Energetics, and NMR and vibrational characteristics of possible sulfur species in silicate melts: An ab initio calculation

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Sulfur oxides, next to H2O and CO2, constitute an important volatile component in natural magmas. The behavior of sulfur in silicate melts and glasses is also of interest for radioactive waste storage and industrial glass refining. Sulfur is located, in the periodic table, below oxygen, the dominant anion in silicates, and in between phosphorous (usually 5+) and clorine (usually 1-). As a result of its intermediate electronegativity, sulfur exhibits a rich variety of valence states even under natural conditions, ranging from 2- (as S2- substituting O2-) to 6+ (forming SO4 tetrahedra, similar to SiO4 or PO4). The solubility and speciation of sulfur in silicate melts and glasses are thus expected to be complicated and highly depend on the oxidation state. Until recently, there had been only limited direct spectroscopic studies on the dissolution mechanisms of sulfur in silicate melts and glasses. Recently, we have carried out a systematic Raman and NMR study on the structure of sodium silicate glasses (quenched melts) synthesized from starting materials containing sulfur of various valence states (for Na2S to Na2SO4) (see the accompanying presentation by Tsujimura et al.). In order to gain insight into the energetics of various sulfur species possibly present in silicate melts and to assist interpretation of the NMR and Raman spectra, we have performed ab initio molecular orbital calculations on clusters containing S2- and SO42- species of various linkages.

All the calculations have been carried out using the Gaussian 98 program. Geometry optimization and vibrational properties have been performed at B3LYP/6-31+G(d,p), which is known to yield reliable geometries and vibrational frequencies even without correction. The 29Si NMR shielding have been calculated with the above geometry at HF/6-311+G(2df,p), a level that has been found to well reproduce the 29Si NMR chemical shifts of silicates.

For the S2- state, we have found that the sulfur species becomes energetically less favorable in the order M-S (free sulfur), Si-S-M (nonbridging sulfur), and Si-S-Si (bridging sulfur). We have also evaluated the 29Si chemical shifts for Si coordinated to zero to four sulfur neighbors (Si(O,S)4), and found a systematic trend toward less negative chemical shift with increasing sulfur neighbors, at a rate of about 30 ppm per additional sulfur neighbor.

For the SO42- state (S6-), we have found that the energy penalty is the largest for polymerized sulfates (e.g. S2O7), intermediate for SO4 groups linked to the silicate network, and the lowest for isolated SO4 groups. Such a distinction is important because the effect of SO4 groups on the properties of silicate melts critically depend on how they are incorporated. We have also calculated the 29Si NMR chemical shifts and vibrational frequencies for each, and found that 29Si chemical shift is not sensitive enough to distinguish Si with or without SO4 neighbors, whereas the S-O vibrational frequencies should be a useful diagnostic parameter.

These calculation results will be compared with the available experimental NMR and Raman data to unravel the variety of dissolution mechanisms of sulfur in silicate melts.