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Power law relationships between bond length, bond strength and electron density distributions

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Abstract The strength of a bond, defined as $p=s/r$, where s is the Pauling bond strength and r is the row number of an M cation bonded to an oxide anion, is related to a build-up of electron density along the MO bonds in a relatively large number of oxide and hydroxyacid molecules, three oxide minerals and three molecular crystals. As p increases, the value of the electron density is observed to increase at the bond critical points with the lengths of the bonds shortening and the electronegativities of the M cations bonded to the oxide anion increasing. The assertion that the covalency of a bond is intrinsically connected to its bond strength is supported by the electron density distribution and its bond critical point properties. A connection also exists between the properties of the electron density distributions and the connectivity of the bond strength network formed by the bonded atoms of a structure.

Introduction

The single most characteristic property of a chemical bond is its length, the shorter a particular bond, the greater its strength (Pauling 1940). A number of expressions have been proposed relating bond length, R, and bond strength, s (See Brown and Shannon 1973=B&S). One of the simplest has the form of the power law equation $s=(R_o/R)^{-N}$ *v.u.*. The constants (R_o, N) in this equation were derived by B&S for the observed bond lengths in a wide variety of oxide crystals under the constraint that the sum of the strengths of the bonds reaching each cation in a structure is equal to its valence. Constants were not only derived by B&S for individual power law equations for ~25 different cations, but they were also derived for three universal power law equations for first, second and third row cations (see also, Brown 1981). The sum of the strengths of the bonds reaching each atom in the oxides, when calculated with these equations, agree to within ~0.05 valence units with the valence of the atom, regardless of whether the bond type is a closed shell or a shared interaction (Bader 1990). The B&S bond strength model has since found widespread use in assessing the probable "correctness" of a crystal structure and the factors that govern the coordination numbers of its cations (Brown 1988). It has also been used to identify atoms in structures that are difficult to distinguish by X-ray diffraction methods as well as to identify the valence states of atoms in mixed-valence compounds (Brown 1981, 1992) and as an aid in the determination of crystal structures (Garrett et al. 1982).

The results of a relatively large number of molecular orbital calculations, completed for a variety of oxide and hydroxyacid molecules containing first and second row cations (Gibbs et al. 1987), have also been used to derive a set of theoretical constants that are in fairly good agreement with those derived by B&S for oxide crystals. With the definition of bond strength as $p=s/r$ *v.u.*, where s is the strength of an electrostatic bond and r is the row number of the cation, it was discovered that R, the average MO bond length, for both main group and closed shell transition cations for all six rows of the periodic table, can be modeled with the power law equation $R=1.39\times p^{-0.22}$ such that ~95% of the variation in $\ln(R)$ can be explained in terms of a linear dependence on $\ln(p)$ (Gibbs et al. 1987).

The following year, Boisen et al. (1988) forged a graph-theoretic algorithm for calculating the resonance bond numbers, n, for the bonds of a representative fragment of a silicate and found that more than 95% of the bond length variations recorded for ten silicate crystals can be modeled with the expression $R=1.39\times(n/r)^{-0.22}$. The fact that the same expression with s replaced by n

This paper is dedicated to Dr. Charles T. Prewitt upon his retirement as Director of The Geophysical Laboratory to return to one of the joys in his life, the study of mineral physics.

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models bond length variations equally well indicates that both n and s measure related properties of an *M*O bonded interaction. In effect, the valence electrons of a metal atom are pictured as resonating among alternative bonded positions of the coordinated polyhedra of a crystal, resulting in a partitioning of the electrons among the bonded network such that the bond numer of the bond tends to be numerically equal to the Pauling bond strength. This corresponds with Pauling's (1947) definition of bond number for a bond in a metal or an intermetallic compound as $n=z/\nu$ *v.u.*, where z is the number of single bonds that resonate among a central atom and its ν coordinated atoms. In the graph-theoretic model, it is assumed that the bonding is covalent with the sum of valence electrons in the bonds associated with each atom conferring a neutral configuration on each oxyen atom. One might conclude from this result that the bonding in silicates is largely covalent in character, but this would clearly be unjustified just as it would be unjustified to conclude that the bonding is largley ionic simply because Pauling's (1929) electrostatic valence rule is satisfied exactly for minerals like quartz, garnet and olivine.

