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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.

INTRODUCTION

Fluorine is one of the most abundant volatile components in evolved volcanic suites and late-stage granitic systems with a solubility in excess of 10 wt% at elevated pressures and natural abundances reaching 5 wt% or higher (Carroll and Webster 1994; Congdon and Nash 1988). It strongly affects the density and viscosity of silicate melts, fluid-melt partition coefficients of trace elements, mineral-melt equilibria, and cation diffusion rates in melts (e.g., Dingwell et al. 1985; Dingwell et al. 1993; Snow and Kidman 1991; Manning et al. 1980; Manning 1981; Burnham and Nekvasil 1986). All of these effects arise from the interaction of F with the silicate melt structure; therefore, understanding the macroscopic properties requires knowledge of the structural role and solubility mechanism of F in silicate melts. Nuclear magnetic resonance studies have been particularly important in elucidating the structural role of F in glasses.

^{27}Al MAS-NMR experiments and ^{19}F – ^{27}Al cross-polarization MAS-NMR experiments on glasses of jadeite + NaF and jadeite + cryolite compositions synthesized at 3.0–3.5 kbar (Kohn et al. 1991) show three primary resonances that have been assigned to Al species coordinated with fluorine. These peaks have been assigned to $^{[4]}$Al (at 56 ppm), $^{[5]}$Al (at 22 ppm), and $^{[6]}$Al (at –4 ppm). The narrowness of the three peaks suggested to Kohn et al. (1991) that each of the species has a small QCC (quadrupolar coupling constant).

The multinuclear NMR and ^{19}F to ^{29}Si cross-polarization MAS NMR results of Schaller et al. (1992) on jadeite and albite glasses synthesized at ambient pressure with F substituting for O showed no evidence of F-Si complexing. They instead suggest the likelihood of Al-F complexing. In spite of the compositional differences of the glasses, the ^{27}Al NMR spectra of Schaller et al. (1992) resemble those of Kohn et al. (1991). However, the distinct peak at 22 ppm interpreted by Kohn et al. (1991) as indicative of 5-coordinated Al species was reflected in the data of Schaller et al. (1992) only as a shoulder on the low-frequency side of the 52 ppm resonance. Because this difference may reflect the poor resolution induced by the 11.7 T magnetic field used, Schaller et al. (1992) accepted the previous assignment of the $^{[6]}$Al species to AlF_6^{3-}. Based on their more recent ^{19}F data on fluoridated albite glass, Zeng and Stebbins (2000) also assigned the dominant ^{19}F peak (at about –188 ppm) to Al-F-Na(n) complexes. Although assignment of species producing this peak is not fully conclusive, upon comparison with the ^{19}F spectra of crystalline cryolite, it is likely that the largest contribution to this peak is from AlF_6^{3-}. Zeng and Stebbins (2000) have suggested that further contributions to this peak may arise from F bonded to Al in 4- and 5-fold coordination.

$^{[4]}$AL SPECIES

Because of the relatively low F contents of the glasses used by Kohn et al. (1991) and Schaller et al. (1992), $^{[4]}$Al species must be dominated by AlO_4^{5-} tetrahedra. Kohn et al. (1991) have suggested that in addition, a small amount of AlF_4^- might also be present. AlF_4^-, however, is very rare in crystalline materials (Herron et al. 1993) and there is only limited evidence for the presence of AlF_4^- in molten salts (Gilbert et al. 1974, 1988; Colton and Eller 1989; Robert et al. 1999). Instead, perhaps Al is linked with one, two, three or four F atoms [i.e, $AlF(O_{bridging}\ldots)_3^-$,

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$AlF_2(O_{bridging...})_2^-$ and $AlF_3(O_{bridging...})^-$]. As pointed out by Schaller et al. (1992), each F could represent a terminal atom linked to an Al tetrahedron, a bridging atom linking two Al octahedra coordinated by both O and F, or even be representative of two tetrahedral Al-F complexes.

