BOND ENERGY INVESTIGATIONS FOR ALUMINUM(III)-FLUORIDE COMPLEXES RELATIVE TO CRYOLITIC MELTS. 
PART I: POTENTIAL ENERGY SURFACE FOR THE DISSOCIATION OF PURE ISOLATED COMPLEXES

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ABSTRACT

Experimental techniques for structural and dynamics studies are difficult to use in cryolite melts. Therefore a theoretical approach based on quantum chemical calculations (with the formalism of the Density Functional Theory) have been carried out. Results concerning stable structures and Al-F bond dissociations of aluminum(III)-F(-I) complexes are presented. It is shown that energy barriers can be obtained by breaking Al-F chemical bond and the relaxation effects on its neighbouring bonds. Potential energy surface relative to bond dissociations is given.

INTRODUCTION

Several experimental techniques, such as X-ray diffractions(1-4), neutron diffusion scattering(5-10), IR and Raman spectroscopies(11-17), are useful for studying structures in molten salts. Due to hard experimental conditions (high working temperatures, corrosiveness, toxicity, ...), some melts are difficult to investigate.

Very few experimental data on structural entities in such melts are available. Only conformational and vibrational studies have been investigatned on melts at lower temperature and comparisons with structural species determined in such experimental conditions have been proposed. Therefore theoretical studies have been recently developed(18-25), most often based on quantum chemical computations and molecular dynamics calculations. These techniques can give vibrational spectra and conformational analyses, that are important for chemical aspects and reactivity. In our laboratory, such theoretical simulations are currently in progress, by using these approaches as analytical and predictive tools to be compared with results of experimental methods.
The subject of this paper is to acquire fundamental data on Al(III)-F(-I) complexes required for the study of the molten cryolite structure by molecular dynamics calculations. In fact, for obtaining a realistic model of such a complex melt, dynamics studies should be performed by taking into account the possibility for all complexes to be dissociated or formed. The notion of breaking bonds and bond formation has been advanced(26), and can be a progress for dynamics calculations to have realistic interaction potentials.

Before studying the melts by a dynamics way, we have to establish the structure of species that could be present in molten cryolite. The calculations reported here have been performed in order to simulate dissociation pathways of AlF$_6^{3-}$ and AlF$_5^{2-}$ by loosing one or two fluoride ions.

**COMPUTATION ELEMENTS**

**Approximation levels**

Our choice for computational software turned in favour of local density functional (LDF) approach, because of its accuracy in convergence and the computational effort for this method that grows to leading order with the cube of the molecule size. Furthermore the density functional approach has been much used in electronic structure calculations on molecules and solids(27-28). Currently, LDF is becoming an increasingly important method in quantum chemistry, as it leads to much more reliable predictions for large molecules. The power of LDF methods has been demonstrated in numerous applications(29-31).

All theoretical computations were carried out with the DMol software ((32), distributed by Biosym Technologies(33)), for which the mathematical formalism is described elsewhere(32-34). The use of DFT has several advantages. For one, this method employs numerical (in the case of DMol) basis sets obtained by solving the atomic DFT equations numerically; thus the use of the exact DFT atomic orbitals implies that the molecule can be dissociated exactly to its constituents atoms within the DFT context. Because of the quality of these orbitals, basis sets superposition effects are minimized (32), and an excellent description of even weak bonds is possible.

All quantum calculations were done at a local approximation using the UHF (Unrestricted Hartree-Fock) level. The DNP basis sets (double numerical functions, augmented by polarization ones) were chosen. The quality of this type of basis sets is similar to the gaussian 6-31G** sets.

**Model for the dissociation processes**

The following dissociation pathways have been studied: AlF$_6^{3-}$ <-> AlF$_5^{2-}$ + F$, $ AlF$_5^{2-}$ <-> AlF$_4^-$ + F$, $ AlF$_6^{3-}$ <-> AlF$_4^-$ + 2F$, by breaking one Al-F bond for the two first reactions and simultaneously two Al-F bonds in the last dissociation.