In this paper, bond strength will be examined in terms of Bader's (1990) bond critical point properties of theoretical and experimental electron density distributions for the bonds reported for a relatively large number of molecules, three minerals and three molecular crystals. It will be shown that it correlates linearly with the average value of the electron density distribution, $\langle\rho(\mathbf{r}_c)\rangle$, evaluated at the (3,–1) critical points, $\mathbf{r}_c$, along the bonds of the individual coordinated polyhedra and that $\langle\rho(\mathbf{r}_c)\rangle$ is related to bond length by a power law expression in the same way that s, p and n are each related to bond length. A connection will be made between the strength of a bond and the electronegativity of the M atom comprising the bond.

Power law relationships

In a recent study of the bond critical point properties calculated for a large number of oxide and hydroxyacid molecules containing first and second row cations, Hill et al. (1997) optimized the geometries of the molecules at the Hartree-Fock/6-311++G** level. The average bond lengths, R, obtained for each molecule in these calculations are plotted against p in Fig. 1 as is the average BeO bond length observed for bromellite (BeO) (Downs 1991), the average CaO, BO and SiO bond lengths observed for danburite ($CaB_2Si_2O_8$) (Downs and Swope 1992), the average SiO bond lengths observed for coesite (SiO_2) (Downs 1995), the average CO bond lengths observed for crystalline L-alanine ($C_3H_7NO_2$) (Gatti et al. 1992), citrinin ($C_{13}H_{14}O_5$) (Roversi et al. 1996) and the average LiO and NO bond lenghs observed for Li bis(tetramethylammonium) hexanitrocobaltate (III) ($Li[N(CH_3)_4]_2[C0(NO_2)_6]$) (Bianchi et al. 1996). As expected, the agreement between the two data sets in Fig. 1 is fairly good with the average bond lengths for the three minerals and the three molecular crystals falling fairly close to the line defining the power curve fit to the data for the molecules (Gibbs et al. 1987). The resulting power equation ($R=1.39\times p^{-0.23}$) calculated for the oxide and hydroxyacid molecular data and graphed in Fig. 1 is statistically identical with that obtained earlier by Gibbs et al. (1987) for oxide molecules and crystals.

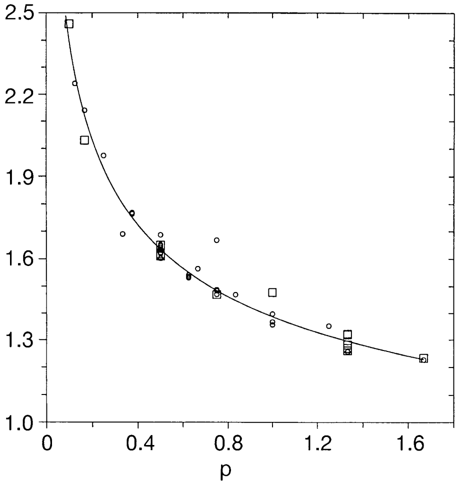

Fig. 1 A scatter diagram of the average geometry optimized bond lengths, R (Å) plotted as *open circles* against the bond strength, p, (v.u.) for hydroxide and oxide molecules (data taken from Table 1, Hill et al. 1997). The average bond length data for the BeO bond in bromellite, the average bond length data for the CaO and BO bonds in danburite, the average SiO bond length in coesite and danburite and the average CO bond lengths in L-alanine, citrinin and Li bis(tetramethylammonium) hexanitrocobaltate (III) (Downs 1991, 1995; Downs and Swope 1992; Gatti et al. 1992; Roversi et al. 1996; Bianchi et al. 1996) are plotted against the value of p as *open squares*

