Ab initio Studies of Aluminium Halides

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Abstract

The catalytic fluorination of hydrocarbons facilitates the large-scale production of chlorofluorocarbons for a wide range of applications including aerosol propellants, refrigerants and solvents. Lewis acid catalysts, such as Swarts catalysts based on antimony pentafluoride, are commonly used. Recently, a sol-gel based synthesis method has been developed which yields very high surface area aluminium fluoride (HS-AlF$_3$) that has a Lewis acidity comparable to that of the Swarts catalysts. This makes HS-AlF$_3$ a promising candidate for use in several Lewis acid catalysed reactions. Despite the importance of the surface in the catalytic process little is known about the detailed atomic scale structure of AlF$_3$ surfaces.

Surface thermodynamics calculations, based on hybrid-exchange density functional theory, are employed to predict the composition and structure of AlF$_3$ surfaces. The surfaces of AlF$_3$ expose under coordinated Al ions that are potential Lewis acid sites. Under standard atmospheric conditions the AlF$_3$ surfaces are shown to adsorb water above the under coordinated Al ions. Theoretical characterisation of the under coordinated Al ions shows that the most reactive type of site is not exposed on crystalline $\alpha$-AlF$_3$ samples, however, it is predicted to occur in small quantities on $\beta$ crystallites. It is speculated that such sites occur in higher quantities on the high surface area materials. This result may explain the different reactivity of $\alpha$-, $\beta$- and HS-AlF$_3$. Our detailed understanding of AlF$_3$ surfaces allows us to propose a reaction centre and mechanism for the dismutation of CCl$_2$F$_2$ on $\beta$-AlF$_3$.

Aluminium chloride is extensively used as a catalyst in Friedal-Crafts reactions. It is therefore, commonly assumed that pure crystalline AlCl$_3$ is strongly Lewis acidic. Ab initio surface thermodynamics calculations are used to study the surfaces of crystalline AlCl$_3$ and show that it is chemically inert.
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List of Publications

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Chapter 1

Introduction

1.1 Introduction

Strong Lewis acid catalysts are widely used in a variety of industrial processes, including Friedal Crafts and halide exchange reactions. Aluminium chloride is extensively used as such a catalyst. Recently, high surface area aluminium fluoride has been synthesised that has a Lewis acidity comparable to that of the widely used Swartz catalyst (SbF$_5$) \[1\]. It therefore has great potential as an industrial solid Lewis acid catalyst. Studies of these materials has generally concentrated on the synthesis of the materials and the investigation of their catalytic properties. To improve the efficiency of the catalysts it is important that we understand why and how the materials catalyse reactions. This requires surface characterisation studies and theoretical studies on the atomic scale description of their surfaces. \textit{Ab initio} methods are now sufficiently robust and accurate that they can play a significant role in characterising complex materials. In this study we use \textit{ab initio} methods and atomistic thermodynamics to characterise the surfaces of aluminium chloride (AlCl$_3$) and aluminium fluoride (AlF$_3$).

In this chapter we summarise the existing knowledge of the materials that are the subject of this study and their importance in fluorine chemistry. We start with a discussion
of Lewis acidity as this is the property that is of paramount interest in the chemistry of these materials. We then discuss the uses and properties of aluminium chloride and aluminium fluoride. The majority of the work in this thesis concerns the study of aluminium fluorides, consequently we discuss the synthesis methods and outline some of the experimental characterisation studies that has been performed on these materials. Finally we discuss what we intend to achieve as a result of this study and outline the structure of this thesis.

1.2 Lewis Acidity

There are two different definitions of acidity. The most well known one is Brønsted acidity. This is a measure of the ability of a substance to donate a proton. The other type of acidity is known as Lewis acidity. A Lewis acid is an electrophile or electron acceptor. There is no universal system that is used to measure Lewis acidity.

The fluorine affinity (FlA) method, as proposed by Christe et al [12] is designed to provide a quantitative measure of Lewis acidity. The FlA is a measure of the energy required for the process \( \text{COF}_3^- + A \rightarrow \text{COF}_2 + \text{AF}^- \). A pF scale is commonly used to present the results with a pF value obtained by dividing the FlA by 10 kcal mol\(^{-1}\). FlAs of all gaseous MX\(_3\) compounds (M = Al, Ga, In; X = F, Cl, Br, I) have previously been calculated using *ab initio* methods [13]. Experimentally FlA values can be deduced from cyclotron resonance (ICR) experiments [14, 15, 16] or from Born-Haber (BH) thermodynamic cycles [17, 18]. Schrobilgen et al have extended the concept of FlAs to electron pair affinities (EPA) [19]. This theory is based on the idea that a free single electron pair would be the strongest possible Lewis base, therefore, acidity can be quantified relative to this ideal. Calculated EPA values agree well with FlA values. A disadvantage, however, of this method is that it is not possible to measure EPAs experimentally.

To some extent Lewis acidity can also be characterised from the activity of suitable
catalytic test reactions. Catalytic activity, however, is not only determined by Lewis acidity but by other factors such as steric hindrances and porosity. As a consequence of this, catalytic activity can be higher in one material than another for a given test reaction, yet the ordering may be reversed for a different test reaction.

The Lewis acidity of a material can also be studied by consideration of its binding energy with a Lewis base; the greater the binding energy, the stronger the Lewis acid. The binding energy of NH$_3$, is commonly used to quantify the strength of a Lewis acid [20, 21, 22]. Density functional theory (DFT) calculations (using the generalised gradient approximation) for the zeolite, Mordenite, [20] show a range of Lewis acid sites; from very weak sites with NH$_3$ binding energies as small as -0.2 eV to very strong sites with binding energies of up to -1.7 eV.

An alternate method of quantifying Lewis acid site strength is to study the photo-acoustic IR spectra of adsorbed species, such as pyridine or CO. In pyridine IR spectra, bands at 1454 and 1620 cm$^{-1}$ are typical when pyridine is adsorbed at a strong Lewis acid site [23]. A band at 1490 cm$^{-1}$ is, however, the result of pyridine adsorption at Brønsted acid sites. Pyridine adsorption is hence a particularly useful method for differentiating Lewis acid sites from Brønsted acid sites. It is less useful at quantifying the strength of Lewis acid sites as the IR spectra only shifts by very small amounts as a function of Lewis acid strength. CO is more useful in the quantification of Lewis acid strength as the CO vibration band in the IR spectrum is much more sensitive to the strength of the Lewis acid site [24, 25].

1.3 Aluminium Chloride

In the US alone, 25,000 tonnes of AlCl$_3$ are produced each year [26]. It is usually produced by the direct exothermic reaction of its constituent elements. It is widely used in the chemical industry as a catalyst for Friedel-Crafts reactions [27], both for acylations
Figure 1.1: The reaction mechanism of a Friedel-Crafts alkylation [7].

The Friedel-Crafts alkylation and acylation reaction mechanisms involve an electrophilic aromatic substitution. Alkylation reactions involve an aromatic ring with an alkyl halide. The mechanism is usually described as follows. The first step of the reaction, shown in figure 1.1, involves the alkyl halide attaching itself via its Cl ion to the AlCl₃ catalyst. The carbon attached to the chlorine in the R-Cl-AlCl₃ complex becomes positively charged. The π electrons in the benzene ring are mildly electrophilic, and hence attack the partially positive carbon to create a non-aromatic intermediate as shown in figure 1.1. Elimination of a proton re-establishes the aromaticity of the ring, and the AlCl₃ catalyst is regenerated along with a molecule of hydrochloric acid. Acylation reactions follow a similar reaction mechanism to alkylations.

The Friedel-Crafts reaction mechanism requires a catalyst with strong Lewis acid properties to enable the formation of a positively charged R group. This has led to a common assumption that pure crystalline AlCl₃ must be a strong Lewis acid. In its solid crystalline form, AlCl₃ consists of hexagonal close-packed layers of chlorine ions in which two-thirds of the octahedral holes between every other chlorine layer are occupied by six-fold coordinated aluminium ions. At its melting point of 192.4°C the structure undergoes a dramatic reconstruction, the aluminium becomes 4-fold coordinated; the co-
valent molecular dimer $\text{Al}_2\text{Cl}_6$ is formed. The volume of the material increases by 85%. The covalently bonded molecular dimers are also the main species in the gas phase at low temperatures (150-200$^\circ$C). At higher temperatures the molecules tend to disassociate into $\text{AlCl}_3$ molecules. The different phases of $\text{AlCl}_3$ are shown in figure 1.2.

1.4 Aluminium Fluoride

Aluminium fluorides are of great interest as potential strong Lewis acid solid catalysts for many halide exchange reactions. Despite this, very little is known about the detailed surface structure of these fluorides although models have been suggested based on observations of chemical activity [28].
1.4.1 The Crystalline Phases of AlF$_3$

There are several different phases of crystalline AlF$_3$. Their structures consist of corner sharing AlF$_6$ octahedra. The most stable phase is $\alpha$-AlF$_3$. This structure, shown in figure 1.3, is closely related to the corundum structure adopted by $\alpha$-Al$_2$O$_3$ but with one of the aluminium sites occupied in the oxide being vacant in the fluoride. At temperatures between 450°C and 650°C all the other known phases of crystalline AlF$_3$ will irreversibly transform to this phase.

The search for different phases of pure AlF$_3$ began in the 1960s. It was motivated by the hope of finding phases with better catalytic properties than $\alpha$-AlF$_3$. Phases that have been reported in the literature include the $\beta$, $\gamma$, $\epsilon$, $\eta$, $\theta$ and $\kappa$ phases. It has, however, since been shown that the $\gamma$, and $\epsilon$ phases were actually either impure or mixtures of better characterised phases [29].

The most common metastable phase is $\beta$-AlF$_3$ [30, 6]. This phase, shown in figure 1.3, is related to the hexagonal tungsten bronze structure. It is commonly obtained by dehydrating $\alpha$-AlF$_3$·3H$_2$O or from the thermal decomposition of NH$_4$AlF$_4$ [31]. The irreversible transition from $\beta$ to $\alpha$ occurs slowly at temperatures between 500°C and 650°C. $\beta$-AlF$_3$ is known to be a moderate Lewis acid and will catalyse many halide exchange reactions.
1.5 HS-AlF$_3$

High surface area aluminium fluoride (HS-AlF$_3$) has recently been prepared that has the characteristics of a very strong Lewis acid. The material catalyses reactions that could previously only be catalysed by very strong Lewis acids such as the widely used Swartz catalysts that are based on antimony pentafluoride (SbF$_5$) [11]. This makes HS-AlF$_3$ a promising candidate for use in many Lewis acid catalysed reactions, including halide exchange reactions and in the production of hydrofluorocarbons [32, 33, 34].

There are many potential advantages of using HS-AlF$_3$ as a strong Lewis acid catalyst instead of SbF$_5$. For example, SbF$_5$ will react irreversibly with water and must always be kept in an anhydrous environment whereas HS-AlF$_3$ reacts reversibly. SbF$_5$ is a liquid catalyst, which makes product separation difficult whereas HS-AlF$_3$ is a solid catalyst which eliminates the problem of product separation.

1.5.1 Synthesis of HS-AlF$_3$

A number of methods, including sol-gel [8, 35], plasma [36, 37] and microwave assisted processes [38, 9], can be used to synthesise HS-AlF$_3$. The method that has received most attention, and is probably the most well developed, is the sol-gel method, first applied to AlF$_3$ by the group led by Professor Erhard Kemnitz at the Humboldt University in Berlin [8, 35].

The sol-gel process typically involves the reaction of aluminium tri-isopropoxide Al(OiPr)$_3$ with a non aqueous HF solution in an organic solvent. The overall reaction is

$$\text{Al(OiPr)$_3$ + xHF} \rightarrow \text{AlF}_x\text{(OiPr)$_{3-x}$ + xPrOH} \quad (1.1)$$

The reaction is thought to proceed as shown in figure 1.4. The reaction first involves the displacement of OiPr groups by F ions (figure 1.4b). A network of Al$^{3+}$ ions linked
by F and O\textsubscript{iPr} ions is then formed (figure 1.4c). The presence of O\textsubscript{iPr} groups in the final product is due to incomplete fluorination of the alkoxide. The product, referred to as the precursor, is a transparent gel which consists of a 3D network of predominately Al(F,O\textsubscript{iPr})\textsubscript{6} octahedra.

To form HS-AlF\textsubscript{3} a full fluorination of the precursor is required. This can be achieved by heating it in a stream of a mild fluorinating agent, such as a gaseous CCl\textsubscript{2}F\textsubscript{2} or CHClF\textsubscript{2} at temperatures between 250\degree C and 300\degree C. These gases almost fully fluorinate the aluminium alkoxide fluoride while still maintaining the disorder of the amorphous mesoporous precursor. The elemental composition (by mass) of the product is 32.13% Al and 67.87% F. Trace elements in the product include Cl, C and O. A BET surface area of up to 300 m\textsuperscript{2} g\textsuperscript{-2} has been achieved using this methodology.

HS-AlF\textsubscript{3} can also be obtained from the sol-gel precursor material by subjecting it to microwave assisted heating followed by mild fluorination using gaseous F\textsubscript{2} \cite{9}. This method results in the formation of crystalline HS-AlF\textsubscript{3} with a BET surface area of up to 300 m\textsuperscript{2} g\textsuperscript{-2}.  

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{struct_models.png}
\caption{The structural models showing how reaction 1.1 is thought to proceed [8]. (a) Al(O\textsubscript{iPr})\textsubscript{3}, (b) [Al(F,O\textsubscript{iPr})\textsubscript{6}]\textsubscript{n} tetrameric intermediate; (c) [Al(F,O\textsubscript{iPr})\textsubscript{6}]\textsubscript{n} polymer. In each of the diagrams the O represents isopropoxy groups.}
\end{figure}
1.5.2 Characterisation of HS-AlF$_3$

Characterisation of $\alpha$-AlF$_3$, $\beta$-AlF$_3$ and amorphous and crystalline HS-AlF$_3$ from X-ray adsorption near-edge structure (XANES) show that their electronic structures are very similar [39]. This is due to the strong ionic nature of their bonding, resulting in the formation of corner sharing AlF$_6$ octahedra. This suggests that it is the geometric and electronic structure of their surfaces that is responsible for the differences in their Lewis acidity, and hence their catalytic properties.

High resolution transmission electron microscopy (HRTEM) reveals that the crystalline HS-AlF$_3$ material, obtained using microwave assisted heating, consists of particles of two different sizes. The larger particles have a diameter of approximately 50 nm while the diameter of the smaller particles is approximately 10 nm. Powder X-ray diffraction (XRD) reveals two well defined peaks which are characteristic of $\alpha$-AlF$_3$. Additionally, two, less intense, broad peaks are also observed, for which no satisfactory indexing has been possible. Given the broad nature of these peaks, it is suggested that they are a result of the smaller (10 nm) particles and that the larger particles consist of $\alpha$-AlF$_3$. Regular shaped particles of radii 10 nm have surface areas of approximately 200 m$^2$g$^{-1}$. This implies that the surface of HS-AlF$_3$ is dominated by the smaller type of particle.

Fourier Transform Infrared (FT-IR) spectroscopy of adsorbed pyridine suggests a concentration of Lewis acid sites of approximately 1.1 nm$^{-2}$ (calculated using the BET surface area) [9]. Furthermore, this method also shows that there are no Brönsted sites present at the surface, as the adsorption peaks associated with such sites are absent. FT-IR spectroscopy of adsorbed pyridine was studied on several other surfaces to enable a comparison to be made between the materials. Two sets of results were obtained, firstly the pyridine was out-gassed at room temperature and secondly the pyridine was out-gassed at 300°C. At 300°C pyridine should only adsorb to the stronger Lewis acid sites. The number of sites, as a function of surface area, are shown graphically in figure 1.5. The ratio
of Lewis sites to surface area remains approximately constant for each of these materials considered. It is particularly interesting to note this is true even when only relatively strong Lewis acid sites are measured. This suggests that the type of Lewis acid sites that pyridine can adsorb to at 300°C are not necessarily strong enough to produce a catalytically active surface.

Figure 1.6 shows the temperature programmed desorption (TPD) curve of NH$_3$ from $\beta$-AlF$_3$ and amorphous HS-AlF$_3$ [10]. (Data for ACF is also present, but it is not relevant to this discussion.) It can be seen that both AlF$_3$ phases have a peak at around 340°C. HS-AlF$_3$ also has a peak at around 250°C, while $\beta$-AlF$_3$ appears to have a small shoulder at around this value. At higher temperatures there is a much larger shoulder for the HS-AlF$_3$ compared to $\beta$-AlF$_3$, this may be related to why HS-AlF$_3$ acts as a stronger Lewis acid than $\beta$-AlF$_3$. FT-IR studies of CO adsorbed to amorphous HS-AlF$_3$ and $\beta$-AlF$_3$ also suggest that there are proportionally more very strong Lewis acid sites on HS-AlF$_3$ than $\beta$-AlF$_3$; this data will be discussed in detail in chapter 9.
1.5.3 Catalytic Activity of AlF$_3$

The catalytic properties of AlF$_3$ materials are typically quantified through use of several test reactions. The reactions that are commonly considered are

$$\text{2CCl}_2\text{F}_2 \rightarrow \text{CCl}_3\text{F} + \text{CClF}_3$$  \hspace{1cm} (1.2)

$$\text{CCl}_2\text{FCClF}_2 \rightarrow \text{CCl}_3\text{CF}_3$$  \hspace{1cm} (1.3)

$$\text{CBrF}_2\text{CBrFCF}_3 \rightarrow \text{CF}_3\text{CBr}_2\text{CF}_3$$  \hspace{1cm} (1.4)

Crystalline $\alpha$-AlF$_3$ does not catalyse any of these reactions. HS-AlF$_3$ enables almost 100% conversion of reaction 1.2 at temperatures as low as 50°C [35]. This reaction proceeds on $\beta$-AlF$_3$, but it requires temperatures of around 400°C [37]. Reaction 1.3 proceeds on HS-AlF$_3$ with more than 90% conversion at a temperature of 100°C [10], this reaction only proceeds on $\beta$-AlF$_3$ at temperatures of 320°C or above. To obtain more
than 90% conversion a temperature of 420°C is required [40]. The third reaction (1.4) proceeds, to almost 100% conversion, at room temperature on amorphous HS-AlF₃ [35] and to approximately 18% conversion on crystalline HS-AlF₃; it does not occur at all on β-AlF₃. In comparison, the widely used SbF₅ catalyst requires temperatures of around 80°C before it can catalyse reaction [1.4]. In conclusion, the amorphous HS-AlF₃ is the most catalytically active material, crystalline HS-AlF₃ is also highly active, while β-AlF₃ is moderately active and α-AlF₃ is relatively inert.

1.6 Objectives of this Study

This study was part of a European Union Framework Programme Six (FP6) project on functionalised metal fluorides (FUNFLUOS). The FUNFLUOS project involved participants from six scientific groups across Europe, including one industrial partner. The members of the project brought together an expertise in a range of experimental, surface characterisation and theoretical methods. The aim of the FUNFLUOS project was to develop, characterise, and exploit, the industrial applicability of new inorganic fluorinated solid materials which have outstanding potential as industrial catalysts.

The search for new materials with specific properties involves the synthesis and characterisation of a large selection of related materials. Understanding the composition, structure and properties of any newly synthesised material is essential in this development process. Of even greater importance, however, is the understanding of how the composition of a material, its structure and its properties are all related to each other. If these relationships can be understood then predictions can be made upon the modifications required to synthesis a material with desired properties. This detailed understanding of these relationships allows us to develop a conceptual framework for a given group of related materials. In general, the relationships are very hard to establish using only experimental techniques. This is because it is not possible to have complete control over
the synthesis procedure or to have detailed knowledge of the structure and composition of a material, nor is it always possible to measure the key properties of a material. Theoretical modelling techniques are essential in the development of a conceptual framework. In theoretical modelling the exact composition and structure of the material investigated can be controlled and, in many cases, reliable calculations of relevant properties can be performed. In this way a detailed understanding of the relationship between structure, composition and properties of a material can be obtained.

We apply \textit{ab initio} modelling techniques to the study of aluminium fluorides. We predict the detailed structure of crystalline $\alpha$- and $\beta$-AlF$_3$ surfaces. We then extend this work to make predictions of the true nature of the synthesised HS-AlF$_3$ materials. An understanding of how the two differ may lead to improved synthesis methods that allow the production of materials with preferred characteristics.

Only in recent years has the accuracy, reliability and the efficiency of \textit{ab initio} calculations allowed us to study realistic models of complex materials for which detailed experimental characterisation is missing. In the real world, many important chemical reactions take place under high temperature and high pressure conditions. \textit{Ab initio} calculations have traditionally been thought of as zero-temperature, zero-pressure techniques, however they can be combined with atomistic thermodynamics to include the effects of finite temperatures and pressures. This allows predictive modelling of surface composition and structure under realistic conditions. This is the first time that such methods have been applied in the field of fluorine chemistry. These methods are of great importance as they can also be applied to a wide range of different materials in many other fields of research.

1.7 Outline of Thesis

In chapter 2 we discuss the theoretical framework of \textit{ab initio} calculations. We also describe some of the surface science techniques discussed in this study. All the \textit{ab initio}
calculations in this study are made using the CRYSTAL code. In chapter 3 we discuss how this code is used and factors that must be considered to obtain accurate and reliable results. Several new methodologies have been developed during the course of this project. This has resulted in the development of new software some of which has been implemented within CRYSTAL. These are discussed in Chapter 4.

In Chapters 5 to 12 we discuss the scientific work achieved in this study. In each of these chapters we start with an introduction and a description of the specific methodologies used. We then discuss the results obtained and make a series of conclusions based upon our results. In chapter 5 we investigate the surface of the natural cleavage plane of AlCl$_3$. The clean surfaces of $\alpha$-AlF$_3$ are investigated in Chapter 6. This study is then extended to consider the stable structures of two of these surfaces as a function of an environment containing gaseous H$_2$O and HF. In Chapter 7 we investigate the structure of the clean $\beta$-AlF$_3$ surface. In chapters 8 and 9 we quantify the strength of the Lewis acid sites on the stable surfaces of $\beta$-AlF$_3$. This is achieved through the investigation of the binding energies of the Lewis acid base, NH$_3$ to the surface and the stretch frequencies of adsorbed CO. In chapter 10 the adsorption of HF and HCl at the surface of $\beta$-AlF$_3$ is studied. The kinetics and energetics of the $\beta$-AlF$_3$ (100) surface is studied in chapter 11 and this work is then extended to consider the reaction mechanism for the dismutation of CCl$_2$F$_2$ in chapter 12. Finally, in chapter 13 we summarise the work.
Chapter 2

Theoretical Background

2.1 Introduction

In this chapter we discuss the background methods and notations used in this thesis. It is divided into two sections. In the first section we discuss electronic structure theory; predominately we deal with finding solutions to the Schrödinger equation. In the second section some of the experimental techniques that are referred to in this thesis are described.

2.2 Electronic Structure

2.2.1 The Schrödinger Equation

In first principles calculations we often want to find approximate solutions to the Born Oppenheimer non-relativistic time-independent Schrödinger equation [41]

\[ \hat{H}\Psi = E\Psi \]  

(2.1)
were $\Psi$ is the wavefunction, $\mathcal{E}$ is the electronic energy and $\hat{\mathcal{H}}$ is the Hamiltonian operator given, in atomic units, by

$$
\hat{\mathcal{H}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A \frac{1}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}
$$

(2.2)

where $r_{iA}$ is the distance between the $i$th electron and the $A$th nucleus, $r_{ij}$ is the distance between electrons $i$ and $j$ and $Z_A$ is the charge of nucleus $A$. $N$ is the number of electrons and $M$ in the number of nuclei in the system. In the proceeding discussions the summations limits will be dropped. The first term in equation 2.2 represents the kinetic energy of the electrons, the second term represents the Coulomb attraction between the electrons and nuclei and the third term describes the Coulomb repulsion between the electrons.

### 2.2.2 The Variational Principle

For a Hamiltonian, $\hat{\mathcal{H}}$, and any normalisable function $\Psi$, we can define the functional

$$
\mathcal{E}[\Psi] = \frac{\langle \Psi | \hat{\mathcal{H}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}
$$

(2.3)

The variational principle states that the expectation value of the Hamiltonian will be greater than or equal to the expectation value of the ground state wavefunction, that is

$$
\mathcal{E}[\Psi] \leq \mathcal{E}_0
$$

(2.4)

If $\mathcal{E}[\Psi] = \mathcal{E}_0$ then the wavefunction $\Psi$ is equal to the wavefunction of the ground state of the system.
2.2.3 The Hartree-Fock Approximation

Pauli’s antisymmetry principle states that a wavefunction should be antisymmetric with respect to the interchange of the space-spin coordinates of any two Fermions. Approximating $\Psi$ as an antisymmetrised product of $N$ orthonormal spin orbitals, $\chi_i(x)$, each a product of a spatial orbital, $\psi(r)$, and a spin functional, $\alpha(\omega)$ we can write

$$\Psi(x_1, x_2...x_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{ccc} \chi_1(x_1) & \chi_2(x_1) & \ldots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \ldots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \ldots & \chi_N(x_N) \end{array} \right|$$

(2.5)

$$= \frac{1}{\sqrt{N!}} \det[\chi_i, \chi_j \ldots \chi_k]$$

This is known as a Slater determinant. In the Hartree Fock approximation the Schrödinger equation is solved for this determinantal form of $\Psi$.

$$E_{HF} = \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \sum_i \int \chi_i^*(x) \left( -\frac{1}{2} \nabla_i^2 + \sum_A Z_A r_i^{-1} \right) \chi_i(x) dx$$

$$+ \frac{1}{2} \sum_{i,j} \int \int \chi_i^*(x_1) \chi_j(x_1) \chi_j^*(x_2) \chi_j(x_2) r_{12}^{-1} dx_1 dx_2$$

$$- \frac{1}{2} \sum_{i,j} \int \int \chi_i^*(x_1) \chi_j(x_1) \chi_i^*(x_2) \chi_j(x_2) r_{12}^{-1} dx_1 dx_2$$

(2.6)

The first term in equation 2.6 represents the electron kinetic energy and the electron-nuclei interactions. The second and third terms are two electron operators, $x_1$ and $x_2$ represent the coordinates of the pairs of electrons. The second term represents the Coulomb interaction of an electron in spin orbital $\chi_i$ with the average charge distribution of the system. The third term is more difficult to describe as it does not have a simple classical analogue. It arises from the antisymmetry requirement of the wavefunction. It is similar to
the Coulomb term except that there is an exchange of electron labels. The double summations in equation 2.6 include the \( i = j \) terms as the second and third terms cancel when \( i = j \).

The Hartree-Fock energy given by equation 2.6 must be minimised with respect to changes in the orbitals,

\[
\frac{\partial E}{\partial \chi_i} = 0 \quad (2.7)
\]

under the constraint that the orbitals remain orthonormal.

\[
\int \chi_i^*(x)\chi_j(x) = \delta_{ij} \quad (2.8)
\]

This results in the Hartree-Fock differential equations

\[
\hat{F}\chi_i(x) = \sum_j \epsilon_{ij}\chi_j(x) \quad (2.9)
\]

where

\[
\hat{F} = \hat{h} + \hat{j} - \hat{k} \quad (2.10)
\]

and

\[
\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A Z_A r_{iA}^{-1} \quad (2.11)
\]

\[
\hat{j}(x_1)f(x_1) = \sum_j \int \chi_j^*(x_2)\chi_j(x_2)r_{i1}^{-1} f(x_1)dx_2 \quad (2.12)
\]

\[
\hat{k}(x_1)f(x_2) = \sum_j \int \chi_j^*(x_2)\chi_j(x_2)r_{i2}^{-1} f(x_2)dx_2 \quad (2.13)
\]

where \( f(x_1) \) is an arbitrary function.

The Hartree-Fock equations can be solved in the space spanned by a set of basis
functions. These are then known as the Hartree-Fock-Roothaan equations. The orbital
basis functions can be written as a linear combination of atomic orbital basis functions,
\( \tilde{\chi} \):

\[
\chi_i = \sum_{\mu=1}^{K} C_{\mu i} \tilde{\chi}_\mu
\]  \hspace{1cm} (2.14)

for each spin orbital \( i \). Inserting these into the Hartree-Fock equation we obtain

\[
\hat{F} \sum_{\mu=1}^{K} C_{\mu i} \tilde{\chi}_\mu(x) = \sum_{j} \epsilon_{ij} \sum_{\mu=1}^{K} C_{\mu j} \tilde{\chi}_\mu(x)
\]  \hspace{1cm} (2.15)

Multiplying by \( \tilde{\chi}^*_\mu(x_1) \) and integrating we obtain

\[
\sum_{\nu} C_{\nu i} \int d\mathbf{x}_1 \tilde{\chi}^*_\mu(x_1) \hat{F} \tilde{\chi}_\nu(x) = \epsilon_i \sum_{\nu} C_{\nu i} \int d\mathbf{x}_1 \tilde{\chi}^*_\mu(x_1) \tilde{\chi}_\nu(x_1)
\]  \hspace{1cm} (2.16)

This matrix equation can be simplified by the introduction of

\[
S_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}^*_\mu(x_1) \tilde{\chi}_\nu(x_1)
\]  \hspace{1cm} (2.17)

\[
F_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}^*_\mu(x_1) \hat{F} \tilde{\chi}_\nu(x_1)
\]

This allows us to write the Hartree-Fock-Roothaan equations in matrix form

\[
\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}
\]  \hspace{1cm} (2.18)

or even more simply, they can be written as

\[
\mathbf{FC} = \mathbf{SC}\epsilon
\]  \hspace{1cm} (2.19)

where \( \epsilon \) is the diagonal matrix of the orbital energies \( \epsilon_i \). This would be equivalent to an
eigenvalue equation if it were not for the overlap matrix \( \mathbf{S} \). To eliminate \( \mathbf{S} \) the basis set is
transformed to an orthogonal basis set. The problem is then simplified to an eigenvalue equation. The equation must be solved iteratively as the orbitals \( \chi_i \) that solve the equation also appear in the operator \( F \). The Hartree-Fock method is consequently a self consistent field (SCF) method.

### 2.2.4 Beyond Hartree-Fock Theory

The Hartree-Fock equations describe non-interacting electrons in a mean field potential consisting of a classical Coulomb potential and a non-local exchange potential. Electron correlation is, however, neglected in this method. This can lead to results that differ substantially from experimental values. Several methodologies have been developed to include correlation in the electron wavefunction. An outline of some of these methods is given below.

The Schrödinger equation can be solved exactly if \( \langle \Psi | \hat{H} | \Psi \rangle \) is minimised by considering all possible values of \( \Psi \) obtained through linear combinations of the N-electron determinants made up from a total of M basis states, such that they define a complete basis set, \((M \gg N)\), this is known as full configuration interaction (CI). This method becomes impractical for modelling systems containing more than a few tens of electrons as there are

\[
M^C_N = \frac{M!}{N!(M-N)!}
\]  

N-electron determinants. This requires the diagonalisation of a matrix of dimension \( M^C_N \). For all but systems consisting of just a few electrons this method becomes prohibitively expensive. In practice the CI method is limited to determinants that are very similar to the Hartree-Fock ground state determinant. In single excitation CI one spin orbital is swapped with a virtual orbital, in doubly excited CI two spin orbitals are swapped for virtual orbitals. These methods limit the number of determinants in the expansion. The
computational cost required to solve these methods for systems containing more than a few 10’s of atoms used to be very high. In the last few years CI methods have been developed that scale linearly with system size, this is now allowing much larger systems to be studied using these techniques.

An alternate method is to use Perturbation theory. This method is based on the idea that if we can solve the Schrödinger equation for one system, that is for one Hamiltonian operator, then if we want to solve for a similar Hamiltonian we consider the difference between the operators as a small perturbation to the first solution. The solution to the second problem is written in terms of the first solution and various powers of the perturbation. A method of applying perturbation theory to the Schrödinger equation was derived by Møller and Plesset in 1933 [42] and is known as the MP\(n\) method. The \(n\) represents the highest power of the perturbation that is included in the calculation. The first important correction is the second order term and this leads to MP2. MP2 is relatively economic to evaluate and gives a reasonable proportion of the correlation energy and has recently been implemented for periodic systems. Higher order terms become more and more expensive. MP3 does not seem to give much improvement over MP2. MP4 gives reasonable results but it is much more expensive than MP2. Higher order terms are rarely evaluated. The computational cost required to solve these methods for systems containing more than a few 10’s of atoms used to be very high. In the last few years local correlation techniques have been developed that scale linearly with system size, this is now allowing much larger systems to be studied using these techniques.

Another alternate method of solution is to use the Quantum Monte Carlo technique [43]. In this method the full set of \(MC_N\) is sampled using a Monte Carlo technique. Strictly this method is only exact if every \(MC_N\) value is sampled. It has, however, been shown to converge very closely to the exact result for a finite number of samples. Recent code developments have lead to algorithms in which this method almost scales linearly with the number of atoms. It is still very expensive, however, as the pre-factor in the
scaling is large.

2.2.5 Density Functional Theory

The Hamiltonian operator, $\hat{H}$, consists of single electron and electron-electron interactions. That is, operators that require only the knowledge of one or two electrons. To compute the total energy of a system it is not necessary to have the full $3N$ dimensional wavefunction. Knowledge of the two particle probability density, that is, the probability of finding an electron at $r_1$ and an electron at $r_2$ is sufficient. Density Functional Theory (DFT) is based on the idea that only knowledge of the particle density is required to obtain an exact solution of the ground state energy of a system.