$^{[5]}$Al species

Based on their contact time analysis of $^{19}F \rightarrow {}^{27}Al$ cross-polarization NMR data, Kohn et al. (1991) assigned five-coordinated $^{[5]}$Al to AlF_5^{2-}. Tossell (1993), however, ruled out the possibility of AlF_5^{2-} species on the basis of his ab initio calculations and suggested instead that $^{[5]}$Al complexes involve 3F and 2 bridging O (i.e., AlF_3O_2....). However, his pioneering study involved a low calculation level-(HF/3-21G*). This level causes large errors even for comparisons of the differences of the NMR shielding tensors between different species. For example, geometry optimization at B3LYP/6-31G* and NMR calculations at the HF/6-311+G(2df,p) level yield an Al shielding difference between AlF_4^- and AlF_6^{3-} of 55 ppm, while geometry optimization and NMR calculations both at the HF/3-21G* level give a difference of 25 ppm. This latter result differs distinctly from the experimental result of approximately 53 ppm (–4 ppm for AlF_6^{3-} from Kohn et al. 1991; 49.2 ppm for AlF_4^- from Herron et al. 1993).

The ^{27}Al NMR shielding tensor depends upon both the nearby atoms and the nearest bridging oxygen angle ∠Al-O-T (where T is another tetrahedral cation, such as Si). Hence, before unequivocal assignment of species to observed resonances is possible through computational analysis, assessment of the dependence of the calculated ^{27}Al NMR chemical shift positions on the Al-O-Si bond angle and evaluation of the possibility of other structural effects are needed.

Computational methods and cluster models

Geometry optimization

All geometry calculations were performed using GAUSSIAN 98 (Frisch et al. 1998). Potential energy minima were located with the Berny algorithm using redundant internal coordinates (Peng et al. 1996). All geometry calculations used the B3LYP DFT method. The chosen basis set was the standard polarized split-valence 6-31G*, because the geometry results of 6-31G* often have an accuracy equivalent to that of much bigger basis sets (Foresman and Frisch 1996).

NMR calculations

The NMR shielding tensor calculations were performed using the gauge-including atomic orbital (GIAO) method [the ab initio version first published by Ditchfield (1974)]. The GIAO method, used as the default NMR method in both Gaussian 94 and 98 because of its faster convergence (Wolinski et al. 1990), computes chemical shieldings for nuclei based on coupled perturbation theory that involves solving for the second derivative of the energy with respect to the magnetic field and the magnetic moment of the nucleus.

The calculated isotropic chemical shifts from both Hartee-Fock and DFT methods are quite similar and accurate for most cases without large electron correlation effects (Cheeseman et al. 1996). With the exception of the pure aluminofluoride species considered (i.e., AlF_4^- and AlF_5^{2-}), the aluminosilicate bonding environments evaluated here are without large electron correlation effects because they lack features such as multiple bonding and super valences. To verify that equivalence between the two methods is valid for the clusters under study here, we compared the results from a variety of parallel calculations using each method. For example, applying the HF method to the typical cluster $AlF_2O_2(SiH_3)_2^-$ yields an isotropic chemical shift of 59.0 ppm; the DFT method yields 60.3 ppm for the same basis set 6-311+G(2df,p) (see below). Because the EFG results are also quite similar, the final peak positions are almost the same (58.8 ppm and 59.9 ppm respectively for this case). Relative to species involving mixed O and F linkages, the aluminofluoride species have stronger electron correlation effects, with HF and B3LYP chemical shift calculations producing a 3–5 ppm difference. For example, the HF peak position for AlF_5^{2-} is 20.1 ppm while the B3LYP result is 25.0 ppm. The experimental peak position is 22 ppm. Both results are within the range of experimental uncertainty. This is the case for all of the alumino-fluorides investigated. Because of its greater stability, the HF method was used for NMR calculations instead of B3LYP. The 6–311+G(2df,p) basis set was also used in these calculations. This decision was reached by testing sequentially higher level calculations and determining the lowest level at which little further change in results would occur over the next higher levels.