In a bond critical point analysis of the molecules using the strategies outlined by Bader (1990), the values of the electron density, $\rho(\mathbf{r}_c)$, were calculated for each *M*O bond (Hill et al. 1997). The average value of the electron density, $\langle\rho(\mathbf{r}_c)\rangle$, determined at the critical points of the coordinated polyhedra for each molecule, decreases nonlinearly with increasing R (Fig. 2) as defined by the power equation $R=1.60\times\langle\rho(\mathbf{r}_c)\rangle^{-0.22}$. This relationship is similar to the empirical bond strength-bond length curves derived by B&S for the oxides, particularly for the second row cations where $R=1.620\times s^{-0.23}$. It is striking that the exponent of this equation matches that obtained for the universal power law expression that relates R to $\langle\rho(\mathbf{r}_c)\rangle$, p and n/r, respectively. The same exponent and similar universal power law expressions also obtain between R and p for nitride, sulfide and fluoride molecules and crystals (Buterakos et al. 1992; Bartelmehs et al. 1989; Nicoll et al. 1994). Hence, it is apparent that a similar connection may exist between p, $\langle\rho(\mathbf{r}_c)\rangle$ and R for these materials as well.

The average values of the electron density distribution measured at the critical points for the bonds in the coordinated polyhedra of bromellite, danburite, coesite and crystalline L-alanine, citrinin and Li bis(tetramethylammonium) hexanitocobaltate (III) are also plotted in

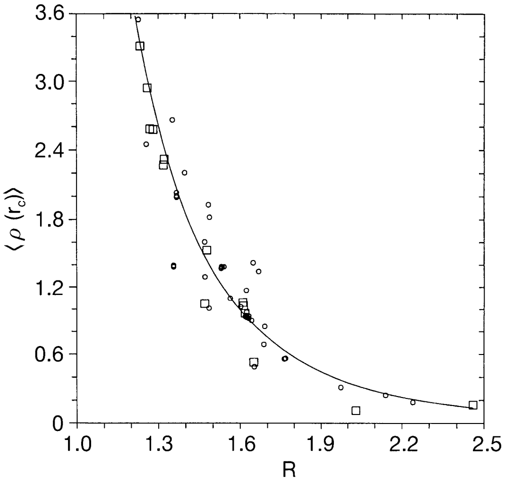

Fig. 2 A scatter diagram of the average value of the electron density at the bond critical points, $\langle\rho(\mathbf{r}_c)\rangle$ (e/Å^3), calculated for hydroxyacid and oxide molecules plotted against the average geometry optimized bond length R (Å). The data observed for bromellite, danburite, coesite, L-alanine, citrinin, Li bis(tetramethylammonium) hexanitrocobaltate (III) are plotted as *open squares* whereas the data for the molecules are plotted as *open circles* (see the legend of Fig. 1 four sources of data)

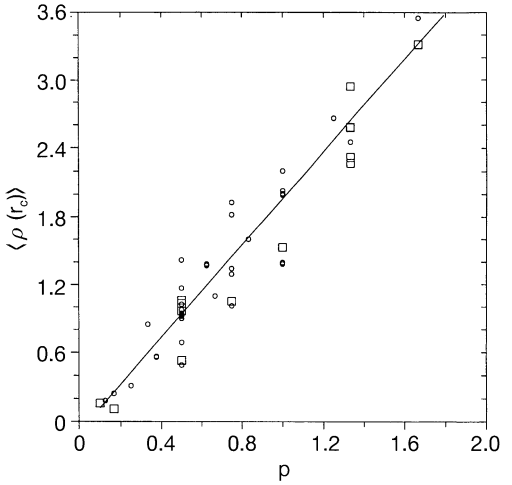

Fig. 3 A scatter diagram of the average value of the electron density, $\langle\rho(\mathbf{r}_c)\rangle$ (e/Å^3), calculated at bond critical points for oxide and hydroxyacid molecules and plotted against the bond strength, p. The data for three minerals and the two molecular crystals are plotted as *open squares* and that for the molecules are plotted as *open circles* (see the legend of Fig. 1 for sources of data)