2.2.6 Thomas-Fermi Theory

The first form of DFT was developed in the 1920’s by Thomas and Fermi [44, 45]. This was the first time in which the electronic charge density was considered as a fundamental variable as opposed to the wavefunction. The local charge density, $\rho(r)$ is considered to be equal to that of an equivalent uniform homogeneous electron gas. The number of electrons in a given element $dr$ is equal to $\rho(r)dr$. The energy, as a function of $\rho(r)$, is given by

$$
E_{TF}[\rho(r)] = \int \nu(r)\rho(r)dr + \int \frac{3}{10} \left(\frac{3\pi^2}{2}\right)^{2/3} \rho^{2/3}(r)dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} drdr' \tag{2.21}
$$

The first term is the classical Coulomb interaction energy between the nuclei and electrons. The second term is the kinetic energy associated with a system of non-interacting electrons in a homogeneous electron gas. The third term is the classical electron-electron Coulomb interaction energy. The variational principle (equation 2.4) can be applied to
minimise the energy, $E_{TF}$, subject to the condition that

$$\int \rho(r) dr = N$$  \hspace{1cm} (2.22)

This leads to the Thomas-Fermi self-consistent equations

$$\nu(r) + \frac{1}{2} \left( \frac{3\pi^2}{2} \right)^{\frac{2}{3}} \rho^{\frac{2}{3}} + \int \frac{\rho(r')}{|r-r'|} dr' - \mu = 0.$$  \hspace{1cm} (2.23)

These equations can be solved to obtain the ground state density, $\rho_0$. This approach is very simple and is qualitatively correct for atoms. However, it suffers from a number of deficiencies. The most serious being that it does not predict bonding between atoms, hence molecules and solids cannot form according to this theory. The main source of error comes from the approximation used for the kinetic energy. The electron-electron interactions are also only considered classically, this also introduces errors into the calculation. To overcome these problems it is necessary to move on to the work of Hohenburg, Kohn and Sham.

2.2.7 The Hohenburg-Kohn Theorem

The Hohenburg-Kohn theorem states that given a ground state density, $\rho_0(r)$ it is possible, in principle, to calculate the corresponding ground state wavefunction, $\Psi_0$. This implies that there is a one to one mapping between $\rho_0(r)$ and $\Psi_0$. $\Psi_0$ is a functional of $\rho_0(r)$ and all ground state observables are functionals of $\rho_0(r)$.

For a given $\rho_0(r)$, the ground state energy can be written as

$$E_0 = \min_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{H} | \Psi \rangle$$  \hspace{1cm} (2.24)

that is, for a given density $\rho_0(r)$ the ground state wavefunction, $\Psi_0$ is one that reproduces
\( \rho_0(\mathbf{r}) \) and minimises the energy. For an arbitrary density \( \rho(\mathbf{r}) \) we define the functional

\[
E[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \mathcal{H} | \Psi \rangle
\] (2.25)

If \( \rho \neq \rho_0 \) then \( \Psi \neq \Psi_0 \) and, hence, according to the variational principle \( E[\rho] > E_0[\rho_0] \) and the function \( E[\rho] \) is minimised by the ground state density \( \rho_0 \).

### 2.2.8 The Kohn-Sham Equations

In section 2.2.1, we showed that the electronic Hamiltonian is a sum of three terms, the kinetic energy, the electron-electron interaction and the electron-nuclei interaction. We can write the energy functional as a sum of these terms

\[
E[\rho] = T[\rho] + E_{ee}[\rho] + E_{eN}[\rho]
\] (2.26)

the electron-nuclei interaction is given by

\[
E_{eN}[\rho] = \int \tilde{E}_{eN}[\rho(\mathbf{r})]d\mathbf{r}
\] (2.27)

The kinetic and potential energy functionals are unknown. Kohn and Sham [46] developed a methodology to approximate these functionals. A fictitious system of \( N \) non-interacting electrons is described by a single determinant wavefunction in \( N \) orbitals, \( \phi_i \). The kinetic energy for this fictional system is given by

\[
T_{KS}[\rho] = -\frac{1}{2} \sum_{i}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle
\] (2.28)

and the electron density is given by

\[
\rho(\mathbf{r}) = \sum_{i}^{N} |\phi_i|^2
\] (2.29)
The electron-electron interaction can be described to an approximate level by considering
the classical Coulomb interaction, also known as the Hartree energy.

\[ E_H[\rho] = \frac{1}{2} \int \rho(\mathbf{r})\rho(\mathbf{r}') \frac{|\mathbf{r} - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' \]  \hspace{1cm} (2.30)

The energy functional can be rewritten as

\[ E[\rho] = T_{KS}[\rho] + E_H[\rho] + E_{eN}[\rho] + E_{xc}[\rho] \]  \hspace{1cm} (2.31)

where \( E_{xc} \) is the sum of the errors in the approximation made in assuming a non-interacting
kinetic energy term and in treating the electron-electron interaction classically. Writing
equation \( 2.31 \) explicitly in terms of the density built from the non-interacting orbitals, and
applying the variational theory, the optimal \( \phi_i \) satisfy

\[ \left[ -\frac{1}{2} \nabla^2 + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \nu_{ext}(\mathbf{r}) + \nu_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \]  \hspace{1cm} (2.32)

where

\[ \nu_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \]  \hspace{1cm} (2.33)

This set of equations are known as the Kohn-Sham equations. They describe a set of non
interacting electrons in an effectively local potential. Given the exact \( E_{xc} \) functional, the
exact ground state energy can be calculated. The equations are very similar in form to the
Hartree-Fock equations, only the non local exchange potential in the Hartree-Fock equa-
tions is replaced with the local exchange-correlation potential. It is, however, important to
remember that \( \nu_{xc} \) is not the sum of the exchange and correlation energies as understood
by Hartree-Fock theory as it also contains an element of the kinetic energy.

The exact form of \( \nu_{xc} \) is currently not known. The functional is, however, universal
and not dependent on the material being studied. Many approximations to $E_{xc}$ have been developed, the accuracy of any given functional depends, in part, on the type of system being studied. It is important to understand the derivation and structure of the functionals to enable an informed decision to be made on which functional to use for any particular study.

2.2.9 The Local Density Approximation

In the 1920’s Thomas and Fermi studied the homogeneous electron gas (see section 2.2.6). The kinetic energy of a non-interacting homogeneous electron gas is given by

$$T[\rho] = 2.87 \int \rho^{\frac{5}{3}}(r)dr$$ (2.34)

and the exchange energy is given by

$$E_x[\rho] = 0.74 \int \rho^{\frac{7}{3}}(r)dr$$ (2.35)

This suggests that $E_{xc}$ for an inhomogeneous system could be approximated in the form

$$E_{xc}[\rho] \approx \int \rho(r)\epsilon_{xc}[\rho(r)]dr$$ (2.36)

$\epsilon_{xc}$ can be separated into contributions from the exchange and the correlation,

$$\epsilon_{xc}[\rho] = \epsilon_x[\rho] + \epsilon_c[\rho]$$ (2.37)

Using equation (2.35) we can write

$$\epsilon_x[\rho] = -C\rho^{\frac{5}{3}}$$ (2.38)
The constant C can be determined from the homogeneous electron gas, but for generality it has been left as a free constant.

The functional form of the correlation energy density was first estimated in 1938 by Wigner [47] to be

\[ \epsilon_c(\rho) = -\frac{0.44}{r_s + 7.8} \]  

where \( r_s \) is the radius of a sphere containing one electron. In 1980 Ceperley and Alder calculated the form of \( \epsilon_c(\rho) \) by simulating the electron gas using an (almost) exact solution to the Schrödinger equation using the Quantum Monte Carlo method [48]. \( \epsilon_c \) has since been fitted to a number of analytical forms, all of which yield similar results and are collectively known as Local Density Approximation (LDA) functionals.

The LDA has been shown to provide very good approximations to the ground state solution of the Schrödinger equation. Its prediction of the total energy of a system is not accurate, however, in many cases the shape of the energy surface is accurately predicted. It typically gives bond lengths to an accuracy of around 1%. It can predict geometries, vibrational frequencies, elastic moduli and phase stability of molecules and solids remarkably well. It is less accurate, however, in the calculation of binding energies. It typically over-estimates them by around 20% and under-estimates energy barriers in diffusion processes or chemical reactions. Given the simplicity of the approximation, it is surprising just how well this functional works.

The reason that the LDA approximation is so accurate is, in part, due to the way in which errors made within the approximation are cancelled out. It has been shown that the functional under-estimates the exchange energy but over-estimates the correlation energy [49]. Another reason for the success of the LDA functional is that it makes a good approximation of the spherically averaged exchange-correlation hole, despite making a poor estimate of its functional form. The exchange-correlation hole is a feature that arises
from the interaction of electrons. It can be thought of as the hole that an electron at \( r_1 \) digs for itself in the surrounding density. The reduction in the surrounding density should be equal to one electron, that is,

\[
\int P_{xc}(r_1, r_2) dr_2 = -1
\]  

(2.40)

where \( P_{xc}(r_1, r_2) \) describes the electron density at \( r_2 \) given an exchange-correlation hole centred at \( r_1 \).

In many systems the exchange energy is much greater than the correlation energy. Therefore, an improvement on the LDA may be to calculate the non-local exchange potential exactly, as in Hartree-Fock theory and the correlation potential in the LDA,

\[
E_{xc} \approx E_{Fock} + E_{c}^{LDA}
\]  

(2.41)

However, because in part the accuracy of LDA depends on the cancellation between the errors in the exchange and correlation energies, in general using the exact exchange does not yield good results. The Hartree-Fock non-local exchange potential gives a very good local and semi-local description but introduces a pathological non local feature into the exchange-correlation hole distribution function. To improve on the LDA it is necessary to incorporate some of the features of the exact exchange interaction but to also include methods that preserve the analytical properties of the exchange-correlation holes.

### 2.2.10 The Generalised Gradient Approximation

The LDA is a zeroth order approximation to the semi-classical expansion of the density matrix in terms of the density and its derivatives. An obvious improvement to this estimation is to include the first order gradient terms. This, however, leads to a number of approximations to the exchange hole, for instance it does not normalise to -1 (equa-
The generalised gradient approximation (GGA) has added constraints that ensure that the normalisation condition is applied. The energy functional depends both on the density and its gradient while retaining the analytical properties of the LDA energy functional. The GGA functional is written as

$$E_{xc} \approx \int \rho(r) \epsilon_{xc}(\rho, |\nabla \rho|) dr$$ (2.42)

A number of functionals within the GGA family have been developed. The GGA improves significantly on the LDA on the prediction of binding energies of molecules. A full description of its performance will be presented in section 2.2.12.

Recently, GGA functionals have been extended to include the semi-local information of the electron density and/or the kinetic energy, \(\tau\), where

$$\tau = \frac{1}{2} \sum_i |\nabla \chi_i|^2$$ (2.43)

These functionals are known as meta-GGA functionals, they typically take the form of

$$E_{xc} \approx \int \rho(r) \epsilon_{xc}(\rho, |\nabla \rho|, |\nabla^2 \rho|, \tau) dr$$ (2.44)

### 2.2.11 Hybrid Exchange Functionals

An exact connection can be made between a non-interacting DFT system and a fully interacting many body system via the integration of the work done in gradually turning on the electron-electron interactions. Hartree Fock theory describes the system in which there are no electron-electron interactions. The LDA and GGA functionals provide excellent approximations for a fully interacting homogeneous electron gas. It is, therefore, reasonable to approximate the solution of the Schrödinger equation by using an exchange
correlation functional given by

\[ E_{xc} \approx \alpha E_{\text{Fock}} + \beta E_{xc}^{\text{GGA}} \]  \hspace{1cm} (2.45)

where the coefficients \( \alpha \) and \( \beta \) can be determined with reference to a system for which exact results are known. This is the method that Becke [50] adopted. He calculated co-efficients to fit a wide range of data of observed atomisation energies, ionisation potentials, proton affinities and total atomistic energies for a small number of molecules. The resultant energy functional is

\[ E_{xc} \approx E_{xc}^{\text{LDA}} + 0.2(E_{x}^{\text{Fock}} - E_{x}^{\text{LDA}}) + 0.72\Delta E_{x}^{\text{B88}} + 0.81\Delta E_{c}^{\text{PW91}} \]  \hspace{1cm} (2.46)

were \( \Delta E_{x}^{\text{B88}} \) and \( \Delta E_{c}^{\text{PW91}} \) are the widely used GGA corrections [51, 52] to the LDA exchange and correlation energies respectively.

Hybrid functionals have been enormously successful and are widely used in many chemical applications most commonly with the B3LYP functional. This functional is similar to the one given in equation 2.46 only a different GGA functional is used to describe the correlation. As will be shown in the next section, binding energies, geometries and frequencies are calculated more accurately using this method than with the best GGA functionals.

\[ \text{2.2.12 Performance of Different Functionals} \]

The development of new functionals in DFT has led to an overall increase in the accuracy of the method. In general, the hybrid exchange functionals are the most accurate, followed by the meta-GGA functionals, then the GGA, then the LDA functionals for calculation of observables of a wide range of materials.

In general there are two methodologies that are used in the production of functionals.
The first method is to use the exact properties of the functional to derive its structure and parameters. Alternatively, functionals can be further parameterised to obtain better fitting to a given set of reference data. This method is largely empirical in its approach. Some functionals can be considered to be on the boundaries between both of these methods.

Several commonly used functionals are listed and characterised in table 2.1. The ability of these functionals to accurately predict several properties of a range of molecular and crystalline systems have recently been benchmarked by Kurth et al [53] and Adamo et al [54]. In table 2.2 we summarise some of the results from these studies.

It can be seen that the LDA has a tendency to over-predict binding energies by around 20%. The GGA functionals predict binding energies significantly more accurately. The highly parameterised GGA functional (HCTH) improves upon the other GGA functionals and compares well with the meta GGA functionals. The lightly parameterised hybrid functional performs as well as the best (highly parameterised) meta-GGA functional.

In consideration of the predicted structures the LDA compares well with the GGA and meta-GGA functionals. It is interesting to note that the highly parameterised meta-GGA functional (VS98) is more accurate than the unparameterised meta-GGA functional (PKZB) for molecules but this situation is reversed for crystals. This is, in part, because highly parameterised functionals are often developed to fit molecular data and hence have a bias towards molecular systems.

<table>
<thead>
<tr>
<th>Mnemonic</th>
<th>Family</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA [55]</td>
<td>Local</td>
<td>-</td>
</tr>
<tr>
<td>PBE [56]</td>
<td>GGA</td>
<td>-</td>
</tr>
<tr>
<td>BLYP [57]</td>
<td>GGA Light</td>
<td></td>
</tr>
<tr>
<td>HCTH [58]</td>
<td>GGA 18</td>
<td></td>
</tr>
<tr>
<td>PKZB [59]</td>
<td>Meta GGA 1</td>
<td></td>
</tr>
<tr>
<td>VS98 [60]</td>
<td>Meta-GGA 21</td>
<td></td>
</tr>
<tr>
<td>B3LYP [50]</td>
<td>Hybrid-exchange 3</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.2: The maximum relative errors (MRE) and mean absolute errors (MAE) for the atomisation energies, structures, bulk moduli and vibrational spectra for a collection of molecules and crystalline materials. Maximum values for any molecule or crystal are given in brackets. The MRE for atomisation energies are for a collection of 20 molecules and the MAE is for a collection of 148 molecules. The structure MRE value is for cell volumes of 12 crystals and the MAE value is for the bond lengths of 23 molecules. The bulk moduli data is for a sample of 12 crystals and the vibrational frequencies are for a sample of 55 molecules.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Atomisation Energies</th>
<th>Structures</th>
<th>Bulk Moduli</th>
<th>Vibrational Frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MRE (%) MAE (kcal mol(^{-1}))</td>
<td>MRE (%) MAE (Å)</td>
<td>MRE (%) MAE</td>
<td>MRE (%) MAE (cm(^{-1}))</td>
</tr>
<tr>
<td>LDA</td>
<td>22 -</td>
<td>5 -</td>
<td>19 -</td>
<td>-</td>
</tr>
<tr>
<td>PBE</td>
<td>7 17 (51)</td>
<td>4 0.011 (0.064)</td>
<td>10 -</td>
<td>65(-194)</td>
</tr>
<tr>
<td>BLYP</td>
<td>5 -</td>
<td>8 -</td>
<td>22 -</td>
<td>-</td>
</tr>
<tr>
<td>HCTH</td>
<td>3 -</td>
<td>6 -</td>
<td>20 -</td>
<td>-</td>
</tr>
<tr>
<td>PKZB</td>
<td>3 5 (38)</td>
<td>3 0.019 (0.111)</td>
<td>9 -</td>
<td>72 (144)</td>
</tr>
<tr>
<td>VS98</td>
<td>2 3(12)</td>
<td>8 0.008 (0.08)</td>
<td>29 -</td>
<td>33 (-109)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>- 3 (20)</td>
<td>- 0.007 (0.062)</td>
<td>-</td>
<td>40 (-209)</td>
</tr>
</tbody>
</table>

In calculations of bulk moduli it can be seen that in general the lightly parameterised functionals provide the most accurate results. The accuracy improves as we move from LDA to GGA to meta-GGA functionals. There is also a general trend in which vibrational frequencies become more accurate as we move from GGA to meta-GGA to hybrid methods.

Overall it can be seen that there is trend in which the accuracy improves as we move from LDA to GGA to meta-GGA to hybrid functionals. The highly parameterised functionals describe molecular systems well but generally do not transfer well to crystal structures. In our studies of crystalline metal halide systems we will, hence, use the B3LYP hybrid functional.


### 2.3 Experimental Techniques

#### 2.3.1 BET Surface Area

The BET method is commonly used to determine the surface areas of solids by measurement of the physical adsorption of gas molecules. The method was developed by Stephen Brunauer, Paul Emmett, and Edward Teller in 1938 [61]. It is assumed that gas molecules physically adsorb on a solid in layers, that there is no interaction between each adsorption layer and that the Langmuir theory of adsorption can be applied to each layer. The total surface area of a material is given by

$$ S_{\text{total}} = \frac{\nu_m N \sigma}{m} $$

(2.47)

where $\nu_m$ is the mass of the monolayer of adsorbed gas, $N$ is Avogadro’s number, $\sigma$ is the adsorption cross section and $m$ is the molecular mass of the adsorbate. Nitrogen is commonly used as the adsorbate to measure the BET surface area of AlF$_3$ surfaces. $\beta$-AlF$_3$, for example, typically has a BET surface area of around 25 m$^2$g$^{-1}$ [10].

#### 2.3.2 Temperature Programmed Desorption

Temperature programmed desorption (TPD) can be used to experimentally determine the binding energy of a molecule to a given surface. The desorption of molecules from a surface is observed as the surface temperature is increased. The rate of desorption can then be used to determine approximate binding energies of the gas to the surface. Assuming that the vibrational frequency ($\nu$) of the adsorbate and the energy of desorption ($E_{\text{des}}$) are independent of the adsorbate concentration, $\sigma$, the energy of desorption (assuming first order desorption and that readsorption does not occur) is given by the Redhead
where the temperature rise is given by $T = T_0 + \alpha t$. $T_p$ is the temperature at which the desorption peak occurs and $R$ is the molar gas constant.

### 2.3.3 Infra Red Spectroscopy

Infrared (IR) spectroscopy exploits the fact that photon energies associated with the IR spectrum can cause bonded atoms to rotate and vibrate. The frequency of the vibrations and rotations can be associated with a particular bond type. IR spectroscopy involves passing IR light through a sample and observing the transmitted light. The vibrational frequencies of the sample can then be obtained from the resultant absorption spectrum and information about its structure can be deduced.

### 2.3.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that can provide information on the elemental composition and electronic state of elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that are emitted from the top few nm of the material. The binding energy (BE) of each of the emitted electrons is given by

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi$$  \hspace{1cm} (2.49)

where $E_{\text{binding}}$ is the binding energy of the electron emitted from one electron configuration within the material, $E_{\text{photon}}$ is the energy of the X-ray photons being used, $E_{\text{kinetic}}$
is the kinetic energy of the emitted electron as measured by the instrument and $\phi$ is the work function of the spectrometer.

Each element produces XPS peaks at characteristic binding energy values that directly identify the element type that exists in or on the surface of the material being analysed. These characteristic peaks correspond to the configuration of the electrons within the atoms: 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area irradiated. Furthermore, the binding energy of the peaks is also sensitive to the electronic configuration of the element, hence, information about the electronic and geometric structure of a given material can also be obtained.
Chapter 3

The CRYSTAL Code

3.1 Introduction

The CRYSTAL code [63] is used for all the ab initio calculations in this thesis. CRYSTAL implements Hartree-Fock theory and density functional theory (DFT) using local Gaussian basis sets for systems periodic in three, two, one and no dimensions. The code is jointly developed by the Theoretical Chemistry group at Turin University in Italy and the Computational Materials Science Group in the STFC in the UK, of which I am a member.

This chapter is split into three sections. In the first section we briefly discuss the implementation of Hartree-Fock theory and DFT in periodic systems. In the second section the implementation of basis sets in CRYSTAL is discussed and the basis sets used in this thesis are presented. In the third section we discuss some of the factors that must be considered in order to obtain reliable and accurate results from the CRYSTAL code.

3.2 Periodic Systems

We consider a finite chain of $N$ evenly spaced atoms and eliminate end effects by assuming that the chain is repeated an infinite number of times. The wavefunction of the
electrons will vary along the chain. We apply periodic boundary conditions, hence the wavefunction goes back to the same value after $N$ lattice spacings. This can be written as

$$\Psi(x + Na) = \Psi(x) \quad (3.1)$$

where $a$ is the lattice spacing between atoms and $\Psi(x)$ is the wavefunction at position $x$. The spacing of atoms is uniform, hence the electron density along the chain must be unchanged if we translate the chain by one lattice spacing,

$$\rho(x + a) = \rho(x) \quad (3.2)$$

where $\rho$ is the electron density, given by

$$\rho(x) = \Psi^*(x)\Psi(x) \quad (3.3)$$

It must therefore be true that

$$\Psi(x + a) = \mu \Psi(x) \quad (3.4)$$

where $\mu$ is a complex number such that $\mu^*\mu = 1$. The effect of translation through a number of lattice spacings is given by

$$\Psi(x + na) = \mu^n \Psi(x) \quad (3.5)$$

where $n$ is an integer. It can be seen from equations 3.1 and 3.5 that $\mu^N = 1$ and hence,

$$\mu = \exp(2\pi ip/N) = \exp(ika) \quad (3.6)$$
where $p$ is an integer and $k$ is given by

$$k = \frac{2\pi p}{Na} \quad (3.7)$$

$k$ is often referred to as the wavenumber. Equation 3.7 defines distinct allowed states for $k$, it only takes values that are a multiple of $2\pi/Na$. Returning to equation 3.4 we can write

$$\Psi(x + a) = \exp(ika)\Psi(x) \quad (3.8)$$

A general solution for $\Psi$ is

$$\Psi(x) = \exp(ikx)u(x) \quad (3.9)$$

where $u(x)$ is any periodic function that satisfies

$$u(x + a) = u(x) \quad (3.10)$$

$\Psi$ is known as a Bloch function. Bloch functions are often constructed from overlapping atomic orbitals. The orbitals on each atom form the periodic function $u(x)$ while the amplitude of the wavefunction is modulated by the $\exp(ikx)$ term. The functions have a wavelike form with a wavelength, $\lambda$ given by

$$\lambda = \frac{2\pi}{k} \quad (3.11)$$

De Broglie’s formula relates the wavelength of a particle to its momentum, $p$,

$$p = \frac{\hbar}{\lambda} \quad (3.12)$$
Combining this with equation 3.7 we obtain

\[ p = \hbar k \]  \hspace{1cm} (3.13)

Hence it can be seen that \( k \) is proportional to the momentum of an electron. These equations can easily be extended to two and three dimensions. In multiple dimensions \( k \) will have a direction associated with it. It becomes a vector quantity, \( k \), and is referred to as a wavevector.

### 3.2.1 Implementation in CRYSTAL

In the CRYSTAL code, Hartree-Fock and density functional theory are implemented using a crystalline orbital method. This is an extension of the standard linear combination of atomic orbitals (LCAO) technique to periodic systems. The local functions \( \psi_\mu(r) \) define the Bloch functions, \( \phi_\mu(r; k) \), defined in equation 3.10. Each crystalline orbital, \( \psi_i(r; k) \) is defined as a linear combination of the Bloch functions.

\[
\phi_\mu(r; k) = \sum_g \phi_\mu(r - C_\mu - g) \exp(ik \cdot g) \hspace{1cm} (3.14)
\]

\[
\psi_i(r; k) = \sum_\mu c_\mu(k) \phi_\mu(r; k) \hspace{1cm} (3.15)
\]

where \( c_\mu \) are the expansion coefficients of the Bloch functions, \( C_\mu \) denotes the coordinate of the nucleus in the zero reference cell on which \( \psi_\mu \) is centred and the \( \sum_g \) is the sum over all lattice vectors, \( g \).

### 3.3 Basis sets

In the CRYSTAL code \textit{ab initio} methods are implemented using Gaussian basis sets. There are many other \textit{ab initio} codes, however, that describe the basis sets using plane
waves. Examples of such codes include the widely used CASTEP [64], VASP [65], CPMD [66] and ABINIT [67] programmes. There are several advantages and disadvantages of using Gaussians instead of plane waves in calculations.

In plane wave calculations the electron density is described in terms of linear combinations of functions of the form

\[ \Psi_k(r) = \sum_g c_g^k \exp(i(\mathbf{k} + \mathbf{g}) \cdot \mathbf{r}) \]  

An infinite number of basis functions would be required to exactly recreate the true wave-function. In practice, a finite set of plane waves must be used, restricting the detail that can be revealed in real space to the extent that it is not practical to describe the core electrons in this manner. Therefore it is necessary to either use additional functionals (such as the (F)LAPW or PAW schemes) or to describe the core electrons using pseudopotentials. The set of basis functions is universal. It does not depend on the type of atom or their positions in the unit cell. It is, therefore, not necessary to construct a new basis sets for every atom in the periodic table or modify them for use in different materials as is required with Gaussian basis sets.

In contrast, Gaussian basis sets allow accurate descriptions of the electronic distributions both in the valence and the core regions with a limited number of basis functions. The local nature of the basis sets allows treatment of both finite systems and those which are periodic in either one, two or three dimensions. A big advantage of this is that it allows molecules, polymers and surfaces to be modelled without imposing artificial periodicity. Conversely, in plane wave codes only three dimensionally periodic systems can be studied. To study a system that is finite in a given dimension it is necessary to include a large vacuum gap between repeating images of the system. Having an atomic-like basis set allows easier population analysis and computation of properties such as projected densities of state and pre SCF alterations of orbital occupations. The choice of whether to use plane
wave or Gaussian basis sets often depends upon the type of system being investigated. In general, systems in which the electrons are highly localised, such as very ionic systems Gaussian basis sets should be used. Conversely, in systems where the electrons are non-localised, for instance in bulk free electron metals such as lithium and aluminium, plane wave methodologies are often preferable.

3.3.1 Gaussian Basis Sets

In periodic systems, as in molecules, the fundamental idea behind using localised Gaussian-type functions is the ‘atoms in molecules’ concept. That is molecules can be described as an assembly of slightly perturbed atoms.

The wavefunction must have a cusp at the nucleus, due to the singularity of the potential at a point with a charge of $+Z$. At the other extreme, an electron far from a molecule must see the molecule as a positive charge with no particular structure and the wavefunction must decay exponentially. Exponential functions are hence a suitable choice for describing the basis functions. Historically, Slater type orbitals (STOs) have been used to describe basis functions.

Slater-type orbitals, however, are not suitable for the fast calculation of multi-centre integrals. Gaussian type functions (GTFs) are hence used in quantum chemistry calculations. In Cartesian form these can be written as

$$\chi^{\text{GTF}} = \exp(-\alpha r^2) x^l y^m z^n$$

(3.17)

where $\alpha$ is the exponent and $l$, $m$ and $n$ are not quantum numbers but simply integer exponents of the Cartesian coordinates. In this form, referred to as Gaussian primitives, the orbitals can be factorised into their Cartesian components.

$$\chi^{\text{GTF}} = \chi_x^{\text{GTF}} \chi_y^{\text{GTF}} \chi_z^{\text{GTF}}$$

(3.18)
where each component has the form

\[ \chi_x^{\text{GTF}} = (x - x_a)^l \exp \left( -\alpha (x - x_a)^2 \right) \]  

(3.19)

where each Gaussian is centred at position \( x_a \). This greatly simplifies the calculation of the integrals. Slater type orbitals are not separable into Cartesian components due to the \( r \) term in their exponential term.

The absence of the pre-exponent factor \( r^{n-1} \) restricts single Gaussian primitives to only approximating 1s, 2p, 3d etc. orbitals (i.e. not 2s, 3p etc). However combinations of Gaussian primitives can be used to approximate the correct nodal properties of atomic orbitals if the primitives are included with different signs. The sum of the exponents of Cartesian coordinates, \( L = l + m + n \) is analogous to the angular momentum quantum number. s-type Gaussian orbitals are represented by \( L = 0 \), p-type by \( L = 1 \), d type by \( L = 2 \) and so on.

It is desirable to describe orbitals as accurately as possible using a minimum number of basis sets. To achieve this, Gaussian type basis functions are expanded as a linear combination of individually normalised Gaussian primitives. These all have the same centre and angular momentum quantum numbers, but with different exponents,

\[ \chi_i(r) = \sum_{j=1}^{L} d_j g_j(r) \]  

(3.20)

where

\[ g_j(r) = g(r, \alpha, l, m) = N_{lm}(\alpha)r^l Y_{lm}(\theta, \phi) \exp(-\alpha_j r^2) \]  

(3.21)

where \( L \) is the length of the contraction, \( \alpha_j \) are the contraction exponents, \( d_j \) are the contraction coefficients. The Gaussian primitives are written in terms of spherical harmonics, including a normalisation factor. With the correct choice of values for \( L, \alpha_j \) and \( d_j \) con-
tracted Gaussians’ can be produced with any desired functional form consistent with the primitive functions used. The same radial functions can be used for an s and p shell with the same principal quantum number. This gives rise to the contracted sp shells.

In basis set contraction schemes the orbitals are grouped into shells. The shells are constructed from contractions of Gaussians. The number of shells used to represent a single Slater orbital (i.e. zeta) is used as a measure of quality of the set. A single zeta basis set uses a single shell for each of the atomic orbitals, a double zeta uses two and a triple zeta uses three and so on. Often more terms are used to describe valence orbitals than core orbitals, this effectively allows the core orbitals to ‘breathe’. The term split-valence is used to describe this. For example DZV (double zeta valence) would refer to a basis set with one shell for core orbitals and two for valence orbitals.

Polarisation functions are functions of higher angular quantum number than the highest occupied orbital in the system. This allows polarisation of charge. For instance, adding a p-type function to a hydrogen atom that is placed in a non uniform field allows its charge distribution to become asymmetric, polarising the atom. A hydrogen atom in a molecule experiences a similar non uniform field.

There are many other notations used to describe basis sets. The other most commonly used system uses notation of the form 6-31G*. This denotes a basis set with six Gaussians describing each of the core atomic shells, and two valence shells, the inner one is expanded in three Gaussians and the outer one is uncontracted. It is usual for the most diffuse basis function to be left uncontracted as the outer part of the valence is very distorted from the atomic picture and hence flexibility is more important than atomic resemblance. The * represents the presence of a polarisation functions (2 *’s would denote two polarisation functions).
3.3.2 Basis Set Super-position Error

A problem associated with non-complete basis sets is one of basis set super-position error (BSSE). If we consider a system comprising of two fragments, A and B, the basis sets on A and B will, in practice, be incomplete. This means that fragment A can make use of the basis set on fragment B in order to better describe its own basis set orbitals and hence lower its total energy and *vice versa*. This will occur whether there is a genuine binding interaction between the two fragments or not. The overall effect of this is to lower the total energy of the combined system, effectively producing a spurious increase in the binding energy between the two fragments.

The most common approach for estimating BSSE is to use the counterpoise correction method [5]. The energy of the fragments A and B are calculated in isolation from each other. The geometries used in these calculations are the geometries adopted by the fragments when they are part of the combined A+B system. The energies of these fragments are then calculated again, only this time the basis functions of the other fragment are left behind. The difference between these two energy calculations on each fragment provides a good estimate of the BSSE.

In general, the majority of BSSE is due to the tails of one basis set being used to improve the description of the core basis set in another atom. Therefore, to reduce the amount of BSSE a better description of the core basis sets is usually required. The core basis set has a very small effect on the final geometry of a system as core electrons are not involved in binding between atoms. The evaluation of BSSE is hence generally only of importance when an accurate estimation of the binding energy is required. Examples of such calculations are studies of molecules adsorbed on surfaces.
3.3.3 Mulliken Population Analysis

There is no unique definition of how many electrons are attached to an atom in a crystal or molecular structure. It is, however, often very useful to be able to perform such a population analyses. Due to its simplicity, the Mulliken population analysis is one of the most popular methods for assigning electrons to specific atoms.

The terms in the electron density matrix are partitioned democratically to the individual orbitals. The total number of electrons assigned to a particular atom is given by the sum of the density on each of its orbitals. As with other schemes of partitioning the electron density, Mulliken population analysis is arbitrary and strongly dependent on the particular basis set employed. A comparison of population analyses for a series of molecules is, however, useful for a quantitative description of intra-molecular interactions, chemical reactivity and structural features.

3.3.4 The Basis Sets used in this Thesis

Polarised triple valence Gaussian basis sets were used for all ab initio calculations in this thesis. The Al, Cl and F basis sets used to describe AlCl₃ and AlF₃ are shown in tables 3.1 and 3.2. An 85-11G* basis set was used for aluminium. This basis set was originally obtained by minimisation of the energy of the isolated atom. The 4sp and 3d exponents were subsequently optimised in bulk Al₂O₃ [68]. An 8-6-311G* basis set was used for chlorine and a 7-311G* basis set was used for fluorine. These basis sets were originally obtained from optimisation of isolated Cl⁻ and F⁻ ions [69]. They are therefore good for ionic crystals, such as AlCl₃ and AlF₃ [70].

