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Theoretical studies of the speciation of Al in F-bearing aluminosilicate glasses

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ABSTRACT

Recently the existence of AlF_5^{2-} or $AlF_3(O-)_2^{2-}$ complexes in F-bearing aluminosilicate glasses was suggested to explain features in their Al NMR spectra (Kohn et al., 1991). We have used ab initio quantum mechanical methods to calculate equilibrium structures, vibrational spectra, electric field gradients at Al, and Al and F NMR shieldings for AlF_4^-, AlF_5^{2-}, AlF_6^{3-}, $Al(OH)_4^-$, $Al(OH)_5^{2-}$, $AlF(OH)_3^-$, $AlF_2(OH)_2^-$, $AlF_3(OH)_2^{2-}$, and $AlF_2(OH)_3^{2-}$ to assist in determining Al speciation in these glasses. The Al nucleus in AlF_5^{2-} is calculated to be deshielded by only about 12 ppm compared with that in AlF_6^{3-}, which is considerably smaller than the experimentally observed separation of ~23 ppm between the peaks assigned to sixfold- and fivefold-coordinated Al in the aluminosilicate glasses. Similarly, the ^{19}F NMR spectra of such glasses show a F resonance deshielded by about 30 ppm compared with AlF_6^{3-}, whereas the calculated ^{19}F NMR shielding difference between AlF_6^{3-} and AlF_5^{2-} is only 18 ppm. On the other hand, the mixed F,O fivefold-coordinated Al species that we model as $AlF_3(OH)_2^{2-}$ is calculated to be deshielded by 25 ppm in Al NMR and by about 30 ppm in F NMR. This species also shows a very small electric field gradient at Al, consistent with the observed narrowness of the Al NMR peak assigned to $^{[5]}Al$. The protons in this $AlF_3(OH)_2^{2-}$ model compound are employed only to terminate dangling bonds and to reduce the total charge. The real identity of the atoms that are next-nearest neighbors to Al have not yet been determined, so it is not clear if this species is still part of the polymeric network.

INTRODUCTION

Dissolved volatile components in magmas can strongly influence their physical properties and volcanic eruptive behavior. F is one of the most important volatile components, significantly influencing phase relations (Manning, 1981), lowering viscosity (Dingwell, 1989), and increasing diffusion coefficients (Dingwell, 1985). F is also an important additive to industrial silica glasses, where it is primarily used to lower the index of refraction (Duncan et al., 1986). The speciation of F in silicate and aluminosilicate glasses has been inferred from phase relationships (Manning et al., 1980) and has recently been studied by Raman spectroscopy (Mysen and Virgo, 1985), by Al NMR (Kohn et al., 1991), and by F NMR (Schaller et al., 1991a, 1991b). Although some features in the Al and F NMR could be assigned fairly confidently on the basis of comparison with crystalline model compounds, certain weak features could not be so confidently assigned. For example, the Al NMR showed a weak peak deshielded by about 23 ppm from that attributed to $^{[6]}Al$. The ^{19}F NMR showed one or more weak features about 30 ppm deshielded from the resonance assigned to AlF_6^{3-} (on the basis of an almost exact match with the F shielding of M_3AlF_6). The weak Al NMR peak was enhanced by ^{19}F-^{27}Al cross-polarization, indicating that F was bound to the Al, and the resonance was narrow, indicating a small electric field gradient (EFG) at Al.

In both Si and Al NMR, an increased coordination number is associated with increased shielding of the nucleus. For example, fivefold-coordinated Al is more highly shielded than fourfold-coordinated (Alemany and Kirker, 1986; Alemany et al., 1991), just as for $^{[4]}Si$ and $^{[5]}Si$ (Stebbins and McMillan, 1989). However, substitution of F for O also deshields the tetrahedrally coordinated nucleus, T, whether Si or Al. Decreasing the polymerization of the aluminosilicate network, i.e., converting bridging O atoms in T-O-T linkages to nonbridging O in T-O-H or T-O-M linkages, on the other hand deshields T (Mägi et al., 1984). Finally, the particular value of the <T-O-T also influences both Si and Al shieldings (Lippmaa et al., 1986). Considerable ambiguity can thus arise in the assignment of an Al NMR resonance to a particular species.