Fig. 2 against R where it is seen that the data for the crystals plot within the confines of the scatter of the theoretical data calculated for the molecules. As both p and $\langle\rho(\mathbf{r}_c)\rangle$ are related to R by a power law equation with the same exponent, p can obviously be expected to be linearly correlated with $\langle\rho(\mathbf{r}_c)\rangle$ as displayed in Fig. 3 where nearly 90% of the variation in $\langle\rho(\mathbf{r}_c)\rangle$ can be explained in terms of a linear dependence on p. Again the data for the minerals and the molecular crystals fall within the confines of the theoretical data calculated for the molecules. Indeed, a regression analysis of the individual $\rho(\mathbf{r}_c)$ values and the individual CO bond lengths measured in a charge density study of crystalline citrinin (Roversi et al. 1996) yields a power law expression ($R=1.65\times\rho(\mathbf{r}_c)^{-0.28}$) that is statistically identical with the one graphed in Fig. 2 and the one calculated by Hill et al. (1997). The agreement between the $\langle\rho(\mathbf{r}_c)\rangle$ values observed for the crystals and the theoretical values calculated for the molecules is fairly good given that the Hartree-Fock formalism utterly ignores electron correlation. Typically, the agreement is poor in regions where the electron density is small and may explain why the $\langle\rho(\mathbf{r}_c)\rangle$ value calculated for the LiO bond departs significantly from that observed for the bond in Li bis(tetramethylammonium) hexanitrocobaltate (III) ($Li[N(CH_3)_4]_2[C0(NO_2)_6]$) (Bianchi et al. 1996).

A bond critical point model for electronegativity

Pauling (1940) originally assumed in the construction of his atomic electronegativity scale that each atom has a unique electronegativity value, χ, regardless of its environment. He found that not only does the value of χ for the atoms within a given row of the periodic table increase from left to right, but that it also decreases from top to bottom within a given column. Allen (1989) has argued that electronegativity is the third dimension of the periodic table, playing a key role in systematizing the properties of a vast array of known materials and in characterizing the forces that bind atoms in molecules and crystals. More recently, with the elucidation of the effects of charge and hybridization, electronegativity has evolved from a single valued quantity to a range of values that depend on the environment of an atom in a molecule or a crystal (Hinze et al. 1963; Mullay 1987; Bergmann and Hinze 1996). For example, the electronegativity of hybridized orbitals on C has been found to decrease in the series sp>sp^2>sp^3 as the s-character of the bonded interaction decreases (simply because s electrons have a lower energy than p electrons), the multiple bond character decreases and the coordination number of C increases (Allen 1989).

Despite the observation that a number of chemical phenomena can be explained in terms of the electron density distribution and electronegativity, only recently has an attempt been made to relate the bcp properties of the electron density distribution of a molecule to the electronegativities of its atoms (Boyd and Edgecombe 1988). In this study, an electronegativity factor is defined to be

$$F_M = r_b(X)/(N_M \times \rho(\mathbf{r}_c) \times R(MX)) \qquad (1)$$

for 21 diatomic hybride molecules where $r_b(X)$ is the bonded radius of X atom (X=H in this case), N_M is the number of valence electrons that atom M contributes to the molecule, $\rho(\mathbf{r}_c)$ is the value of the electron density at r_c and $R(M\,X)$ is the minimum energy MH bond length. Assuming that the electronegativity of an atom M can be expressed by the power law expression, $\chi_M = a \times F_M^b$, and selecting the constants a=1.938 and b=–0.2502 to yield an electronegativity of 1.0 for Li and 4.0 for F, they found that the χ_M values calculated for the molecules matching Pauling's (1940) χ-values to within 0.1, on average, with a linear coefficient of determination of r^2=0.98. As R(MH) is highly correlated with r_b(H), Hill et al. (1997) redefined Eq. 1 to read

$$F_M = r_b(X)/(N_M \times \rho(\mathbf{r_c})) \tag{2}$$

and recalculated a=1.31 and b=–0.23 for the χ-values of 1.0 and 4.0 for Li and F (the constants a and b were derived for bcp properties calculated in Å-units). A recalculation of the χ_M values with the expression