Using the GIAO formalism, the isotropic shielding δ_{iso} is obtained by averaging the three principal tensor components, σ_{xx}, σ_{yy}, and σ_{zz}. Isotropic chemical shifts δ_{iso} were calculated using the relationship $\delta_{iso} = \sigma_{iso}^{ref} - \sigma_{iso}^{molecule}$, where σ_{iso}^{ref} is the chemical shielding value of a reference substance [chosen here to be $Al^{3+}\cdot 6(H_2O)$] calculated at the same level. Nuclei with a nuclear spin quantum number of $I > 1$, (e.g., ^{27}Al) will have nonspherical nuclear charge distributions and hence an electric quadrupolar moment Q. For such cases, the experimental peak,

$$\delta_{peak} = \delta_{iso} - \delta_{qs}$$

where δ_{peak} is the observed peak, δ_{iso} the isotropic chemical shift, and δ_{qs} the quadrupolar shift. To compare the calculation results directly against experimental spectra, the δ_{qs} is needed. It can be calculated from the equation

$$\delta_{qs} = -\frac{3}{40}\frac{QCC^2}{\omega_L^2}\frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2}\left(1+\frac{\eta^2}{3}\right)$$

(Samoson 1985) where the QCC (quadrupolar coupling constant) = e^2Qq, and consists of the nuclear quadrupolar moment Q, the electric field gradient q, and the fundamental constant e. The asymmetry parameter $\eta = |(q_{xx} - q_{yy})/q_{zz}|$ where q_{xx}, q_{yy}, and q_{zz} are the principal tensor components of the electric field gradient (EFG). For highly symmetric molecules such as AlF_6^{3-} and $Al^{3+}\cdot(6H_2O)$, the QCC is zero; thus, the δ_{qs} of such clusters is also zero.

For all of the work discussed below, the same B3LYP/6-31G* geometry and HF/6-311+G(2df,p) level was used for EFG calculations. Based on assorted tests conducted in conjunction with this work, it appears that the EFG is very sensitive to the choice of basis sets but not to the different levels HF, DFT, or MP2. With expanding basis sets, a slow asymptotic trend toward

a limiting value is observed. Although it is not easy to find the limiting point and get an accurate EFG, we are confident that our 6-311+G(2df,p) basis set results are close to the limiting value. Another significant factor to be considered in the EFG calculation, however, is selection of the cluster model size.

Cluster models

NMR shielding properties reflect primarily the local chemical environment of a given nucleus. Standard cluster models (e.g., Gibbs 1982) have proven especially useful for the interpretation of "local" properties and thus should be particularly applicable to NMR investigations. Furthermore, the cluster model method may be the only way to study materials without periodic structure or long range order.

The calculations presented here are based on the classic assumption that small molecular clusters terminated by H can be used to calculate shielding tensors of complexly polymerized units, particularly when care is taken to place the nucleus of interest in the center of the cluster and to represent all primary linkages in the cluster. Valid application of this assumption requires identification of the minimum size cluster that contains all of the major linkages to the atom of interest. For example, a $^{[4]}$Al coordinated to three F atoms and one bridging oxygen where the bridging O is further linked to a silica tetrahedron. Three cluster models can be used to represent this situation (Fig. 1) and are used for calculation of the ^{27}Al NMR properties of these clusters (see Table 1 and Fig. 2). The simplest cluster (A) is one in which protons replace all additional linkages. Cluster B includes a Si atom linked to the bridging O and balanced by three H atoms. Cluster C has a Si-O tetrahedron linked to the bridging O and charge-balanced by 3 hydrogen atoms. In Cluster C, the 3 ∠Si-O-H are fixed at 140° (in order to simulate the ∠Si-O-T in crystalline silicates). The calculated ^{27}Al NMR properties of these clusters are in Table 1 and Figure 2.

Comparison of the NMR calculation results for the three clusters yields several important issues for consideration:

The cluster size problem. None of the three cluster models shown (Fig. 1) can produce a reasonable nearest bridging angle ∠Al-O-Si if the geometry is freely optimized. This problem is directly caused by neglecting additional linkages that form units such as 4-membered, 6-membered, or even larger tetrahedral rings and by neglecting cation effects. It is not easily remedied by using slightly larger clusters. The intermediate level ab initio ^{29}Si NMR calculations of Bussemer et al. (1997) suggest that very large clusters with at least 5 coordination layers of atoms around the central Si atom in a zeolite are needed before reliable ∠T-O-T (in their case, T = Si) are obtained. The largest cluster model used in Figure 2—Cluster C—has a 3-layer coordination configuration of atoms around the central Al atom, but only in one direction. A complete 5-layer coordination model would require a prohibitively large amount of computer power for high level NMR calculations. Fortunately, this problem can be bypassed through the recognition that the disordered state of glassy material assures the presence of a distribution of T-O-T angles. The lack of quantified information on this distribution can be sidestepped by allowing the ∠T-O-T angle to vary in the analysis. Here, simple cluster models were used in which the ∠Al-O-Si is varied systematically around the average ∠T-O-T

