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The ionicity of the Si–O bond in low-quartz

R. F. STEWART

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

M. A. WHITEHEAD

Department of Chemistry

AND GABRIELLE DONNAY

Department of Geological Sciences
McGill University, Montreal, Canada

Abstract

Accurate structure factors for synthetic low-quartz permit the evaluation of residual charges of +1.0±0.1 e.u. on pseudoatom Si and −0.5±0.1 e.u. on pseudoatom O. A new definition of ionicity, based on experimental data exclusively, sets it equal to the ratio of residual charge to formal charge thus giving the Si–O bond in quartz an ionicity of 25%. The value that is calculated from orbital electronegativity theory, taking the observed interbond angles into account, is 25.36%.

Introduction

The theory of bonding is based on energy, whereas the X-ray experiment gives the electron density. The relation of the energy of a many-electron, many-nucleus molecule to the $\bar{\rho}$ of the corresponding molecular crystal structure is still unknown, so that the interpretation of electron-density ($\bar{\rho}$) maps and electron-density-difference ($\Delta\bar{\rho}$) maps in terms of chemical bonding is fraught with difficulties. It was hoped that reliable measurements of the structure factors $F(hkl)_{obs}$ would help us understand the nature of the chemical bond, but while it may be easy to map $\Delta\bar{\rho}$ and to explore a number of physical properties inherent in F(*hkl*), there is no unique way of decomposing the mean thermal charge density (or electron density $\bar{\rho}$ at room temperature) into constituent parts. Thus, from only $\bar{\rho}$, it is impossible to determine the natural spin orbitals (Löwdin, 1955)[1] of the spinless first order density matrix, and $\bar{\rho}$ yields neither direct information on paired spins of electrons nor a simple description of valence-bond structures. Conversely, valence-bond structures cannot be uniquely converted into one-electron density functions (Coppens, 1977; Bader *et al.*, 1979).

Current theoretical approaches equate the number of bond paths to the number of chemical linkages but not to electron-pair bonds (Bader *et al.*, 1979) and conceive of the molecule, whether finite or infinite, as made up of atom-like virial fragments (Srebrenik *et al.*, 1978). These developments imply that a molecule is not the sum of the atoms of which it is composed, and the term "pseudoatom" is used to refer to atoms in a compound. In 1932 Pauling introduced the *atomic* electronegativity scale. Mulliken (1934) extended the concept so that *orbital* electronegativities could be introduced by Hinze and Jaffé (1962) and applied to σ and π orbitals (Hinze *et al.*, 1963) to generate σ and π polar character and to give, as a sum of effects, the ionic character of a bond (Baird *et*

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[1] Natural spin orbitals u_i have the property that the total charge density is given rigorously by

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1),$$

where n_i is the occupation number between zero and unity measuring that part of the charge arising from the ith spin orbital. Normally when the charge density is expressed in terms of a basic set of spin orbitals ϕ_i, cross terms $\phi_i^*\phi_j$ with coefficients c_{ij} occur. Linear combinations of these original ϕ_i's to give u_i's, where only i = j is possible, generate natural spin orbitals (Slater, 1975, p. 253).

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al., 1968). Thus, if in an AB molecule there were multiple bonding σ and π, the two electron-pair bonds could be more or less polar and show parallel or antiparallel polarities: if the σ bond were $A^{0.5}B^{-0.5}$ and the π bond $A^{-0.3}B^{0.3}$, then the molecule as a whole would show the residual charges $A^{0.2}B^{-0.2}$, which are obtained in an absolute electron-density study.

Later the electronegativity concept developed into a molecular orbital and density functional format. It was shown that, while energy rather than electronegativity determines whether a chemical bond will form, the charge transfers which accompany bond formation are determined by the electronegativity differences, and neutralization occurs with all the electronegativities equal in the final molecule. Thus we return to Pauling's atomic picture where the charge transfer that occurs between atoms to give neutrality is proportional to the electronegativity difference (Parr *et al.*, 1978).

The bonds in SiO_2

When accurate X-ray data available for α-quartz (Le Page and Donnay, 1976) are employed to evaluate its three-dimensional electron-density function, it cannot be assumed that information on single and double bond character will be forthcoming or that lone pairs will be discovered. The difference map $\Delta\bar{\rho}$ shows only charge-density displacements, as it measures the difference between observed and calculated electron density where the latter is based on an SiO_2 structure composed of free Si and O atoms which are spherically averaged. (The quadrupole component of these ^3P ground-state atoms is neglected in the reference-model density.) In some cases the deformation density in $\Delta\bar{\rho}$ maps can be *interpreted* in terms of preconceived chemical bonding on the assumption that a molecular orbital resembles its constituent atomic orbital basis.