$$\chi_M = 1.31 \times F_M^{-0.23} \tag{3}$$

using the F_M values given by Eq. 2 for the diatomic hydride molecules yields values that match Pauling's values with the same agreement as obtained with the F_M values generated with Eqs. 1 and 3. The question that comes to mind is "Why does Eq. 3 work?" The answer is not clear-cut. However, we know that as electronegativity increases from left to right within a given row of the periodic table that (1) r_b(H) decreases nonlinearly; (2) $\rho(\mathbf{r_c})$ increases nonlinearly; (3) that Z-effective increase linearly as N_M increases from left to right. Hence, the electronegativity of an atom is expected to increase with decreasing r_b(H) and increasing $\rho(\mathbf{r_c})$ and N_M. However, contrary to the assumption made by Boyd and Edgecombe (1988), R(MH) actually decreases rather than increases within a row from left to right in the periodic table as electronegativity increases.

When Hill et al. (1997) applied Eqs. 2 and 3 to the bcp properties calculated for more than 50 oxide and hydroxyacid molecules, they found that several of the critical point properties vary linearly with χ_M. As R(MO) decreases and $\rho(\mathbf{r_c})$ increases, the orthogonal curvatures ($|\lambda_1|$ and $|\lambda_2|$) of $\rho(\mathbf{r_c})$ measured perpendicular to the bond path and the curvature measured along the path, λ_3, for a given bond each increase linearly with χ_M. Also, with the exception of the NO bond data, the Laplacian of $\rho(\mathbf{r_c})$, $\nabla^2 \rho(\mathbf{r_c})$, increases linearly with χ_M. In other words, as R(MO) decreases and $\rho(\mathbf{r_c})$ increases in value, the electron density can be pictured as being concentrated radially toward the bond path and away from the interatomic surface toward the basins of the bonded atoms. Also, for the more electronegative atoms, the local energy density, $H(\mathbf{r_c})$ (Cremer and Kraka 1984), was found to decrease linearly with χ_M, indicating that the build-up of electron density at $\mathbf{r_c}$ has a stabilizing effect on the molecules with the bond becoming progressively more covalent as χ_M increases. Similar trends are observed for the MN and MS bonds in a comparable number of nitride and sulfide molecules (Feth et al. in press; G.V. Gibbs et al., in preparation).

Gibbs et al. (accepted) have since found evidence in a comparative study of the bcp properties for SiO and GeO bonds in a variety of silicate and germanate molecules that Ge has a slightly larger electronegativity than Si in contrast to Pauling (1940) who found them to have identical electronegativities (1.8). To learn how the electronegativities of Si and Ge vary with bond length and coordination number, calculations were completed for molecules with 4-, 6- and 8-coordinated Si and Ge. As expected, the minimum energy bond lengths calculated for the molecules were found to increase with increasing coordination number. Also, the χ_M values for Si and Ge calculated with Eqs. 2 and 3 decrease in a regular way with increasing coordination number (denoted by a Roman numeral):

χ IVSi	χ IVGe	χ VISi	χ VIGe	χ VIIISi	χ VIIIGe
1.81	1.83	1.70	1.75	1.46	1.55.

In each case, the electronegativity of Ge, rather than being equal to that of Si, is indicated to be ~0.05 larger. Not only does this indicate that the electronegativity of Ge is larger than that of Si as observed by Allred and Rochow (1958) and Allen (1989), but it also indicates that the GeO bond is slightly more covalent than the SiO bond, all other thing being equal.

It is important to note that Hill et al. (1997) and Gibbs et al. (accepted) were unable to obtain in their studies, the electronegativity, χ_O, for the oxide anion (no more than we were able in this study to obtain the electronegativity of the oxide ions in the six crystals). This complicates the situation because as χ_M changes for each M cation, so then should χ_O change. Inasmuch as the character of the bond is believed to be related to the electronegativity differences, $|\chi_M - \chi_O|$ (Pauling 1940), it then follows that our assumption that the covalency of an MO bond increases with increasing χ_M may not be valid. Nonetheless, as the trends reported here and by Hill et al. (1997), Feth et al. (in press) and Gibbs et al. (accepted) between χ_M, bond character and the bcp properties seem to conform with chemical intuition, we believe that they are qualitatively correct and meaningful.