In chapter 6 hydroxylation of the AlF₃ surface is considered. The basis sets used to describe O and H are given in table 3.3. Oxygen is described using a 6-31G* basis set, which was originally optimised for SiO₂ (α-quartz) and AlPO₄ [71]. Hydrogen is described using an 821G* basis set, this has been optimised for the H atom [72]. H₂O, HF
Table 3.1: The aluminium and chlorine basis sets.

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<tr>
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<th></th>
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<th></th>
</tr>
</thead>
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<td>p co-eff</td>
<td>Exponent</td>
</tr>
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<td>19440</td>
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<tr>
<td></td>
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<td>163.1</td>
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<td>111.1</td>
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<td>0.50</td>
<td>1.0 (d co-eff)</td>
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</tbody>
</table>

and HCl molecules were also described using the basis sets discussed so far. In chapter 8 adsorption of NH₃ to the AlF₃ surfaces is considered. The NH₃ basis sets are given in table 3.4. An H basis set that is less diffuse than that used to define H₂O, OH and HF species is used for NH₃ due to numerical difficulties associated with strong H-F and H-H overlap at high coverage. The basis sets for CO are given in table 3.5. A higher quality basis set for O was used for CO to improve the description of the dipole moment on the CO molecule. At the DFT level of theory the charge on the O in CO is predicted to be positive, while experimentally it is known to be slightly negative. Improving the O basis set reduced size of the positive charge on the oxygen from 0.17 to 0.08 |e|. 

73
Table 3.2: The fluorine basis set.

<table>
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<tr>
<th>Orbital</th>
<th>Exponent</th>
<th>s co-eff</th>
<th>p co-eff</th>
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Table 3.3: The oxygen and hydrogen basis sets used for OH⁻ and H₂O. (The hydrogen basis set is also used in HF and HCl.)

<table>
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<th>Oxygen</th>
<th>Hydrogen</th>
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<td>----------</td>
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### Table 3.4: The nitrogen and hydrogen basis sets used for NH₃.

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<th>Exponent</th>
<th>s co-eff</th>
<th>p co-eff</th>
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<td></td>
<td>Hydrogen</td>
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<td></td>
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<td></td>
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### Table 3.5: The carbon and oxygen basis sets used for CO.

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<th>p co-eff</th>
<th>Exponent</th>
<th>s co-eff</th>
<th>p co-eff</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>Oxygen</td>
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</tr>
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<td></td>
<td>1.292</td>
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</tr>
</tbody>
</table>
3.4 Using the CRYSTAL code

To obtain reliable results from the CRYSTAL code it is important that the numerical approximations employed are carefully considered in order to achieve a balance between accuracy and computational cost.

3.4.1 k-space Sampling

Integration in reciprocal space is an important aspect of \textit{ab initio} calculations for periodic systems. It is required for the calculation of the Fermi energy, $\epsilon_F$, for calculating the one-electron density matrix in the SCF procedure and in the Ewald summation of the Coulomb and exchange interactions. It is also required after self consistency has been achieved for calculating the density of states (DoS) and a number of other observable quantities.

The Fermi energy and the density matrix are evaluated starting from the knowledge of the eigenvalues and the eigenvectors at a given set of sampling points. In three dimensions the sampling points, known as the Monkhorst net \cite{73}, belong to a lattice with basis vectors $b_1/s_1$, $b_2/s_2$ and $b_3/s_3$ where $b_1$, $b_2$ and $b_3$ are the reciprocal lattices vectors and $s_1$, $s_2$ and $s_3$ are the integer shrinking factors. Calculations for slabs require two shrinking factors and polymers require one shrinking factor. The value of the shrinking factor is set by the CRYSTAL user. It is necessary to test the convergence of a particular system with respect to k-space sampling before deciding on values to be used for a given set of calculations.

In conducting systems a second parameter, known as the Gilat shrinking factor, which defines a Gilat net \cite{74}, must also be defined. This value should in general be significantly larger than those of the Monkhorst factors, resulting in a denser net. The Fermi energy is determined from integrals of the electron density on the Gilat net. An accurate estimate of the Fermi energy is not required for the final solution for non-conducting systems. However, these systems may give rise to conducting solutions in the initial stages of the
SCF cycle where an accurate determination of the Fermi energy is required.

3.4.2 The Coulomb and Exchange Summations

The accuracy of the summation of the Coulomb interactions and the exchange integrals are determined by five overlap criteria (ITOL1 - ITOL5). These are (1) the overlap threshold for the Coulomb integrals, (2) the penetration threshold for the Coulomb integrals, (3) the overlap threshold for the HF exchange integrals, (4) the part truncation of the HF exchange series and (5) the further truncation of the HF exchange series. When the overlap between two atomic orbitals is smaller than $10^{-\text{ITOL}}$, the corresponding integral is disregarded or evaluated in a less precise way. In general, the value of the fifth tolerance should be twice that of the other ITOL values, which should be set to the same value. This ensures that each of the summation terms is calculated efficiently and to a similar degree of accuracy.

3.4.3 Functionals

Several different DFT functionals are implemented in the CRYSTAL code. The exchange potential can be defined in terms of a fraction of the Hartree-Fock exchange with a fraction of a defined DFT exchange potential. The Hybrid functionals B3PW [52] and B3LYP [50] are implemented in CRYSTAL.

3.4.4 Grid Sampling

The matrix elements of $V_{xc}[\rho]$ cannot be determined analytically. Their values are calculated numerically at a large number of defined grid points that are centred on the atoms. The more grid points used, the more accurate the calculation. An indication of the accuracy obtained from a particular grid is given by the value of the integrated density of the system. If the value of the integrated charge density deviates by more than $10^{-3}$ of an
electron from the known number of electrons in the system then a larger grid should be considered.

### 3.4.5 Geometry Optimisation

Geometry optimisation is performed in symmetrised Cartesian coordinates. Forces on atoms within a defined lattice are calculated using analytical gradients of the energy. In CRYSTAL06 Pulay forces [75] and analytical stresses have been implemented for the optimisation of cell parameters. In CRYSTAL03 the forces are calculated by numerical difference with respect to the lattice parameters.

In this thesis geometry optimisation was performed by energy minimisation using a combination of an unconstrained Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm as implemented in the DOMIN software [76] and a damped molecular dynamics optimiser which is described in section 4.5. Structures were considered fully optimised when the residual forces on all the atoms were below $1 \times 10^{-4}$ Hartree Bohr$^{-1}$.

### 3.4.6 Phonon Calculations

Frequency calculations, at the $\Gamma$ point, can be calculated using the CRYSTAL code. The second derivatives of the energy are computed from numerical differences of the analytical first derivatives. Frequencies are then obtained by diagonalising the mass-weighted Hessian matrix [77]. The calculation of a full Hessian matrix for large systems is a computationally demanding task. If the frequency of interest is not strongly coupled to the whole system under consideration then a good estimation of it can be calculated from the formation of a partial Hessian matrix, constructed from the displacements of a selection of the atoms within the full system.
3.4.7 Running CRYSTAL calculations

All \textit{ab initio} calculations in this thesis have been run using the hybrid exchange B3LYP functional. This functional has been shown to produce accurate results for a wide range of materials. A comparison of this functional to other DFT functionals is given in section 2.2.12. The calculations, unless stated otherwise, were run with the overlap criteria (ITOL1 - ITOL5) set to 8, 8, 8, 8 and 16. A sampling grid consisting of 75 radial points and 974 angular points in the region of chemical interest (referred to as an Extra Large grid) was used. A shrinking factor of 8 was used in K space and a denser Gilat net consisting of 16 points was used in the evaluation of the Fermi energy and density matrix.

3.4.8 Reducing the CRYSTAL tolerances

The numerical tolerances used in our CRYSTAL calculations were selected to provide very high numerical accuracy, and in some cases, were more accurate than necessary. In chapter 12, mechanisms for the catalysis of halogen exchange reactions at AlF$_3$ surfaces are considered. This involves running a very large number of CRYSTAL calculations. Reducing the numerical accuracy in order to obtain a speed up in the time to solution was therefore considered. The effect of changing the numerical tolerances in CRYSTAL on the total energy and the bulk lattice parameters of $\beta$-AlF$_3$ were analysed in detail and are summarised in tables 3.6 to 3.8. It can be seen from these tables that reducing the overlap tolerances from 8, 8, 8, 8 and 16 to 6, 6, 6, 6 and 12, reducing the k space sampling from 8 and 16 to 2 and 4 and using a less dense numerical grid (defined as Large as opposed to Extra Large) results in a change of $1.8 \times 10^{-3}$ eV in the total energy of the system and a maximum change of 0.002 Å in any of the lattice parameters. The time for calculation of bulk $\beta$-AlF$_3$ is reduced by a factor of four. In the proceeding discussion we shall refer to the two sets of tolerances discussed here as the higher and lower sets of numerical tolerances.
Table 3.6: The effect of changing the overlap criteria. These calculations were run using an XL grid and shrinking factors of 8 and 16.

<table>
<thead>
<tr>
<th>Overlap criteria</th>
<th>Δ Energy (eV)</th>
<th>Lattice parameters (Å)</th>
<th>Time to solution (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8, 8, 8, 8, 16</td>
<td>-</td>
<td>7.036, 12.185, 7.261</td>
<td>225</td>
</tr>
<tr>
<td>7, 7, 7, 7, 14</td>
<td>1.1 × 10⁻⁴</td>
<td>7.036, 12.185, 7.261</td>
<td>169</td>
</tr>
<tr>
<td>6, 6, 6, 6, 12</td>
<td>4.0 × 10⁻³</td>
<td>7.035, 12.185, 7.260</td>
<td>145</td>
</tr>
<tr>
<td>5, 5, 5, 5, 10</td>
<td>1.6 × 10⁻³</td>
<td>7.016, 12.152, 7.234</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 3.7: The effect of changing the shrinking factors. These calculations were run using overlap criteria of 6, 6, 6, 6, and 12 and an XL grid.

<table>
<thead>
<tr>
<th>k-space sampling</th>
<th>Δ Energy (eV)</th>
<th>Lattice parameters (Å)</th>
<th>Time to solution (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8, 16</td>
<td>-</td>
<td>7.035, 12.185, 7.260</td>
<td>145</td>
</tr>
<tr>
<td>6, 12</td>
<td>&lt; 10⁻⁸</td>
<td>7.035, 12.185, 7.260</td>
<td>112</td>
</tr>
<tr>
<td>5, 10</td>
<td>&lt; 10⁻⁸</td>
<td>7.016, 12.152, 7.234</td>
<td>101</td>
</tr>
<tr>
<td>4, 8</td>
<td>&lt; 10⁻⁸</td>
<td>7.016, 12.152, 7.234</td>
<td>91</td>
</tr>
<tr>
<td>3, 6</td>
<td>4.3 × 10⁻⁷</td>
<td>7.016, 12.152, 7.234</td>
<td>92</td>
</tr>
<tr>
<td>2, 4</td>
<td>1.3 × 10⁻⁴</td>
<td>7.016, 12.152, 7.234</td>
<td>71</td>
</tr>
<tr>
<td>1, 2</td>
<td>8.2 × 10⁻³</td>
<td>7.041, 12.196, 7.265</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 3.8: The effect of changing the grid size. These calculations were run using overlap criteria of 6, 6, 6, 6, and 12 and shrinking factors of 2 and 4.

<table>
<thead>
<tr>
<th>Grid size</th>
<th>Δ Energy (eV)</th>
<th>Lattice parameters (Å)</th>
<th>Time to solution (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XL</td>
<td>-</td>
<td>7.035, 12.185, 7.260</td>
<td>71</td>
</tr>
<tr>
<td>L</td>
<td>2.2 × 10⁻³</td>
<td>7.037, 12.185, 7.259</td>
<td>56</td>
</tr>
<tr>
<td>M</td>
<td>1.1 × 10⁻²</td>
<td>7.036, 12.178, 7.262</td>
<td>46</td>
</tr>
</tbody>
</table>
Table 3.9: The energies of three $\beta$-AlF$_3$ surfaces calculated using the higher and lower sets of numerical tolerances.

<table>
<thead>
<tr>
<th>Surface Structure</th>
<th>Surface Energy (Jm$^{-2}$)</th>
<th>Higher tolerances</th>
<th>Lower tolerances</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100 T1</td>
<td>0.8533</td>
<td>0.8595</td>
<td></td>
</tr>
<tr>
<td>B100 T6</td>
<td>0.8574</td>
<td>0.8622</td>
<td></td>
</tr>
<tr>
<td>B010</td>
<td>0.7356</td>
<td>0.7377</td>
<td></td>
</tr>
</tbody>
</table>

To further investigate the effect of these approximations to the numerical accuracy within CRYSTAL the energies of several $\beta$-AlF$_3$ surfaces are considered. The results obtained from both the higher and lower sets of numerical tolerances are shown in Table 3.9. The surface energies calculated using the set of lower set of numerical tolerances are to within 0.005 Jm$^{-2}$ of the energies calculated using the higher set of numerical tolerances. The relative energetics between the surfaces are accurate to within 0.003 Jm$^{-2}$.

The majority of calculations in this project have been run using the higher set of numerical tolerances. In hindsight, given the four fold increase in calculation speed and the very high level of numerical accuracy obtained by using the lower set of numerical tolerances, more care should have been taken at the start of this project to consider the numerical tolerances used.
Chapter 4

New Methodologies

4.1 Introduction

There are four main areas in which I have developed new methodologies or implemented new optimisation methods within the CRYSTAL code.

Density functional theory has traditionally been thought of as a zero-temperature, zero-pressure technique. In the real world, many important chemical reactions take place under high temperature and high pressure conditions. Conversely, many surface science experimental techniques take place in ultra high vacuum (UHV) conditions. The need to bridge this gap between 'real life' high temperature, high pressure environments and UHV conditions is one of the main challenges in modern surface science. Recently it has been shown that the effect of an external atmosphere at a finite temperature can be included in calculations via \textit{ab initio} atomistic thermodynamics. This allows connections to be made between 'real life' and UHV conditions. In section \ref{sec:4.2} we describe the methodology that has previously been used on metal oxide systems and apply it to metal halide systems.

In chapter \ref{chap:8} the binding energies of NH$_3$ to $\beta$-AlF$_3$ surfaces are calculated. Experimentally, temperature programmed desorption (TPD), described in section \ref{sec:2.3.2} has been used to study adsorption of NH$_3$ to the surface of $\beta$-AlF$_3$. To enable a comparison be-
tween our theoretical binding energies and experimental TPD curves a kinetic Monte Carlo desorption simulation programme has been developed. This programme, described in section 4.3 uses our calculated binding energies to predict a TPD curve.

In chapter 11 the mobility of surface fluorine atoms on the β-AlF₃ (100) surface is investigated, and in chapter 12 the dismutation of CCl₂F₂ on this surface is studied. The calculation of energy barriers for these diffusion events and reactions, are hence, required. A popular method for locating reaction pathways, and in particular transition states and energies, when the end points are known is the Nudged Elastic Band (NEB) algorithm [78]. I have implemented this method into the CRYSTAL code. The algorithm and my implementation of it is in CRYSTAL are described in section 4.4.

The geometry optimisation methods implemented in CRYSTAL, when this project was started, were not very efficient for systems far from their equilibrium geometry. As a consequence of this I have developed a robust damped molecular dynamics (DMD) algorithm in CRYSTAL. This algorithm and its implementation are described in section 4.5.

4.2 Surface Thermodynamics

The relative stability of surfaces with different stoichiometries is determined by the comparison of their surface free energy. The methodology used to calculate the surface free energy at a finite temperature and pressure has been developed for metal oxide systems [79, 80, 81] and extended to multicomponent environments [82]. We have applied this methodology to metal halide systems and extended it to include surfaces exposed to a multicomponent environment of gaseous HF and H₂O. Although expressed in terms of AlF₃ the method is applicable to any multicomponent gas phase environment.

At a given temperature a solid is in equilibrium with its vapour when

\[ \mu_{\text{vapour}}(T, P_{\text{vap}}) = \mu_{\text{solid}}(T, P_{\text{tot}}) \]  

(4.1)
where \( P_{\text{vap}} \) is the vapour pressure of the material and \( P_{\text{tot}} \) is the total pressure of the system. \( P_{\text{tot}} \) enters equation \( 4.1 \) via the pressure dependence of the \( PV \) term in the Gibbs free energy of the solid. Consequently, the variation depends upon \( P_{\text{tot}} \) rather than any individual partial pressure. In the following derivation any terms which have a dependency on \( P_{\text{tot}} \) will be in the solid phase but could be rewritten in terms of the vapour pressure of that phase.

As an example we consider an AlF\(_3\) slab with adsorbed hydroxyl groups, water and HF exposed to an atmosphere containing gaseous H\(_2\)O, H\(_2\) and HF. The methodology is trivially extended to other systems. Modelling the AlF\(_3\) surface as a slab of material periodic in two dimensions and of finite thickness in the third, we define the surface free energy as

\[
\gamma(T, P_{F_2}, P_{O_2}, P_{H_2}, P_{\text{tot}}) = \frac{1}{2A} \left[ G_{\text{slab}}(T, P_{\text{tot}}) - N_{\text{Al}} \mu_{\text{Al}}(T, P_{\text{tot}}) - N_{F_2} \frac{1}{2} \mu_{F_2}(T, P_{F_2}) - N_{O_2} \frac{1}{2} \mu_{O_2}(T, P_{O_2}) - N_{H_2} \frac{1}{2} \mu_{H_2}(T, P_{H_2}) \right]
\]

(4.2)

where \( A \) is the surface area of the unit cell (the factor of 2 accounts for both sides of the slab). \( G_{\text{slab}} \) is the Gibbs free energy per unit cell of the slab and \( N_{\text{Al}}, N_{F_2}, N_{O_2} \) and \( N_{H_2} \) are respectively the total number of aluminium, fluorine, oxygen and hydrogen ions within the slab. \( P_{F_2}, P_{O_2} \) and \( P_{H_2} \) are the partial pressures of the F\(_2\), O\(_2\) and H\(_2\) molecules respectively and \( P_{\text{tot}} \) is the total pressure of the system. \( \mu_{\text{Al}}, \mu_{F_2}, \mu_{O_2} \) and \( \mu_{H_2} \) are the chemical potentials for aluminium, fluorine, oxygen and hydrogen respectively.

It is assumed that bulk aluminium fluoride is in equilibrium with aluminium and fluorine in their natural states, consequently

\[
G_{\text{bulk}}(T, P_{\text{tot}}) = \mu_{\text{Al}}(T, P_{\text{tot}}) + \frac{3}{2} \mu_{F_2}(T, P_{F_2})
\]

(4.3)
where \( G_{\text{bulk}} \) is the Gibbs free energy per formula unit of the bulk crystal having stochiometry \( \text{AlF}_3 \). Similarly, HF and \( \text{H}_2\text{O} \) are in equilibrium with their constituent atoms, hence

\[
\frac{1}{2} \mu_{\text{H}_2}(T, P_{\text{H}_2}) + \frac{1}{2} \mu_{\text{F}_2}(T, P_{\text{F}_2}) = \mu_{\text{HF}}(T, P_{\text{HF}}) \tag{4.4}
\]

\[
\mu_{\text{H}_2}(T, P_{\text{H}_2}) + \frac{1}{2} \mu_{\text{O}_2}(T, P_{\text{O}_2}) = \mu_{\text{H}_2\text{O}}(T, P_{\text{H}_2\text{O}}) \tag{4.5}
\]

Using equations 4.3, 4.4 and 4.5 we can eliminate \( \mu_{\text{Al}}, \mu_{\text{F}_2} \) and \( \mu_{\text{O}_2} \) from equation 4.2.

\[
\gamma(T, P_{\text{HF}}, P_{\text{H}_2\text{O}}, P_{\text{H}_2}) = \frac{1}{2A} \left\{ G_{\text{slab}}(T, P_{\text{tot}}) - N_{\text{Al}} G_{\text{bulk}}(T, P_{\text{tot}}) \right.&
\left. - (N_F - 3N_{\text{Al}}) \left[ \mu_{\text{HF}}(T, P_{\text{HF}}) - \frac{1}{2} \mu_{\text{H}_2}(T, P_{\text{H}_2}) \right] \right.
\left. - N_O \left[ \mu_{\text{H}_2\text{O}}(T, P_{\text{H}_2\text{O}}) - \mu_{\text{H}_2}(T, P_{\text{H}_2}) \right] \right.
\left. - N_H \frac{1}{2} \left[ \mu_{\text{H}_2}(T, P_{\text{H}_2}) \right] \right\} \tag{4.6}
\]

Re-arranging this equation we obtain

\[
\gamma(T, P_{\text{HF}}, P_{\text{H}_2\text{O}}, P_{\text{H}_2}) = \frac{1}{2A} \left\{ G_{\text{slab}}(T, P_{\text{tot}}) - N_{\text{Al}} G_{\text{bulk}}(T, P_{\text{tot}}) \right.&
\left. - (N_F - 3N_{\text{Al}}) \mu_{\text{HF}}(T, P_{\text{HF}}) - N_O \mu_{\text{H}_2\text{O}}(T, P_{\text{H}_2\text{O}}) \right.
\left. - \frac{1}{2} \left( 3N_{\text{Al}} - N_F - 2N_O + N_H \right) \mu_{\text{H}_2}(T, P_{\text{H}_2}) \right\} \tag{4.7}
\]

For a slab of stoichiometry \( \text{AlF}_{3-x}(\text{OH})_x \) with or without molecular HF or \( \text{H}_2\text{O} \) adsorbed at its surface, the term involving \( \mu_{\text{H}_2} \) is eliminated from equation 4.7, consequently, if the stable surfaces only consist of such slabs their relative stabilities can be written as a function of \( \mu_{\text{H}_2\text{O}} \) and \( \mu_{\text{HF}} \). To illustrate this, consider a slab consisting of \( m \) \( \text{AlF}_{3-x}(\text{OH})_x \) units, \( n \) HF and \( p \) \( \text{H}_2\text{O} \) molecules; \( N_{\text{Al}} = m, N_F = m(3 - x) + n, N_O = mx + p \) and...
\[ N_H = mx + n + 2p \] hence,

\[
3N_{Al} - N_F - 2N_O + N_H \\
= 3m - (m(3 - x) + n) - 2(mx + p) + (mx + n + 2p) \\
= 0.
\] (4.8)

The chemical potential of an ideal gas can be written as

\[
\mu_X(T, P_X) = \mu_X(T, P_X^\circ) + kT \ln \left( \frac{P_X}{P_X^\circ} \right)
\] (4.9)

We can therefore calculate the chemical potential at any pressure if we know the value of \( \mu_X(T, P_X) \) at a given pressure \( P_X^\circ \).

The above derivation is relative to the energy zero of classical thermodynamics where the energy of formation of an element in its standard state at standard temperature and pressure is zero. However, we need to convert to the energy zero of the DFT calculations so that \( G_{bulk} \) and \( G_{slab} \) are simply the DFT total energies of the system. To do this we write equation 4.9 as

\[
\mu_X(T, P_X) = \mu_X(0, P_X^\circ) + [\mu_X(T, P_X^\circ) - \mu_X(0, P_X^\circ)] + kT \ln \left( \frac{P_X}{P_X^\circ} \right)
\] (4.10)

where the term in square brackets is now the change in the chemical potential in moving from \( T = 0 \) to \( T = T \) at constant pressure \( P_X^\circ \).

\[
\mu_X(T, P_X) = \mu_X(0, P_X^\circ) + \Delta \mu_X(P_X^\circ) \bigg|_{T=0}^{T=T} + kT \ln \left( \frac{P_X}{P_X^\circ} \right)
\] (4.11)

we can define the chemical potential on the DFT energy scale as

\[
\mu'_X(T, P_X) = \mu_X(T, P_X) - \mu_X(0, P_X^\circ) + E_{DFT}(T = 0)
\] (4.12)
Traditionally, phase diagrams in the literature \([80, 81]\) have been plotted as a function of

\[
\mu^*_X(T, P_X) = \Delta \mu_X(P_X^0) \bigg|_{T=T=0}^T + kT \ln \left( \frac{P_X}{P_X^0} \right)
\]  

(4.13)

which does not include the term \(\mu_X(0, P_X^0)\) which is the enthalpy of the compound at \(T = 0K\).

The term \(\Delta \mu_X(P_X^0) \bigg|_{T=T=0}\) in equations 4.11 and 4.13 and implicitly in equation 4.12 can be obtained from thermodynamical reference tables \([1]\), as described in section 4.2.2. The values that we have used in this thesis are displayed in table 4.1. Formally \(\mu\) is a Gibbs free energy while \(E_{DFT}\) is an enthalpy, \(H\). These are related via

\[
G(T, P) = H(T, P) - TS(T, P)
\]  

(4.14)

where \(S\) is the entropy of the system, but at \(T = 0\), \(G\) and \(H\) become identical.

The Gibbs free energies of the slab and bulk crystal are computed at the athermal limit and their temperature dependence is ignored as it is negligible compared to that of the gas. Correction to finite temperature is possible by either molecular dynamics simulation or the calculation of the lattice dynamics and the use of the quasiharmonic approximation. However, as the current article is concerned with the qualitative behaviour of the surface stability rather than a quantitative determination of the absolute surface formation energy these small corrections have not been computed. The small PV term due to the change in volume of the surface and bulk phases is also neglected. This approximation is in line with previous studies \([79, 80, 81]\).

Substituting equation 4.11 into equation 4.12 allows us to express the variation of
Table 4.1: Calculated values $\Delta \mu$ at 1 atm obtained from thermochemical tables [1].

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$\Delta \mu_{\text{Cl}_2}$ (eV)</th>
<th>$\Delta \mu_{\text{F}_2}$ (eV)</th>
<th>$\Delta \mu_{\text{H}_2\text{O}}$ (eV)</th>
<th>$\Delta \mu_{\text{HF}}$</th>
<th>$T=0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-0.57</td>
<td>-0.54</td>
<td>-0.48</td>
<td>-0.45</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>-1.27</td>
<td>-1.18</td>
<td>-1.11</td>
<td>-1.03</td>
<td></td>
</tr>
</tbody>
</table>

$\mu'_{X}(T, P_X)$ with pressure at fixed $T$ as

$$
\mu'_{X}(T, P_X) = E_{DF}(T = 0) + \Delta \mu_{X}(P_X^o)_{T=0} + kT \ln \left( \frac{P_X}{P_X^o} \right) \quad \text{(4.15)}
$$

Equation 4.7 can be used along with equation 4.15 for HF and H$_2$O allowing us to evaluate the surface energies of different clean and hydroxylated AlF$_3$ surfaces as a function of HF and H$_2$O partial pressure at fixed temperature. The lowest energy surfaces can then be plotted as a function of $\mu_{\text{HF}}$ and $\mu_{\text{H}_2\text{O}}$.

### 4.2.1 Limiting Values

In principle the limiting values of $\mu_X(T, P_X)$ can be estimated or calculated. The lower limit is the value at which the compound decomposes into its constituent elements. At this point

$$
\mu_{XY}(T, P_{XY}) = \mu_X(T, P_X) + \mu_Y(T, P_Y) \quad \text{(4.16)}
$$

this limit can be obtained either from thermodynamic tables or via calculation of the energy of the components of the system in their standard states.

For example, considering the lower limit of F$_2$, below which AlF$_3$ decomposes into Al$_{(s)}$ and F$_2$, we obtain

$$
\Delta G_{\text{reaction}} = G_{\text{bulk}}^{\text{AlF}_3} - G_{\text{bulk}}^{\text{Al}} - \frac{3}{2} G_{\text{F}_2} \quad \text{(4.17)}
$$
\[ kT \ln \left( \frac{P_{F_2}}{P^\circ_{F_2}} \right) = \min[\mu_{F_2}] = \frac{2}{3} \left[ G_{AlF_3}^{Al} - G_{bulk}^{Al} \right] \] (4.18)

This value can be obtained via the calculation of the energy of bulk Al and AlF₃. However, often it is not possible within the given calculational scheme to obtain accurate results for both a metallic and ionic solid. It may therefore be preferable to obtain values from thermodynamical tables. The free energy of formation of crystalline AlF₃ is -14.8 eV at standard temperature and pressure. This is equivalent to a partial pressure of F₂ of 10⁻¹⁷ atm at 300K. Thus in this case the lower limit would be determined by the quality of the vacuum in the experiment.

Similarly, an upper limit can be defined as the point at which the constituent gases condense onto the surface of the material.

\[ \mu_{gas}^X(T, P_X) = \mu_{condensed phase}^X(T, P_{tot}) \] (4.20)

This value can again be obtained from thermodynamic tables provided data for a condensed phase exists for the given temperature and pressure. If not, it can be approximated as the point at which

\[ \mu^*_X(T, P_X) = 0 \] (4.21)

For example, the vapour pressure of H₂O at 300K is 3.6 \times 10⁻² atm and at 600K it is 1.2 \times 10⁻¹ atm, this corresponds to \( \mu^* = -0.57 \) eV at 300K and -1.16 eV at 600K. In the temperature range that we are typically interested in data for the condensed phase of F₂ is not apparently available. We therefore take the maximum value of \( \mu_{F_2} \) to be the total energy of an isolated F₂ molecule at T=0K. The vapour pressure of HF at 300K is 1.3 atm, corresponding to \( \mu^* = -0.44 \) eV. At 600K the condensed phase of both HF and H₂O...
are not apparently available hence we set the maximum value of $\mu^*$ to zero.

### 4.2.2 Obtaining $\Delta \mu(P^\circ)$ from Thermodynamic Tables

It is important that the values in equation 4.15 are evaluated correctly. In particular, care should be taken in calculating the term $\Delta \mu_X(P^\circ_X)|_{T=T_0}$. Values in tables are often given with respect to $T = 298.15$ K hence it is important to make a correction to $T = 0$ K.

As an example, we will consider obtaining $\Delta \mu(P^\circ)|_{T=T_0}$ for HF using data from the NIST website [84]. The quantities $C_p^\circ$, $H^\circ - H_{298.15}^\circ$ and $S^\circ$ are given as a function of temperature. For instance, at 600K $C_p^\circ = 29.23$ J mol$^{-1}$ K$^{-1}$, $H^\circ - H_{298.15}^\circ = 8.80$ kJ mol$^{-1}$ and $S^\circ = 194.2$ J mol$^{-1}$ K$^{-1}$.

We can write

$$\Delta \mu_X(P^\circ_X)|_{T=T_0} = H^\circ - H_0^\circ - TS^\circ$$  \hspace{1cm} (4.22)

Hence we also require the value of $H_{298.15}^\circ - H_0^\circ$. This has to be obtained separately, for instance from the CODATA tables [85]. Values for many molecules are also given on their website [86]. For instance, $H_{298.15}^\circ - H_0^\circ = 8.599$ kJ mol$^{-1}$ for HF. Hence,

$$\Delta \mu_{HF}(P^\circ_{HF})|_{T=T_0} = (H^\circ - H_{298}^\circ) + (H_{298}^\circ - H_0^\circ) - TS^\circ$$

$$= 8.80 \text{ kJ mol}^{-1} + 8.599 \text{ kJ mol}^{-1}$$

$$- 600 \text{ K} \times 0.1942 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$= 99.121 \text{ kJ mol}^{-1} = -1.03 \text{ eV}$$ \hspace{1cm} (4.23)

### 4.3 Kinetic Monte Carlo Simulations

In this thesis kinetic Monte Carlo simulations are used to model the desorption of molecules from a surface and for simulating the diffusion of F ions at a surface.
Initially a grid, containing $A$ sites, is set up to represent the surface at time zero. For instance, when modelling the desorption of $\text{NH}_3$ from a surface, each site on the grid represents an adsorbed $\text{NH}_3$ molecule. The rate constant for event $j$ occurring at site $i$ is given by

$$r_{i,j} = \nu_0 \exp \left( -\frac{\Delta E(i,j)}{RT} \right)$$

(4.24)

where $\nu_0$ is the attempt frequency, $R$ is the molar gas constant, $T$ is the temperature of the system and $\Delta E$ is the energy barrier associated with event $j$, its value is also dependent on the occupancy of neighbouring grid sites.

The rate constants are calculated for each grid point. The cumulative function

$$R_m = \sum_{n=1}^{m} r_n$$

(4.25)

is calculated for $m = 1, N$ where $N$ is the total number of possible events. A random number, $u \in [1, N]$, is generated and the event $m$ that satisfies $R_{m-1} < u < R_m$ is selected. The grid is updated to represent the occurrence of this event and the time is updated by

$$t = t + -\ln \left( \frac{u}{N} \right) \Delta t$$

(4.26)

where $\Delta t = 1/R_N$. $\Delta t$ is multiplied by $-\ln(u/N)$ as this captures stochastic nature of the timestep. If the temperature varies as a function of time then this must also be updated. Reaction rates, $R_{ij}$ that change as a consequence of event $m$ occurring are updated (if the temperature changes then all the reaction rates must be updated). Additional reaction rates may now be required, or some rates may need to be deleted, in which case the value of $N$ must also be updated. The cumulative function is recalculated, a new random number generated and the process is repeated.
The simulations are run several times (at least five times) and it is checked that similar results are obtained each time. This is necessary as it is possible that a rare stochastic event could occur that has a knock on effect to the rest of the desorption pattern. If the system is run only once an anomalous result may not be noticed.