To assist in assigning the ^{27}Al and ^{19}F NMR spectra of F-bearing aluminosilicate glasses, we have calculated using quantum mechanics several properties of a number of aluminum fluorides and hydroxyfluorides that serve as models for possible species in the F-bearing aluminosilicate glasses, in particular AlF_4^-, AlF_5^{2-}, AlF_6^{3-}, $Al(OH)_4^-$, $Al(OH)_5^{2-}$, $AlF_3(OH)^-$, $AlF_2(OH)_2^-$, $AlF_2(OH)_3^{2-}$, and $AlF_3(OH)_2^{2-}$. For each species we calculate the minimum-energy geometry using standard self-consistent-field molecular orbital (SCF-MO) methods (Hehre et al., 1986) and medium-sized expansion basis sets. At these optimized geometries, we then calculated the electric field

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gradient at the Al nucleus and the Al and F NMR shieldings. For some species we have also calculated the vibrational spectrum [although in general Raman spectroscopy does not seem to be a particularly good method for studying aluminum fluoride species, since polarizability changes with bond lengths, and therefore Raman intensities are expected to be considerably smaller than in analogous Si species (Mysen and Virgo, 1985)].

COMPUTATIONAL METHODS

Equilibrium geometries have been evaluated using the ab initio SCF-MO program Gamess (Schmidt et al., 1987, 1990) at the SCF level using polarized double zeta bases designated as 3-21G* (Hehre et al., 1986). Such calculations typically produce bond distances a few hundredths of an ångström shorter than these found by experiment and harmonic vibrational frequencies about 10% too high (Hehre et al., 1986). In most cases for the hydroxyfluorides we have assumed a particular symmetry for the complex, corresponding to a particular rotamer of the T-O-H groups and have not established that this rotamer is in fact the global minimum in energy. We do not expect the electric field gradients and NMR shieldings to be particularly sensitive to the choice of rotamer, although the energies may well be. Since our species are only models for condensed phase geometries, further optimization of the geometries seems inappropriate.

Electric field gradients at Al have been calculated at the SCF level using 3-21G* and various larger bases, whereas Al and F NMR shieldings have generally been calculated using the program RPAC (Hansen and Bouman, 1985) interfaced to Gamess. RPAC utilizes the random phase approximation method, equivalent to the coupled Hartree-Fock perturbation theory as used in the program Sysmo (Lazzeretti and Zanasi, 1980). It can evaluate NMR shieldings using either a common origin for all the orbitals (CHF approach) or using a localized-orbital local-origin method (LORG), in which the occupied canonical molecular orbitals are subjected to a unitary transform generating localized molecular orbitals and the LMO contributions to the shielding are evaluated with the gauge at their charge centroids. This method has yielded good results for many molecules in the past (Facelli et al., 1990). However, we have found it to give unreliable results for trends of Al shielding with coordination number, as we will show. One strength of the LORG method should be its cancellation of shielding effects from distant core electrons, e.g., 1s electrons of F in AlF_n^{3-n}. We have previously shown that this cancellation can be enforced by conventional CHF calculations (Tossell, 1990) by simply subtracting the diamagnetic contribution of these distant cores obtained from the formula of Flygare and Goodisman (1968). Such results are reported as core-corrected CHF values below. For AlF_5^{2-} we have also calculated the Al shielding with the same geometry and basis using the Sysmo program to establish the expected equivalence of Sysmo and RPAC CHF results. $AlF_3(OH)_2^{2-}$ has been studied using only Sysmo, since the difficulty of the RPAC calculation increases more rapidly with molecule size than does the Sysmo calculation (at least for our version of RPAC and our computational conditions).

