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Molecular orbital calculations on aluminosilicate tricluster molecules: Implications for the structure of aluminosilicate glasses

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ABSTRACT

Ab initio, molecular orbital calculations were carried out to study the energetic stability and NMR characteristics of "triclusters" of composition $[T(XO)(OH)_2]O[Al(OH)_3][T(OH)_3]$ (X = no atom, H^+, Li^+, Na^+, K^+, Mg^{2+}, or Ca^{2+}; T = Si^{4+} or Al^{3+}). These triclusters consist of a central oxygen atom in trigonal coordination (^{III}O) surrounded by three tetrahedrally coordinated, network-forming cations (Al and Si). All tricluster configurations modeled are predicted to be dynamically stable except for one containing three Al^{3+} cations. Tricluster viability was further tested by computing energetic stabilities relative to $Al(OH)_3$ and dimers with non-bridging oxygen atoms (NBO). With these species as reactants and T = Si^{4+}, calculated reaction energies vary from –87 kJ/mol with X = H^+, to –253 kJ/mol with X = Mg^{2+}. For the case of X = Ca^{2+}, where structures with 1 Si and 2 Al were also modeled, the reaction energy was found to be over 50 kJ/mol more negative in the latter case (–278 kJ/mol compared to –222 kJ/mol). However, when the energy of the triclusters $[Si(Na^+O)(OH)_2]O[Al(OH)_3][Si(OH)_3]$ and $[Al(Ca^{2+}O)(OH)_2]O[Al(OH)_3][Si(OH)_3]$ was calculated relative to isochemical chains of three tetrahedra without NBO or ^{III}O, the triclusters were predicted to be +124 and +142 kJ/mol less stable than the corresponding trimer chains. Although these latter computed energy changes do not preclude formation of triclusters, they imply that such species should occur only in minor concentrations.

To help identify ^{III}O within aluminosilicate glasses, predictions of ^{17}O NMR chemical shifts ($\delta^{17}O$), quadrupolar coupling constants (QCCs), and asymmetry parameters (η) are also presented. When compared with predictions of ^{17}O NMR parameters in a number of molecules representing Si and Al-bearing Q^4 species, it is found that the calculated parameters for ^{III}O are generally within the range of normal bridging oxygen atoms (BO). Thus, if ^{III}O are a minor percentage of oxygen atoms within a glass, we conclude that their identification may be difficult using NMR spectroscopy.