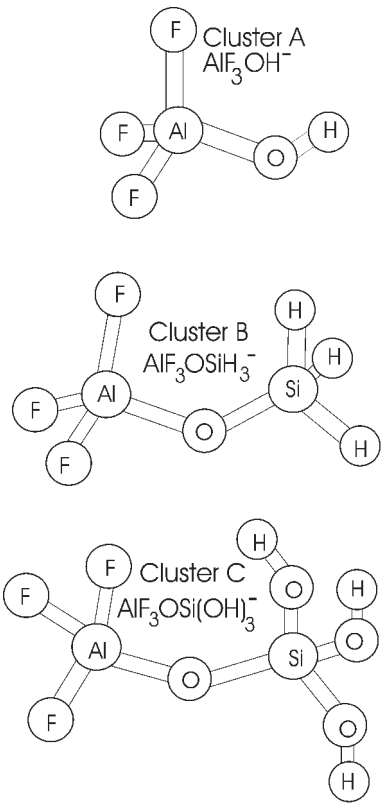

FIGURE 1. Schematic of clusters A, B, and C used in NMR calculations.

TABLE 1. Calculated isotropic chemical shift, QCC, quadrupolar shift, and peak position for Clusters A, B, and C for a variety of ∠Al-O-Si (or ∠Al-O-H)

Cluster	Fixed ∠Al-O-Si*	δ_{iso} ppm	QCC MHz	δ_{qs}† ppm	Peak Position ppm
Cluster A	126°	59.2	3.86	3.1	56.1
	132°	57.5	3.42	2.5	55.0
AlF_3OH^-	138°	55.6	2.84	1.7	53.9
	144°	53.6	2.17	1.0	52.6
	150°	51.6	1.52	0.5	51.1
	160°	48.7	0.59	0.1	48.6
	170°	46.8	0.06	0.0	46.8
	180°	46.1	0.21	0.0	46.1
Cluster B	126°	58.0	2.23	1.0	57.0
	132°	57.2	1.65	0.6	56.6
$AlF_3OSiH_3^-$	138°	56.4	1.04	0.22	56.2
	144°	55.6	0.99	0.22	55.4
	150°	54.9	1.21	0.3	54.6
	160°	54.1	1.98	0.9	53.2
	170°	53.6	2.40	1.2	52.4
	180°	53.5	2.44	1.3	52.2
Cluster C	126°	57.6	2.73	1.7	55.9
	132°	56.7	2.78	1.7	55.0
$AlF_3OSi(OH)_3^-$	138°	55.7	2.42	1.2	54.5
	144°	55.1	1.69	0.6	54.5
	150°	54.3	0.81	0.2	54.1
	160°	53.3	0.91	0.2	53.1
	170°	52.7	1.51	0.5	52.2
	180°	52.6	1.32	0.4	52.2

Note: All NMR and EFG calculations were at HF/6-311+G(2df,p) using geometries from B3LYP/6-31G.
* Or ∠Al-O-H
†The calculated quadrupolar shift is for a magnetic field strength of 14.1 T.

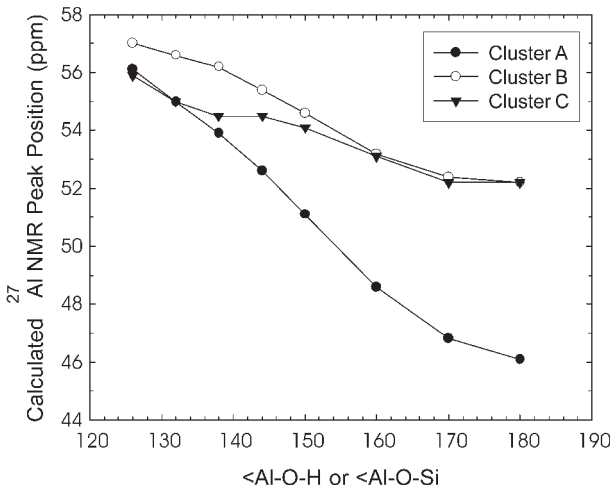

FIGURE 2. Calculated ^{27}Al NMR chemical shift (peak position) as a function of bridging oxygen angle for the clusters A, B, and C of Figure 1.

angle in aluminosilicate glasses (138°, Geisinger et al. 1985) within the range 126 to 150°.

