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Ab initio studies of possible fluorine-bearing four- and fivefold coordinated Al species in aluminosilicate glasses

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ABSTRACT

Ab initio NMR gauge-including atomic orbital (GIAO) calculations were used to constrain assignments of resonances in ^{27}Al NMR spectra of F-bearing alkali aluminosilicate glasses. The effect of bond angles within the range 126–150° on the chemical shift was investigated using cluster models of next-nearest atoms that are charge balanced by hydrogen atoms. GIAO calculations used geometries obtained through optimization at fixed Al-O-Si bond angles. The calculated peak positions for all of the 4-fold coordinated Al species yielded calculated ^{27}Al NMR peak positions in good agreement with the experimental data, suggesting that any or all of the species AlF_4^-, $AlF_3O(SiH_3)^-$, $AlF_2O_2(SiH_3)_2^-$, and $AlFO_3(SiH_3)_3^-$ may be present. Three of the investigated 5-fold coordinated species AlF_5^{2-}, $AlF_3O_2(SiH_3)_2^{2-}$, and $AlF_2O_3(SiH_3)_3^{2-}$ fit the experimental requirements well, whereas the remaining 5-fold coordinated species that were tested [$AlF_4O(SiH_3)^{2-}$, and $AlFO_4(SiH_3)_4^{2-}$] did not.