4.4 The Nudged Elastic Band Algorithm

The rate of chemical reactions and diffusion events are all, in part, determined by the energy barrier between the reactants and the products. The transition state is a saddle point on the potential energy surface. Locating saddle points on a high dimensional surface is not a straight forward task. Several methods have been developed to accomplish this task. There are algorithms that require second derivative information, and others that only require first derivatives to be calculated. The current version of CRYSTAL does not have the ability to calculate analytical second derivatives. We are thus limited to methods that only require first derivatives. Methods that have been developed include Conjugate Peak Refinement, Drag, Nudged Elastic Band and Ridge. These methods have been reviewed and the Nudged Elastic Band (NEB) method has been shown to be the most efficient and reliable [87]. I have implemented this method in the CRYSTAL code.

The NEB algorithm requires that the structure of both the reactants and the products are known. The NEB algorithm takes an initial estimate of the minimum energy path (MEP) and iterates towards a local MEP. If the local MEP is the global MEP of the system then the highest point along the MEP is, by definition, the transition state.

Several images are constructed along the initial estimate of the MEP (these are usually obtained from linear interpolation between the two minima). This forms a band of N+1 images (typically 3-10 images are used, excluding the fixed end points). These images can be denoted by $[\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots, \mathbf{R}_{N-1}]$ where $\mathbf{R}_i$ defines the coordinates of image $i$. $\mathbf{R}_0$ and $\mathbf{R}_N$ are the end points and remain fixed throughout the calculation. Spring forces between
adjacent images are added to encourage continuity and equal spacing of the images along the band. The minimisation of the total forces acting on the images results in convergence to a local MEP. The main distinguishing feature of this method to other band methods is its use of force projections to eliminate interferences between the spring forces and the true forces. The tangent of the band at each image point is estimated. The spring force is projected out parallel to the tangent while the true force is projected out perpendicular to the tangent as shown in figure 4.1. The total force acting on each image is

$$ F_i = F_{spr}^i \parallel - \nabla E(R_i) \perp $$ (4.27)

where $F_{spr}^i \parallel$ is the force due to the spring interactions and $E(R_i \perp)$ is the energy of the image at position $R_i$.

The tangent estimation used is the one proposed by Henkelman and Jónsson [78]. It is defined as the vector joining up image $i$ with either image $i + 1$ or $i - 1$, depending on which has the highest energy. The tangent is then normalised.
The spring force is defined as

\[ F_{i}^{spr} \parallel = k ( | R_{i+1} - R_{i} | - | R_{i} - R_{i-1} | ) \hat{\tau}_{i} \]  (4.28)

This ensures equal spacing of the images when the same spring constant, \( k \), is used for all the springs. It may be preferable to have higher resolution of the MEP close to the saddle point. This can be achieved by the use of stronger springs close to the saddle point. A variable spring constant scheme has been implemented in CRYSTAL; the spring constant depends linearly on the energy of the images, such that images with higher energies are connected via stronger spring constants [88].

\[ k_{i} = \begin{cases} k_{\text{max}} - \Delta k \left( \frac{E_{\text{max}} - E_{i}}{E_{\text{max}} - E_{\text{ref}}} \right) & \text{if } E_{i} > E_{\text{ref}} \\ k_{\text{max}} - \Delta k & \text{if } E_{i} < E_{\text{ref}} \end{cases} \]  (4.29)

where

\[ E_{i} = \max(E_{i}, E_{i-1}) \]  (4.30)

\( E_{\text{max}} \) is the maximum value of \( E_{i} \) over the whole band and \( E_{\text{ref}} \) is a reference value for the energy. It is set to the higher energy of the two end points.

Once all the forces have been calculated the images are instantaneously moved along the force vectors using a velocity Verlet algorithm.

\[ \mathbf{R}(t + \delta t) = \mathbf{R}(t) + \mathbf{v}(t)\delta t + \frac{1}{2} \mathbf{a}(t)\delta t^{2} \]  (4.31)

\[ \mathbf{v}(t + \frac{\delta t}{2}) = \mathbf{v}(t) + \frac{1}{2} \mathbf{a}(t)\delta t \]  (4.32)

\[ \mathbf{v}(t + \delta t) = \mathbf{v}(t + \frac{\delta t}{2}) + \frac{1}{2} \mathbf{a}(t + \delta t)\delta t \]  (4.33)

where \( \mathbf{a} = -\frac{1}{m} \nabla E(\mathbf{r}) \) is the acceleration at time \( t \). \( \mathbf{v}(t) \) is the velocity at time \( t \) and \( m \) is the mass of a hydrogen atom. The timestep is a constant. If this is set too small
the convergence to an MEP will be very slow, if it is set too large then the system may oscillate or become unstable. The velocity is initially zero and is allowed to increase after each timestep in the direction of the current force. To obtain a minimisation using this method, it is necessary to damp the kinetic energy. This is achieved by keeping only the velocity component which is parallel to the force at the current step. Hence the quenched velocity is given by

\[ \nu(t + \delta t) = \nu(t + \delta t) \times \frac{\nu(t + \frac{\delta t}{2}) \cdot \mathbf{a}(t)}{|\mathbf{a}(t)|} \]  

(4.34)

and it is applied after equation 4.32 \[89\].

### 4.4.1 The Climbing Image NEB Algorithm

In the implementation of NEB described so far, a common problem is that a large number of images are required to get a good resolution of the transition state. A solution to this problem is to use the Climbing Image (CI) NEB algorithm. This method allows the image that is highest in energy to move along the MEP to the highest point \[88\].

This is achieved by modifying the calculation of the force acting on the image with the highest energy. The spring force acting on this image is ignored and instead the parallel component of the force is calculated as the inverse of the true parallel force.

\[ F_{i_{\text{max}}} = -\nabla E(R_{i_{\text{max}}}) + 2 \nabla E(R_{i_{\text{max}}}) \cdot \| \| \]  

(4.35)

This modified force is normally implemented after several iterations of the standard NEB algorithm.
4.4.2 Implementation in CRYSTAL

The NEB method has been implemented in the CRYSTAL code as a separate module that interacts with the main code via calls to functions in CRYSTAL to calculate the energy and first derivatives. This modular implementation allows the NEB code and CRYSTAL to be developed independently and minimises complexity due to interdependency.

The method has been implemented to allow it to be run in parallel across the images. Almost all of the CPU time is spent in the calculation of the energy and forces for each of the images. The calculation for each image is completely independent of any of the other images, hence this part of the calculation can be run in parallel very efficiently. This makes the NEB algorithm a perfect candidate for running on large parallel machines.

Figure 4.2 shows the basic structure of the parallelisation of the algorithm. In this example 32 processors is just an example of the number of processors a single image is run on. This could be much larger if the system is sufficiently large.
Table 4.2: Comparison of transition state energies obtained by NEB in CRYSTAL to those available from the NIST website [2].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Transition Energy (kJ mol(^{-1}))</th>
<th>CRYSTAL-NEB</th>
<th>NIST</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{+H} \rightarrow \text{H+H}_2)</td>
<td></td>
<td>69.6</td>
<td>71.1</td>
</tr>
<tr>
<td>(\text{H}_2\text{O+H} \rightarrow \text{OH} + \text{H}_2)</td>
<td></td>
<td>73.9</td>
<td>78.0</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl})</td>
<td></td>
<td>260.8</td>
<td>264.6</td>
</tr>
</tbody>
</table>

4.4.3 Testing and Validation

The code has been rigorously tested on several small molecular systems. A sample of the test cases that have been studied are summarised in Table 4.2. The transition energies obtained using this code have been compared to those from the National Institute for Standards and Technology (NIST) website [2]. The energies are relative to the initial products. Hartree-Fock theory and 3-21G basis sets have been used to obtain the results. Figure 4.3 shows the resultant MEP for the reaction \(\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}\). Several of the images along the MEP are shown diagrammatically.

It is important to be aware that NEB will not necessarily find the lowest transition state for a given reaction. For instance, in the reaction shown in figure 4.3 there are two possible reaction mechanisms, as shown in figure 4.4. The energy barrier along the MEP for mechanism A is 261 kJ mol\(^{-1}\) compared with 638 kJ mol\(^{-1}\) for mechanism B. The MEP found for mechanism B is only a local MEP.

The parallel scalability of the reaction \(\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}\) test case is shown in Figure 4.5. Eight images where used in this calculation. It was run on 1, 2, 4 and 8 processors. It can be seen that the scaling of the method is very good. Problems with scaling will occur, however, when one image takes significantly more time to converge than the other images.
Figure 4.3: The reaction pathway for $\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$.

Figure 4.4: Two alternate mechanisms for the reaction $\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$.
4.5 The Damped Molecular Dynamics Optimiser

The calculation of minimum energy geometries requires an initial guess at the system. The geometry of the system is then optimised until a minimum energy system is obtained. Traditionally CRYSTAL has used the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimisation method [89].

This method involves constructing an approximate Hessian matrix of second order derivatives of the function to be minimised. This approximation of the function’s second order derivatives allows the application of a quasi-Newton fitting method in order to move towards the minimum in the parameter space. The Hessian matrix does not need to be computed at any stage. The method assumes that the function can be locally approximated as quadratic in the region around the minimum.

When the system is far from the minima the local region often can not be approximated as a region with quadratic curvature. In some cases the curvature may even be negative. Using the BFGS optimiser in such circumstances is inefficient. In particular, if the local curvature is negative the BFGS optimiser may take the system further away from the minima.

Figure 4.5: Parallelisation across images.
These problems associated with using the BFGS method where the motivation behind my implementation of a damped molecular dynamics (DMD) optimiser within CRYSTAL. The DMD optimisation method only uses first order derivative information. It uses a velocity Verlet algorithm \[90\] and is very similar to the DMD optimiser used in the optimisation of the MEP in the NEB algorithm (see section 4.4).

\[
R(t + \delta t) = R(t) + \nu(t)\delta t + \frac{1}{2}a(t)\delta t^2
\]  \hspace{1cm} (4.36)

\[
\nu(t + 2\delta t) = \nu(t) + \frac{1}{2}a(t)\delta t
\]  \hspace{1cm} (4.37)

\[
\nu(t + \delta t) = A\nu(t + 2\delta t) + \frac{1}{2}a(t + \delta t)\delta t
\]  \hspace{1cm} (4.38)

where \(A\) is a damping term and

\[
A = \hat{\nu}(t + 2\delta t) \cdot \hat{a}(t + \delta t)
\]  \hspace{1cm} (4.39)

where \(\hat{\nu}\) and \(\hat{a}\) are the unit velocity and acceleration vectors.

A significant advantage of the DMD optimiser over the BFGS optimiser is that it is much more stable. For instance, when converging several of the AlF\(_3\) surfaces discussed in this thesis it was often necessary to manually intervene with the BFGS optimiser to force convergence. This was rarely necessary with the DMD optimiser. It was, however, often necessary to restart the original implementation of the DMD optimiser and update its timestep as an optimisation progresses to ensure efficient convergence.

Modifications to the optimiser have been implemented to automatically modify the timestep to reduce the need for manual intervention during an optimisation calculation. During a DMD optimisation, after a set number of geometry optimisations (5 by default) the magnitude of the two terms of the coordinate update process in equation 4.36 are
Table 4.3: Comparison of the BFGS and DMD optimisers as implemented in CRYSTAL03. The number of iterations required to optimise a bulk cleaved slab of AlCl$_3$ and $\alpha$-AlF$_3$ are displayed. The surfaces are considered optimised when the residual forces are below $5 \times 10^{-4}$ Hartrees Bohr$^{-1}$.

<table>
<thead>
<tr>
<th>System</th>
<th>BFGS</th>
<th>DMD</th>
<th>Modified DMD</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$</td>
<td>21</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>AlF$_3$</td>
<td>248</td>
<td>39</td>
<td>34</td>
</tr>
</tbody>
</table>

compared. If

$$\nu(t)\delta t > 5 \times \left[ \frac{1}{2} a(t)\delta t^2 \right]$$  \hspace{1cm} (4.40)

then the timestep is increased by 10%. Alternatively if the average value of the scaling factor $A$, defined in equation 4.39 is less than 0.5 the timestep is reduced by 10%.

Other functionality has also been implemented to improve the robustness of the algorithm. If the energy of the system increases significantly from one optimisation step to the next, then the subsequent geometry is calculated as an average of these previous two systems and the timestep is reduced by 50%. The maximum step size between two optimisation steps has been set by default to 0.1 Bohr.

This algorithm has been shown to be very effective compared to the BFGS optimiser. Table 4.3 compares the number of iterations required to optimise the (001) AlCl$_3$(001) and the $\alpha$-AlF$_3$(01T2) surfaces using the BFGS, the original DMD and the modified DMD algorithms. These test cases are examples of systems that have been calculated as part of this project. The surfaces are considered converged when their maximum symmetry allowed displacement were below $5 \times 10^{-4}$ Hartrees Bohr$^{-1}$. The reconstruction of the AlCl$_3$ surface is relatively small, while the AlF$_3$ surface reconstruction is much more dramatic.

It can be seen that both the DMD algorithms converge the AlCl$_3$ more efficiently than the BFGS optimiser. The modified version of the DMD optimiser does not alter the
timestep in this optimisation, hence its optimisation is identical to that of the unmodified version. The optimisation of AlF$_3$ using the BFGS optimiser required four manual restarts of the optimiser before it was able to fully converge the system. In contrast, the DMD methods optimised the structure in significantly fewer steps and with no manual intervention. In this optimisation it can be seen that the modified version optimised the system more efficiently than the original method. It is clear from these simple test cases that the DMD method outperforms the BFGS and hence I use this (modified) method as a starting point for all the optimisations in this study. I only change to using the BFGS optimiser when the DMD optimisation appears to be running inefficiently, as sometimes occurs when the structure is very close to the fully converged state. When it is close to the fully converged state, the BFGS optimiser should be very efficient, as to a good approximation the curvature of the surface is likely to be quadratic.

It should be noted that the release of CRYSTAL06 includes much modified optimisation routines, which in most cases outperform the DMD scheme. The DMD optimisation method, is however, still useful in the initial stages of the optimisation of a system that is far from equilibrium.
Chapter 5

The Composition and Structure of the (001) AlCl$_3$ Surface

5.1 Introduction

In its solid crystalline form, AlCl$_3$ consists of hexagonal close-packed layers of chlorine ions in which two-thirds of the octahedral holes between every other chlorine layer are occupied by six-fold coordinated aluminium ions. The bulk unit cell of AlCl$_3$ is monoclinic and it is described by the C$_2$/m symmetry group. The structure is defined by ten parameters; these consist of four lattice parameters and six fractional coordinates that define the atom positions. The lattice parameters are the $a$, $b$ and $c$ lattice vectors of the unit cell and the angle between the $b$ lattice vector and the $ac$ plane. Five parameters are required to define the fractional positions of the chlorine ions and one parameter is required to define the positions of the aluminium ions.

There are many materials, such as graphite and molybdenum sulphide (MoS$_2$), that have similar layered structures. These compounds cleave parallel to their basal plane. In graphite this ease of cleaving accounts for its flaky appearance, softness and its use as a lubricant. The structure, appearance and feel of MoS$_2$ is very similar to that of
graphite; it consists of layers of molybdenum atoms between layers of sulphur atoms. Again, the weak interactions between the sulphur layer lead to its lubrication properties. It is therefore expected that the crystalline surface of AlCl$_3$ is also likely to predominately cleave parallel to its basal plane, which is the (001) surface.

There is a common assumption that crystalline AlCl$_3$ is Lewis acidic. In collaboration with Kemnitz’s group at the Humboldt University of Berlin a combination of experimental and theoretical techniques indicate that this assumption is incorrect [10]. The ability of five different catalysts; AlCl$_3$, aluminium chlorofluoride (ACF) and three different phases of aluminium fluoride (AlF$_3$) ($\alpha$, $\beta$ and amorphous high surface area) to catalyse the isomerisation reaction

$$\text{CCl}_2\text{FCClF}_2 \rightarrow \text{CCl}_3\text{CF}_3$$

was investigated. This particular reaction was selected as it is specifically Lewis acid catalysed and truly heterogeneous and therefore, unlike in Friedel-Crafts reactions, the AlCl$_3$ does not become dissolved in the reaction mixture. It was shown that AlCl$_3$ only catalysed the reaction after the reactant was first refluxed over the catalyst. In contrast, the ACF catalyst was active with immediate effect. It was concluded that the AlCl$_3$ only becomes active after some of its chlorines have been replaced by fluorines resulting in the partial formation of ACF.

In an attempt to improve our understanding of the catalytic properties of AlCl$_3$ we have used ab initio calculations to predict the composition and structure of its (001) surface [10]. We believe that this is the first time that AlCl$_3$ has been modelled as a crystalline material using ab initio methods. Previously, ab initio calculations have been performed to investigate the catalytic properties of molecular AlCl$_3$ for a variety of Lewis acid catalysed reactions. For example, the Diels-Alder reaction mechanism between (E)-methyl cinnamate and cyclopentadiene has been studied in the presence of an AlCl$_3$ molecule.
Table 5.1: Comparison of the computed and observed bulk AlCl$_3$ lattice parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Theory</th>
<th>Experiment [3]</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>6.053</td>
<td>5.914</td>
<td>2.3</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>10.521</td>
<td>10.234</td>
<td>2.7</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>6.161</td>
<td>6.148</td>
<td>0.2</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>107.04</td>
<td>108.25</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5.2: The calculated atom positions of bulk AlCl$_3$. The values shown in italics are constrained by symmetry. The observed atomic positions are displayed in brackets [3].

<table>
<thead>
<tr>
<th>Atom</th>
<th>x(fractional)</th>
<th>y(fractional)</th>
<th>z(fractional)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.0</td>
<td>0.166 (0.166)</td>
<td>0.0</td>
</tr>
<tr>
<td>Cl$_1$</td>
<td>0.203 (0.218)</td>
<td>0.0</td>
<td>0.225 (0.226)</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>0.252 (0.248)</td>
<td>0.182 (0.179)</td>
<td>0.224 (0.225)</td>
</tr>
</tbody>
</table>

[91] and the AlCl$_3$ catalysis of an amide bond formation in a reaction between acetic acid and methylamide has been studied [92]. In both of these investigations it was shown that the aluminium of the molecule acted as an electron pair acceptor.

## 5.2 Methodology

A full structure optimisation of the bulk geometry of AlCl$_3$ was performed, as described in section 3.4.5. The resultant lattice parameters and ion positions are compared to observed values in table 5.1 and table 5.2 respectively. The maximum deviation of any lattice parameter from the observed value is 2.7% and as expected from a B3LYP calculation of an ionic material, the predicted bond lengths are slightly too long.

The (001) AlCl$_3$ surface was modelled by cleaving the bulk crystal to produce a two dimensional slab with two identical surfaces. The positions of the ions within the slabs were allowed to relax in all directions consistent with maintaining either a glide or a mirror symmetry operator in the plane of the surface, depending on the thickness of the slab.
Table 5.3: The surface energies of stoichiometric (001) AlCl₃ slabs as a function of slab thickness.

<table>
<thead>
<tr>
<th>No. of Cl-Al-Cl layers</th>
<th>Surface Energy (Jm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.037</td>
</tr>
<tr>
<td>2</td>
<td>0.034</td>
</tr>
<tr>
<td>3</td>
<td>0.033</td>
</tr>
<tr>
<td>4</td>
<td>0.033</td>
</tr>
</tbody>
</table>

The initial termination considered consisted of a slab terminated by a complete layer of chlorine atoms. Due to the stability of the individual Cl-Al-Cl layers it was predicted that this would be the most stable surface structure. Initial surface geometry and energy convergence tests with respect to slab thickness where carried out on this surface. Six further surface structures of AlCl₃ were then considered. These were obtained by successive removal or addition of Cl ions. These surfaces are terminated by a layer containing between zero and six Cl ions. Their surface energies, as a function of chlorine chemical potential and partial pressure at 300K, were calculated using the methodology described in section 4.2.

5.3 Results and Discussion

5.3.1 Slab Thickness Convergence Tests

The surface energies of the stoichiometric slab, as a function of slab thickness, are given in table 5.3. The geometry and surface energies converge to better than 0.01 Å and 0.001 Jm⁻² for a slab consisting of three Cl-Al-Cl layers, hence this was used in all subsequent calculations.

The surface energy of a stoichiometric slab is constant as a function of chlorine chemical potential, hence it is also independent of chlorine partial pressure and temperature. The surface energy of non-stoichiometric slabs depends linearly on the chlorine chemi-
Figure 5.1: The surface energies of the seven differently terminated slabs as a function of chlorine chemical potential and chlorine partial pressure at 300K.

cal potential. The gradient of the line is proportional to the chlorine surface excess, as discussed in section 4.2. The surface energies as a function of both chlorine chemical potential and chlorine partial pressure at 300K are plotted in figure 5.1 for each of the seven terminations considered.

The stoichiometric termination involving a complete Cl-Al-Cl surface layer is the most stable surface at all chlorine chemical potentials. The surface energy of this termination is 0.03 Jm\(^{-2}\). This is likely to be an under-estimate of the surface energy as the individual layers of AlCl\(_3\) interact only via van-der-Waals interactions, which are underestimated by density functional calculations. At zero chemical potential the energy of the stoichiometric 3Cl termination and the 5Cl termination are equivalent. This is because after relaxation the 5Cl termination becomes equivalent to the 3Cl termination and a gas phase Cl\(_2\) molecule which does not interact with the surface.

The stoichiometric 3Cl termination has undergone only a very small reconstruction from the bulk cleaved termination. The largest single atom displacement is 0.016 Å. The
optimised structure is shown in figure 5.2. The Mulliken analysis shows that there is very little difference in the ionic charges between the bulk terminated and the relaxed surfaces for the stable 3Cl system. The charge on the bulk aluminium is +1.91 $|e|$ compared to +1.89 $|e|$ on the aluminium ions in the surface layer. The charges on the bulk chlorine ions are -0.64 and -0.63 $|e|$, the charges on the chlorine ions in the surface layer are -0.60 and -0.60 $|e|$ respectively. This is to be expected as the geometry of the surface layer is almost identical to that of the bulk layers.

As discussed in section 1.2, a Lewis acid is an electrophile or electron acceptor. A Lewis acid will usually have a vacant orbital and/or an available LUMO. Species with a full or partial positive charge usually behave as Lewis acids. Acid sites on the surface may, therefore, be characterised from the electrostatic potential on a plane above the surface. A large positive potential would indicate an electron acceptor species and hence likely Lewis acidity. The electrostatic potential of the 3Cl termination, 2.34 Å above the surface Al ions, in the (001) plane is shown in figure 5.3. The value of 2.34 Å was chosen as this is the Al-Cl distance in AlCl$_3$. The electrostatic potential cuts through the ionic radius of the surface Cl ions hence a large positive potential is seen above these ions. The potential above the Al ions is approximately zero, hence it is likely that the aluminium ions do not act as Lewis acid sites. In comparison the potential above the Al ions (at 1.82 Å above the Al ions, as this is the Al-F bond length in bulk $\beta$-AlF$_3$) on the $\beta$-AlF$_3$ T1 termination (described in section 7.3), which is known to be a reasonably strong Lewis acid [93, 94], is 0.16 Hartrees $|e|^{-1}$. A more quantitative method of measuring the Lewis acidity of sites is to measure the binding energies and vibrational spectra of Lewis bases such as NH$_3$ or CO. These methodologies are applied to AlF$_3$ surfaces in Chapters 8 and 9.
Figure 5.2: A side on view of the stoichiometric $3\text{Cl}$ terminated $\text{AlCl}_3$ slab. The $\text{Al}$ ions are represented by small spheres and the $\text{Cl}$ ions by large spheres.

Figure 5.3: The electrostatic potential in the (001) plane, 2.34 Å above the surface most $\text{Al}$ ions. The contours shown are on a scale ranging from 0.15 (red) to -0.15 (blue) in units of Hartrees $|e|^{-1}$. There are a total of 100 contour lines across this range. The contours above the $\text{Al}$ ions are green which represents a potential of approximately zero. This is the same scale that is used for $\beta$-$\text{AlF}_3$, shown in figure 7.6. The electrostatic potential cuts through the ionic radius of the surface $\text{Cl}$ ions hence a large positive potential is seen above these ions.
5.4 Conclusions

The basal plane of the AlCl$_3$ surface has been studied using total energy calculations based on hybrid exchange density functional theory. A variety of surface terminations have been considered and their relative stability as a function of external chlorine chemical potential has been evaluated. It has been shown that under all reasonable reaction conditions, the surface would be terminated by a layer containing three Cl ions and that it has a very low surface energy. The electrostatic potential above the surface indicates that the Cl ions mask the Al ions from the surrounding environment and, therefore, the surface is not Lewis acidic. This observation is fully consistent with a recent experimental observation that shows that the ideal AlCl$_3$ surface is chemically inert and does not act as a Lewis acid catalyst \[\text{[10]}\].
Chapter 6

The surface structure of $\alpha$-AlF$_3$ as a function of HF and H$_2$O chemical potential.

6.1 Introduction

The structure of crystalline AlF$_3$ is very different to that of AlCl$_3$. As discussed in chapter 5, crystalline AlCl$_3$ consists of Cl-Al-Cl layers. The Al ions, which are at the centre of each layer, polarise the Cl ions and consequently the Cl ions in neighbouring layers do not repel one another. F$^-$ ions are more electronegative than Cl$^-$ ions, hence they are smaller and less polarisable, consequently F ions would strongly repel one another in this type of lattice [26]. The various crystalline forms of AlF$_3$ consist of arrangements of corner sharing AlF$_6$ octahedra [4, 95, 6]. The thermodynamically stable phase is $\alpha$-AlF$_3$. The bulk structure of $\alpha$-AlF$_3$, shown in figure 6.1 is closely related to the corundum structure adopted by $\alpha$-Al$_2$O$_3$ but with one of the aluminium sites occupied in the oxide being vacant in the fluoride [4, 95]. The surfaces of $\alpha$-AlF$_3$ are known to be less catalytically active than the surfaces of the moderately catalytic $\beta$ phase and the highly catalytic amor-
phous high surface area material (HS-AlF₃) [96]. It is not understood, however, how the surface structure of the different phases of AlF₃ leads to the observed differences in their catalytic activity.

X-ray diffraction studies have shown that crystallites of α-AlF₃ predominately expose the (0112) surface [97]. We have, therefore, initially studied the (0112) termination of α-AlF₃. We also consider the stability of the {0001}, {1011}, {2110} and {1014} surfaces and use this data to construct a Wulff plot [98] and predict the equilibrium morphology of α-AlF₃ crystallites.

It is well known that the surfaces of AlF₃ strongly hydrolyse and adsorb water. Hydroxylated surfaces are expected to have different catalytic properties (possibly including Brønsted acidity) to those of clean surfaces. HF is often used as a fluorination agent to refluorinate hydroxylated AlF₃ surfaces. Examining the surface structure and stoichiometry under typical reaction conditions is therefore of great importance to enable a better understanding of the catalytic nature of AlF₃ surfaces. In this study the hydroxylation of two α-AlF₃ surfaces is considered along with the adsorption of H₂O and HF to their under-coordinated Al ions. The relative energetics of these surfaces are used to predict the stability of α-AlF₃ surfaces as a function of HF and H₂O chemical potential.

6.2 Methodology

There is some confusion in the literature regarding the space group of bulk α-AlF₃. This has been reported variously as either R₃ [4] or R₃c [95]. We performed calculations within the R₃ space group which is consistent with both possibilities; the R₃c space group is a special case of the R₃ space group. The bulk unit cell of α-AlF₃, within the R₃ space group, is defined by four parameters; the a and c lattice vectors of the unit cell and the fractional coordinates of the F ions. The Al ions are located at the positions (0.0, 0.0, 0.0) and (0.0, 0.0, 0.5) while the F ion is located at position (x, 0.3333, y).
A full structure optimisation of the bulk geometry of $\alpha$-AlF$_3$ was performed, as described in section 3.4.5. The optimised lattice parameters and the (unrestrained) atom positions are displayed in table 6.1, along with results obtained experimentally using X-ray powder diffraction methods. The calculated equilibrium lattice constants for the unit cell agree with those observed to within 2% and as expected from a B3LYP calculation of an ionic material, the predicted bond lengths are slightly too long.

Terminations of the $\alpha$-AlF$_3$ (01T2), (0001), (10T1), (2110) and (10T4) surfaces were obtained by cleaving the bulk crystal along different layers within these five planes. Obviously, the surface may undergo reconstruction, but in the absence of experimental data...
we considered the smallest unit cell in which a stoichiometric surface could be obtained. The geometry of each slab was relaxed to minimise its total energy. Initial surface geometry and energy convergence tests with respect to slab thickness were carried out for the stoichiometric \((01\overline{2})\) \((1 \times 1)\) termination.

The relative stability of surfaces with different stoichiometries is determined by the comparison of their surface free energy, using the methodology described in chapter 4. It is applied here to calculate the relative free energies of low index \(\alpha\)-\(\text{AlF}_3\) surfaces as a function of fluorine chemical potential. The most stable surface along each plane has then been used to calculate a Wulff plot \cite{98} for \(\alpha\)-\(\text{AlF}_3\). The \textit{ab initio} thermodynamics method is then extended to multicomponent environments \cite{82}, as described in chapter 4. This methodology is used to calculate the free energy of clean, hydroxylated and hydrated \(\text{AlF}_3\) surfaces as a function of the chemical potentials of HF and \(\text{H}_2\text{O}\).

To obtain an accurate phase diagram requires calculations of the free energies of every structure that may conceivably occur. Our studies of the clean \(\alpha\)-\(\text{AlF}_3\) surfaces will show (in sections \ref{6.3.2} and \ref{5.3.2}) that the dominant theme governing the stability of \(\text{AlF}_3\) surfaces is stoichiometry. The strong ionic character of \(\text{Al}^{3+}\) and \(\text{F}^-\) ions implies that only stoichiometric slabs which maintain charge balance will be present in the phase diagram. \(\text{OH}^-\) ions must, therefore, be substituted for \(\text{F}^-\) ions, maintaining a stoichiometry of \(\text{AlF}_{3-x}(\text{OH})_x\). In this study we consider replacing up to three surface \(\text{F}^-\) ions for \(\text{OH}^-\) ions on each surface of interest. The energies of all possible structures in which one, two or three of the surface \(\text{F}^-\) ions are replaced by \(\text{OH}^-\) ions were calculated. Adsorption of HF and \(\text{H}_2\text{O}\) above the under coordinated \(\text{Al}\) ions on each of the clean and hydroxylated surfaces are also calculated. A very large number of calculations were required, hence, approximate calculations using CRYS'TAL, but with a lower level of numerical accuracy (the overlap criteria, the shrinking factors and the size of the integration grid were all reduced), as described in section \ref{3.4.8}, were initially performed to predict which surfaces were candidates for inclusion in the phase diagrams. Comparisons between the accurate
and approximate calculations showed that relative differences in the surface energies of structures with identical stoichiometries were calculated to within 0.005 Jm$^{-1}$. Accurate calculations were performed for each system that had a surface free energy within 0.01 Jm$^{-1}$ of the lowest energy surface for each possible stoichiometry.

### 6.3 Results and Discussion

#### 6.3.1 Slab thickness convergence tests

The surface energies of the stoichiometric (01T2) (1 × 1) termination, as a function of slab thickness were calculated. There are two possible ways of maintaining top-bottom symmetry; either a mirror or a glide symmetry operation can be applied to the slab. The slabs obtained from these two different symmetry operations are shown in figure 6.2. When a glide symmetry operation is applied, the Al ions at the centre of the slab buckle when the slab is relaxed. This relaxation effect results in an energy lower than the true value of the surface energy. When a mirror symmetry operation is applied the symmetry constraint does not allow any buckling of the centre most layer of ions. Therefore, increasing the slab thickness results in a decrease of the surface energy as relaxation of ions can occur further away from the surface. The results of these convergence tests are displayed in table 6.2. The surface energy converges to within 0.01 Jm$^{-2}$ for a slab consisting of eight Al ions, this corresponds to a slab thickness of 11.2 Å, measured between surface Al ions on either side of the slab. In all subsequent calculations a similar thickness of slab and a glide symmetry operation are used.
Figure 6.2: The 3F (012) $\alpha$-AlF$_3$ slab containing 8 Al ions. (a) a glide symmetry operator has been applied in the z direction (b) a mirror symmetry operator has been applied in the z direction.

Table 6.2: The surface energies of the stoichiometric $\alpha$-AlF$_3$ (0112) (1×1) termination. The magnitude of the buckling to the centre-most row of Al ions is also displayed for the slab containing the glide symmetry operator (figure 6.2a).

<table>
<thead>
<tr>
<th>No. of Al ions</th>
<th>Surface energy (Jm$^{-2}$)</th>
<th>bulk Al buckle (Å)</th>
<th>Surface energy (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.917</td>
<td>0.232</td>
<td>0.973</td>
</tr>
<tr>
<td>8</td>
<td>0.938</td>
<td>0.151</td>
<td>0.955</td>
</tr>
<tr>
<td>10</td>
<td>0.945</td>
<td>0.037</td>
<td>0.949</td>
</tr>
<tr>
<td>12</td>
<td>0.946</td>
<td>0.039</td>
<td>0.948</td>
</tr>
</tbody>
</table>
6.3.2 The fluorine terminated surfaces

The (01\textit{1}2) surface

The surface free energies of the \(\alpha\)-\(\text{AlF}_3\) (01\textit{1}2) terminations, within a \((1 \times 1)\) cell, as a function of fluorine chemical potential and fluorine partial pressure at 300K are plotted in figure 6.3. The surfaces are labelled according to the number of F ions present. The 3F structure represents a stoichiometric slab. The 2F surface contains one less F ion per \((1 \times 1)\) cell and, similarly, the 4F surface contains an additional F ion compared to the 3F surface.