Next-nearest neighbors (NNN, here taken to be Si) can contribute significantly to NMR properties. Although at small angles the results for all three clusters investigated are similar, the calculated chemical shifts for cluster A (no NNN and hence, the configuration least like that expected in the glass) quickly diverge from B and C with increasing ∠Al-O-Si (or ∠Al-O-H for Cluster A).

Atoms beyond the NNN atoms contribute little to the NMR resonances if all of the ∠Al-O-Si are fixed. Both Cluster B and C have tetrahedral NNN atoms, but Cluster C contains further linkages. The calculated results for the two clusters are quite similar, showing only a small difference at small angles. At small angles (e.g., 126 to 132°), strong hydrogen bonding occurs between F and H in Cluster C (albeit weakened by the fixed ∠Si-O-H of 140°). Such H bonding is purely an artifact of the cluster model used and unrealistic for anhydrous glass. Without this artificially induced H bonding, the NMR results of Cluster C are likely to be quite similar to those of Cluster B over the whole ∠Al-O-Si range. Because of its obvious advantages, Cluster B has been used here as the cluster of choice for further calculations.

Cation effects. The presence of charge-balancing cations will affect the ∠T-O-T angle since they are directly linked to the O atoms. By changing the ∠T-O-T angles over a possible range this effect is indirectly included in the cluster model method used here. Any further possible cation effects are ignored because the distance between Al and the charge-balancing cation (i.e. Na^+) is about 3.0 to 3.5 Å—a distance at least as far as the NNN atoms. Because the effects of long-range interactions on NMR shielding constants are proportional to R^{-4} (Barszczewicz et al. 1996) this distance should preclude large effects on the NMR properties. For example, the cluster $AlFO_3(SiH_3)_3^-$ (Fig. 3) with the three ∠Al-O-Si fixed at 144° has a calculated isotropic shift of 61.9 ppm for ^{27}Al, without Na^+, but 61.6 ppm if the Na^+ lies at a distance of 3.5 Å from Al.

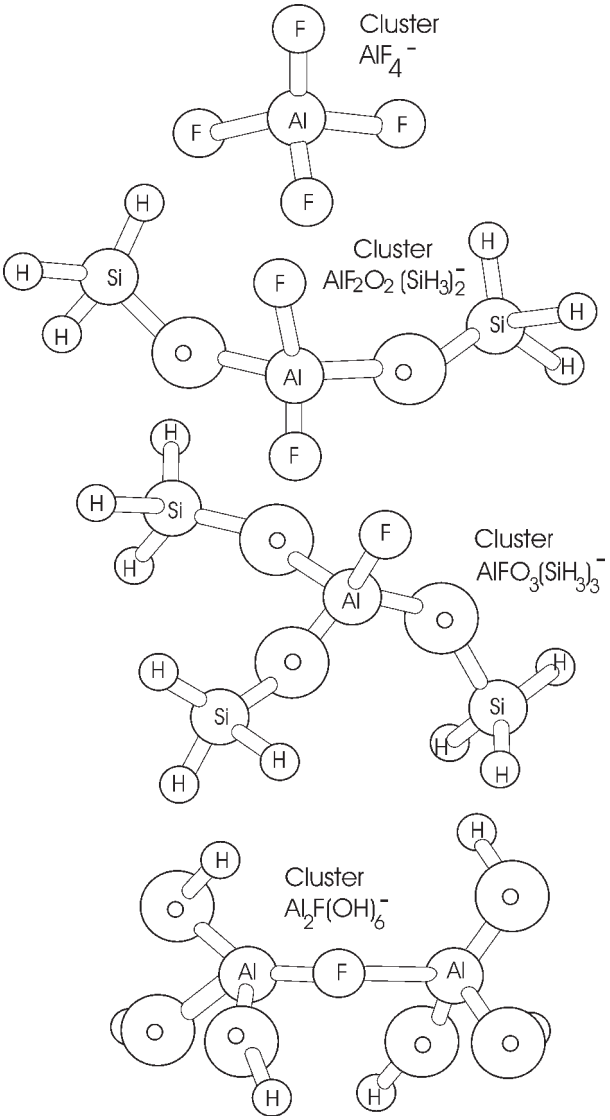

FIGURE 3. Clusters involving $^{[4]}$Al used in the NMR calculations.

