Cluster model investigation of chemical bonding of elements in silica and water

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Abstract. Chemical bonding of different elements in the periodic table is investigated by the DV-Xα molecular orbital method for silicon oxide cluster and aqueous cluster models. The molecular orbital calculations reveal the distinctiveness of phosphorus-oxygen and calcium-oxygen bonds in the silica based cluster model. The former shows very strong covalency and the latter shows negative covalency. Because silica is ubiquitous in the Earth's crust, these characteristics seem to be important for the selection of elements in natural eco-systems.

1. Introduction
For development of an ecological system, it is important to understand the distribution of elements and the selection of elements in nature [1, 2]. There are great nanoscopic eco-machines [3] and nature provides clues for materials science and engineering. Earth's surface layer is divided into solid, liquid and gaseous parts, called the lithosphere, hydrosphere and atmosphere, respectively. The biosphere is present on the Earth's surface. The lithosphere consists mainly of soil and rock. The hydrosphere consists mainly of water in oceans, rivers and lakes. In the Earth's crust, the most abundant element is oxygen and the second most abundant element is silicon [4]. Silica and silicate minerals are dominant in rocks. Silica and silicates have building units of tetrahedral SiO₄ where four oxygen atoms surround a central silicon atom. Water is familiar but has complex properties. It is a solvent and forms complex solutions in oceans, rivers and lakes.

Natural eco-systems seem to be built around Si-O and H-O bond networks, because Si-O networks are dominant in the lithosphere and H-O networks are dominant in the hydrosphere. Thus, an investigation of the properties of elements in Si-O and H-O networks can form the basis for understanding eco-systems. In this paper, the chemical bonding of elements is investigated by the DV-Xα molecular orbital method in a silica based cluster model [5, 6] and an aqueous cluster model with water molecules as ligands.

2. Computational method
DV-Xα molecular calculations were carried out using the SCAT code developed by Adachi et al. [7]. Calculations were based on the Hartree-Fock-Slater approximation with an exchange correlation between electrons based on the Slater local exchange-correlation potential V_{xc} given by

\[ V_{xc} = -3\alpha \left[ \frac{3}{8\pi} \rho(\vec{r}) \right]^{1/3}, \]

(1)
where $\rho(\vec{r})$ is the local electron density at a position $\vec{r}$ [7-9]. In this calculation, the parameter $\alpha$ is fixed at a constant value of 0.7 and the self-consistent charge approximation is employed. The molecular orbital wave function $\phi$ is expressed by a linear combination of atomic orbitals (LCAO) as

$$\phi_n = \sum_i c_i^n \chi_i,$$

where $\chi_i$ is a basis function. Numerical atomic orbitals are employed as the basis functions in the DV-Xα method.

Figure 1 shows the model clusters analyzed in the present work. (a) M(SiO$_4$)$_4$ and (b) M(H$_2$O)$_6$. In both the M(SiO$_4$)$_4$ and M(H$_2$O)$_6$ clusters, the central site atom is M, as indicated by arrows in Figure 1. The M(SiO$_4$)$_4$ cluster is based on crystalline $\alpha$-quartz with a lattice constant $a=0.491$ nm (M-O distance=0.161 nm) [10] and the M(H$_2$O)$_6$ cluster is based on an octahedral aqua complex (M-O distance=0.140 nm). DV-Xα molecular calculations are performed for these model clusters, where M = H – Sn across the periodic table. The atomic positions are fixed in the calculations for all the cluster models. The atomic basis functions used in the present calculations are 1s for H and He, 1s-2p for Li – Ne, 1s-3d for Na – Cl, 1s-3p for Ar, 1s-3p, 4s and 4p for K and Ca, 1s-4p for Sc – Kr, 1s-4p and 5s for Rb and Sr and 1s-5p for Y – Sn. No point groups are used to produce symmetry orbitals. Self-consistency within 0.001 electrons is obtained for the final orbital populations. A Mulliken population analysis [11] is employed for evaluation of the net charge and the bond overlap population. Non-spin-polarized cases are considered in the molecular orbital calculations.

3. Results and discussion

Figure 2 shows the bond overlap population between the central atom M and neighboring O atoms in the cluster (a) M(SiO$_4$)$_4$ and (b) M(H$_2$O)$_6$, for M = H – Sn across the periodic table. In the M(SiO$_4$)$_4$ clusters, self-consistency within 0.001 electrons was not achieved in the calculations for M = V, Se and Ag. Self-consistency was achieved within 0.014 electrons for M = V, within 0.018 electrons for M = Se and within 0.037 electrons for M = Ag. In the M(SiO$_4$)$_4$ cluster models, the maximum value of the bond overlap population is observed for M = P, and minima are observed for M = Ca and Sr. An M atom is at the center of four SiO$_4$ tetrahedral units, and an M atom and four neighboring O atoms also form one MO$_4$ tetrahedral unit. In the present calculations, the M-O distances are set to be the same as for Si-O (0.161 nm). Of course, each stable structure for the M-O cluster is not necessarily tetrahedral, and both the coordination number with oxygen and the distance from oxygen are different from the case of Si-O for different elements in the periodic table. However, Figure 1 does show the individual characteristics of each element in Si-O tetrahedral networks.

