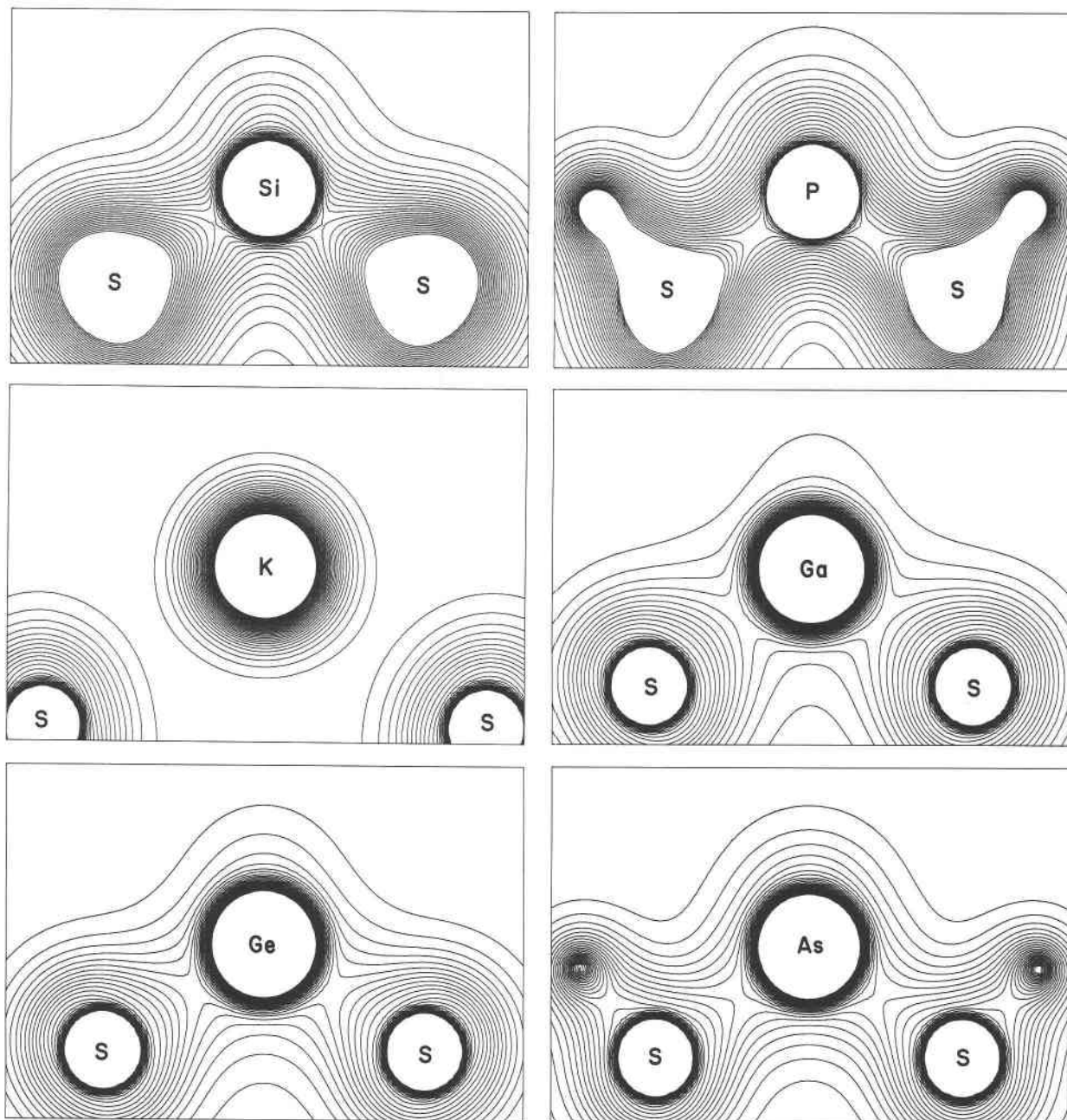
Fig. 5—*Continued.*

their very nature, lead to a set of radii that reproduce bond lengths. But, these radii, unlike the bonded radii, may not reflect physical reality.

In conclusion, electron-density maps calculated by Finger and Gibbs (1985) for the molecules H_4SiO_4, H_8SiN_4, SiF_4, H_4SiS_4, and $SiCl_4$ indicate that the bonded radius for Si is smaller when it is bonded to the first-row anions N^{3-}, O^{2-}, and F^- than when it is bonded to the second-row anions S^{2-} and Cl^-. The bonded radii of the cations

for sulfides determined in this study (Table 1) conform with this observation with the cations being 0.12 Å larger, on average, than those observed by Finger and Gibbs (1985) for the oxides. Also, the bonded radius of S^{2-} for a given bond is 0.41 Å larger, on average, than those for oxides. The larger cation radii for the sulfides may be related to the more diffuse distribution of the valence electrons on S^{2-}. A comparison of the electron-density maps for sulfides presented in this paper with those cal-
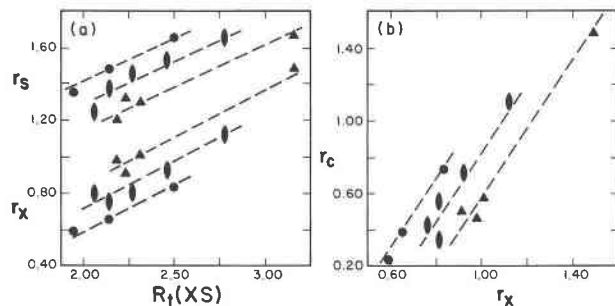
Fig. 6. (a) A plot of the bonded radii for the sulfide anion, r_S, and the bonded radii, r_X vs. the theoretical bond lengths, $R_t(XS)$ for first-, second-, and third-row X cations. (b) A plot of the crystal radii, r_c, determined by Shannon (1981) vs. the bonded radii r_X for first-, second-, and third-row X cations for sulfides.

culated by Finger and Gibbs (see Gibbs and Boisen, 1986) for oxides show that the charge density for S^{2-} for a given bond is more diffuse than that for the corresponding bond involving O^{2-}.

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