Multiple ∠Al-O-Si. When there are more than two ∠Al-O-Si in one tetrahedron or pentahedron, (such as in the cluster $AlF_2O_2(SiH_3)_2^-$, Fig. 3), little difference is seen in the calculated isotropic shift when using an average value of the two angles or the actual value for each individual angle. Likewise, the QCC shows only a small change. Thus, the results reported here for an average ∠Al-O-Si from 126° to 150° are actually applicable to a much larger distribution of individual ∠Al-O-Si.

EFG errors. Because the calculated QCC for each of the three types of clusters analyzed is different, it is possible that even the cluster model with NNN atoms may not be big enough for accurate EFG calculation. Further test calculations have confirmed this problem. Inclusion of cations in these small clusters induces yet additional problems for EFG calculation because of problems in maintaining electric field balance. Fortunately, the fixed-angle NNN model is cation-free and yields a large part of the EFG. This is also ameliorated by clusters in which Al is in

the center of a nearly rigid tetrahedron. (Other atoms, such as O in these clusters, can be strongly affected by slight changes in structural conformation.) Because most of the QCC values dealt with here are less than 3 MHz, for a 14.1 T magnetic field, they yield no more than a 5 ppm quadrupolar shift. With even a 40% error in the EFG calculation the peak position change is no more than 2 ppm. The EFG values presented here are similar to available experimental data (e.g. to those of Dirken et al. (1995), who obtained an Al QCC of 3.9 MHz for glass of composition $NaAlSi_{5.3}O_{12.6}$).

Results and discussion

$^{[4]}$Al species.

According to the experimental data of Kohn et al. (1991) acquired at 14.1 T, any proposed four-coordinated species must have a ^{27}Al NMR peak position around 56 ppm and a small QCC.

For comparison, AlF_4^- in solution has an ^{27}Al NMR chemical shift of 49.2 ppm (Herron et al. 1993). NMR calculations on an AlF_4^- cluster have yielded a chemical shift peak position at 52.7 ppm and a QCC of zero. Because many kinds of effects can be envisioned to be specific to the aqueous rather than glassy environment (e.g., possible F-H hydrogen bonding, a non-zero QCC), the 3.5 ppm difference appears reasonable. Small changes in this chemical shift (to 51.4 ppm) occurs if the structure was optimized at MPZ/6-31G*. Slight variations in the Al-F bond length, i.e., by 0.02 Å, from 1.693 Å to 1.713 Å, changes the ^{27}Al NMR peak position to 49.2 ppm. Perhaps the aqueous environment induces relaxation of the AlF_4^- structure by lengthening the Al-F bonds. These results are consistent with the presence of some AlF_4^- as a species in the glass.

The results of NMR calculations on Cluster B (in which Al is linked to 3 F atoms and one bridging oxygen, Fig. 1) over the entire bond angle range indicate little effect of bond angle on chemical shift for this species. The agreement between the calculated chemical shift values and that obtained experimentally (at 55 ppm) as well as the small QCC value (Table 1) suggest that this species may be present in significant quantity in the glass.

Calculated NMR results for clusters representing species with Al linked to 1 and 2 F atoms (Fig. 3) are given in Table 2. Within the 126–150° range in bond angle, none of these species have a NMR peak position of 56 ppm. The closest agreement is for ∠Al-O-Si close to 160°. Therefore, it is possible that species $AlFO_3(SiH_3)_3^-$ and $AlF_2O_2(SiH_3)_2^-$ with large ∠Al-O-Si are present in the glass. If this is the case, then F must not only break Al-O bonds but also allow the structure to become more relaxed and hence, less dense, because it results in a larger ∠Al-O-Si for the intact linkage. In the case of two tetrahedral Al sharing one F as an Al-F-Al linkage [$Al_2F(OH)_6^-$, Fig. 3], the calculated ^{27}Al NMR isotropic chemical shift is 60.0 ppm. However, the QCC for this species is very high (16.8 MHz) which makes the quadrupolar shift very large and the peak position close to 0 ppm. Its large QCC precludes it from being present in sufficient quantities as to be identifiable in ^{27}Al NMR spectra.

