Nature of Si-O bonding via molecular orbital calculation

NORITAKE, Fumiya[1]* ; KAWAMURA, Katsuyuki[1]

[1]Okayama University

Understanding the nature of Si-O bonding and Si-O-Si bridging is important for mineralogy, material science and metallurgy. It is well known that the variation of Si-O-Si angle in silicates is caused by difference of composition, temperature and pressure. The change of angle of Si-O-Si bridging affects the strength of Si-O bonding. For instance, the increase of Si-O-Si angle decreases the Si-O bond length in coesite crystal (Gibbs et al. 1977). The decrease of Si-O-Si angle of liquid silicates as a result of compression is reported by various researchers (e.g. Navrotsky et al., 1985 Ohtani et al., 1985, Sakamaki et al., 2012). The decrease of Si-O-Si angle is thought to be the trigger of decrease of viscosity of liquid silicates. (Navrotsky et al., 1985, Noritake et al., 2012). Quantum chemical properties of Si-O-Si bridging is investigated to understand the relationship between Si-O-Si angle, Si-O bond length and its strength (e.g., Newton and Gibbs 1980, Tsuneyuki 1996, Kubicki and Sykes 1993). Newton and Gibbs (1980) reports the pyrosilisic acid molecule has energy minimum at Si-O-Si angle of 145 ^{0} using STO-3G basis set (Hehre et al 1969) by Hartree-Fock method. Tsuneyuki (1996) reports that the bending of Si-O-Si is not reproduced using double-zeta function basis set nevertheless the increase of the number of basis function generally increase the reproducibility. However, the nature of Si-O-Si bridgings seems not to be reproduced by increase of basis function using Hartree-Fock method. In this paper, we show the molecular orbital calculation about pyrosilisic acid molecule using post-Hartree-Fock method and more precise basis set to understand the nature of Si-O-Si bridging.

Molecular orbital calculations were performed using the GAUSSIAN 09 code. We firstly calculate the optimized structure of disiloxane (Almenningen et al., 1963) by Hartree-Fock (HF), second-order Moller-Plesset perturbation theory (MP2) , and two density functional theory (Becke's density functional (Becke, 1988) with three correlation functionals by Lee, Yang and Parr (B3LYP) (Lee et al., 1988), and generalized gradient approximation by Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996)) with 6-311G(d,p) split valence double zeta basis set (Raghavachari et al., 1980). The bending of Si-O-Si bridging is not reproduced by HF method as shown in Tsuneyuki (1996). The bending of Si-O-Si bridging is reproduced by use of MP2 and density functional theory with PBE. The optimized angle of Si-O-Si in disiloxane molecule by MP2 is closer to experimental value than that by PBE. Then we apply the MP2 method with 6-311G(d,p) basis set to the calculation of pyrosilisic acid, $H_6Si_2O_7$. NBO analysis (Foster and Weinhold, 1980, Reed et al., 1985; 1988) is used to analyze the electronic state of bonding.

We found the equilibrium geometries for bended two pyrosilisic acid molecules (C_{2V} and 60 ^{0} torsion) using Moller-Plesset perturbation theory and with 6-311G(d,p) split valence double zeta basis set. We calculated the energy surface with varying Si-O_{br} length and Si-O-Si angle and found the relationship between Si-O_{br} length and bridging angle. From the energy surface, the stable Si-O bond length decrease with spreading Si-O-Si angle. The bending of Si-O-Si angle in equilibrium geometries can be explained by explained by the balance of Coulombic repulsion between tetrahedra and lone pair electrons of bridging oxygen atom without concerning the contribution of d-p π-bonding. The Si-O bonding strengthen with increasing Si-O-Si angle because of stabilization in energy of Si-O bonding orbital with decreasing the hybridization index λ in spλ orbital of bridging oxygen and increase of coulombic interaction between Si and bridging oxygen atom.

Keywords: Molecular orbital calculation, Si-O-Si bridging