One challenge in the analysis of measured structure factors for α-quartz lies in the derivation of accurate phases, since the space group ($P3_221$) is acentric. The approach taken by one of us consisted in using the many-center, finite multipole expansion for the Si and O pseudoatoms (Stewart, 1976). With suitably flexible radial functions, a large number of static-charge physical properties are projected out from the observed structure factors (Stewart, 1977). The charge of each pseudoatom is given by the monopole populations and in general is dependent on the monopole form-factor as well as on the selection of higher multipoles. It is emphasized here that projection methods (or least-squares fits) with rigid pseudoatoms can accurately represent the electron-density distribution, including effects of chemical bonding. For the several models used, which included optimization of the radial, multipole form factors, the residual charge of +1±0.1 electron units (e.u.) was found on the pseudoatom Si and −0.5±0.1 e.u. on the pseudoatom O. A large octopolar component of electron-charge density about Si is presumably due to the tetrahedral environment of Si. (The site symmetry of Si is 2 so that the three components of the octopole were included in the analysis.)

We define the ionicity (or ionic character) *i*, expressed as a percentage, as follows:

$$i = 100 \times \text{residual charge/formal charge}$$

For a residual charge of +1 e.u. on Si^{4+}, the ionicity is 25%, and each of the four very nearly equal Si–O bonds has thus 75% covalent character. Since residual charges like those on Si and O are obtainable from accurate X-ray diffraction data, the re-defined ionicity *i* is determined experimentally and does not depend on any electronegativity scale. As will be shown below, this *i* value agrees with the one calculated from the orbital electronegativity theory. If such agreement should be forthcoming for many other A–B bonds, a curve of ionicity *vs.* difference in orbital electronegativity would be meaningful.

Orbital electronegativity theory

Following Hinze *et al.* (1963), we express the energy of atom A as

$$E_A = a_A + bn_A + cn_A^2 \tag{1}$$

The electronegativity of A is defined as

$$X_A = dE_A/dn = b + 2cn_A \tag{2}$$

where b_A and c_A are constants, and n_A is the number of electrons in the orbital: 0, 1, or 2. The constants are related as follows (Mulliken, 1934; Baird *et al.*, 1968) to the ionization potential I_A of the experimental valence state and the electron affinity E_A:

$$b_A = I_A \tag{3}$$

$$c_A = \tfrac{1}{4}(E_A - I_A) \tag{4}$$

When two orbitals form a bond containing 2 electrons ($n_A + n_B = 2$), the electronegativities are equalized, $\chi_A^* = \chi_B^*$, and charge moves from one orbital to the other, giving ionic character to the bond. The amount of charge moved is governed by the need to equalize the electronegativities (Parr *et al.*, 1978; Sanderson, 1976, p. 75–79). The ionic character is

$$i = \frac{1}{2}\,\frac{\chi_A - \chi_B}{c_A + c_B}$$

where χ_A and χ_B are the initial electronegativities of the orbitals forming the bond.[2] These orbital electronegativities and coefficients are well established (Hinze and Jaffé, 1962; Hinze *et al.*, 1963; Baird *et al.*, 1968). For tetrahedrally bonded Si, we have

$$\chi_{te}^{Si} = 2.25$$

(te = sp^3 hybridization), this orbital being bonded to an oxygen atom in a hybridized state between sp, di, di $\pi^2\pi^2$, and sp^2, tr tr $tr^2\pi^2$, so that the Si–O–Si angle is 143° (the sp hybrid is 180° and the sp^2 hybrid 120°). Since χ_{di}^{O} is 6.23 and χ_{tr}^{O} is 5.54, and since there is a known relation between χ and bond angle (Hinze and Jaffé, 1962), the $\chi_{143^\circ}^{O}$ is

$$\chi_{SiO_2}^{O} = 5.80$$

The values of the coefficients are

$$c_{te}^{Si} = -2.26$$

and from $c_{di}^{O} = -4.8$ and $c_{tr}^{O} = -4.7$ since the c value is directly related to angle (Hinze and Jaffé, 1962)

$$c_{SiO_2}^{O} = -4.74$$

giving $i = 25.36\%$ in agreement with the above value $i = 25\%$ obtained from our interpretation of the X-ray results.