TABLE 1. Al-F and Al-OH distances (in Å) calculated at the 3-21G* SCF level

Species, Symmetry	*R*(Al-F)	*R*(Al-OH)
AlF_4^-, T_d	1.640	—
AlF_5^{2-}, C_{4v}	1.736(eq), 1.691(ap)	—
AlF_5^{2-}, D_{3h}	1.749(ap), 1.709(eq)	—
AlF_6^{3-}, O_h	1.803	—
$AlF(OH)_3^-$, C_{3v}	1.663	1.740
$AlF_2(OH)_2^-$, C_{2v}	1.654	1.729
$AlF_2(OH)_3^{2-}$, D_{3h}	1.753(ap)	1.793
$AlF_3(OH)_2^{2-}$, C_S	1.733, 1.706(×2)	1.870
$Al(OH)_4^-$, S_4	—	1.743
$Al(OH)_5^{2-}$, C_S	—	1.930, 1.864, 1.816, 1.810(×2)

Note: The D_{3h} form of AlF_5^{2-} is more stable by 11.0 kJ/mol at the 3-21G* SCF level.

It is important to understand that some of the species we shall consider are merely simple models for materials with the same nearest-neighbor composition about Al. For example, our use of the molecular cluster model $AlF_3(OH)_2^{2-}$ does not imply that a species with OH groups exists in anhydrous samples—rather this species is a simple model for a real condensed phase species in which Al has three F and two O nearest neighbors.

RESULTS

Calculated bond distances are presented in Table 1. Our calculated Al-F distances are consistently about 0.05–0.08 Å shorter than those calculated by O'Keeffe (1986) at the 6-31G* SCF level. For AlF, for which an accurate bond distance of 1.65437 Å is available from experiment (Lide, 1965), we calculate 1.603 Å, whereas O'Keeffe obtained 1.67 Å. The calculated increases in bond length with increasing coordination number are as expected. The apical Al-F bonds are calculated to be longer than the equatorial for D_{3h} symmetry AlF_5^{2-}. The D_{3h} isomer is also calculated to be more stable than the C_{4v} symmetry isomer by 11.0 kJ/mol. In the mixed hydroxyfluorides, substitution of OH for F leads to increased distances for the remaining Al-F bonds. At the same time, the Al-OH bond distance is reduced when some OH are replaced by F.

In Table 2 we compiled Al NMR shieldings, σ^{Al}, where $H_{effective} = (1 - \sigma)\ H_{applied}$ in the NMR experiment. For AlF_4^- and $AlF_5^{2-}(D_{3h})$ we have also used a slightly larger basis set (6-31G*) to establish that trends are not strongly influenced by small basis set variations. Calculated F NMR shieldings are shown in Table 3 for the same geometries and basis sets.

Several general principles emerge from the results shown in Tables 2 and 3. First, the NMR shielding of Al increases with increasing coordination number and decreases as OH is substituted for F. Note that an increase in σ^{Al} corresponds to a more negative value for the Al NMR shift, δ^{Al}. In Table 2 we also include results for simpler models

TABLE 2. Calculated Al NMR isotropic shieldings using 3-21G* optimized geometries, a 3-21G* basis and the program RPAC

Species, Symmetry	CHF	Core-corrected CHF	LORG
AlF_4^-	638.4 (648)	592.6	655.5
AlF_5^{2-}, D_{3h}	661.3 (673)	606.8	603.4
AlF_5^{2-}, C_{4v}	660.7	606.3	597.9
AlF_6^{3-}	680.2	617.7	595.6
$Al(OH)_4^-$ ≤ 143.3°	628.4	585.3	
$Al(OH)_4^-$, S_4*	586.6	543.5	
AlO_4^{5-}, T_d**	552.9	509.8	
$Al(OH)_5^{2-}$, C_S	632.6†	589.5	
AlO_5^{7-}, D_{3h}**	600.4	549.5	
$AlF(OH)_3^-$	596.6	552.9	
$AlF_2(OH)_2^-$	612.4	568.0	
$AlF_3(OH)_2^{2-}$	645.4†	592.4	

Note: 6-31G* values in parentheses.

* The 3-21G* equilibrium value, <Al-O-H = 106.5°.

** Symmetrized bare oxide anion with distances from aluminum hydroxide optimizations.

† Calculated with the conventional (common origin) coupled Hartree-Fock program Sysmo.