At all but very high fluorine chemical potentials the stoichiometric termination has the lowest surface energy. At very high fluorine chemical potentials the 5F structure is most stable, however, this structure, after optimisation is equivalent to the stoichiometric (3F) slab with an \(\text{F}_2\) molecule adsorbed at its surface; with a binding energy of 0.1 eV. The stoichiometric (3F) structure, shown in figure 6.4a, consists of alternating 6-fold and 5-fold coordinated Al ions. The Al ions are each bound to five bidentate F ions, the 6-fold Al ions, in addition are also coordinated to a monodentate F ion. The surface energy of this structure is \(0.94 \text{ Jm}^{-2}\). It will be shown in chapters 8 and 9 that the 5-fold Al ion on this termination acts as a strong Lewis acid. \(\alpha\)-\(\text{AlF}_3\) is known to be less catalytically active than \(\beta\)-\(\text{AlF}_3\) [96]; this suggests that there may be a more stable and less Lewis acidic termination of the \(\alpha\)-\(\text{AlF}_3\) (01\textit{1}2) surface.

Analysis of the structures and the energetics of the \(\beta\)-\(\text{AlF}_3\) surfaces (to be discussed in chapter 7) suggested that a lower energy \(\alpha\)-\(\text{AlF}_3\) (01\textit{1}2) surface could be obtained within an \((\sqrt{2} \times \sqrt{2})\) cell. The predicted structure was optimised. The structure of this surface is shown in figure 6.4b, it has a surface energy of \(0.76 \text{ Jm}^{-2}\), hence it is more stable than the \((1 \times 1)\) termination. The surface Al ions on the \((\sqrt{2} \times \sqrt{2})\) termination are bound to four bidentate F ions and one monodentate F ion.
Figure 6.3: The surface energies of the various terminations of the (01̅12) (1 × 1) α-AlF₃ surfaces as a function of fluorine chemical potential and fluorine partial pressure at 300K.

Figure 6.4: The structures of (a) the (01̅12) (1 × 1) termination and (b) the (01̅12) (√2 × √2) termination. The F ions are represented by large spheres and the Al ions by small spheres.
Figure 6.5: The surface energies of the various terminations of the (0001) (1×2) α-AlF₃ surfaces as a function of fluorine chemical potential and fluorine partial pressure at 300K.

The (0001) surface

The smallest cell required to obtain a stoichiometric termination is either a (1×2) or a (2×1) cell; these two cells are indistinguishable from one another. The surface free energies of the α-AlF₃ (0001) terminations, within a (1×2) cell, as a function of fluorine chemical potential and fluorine partial pressure at 300K are plotted in figure 6.5. The stoichiometric termination is the most stable at all realistic fluorine chemical potentials. At zero chemical potential the surface energy of the 5F surface is identical to that of the 3F surface. This is because the optimised 5F surface consists of the 3F surface and a gas phase F₂ molecule.

Two possible stoichiometric terminations, calculated within a (1×2) cell, were obtained and labelled Type A and Type B, both had very similar surface energies of 1.18 and 1.19 Jm⁻² respectively. Given this small difference in energies it is expected that both terminations will occur on the (0001) surface. The structures of these two terminations are shown in figure 6.6. Both terminations contain a 4-fold and a 5-fold coordinated
surface Al ion. The 4-fold Al is almost perfectly tetrahedrally coordinated whereas the 5-fold Al ion is in a distorted and truncated octahedral geometry. The differences between the two terminations arises from the rotation of the tetrahedral Al ion by approximately $60^\circ$; the Al ion binds to different F ions in the two structures.

The phase diagrams for the (01T2) and (0001) terminations show that the dominant theme governing surface stability is stoichiometry. For every Al ion present in the stable slabs there are three negative ions present allowing the formation of an Al$^{3+}$ and three F$^-$ ions. Consequently our studies of the (10T1), (2110) and (10T4) surfaces only involve the determination of stoichiometric surface structures and energetics.

The (10T1) surface

Two possible structures of the (10T1) surface have also been obtained, with energies of 1.15 and 1.20 Jm$^{-2}$, these structures are essentially equivalent to the (0001) type A and type B terminations respectively. The most significant difference is that the unit cell of the (10T1) surface is approximately 1.6% larger than the unit cell of the (0001) surface.
Figure 6.7: The structure of the (\(\overline{2}110\)) termination (\(E=1.04\ \text{Jm}^{-2}\)). The F ions are represented by large spheres and the Al ions by small spheres.

The \((\overline{2}110)\) surface

The relaxed stoichiometric \((\overline{2}110)\) termination, shown in figure 6.7, has a surface energy of \(1.04\ \text{Jm}^{-2}\). The surface Al ions are coordinated to four bidentate F ions and a monodentate F ion. The local structure of this surface is very similar to that of the \((01\overline{1}2)\) \((\sqrt{2} \times \sqrt{2})\) termination. The most significant difference between the two surfaces is the density of Al ions. On the \((01\overline{1}2)\) termination there are 3.9 surface Al ions per nm\(^2\) compared with 5.5 per nm\(^2\) on the \((\overline{2}110)\) termination. The ratio of the density of sites \((3.9/5.5 = 0.71)\) is similar to the ratio of the surface energies, \((0.76/1.04 = 0.73)\). In chapter [7] we show that the surface energies of AlF\(_3\) can be predicted by consideration of the density and local geometry of surface Al ions.

The \((10\overline{1}4)\) surface

The relaxed stoichiometric \((10\overline{1}4)\) termination has been calculated and it is essentially equivalent to the \((\overline{2}110)\) termination. It has a surface energy of \(1.06\ \text{Jm}^{-2}\) and its unit cell is 1.2\% smaller than that of the \((\overline{2}110)\) termination.
Crystal Morphology

The predicted morphology of an $\alpha$-AlF$_3$ crystal, calculated from the lowest energy {01T2}, {0001}, {10T1}, {2110} and {10T4} surfaces is shown in figure 6.8. The effect of line defects and point defects at the regions were two or more surfaces meet are not considered in the construction of this morphology plot. It should be noted, however, that for nano-crystallites these may make a significant contribution to the surface structure of such a crystallite. The {0001} and {10T1} surfaces are essentially identical as are the {2110} and {10T4} surfaces. The surface of the crystal is composed of approximately 82% {01T2} surfaces, 14% {2110} and {10T4} surfaces and 4% {0001} and {10T1} surfaces. In a previous study, Chaudhuri et al [99] used an atomistic molecular dynamics approach to study initially cubic nanoparticles of AlF$_3$. In their study they started with a cubic nanoparticle displaying the {0001} surface and performed a molecular dynamics simulation in order to obtain an equilibrium morphology for an $\alpha$-AlF$_3$ nanoparticle. The dominance of the {0001} surface in their resultant structure is likely to be an artifact of their choice of initial geometry which prevented thermodynamic equilibrium from being reached during the time scale of the simulation.

6.3.3 Hydroxylation and adsorption of H$_2$O and HF

The structure and stability of the $\alpha$-AlF$_3$ surfaces as a function of HF and H$_2$O partial pressure is now considered. The $\alpha$-AlF$_3$ (0001) and the (01T2) terminations are considered as they are significant in the crystal morphology plot. The ($\bar{2}$110) termination has not been considered, even though it is predicted to occur on real crystallites, as its surface structure is similar to the (01T2) ($\sqrt{2} \times \sqrt{2}$) termination. The stability of both the $\alpha$-AlF$_3$ (01T2) (1×1) and ($\sqrt{2} \times \sqrt{2}$) terminations are initially considered separately. The resultant phase plots are then used to produce a combined phase plot for the (01T2) surface.
Figure 6.8: Equilibrium morphology of an $\alpha$-AlF$_3$ crystal predicted from the energies of the $\{01\bar{1}2\}$, $\{0001\}$, $\{10\bar{1}1\}$, $\{\bar{2}1\bar{1}0\}$ and $\{10\bar{1}4\}$ surfaces.

The (01T2) ($\sqrt{2} \times \sqrt{2}$) termination

The phase diagram for the (01T2) ($\sqrt{2} \times \sqrt{2}$) termination is shown in figure 6.9. The clean (non hydroxylated) termination is labelled the 3F termination, the hydroxylated surfaces are labelled according to the number of F ions that are replaced by OH ions per surface unit cell (i.e. 2F-1OH, 1F-2OH and 3OH). The structures of the 2F-1OH, 1F-2OH and 3OH terminations, that occur in the phase diagram, are shown in figure 6.10. A number of simple rules governing OH substitution for F ions emerge from the large number of slab calculations that were performed. The bidentate F ions are preferentially substituted for OH ions. Furthermore, it is preferable to replace F ions at positions where the Al-F-Al angle is relatively small ($\approx 140^\circ$). Replacing an F ion where the Al-F-Al angle is larger ($\approx 165^\circ$) is energetically unfavourable as it results in a large distortion of the surface, to form an Al-O-Al angle of approximately 140°.

Adsorption of HF to the 3F termination results in very strong hydrogen bonds, of length 1.22 Å, forming between the HF molecule and nearby monodentate F ions, as shown in figure 6.11a. As will be shown in chapter 10, similar structures are predicted for
Figure 6.9: The stable terminations of $\alpha$-AlF$_3$ (0112) ($\sqrt{2} \times \sqrt{2}$) as a function of HF and H$_2$O effective chemical potential and partial pressure and temperature. The area within the small rectangle is the accessible region of the phase diagram at 300K and the region within the large rectangle is the accessible region at 600K (see text for details).

Figure 6.10: The structures of (a) the 2F 1OH, (b) the 1F 2OH and (c) the 3OH $\alpha$-AlF$_3$ (0112) ($\sqrt{2} \times \sqrt{2}$) terminations. The F ions are represented by large spheres and the Al ions by small spheres.
Figure 6.11: The structures of (a) HF adsorbed on the 3F (0112) \((\sqrt{2} \times \sqrt{2})\) termination, (b) \(\text{H}_2\text{O}\) adsorbed on the 3F termination and (c) \(\text{H}_2\text{O}\) adsorbed on the 1F-2OH termination. The F ions are represented by large spheres and the Al ions by small spheres.

The adsorption of HF, at half monolayer coverage, to \(\beta\)-AlF\(_3\). Adsorbed HF may act as a strong Brønsted acid as it could give up its proton, for instance, to protonate nearby OH\(^-\) groups. It may be that the catalysis of some reactions requires the availability of both a strong Lewis acid site and a Brønsted acid site. The stoichiometry of an \(x\text{F}-(3-x)\text{OH} + \text{HF (}x = 0,1 \text{ or 2)}\) termination is the same as an \((x+1)\text{F}-(2-x)\text{OH} + \text{H}_2\text{O}\) termination. It is always energetically favourable to form the termination consisting of an adsorbed \(\text{H}_2\text{O}\) molecule, consequently hydroxylated surfaces with adsorbed HF are not present in the phase diagram. Adsorption of \(\text{H}_2\text{O}\) to the 3F termination is shown in figure 6.11b. The \(\text{H}_2\text{O}\) molecules form strong hydrogen bonds to nearby monodentate F ions. Adsorption on the hydroxylated surfaces occurs in an analogous manner; adsorption on \(\text{H}_2\text{O}\) to the 1F-2OH termination is shown in figure 6.11c.

The phase diagram in figure 6.9 is plotted for effective chemical potentials ranging from 0.0 to -2.9 eV. The corresponding partial pressures at room temperature (300K) and at a typical reaction temperature (600K) are also displayed. The full range of the phase diagram, shown in figure 6.9, is not accessible at any given temperature. Regions of the phase diagram that are accessible at 300K and 600K are marked by rectangles in figure 6.9. The lower limits for the \(\text{H}_2\text{O}\) and HF partial pressures are set at \(10^{-10}\) and \(10^{-15}\) respectively. These values are estimates of typical partial pressures expected
under UHV conditions. The partial pressure of HF is significantly less than that of O\textsubscript{2} in normal atmospheric conditions, hence a value of $10^{-15}$ is used as an estimate of UHV conditions. The upper limits are obtained from the vapour pressure of H\textsubscript{2}O and HF. At 300K the vapour pressures of H\textsubscript{2}O and HF are 0.036 atm and 1.3 atm respectively. The vapour pressure of H\textsubscript{2}O at 600K is 0.12 atm. The upper HF partial pressure is limited by experimental procedures and safety concerns, a maximum pressure of 5 atm is assumed.

Competition between hydroxylation and fluorination leads to a number of stable phases. Relatively small changes in reaction conditions can alter the surface very significantly. At 300K, under most conditions, the 3F termination with H\textsubscript{2}O adsorbed above the under-coordinated Al ions is predicted to occur. At low H\textsubscript{2}O partial pressure and high HF partial pressure the adsorbed H\textsubscript{2}O molecule will be substituted by an HF molecule. At very low HF partial pressure the surface will be partially hydroxylated. At 600K the 3F termination is expected to dominate, unless the HF partial pressures is low and the H\textsubscript{2}O partial pressure is high, under which circumstances the surface is predicted to be hydroxylated. At very low partial pressures of HF and high partial pressures of H\textsubscript{2}O the surface is unstable with respect to complete hydroxylation of the crystallite. Observations of amorphous HS-AlF\textsubscript{3} have shown that, left exposed to air over a period of several months, it will undergo a transition to a hydroxylated pyrochlore structure \[100\].

The (01\textbar 2) (1\times1) termination

The resultant phase plot for the (01\textbar 2) (1\times1) termination is shown in figure 6.12. As for the (01\textbar 2) (\sqrt{2} \times \sqrt{2}) termination, the bidentate F ions are preferentially substituted for OH ions. The structure of the stable 2F-1OH termination is shown in figure 6.13a. The Al-F-Al angles are between 165° and 170° on the 3F termination. After hydroxylation the Al-F-Al angles reduce by around 10° and the Al-O-Al angles are between 140° and 145°. The 2F-1OH termination does not occur in the phase diagram. Hydroxylation of the 3F termination occurs at similar values of HF and H\textsubscript{2}O chemical potentials as for the
stable (01\(\bar{1}\)2) termination. The binding energies of HF and H\(_2\)O to these terminations are greater than for the analogous (01\(\bar{1}\)2) (\(\sqrt{2} \times \sqrt{2}\)) terminations. Stronger hydrogen bonding also occur on the (1×1) termination compared to the (\(\sqrt{2} \times \sqrt{2}\)) termination. The H\(_2\)O molecule hydrogen bonds via both of its hydrogens on this termination. After adsorption of HF, the HF bond length and its hydrogen bond with a nearby F ion are of the same length, 1.15 Å that is, an FHF\(^-\) species is formed. This behaviour is seen after full monolayer adsorption of HF on \(\beta\)-AlF\(_3\) surfaces, as will be shown in chapter 10. The structures of the 3F termination after adsorption of HF and H\(_2\)O are shown in figures 6.13b and 6.13c respectively.

At 300K the clean 3F termination with H\(_2\)O adsorbed above the under-coordinated Al ions is predicted to occur at most realistic HF and H\(_2\)O partial pressures. At 600K this termination is also expected to dominate at high HF and H\(_2\)O partial pressures. If the H\(_2\)O partial pressure is less than 10\(^{-4}\) atm then the 3F termination is predicted to occur. HF adsorbs to this termination if the HF partial pressure is above 5x10\(^{-2}\) atm. At low values of HF partial pressure and high values of H\(_2\)O partial pressure the surface will be hydroxylated.

The combined (01\(\bar{1}\)2) (1×1) and (\(\sqrt{2} \times \sqrt{2}\)) terminations

The phase diagram for the (01\(\bar{1}\)2) (\(\sqrt{2} \times \sqrt{2}\)) and the (1×1) terminations have been combined to produce a complete phase diagram for the (01\(\bar{1}\)2) surface. The resultant phase diagram is shown in figure 6.14. The structures that appear in this phase diagram are all derived from the (\(\sqrt{2} \times \sqrt{2}\)) 3F termination, except for the 3F+H\(_2\)O and 3F+HF terminations, which are derived from the (1×1) 3F termination. HF and H\(_2\)O bind more strongly to the (1×1) 3F termination compared to the (\(\sqrt{2} \times \sqrt{2}\)) 3F termination, as can be seen from table 6.3. Consequently, the (1×1) 3F terminations with adsorbed HF or H\(_2\)O are more stable than the corresponding structures derived from the (\(\sqrt{2} \times \sqrt{2}\)) 3F termination.
Figure 6.12: The stable terminations of (0112) (1×1) α-AlF$_3$ as a function of HF and H$_2$O effective chemical potential and partial pressure and temperature. The area within the small rectangle is the accessible region of the phase diagram at 300K and the region within the large rectangle is the accessible region at 600K (see text for details).
Figure 6.13: The structures derived from the (01\(\overline{2}\)) (1 \times 1) termination. (a) The 1F-2OH termination, (b) HF adsorbed on the 3F termination and (c) H\(_2\)O adsorbed on the 3F termination. The F ions are represented by large spheres and the Al ions by small spheres.

Table 6.3: The binding energy of H\(_2\)O and HF to the various \(\alpha\)-AlF\(_3\) 3F terminations. (The binding energies are corrected for BSSE using the counterpoise scheme \([5]\).)

<table>
<thead>
<tr>
<th>Termination</th>
<th>H(_2)O Binding energy (eV)</th>
<th>HF Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(01(\overline{2})) (1 \times 1)</td>
<td>-1.60</td>
<td>-1.26</td>
</tr>
<tr>
<td>(01(\overline{2})) ((\sqrt{2} \times \sqrt{2}))</td>
<td>-1.06</td>
<td>-0.81</td>
</tr>
</tbody>
</table>

It is important to note that the phase diagram is only based on thermodynamic considerations. The kinetic barriers to phase transitions are not considered. There is likely to be a considerable barrier to the transition from the (1 \times 1) to the (\(\sqrt{2} \times \sqrt{2}\)) structure as it requires the cleavage and formation of several Al-F bonds. \(\alpha\)-AlF\(_3\) is usually synthesised at elevated temperatures, at which the (\(\sqrt{2} \times \sqrt{2}\)) 3F termination will dominate. It may be that the transition to the (1 \times 1) 3F + H\(_2\)O termination upon cooling to room temperature is kinetically hindered. Conversely, catalytically active HS-AlF\(_3\) is synthesised using sol-gel methods that proceed at lower temperatures \([8, 101]\). It is speculated that under these conditions the formation of surfaces similar to the (1 \times 1) 3F termination are favoured over surfaces that are similar to the (\(\sqrt{2} \times \sqrt{2}\)) 3F termination. The surface structure of AlF\(_3\) has not been determined from experimental methods due to the difficulties in obtaining sufficiently large crystals for surface science experiments.
Figure 6.14: The stable $\alpha$-AlF$_3$ (01T2) surfaces, including terminations derived from the $(1 \times 1)$ and $(\sqrt{2} \times \sqrt{2})$ 3F terminations, as a function of HF and H$_2$O effective chemical potential and partial pressure and temperature. The terminations derived from the $(1 \times 1)$ 3F termination are denoted by an asterisk. The area within the small rectangle is the accessible region of the phase diagram at 300K and the region within the large rectangle is the accessible region at 600K (see text for details).
The (0001) termination

The phase plot for the (0001) (1×2) surface is shown in figure 6.15. This surface hydroxylates more readily than the (01\bar{1}2) termination. The 2F-1OH termination, shown in figure 6.16a, is based on the Type B structure; the bidentate F ion is substituted for an OH group. The OH group points towards a nearby monodentate F ion, with which it forms a hydrogen bond. The flexibility of the monodentate F ions on this surface enables the formation of hydrogen bonds, this explains, at least in part, why the surface is easily hydroxylated. Subsequent hydroxylation of the surface occurs via substitution of the two monodentate F ions for OH ions. Hydroxylation of F ions below the surface Al ions was not considered. It is interesting to note that while the 3F Type A termination is more stable than the Type B termination, the hydroxylated Type B terminations are more stable than their Type A counterparts. This is due to the formation of a bridging OH ion on the type B termination.

There are both 5-fold and 4-fold Al ions exposed at the (0001) surface. It is possible to adsorb up to three molecules per unit cell; two to the 4-fold Al and one to the 5-fold Al. This leads to a very large number of possible permutations of molecular adsorption geometries. The most stable surfaces that involve adsorbed molecules are those where the molecules form strong hydrogen bonds to surface F and OH ions. Such bonds are usually formed to monodentate ions due to their greater flexibility compared to bidentate F ions. Consequently, in almost all cases, the stable surfaces involving adsorbed molecules are based on the Type A structure. The structures of the 3F terminations after adsorption of two H₂O and two HF molecules are shown in figures 6.16b and 6.16c respectively. After adsorption of two HF molecules to the 3F termination, one of the molecules forms an FHF⁻ species, where the two H-F bonds are of equal length, while the other forms a strong hydrogen bond. In the later case the HF bond length is 1.05 Å and the hydrogen bond is of length 1.30 Å. The (0001) surface generally adsorbs HF and H₂O molecules.
Figure 6.15: The stable $\alpha$-AlF$_3$ (0001) surfaces as a function of HF and H$_2$O effective chemical potential and partial pressure and temperature. The area within the small rectangle is the accessible region of the phase diagram at 300K and the region within the large rectangle is the accessible region at 600K (see text for details).

Figure 6.16: The structures derived from the (0001) surface. (a) The 2F-1OH termination, (b) HF adsorbed on the 3F termination and (c) H$_2$O adsorbed on the 3F termination. The F ions are represented by large spheres and the Al ions by small spheres.
more strongly than the (01T2) \((\sqrt{2} \times \sqrt{2})\) termination, due to the formation of hydrogen bonds, but not as strongly as the (01T2) \((1 \times 1)\) termination. Hydroxylated surfaces with adsorbed HF are not present in the phase diagram for the same reasons as discussed in section 6.3.3.

At 300K a range of terminations can be expected, depending on the HF and H\textsubscript{2}O partial pressures. Under normal laboratory conditions, three H\textsubscript{2}O molecules are predicted to adsorb on the 3F termination. At 600K, a large number of different terminations occur. Under typical reaction conditions, for instance 20\% humidity and an HF partial pressure between \(10^{-1}\) and \(10^{-5}\) atm two H\textsubscript{2}O molecules are predicted to adsorb on the 3F termination.

### 6.4 Conclusions

The structure and energetics of \(\alpha\)-AlF\textsubscript{3} surfaces have been calculated. It is shown that the stable surfaces are always stoichiometric, due to the highly ionic nature of AlF\textsubscript{3}. The morphology of \(\alpha\)-AlF\textsubscript{3} crystallites has been predicted. It is shown that the \{01T2\} surface dominates the crystallites. Under-coordinated Al ions are always exposed at the surface of \(\alpha\)-AlF\textsubscript{3} crystallites. These Al ions are either coordinated to four or five F ions.

The surface structure of the (01T2) and (0001) terminations of \(\alpha\)-AlF\textsubscript{3} were calculated as a function of HF and H\textsubscript{2}O chemical potentials. The phase diagrams for these surfaces showed many similarities. Formation of hydrogen bonds between the OH\textsuperscript{−}, HF and H\textsubscript{2}O species to nearby F and O ions occurred readily and the stable surfaces always maximised such bonding. Under standard atmospheric conditions the surfaces were predicted to adsorb water above under-coordinated Al ions. To expose the under-coordinated Al ions the surfaces must be heated up and put under conditions of low H\textsubscript{2}O partial pressure and high HF partial pressure.

The phase diagram for the (01T2) termination contains phase boundaries between the
structures derived from the \((1 \times 1)\) and the \((\sqrt{2} \times \sqrt{2})\) surfaces. The \((1 \times 1)\) 3F termination consists of very strong Lewis acid sites, however it is only thermodynamically stable when its Lewis acid sites are saturated by HF or H\(_2\)O. This suggests that to obtain catalytically active AlF\(_3\) it is necessary to desorb these molecules at a temperature below that at which the surface reconstructs to form the inactive \((\sqrt{2} \times \sqrt{2})\) phase. The sol-gel process used to obtain catalytically active HS-AlF\(_3\) satisfies this condition \[8, 101\].
Chapter 7

The surface structure and crystal morphology of $\beta$-AlF$_3$

7.1 Introduction

$\beta$-AlF$_3$ surfaces are known to be moderately catalytically active, unlike $\alpha$-AlF$_3$ which is relatively inert, however, it is not as catalytically active as high surface area (HS) AlF$_3$ [96]. Understanding the similarities and differences in the structure of the $\alpha$- and $\beta$-AlF$_3$ surfaces may lead to an understanding of the relationship between surface structure and catalytic activity. This in turn may enable a better understanding of, and an ability to control, the catalytic properties of HS-AlF$_3$.

$\beta$-AlF$_3$, shown in figure 7.1, is related to the hexagonal tungsten bronze structure. The bulk unit cell of $\beta$-AlF$_3$ is orthorhombic and is described by the Cmm space group. It is defined by eleven parameters; the $a$, $b$ and $c$ lattice vectors of the unit cell and the fractional coordinates of the six F ions. The two Al ions are located at positions (0.0, 0.5, 0.0) and (0.25, 0.25, 0.0) and are constrained by symmetry.

Previously, models of the catalytically active $\beta$-AlF$_3$ surface have been suggested on the assumption that the (100) plane provides the dominant surface [23]. We therefore start
by studying the (100) surface. We show that there are two low energy terminations of this surface, both with very similar surface energies. These terminations are labelled the T1 and T6 terminations. It is expected that the (100) surface exposes both terminations and thus steps must occur between the two terminations. We therefore investigated two model stepped systems: One consisting of a T1 upper terrace and a T6 lower terrace and a second system in which the character of the two terraces is reversed. In the case of the T6 upper and T1 lower terrace the surface structure consists of microfacets of the (010) plane. We have therefore studied the (010) plane, and for completeness the (001) plane of $\beta$-AlF$_3$. On the basis of these calculations we have constructed an approximate Wulff plot [98], enabling us to predict the crystal morphology for this material.

### 7.2 Methodology

A full structure optimisation of the bulk geometry of $\beta$-AlF$_3$ was performed, as described in chapter [3.4.5]. The optimised lattice parameters and the atom positions are displayed
Table 7.1: The lattice parameters for the optimised bulk β-AlF₃ structure compared to values obtained from an X-ray powder diffraction study [6].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This study (Å)</th>
<th>Experiment (Å)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>7.036</td>
<td>6.931</td>
<td>1.5</td>
</tr>
<tr>
<td>b</td>
<td>12.185</td>
<td>12.002</td>
<td>1.5</td>
</tr>
<tr>
<td>c</td>
<td>7.261</td>
<td>7.134</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 7.2: The atom positions for the optimised bulk β-AlF₃. The values shown in italics are constrained by symmetry and were not optimised. The values shown in brackets were obtained from an x-ray powder diffraction study [6].

<table>
<thead>
<tr>
<th>Atom</th>
<th>x(fractional)</th>
<th>y(fractional)</th>
<th>z(fractional)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₁</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Al₂</td>
<td>0.25</td>
<td>0.25</td>
<td>0.0</td>
</tr>
<tr>
<td>F₁</td>
<td>0.0</td>
<td>0.2124 (0.2125)</td>
<td>0.5001 (0.5257)</td>
</tr>
<tr>
<td>F₂</td>
<td>0.3186 (0.3161)</td>
<td>0.1062 (0.1054)</td>
<td>0.0005 (-0.0200)</td>
</tr>
<tr>
<td>F₃</td>
<td>0.5</td>
<td>0.9996 (0.0177)</td>
<td>0.25</td>
</tr>
<tr>
<td>F₄</td>
<td>0.24970</td>
<td>0.2502 (0.2352)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

in tables 7.1 and 7.2 along with results obtained experimentally from X-ray powder and single-crystal diffraction methods [6]. It can be seen that the theoretical calculations are in close agreement with the experimental parameters, in each case, as expected, B3LYP slightly over-estimates the cell parameters. The maximum deviation in the lattice parameters is 1.7%.

Terminations of the β-AlF₃ (100), (010) and (001) surfaces were obtained by cleaving the bulk crystal along different layers within these three planes. Obviously, the surface may undergo reconstruction, but in the absence of experimental data we initially only consider the (1×1) terminations. The geometry of each slab was relaxed to minimise its total energy, as described in chapter 5. Due to the large size of the unit cell, full convergence tests with respect to slab thickness were performed using CRYystal, but with the lower level of numerical accuracy described in section 3.4.8.

The bulk unit cell of β-AlF₃ has Cmcm symmetry. However, it is very close to the
Figure 7.2: The bulk $\beta$-AlF$_3$ structure. The lines indicate the (100), (130) and (\overline{1}30) planes.

higher symmetry $P6_322$ group. Therefore, to a very good approximation the (100) plane is equivalent to the (130) and (\overline{1}30) planes of $P6_322$ symmetry. These planes are shown in figure 7.2. Similarly, the (010) plane is almost identical to the (110) and (\overline{1}10) planes. We can therefore approximate the energies of these surfaces to be the same as their (100) and (010) counterparts. These surface energies are used to calculate an approximate Wulff plot for $\beta$-AlF$_3$ [98].

7.3 Results and Discussion

7.3.1 Slab thickness convergence tests

The surface energies of the two stoichiometric terminations (T1 and T6) of the (100) surface are shown in table 7.3. The surface energies converge more slowly for the T1 termination than the T6 termination. The T1 termination is converged to better than 0.01 Jm$^{-2}$ for a slab containing 26 Al ions, this corresponds to a slab thickness of 13.8 Å, measured between surface Al ions on either side of the slab. In all subsequent calculations
Table 7.3: The surface energies of the two stoichiometric \( \beta \)-AlF\(_3\) (100) terminations. Note that the calculations were run with reduced CRYSTAL tolerances, as discussed in the text.

<table>
<thead>
<tr>
<th>T1</th>
<th>T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of Al ions</td>
<td>Surface Energy (Jm(^{-2}))</td>
</tr>
<tr>
<td>32</td>
<td>0.872</td>
</tr>
<tr>
<td>26</td>
<td>0.860</td>
</tr>
<tr>
<td>20</td>
<td>0.848</td>
</tr>
<tr>
<td>14</td>
<td>0.809</td>
</tr>
</tbody>
</table>

a similar thickness of slab is used.

7.3.2 The \( \beta \)-AlF\(_3\) (100) surface

The surface free energies of the \( \beta \)-AlF\(_3\) (100) terminations, within a (1\( \times \)1) cell, as a function of fluorine chemical potential and fluorine partial pressure at 300K are plotted in Figure 7.3. The stoichiometric terminations have significantly lower energies than the other terminations at all fluorine partial pressures. These terminations, labelled T1 and T6 and shown in figures 7.4 and 7.5 have very similar surface energies of 0.85 and 0.86 Jm\(^{-2}\) respectively.

The T1 termination, shown in figure 7.4 contains three rows of surface Al ions that run parallel to the channels in the bulk material. The upper most row of Al ions and an adjacent row form four member rings (-F-Al-F-Al-), each ring consisting of an Al ion from each row. The Al-F bond lengths of these four member rings are no more than 8% larger than those of bulk Al-F (1.82 Å). It is energetically unfavourable to also form four member rings with the Al ions on the other row, consequently, alternate Al ions on this row and the upper most row are under-coordinated. The Al ions in these two rows are all bound to five bidentate F ions and each alternate Al ion is also capped by a monodentate F ion. This results in two potential Lewis acid sites; those above the upper row of Al ions and those above the lower row of Al ions, indicated in figure 7.4.
Figure 7.3: Surface free energies of the six differently terminated slabs as a function of fluorine chemical potential and fluorine partial pressure at 300K. The surface energies for the T1 and T6 are almost identical, hence the T1 and T6 lines are not distinguishable.

Figure 7.4: A side on view (left) and a plan view (right) of the $\beta$-AlF$_3$ (100) T1 termination. The Al ions are represented by small spheres and the F ions by large spheres.
The T6 termination, shown in figure 7.5, contains two symmetric rows of surface Al ions per unit cell, which are separated by an open channel. Each of these Al ions is bound to four bidentate F ions and a monodentate F ion, hence, it is under-coordinated. Molecules can adsorb to these under-coordinated Al ions in two different ways; either from above the channel or within it. This concept is described in more detail in chapter 8. The density of under-coordinated Al ions on this surface is twice that of the T1 termination.

The under-coordinated Al ions on the T1 and T6 terminations are expected to exhibit Lewis acidity. The binding of F ions to their under-coordinated Al ions differs hence it is expected that their Lewis acidities will also differ. In an attempt to characterise these possible Lewis acid sites the electrostatic potential on a plane 1.82 Å (the Al-F bond distance in bulk $\beta$-AlF$_3$) above the under-coordinated Al ions is calculated using the same methods as described in section 5.3. Figure 7.6 displays the potential above the under-
Figure 7.6: The surface potentials 1.82 Å above the different under-coordinated Al ions on the T1 and T6 terminations. (a) The potential above the upper row of Al ions on the T1 termination. (b) The potential above the lower row of Al ions on the T1 termination. (c) The potential above the Al ions on the T6 termination. The contours run from +0.15 (red) to -0.15 (blue) in units of Hartrees $|e|^{-1}$. There are a total of 100 contour lines across this range. This is the same scale as used in figure 5.3 for the (001) surface of AlCl₃.

coordinated Al sites; two on the T1 termination and one on the T6 termination. There are regions of large positive potential above both the under-coordinated Al ions on the T1 termination. The maximum value of the potential is 0.156 Hartrees $|e|^{-1}$ above the upper row of under-coordinated Al ions and 0.159 Hartrees $|e|^{-1}$ above the lower row. Where the potential slice cuts through F ions it becomes very positive. This is because it cuts through regions where the fluorine nucleus is not shielded by electrons, hence this region should be ignored.