This analysis shows that the ^{27}Al NMR experimental data obtained by Kohn et al. (1991) and Schaller et al. (1992) alone do not yield a ready means of distinguishing among AlF_4^-, Al-$F_3OSiH_3^-$, $AlFO_3(SiH_3)_3^-$ and $AlF_2O_2(SiH_3)_2^-$. Similarly, because it is not possible to determine if Q^0 (i.e., an Al species without bridging oxygen such as AlF_4^-), Q^1 (e.g., $AlF_3O^-_{br}$), Q^2 [e.g., $AlF_2(O_{br...})_2^-$)], or Q^3 [e.g., $AlF(O_{br...})_3^-$] formation is preferred upon the addition of F to an alkali aluminosilicate glass, the extent of depolymerization induced by the addition of F remains an important question.

Table 2. ^{27}Al NMR results for $AlFO_3(SiH_3)_3^-$ and $AlF_2O_2(SiH_3)_2^-$ at different ∠Al-O-Si

∠Al-O-Si	$AlFO_3(SiH_3)_3^-$		$AlF_2O_2(SiH_3)_2^-$	
	δ_{peak}* ppm	QCC MHz	δ_{peak}* ppm	QCC MHz
126°	68.0	3.2	60.7	4.1
132°	65.5	2.8	60.5	3.1
138°	64.1	1.4	59.8	2.0
144°	61.7	1.1	58.8	1.0
150°	59.5	0.7	57.4	0.6
160°	56.5	1.0		

* ($\delta_{peak} = \delta_{iso} - \delta_{qs}$), δ_{qs} calculated at 14.1 T, matching the experimental conditions of Kohn et al. (1991).

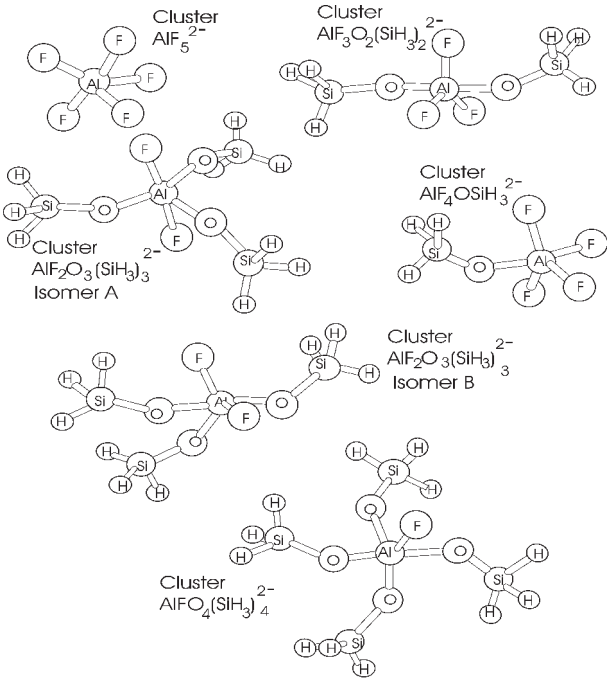

Figure 4. Clusters involving $^{[5]}$Al used in the NMR calculations.

$^{[5]}$Al species

According to the experimental data of Kohn et al. (1991), any proposed five-coordinated species must have a ^{27}Al NMR peak position around 22 ppm at 14.1 T and a small QCC.

Calculations on the species AlF_5^{2-} (Fig. 4) yield a QCC of 4.97 MHz. and a ^{27}Al NMR peak position of 20.1 ppm, thereby suggesting that this species may be responsible for the peak observed by Kohn et al. (1991). The results of calculations on the $AlF_4OSiH_3^{2-}$ cluster which includes 4 F atoms and one bridging oxygen (Fig. 4) are shown in Table 3. The calculated NMR peak position is maintained at 27 ppm throughout the –Al-O-Si range until the angle is widened to 180°. Because there is no recognizable shoulder to the left of the primary feature at 22

ppm (Kohn et al. 1991), this species is not present in detectable quantities. The presence of the species $AlF_3O_2H_2^{2-}$ has been suggested by Tossell (1993). Using the slightly larger model cluster $AlF_3O_2(SiH_3)_2^{2-}$ (Fig. 4), the calculated chemical shift is in good agreement with the experimental requirements when its ∠Al-O-Si is close to 138° (Table 3). Furthermore, it has a calculated QCC similar to that of AlF_5^{2-}. The similarities between the calculated NMR parameters of $AlF_3O_2(SiH_3)_2^{2-}$ and AlF_5^{2-} indicate that the spectra of Kohn et al. (1991) do not permit distinguishing between these two species and that either or both may be present in significant abundances in the glass.