TABLE 3. Calculated F isotropic NMR shieldings using a 3-21G* basis and 3-21G* optimized geometries

Species, Symmetry	CHF	Core-corrected CHF
AlF_4^-	533	476
AlF_5^{2-}, C_{4v}	540(eq), 549(ap)	487 av
AlF_5^{2-}, D_{3h}	543(eq), 541(ap)	488 av
AlF_6^{3-}	577	505
$AlF(OH)_3^-$	527	471
$AlF_2(OH)_2^-$	522	465
$AlF_3(OH)_2^{2-}$	532, 530	477, 476
SiF_6^{2-}	528	472

for Al fourfold- and fivefold-coordinated with O, i.e., AlO_4^{5-}, T_d and AlO_5^{7-}, D_{3h}. In each case we have averaged the equilibrium distances calculated for $Al(OH)_4^-$ and $Al(OH)_5^{2-}$ and used these for the higher symmetry bare oxide clusters, AlO_4^{5-} and AlO_5^{7-}. Although the absolute values of σ^{Al} are changed by this deprotonation, the fourfold- to fivefold-coordinated shielding difference is hardly affected. Thus, such bare clusters are probably adequate for determining changes in shielding with coordination number. We also show results for an $Al(OH)_4^-$ species with the <Al-O-H increased from the calculated equilibrium value of 106.5° to the value of 143.3°, closer to typical <Al-O-Si in aluminosilicates. Such an increase in angle is a very simple way to model some of the effects of increasing polymerization of the aluminosilicate network. As discussed in Tossell (1991), such modeling could be done almost equally well in terms of a TO_4^{4-} group stabilized by point charges at the H positions. The results for $Al(OH)_4$ show that σ^{Al} also increases with increasing <Al-O-H. The latter trend is related to the increase in σ^{Al} with increasing <Al-O-T and in general with increasing polymerization. The trends with coordination number and <T-O-T are the same as those seen in experimental or theoretical studies of Si compounds, although the changes are smaller in absolute parts per million (Tossell, 1991).

Trends in F NMR shielding appear to be fairly closely related to those for Al. For example, σ^F in AlF_n^{3-n} increases with increasing Al coordination number and decreases as OH is substituted for F. The σ^F value also decreases if F is bonded to Si rather than Al. All these shielding changes are of similar, modest size, so a decrease in F shielding compared with a highly shielded reference species like AlF_6^{3-} might arise from a lowered Al coordination number, substitution of OH (or O-T) for F, or coordination of the F to Si. The calculated difference in F shielding between AlF_6^{3-} and SiF_6^{2} is 33 ppm, in reasonable agreement with the results in Schaller et al. (1991b) of a shift of 38 or 39 ppm from M_3AlF_6 to M_2SiF_6.

So far our discussion of Al and F NMR shieldings has been based on the core-corrected CHF values in Tables 2 and 3. We have found it difficult to obtain LORG results consistent with experimental results. For example, the LORG-calculated values for Al shieldings actually decrease as the Al coordination number is increased, as shown in Table 2, clearly contrary to experimental results. The problem can be traced to the high polarity of the change distribution, in which almost all the valence electrons reside on F, so that even the four LMO of AlF_4^- that are expected to be of the Al-Fσ bond type and that give strong paramagnetic contributions to σ^{Al} have their centroids outside the F atoms. The LORG method actually used in RPAC is technically a modified LORG approach, in which the contributions of the σ bonding LMO are supposed to actually be evaluated with the Al rather than the LMO centroid as gauge origin. This is enforced by pulling the origin for all LMO within a certain distance of the Al onto the Al nucleus. Such a modified LORG procedure works well when such a pulling distance can be chosen to evaluate the contributions of LMO in σ bonding at Al but keep the F2s and F2p lone pair contributions evaluated at their centroids, near or slightly outside the F. For AlF_4^- such a distance can't be easily found, since the σ-bonding and F2p lone pair LMO centroids are at almost the same distance from the Al. A proper choice of gauge origins for the different LMO contributions can be made ad hoc, as seen in Table 4, but adding up the most appropriate LMO contributions then becomes rather complicated. Also, for different AlF_n^{3-n} complexes to be treated comparably, the pulling distance must change with the Al-F distance or coordination number. For example, in AlF_5^{2-} a pulling distance of 1.60 Å yields the right origin for the σ type LMO so that the core-corrected CHF and LORG results are very similar. It may be possible to develop a systematic procedure to obtain good LORG results by changing the pulling distance with the Al-F distance, but it presently seems simpler to use a core-corrected CHF approach.