The potential above the T6 termination is much harder to analyse. This is because the Al ions are shielded from above by the monodentate F ions at the surface. It is likely, as the energy surface is very flat, that under reaction conditions these F ions would rotate either towards or away from the surface and expose the Al ions to a larger extent. There is a positive potential (yellow in colour) in the surface regions close to the under-coordinated Al ions. The maximum value of this potential at any point is 0.088 Hartrees $|e|^{-1}$. This value can not be compared directly to those on the T1 termination as it is not taken from
In comparison to the surface potential above AlCl$_3$ (see section 5.3), it is clear that there is a much stronger potential above these surfaces. This is indicative of Lewis acid sites, but to better quantify the Lewis acidity above the $\beta$-AlF$_3$ surfaces alternative methods of characterisation are required. In zeolite chemistry, the strength of Lewis acid sites have been quantified from calculations of the binding energy and stretching frequencies of NH$_3$ and CO absorbed at the zeolite’s acid sites [20, 25]. In chapter 8 the binding energy of NH$_3$, to the under-coordinated Al ions is calculated and in chapter 9 the binding energy of CO and its stretching frequency are calculated.

The very similar surface energies of the T1 and T6 terminations suggests that both terminations occur at the surface. Consequently a relatively high concentration of steps is expected. Two model stepped surfaces were considered within a (2×1) cell; a system consisting of a T1 upper/T6 lower terrace and a system consisting of a T6 upper/T1 lower terrace. The relaxed geometries of these systems are shown in figure 7.7. The T1 upper terrace/T6 lower terrace termination converges to a structure little different from a straight superposition of the two relaxed individual terminations. The surface energy is very similar to that of the T1 and T6 terminations individually at 0.85 Jm$^{-2}$. The under-coordinated Al ions on the T1 and T6 terminations are still present.
The termination with a T6 upper terrace/T1 lower terrace is more interesting. The optimised structure appears to show the formation of microfacets along the (010) direction. The surface Al ions that are obtained from the T1 cut of the slab all have six nearest neighbour F ions and form four-member rings, containing two Al ions (-F-Al-F-Al-). On the T1 termination only half of the surface groups form such rings, as can be seen in figure 7.4. The other surface Al ions alternate between five and six fold coordination, as it is energetically unfavourable to form these four member rings close to one another. The under-coordinated Al ions present on the T6 termination are still present on this reconstructed termination. This termination has an energy slightly lower than the other terminations at 0.84 Jm$^{-2}$ suggesting that the presence of (010) microfacets leads to a stabilisation of the surface. It should be noted that the nature of these reconstructions leads to final structures in which parts of the slab are rather thin and consequently the surface energies are unlikely to be fully converged with respect to slab thickness. However, despite this, the formation of the microfacetted structure does suggest that the (010) surface may be lower in energy than the (100) surface.

Furthermore, although it is not initially obvious, the T1 and T6 terminations also show microfaceting to the (010) plane. The high periodicity of these surfaces results in microfaceting occurring on a smaller scale, it simply becomes much more obvious on the T6/T1 stepped termination. This behaviour is commonly seen at the surface of many cubic metals where, for instance, the \{110\} surface spontaneously reconstructs giving rise to the (1\times2) missing row reconstruction [102], this results in ribbons of \{111\} like microfacets across the surface, although the initial structure also shows small microfacets of the \{111\} surface.
7.3.3 The $\beta$-AlF$_3$ (010) surface

It would be possible to perform a full analysis of all possible terminations of the (010) surface within a (1×1) cell and investigate the phase stability as a function of fluorine chemical potential. However, as for the $\alpha$-AlF$_3$ (2110) surface in section 6.3.2, we use the fact that stable terminations are always stoichiometric and consequently only consider such terminations here. Within a (1×1) unit cell there are two stoichiometric terminations of the (010) surface.

The relaxed geometries of the (010) surface are shown in figure 7.8. The surface energies are 0.74 Jm$^{-2}$ and 0.93 Jm$^{-2}$ for the S1 and S2 terminations respectively. As the S1 termination is significantly lower in energy it is expected that this termination will dominate on real crystals. The surface Al ions on the S1 termination are all bound to four bidentate F ions and a monodentate F ion. Their local geometries are almost identical to those of the Al ions on the T6 termination, however, the orientation of the Al-F groups is different on the two terminations. On the S1 termination the bond between the Al and the monodentate F ion is perpendicular to the surface, while on the T6 termination the bond makes an angle of approximately 60$^\circ$ to the surface and the monodentate F ions along adjacent rows point towards one another. There are 3.9 under coordinated Al sites per nm$^2$ on the S1 termination compared to 4.5 per nm$^2$ on the T6 termination. It is likely that this is, at least in part, why the S1 termination is more stable than the T6 termination. The S2 termination consists of a checker board like pattern in which all the Al ions are bound to five bidentate F ions and alternating ions are also bound to a monodentate F ion. The local geometries of these Al ions are similar to the alternating rows of 5-fold and 6-fold coordination on the T1 termination. There are 3.9 under-coordinated Al sites per nm$^2$ on the S2 termination compared to 2.3 per nm$^2$ on the T1 termination. Again, this may explain, at least in part, why the surface energy of the S2 termination is greater than that of the T1 termination. The comparison of the density of under-coordinated sites explains,
at least in part, the relative stability of terminations which have the same local structure (S1/T6 and S2/T1). The relative energetics of terminations with different local structures will be discussed in section 7.3.5.

7.3.4 The $\beta$-$\text{AlF}_3$ (001) surface

Three possible stoichiometric terminations, obtained from the (010) surface within a $(1 \times 1)$ cell, are considered. The relaxed structures of these terminations are shown in figure 7.9. The terminations are perpendicular to the channels that run through the $\beta$-$\text{AlF}_3$ structure. The surface energies of these terminations are 0.79, 0.93 and 1.24 Jm$^{-2}$ for the R1, R2 and R3 terminations respectively. It is therefore expected that the R1 termination will dominate this surface. The outer-most Al ions on this termination all display tetrahedral coordination. Half of the outer-most Al ions are each bound to three bidentate and one monodentate F ion, while the other Al ions are each bound to two bidentate and two monodentate F ions. The R2 termination consists of equal amounts of five-fold and six-fold surface Al ions. This termination has similarities to the T1 and S2 terminations.
Figure 7.9: The relaxed stoichiometric (001) terminations. The Al ions are represented by small spheres and the F ions by large spheres.

It has a density of 3.5 under-coordinated Al ions per nm$^2$. The high energy R3 termination consists of two Al ions per unit cell in its outer-most layer. These are both bound to four F ions, one type bound to one monodentate F ion and the other to two monodentate F ions. These species are approximately tetrahedral, although significantly more distorted than those found on the stable R1 termination.

7.3.5 Predicting Surface energies

Analysis of these terminations suggests that a simple model could be used to predict their surfaces energies. We define the Al effective coordination number as the number of bidentate F ions it is bound to multiplied by one half added to the number of monodentate F ions it is bound to. For example, an Al ion bound to six F ions, one of which is monodentate, has an effective coordination number of 3.5 ($5 \times 0.5 + 1$). Three factors contribute to the surface energies; the density of 5-fold and 4-fold Al ions and the density of Al ions that do not have an effective coordination number of three. Analysis of our data shows that the surface energies can be estimated using

$$E = \frac{1}{A} \{19.0 \times (\text{No. of 5-fold Al ions}) + 27.4 \times (\text{No. of 4-fold Al ions})$$
$$+ 2.6 \times (\text{No. of Al eff. coord} \neq 3)\}. \quad (7.1)$$
where \( A \) is the area of the termination and the pre-factors are obtained from numerical fits to the data.

The results from this analysis are shown in table 7.4. We have also included the \( \alpha \)-AlF\(_3\) terminations discussed in chapter 6 in this table. The two \( \alpha \)(0001) surfaces appear identical from this analysis, but are structurally different. Both surfaces contain two monodentate F ions. In one case they are both attached to the same Al ion, while on the other each is attached to a separate Al ion. It can be seen that this model can accurately predict the surface energies. The only large discrepancy is for the (100) T1 termination where the model under-estimates the surface energy. This is most probably because the model does not take into account the distorted four-member rings that occur on this termination. The (001) R1 and R2 surface energies are over-estimated by around 10%. These terminations cut perpendicularly through the channels of \( \beta \)-AlF\(_3\), hence the problem may be in the non uniform distribution of the atoms in the surface plane. The accurate prediction of the (001) R3 termination may be due to this error being cancelled by the neglect of the distorted nature of its Al tetrahedra.

7.3.6 Crystal morphology

The predicted equilibrium morphology of a \( \beta \)-AlF\(_3\) crystal, calculated from the lowest energy \{100\}, \{010\} and \{001\} planes and assuming \( P6_322 \) symmetry, as discussed in section 7.2, is shown in figure 7.10. The surface area of the crystal is composed of; 4\% \{001\} surface, 59\% \{010\} surface and 38\% \{001\} surface.

7.4 Conclusions

We have shown that the (100) surface is unstable with respect to the formation of microfacets consisting of the (010) crystallographic plane. We have consequently calculated the surface structure of the (010) surface, and for completeness the (001) surface. The en-
Table 7.4: The parameters used to predict the surface energies of the surface using equation [7.7]. The predicted energies and those calculated from our DFT energy calculations are displayed.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Surface area ( (\text{Å}^2) )</th>
<th>No. of 5-fold Als</th>
<th>No. of 4-fold Als</th>
<th>No. of Als coord ( \neq 3 )</th>
<th>Predicted energy ( (\text{Jm}^{-2}) )</th>
<th>Calculated energy ( (\text{Jm}^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta(100) ) T1</td>
<td>88.5</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>0.55</td>
<td>0.85</td>
</tr>
<tr>
<td>( \beta(100) ) T6</td>
<td>88.5</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>( \beta(010) ) S1</td>
<td>51.1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>( \beta(010) ) S2</td>
<td>51.1</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>( \beta(001) ) R1</td>
<td>85.7</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0.70</td>
<td>0.79</td>
</tr>
<tr>
<td>( \beta(001) ) R2</td>
<td>85.7</td>
<td>3</td>
<td>0</td>
<td>6</td>
<td>0.85</td>
<td>0.93</td>
</tr>
<tr>
<td>( \beta(001) ) R3</td>
<td>85.7</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>1.24</td>
<td>1.24</td>
</tr>
<tr>
<td>( (1 \times 1) \alpha(01\overline{1}2) )</td>
<td>25.7</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>( (\sqrt{2} \times \sqrt{2}) \alpha(01\overline{1}2) )</td>
<td>51.6</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.74</td>
<td>0.76</td>
</tr>
<tr>
<td>( \alpha(0001) ) A</td>
<td>44.0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1.17</td>
<td>1.18</td>
</tr>
<tr>
<td>( \alpha(0001) ) B</td>
<td>44.0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1.17</td>
<td>1.19</td>
</tr>
<tr>
<td>( \alpha(2110) )</td>
<td>36.6</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1.04</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure 7.10: The morphology of a \( \beta \)-\text{AlF}_3\) crystal predicted from the approximate Wulff plot of the \{100\}, \{010\} and \{001\} lowest energy surfaces.
ergetics of these surfaces have been used to predict the morphology of a \( \beta \)-AlF\(_3\) crystal. We have shown that only a small amount of the \( \{100\} \) surface is expected to be exposed on such crystals. There are many similarities between many of the stoichiometric \( \{100\} \), \( \{010\} \) and \( \{001\} \) terminations. However, the lowest energy \( \{001\} \) surface has a significantly different structure to any of the \( \{100\} \) and \( \{010\} \) terminations. Furthermore, the analysis of these surfaces reveals that their energies can be approximately predicted from their surface structure alone. To enable a full understanding of the catalytic properties of \( \beta \)-AlF\(_3\) and related high surface area AlF\(_3\) materials it is imperative that future studies and models of chemical reactivity consider all of these different low energy surfaces.
Chapter 8

Characterisation of Lewis acid sites on \( \alpha \)- and \( \beta \)-AlF\(_3\) surfaces: Adsorption of NH\(_3\)

8.1 Introduction

The structures of the \( \alpha \)- and \( \beta \)-AlF\(_3\) surfaces have been studied in chapters 6 and 7 respectively. The surfaces all contain Al ions that are under-coordinated, which are predicted to be Lewis acid sites [103]. The local structure around these sites differs on the different surfaces. The Al ions bind to either four or five F ions and up to two of these F ions may be monodentate.

It might be expected that 4-fold coordinated Al ions would be more reactive than the 5-fold Al ions [99]. However, the difference in the coordination geometries of these sites also exerts a strong influence on the reactivity of the sites. In metal oxide systems, tetrahedral coordination generally occurs for metal ions with radii less than 0.5 Å and octahedral coordination for radii between 0.5 and 0.8 Å [104]. The ionic radius of F\(^-\) is 1.33 Å compared to 1.36 Å for O\(^{2-}\) [105], hence we can expect the coordination properties
of metal halides to be similar to those of their corresponding metal oxides. The ionic radii of Al\(^{3+}\) is 0.54 Å \[105\] which is close to the boundary between tetrahedral and octahedral coordination and consequently the formation of a tetrahedral AlF\(_4\) site in the current system is not surprising. This observation is of great significance. Previously it has been suggested that the very strong Lewis acid sites on AlF\(_3\) materials may be due to 4-fold Al ions \[99\]. However, the formation of stable tetrahedral structures, found here, suggests that such sites may be only moderately Lewis acidic. Conversely, the 5-fold coordinated Al ions, being in a distorted and truncated octahedra, may be expected to show stronger Lewis acidity.

The binding energy of NH\(_3\) is commonly used to quantify the strength of a Lewis acid \[25, 21, 22\]. DFT calculations on the zeolite, Mordenite, \[25\] suggest a range of Lewis acid sites; from very weak sites with NH\(_3\) binding energies as small as -0.2 eV to very strong sites with binding energies of up to -1.7 eV. The DFT (using the GGA approximation) calculated binding energy of NH\(_3\) to sites on the V\(_2\)O\(_5\) (010) surface is around -1.3 eV \[106\], which is again typical of a strong Lewis acid site. Lewis acidity can also be characterised by the vibrational spectrum of an adsorbed species such as pyridine, CO or CD\(_3\)CN. However, the vibrational spectra of adsorbed NH\(_3\) is not a reliable method of quantifying Lewis acidity, in part, because the vibrational frequencies are very sensitive to the formation of hydrogen bonds between the adsorbed NH\(_3\) molecules and the surface to which they adsorb.

In this chapter the binding energy of NH\(_3\) to sites on the surfaces predicted to be exposed on \(\alpha\)- and \(\beta\)-AlF\(_3\) crystallites is calculated. The adsorption of NH\(_3\) is then considered in more detail at the \(\beta\)-AlF\(_3\) (100) T1 and T6 terminations. The variation in binding energy as a function of NH\(_3\) coverage is studied and these results are used to develop a kinetic Monte Carlo model which is used to predict the temperature programmed desorption (TPD) spectra. Comparison with experimental TPD studies of NH\(_3\) from \(\beta\)-AlF\(_3\) provides strong evidence to support these models of the surface. The mechanism by which NH\(_3\)
bonds to these surfaces is investigated by studying the charge transfer and the electrostatic interaction energy between NH$_3$ molecules and the $\beta$-AlF$_3$ (100) T1 and T6 terminations.

### 8.2 Methodology

NH$_3$ molecules were assumed to adsorb above under-coordinated Al ions via their nitrogen atom. Structures were then fully optimised. The counterpoise scheme [5] was used to estimate the basis set superposition error (BSSE) between the adsorbed NH$_3$ molecules and the surface. Temperature programmed desorption was simulated using a kinetic Monte Carlo model, as described in section 4.3.

### 8.3 Results and Discussion

#### 8.3.1 Comparison of Lewis acid sites

The binding energies of NH$_3$ to the under-coordinated Al ions on the surfaces predicted to be exposed on crystallites of $\alpha$ and $\beta$-AlF$_3$ are tabulated in table 8.1. In addition, the binding energy for adsorption to the metastable $\alpha$-AlF$_3$ (01$\bar{1}$2) (1×1) is also presented. The binding energies to the $\alpha$-AlF$_3$ (10$\bar{1}$4) and (10$\bar{1}$1) are not considered as sites on these terminations are essentially identical to sites on the (2110) and (0001) terminations respectively.

The under-coordinated Al sites on the $\beta$-AlF$_3$ (100) T1 termination and on the (1×1) $\alpha$-AlF$_3$ (01$\bar{1}$2) termination bind NH$_3$ significantly more strongly than the Al sites on the other terminations. The Al ions on these terminations are bound to five bidentate F ions. As discussed previously, the $\alpha$-AlF$_3$ (01$\bar{1}$2) (1×1) termination is not predicted to occur on the $\alpha$ crystallite. This type of under-coordinated Al site is, therefore, only expected to occur on the $\beta$-AlF$_3$ surface, where it is predicted to occur only as a minor surface phase (see section 7.3.6). This may explain why $\beta$-AlF$_3$ is significantly more
Table 8.1: The binding energy of NH₃ to the various α- and β-AlF₃ terminations. (The binding energies are corrected for BSSE using the counterpoise scheme [5].)

<table>
<thead>
<tr>
<th>Termination</th>
<th>Al ion coordination</th>
<th>No. of monodentate F ions</th>
<th>Density of NH₃ (nm⁻²)</th>
<th>Hydrogen bonds formed (Å)</th>
<th>NH₃ binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0112)*</td>
<td>5</td>
<td>0</td>
<td>3.9</td>
<td>2.05, 2.05</td>
<td>-1.79</td>
</tr>
<tr>
<td>(0112)**</td>
<td>5</td>
<td>1</td>
<td>3.9</td>
<td>1.92</td>
<td>-1.34</td>
</tr>
<tr>
<td>(2110)</td>
<td>5</td>
<td>1</td>
<td>5.5</td>
<td>1.64, 2.06</td>
<td>-1.38</td>
</tr>
<tr>
<td>(0001) Type A</td>
<td>5</td>
<td>2</td>
<td>2.3</td>
<td>1.76, 1.79</td>
<td>-1.46</td>
</tr>
<tr>
<td>(0001) Type A</td>
<td>4</td>
<td>1</td>
<td>2.3</td>
<td>1.61</td>
<td>-1.56</td>
</tr>
<tr>
<td>(0001) Type B</td>
<td>5</td>
<td>1</td>
<td>2.2</td>
<td>1.72</td>
<td>-1.52</td>
</tr>
<tr>
<td>(0001) Type B</td>
<td>4</td>
<td>1</td>
<td>2.2</td>
<td>1.68</td>
<td>-1.44</td>
</tr>
<tr>
<td>(100) T1</td>
<td>5</td>
<td>0</td>
<td>2.3</td>
<td>1.97</td>
<td>-1.73</td>
</tr>
<tr>
<td>(100) T6</td>
<td>5</td>
<td>1</td>
<td>4.5</td>
<td>1.99</td>
<td>-1.40</td>
</tr>
<tr>
<td>(010) S1</td>
<td>5</td>
<td>1</td>
<td>3.9</td>
<td>1.98</td>
<td>-1.37</td>
</tr>
<tr>
<td>(001) R1</td>
<td>4</td>
<td>1</td>
<td>1.2</td>
<td>1.94</td>
<td>-1.43</td>
</tr>
<tr>
<td>(001) R1</td>
<td>4</td>
<td>2</td>
<td>1.2</td>
<td>-</td>
<td>-1.00</td>
</tr>
</tbody>
</table>

* The surface predicted within a (1×1) cell.
** The surface predicted within a (√2×√2) cell.

catalytically active than α-AlF₃. Furthermore, this type of site may be present in much larger quantities on HS-AlF₃, which is highly catalytically active. The binding energies of NH₃ to 5-fold Al ions bound to one or two monodentate F ions and 4-fold Al ions bound to one monodentate F ion are all similar in magnitude. Given that the binding energy is also dependent on the overall coverage of NH₃ (it decreases with increased coverage as will be shown in sections 8.3.2 and 8.3.3) and the formation of hydrogen bonds with nearby F ions [107] it is not possible to distinguish between the strength of these acid sites by using the NH₃ binding energies alone. The binding energy of NH₃ to the 4-fold Al ion bound to two monodentate F ions on the β-AlF₃ (010) termination is significantly less in comparison to the other under-coordinated Al sites considered.

In chapter 7 we introduced the concept of an effective coordination number, which we used in a simple model in order to predict surface energies from the density and local environment of the surface Al ions. The effective coordination number can also be used
to understand the variations in the NH$_3$ binding energies. Under-coordinated Al ions that are bound to five bidentate F ions have an effective coordination number of 2.5 (each F ion is shared between two Al ions). Under-coordinated Al ions that are bound to four bidentate F ions and one monodentate F ion have an effective coordination number of 3.0 ($4 \times 0.5 + 1$). The Al ions bound to five bidentate F ions are therefore in a less stable chemical environment than those bound to four bidentate and a monodentate F ion. This may explain why the Al ions bound to five bidentate F ions bind NH$_3$ more strongly.

Tetrahedrally bonded Al ions that are bound to one or two monodentate F ions have an effective coordination number of 2.5 and 3.0 respectively, but do not bind NH$_3$ as strongly as the 5-fold Al ions with the equivalent effective coordination number. This is because, as discussed in section 8.1, the tetrahedral environment is more stable than the truncated octahedral environment of the 5-fold Al ions.

The calculated binding energies, shown in table 8.1, range from -1.00 eV to -1.79 eV. These values are typical of those obtained for materials displaying moderate to strong Lewis acidity; for instance, the binding energy for NH$_3$ at strong Lewis acid sites on Mordenite is -1.7 eV [20] (calculated using the GGA functional) and on the V$_2$O$_5$(010) surface sites it is around -1.3 eV [106] (calculated using the B88-LYP functional). The $\alpha$- and $\beta$-AlF$_3$ surfaces hence show characteristics of Lewis acid materials, although the strongest sites are predicted to occur only at the $\beta$ surface.

In sections 8.3.2 to 8.3.5 we consider, in much more detail, adsorption of NH$_3$ to the $\beta$-AlF$_3$ (100) T1 and T6 terminations. These terminations have been chosen as they represent both the strongest Lewis acid site predicted to occur on $\beta$-AlF$_3$ and a site that is typical of the other sites found on the surfaces of both $\alpha$- and $\beta$-AlF$_3$ crystallites.
Figure 8.1: Adsorption of NH$_3$ above under-coordinated Al ions on the β-AlF$_3$ (100) T1 termination. (a) Adsorption on T1A sites. (b) Adsorption on T1B sites. (c) Adsorption on T1A and T1B sites.

8.3.2 The T1 surface

The relaxed T1 termination, shown previously in figure 7.4, contains two rows of ions in which alternate Al ions are under-coordinated. The upper row of under-coordinated Al ions are labelled T1A sites and those on the alternate row, T1B sites. There is one T1A and one T1B site per unit cell. Side views of the terminations, after adsorption of NH$_3$ at half and full monolayer coverage, are shown in figure 8.1. The Al-N bond length is 2.0 Å. The NH$_3$ molecules form hydrogen bonds with adjacent monodentate F ions, the H-F bond length is 2.0 Å. These bond lengths are independent of adsorption site and coverage. A plan view of the T1 termination with a full monolayer coverage of NH$_3$ is shown in figure 8.2. Each NH$_3$ molecule has two NH$_3$ neighbours, with an N-N separation of 5.4 Å, the next nearest neighbours (nnn) have an N-N separation of 7.3 Å.

The binding energies of NH$_3$, as a function of the occupancy of neighbouring sites, are displayed in table 8.2. Overall, the binding energies are approximately 0.1 eV greater for adsorption on T1A sites than on T1B sites. The binding energy per molecule decreases as the level of coverage of neighbouring sites is increased. This variation in binding energies will be discussed in section 8.3.4.
Figure 8.2: A plan view of NH$_3$ adsorption on the β-AlF$_3$ (100) T1 termination at full monolayer coverage. There are two adsorbed NH$_3$ molecules per unit cell. The channels in the bulk material are parallel to the $<$001$>$ direction.

Table 8.2: Binding energies (BE) of NH$_3$ as a function of the occupation of neighbouring and next nearest neighbouring (nnn) sites. Nearest neighbour sites are of an opposite site type while next nearest neighbour sites are of the same type.

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>No. of nearest neighbours</th>
<th>BE with no nnn (eV)</th>
<th>BE with both nnn (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1A</td>
<td>0</td>
<td>-1.96</td>
<td>-1.86</td>
</tr>
<tr>
<td>T1A</td>
<td>1</td>
<td>-1.86</td>
<td>-1.68</td>
</tr>
<tr>
<td>T1A</td>
<td>2</td>
<td>-1.72</td>
<td>-1.54</td>
</tr>
<tr>
<td>T1B</td>
<td>0</td>
<td>-1.86</td>
<td>-1.77</td>
</tr>
<tr>
<td>T1B</td>
<td>1</td>
<td>-1.75</td>
<td>-1.64</td>
</tr>
<tr>
<td>T1B</td>
<td>2</td>
<td>-1.57</td>
<td>-1.50</td>
</tr>
</tbody>
</table>
8.3.3 The T6 surface

The T6 termination, previously shown in figure 7.5, contains two symmetric rows of under-coordinated surface Al ions per unit cell, which are separated by an open channel. Each of these Al ions is bound to a monodentate F ion, which is free to rotate to either open or close the surface channel. There are four under-coordinated Al sites per unit cell on the T6 termination, twice as many as on the T1 termination. There are two mechanisms by which NH₃ can bind to these under-coordinated Al ions. NH₃ can adsorb above the Al ions, this results in the surface F ions rotating downwards, by approximately 35°; this adsorption site is referred to as a T6A site. Alternatively, the F ions can rotate upwards, by approximately 45° and NH₃ molecules can adsorb from below the monodentate F ions; this adsorption site is referred to as a T6B site. Consequently, there are many different ways of adsorbing NH₃ molecules within a unit cell; there are four sites and each site can adsorb a molecule in two possible ways. Initial calculations showed that if an NH₃ molecule is adsorbed from above (to a T6A site) then at the adjacent sites there is a strong preference for adsorption at T6B sites and vice versa. For example, if at full monolayer coverage the occupied sites are all T6A, all T6B or alternating T6A and T6B, then the binding energies are -0.52, -0.20 and -1.40 eV respectively. In what follows we therefore assume that the adsorption sites on the T6 termination alternate between T6A and T6B sites.

Side views of the adsorption geometries at half and full monolayer coverage are shown in figure 8.3. The N-Al bond length is 2.0 Å, the same as that for adsorption to the T1 termination. The NH₃ molecules form a hydrogen bond with a nearby F ion with a bond length of around 2.0 Å. These bond lengths are independent of adsorption site and coverage. Figure 8.4 is a plan view of full monolayer coverage on this termination. Each molecule has five neighbours within a radius of 7.0 Å, as shown in figure 8.4. For a molecule adsorbed on an T6A site the five neighbours consist of two molecules adsorbed
Figure 8.3: Adsorption of NH$_3$ above under-coordinated Al ions on the β-AlF$_3$ (100) T6 termination. (a) Adsorption on T6A sites. (b) Adsorption on T6B sites. (c) Adsorption on T6A and T6B sites on adjacent T6A sites, labelled as (I) in figure 8.4, two molecules adsorbed on adjacent T6B sites, labelled as (II) in figure 8.4 and one molecule that is adsorbed on the T6B site across the channel, labelled as (III) in figure 8.4. Similarly, for a molecule adsorbed on a T6B site, it has two neighbours on adjacent T6B sites, two neighbours on adjacent T6A sites and a neighbour on a T6A site across the channel.

The binding energies as a function of the occupation of these five nearest neighbour sites have been calculated for the adsorption of NH$_3$ on both T6A and T6B sites. There are 32 ways to occupy 5 sites ($2^5$), after removing symmetrically equivalent possibilities this is reduced to 20. The resulting binding energies are displayed in table 8.3. The binding energy of NH$_3$ at a T6A (T6B) site is most sensitive to the occupancy of the nearest T6A (T6B) site. These variations in binding energy are discussed further in section 8.3.4.

### 8.3.4 Properties of NH$_3$ adsorption on β-AlF$_3$ (100)

The Mulliken charges on the nitrogen and hydrogen atoms in an isolated NH$_3$ molecule are -0.91 $|e|$ and +0.30 $|e|$ respectively. The charges on the N, H, and the surface Al and F ions after full monolayer adsorption on the T1 and T6 terminations are shown in table 8.4. The charges on the N and H were corrected for BSSE by subtraction of the
Figure 8.4: A plan view of NH$_3$ adsorption on the β-AlF$_3$ (100) T6 termination at full monolayer coverage. There are four NH$_3$ molecules adsorbed per unit cell. Arrows point to the five nearest neighbours of an T6A and T6B site. The channels in the bulk material are parallel to the <001> direction.
Table 8.3: Binding energies of NH$_3$ adsorbed on the T6 termination as a function of the occupancy of the its nearest neighbour sites.

<table>
<thead>
<tr>
<th>Binding energy (eV)</th>
<th>Adsorption on T6A sites</th>
<th>Adsorption on T6B sites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of NH$_3$ at nearby T6A sites</td>
<td>No. of NH$_3$ at adjacent T6B sites</td>
</tr>
<tr>
<td>-1.55</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>-1.54</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-1.51</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>-1.46</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>-1.45</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>-1.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-1.40</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-1.34</td>
<td>1</td>
<td>1*</td>
</tr>
<tr>
<td>-1.34</td>
<td>1</td>
<td>1**</td>
</tr>
<tr>
<td>-1.33</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>-1.31</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>-1.29</td>
<td>1</td>
<td>1*</td>
</tr>
<tr>
<td>-1.27</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-1.26</td>
<td>1</td>
<td>1**</td>
</tr>
<tr>
<td>-1.24</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>-1.23</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>-1.22</td>
<td>2</td>
<td>2</td>
</tr>
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<td>-1.18</td>
<td>2</td>
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<td>-1.17</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>-1.15</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

* The T6A site and T6B site that are occupied are adjacent to one another
** The T6A site and T6B site that are occupied are not adjacent to one another
Table 8.4: The Mulliken charges, in units of |e|, on the different surface species at full monolayer coverage, after correction for BSSE. The changes in the charges are given with respect to the clean surface and an isolated NH\textsubscript{3} molecule. An isolated NH\textsubscript{3} molecule has a charge of -0.91 |e| on the nitrogen and +0.30 |e| on the hydrogens.

<table>
<thead>
<tr>
<th>Species</th>
<th>T1 A</th>
<th>T1 B</th>
<th>T6 A</th>
<th>T6 B</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-0.91</td>
<td>-0.91</td>
<td>-0.88</td>
<td>-0.90</td>
</tr>
<tr>
<td>H</td>
<td>0.37</td>
<td>0.37</td>
<td>0.35</td>
<td>0.39</td>
</tr>
<tr>
<td>H</td>
<td>0.36</td>
<td>0.36</td>
<td>0.35</td>
<td>0.36</td>
</tr>
<tr>
<td>H (H bonded)</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.34</td>
</tr>
<tr>
<td>(\Delta) NH\textsubscript{3}</td>
<td>0.20</td>
<td>0.19</td>
<td>0.018</td>
<td>0.19</td>
</tr>
<tr>
<td>(\Delta) Al</td>
<td>-0.02</td>
<td>-0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>(\Delta) bidentate Fs*</td>
<td>-0.13</td>
<td>-0.10</td>
<td>-0.08</td>
<td>-0.08</td>
</tr>
<tr>
<td>(\Delta) monodentate F</td>
<td>-0.05</td>
<td>-0.08</td>
<td>-0.12</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

* The Al adsorption sites on the T1 termination are bound to five bidentate F ions and on the T6 termination they are bound to four bidentate F ions.

following two terms. (1) The charge that is transferred to the N and H basis functions in a calculation of the AlF\textsubscript{3} surface in the configuration it adopts after adsorption of NH\textsubscript{3}, in the presence of the NH\textsubscript{3} basis functions; (2) The increase in the charge on the N and H atoms of an NH\textsubscript{3} molecule in the configuration it adopts after adsorption, when it is calculated in the presence of the AlF\textsubscript{3} basis functions compared to when it is calculated in the absence of the AlF\textsubscript{3} basis functions. Analogous corrections for BSSE were made for the charges on the surface Al and F ions. After adsorption to the T1 termination, around 0.2 |e| is transferred from the NH\textsubscript{3} to the surface. This charge is transferred to the F ions neighbouring the Al adsorption site to the hydrogen bonded F ion. There is no significant change in the charge on the Al adsorption site. On the T6 termination the transfer of charge is similar. Approximately 0.2 |e| is transferred from the NH\textsubscript{3} molecule to the neighbouring monodentate and bidentate F ions. In the absence of BSSE corrections the charge transfer from the NH\textsubscript{3} molecule is approximately 0.10 |e| and 0.08 |e| for the T1 and T6 terminations respectively.

Although the assignment of charge is sensitive to the charge partition method and
basis sets that are used, it appears that the charge transfer that is observed on these AlF$_3$ surfaces is less than that which has been calculated on other Lewis acid surfaces [106, 20]. For instance, it is reported that after adsorption to Lewis acid vanadium sites on the V$_2$O$_5$ (010) surface, between 0.3 and 0.4 $|e|$ is transferred from the NH$_3$ molecule to the surface [106]. Previous computational studies on molecular systems have shown that there is no correlation between the degree of charge transfer and binding energies, but that observed trends can be quantitatively explained using simple electrostatic models [108].

In chapter 7 we showed that there is a large electrostatic potential above the exposed under-coordinated Al ions on the $\beta$-AlF$_3$ (100) terminations. A simple model is now used to estimate the electrostatic contribution to the binding energy. A single NH$_3$ molecule is removed from the surface and the electrostatic potential is computed at the points in space previously occupied by the N and H ions. The electrostatic contribution to the binding energy is then estimated by multiplying the potential by the charge on the N and H atoms of an isolated NH$_3$ molecule computed at the structure of the adsorbed molecule. The resultant energies are displayed in table 8.5 for adsorption sites on the T1 termination, and in table 8.6 for adsorption sites on the T6 termination, at a range of surface coverages. These electrostatic contributions suggest that the total binding energy of the molecule to the surface is dominated by electrostatic interactions. The electrostatic energies are greater than the calculated binding energies, in part, because the repulsive forces between the NH$_3$ molecule and the surface are not considered in this analysis. The contribution to the binding energy of the relaxation of the adsorption site and NH$_3$ molecule is also neglected, this contribution reduces the energy of the system by around 0.7 eV on the T1 termination and between 0.7 eV and 0.9 eV on the T6 termination.