The bond overlap population was derived from the DV-Xα orbitals in calculations considering only the Xα exchange correlation, without electron correlation. Although the finer details with respect to
energy are rather sensitive to the way electron correlation is included, information concerning the wave functions is insensitive to electron correlation and such DV-Xα calculations can be considered reliable [7-9, 12, 13].

![Figure 2](image_url)

**Figure 2.** Bond overlap population of M-O in (a) M(SiO₄)₄ and (b) M(H₂O)₆, where M = H–Sn. The M-O distances are 0.161 nm in M(SiO₄)₄ and 0.140 nm in M(H₂O)₆ respectively.

In the M(H₂O)₆ cluster model, the maximum value of the bond overlap population is observed for M = S, and minima are observed for M = Ca and Sr. The peak shapes are similar for the M(SiO₄)₄ and M(H₂O)₆ cluster models, but the maximum peak elements are different. The strength of the covalent bonding is estimated by the bond overlap population. The elements Si, P and S show strong covalency with O. On the other hand, the elements Ca and Sr show negative covalency. Especially in the case of M(SiO₄)₄ models, P and Ca seem to be distinctive elements.

It is interesting to note that Ca and P are also distinctive elements in biological systems. Ca acts as a messenger in cells and P is essential to all life, being a component of DNA and ATP [4]. In mammals, bone contain both Ca and P, often paired with each other. In the present calculations, although the bond overlap population curve for M(H₂O)₆ is similar to that for M(SiO₄)₄, the distinctiveness of Ca and P is clear for M(SiO₄)₄. In addition, a local minimum is observed for Zn in M(SiO₄)₄, and Zn is the second cell messenger [14]; however, this minimum is not observed in M(H₂O)₆.

Si-O networks are the dominant forms in the Earth and in the universe, the non-living world. In the Earth, they are found in the crust and mantle, as silica and/or silicate minerals. In the universe, they are found in cosmic dust, asteroids, terrestrial planets, and so on. Si-O networks are therefore ubiquitous. The essentiality of Si in life has been pointed out despite a failure to describe any mechanism of action [15, 16]. It seems that the characteristics of Ca-O and P-O bonds in Si-O networks are important for the selection of elements in eco-systems in nature.
4. Conclusions

The nature of chemical bonding with oxygen is investigated by the DV-X\alpha molecular orbital method for silica based cluster and water based cluster models. The effect of substitution at the central silicon site in \(-\)quartz silica based tetrahedral cluster models is investigated for elements from hydrogen to tin in the periodic table. Central site substitution effects in clusters based on an octahedral aqua complex are also evaluated. The phosphorus-oxygen bonds show very strong covalency and calcium-oxygen bonds show negative covalency. This tendency is more clear in the silica based model than in the octahedral aqua complex model. The characteristics of phosphorus-oxygen and calcium-oxygen bonds in the silicon-oxygen networks seem to be important for element selection rules in natural ecosystems.

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References

[1] Williams R J P and Frausto da Silva J J R 2000 Coordin. Chem. Rev. 200-202 247
[2] Williams R J P 2006 J. Inorg. Biochem. 100 1908
[3] Brunner E, Gröger C, Lutz K, Richthammer P, Spinde K and Sump M 2009 Appl. Microbiol. Biotechnol. 84 607
[4] Emsley J 2001 Nature's Building Blocks (Oxford: Oxford University Press)
[5] Takahara W and Minami F 2006 Bull. Soc. DV-X\alpha 19 186
[6] Takahara W 2007 Bull. Soc. DV-X\alpha 20 110 (in Japanese)
[7] Adachi H, Tsukada M and Satoko C 1978 J. Phys. Soc. Jpn. 45 875
[8] Adachi H 1997 Adv. Quant. Chem. 29 49
[9] Adachi H 1997 Mater. Trans., JIM 38 485
[10] Villars P and Calvert L D 1991 Pearson's Handbook of Crystallographic Data for Intermetallic Phases Second Edition (Materials Park, OH: ASM International) p 4760
[11] Mulliken R S 1955 J. Chem. Phys. 23 1833
[12] Morinaga M, Nasu S, Adachi H, Saito J and Yukawa N 1991 J. Phys.: Condens. matter 3 6817
[13] Takahara W, Maeda H and Minami F 2003 Adv. Quant. Chem. 42 275
[14] Yamasaki S, Sakata-Sogawa K, Hasegawa A, Suzuki T, Kabu K, Sato E, Kurosaki T, Yamashita S, Tokunaga M, Nishida K and Hirano T 2007 J. Cell. Biol. 177 637
[15] Exley C 1998 J. Inorg. Biochem. 69 139
[16] Exley C 2009 Trends Biochem. Sci. 34 589