Another parameter of value in determining Al speciation is the electric field gradient at Al, q, which is measured indirectly through the nuclear quadrupole coupling

TABLE 4. AlF_4^- contributions to σ^{Al}, 3-21G* basis at optimized geometry

Localized orbital	CHF	Core-corrected CHF	LORG RMIN = 1.20 Å	LORG RMIN = 1.60 Å	LORG Corrected
Al1s	455.5	455.1	455.5 (Al)	455.5 (Al)	455.5
Al2s,2p	75.1 × 4	75.1 × 4	70.9 × 4 (Al)	72.9 × 4 (Al)	72.9 × 4
Fls	8.9 × 4	−2.5 × 4	0.0 × 4 (F)	0.7 × 4 (F)	0.71 × 4
σ[a]	−18.9 × 4	−18.9 × 4	−2.1 × 4 (~F[b])	−3.23 × 4 (~F)	0.71 × 4
F2s	−6.45 × 4	−6.45 × 4	−2.2 × 4 (~F)	−6.8 × 4 (Al)	−6.8 × 4
F2pn,π	−6.45 × 8	−6.45 × 4	−2.2 × 8 (~F)	−6.8 × 8 (Al)	−6.8 × 4
TOTAL	638.5	592.6	704.3	655.4	592.6

Note: Origins given in parentheses.

[a] The σ LMOs have their centroids outside of F atoms.

[b] The symbol ~F indicates that the centroid of the LMO is near the F nucleus.

constant, NQCC = e^2qQ/h, and can be inferred from the width of the Al NMR resonance. The EFG is a purely ground-state property but is still fairly difficult to calculate accurately, since it is strongly influenced by basis set choice and by electron correlation (Jost and O'Konski, 1983). Since only the NQCC can be measured directly, the nuclear quadrupole moment, *eQ*, is also uncertain unless *q* can be calculated very accurately for some simple case. Our interest is in assessing reasonable relative values of *q* for these complex Al-containing molecules rather than obtaining an extremely accurate value for a simple case. Using a commonly employed value of 1.5×10^{-1} barns for *eQ* of Al (Fuller, 1976), we have calculated NQCC values for the AlF diatomic molecule at the SCF level for various basis sets, as shown in Table 5. The large polarized Dunning-Hay basis (Dunning and Hay, 1977) gives a result matching experimental results closely, but this agreement depends strongly on our choice of *eQ*. For the 3-21G* basis, the calculated *eq* value is only about two thirds as large. If the polarized Dunning-Hay value of *eq* represents the Hartree-Fock limit, we would expect this value to be reduced somewhat by electron correlation. In Table 6 we present *q* and NQCC values calculated from 3-21G* bases at optimized 3-21G* geometries for several fluorides and hydroxyfluorides. Given the possible modification of *q* due to other atoms within the real condensed-phase material, use of more elaborate basis sets would probably represent wasted effort.