It was shown in sections 8.3.2 and 8.3.3 that the binding energy of NH$_3$ at a given site is strongly dependent on the occupancy of neighbouring sites. In general, the binding energy decreases as the NH$_3$ coverage increases. It is proposed that repulsive interactions between neighbouring NH$_3$ molecules account for the observed variations in binding en-
Table 8.5: Estimations of the electrostatic interaction energy between the T1 termination and adsorbed NH$_3$ molecules. The calculated binding energies are given for comparison.

<table>
<thead>
<tr>
<th>Binding site</th>
<th>Binding energy (eV)</th>
<th>Electrostatic interaction (eV)</th>
<th>Occupied neighbouring sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1A</td>
<td>-1.96</td>
<td>-2.20</td>
<td>None</td>
</tr>
<tr>
<td>T1A</td>
<td>-1.86</td>
<td>-2.13</td>
<td>One at nearby B site</td>
</tr>
<tr>
<td>T1A</td>
<td>-1.72</td>
<td>-2.04</td>
<td>Two at nearby B sites</td>
</tr>
<tr>
<td>T1B</td>
<td>-1.86</td>
<td>-2.14</td>
<td>None</td>
</tr>
<tr>
<td>T1B</td>
<td>-1.75</td>
<td>-2.04</td>
<td>One at nearby A site</td>
</tr>
<tr>
<td>T1B</td>
<td>-1.57</td>
<td>-1.96</td>
<td>Two at nearby A sites</td>
</tr>
</tbody>
</table>

Table 8.6: Estimations of the electrostatic interaction energy between the T6 termination and adsorbed NH$_3$ molecules. The calculated binding energies are given for comparison.

<table>
<thead>
<tr>
<th>Binding site</th>
<th>Binding energy (eV)</th>
<th>Electrostatic interaction (eV)</th>
<th>Occupied neighbouring sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>T6A</td>
<td>-1.54</td>
<td>-1.98</td>
<td>None</td>
</tr>
<tr>
<td>T6A</td>
<td>-1.33</td>
<td>-1.82</td>
<td>One at nearby A site</td>
</tr>
<tr>
<td>T6A</td>
<td>-1.23</td>
<td>-1.80</td>
<td>Two at nearby A sites</td>
</tr>
<tr>
<td>T6B</td>
<td>-1.60</td>
<td>-2.21</td>
<td>None</td>
</tr>
<tr>
<td>T6B</td>
<td>-1.40</td>
<td>-2.07</td>
<td>One at nearby B site</td>
</tr>
<tr>
<td>T6B</td>
<td>-1.21</td>
<td>-2.03</td>
<td>Two at nearby B sites</td>
</tr>
</tbody>
</table>
Table 8.7: Estimation of the repulsive dipole interaction energy between neighbouring \( \text{NH}_3 \) molecules in the absence of the \( \text{AlF}_3 \) surface. The termination and adsorption sites describe the positioning of the \( \text{NH}_3 \) molecules. The interaction energy includes the interactions from both nearest neighbours.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Adsorption sites</th>
<th>Dipole Interaction (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>T1A+T1B</td>
<td>0.056</td>
</tr>
<tr>
<td>T6</td>
<td>T6A</td>
<td>0.044</td>
</tr>
<tr>
<td>T6</td>
<td>T6B</td>
<td>0.052</td>
</tr>
</tbody>
</table>

Energy. These interactions can either be direct, e.g. dipolar repulsion, or indirect, that is, surface mediated. In order to analyse this, the direct interactions are estimated as follows. A periodic array of \( \text{NH}_3 \) molecules, constrained in the positions they adopt after adsorption to the surface, is considered. An electric field is applied perpendicular to the plane of the molecular net with the field strength chosen to produce charges on the N and H ions similar to those found after adsorption on the \( \text{AlF}_3 \) surface. The energy per molecule of the net is calculated and the calculations are then repeated with alternate \( \text{NH}_3 \) ions removed. The difference in the energy per molecule is used to estimate the direct nearest neighbour interactions, the resultant energies are displayed in table 8.7. The total \( \text{NH}_3 \) binding energy decreases by approximately 0.3 eV per molecule when nearest neighbours are present. It can therefore be concluded that variations in the binding energy of \( \text{NH}_3 \) as a function of coverage are due to both direct and indirect interactions of similar magnitude.

8.3.5 Temperature Programmed Desorption Simulations

The binding energy of \( \text{NH}_3 \) to the \( \beta \)-\( \text{AlF}_3 \) (100) T1 and T6 terminations is strongly dependent on the local coverage. To enable a comparison of these results with TPD data we have used kinetic Monte Carlo simulations to predict the rate of desorption as the temperature is increased at a rate of 7.5 K min\(^{-1}\). In these simulations the initial lattice represents a full monolayer coverage on either the T1 or T6 termination. The simulations
are performed using a periodic unit cell consisting of 250,000 adsorption sites and the desorption simulation is run five times for each termination. The probability of desorption from each site is calculated using the first order Redhead equation, defined previously in section 2.3.2 (equation 2.48), the DFT computed binding energies tabulated in tables 8.2 and 8.3 and the attempt frequency, $\nu_0$, that is estimated from the vibrational frequency of the Al-N bond. The frequency is computed by construction of the force constant matrix via finite differencing of the analytical gradients followed by diagonalisation of the resultant dynamical matrix. Analysis using a partial force constant matrix computed by displacing the atoms of the Al-NH$_3$ motif indicates that the Al-N stretch frequency varies by around 50 cm$^{-1}$ ($1.5 \times 10^{12}$ s$^{-1}$) as the adsorption site and surface coverage are varied. Determination of an accurate rate of desorption is dominated by the calculation of the binding energy hence a single representative frequency of $1.7 \times 10^{13}$ s$^{-1}$ was used in our kinetic Monte Carlo simulations, calculated from the full force constant matrix of the T1 surface at full monolayer coverage. It is assumed that readsoption of the NH$_3$ molecules does not occur. Simulations of desorption from the T1 termination take into account the occupancy of nearest and next nearest neighbour sites. The DFT calculation required when a single next nearest neighbour site is occupied is prohibitively expensive so this is approximated by the average binding energy of the cases where there are none or two nearest neighbours present. This is expected to be accurate to within, at worst, 0.04 eV per NH$_3$ molecule, based on the binding energies calculated as a function of nearest neighbour occupancy. All other binding energies are taken directly from table 8.2. On the T6 termination the occupancy of the five next nearest neighbours, shown in figure 8.4 are considered.

Figure 8.5 contains the predicted desorption curve from the $\beta$-AlF$_3$ (100) T1 and T6 terminations. The predicted spectra contains three peaks. These can be assigned to the superposition of two spectra from each termination, each containing two peaks, as shown in figure 8.5. The peak that occurs at the lower temperature from each termination is due
to desorption at high local coverage while the peak that occurs at the higher temperature is due to desorption when most, or all, neighbouring sites are unoccupied. These peaks occur at around 220°C and 350°C from the T1 termination and at around 130°C and 220°C from the T6 termination. The two central peaks overlap. The peaks associated with desorption from the T1 termination occur at 80% and 23% of the initial coverage, the peaks associated with desorption from the T6 termination occur at 79% and 26% of the initial coverage.

Experimental TPD spectra for NH$_3$ on β-AlF$_3$ obtained by Kemnitz et al [10] are shown in figure 8.6. There are three distinct peaks/shoulders, at around 200°C, 300°C and 420°C. It is tempting to suggest that these three features correspond to the three peaks predicted from our kinetic Monte Carlo simulations, shown in figure 8.5, even though the peaks/shoulders obtained from the experimental procedure occur at temperatures that are systematically around 70°C higher than those computed.
Figure 8.6: The TPD curves obtained by Kemnitz et al. (Top) The three experimental results were obtained from different $\beta$-AlF$_3$ samples. Experiment A used untreated $\beta$-AlF$_3$, experiment B used a $\beta$-AlF$_3$ sample that was first fluorinated using CCl$_2$F$_2$ and in experiment C the sample was fluorinated using CHClF$_2$. The fluorination process is used to reverse surface hydrolysis. (Bottom) This graph is identical to the one on the left but also includes the results obtained from our kinetic Monte Carlo simulations, shifted by 70°C to higher temperatures.
There are several factors which may cause this slight discrepancy in absolute temperatures. Experimentally it is difficult to increase the temperature uniformly at the surface and to measure it accurately. Consequently, the temperature of the surface may be overestimated. In the Monte Carlo simulations it is assumed that there is no barrier to the desorption process, if this is not true, the temperature at which desorption occurs will be under-estimated in our simulations. In the DFT approach used here the calculations of relative binding energies are much more accurate than the absolute energies, yet, an error in the absolute binding energy of 0.1 eV changes the temperature at which peak desorption occurs by approximately 30°C. It is known that hydrolysis and hydroxylation occurs at the surface of real samples of β-AlF₃ [109], two of the experimental samples have been fluorinated to limit hydroxylation and hydration of the surface, however, it can clearly be seen that the TPD of NH₃ is sensitive to such factors. Despite the effects of these possible errors and approximations, it is very encouraging to see that the predictive relative temperatures at which desorption peaks occur are in extremely good agreement with those observed.

The simulation of TPD from the (100) surface suggests that the predicted local surface geometries are representative of the geometries that occur on real β-AlF₃ surfaces. Although we have not specifically modelled the sites on the (010) and (001) surfaces, our initial studies showed that the binding energies of NH₃ to these sites is similar to those for the (100) T6 termination. If these surfaces were included in our TPD simulations it is likely that the resultant TPD curve would be much smoother and more closely represent the experimental results. The number of T1A and T1B sites exposed on β-AlF₃ crystallites is predicted to be relatively low (see section 7.3.6), however, the shoulder in the experimental TPD curves at high temperatures strongly suggests that they do occur. The ability to assign TPD peaks to the local structure of adsorption sites may provide a method for studying how different synthesis methods affect the local structure of β-AlF₃ and HS-AlF₃ surfaces. For example, from figure 8.6 it can be seen that the experimental
sample that was post fluorinated with CHClF₂ has a more defined shoulder at low temperatures compared to the other samples. The analysis developed here implies that this is because the sample’s surface presents more sites of the type seen on the T6 termination. This study also illustrates that even the number of different adsorption sites at an AlF₃ surface cannot be derived directly from the TPD spectra as the analysis requires a careful consideration of the coverage dependence of the adsorption energies.

8.4 Conclusions

We have shown that NH₃ binds strongly to under-coordinated Al ions on the α- and β-AlF₃ surfaces. Our calculated binding energies are typical of values obtained for strongly Lewis acidic zeolite materials. Al ions bound to four F ions form stable tetrahedral structures, which are shown to bind the Lewis base, NH₃, less strongly than the distorted octahedral environment of 5-fold coordinated Al ions. NH₃ binds most strongly to under-coordinated Al ions that are bound to five bidentate ions, these sites are not predicted to occur at the surface of α-AlF₃ crystallites. We showed that the binding energy is predominately due to the interaction of the NH₃ with the large electrostatic potential above the under-coordinated Al ions. The binding energy of NH₃ is shown to decrease with increased surface coverage, due to a combination of direct repulsive interactions between neighbouring NH₃ molecules and a surface mediated interaction due to surface relaxations upon adsorption. We have simulated the TPD spectrum for the β-AlF₃ (100) T1 and T6 terminations and compared our results with experimental TPD data. Our results suggest that the types of local sites seen on the T1 and T6 terminations occur on real β-AlF₃ surfaces and that the structural models and binding mechanisms described here are a close approximation to those that occur on real AlF₃ surfaces.
Chapter 9

Characterisation of the Lewis acid sites on the $\beta$-AlF$_3$(100) surface: Adsorption of CO

9.1 Introduction

AlF$_3$ surfaces are known to hydroxylise under certain reaction conditions, as was shown in chapter 6. Understanding how the effectiveness of an AlF$_3$ catalyst is dependent on the extent to which its surface is hydroxylated is important in the drive to a better understanding of, and an ability to control its catalytic properties. In this chapter we characterise the Lewis acidity of hydroxylated AlF$_3$ surfaces. In chapter 8 we characterised the Lewis acidity of non-hydroxylated AlF$_3$ surfaces from calculations of the binding energy of NH$_3$. This is not, however, a reliable method for characterising the acidity of hydroxylated surfaces as NH$_3$ interacts strongly with OH$^-$ groups and in some situations adsorbed NH$_3$ will deprotonate OH$^-$ groups to form NH$_4^+$ ions.

An alternative method for characterising the strength of Lewis acid sites is to consider the stretch frequency of adsorbed CO molecules. The CO stretch frequency is shifted to
higher wavenumbers after it is adsorbed on Lewis acid centres compared to an isolated CO molecule. In general, the greater the blue shift, the stronger the Lewis acid. The highest occupied molecular orbital (HOMO) for CO is the $5\sigma$ orbital; this orbital is slightly anti-bonding. Withdrawing electrons from this orbital, hence, strengthens the CO bond, resulting in a blue shift of the CO stretch frequency. The withdrawal of electrons from this bond occurs after adsorption to a Lewis acid centre. Brönsted acid sites can also be characterised from CO adsorption. A CO molecule can form weak hydrogen bonds to surface OH$^-$ groups; this interaction blue shifts both the CO and the OH stretch frequencies.

In this chapter we initially calculate the stretch frequency of CO adsorbed to the $\alpha$ and $\beta$-AlF$_3$ terminations predicted to be exposed at crystalline surfaces. These results are compared to the binding energies of NH$_3$ to these surfaces, calculated in chapter 8. In the second part of this study we investigate how the strength of a Lewis site depends on the hydroxylation of neighbouring anionic sites. The CO stretching frequency is calculated after adsorption to under-coordinated Al ions on hydroxylated $\beta$-AlF$_3$ (100) T1 and (010) terminations. Our collaborators at the Laboratory of Catalysis and Spectrometry at the ENSI (École Nationale Supérieure d’Ingénieurs) in Caen and the University of Caen have measured the IR spectrum for CO adsorbed to clean and hydroxylated $\beta$-AlF$_3$ [110]. Our results are used to interpret the data obtained from these experiments, enabling a greater understanding of the structure of AlF$_3$ surfaces than could have been obtained from theory or experiment alone.

### 9.2 Methodology

CO molecules were assumed to adsorb above under-coordinated Al ions via their C atom. Structures were then fully optimised. The counterpoise scheme [5] was used to estimate the basis set superposition error (BSSE) between the adsorbed CO molecules and the surface which was confirmed to be a small contribution of the total binding energy. The
vibrational frequencies of the molecules were computed by construction of the force constant matrix via finite differencing of the analytic gradients followed by diagonalisation of the dynamical matrix [77]. There was no attempt to correct for BSSE in these calculations. The calculation of a full force constant matrix for large systems is a computationally demanding task. The stretch vibrational modes of CO adsorbed to a partially hydroxylated $\beta$-AlF$_3$ (100) T1 termination were calculated twice using different partial force constant matrices. The first partial force constant matrix was constructed from the displacements of half of the AlF$_3$ slab (the atoms closest to the surface) and the CO molecules. The second force constant matrix was constructed from the displacements of the CO molecules only. The frequencies obtained from these two calculations for the CO stretch vibration were to within 0.04 cm$^{-1}$ of one another. A partial matrix consisting of the displacements of the CO molecules was, therefore, used in all frequency calculations in this study.

The experimental data discussed in this chapter were obtained from our collaborators at the Laboratory of Catalysis and Spectrometry at the ENSI Caen and the University of Caen. An outline of their methodology is given here, a full description can be found elsewhere [110, 111]. Samples of $\beta$-AlF$_3$, amorphous HS-AlF$_3$, $\beta$-AlF$_{2.6}$(OH)$_{0.4}$ and $\beta$-AlF$_{2.7}$(OH)$_{0.3}$ were studied. The $\beta$-AlF$_3$ sample was prepared by thermal decomposition of $\alpha$-AlF$_3$·3H$_2$O, the resulting material had a surface area of 33 m$^2$g$^{-1}$. The HS-AlF$_3$ sample was obtained using the sol-gel process. This material had a surface area of 317 m$^2$g$^{-1}$ and it was activated in situ by the fluorination agent CHCIF$_2$ before CO was adsorbed to its surface. The $\beta$-AlF$_{2.6}$(OH)$_{0.4}$ sample was obtained using microwave assisted synthesis. The sample had a surface area was 140 gm$^{-2}$ and it was activated in situ by the fluorination agent CHF$_3$, before CO was adsorbed to its surface. The sample was then fluorinated by F$_2$ at 225°C, after this procedure the sample has stiochiometry AlF$_{2.7}$(OH)$_{0.3}$. CO was adsorbed in discrete doses to each of the samples at 77K. After exposure to each dose of CO an IR spectrum was recorded. This procedure was repeated until no new features were observed in the spectrum. The sample was then saturated with CO and the
spectrum was recorded.

9.3 Results and Discussion

The observed and calculated stretch frequencies for gaseous CO are 2143 cm\(^{-1}\) and 2220 cm\(^{-1}\) respectively. The calculated value is in line with those in the literature for the B3LYP functional \([112]\). As in general B3LYP over-estimates stretch frequencies, our calculated CO frequencies have been multiplied by a scaling factor of 0.965 (2143/2220) to take into account the discrepancy between experiment and theory.

9.3.1 Clean Surfaces

The binding energies and stretch frequencies for CO adsorbed to under coordinated Al ions on representative terminations of the surfaces predicted to be exposed on \(\alpha\) and \(\beta\)-AlF\(_3\) crystallites and amorphous HS-AlF\(_3\) are tabulated in table 9.1. The highest frequencies for CO adsorbed on the \(\alpha\)- and \(\beta\)-AlF\(_3\) surfaces occur after adsorption on Al ions that are bound to five bidentate F ions. The CO stretch frequencies occur at between 2229 and 2233 cm\(^{-1}\). These sites also bind CO more strongly than the other sites, with a binding energy of around -0.5 eV, and were previously shown to bind NH\(_3\) more strongly than the other sites too. These types of Al ions are present on the \(\beta\)-AlF\(_3\) (100) T1 termination and the \(\alpha\)-AlF\(_3\) (1\times1) (01\(\bar{T}2\)) termination. Crystalline \(\alpha\)-AlF\(_3\) is not predicted to expose the (1\times1) (01\(\bar{T}2\)) termination, crystalline \(\beta\)-AlF\(_3\) is predicted to only expose the (100) surface in small quantities. It is speculated, however, that this type of Al site is exposed in large quantities on HS-AlF\(_3\) and that it is responsible for its catalytic properties.

Adsorption to four fold Al sites bound to one monodentate F ion also gives large CO stretch frequencies of between 2223 and 2231 cm\(^{-1}\), however the corresponding binding energy to these surfaces is much smaller, typically around 0.15 to 0.2 eV. The CO stretch frequencies for adsorption to five fold Al ions bound to one monodentate F ion lie between
Table 9.1: The binding energy and shift in the stretching frequency, relative to gaseous CO (2143 cm\(^{-1}\)), for CO adsorbed on the various \(\alpha\)- and \(\beta\)-AlF\(_3\) terminations. (The binding energies are corrected for BSSE using the counterpoise scheme \([5]\) and the shifts in CO frequency are scaled as discussed in the text.)

<table>
<thead>
<tr>
<th>Termination</th>
<th>Al ion coordination</th>
<th>No. of monodentate F ions</th>
<th>Density of NH(_3) (nm(^{-2}))</th>
<th>CO binding energy (eV)</th>
<th>CO stretch frequency (cm(^{-1}))</th>
<th>Shift in CO stretch freq. (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0112)*</td>
<td>5</td>
<td>0</td>
<td>3.9</td>
<td>-0.52</td>
<td>2230</td>
<td>87</td>
</tr>
<tr>
<td>(01T2)**</td>
<td>5</td>
<td>1</td>
<td>3.9</td>
<td>-0.21</td>
<td>2215</td>
<td>72</td>
</tr>
<tr>
<td>(2110)</td>
<td>5</td>
<td>1</td>
<td>5.5</td>
<td>-0.32</td>
<td>2214</td>
<td>71</td>
</tr>
<tr>
<td>(0001) Type A</td>
<td>5</td>
<td>1</td>
<td>2.3</td>
<td>-0.30</td>
<td>2221</td>
<td>78</td>
</tr>
<tr>
<td>(0001) Type A</td>
<td>5</td>
<td>2</td>
<td>2.3</td>
<td>-0.28</td>
<td>2226</td>
<td>83</td>
</tr>
<tr>
<td>(0001) Type B</td>
<td>5</td>
<td>1</td>
<td>2.3</td>
<td>-0.16</td>
<td>2223</td>
<td>80</td>
</tr>
<tr>
<td>(100) T1</td>
<td>5</td>
<td>0</td>
<td>2.3</td>
<td>-0.48</td>
<td>2233, 2229</td>
<td>89, 86†</td>
</tr>
<tr>
<td>(100) T6</td>
<td>5</td>
<td>1</td>
<td>4.5</td>
<td>-0.32</td>
<td>2213, 2219</td>
<td>70, 76††</td>
</tr>
<tr>
<td>(010) S1</td>
<td>5</td>
<td>1</td>
<td>3.9</td>
<td>-0.26</td>
<td>2217</td>
<td>74</td>
</tr>
<tr>
<td>(001) R1</td>
<td>4</td>
<td>1</td>
<td>1.2</td>
<td>-0.21</td>
<td>2227</td>
<td>84</td>
</tr>
<tr>
<td>(001) R1</td>
<td>4</td>
<td>2</td>
<td>1.2</td>
<td>-0.02</td>
<td>2208</td>
<td>65</td>
</tr>
</tbody>
</table>

* The surface predicted within a \((1\times1)\) cell.
** The surface predicted within a \((\sqrt{2} \times \sqrt{2})\) cell.
† The frequencies are for adsorption to T1A sites and T1B sites respectively.
†† The frequencies are for adsorption to T6A sites and T6B sites respectively.

2215 and 2227 cm\(^{-1}\). In chapter 8 the binding energies of NH\(_3\) to under-coordinated Al ions bound to one monodentate F ion were shown to be significantly weaker than for adsorption to Al ions bound to five bidentate F ions. CO binds very weakly to the four fold Al ions bound to two monodentate F ions and correspondingly the shift in the CO stretch frequency is relatively small, the NH\(_3\) binding energy was correspondingly small for this site. It can therefore be concluded that, with the exception of four fold Al ions bound to one monodentate F ions, that there is good correlation between NH\(_3\) binding energies and CO stretch frequencies.

The binding energies and stretch frequencies, at half and full monolayer coverage on the \(\beta\)-AlF\(_3\) (100) T1 and (010) terminations are given in table 9.2. The stretch frequency
Table 9.2: The binding energy and the CO stretch frequency for CO adsorbed on the \( \beta \)-AlF\(_3\) (100) T1 and (010) terminations at half and full monolayer coverage. (The binding energies are corrected for BSSE using the counterpoise scheme \[5\] and CO frequencies are scaled as discussed in the text.)

<table>
<thead>
<tr>
<th>Termination</th>
<th>Site</th>
<th>Coverage (MLs)</th>
<th>Binding energy (eV)</th>
<th>CO stretch frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) T1</td>
<td>A</td>
<td>0.5</td>
<td>-0.32</td>
<td>2241</td>
</tr>
<tr>
<td>(100) T1</td>
<td>A</td>
<td>1.0</td>
<td>-0.46</td>
<td>2233</td>
</tr>
<tr>
<td>(100) T1</td>
<td>B</td>
<td>0.5</td>
<td>-0.49</td>
<td>2236</td>
</tr>
<tr>
<td>(100) T1</td>
<td>B</td>
<td>1.0</td>
<td>-0.62</td>
<td>2229</td>
</tr>
<tr>
<td>(010)</td>
<td>A</td>
<td>0.5</td>
<td>-0.26</td>
<td>2225</td>
</tr>
<tr>
<td>(010)</td>
<td>A</td>
<td>1.0</td>
<td>-0.27</td>
<td>2217</td>
</tr>
</tbody>
</table>

is reduced by 7-8 wavenumbers as the coverage is increased from half monolayer to full monolayer coverage. The binding energies increase as the coverage is dropped. It has, however, been shown that CO binding energies are not a reliable prediction of Lewis acidity \[25\].

The IR absorption spectra for \( \beta \)-AlF\(_3\) and HS-AlF\(_3\) after adsorption of CO are shown in figure 9.1. There are two high intensity absorption peaks centred at around 2165 and 2150 cm\(^{-1}\) after CO adsorption on \( \beta \)-AlF\(_3\). The peak at 2150 cm\(^{-1}\) is likely to be due to physisorbed CO as the shift in the frequency relative to an isolated CO molecule (2143 cm\(^{-1}\)) is very small. The frequency of the peak at 2165 cm\(^{-1}\) is much smaller than the predicted frequency after adsorption to under-coordinated Al ions on AlF\(_3\) surfaces. It is speculated that the surface may be partially hydroxylated and that this peak may be due to adsorption at Brönsted sites; adsorption on hydroxylated surfaces is the subject of section 9.3.2. The IR spectrum for CO adsorption on HS-AlF\(_3\) contains a peak at 2150 cm\(^{-1}\) and a shoulder at 2170 cm\(^{-1}\). These two features are, again, assigned to physisorbed CO and adsorption at Brönsted sites respectively. The peak at 2170 cm\(^{-1}\) for HS-AlF\(_3\) is less pronounced than the equivalent peak at 2165 cm\(^{-1}\) for \( \beta \)-AlF\(_3\). This observation is consistent with our assignment of the peak to adsorption on Brönsted sites. The HS-AlF\(_3\)
sample was fluorinated in situ before it was exposed to CO hence its surface is expected to contain relatively fewer surface OH groups than the $\beta$-AlF$_3$ sample’s surface.

An additional high intensity adsorption peak is seen for HS-AlF$_3$. This occurs at around 2240-2235 cm$^{-1}$ at low coverages. This peak shifts to 2220 cm$^{-1}$ as the coverage is increased. The equivalent feature occurs as a small shoulder on $\beta$-AlF$_3$ after saturation with CO. At extremely low coverages, however, this adsorption band is the most intense peak, occurring at around 2220 cm$^{-1}$. As the CO coverage is increased this band develops into a broad shoulder between 2230 and 2180 cm$^{-1}$.

Comparison of the theoretical and experimental data suggests that the peak centred at around 2220 cm$^{-1}$ on HS-AlF$_3$ and the broad shoulder between 2230 and 2180 cm$^{-1}$ on $\beta$-AlF$_3$ are due to chemisorption to under-coordinated Al ions. Adsorption at the high frequency end of this band is predicted to be due to adsorption on Al ions bound to five bidentate F ions. High frequencies were also calculated for adsorption on four-fold Al ions bound to one monodentate F ion, however the binding energy of these adsorptions were very low, hence CO is unlikely to adsorb to such sites at low coverage, and adsorption at high frequencies dominate at very low coverages. Al ions bound to five bidentate F ions are only predicted to occur on $\beta$-AlF$_3$ in small quantities, this is in agreement with the measured low intensity of CO adsorption at frequencies above 2220 cm$^{-1}$ on $\beta$-AlF$_3$. It is predicted that frequencies between 2220 and 2190 cm$^{-1}$ are due to CO adsorption on five-fold Al ions bound to one monodentate F ion. This type of Al environment is predicted to dominate on crystallites of $\beta$-AlF$_3$. It is possible that the wide nature of the adsorption band at these frequencies is due to partial hydroxylation of the surface. The effect of hydroxylation is discussed in detail in the next section.

Features in both the $\beta$ and HS spectra shift to lower frequencies as the CO coverage is increased. This is likely to be due to a combination of factors. Our theoretical calculations have shown that, in general, the surfaces that bind CO most strongly have the largest frequency shifts, hence it is likely that CO binds to these types of sites first. Secondly, we
have shown that at full monolayer coverage CO stretch frequencies are reduced by 7-8 wavenumbers compared with adsorption at half monolayer coverage.

9.3.2 Hydroxylated surfaces

The stretch frequencies of CO adsorbed on the hydroxylated (100) T1 and (010) terminations of β-AlF₃ were calculated. The (010) termination was chosen as this type of surface dominates at both α and β surfaces. The (100) T1 termination represents the most active type of Al site, which are predicted to be responsible for the high catalytic nature of HS-AlF₃. The local structure of the Al sites on these two surfaces, before hydroxylation and after adsorption of CO, are shown in figure 9.2.

The calculated CO stretch frequencies after adsorption on Al sites on a range of hydroxylated (010) and (100) surfaces are shown in table 9.3. Calculations were performed at half monolayer coverage. The labelling of the F ions that were substituted for OH ions is shown in figure 9.2. The local geometries after adsorption of CO on a selection of these surfaces are shown in figure 9.3.
Figure 9.2: The local structure of the non hydroxylated surface sites on (a) the (100) T1 termination and (b) the (010) termination after adsorption of CO. Full surface calculations were performed; these pictures just show the local structure of the adsorption site.

Figure 9.3: The local structure of the surface sites after adsorption of CO. The top row shows structures of the sites on the (100) surface while the bottom rows shows structures that occur on the (010) surface. The labelling of the figures refers to the labels given to the structures in table 9.3. Full surface calculations were performed; these pictures just show the local structure of the adsorption site.
The binding energy and shift in the stretching frequency, relative to gaseous CO (2143 cm$^{-1}$), for CO adsorbed on the various $\alpha$- and $\beta$-AlF$_3$ terminations.

It can be seen from table 9.3 that the stretch frequency of CO adsorbed on under-coordinated Al ions is dependent on the extent to which the local ions have been hydroxylated. Substitution of F ions for OH ions reduces the stretch frequency. The position of the substituted OH group in the AlF$_{5-x}$(OH)$_x$ species also affects the CO stretch frequency. When an F ion is substituted for an OH ion the resultant Al-OH-Al angle is always smaller than the equivalent Al-F-Al angle. If the Al-F-Al angle is small (i.e. at the $F_A$ and $F_B$ ions) then the change in the angle after OH substitution is relatively small and the change in the CO shift is correspondingly small. If the Al-F-Al angle is close to 180° (i.e. at the $F_C$ and $F_D$ ions on both surfaces and the $F_E$ ion on the (100) surface) then the change in the angle is much greater, leading to a greater distortion of the surface, consequently, the decrease in the CO shift is much greater. If more than one of these F ions is replaced by an OH group then the distortion induced at the surface is large enough such that the CO will preferentially bind via one or more OH ions (i.e. at a Br"onnsted site) if possible. A Br"onnsted site may not be available if the OH ions preferentially hydrogen bond to the nearby monodentate F or OH ions (structures p and w in table 9.3), in this situation the CO binds very weakly to the Al ion. If a monodentate F ion ($F_E$) is replaced with an OH ion the CO stretch frequency is much reduced. It is thought that this is caused by changes that occur in the electrostatic field in the vicinity of the CO molecule as a result of this OH substitution.

The IR spectra for $\beta$-AlF$_{2.6}$OH$_{0.4}$ and $\beta$-AlF$_{2.7}$OH$_{0.3}$, obtained by our collaborators, are shown in figure 9.4. The main features in these spectra have been labelled A to E. The spectrum for $\beta$-AlF$_{2.6}$OH$_{0.4}$ shows a broad band between 2220 and 2180 cm$^{-1}$ after saturation of CO. This band is assigned to three wide, overlapping peaks at around 2115, 2200 and 2190 cm$^{-1}$, labelled B, C and D in figure 9.4. An intense peak occurs at around 2173 cm$^{-1}$ and is labelled E in the figure. There is significant absorption between 2170
Table 9.3: Shifts in CO frequency, relative to gaseous CO (2143 cm\(^{-1}\)), for adsorption to under coordinated Al ions on the \(\beta\)-AlF\(_3\) (100) T1 and (010) terminations. The labelling of the F ions that are substituted for OH ions is shown diagrammatically in figure 9.2.