In order to describe the reactions in a consistent way, we have to take into account the following effects. The breaking Al-F bond length has to be enhanced for simulating the dissociation mechanism and fixed during each geometry optimization. Furthermore, relaxation effects should be considered for all fluorine atoms that are not fixed during the optimization. So each energy point corresponds to an optimized geometry carried out at these constraint levels.
In this paper, we do not consider the effect of the molten salt environment on Al(III)-F(-I) complexes. This effect will be taken into account in further studies through quantum and molecular dynamics investigations.

RESULTS AND DISCUSSION

The procedure just described is very general and should be applicable to any system. The schemes describe breaking one or two bonds of sixfold- and fivefold-coordinated aluminum complexes. For the reaction involving AlF$_5^{2-}$, total energies have been modified by adding the total energy of F$^-$ ion, so that all energies in all dissociation pathways can be compared. It is important to mention that we consider the complexes loosing an F$^-$ ion, since the Mulliken and Hirshfeld population analyses give a negative charge on F for relatively large bond length. The bond type is thus ionic and the interaction is an electrostatic one.

The potential energy curves of dissociation pathways by DFT calculations are depicted in figure 1. Some interesting trends emerge from these results. The consistency of all theoretical computations is shown on figure 1 because we find again the energy of a stable conformation, AlF$_5^{2-}$ or AlF$_4^-$, added to F$^-$ or 2F$^-$ energies. Regarding structures through the dissociation mechanism of AlF$_5^{2-}$ into AlF$_4^-$, we observe that the conformation of AlF$_5^{2-}$ tends towards a distorted tetrahedral geometry due to the presence of the far-off fluoride atom. Analogous remarks can be mentioned concerning the dissociation of AlF$_6^{3-}$ into AlF$_4^-$ by stretching two fluoride adjacent ions. However, the reaction: AlF$_6^{3-} \leftrightarrow$ AlF$_4^- + 2F^-$ by stretching two opposite F$^-$ ions shows a square plane geometry for long Al-F bond lengths. On the other hand, concerning the dissociation of AlF$_6^{3-}$ into AlF$_5^{2-}$, we can point out a distorted octahedral conformation, that could be underline experimentally in the melt.

The energy differences $\Delta E$ between the initial stable structures and the transient species are reported in table 1. These results suggest that the dissociation of AlF$_6^{3-}$ into AlF$_5^{2-}$ is more favourable than those of AlF$_6^{3-}$ into AlF$_4^-$ or AlF$_5^{2-}$ into AlF$_4^-$. The comparison between the energy gaps and RT=8kJ/mol at 1000K suggests that environment effects should occur. In fact, the model used for dissociation schemes does not include molten salt effects, such as F$^-$ exchanges between two complexes and charge effects that could lower the energy barrier of reactions.

CONCLUDING REMARKS

Stable structures of Al(III)-F(-I) complexes have been studied and dissociation schemes have been proposed. In a theoretical point of view, the procedure used is very general and is applicable to any chemical system. The dissociation pathways relative to these complexes have been studied and energy gaps given. LDF calculations of reaction schemes show that AlF$_6^{3-} \leftrightarrow$ AlF$_5^{2-} + F^-$ involves a lower energy barrier than the other dissociations. These studies will be completed by further investigations in order to consider preponderant effect of molten salt environment (charged and solvation effects). It will be the subject of a forthcoming paper.
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Figure 1: dissociation energies according to the following dissociations:

(1) \( \text{AIF}_6^{3-} \leftrightarrow \text{AIF}_5^{2-} + \text{F}^- \)

(2) \( \text{AIF}_6^{3-} \leftrightarrow \text{AIF}_4^- + 2\text{F}^- \)

(3) \( \text{AIF}_5^{2-} \leftrightarrow \text{AIF}_4^- + \text{F}^- \) axial way

(3') \( \text{AIF}_5^{2-} \leftrightarrow \text{AIF}_4^- + \text{F}^- \) equatorial way

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Reactions} & (1) & (2) & (3) & (3') \\
\hline
\Delta E (kJ/mol) & 35 & 107.6 & 121 & 137.6 \\
\hline
\end{array}
\]

Table 1: energy gaps corresponding to the studied dissociations (see text)
Figure 2: stable structures of AlF$_6^{2-}$, AlF$_5^2$ and AlF$_4^-$. 
Figure 3: a typical electron density map: transition structure for dissociation (1) (scaled from $10^{-2}$ to $10^{-7}$).