Some interesting trends emerge from these results. Perhaps the easiest interpretation of the results is obtained using the partial quadrupole splitting parameter method (Bancroft, 1973; Parish, 1984). For a trigonal bipyramidal complex $MA_2^{ap}B_3^{eq}$ (two A ligands in the apical position and three B ligands in the equatorial positions) the *zz* component of the EFG, q_{zz}, is proportional to (2[A] − 1.5 [B]), where [A] and [B] are the individual ligand contributions to the EFG. (Note that for D_{3h} symmetry $q_{xx} = q_{yy} = -\frac{1}{2}\, q_{zz}$). Since the ligand contribution to the EFG scales as R_{M-L}^{-3}, we would expect $q_{zz} \propto [(2/R^3_{M-A}) - (1.5/R^3_{M-B})]$, so that if the larger numerator for the contribution of the apical A ligands is balanced by a larger R^3_{M-A} in the denominator (i.e., apical distances larger than equatorial) then q_{zz} can be quite small. For AlF_5^{2-}, and particularly for $AlF_3(OH)_2^{2-}$, the apical distances are longer than the equatorial, and q_{zz} is small, whereas for $AlF_2(OH)_3^{2-}$, with an apical distance to F of only 1.753 Å (shorter than the distance of 1.793 to equatorial O) the q_{zz} value is much larger. Thus, to obtain a small EFG for a fivefold-coordinated aluminum hydroxyfluoride (with approximate or true D_{3h} symmetry) we must place the OH^- groups (with intrinsically larger bond distances) in the apical positions. For AlF_5^{2-} and $AlF_3(OH)_2^{2-}$ the calculated q_{zz} values are negative, indicating that the equatorial ligands slightly overbalance the contribution from the apical. It is worthwhile noting that the calculated Al EFG for $Al(OH)_5^{2-}$, as shown in Table 6, is only 2.6 MHz. This is considerably smaller than the 5.9 MHz value observed (Ghose and Tsang, 1973) for the fivefold-coordinated site in andalusite, Al_2SiO_5, which is of basically trigonal bipyramidal geometry but with the fivefold-coordinated polyhedra sharing edges. It is therefore clear that fine details of the geometry can significantly influence the EFG. Of the species considered, $AlF_3(OH)_2^{2-}$ has the smallest EFG, and so it should generate a narrow Al

TABLE 5. Calculated EFG at Al in AlF, *R*(Al-F) = 1.65437 Å (experimental value) using various basis sets

	|*q*| (au)	e^2qQ/h (MHz)[a]
3-21G*	0.8578	26.4
6-31G*	0.9714	29.2
Dunning-Hay*	1.2422	38.3
Exp.[b]	—	37.6

[a] Assuming $eQ = 1.5 \times 10^{-1}$ barns for ^{27}Al (Fuller, 1976).

[b] Lide (1965).

TABLE 6. Calculated EFG at Al in AlF_5^{2-}, $AlF_2(OH)_3^{2-}$, $AlF_3(OH)_2^{2-}$, $AlF(OH)_3^-$, and $AlF_2(OH)_2^-$ from 3-21G* bases at 3-21G* optimized geometries

Species, Symmetry	|*q*| (au)	e^2qQ/h (MHz)[a]
AlF_5^{2-}, C_{4v}	0.1366	4.2
AlF_5^{2-}, D_{3h}	0.0600	1.8
$AlF_2(OH)_3^{2-}$, D_{3h}	0.2815	8.7
$AlF_3(OH)_2^{2-}$, C_S	0.0375	1.2
$Al(OH)_5^{2-}$, C_S	0.0856	2.6
$AlF(OH)_3^-$, C_{3v}	0.1484	4.6
$AlF_2(OH)_2^-$, C_{2v}	0.0377	1.2
AlF, $C_{\infty v}$	0.8578	26.4

[a] Assuming $eQ = 1.5 \times 10^{-1}$ barns for ^{27}Al.

TABLE 7. Calculated harmonic vibrational frequencies (in cm^{-1}) for totally symmetric stretching modes compared with experimental results

Species, Mode	Calc	Exp
AlF_4^-, a_1	717	622*
AlF_5^{2-}, a_1'	621	—
AlF_6^{3-}, a_{1g}	535	555*
$Al(OH)_4^-$, a	664 (634**)	615**
$AlF(OH)_3^-$, a_1	673	—
$AlF_3(OH)_2^{2-}$, a'	607	—

* Gilbert et al. (1975).
** Hess et al. (1988), 6-31G* SCF calculation.

NMR peak. Kohn et al. (1991) considered trigonal bipyramidal $AlF_3(OH)_2^{2-}$ as a candidate for the intermediate peak in their Al NMR spectrum but could not definitely establish on qualitative grounds whether its EFG would be large or small. The present results establish that it would indeed have a small EFG.