Two isomers of $AlF_2O_3(SiH_3)_3^{2-}$ (Fig. 4), one with symmetry close to C_3 (A) and the other distorted (B), were also investigated. At first glance, the results suggest that isomer A might be present in the glass because it has a peak around 22 ppm for an ∠Al-O-Si of about 138° (Table 4). However, its NMR peak position and QCC change markedly with increasing angle. Because of the distribution of ∠Al-O-Si in aluminosilicate glasses, this should result in a broad feature covering the range of chemical shift listed in Table 4. This is not observed in the spectra of Kohn et al. (1991). Hence, it is unlikely that isomer A is abundant in the glass.

The chemical shift of isomer B does not show the strong changes with bond angle of isomer A (Table 4). It approaches the experimental value at higher ∠Al-O-Si while maintaining a low QCC. Surprisingly, it has a slightly lower calculated energy (about 2 kcal/mol) than isomer A. Although an energy difference of this magnitude maybe unreasonable at high *T* and *P*, taken together, these results suggest that although neither isomer is completely compatible with the experimental data, isomer B with large ∠Al-O-Si is likely to be more abundant. Cluster $AlFO_4(SiH_3)_4^{2-}$ behaves similarly to isomer B (see Table 3). With increasing ∠Al-O-Si its NMR peak position changes from 32.3 to 26.5 ppm, not reaching the requisite 22 ppm position until the ∠Al-O-Si has reached 160°. It is thus not likely to be abundant in the glass.

If $AlFO_4(SiH_3)_4^{2-}$, isomer B, or a combination of the two are abundantly present in the glass, then they are required to have large bond-angles and may thus significantly contribute to the decrease in glass density upon the addition of F (Dingwell et al. 1985, 1993). Clearly, however, the net decrease in melt density upon the addition of F cannot be attributed to the formation of a single type of F-bearing unit, but is rather a composite effect of all of the F-bearing species and residual F-free linkages in fluoridated aluminosilicate melts.

TABLE 3. Calculated ^{27}Al NMR data for $AlF_4OSiH_3^{2-}$, $AlF_3O_2(SiH_3)_2^{2-}$ and $AlFO_4(SiH_3)_4^{2-}$ at different ∠Al-O-Si

∠Al-O-Si	$AlF_4OSiH_3^{2-}$		$AlF_3O_2(SiH_3)_2^{2-}$		$AlFO_4(SiH_3)_4^{2-}$	
	δ_{peak}* ppm	QCC MHz	δ_{peak}* ppm	QCC MHz	δ_{peak}* ppm	QCC MHz
126°	27.7	0.8	29.2	2.2	32.3	3.6
132°	27.3	1.3	25.9	3.8		
138°	27.0	1.9	22.9	5.1	30.5	0.6
144°	26.4	2.5	19.5	6.3	28.5	0.5
150°	25.8	3.1	16.1	7.4	26.5	1.2
180°	23.7	4.7	—	—	—	—

* ($\delta_{peak} = \delta_{iso} - \delta_{qs}$), δ_{qs} calculated at 14.1 T, matching the experimental conditions of Kohn et al. (1991).

TABLE 4. ^{27}Al NMR results of two isomers of $AlF_2O_3(SiH_3)_3^{2-}$ at different ∠Al-O-Si

∠Al-O-Si	Isomer A (close to C_3)		Isomer B	
	δ_{peak}* ppm	QCC MHz	δ_{peak}* ppm	QCC MHz
132°	28.4	3.9	31.0	1.5
138°	22.6	5.8	28.2	2.7
144°	14.2	8.3	25.7	3.6
150°	2	10.7	23.8	4.1

* ($\delta_{peak} = \delta_{iso} - \delta_{qs}$), δ_{qs} calculated at 14.1 T, matching the experimental conditions of Kohn et al. (1991).

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