

Si-F bonding in aluminosilicate glasses: Inferences from ab initio NMR calculations

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ABSTRACT

Although it has been well accepted that F-Al linkages dominate in F-bearing alkali aluminosilicate glasses, the possibility of F-Si linkages remains unresolved. Recent ^{19}F NMR results have been interpreted as indicative of not only the presence of the Al-F-Na(n) linkages but also of the presence of Si-F-Na(n) linkages. High level ab initio NMR calculations were performed to investigate the nature of possible species contributing to the ^{19}F spectra.

The B3LYP/6-31G* level was used to optimize structures and a scaling technique applied to the calculation of NMR properties using both HF and B3LYP methods at the 6-311+G(2df,p) level. The applicability of this scaling method was checked by comparing calculated results against experimental data on several crystalline materials; the results are improved over HF or DFT methods alone. The calculation results show that none of the F-Al species investigated can produce the -147 ppm peak of Schaller et al. (1992). However, several species in which F is bonded to fourfold-, fivefold-, and sixfold-coordinated Si produce a ^{19}F chemical shift of approximately -147 ppm. These results verify the assignments of this peak by Zeng and Stebbins (2000) to tetrahedral Si-F and NaSiF_6 -like species, and rule out many other possible species. Several additional species such as a fivefold coordinated Si-F species may further contribute to the -147 ppm ^{19}F peak.