To test further the accuracy of our calculations and to assist in assignment of IR-Raman spectra, we have also calculated the vibrational energies shown in Table 7. Mysen and Virgo (1985) have identified a weak feature in the spectra of F-bearing aluminosilicates with the Raman active A_{1g} vibration of AlF_6^{3-} at about 540-550 cm^{-1} (Gilbert et al., 1975), whereas we calculated 535 cm^{-1}. The totally symmetric Raman active Al-F stretch in AlF_4^- occurs at 622 cm^{-1}, whereas we calculated 717 cm^{-1}. We thus appear to overestimate stretching frequencies by about 10% for the nearly neutral species and to match experimental results (fortuitously) well for the 3^- anion. An estimate of the totally symmetric stretching frequency of AlF_5^{2-} would thus be $0.9(621) \approx 560$ cm^{-1}. For $AlF_3(OH)_2^{2-}$, with somewhat longer average Al-F equatorial distances, we calculate an even lower value for the symmetric stretching vibration. Thus, it appears that AlF_6^{3-} and $AlF_3(OH)_2^{2-}$ will show such similar Raman spectra that distinguishing them would be very difficult.

DISCUSSION

Having established that our calculations reproduce expected trends in bond distance, NMR shielding, electric field gradients, and vibrational spectra, we can use the results to help in assigning the NMR spectra of the F-bearing aluminosilicate glasses. The assignment of the peak at δ ^{19}F of -193 to AlF_6^{3-} (Schaller et al., 1991b) seems reasonable in light of the good match to M_3AlF_6. The Al NMR spectra has a feature at δ ^{27}Al of 55, assigned to fourfold-coordinated Al, very much like those seen in F-free aluminosilicates. We assign this to Al fourfold-coordinated by bridging O, for which our molecular model would be S_4 symmetry $Al(OH)_4^-$ with <Al-O-H increased to some value larger than the equilibrium one of 106.5°. Since replacement of one OH by an F increases the Al NMR shielding by only about 10 ppm, we cannot completely exclude species such as $AlF(OH)_3^-$ contributing to the 55-ppm peak, which would be slightly broader on its low δ (shielded) side. If we assume, on the basis of the ^{19}F Cramps results, that the feature at $\delta = -1$ ppm in the Al spectrum represents AlF_6^{3-}, then the experimental difference of about 56 ppm between fourfold- and sixfold-coordinated species is at least consistent with our results for AlF_6^{3-} vs. $Al(OH)_4^-$, with a difference of between 33 and 74 ppm, depending upon <Al-O-H. Clearly it would be desirable to perform calculations on larger $Al(O\text{-}T)_4$ clusters to substantiate this. Unfortunately, such ambiguity is difficult to eliminate completely in comparing halides and chalcogenides as ligands.

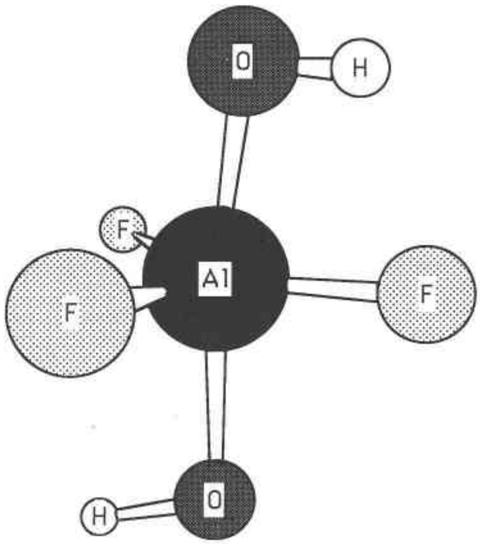

Fig. 1. Structure of $AlF_3(OH)_2^{2-}$, optimized at the SCF 3-21G* level.