Boyd and Edgecombe (1988) concluded in their study of electronegativities that their bcp model can not only be used to obtain the electronegativities of substituents, but it also can be extended to evaluate electronegativities for theoretical and experimental electron density distributions. Figure 4 shows that χ_M increases nonlinearly with increasing p for theoretical and experimental electron density distributions for molecules and crystals. A similar trend has been presented by Brown and Skowron (1990) between electronegativity and Lewis acid strength. As argued by B&S (see also, Brown 1988), Fig. 4 also shows that the Pauling bond strength, s, relates to the electronegativitiy of the coordinated M atom, the greater the value of s, the greater electronegativity of the M cation and the greater the covalency of the MO bond. The data obtained for the minerals and the molecular crystals, as observed in the earlier plots, scatter within the confines of the data for the molecules. This indicates that the critical point properties of the electron density distributions for the molecules, the molecular crystals and the minerals are similar. Indeed, the bond critical point properties of the SiO(br) bonds recently calculated for several hydroxyacid disilicic

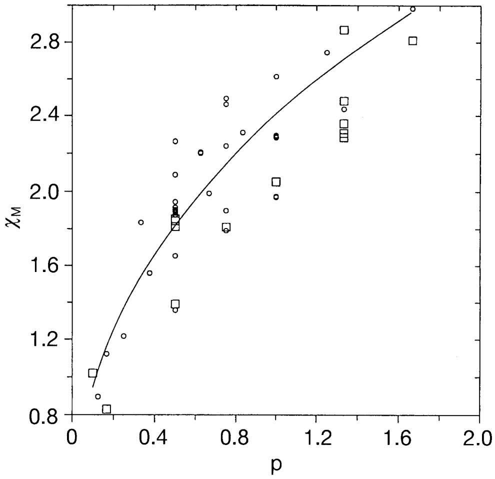

Fig. 4 A scatter diagram of relative electronegativities of the *M* cations, χ_M, generated from the critical point properties of the electron density distributions calculated for oxide and hydroxyacid molecules, plotted as *open circles* against the bond strength, *p*. The data for three minerals and the two molecular crystals are plotted as *open squares* (see the legend of Fig. 1 for sources of data)

acid molecules ($H_6Si_2O_7$) and the hydroxyacid pentasilicic acid molecule, ($H_{12}Si_5O_{16}$), agree with those observed, on average, for coesite and danburite to within ~5% (G.V. Gibbs et al., accepted). Collectively, these results show, as expected, that the geometry and electron density distributions of a silicate and a representative molecule are strikingly similar despite the crystal's much larger size (Gibbs 1982; Gibbs and Boisen in press). They also support the argument that the local force field and the electron density distribution of a silicate SiO_4 tetrahedral oxyanion plays a determinantal role in governing the structure and properties of the tetrahedral frame of a silicate (Gibbs 1982).

Discussion

The correlations between bond strength, electronegativity and the value of the electron density at critical points along the bonds establish an important connection between the strength of a bond and its electron density distribution. As the strength of a particular bond depends on its bond length, it follows that the shorter the bond, the greater the electronegativity of the cation, the greater the build-up of electron density along the bond and the greater the enhancement of electron density toward the bond path. These correlations establish a basis for the connection proposed by B&S between the covalent character of a bond and its bond strength – the greater the bond strength, the more covalent the bond. It likewise conforms with the well-developed correlation between bond strength and Mulliken bond overlap populations established by Gibbs (1982) – the greater the overlap population, the greater the bond strength and the shorter the bonds. The discovery by Brown (1981; 1987; see also Garrett et al. 1982) that an inverted map of the bond strength network of a crystal closely approximates an experimental valence density distribution is a natural result of the close connection that exists between bond strength and the electron density distribution of a bonded interaction. Likewise, it is evident that an intrinsic connection exists between the bond strength network of the B&S model and the topological properties of the electron density distributions, a connection that was suggested to exist nearly 20 years ago by Bader et al. (1980). Finally, the universal power law $R=R_0p^{-N}$ begs a physical interpretation. While we are unable to offer such an interpretation, it does provide grist for the theoretician's mill.

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