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 (\(\text{III}O\)) 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 \([Si(Na^{+}O)(OH)_{2}]O[Al(OH)_{3}]\) and \([Al(Ca^{2+}O)(OH)_{2}]O[Al(OH)_{3}]\) was calculated relative to isochemical chains of three tetrahedra without NBO or \(\text{III}O\), 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 \(\text{III}O\) within aluminosilicate glasses, predictions of \(^{17}\text{O}\) NMR chemical shifts (\(\Delta^{17}\text{O}\)), quadrupolar coupling constants (QCCs), and asymmetry parameters (\(\varepsilon\)) are also presented. When compared with predictions of \(^{17}\text{O}\) NMR parameters in a number of molecules representing Si and Al-bearing \(Q^{4}\) species, it is found that the calculated parameters for \(\text{III}O\) are generally within the range of normal bridging oxygen atoms (BO). Thus, if \(\text{III}O\) are a minor percentage of oxygen atoms within a glass, we conclude that their identification may be difficult using NMR spectroscopy.

INTRODUCTION

The ability to predict the physical and thermodynamic properties of silicate melts is of considerable importance in the Earth and materials sciences. One approach to understanding the variations of macroscopic properties as a function of composition is to interpret them in terms of changes in atomic structure. Therefore, an accurate description of silicate melt structure is essential to this goal. Current models generally assume that Si and Al are tetrahedrally coordinated “network formers” and that the charge deficit on the Al\(^{3+}\) cation is compensated by a metal cation, M\(^{n+}\), such as Na\(^{+}\) or Ca\(^{2+}\) (e.g., Mysen 1988). Additional metal cations in excess of those required to charge balance Al are assumed to break apart the aluminosilicate network through the introduction of non-bridging oxygen atoms (NBOs). Although this model has proven useful, it is becoming increasingly clear that in “framework” glasses (where the molar ratio M\(^{n+}/n\text{Al} = 1\)) atomic structure may be more complex (Toplis et al. 1997, 2000; Stebbins and Xu 1997; Stebbins et al. 2000). For example, viscosity measurements close to the “charge-balanced” join in the system Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\) show that the viscosity maximum expected when Na/Al = 1 is systematically displaced to compositions where Na/Al > 1 (Toplis et al. 1997). This feature was interpreted by those authors to imply the presence of NBOs at the charge-balanced join where none are predicted in conventional models of glass structure. Furthermore, using \(^{17}\text{O}\) NMR spectroscopy, Stebbins and Xu (1997) demonstrated the presence of 5% NBOs in the “fully polymerized” framework glass anorthite (CaAl\(_2\)Si\(_2\)O\(_8\)). The presence of these NBOs implies that a fraction of the Al present is not associated with a charge-balancing cation. Given that no more than 2% of the Al in Ca or Na has been found coordinated to more than four oxygen atoms (Baltisberger et al. 1996; Stebbins et al. 2000), Toplis et al. (1997) and Stebbins and Xu (1997) proposed that a fraction of the Al present is associated with a three-coordinate oxygen atom, a geometry originally proposed by Lacy (1963) and termed a “tricluster.” Oxygen coordinated to a mixture of three tetrahedral Si/Al has not been described in crystalline aluminosilicates, but triclusters containing three Al tetrahedra do exist in CaAl\(_2\)O\(_3\) (grosssite) as discussed recently by Stebbins et al. (2001).

Molecular orbital calculations are useful in helping to iden-