The species yielding the intermediate slightly deshielded Al NMR peak ($\delta^{Al} \sim 22$ ppm) and the deshielded F NMR peaks ($\delta^{F} \sim -165$ ppm) might differ from AlF_6^{3-} by having a lower coordination number, by the substitution of F by O-T or by incorporation in the polymeric network. The absence of any enhancement in the ^{19}F > ^{29}Si CP-MAS spectra compared with the conventional ^{29}Si MAS spectra indicates that there are no direct Si-F interactions. The absence of a peak in the ^{29}Si NMR at the SiF_6^{2-} position further supports the conclusion that SiF_6^{2-} groups are absent, and so these cannot explain the deshielded feature in the ^{19}F NMR. The calculated Al and F deshieldings of AlF_5^{2-} compared with AlF_6^{3-} are only 11 and 18 ppm, respectively, considerably smaller than the experimental peak separations of about 23 and 30 ppm in Al and F NMR, respectively. For the $AlF_3(OH)_2^{2-}$ species, whose calculated structure is shown in Figure 1, the calculated Al deshielding relative to AlF_6^{3-} is 25 ppm, whereas the deshielding of F is about 29 ppm. We can calibrate our calculated shieldings by comparing calculated and experimental effects of the coordination number on the ^{29}Si shielding in various silicon fluorides for which experimental data is available. As shown in Table 8, our calculated (core-corrected) value for the SiF_4-SiF_6^{2-} shielding difference is 64 ppm, whereas

TABLE 8. Si NMR isotropic shieldings for SiF_4, SiF_5^- and SiF_6^{2-}, compared with experimental results

	Previous results*			Present results			
Molecule	*R*(Si-F)	σ(CHF)	σ(core-corrected CHF)	*R*(Si-F)	σ(CHF)	σ(core-corrected CHF)	$\Delta\sigma_{exp}$**
SiF_4	1.556	556	508	1.553	594	546	0
SiF_5^-	—	—	—	1.628, 1.594	634	575	
SiF_6^{2-}	1.685	668	601	1.662	678	610	+74

* Tossell and Lazzeretti (1986).
** Johannesen et al. (1968).

the experimental value is 74 ppm (Johannesen et al., 1968). Our previous calculations (Tossell and Lazzeretti, 1986), which employed considerably larger basis sets, gave a shielding difference (after core correction) of 93 between the fourfold- and sixfold-coordinated species. On the basis of this comparison with Si shieldings, we expect the present calculations to underestimate the change in Al shielding with coordination number by perhaps a sixth. Even with corrections for this underestimation, it still appears that the shielding difference of AlF_6^{3-} and AlF_5^{2-} is too small to allow assignment of the middle Al NMR peak to a AlF_5^{2-} species, rather than to the more deshielded $AlF_3(OH)_2^{2-}$.

Incorporation of the $AlF_3O_2^-$ unit into the aluminosilicate polymer might be modeled by increasing the <Al-O-H by a small amount, which would slightly shield Al and probably F as well. Since the Al-O distance in $AlF_3(OH)_2^{2-}$ is quite long (1.870 Å), such Al-O-T linkages might have fairly small angles (long T-O_{br} distances are generally correlated with small <T-O_{br}-T). $AlF_3(OH)_2^{2-}$ also has a small EFG, consistent with the Al NMR spectra. Another possibility would be $AlF_2(OH)_2^{1-}$, which also has a small EFG, but according to the results in Tables 2 and 3 is probably too deshielded in both Al and F NMR to fit the experimental data. Another species closely related to $AlF_3(OT)_2^-$ would be a species like $AlF_3(ONa)_2^-$, with the T-O-T bonds broken to convert bridging to nonbridging O. Distinguishing the degree of tetrahedral polymerization of such a species from NMR would certainly be difficult.

CONCLUSION

Although calculations using quantum mechanics on even simple gas phase molecules do not exactly match experimental results at the level of rigor used in this paper, and although the molecular models used cannot capture all aspects of the behavior of condensed phase species, we nonetheless feel that semiquantitative estimates of trends in properties can be confidently obtained at this level. On the basis of our results, the fivefold-coordinated Al species identified in the Al NMR spectra of F-bearing aluminosilicate glasses probably has both F and O in its first coordination sphere, a probable molecular model being $AlF_3(OH)_2^{2-}$, rather than AlF_5^{2-}, as previously thought. The major Al NMR peaks may still be confidently identified with $Al(OH)_4^-$ and AlF_6^{3-} species.

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