Conclusion

In the case of α-quartz the orbital electronegativity theory checks the experimental facts. It preserves the chemical bond, is compatible with the concept of pseudoatom and links the residual charges obtained from the $\Delta\bar{\rho}$ map to energetic properties such as ionization potential, electron affinity, nuclear quadrupole resonance (Kaplansky and Whitehead, 1968), nuclear magnetic resonance (Baird *et al.*, 1968), bond length (Zeiss and Whitehead, 1971), and calculated electron-density distribution (Krause and Whitehead, 1973).

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References

Bader, R. W., S. G. Anderson and A. J. Duke (1979) Quantum topology of molecular charge distribution. I. *J. Am. Chem. Soc., 101,* 1389–1395.

Baird, N. C., J. M. Sichel and M. A. Whitehead (1968) A molecular orbital approach to electronegativity. *Theor. Chim. Acta, 11,* 38–50.

Coppens, P. (1977) Experimental electron densities and chemical bonding. *Angew. Chem., Int. Ed., Engl., 16,* 32–40.

Hinze, J. A. and H. H. Jaffé (1962) Electronegativity. I. Orbital electronegativity of neutral atoms. *J. Am. Chem. Soc., 84,* 540–546.

———, M. A. Whitehead and H. H. Jaffé (1963) Electronegativity. II. Bond and orbital electronegativities. *J. Am. Chem. Soc., 85,* 148–154.

Kaplansky, M. and M. A. Whitehead (1968) BEEM-π calculations on chlorine in conjugated molecules. *Mol. Phys, 15,* 149–156.

Kowalczyk, S. P., L. Ley, F. R. McFeely and D. A. Shirley (1974) An ionicity scale based on X-ray photoemission valence-band spectra of A^NB^{8-N} and A^NB^{10-N} type crystals. *J. Chem. Phys., 61,* 2850–2856.

Krause, L. and M. A. Whitehead (1973) BEEM-π calculations for a series of pyridines and their ^{14}N N.Q.R. *Mol. Physics, 26,* 503–506.

Le Page, Y. and G. Donnay (1976) Refinement of the crystal structure of low-quartz. *Acta Crystallogr., B32,* 2456–2459.

Löwdin, P. O. (1955) Quantum theory of many particle systems. I. Physical interpretations by means of density matrices, natural spin orbitals, and convergence problems in the method of configurational interactions. *Phys. Rev., 97,* 1474–1489.

Mulliken, R. S. (1934) A new electron-affinity scale, together with data on valence states and on valence ionization potentials and electron affinities. *J. Chem. Phys. 2,* 782–793.

Parr, R. G., R. A. Donnelly, M. Levy and W. E. Palke (1978) Electronegativity: the density functional viewpoint. *J. Chem. Phys., 68,* 3801–3807.

Pauling, L. (1932) The nature of the chemical bond, IV. The energy of single bonds and the relative electronegativity of atoms. *J. Am. Chem. Soc., 54,* 3570–3582.

Sanderson, R. T. (1976) *Chemical Bonds and Bond Energy,* 2nd ed. Academic Press, New York.

Slater, J. C. (1975) *Solid State and Molecular Theory.* Wiley-Interscience, New York.

Srebrenik, S., R. F. W. Bader and T. Nguyen-Dang (1978) Subspace quantum mechanics and the variational principle. *J. Chem. Phys., 68,* 3664–3679.

Stewart, R. F. (1976) Electron population analysis with rigid pseudoatoms. *Acta Crystallogr., A32,* 565–574.

——— (1977) One-electron density functions and many-centered finite multipole expansions. *Israel J. Chem., 16,* 124–131.

Tossell, J. A. (1977) A comparison of silicon–oxygen bonding in quartz and magnesium olivine from X-ray spectra and molecular orbital calculations. *Am. Mineral., 62,* 136–141.

Zeiss, G. D. and M. A. Whitehead (1971) Hetero-atomic molecules: semi-empirical ($\pi + \sigma$) molecular orbital calculation and prediction of physical properties. *J. Chem. Soc. A,* 1727–1738.

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[2] The ionicity scale based on X-ray photoemission valence-band spectra of A^NB^{8-N} and A^NB^{10-N} crystals (Kowalczyk *et al.*, 1974) and used on SiO_2 (Tossell, 1977) is not considered here, because it has never been clearly related to traditional ideas, either to the SCF-Xα calculations performed by Tossell (1977) or to the X-ray-density results.

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