### The \(\beta\)-AlF\(_3\) (100) T1 termination

<table>
<thead>
<tr>
<th>Label</th>
<th>Al environment</th>
<th>Substituted F ions</th>
<th>CO stretching frequency (cm(^{-1}))</th>
<th>Shift in frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>AlF(_5)</td>
<td>-</td>
<td>2241</td>
<td>98</td>
</tr>
<tr>
<td>b</td>
<td>AlF(_5)</td>
<td>nearby monodentate OH</td>
<td>2230</td>
<td>87</td>
</tr>
<tr>
<td>c</td>
<td>AlF(_4)(OH)</td>
<td>(F_A)</td>
<td>2238</td>
<td>95</td>
</tr>
<tr>
<td>d</td>
<td>AlF(_4)(OH)</td>
<td>(F_B)</td>
<td>2231</td>
<td>88</td>
</tr>
<tr>
<td>e</td>
<td>AlF(_4)(OH)</td>
<td>(F_C)</td>
<td>2221</td>
<td>78</td>
</tr>
<tr>
<td>f</td>
<td>AlF(_4)(OH)(_2)</td>
<td>(F_B, F_C)</td>
<td>2218</td>
<td>75</td>
</tr>
<tr>
<td>g</td>
<td>AlF(_2)(OH)(_3)</td>
<td>(F_B, F_C, F_D)</td>
<td>2167*</td>
<td>24</td>
</tr>
<tr>
<td>h</td>
<td>AlF(_3)(OH)(_4)</td>
<td>(F_B, F_C, F_D, F_E)</td>
<td>2169*</td>
<td>26</td>
</tr>
<tr>
<td>i</td>
<td>Al(OH)(_5)</td>
<td>(F_A, F_B, F_C, F_D, F_E)</td>
<td>2167*</td>
<td>24</td>
</tr>
</tbody>
</table>

### The \(\beta\)-AlF\(_3\) (010) termination

<table>
<thead>
<tr>
<th>Label</th>
<th>Al environment</th>
<th>Substituted F ions</th>
<th>CO stretching frequency (cm(^{-1}))</th>
<th>Shift in frequency (cm(^{-1}))</th>
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<td>k</td>
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<td>AlF(_4)(OH)</td>
<td>(F_A)</td>
<td>2214</td>
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<td>m</td>
<td>AlF(_4)(OH)</td>
<td>(F_B)</td>
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<td>76</td>
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<tr>
<td>n</td>
<td>AlF(_4)(OH)</td>
<td>(F_C)</td>
<td>2210</td>
<td>67</td>
</tr>
<tr>
<td>o</td>
<td>AlF(_4)(OH)</td>
<td>(F_E)</td>
<td>2188</td>
<td>45</td>
</tr>
<tr>
<td>p</td>
<td>AlF(_3)(OH)(_2)</td>
<td>(F_C, F_D)</td>
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<td>40</td>
</tr>
<tr>
<td>q</td>
<td>AlF(_3)(OH)(_2)</td>
<td>(F_A, F_C)</td>
<td>2196</td>
<td>53</td>
</tr>
<tr>
<td>r</td>
<td>AlF(_3)(OH)(_2)</td>
<td>(F_A, F_B)</td>
<td>2209</td>
<td>66</td>
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<tr>
<td>s</td>
<td>AlF(_3)(OH)(_2)</td>
<td>(F_A, F_E)</td>
<td>2175*</td>
<td>32</td>
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<tr>
<td>t</td>
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<td>(F_B, F_C)</td>
<td>2203</td>
<td>60</td>
</tr>
<tr>
<td>u</td>
<td>AlF(_3)(OH)(_2)</td>
<td>(F_B, F_E)</td>
<td>2183</td>
<td>40</td>
</tr>
<tr>
<td>v</td>
<td>AlF(_3)(OH)(_2)</td>
<td>(F_C, F_E)</td>
<td>2177</td>
<td>34</td>
</tr>
<tr>
<td>w</td>
<td>AlF(_3)(OH)(_3)</td>
<td>(F_A, F_B, F_C)</td>
<td>2176</td>
<td>33</td>
</tr>
<tr>
<td>x</td>
<td>AlF(_3)(OH)(_3)</td>
<td>(F_A, F_B, F_E)</td>
<td>2178*</td>
<td>35</td>
</tr>
<tr>
<td>y</td>
<td>AlF(_2)(OH)(_3)</td>
<td>(F_A, F_C, F_D)</td>
<td>2172*</td>
<td>29</td>
</tr>
<tr>
<td>z</td>
<td>AlF(_2)(OH)(_3)</td>
<td>(F_C, F_D, F_E)</td>
<td>2163*</td>
<td>20</td>
</tr>
<tr>
<td>aa</td>
<td>Al(OH)(_4)</td>
<td>(F_A, F_B, F_C, F_D)</td>
<td>2169*</td>
<td>26</td>
</tr>
<tr>
<td>bb</td>
<td>Al(OH)(_4)</td>
<td>(F_A, F_C, F_D, F_E)</td>
<td>2161*</td>
<td>18</td>
</tr>
<tr>
<td>cc</td>
<td>Al(OH)(_5)</td>
<td>(F_A, F_B, F_C, F_D, F_E)</td>
<td>2155*</td>
<td>12</td>
</tr>
</tbody>
</table>

* Adsorption on a Brønsted site
Figure 9.4: The CO stretch region of the IR adsorption spectra for CO adsorbed on $\beta$-AlF$_{2.6}$OH$_{0.4}$ and $\beta$-AlF$_{2.7}$OH$_{0.3}$. The solid lines represent consecutive adsorption of CO and the dashed line represents saturation with CO.
and 2140 cm$^{-1}$, likely to be due to physisorbed CO. There is also a weak band at very high wavenumbers, labelled A. This band is most prominent at very low coverages of CO.

After fluorination with F$_2$ the material has a stoichiometry of $\beta$-AlF$_{2.7}$OH$_{0.3}$. It is assumed that fluorination will have mainly occurred only at the surface of the material. Adsorption of CO results in a similar adsorption band to that before pre-fluorination, however, there are number of important differences between the two spectra. The small peak seen at around 2135 cm$^{-1}$ on $\beta$-AlF$_{2.6}$OH$_{0.4}$ (labelled A) does not occur after adsorption to the fluorinated sample. The peak observed at B increases after fluorination while the peaks at C and D decrease. Comparison to the calculated frequencies suggests that the peak at B is due to CO adsorbed on Al ions which are bound to five F ions, one of which is monodentate. Peaks C and D are due to similar sites, only ones at which one or more of the F ions have been replaced by OH ions. The wide width of the absorption band between 2220 and 2180 cm$^{-1}$ reflects the large number of variations in which surface Al ions can be partially hydroxylated. The calculated stretch frequency for CO adsorbed to Al sites on the (100) surface in which F ions are substituted for OH ions can also be assigned to peaks B and C. Only a low intensity of such sites is predicted and hence they are only likely to make up a minor contribution. The peak that occurs at A is very small for $\beta$-AlF$_{2.6}$OH$_{0.4}$ and disappears completely after fluorination with F$_2$. It is suggested that this peak is caused by Al ions bound to five bidentate F ions. To obtain catalytically active HS-AlF$_3$ its precursor is fluorinated with a gentle fluorination agent such as CCl$_2$F$_2$ at relatively low temperatures over a long period of time. Although it is not clear why peak A disappears after fluorination with F$_2$, one suggestion is that because the sample is fluorinated with a strong agent, the reaction is exothermic, resulting in a reconstruction of the surface in which the newly formed $\beta$-AlF$_{2.7}$OH$_{0.3}$ does not contain these active sites. The peak labelled E can be assigned to both CO that is adsorbed weakly to extensively hydroxylated Al ions and CO that is hydrogen bonded to OH groups, that is, adsorbed on Brönsted sites. This peak decreases after fluorination of the sample, which is consistent
with our assignment of it.

9.4 Conclusions

The strength of Lewis acid sites on clean and hydroxylated AlF$_3$ surfaces have been characterised from experimental and theoretical CO adsorption studies. This study supports our previous assignment, in chapter 8, of very strong Lewis acid sites that occur in small quantities on β-AlF$_3$ and in much higher quantities on HS-AlF$_3$ surfaces. These sites consist of Al ions bound to five bidentate F ions. We show, furthermore, that if this type of site is hydroxylated its Lewis acidity is significantly reduced; typically to the strength of the majority of sites found on crystalline α- and β-AlF$_3$ surfaces.

It is speculated that reactions that are catalysed by HS-AlF$_3$, but not β-AlF$_3$ require a high concentration of Al sites bound to five bidentate F ions. If such sites occur adjacent to one another this may result in an inductive effect or enable larger molecules to bind via multiple adsorption sites. Understanding the structure of the active sites on AlF$_3$ surfaces may enable the development of synthesis methods to create large quantities of such sites.
Chapter 10

Adsorption of HF and HCl on the \(\beta\)-AlF\(_3\) (100) surface

10.1 Introduction

The surface of \(\beta\)-AlF\(_3\) is known to catalyse many fluorination, dismutation and isomerisation reactions involving chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) \[109, 113, 114\]. Understanding the detailed atomic scale mechanisms by which reactions proceed at the active sites of \(\beta\)-AlF\(_3\) surfaces may facilitate the design and synthesis of more efficient and selective catalysts. In many AlF\(_3\) catalysed reactions HF and HCl are present as either reactants or products. As a first step towards a detailed understanding of the reaction mechanisms it is important that the interaction of these simple molecules with the surface is understood. The adsorption of HF and HCl on \(\beta\)-AlF\(_3\) has previously been studied using radiotracer measurements \[115\]. These experiments show that after adsorption and subsequent desorption of HF or HCl, there is significant halide exchange between the gas and the surface. A material that is related to AlF\(_3\), that is also highly catalytically active, is aluminium chlorofluoride (ACF) \[10\]. Studies of the adsorption of chlorine containing compounds onto AlF\(_3\) surfaces may also provide an insight into the...
high catalytic activity of ACF.

In this chapter we investigate the adsorption of HF and HCl to the under-coordinated Al sites on the T1 and T6 terminations of $\beta$-$\text{AlF}_3$ (100). We calculate the binding energies, geometries and vibrational frequencies of the molecules adsorbed to the surface at half and full monolayer coverages, and on the basis of these results, we propose possible reasons for the high catalytic activity of ACF and HS-$\text{AlF}_3$ surfaces for chlorine/fluorine exchange reactions.

### 10.2 Methodology

HF and HCl molecules were assumed to adsorb above under-coordinated Al ions via their fluorine or chlorine atom. Structures were then fully optimised. The binding energies of the molecules were corrected, where possible, for basis set superposition error (BSSE) using the counterpoise scheme [5]. The vibrational frequencies of the molecules were computed, as described in chapter 3.4.6.

### 10.3 Results and Discussion

The T1 termination, shown previously in figure 7.4, consists of two rows of ions that contain under-coordinated Al ions. The sites above these Al ions on the upper-most row are labelled T1A sites, and those on the lower row, T1B sites. The T6 termination, shown previously in figure 7.5 contains two symmetric rows of under-coordinated surface Al ions, which are separated by an open channel. Each of these Al ions is bound to a monodentate F ion, which is free to rotate to either open or close the surface channel. Molecules can adsorb to these under-coordinated Al ions either from above the Al ions, to a T6A site or from below the monodentate F ions, to a T6B site. These adsorption sites on the T6 termination are described in more detail in section 8.3.3. Initial calculations showed that
if an HF or HCl molecule adsorbs to a T6A site then molecules will preferentially bind to the adjacent Al ions via T6B sites and *vice versa*. This enables strong hydrogen bonds to form between the adsorbed molecules and the monodentate F ions, as will be shown in sections 10.3.1 and 10.3.2.

The number of under-coordinated Al sites per unit area on the T6 termination is twice that of the T1 termination. Full monolayer coverage is defined as the adsorption of molecules at all under-coordinated Al ions on a given termination. We consider half monolayer coverage on the T1 termination within the (1x1) cell. The cell contains one T1A and one T1B site. Therefore, we define half monolayer coverage as adsorption above all of the T1A sites or all of the T1B sites. Using larger cells there are other ways to obtain half monolayer coverage, however, these are outside the scope of this study. On the T6 termination half-monolayer coverage is defined as adsorption to alternate Al ions; either all T6A sites or all T6B sites.

### 10.3.1 Adsorption of HF

**Half Monolayer adsorption**

The T1A and T1B sites on the T1 termination are very similar to one another and consequently HF adsorbs in very similar ways. At half monolayer coverage on the T1 termination the HF molecule bonds via its F ion to an under-coordinated Al ion. The adsorbed HF molecule forms a strong hydrogen bond, of length 1.29 Å, with a nearby monodentate F ion, as shown in figure 10.1a. The molecular HF bond is 0.93 Å in gas phase, after adsorption the bond length increases to 1.08 Å.

On the T6 termination we consider two alternative half monolayer coverages; adsorption on T6A sites and adsorption on T6B sites. Adsorption of HF on a T6A site results in the formation of a hydrogen bond, of length 1.50 Å, with a neighbouring monodentate F ion, as shown in figure 10.1b. Adsorption on a T6B site also results in the formation of a
Full Monolayer adsorption

At first sight, the adsorption at full monolayer coverage of HF appears to display similar characteristics to adsorption at half monolayer coverage. However, a closer analysis of the systems shows that the local structure at full monolayer coverage is very different from that found at half monolayer coverage. After full monolayer adsorption to either the T1 or T6 termination the F ions that originate from the HF molecules and the neighbouring monodentate F ions become indistinguishable. The two H-F bond lengths are identical and the system consists of $\text{FHF}^-$ species at the surface. The bond lengths of this group are almost identical to those of the gas phase $\text{FHF}^-$ species, which has calculated bond lengths of 1.16 Å. Consequently, when HF is desorbed there will be a partial exchange of F ions with the surface, as has previously been observed in radiotracer experiments [115]. Structures consisting of a full monolayer of HF adsorbed on the T1 and T6 terminations are shown in figure [10.2]. The resultant Al-F and H-F bond lengths are displayed in table [10.1].
Table 10.1: The binding energies and bond lengths of HF adsorbed on the T1 and T6 terminations. The F ions that form the HF gas are labelled $F_g$ and those that originate from the surface are labelled $F_s$. At full monolayer coverage these F ions become indistinguishable. The binding energies in brackets correspond to values before corrections for BSSE were made.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Coverage (MLs)</th>
<th>Type of site</th>
<th>Figure</th>
<th>Binding energy (eV)</th>
<th>Al-F$_g$ (Å)</th>
<th>H-F$_g$ (Å)</th>
<th>H–F$_s$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1A</td>
<td>10.1a</td>
<td>-1.13 (-1.29)</td>
<td>1.86</td>
<td>1.08</td>
<td>1.29</td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1B</td>
<td>-</td>
<td>-1.15 (-1.30)</td>
<td>1.88</td>
<td>1.08</td>
<td>1.28</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>T6A</td>
<td>10.1b</td>
<td>-0.69 (-0.84)</td>
<td>1.99</td>
<td>0.99</td>
<td>1.52</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>T6B</td>
<td>10.1c</td>
<td>-0.85 (-1.01)</td>
<td>1.98</td>
<td>1.00</td>
<td>1.40</td>
</tr>
<tr>
<td>T1</td>
<td>1.0</td>
<td>T1A</td>
<td>10.2a</td>
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<td>1.83</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>T1</td>
<td>1.0</td>
<td>T1B</td>
<td>-</td>
<td>-1.16 (-1.33)</td>
<td>1.85</td>
<td>1.16</td>
<td>1.17</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6A</td>
<td>*</td>
<td>( -1.32)</td>
<td>1.83</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6B</td>
<td>*</td>
<td>( -1.49)</td>
<td>1.83</td>
<td>1.15</td>
<td>1.15</td>
</tr>
</tbody>
</table>

* It was not possible to make corrections for BSSE using the counterpoise scheme (see text).

**Binding Energies**

The binding energies of HF on the T1 and T6 terminations at half monolayer and full monolayer coverages are shown in table 10.1. At full monolayer coverage, the electronic state of the adsorbed HF molecule is significantly different from that of the gas phase species. This leads to problems in the counterpoise correction scheme. The calculation of the distorted gas phase molecule (corresponding to the adsorbed geometry) in the presence of the empty basis functions of the surface converges to an electronic ground state that differs from the ground state obtained when the empty basis functions are removed. For the T1 termination, the BSSE calculations converge to approximately the right state, although charge transfer into the empty surface orbitals still occurs. However, given that the BSSE is similar to that obtained at half monolayer coverage we believe the counterpoise scheme still provides a good approximation to the BSSE.
The binding energies are significantly greater for adsorption on the T1 termination than on the T6 termination. Previous calculations of the binding energy of NH$_3$ to these terminations also show larger binding energies to the T1 termination than the T6 termination [107, 116]. In chapter 8 we suggested that this is due to the different local geometries of the under-coordinated Al ions on each of the terminations.

On the T1 termination the binding energy is approximately the same at both half and full monolayer coverages. Conversely, the binding energy on the T6 termination increases with increased coverage. It is therefore energetically favourable for HF to segregate into clusters, reducing the overall surface energy of the system. This clustering should be observable in temperature programmed desorption where we would expect very sharp desorption peaks (surface explosions) [117].

**Vibrational Spectra**

There are three types of high frequency vibrational modes that occur on these terminations after adsorption of HF; two bending modes and a stretching mode, as depicted in figure 10.3. The calculation of a full force constant matrix for large systems is a compu-
Table 10.2: The vibrational frequencies of HF adsorbed to the T1 termination calculated from the full and partial force constant matrix. The vertical bending mode and the stretching mode occur at the same frequency on both the T1A and T1B sites.

<table>
<thead>
<tr>
<th>Atoms included in the calculation</th>
<th>Horiz. bend at T1A site (cm(^{-1}))</th>
<th>Horiz. bend at T1B site (cm(^{-1}))</th>
<th>Vert. bend (cm(^{-1}))</th>
<th>Stretch (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>All atoms</td>
<td>1199</td>
<td>1190</td>
<td>1435</td>
<td>1224</td>
</tr>
<tr>
<td>FHF(^-) + Al ions</td>
<td>1198</td>
<td>1190</td>
<td>1435</td>
<td>1211</td>
</tr>
</tbody>
</table>

The calculated vibrational frequencies of the adsorbed molecules and surface F ions at half and full monolayer coverage for both (100) terminations are given in table 10.3. For comparison, calculated stretching frequencies for an isolated HF molecule, an HF dimer and the stretching and bending frequencies of an FHF\(^-\) molecule are given in ta-

Figure 10.3: The three types of high frequency modes that occur. The arrows point in the directions in which the central H ion moves. The other atoms movements are negligible. (a) A horizontal bending mode. (b) A vertical bending mode. (c) A stretching mode.
Table 10.3: The vibrational frequencies of HF adsorbed on the $\beta\text{-AlF}_3$ (100) T1 and T6 terminations.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Coverage (MLs)</th>
<th>Type of site</th>
<th>Figure</th>
<th>Horiz. bend (cm$^{-1}$)</th>
<th>Vert bend (cm$^{-1}$)</th>
<th>Stretch (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1A</td>
<td>10.1a</td>
<td>1151</td>
<td>1347</td>
<td>1654</td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1B</td>
<td>-</td>
<td>1150</td>
<td>1347</td>
<td>1654</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>T6A</td>
<td>10.1b</td>
<td>945</td>
<td>1191</td>
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<td>10.1c</td>
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<td>T1</td>
<td>1.0</td>
<td>T1A</td>
<td>10.2a</td>
<td>1198</td>
<td>1435$^\ast$</td>
<td>1211$^\ast$</td>
</tr>
<tr>
<td>T1</td>
<td>1.0</td>
<td>T1B</td>
<td>10.2b</td>
<td>1190</td>
<td>1147</td>
<td>1580</td>
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<tr>
<td>T6</td>
<td>1.0</td>
<td>T6A</td>
<td>10.2b</td>
<td>1189</td>
<td>1436</td>
<td>1115</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6B</td>
<td>-</td>
<td>1075</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* The vibrational modes of the molecules on the T1A and T1B sites are coupled.

Table 10.4: The stretching frequencies of molecular HF and the bend and stretching frequencies for FHF$^-$ species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Calculated frequency (cm$^{-1}$)</th>
<th>Experimental frequency (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>HF</td>
<td>3940</td>
<td>4138$^{[118]}$</td>
</tr>
<tr>
<td>HF dimer</td>
<td>3803</td>
<td>-</td>
</tr>
<tr>
<td>FHF$^-$ (bend)</td>
<td>1359</td>
<td>1286$^{[119]}$</td>
</tr>
<tr>
<td>FHF$^-$ (stretch)</td>
<td>1451</td>
<td>1331$^{[119]}$</td>
</tr>
</tbody>
</table>

It can be seen from tables 10.3 and 10.4 that the HF stretching frequency decreases dramatically when HF is adsorbed on the $\beta\text{-AlF}_3$ (100) surface; it more closely resembles the stretching frequency of molecular FHF$^-$. The stretching frequency is strongly dependent on the local geometry of the adsorption site and the HF coverage at the surface. At half monolayer coverage on the T1 termination the stretching frequency is 1654 cm$^{-1}$. It is independent of the adsorption site. The vibrational frequencies associated with half monolayer coverage on the T6 termination are unlikely to be observable experimentally as the formation of an evenly distributed half monolayer coverage is energetically un-
favourable. The frequencies have only been included in table 10.3 for completeness. At full monolayer coverage on the T1 termination the HF stretching frequency is 1211 cm$^{-1}$. On the T6 termination, at full monolayer coverage, two distinct stretching frequencies are predicted. The HF molecules that adsorb at T6A sites, forming FHF$^-$ species parallel to the channels have a stretching frequency of 1115 cm$^{-1}$. The FHF$^-$ species that form perpendicular to the channels have a much higher stretching frequency of 1580 cm$^{-1}$, due to the restricted movement of the F ions within their local environment. The very different vibrational frequencies predicted should be visible in surface vibrational spectroscopy and will distinguish between T1 and T6 terminations and the level of saturation of HF.

10.3.2 Adsorption of HCl

Half Monolayer adsorption

Half monolayer adsorption on the T1 termination results in the formation of two distinct types of system. The HCl can either adsorb in analogy to HF or it can dissociate, resulting in an HF molecule and a Cl ion at the surface. The structures of the two alternate resultant geometries are shown in figures 10.4a and 10.4b. Half monolayer adsorption on the T6 termination occurs in an analogous manner, resulting in either an adsorbed HCl molecule hydrogen bonded to a nearby F ion or in the formation of a Cl ion at the surface and an HF molecule which hydrogen bonds to a nearby F ion. Resultant structures after half monolayer adsorption to T6A sites are shown in figures 10.4c and 10.4d. The binding energy at half monolayer coverage on T6B sites, without dissociation of HCl, is approximately zero. The relaxed structure after HCl adsorption and dissociation on T6B sites is shown in figure 10.4e. The bond lengths of the adsorbed species on the T1 and T6 terminations are given in table 10.5. In all of these calculations HCl is initially assumed to adsorb via its Cl ion above an under-coordinated Al ion, dissociation of the HCl ion occurs as a result of the geometry optimisation. The optimisation methods only locate
local minima, and therefore this suggests that there is no energy barrier, or only a very small energy barrier, to the dissociation of the HCl molecule upon adsorption on the T1 and T6 terminations.

Figure 10.4: Half Monolayer adsorption of HCl on (a) T1A sites on the T1 termination without dissociation of HCl, (b) T1A sites on the T1 termination with dissociation of HCl, (c) T6A sites on the T6 termination without dissociation of HCl, (d) T6A sites on the T6 termination with dissociation of HCl and (e) T6B sites on the T6 termination with dissociation of HCl.

Full Monolayer adsorption

Full monolayer adsorption of HCl on the T1 termination leads to two different models of adsorption. The first model is derived from the half monolayer structure where HCl does not dissociate. If further HCl is adsorbed to this surface then the H-Cl bond of all the adsorbed HCl molecules become elongated and H ions chemically bond to nearby monodentate F ions, resulting in the formation of CIHF− species, as shown in figure 10.5a. Alternatively, if the initial HCl molecules dissociate upon adsorption to the surface then

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Table 10.5: Results for the adsorption of HCl on the T1 and T6 terminations. Multiple structures occur for adsorption at each site as HCl may or may not dissociate (see text). The low energy structures are shown in figures 10.4 and 10.5.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Coverage</th>
<th>Site type</th>
<th>Figure</th>
<th>Binding energy (eV)</th>
<th>H—Cl (Å)</th>
<th>H—Cl (Å)</th>
<th>H—F (Å)</th>
<th>H—F (Å)</th>
<th>Al—Cl (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1A</td>
<td>10.4a</td>
<td>-0.67 (-0.80)</td>
<td>1.41</td>
<td>1.08</td>
<td>1.43</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1A</td>
<td>10.4b</td>
<td>-0.65 (-0.80)</td>
<td>1.42</td>
<td>1.08</td>
<td>1.40</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>T1B</td>
<td></td>
<td>-0.63 (-0.75)</td>
<td>1.44</td>
<td>1.08</td>
<td>1.28</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>T6A</td>
<td>10.4c</td>
<td>-0.29 (-0.41)</td>
<td>1.35</td>
<td>1.01</td>
<td>1.56</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>T6A</td>
<td>10.4d</td>
<td>-0.33 (-0.50)</td>
<td>1.35</td>
<td>1.00</td>
<td>1.46</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>1.0</td>
<td>T1A</td>
<td>10.5a</td>
<td>-0.66 (-0.82)</td>
<td>1.54</td>
<td>1.21</td>
<td>2.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>1.0</td>
<td>T1B</td>
<td></td>
<td>-0.62 (-0.77)</td>
<td>1.63</td>
<td>1.11</td>
<td>2.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>1.0</td>
<td>T1B</td>
<td>10.5b</td>
<td>-0.64 (-0.77)</td>
<td>1.51</td>
<td>1.15</td>
<td>2.28, 2.33*</td>
<td>1.15</td>
<td>1.18</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6A</td>
<td></td>
<td>-0.56 (-0.69)</td>
<td>1.50</td>
<td>1.50</td>
<td>2.31, 2.38*</td>
<td>1.50</td>
<td>1.68</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6B</td>
<td></td>
<td>-0.34 (-0.55)</td>
<td>1.71</td>
<td>1.71</td>
<td>2.28</td>
<td>1.07</td>
<td>1.12</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6A</td>
<td>10.5c</td>
<td>-0.16 (-0.40)</td>
<td>1.57</td>
<td>1.57</td>
<td>2.29, 2.36*</td>
<td>1.57</td>
<td>1.70</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6B</td>
<td></td>
<td>-0.55 (-0.74)</td>
<td>1.48</td>
<td>1.48</td>
<td>2.19, 2.37*</td>
<td>1.48</td>
<td>1.70</td>
</tr>
<tr>
<td>T6</td>
<td>1.0</td>
<td>T6A</td>
<td>-</td>
<td>+0.47 (+0.32)</td>
<td>1.37</td>
<td>1.37</td>
<td>2.19, 2.37*</td>
<td>1.37</td>
<td>1.85</td>
</tr>
</tbody>
</table>

* The longer bond length is for the Cl with the shorter H—Cl distance.
additional HCl molecules adsorb to under coordinated Al ions that are adjacent to lone Cl ions and form bonds to them, forming ClFCl\(^{-}\) species, as shown in figure 10.5b. Adsorption to the T6 termination occurs in an analogous manner, resulting either in the formation of ClHF\(^{-}\) structures or in the formation of FHF\(^{-}\) and ClFCl\(^{-}\) species. The most stable structure at full monolayer coverage on the T6 termination is shown in figure 10.5c, this structure consists of of FHF\(^{-}\) groups bridging across the surface channel and ClHCl\(^{-}\) species running parallel to the channel. The bond lengths of the adsorbed species at full monolayer coverage on the T1 and T6 terminations are given in table 10.5.

![Diagram](image)

Figure 10.5: Full monolayer adsorption of HCl on (a) the T1 termination without dissociation of HCl, (b) the T1 termination with partial dissociation of HCl and (c) the T6 termination with partial dissociation of HCl.

### Binding Energies

The binding energies for half and full monolayer coverage on the T1 and T6 terminations are given in table 10.5. In analogy to adsorption of HF, we find the binding energies for adsorption of HCl on the T1 termination are significantly higher than for adsorption on the T6 termination. On the T1 termination the energies, after adsorption of HCl, are all very similar, regardless of the resultant surface geometries. The magnitude of the binding energy is sensitive to the type of binding site and the surface coverage on the...
T6 termination. It is unlikely that the geometries associated with comparatively small binding energies will be observable experimentally.

The very rich variety of different structures that occur after the adsorption of HCl to the T1 and T6 terminations may be correlated to the high catalytic activity towards many HFC and CFC reactions. If CFC and HCFC adsorption is similar to that of HCl then one would expect fluorine/chlorine exchange to be facilitated by the surface. Furthermore, the formation of exposed Cl ions at the surface may result in a very similar surface structure to that of aluminium chlorofluoride (ACF), which is obtained from the partial fluorination of aluminium chloride. ACF is very strongly Lewis acidic, with an acidity comparable to that of HS-AlF$_3$. However, unlike HS-AlF$_3$ it becomes irreversibly inactive if exposed to moisture. Understanding the similarities and differences between these materials may be the key to developing better heterogenous Lewis acid catalysts in the future.

### Vibrational Spectra

The vibrational frequencies for surface species on the low energy systems are displayed in table 10.6. For comparison, the bond lengths and vibrational frequencies of gas phase HF, HCl, ClHCl$^-$ and ClHF$^-$ are given in table 10.7.

On both terminations the most significant change in the vibrational frequencies of the surface ions between half and full monolayer coverage is in the stretching frequency. For example, on the T1 termination this occurs at around 1660 cm$^{-1}$ at half monolayer and at 1029 cm$^{-1}$ and 1332 cm$^{-1}$, at full monolayer coverage. This change in the stretching frequency should provide a method of experimentally characterising AlF$_3$ surfaces.

### 10.4 Conclusions

HF is shown to adsorb above under-coordinated Al sites on $\beta$-AlF$_3$ (100). At low coverage it forms hydrogen bonds to neighbouring monodentate F ions. At high coverage it forms
Table 10.6: The vibrational frequencies of HCl adsorbed to the T1 and T6 $\beta$-AlF$_3$ (100) terminations.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Coverage (MLs)</th>
<th>Species</th>
<th>Site type</th>
<th>Figure</th>
<th>Horiz. bend (cm$^{-1}$)</th>
<th>Vert. bend (cm$^{-1}$)</th>
<th>Stretch (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.5</td>
<td>Cl-H—F</td>
<td>T1A</td>
<td>10.4a</td>
<td>824</td>
<td>1058</td>
<td>1664</td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>F-H—F</td>
<td>T1A</td>
<td>10.4b</td>
<td>1149</td>
<td>1343</td>
<td>1671</td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>Cl-H—F</td>
<td>T1B</td>
<td>-</td>
<td>820</td>
<td>1047</td>
<td>1649</td>
</tr>
<tr>
<td>T1</td>
<td>0.5</td>
<td>F-H—F</td>
<td>T1B</td>
<td>-</td>
<td>1143</td>
<td>1339</td>
<td>1651</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>Cl-H—F</td>
<td>T6A</td>
<td>10.4c</td>
<td>763</td>
<td>837</td>
<td>2329</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>F-H—F</td>
<td>T6A</td>
<td>10.4d</td>
<td>891</td>
<td>909</td>
<td>2602</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>F-H—F</td>
<td>T6B</td>
<td>10.4e</td>
<td>960</td>
<td>1206</td>
<td>2595</td>
</tr>
<tr>
<td>T1</td>
<td>1</td>
<td>F-H—Cl</td>
<td>T1A</td>
<td>10.5a</td>
<td>956</td>
<td>1191</td>
<td>1029</td>
</tr>
<tr>
<td>T1</td>
<td>1</td>
<td>F-H—Cl</td>
<td>T1B</td>
<td>-</td>
<td>957</td>
<td>1168</td>
<td>1332</td>
</tr>
<tr>
<td>T1</td>
<td>1</td>
<td>Cl-H—Cl</td>
<td>T1A</td>
<td>-</td>
<td>771</td>
<td>1017</td>
<td>982</td>
</tr>
<tr>
<td>T1</td>
<td>1</td>
<td>F-H-F</td>
<td>T1B</td>
<td>-</td>
<td>1184</td>
<td>1429</td>
<td>1271</td>
</tr>
<tr>
<td>T1</td>
<td>1</td>
<td>F-H-F</td>
<td>T1A</td>
<td>10.5b</td>
<td>1184</td>
<td>1425</td>
<td>1249</td>
</tr>
<tr>
<td>T6</td>
<td>1</td>
<td>Cl-H—Cl</td>
<td>T6A</td>
<td>10.5c</td>
<td>759</td>
<td>974</td>
<td>1058</td>
</tr>
<tr>
<td>T6</td>
<td>1</td>
<td>Cl-H—Cl</td>
<td>T6B</td>
<td>10.5d</td>
<td>757</td>
<td>959</td>
<td>1117</td>
</tr>
<tr>
<td>T6</td>
<td>1</td>
<td>F-H-F</td>
<td>T6B</td>
<td>10.5e</td>
<td>1063</td>
<td>1124</td>
<td>1624</td>
</tr>
</tbody>
</table>

Table 10.7: The calculated bond lengths and frequencies of molecular HCl, ClHF$^-$ and ClHCl$^-$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond length (Å)</th>
<th>Bending frequency (cm$^{-1}$)</th>
<th>Stretching frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.93</td>
<td>-</td>
<td>3940</td>
</tr>
<tr>
<td>HCl</td>
<td>1.31</td>
<td>-</td>
<td>2877</td>
</tr>
<tr>
<td>ClHCl$^-$</td>
<td>1.59</td>
<td>876</td>
<td>919</td>
</tr>
<tr>
<td>ClHF$^-$</td>
<td>1.89, 0.99*</td>
<td>927</td>
<td>2745</td>
</tr>
</tbody>
</table>

* 1.89 Å is the H-Cl bond length and 0.99 Å is the H-F bond length.
a chemical bond with nearby F ions forming an $\text{FHF}^-$ species. A much more complex situation occurs when HCl is adsorbed at the surface. Not only will it adsorb in ways analogous to HF but additional processes that involve the dissociation of HCl also occur. This leads to the formation of exposed Cl ions at the surface. It is predicted that this type of process may activate the surface, allowing a wide variety of reactions involving CFC and HCFC to be catalysed. This active surface may have similarities with those of highly catalytic ACF materials. Vibrational absorption peaks after adsorption of HF and HCl at half and full monolayer coverages have been calculated and it has been shown that it may be possible to characterise these surfaces from their vibrational spectra.
Chapter 11

Diffusion of Fluorine on the $\beta$-AlF$_3$(100) Surface

11.1 Introduction

In chapters 8 and 9 several AlF$_3$ surfaces where characterised by their interaction with NH$_3$ and CO. As a result of these studies it was suggested that the catalytically most active surfaces consist of Al ions bound to five bidentate F ions, alternate Al ions are also bound to a monodentate F ion. It is suggested that the catalytically active sites are the under-coordinated (uncapped) Al ions. The $\beta$-AlF$_3$(100) surface contains Al ions of this type and hence it is predicted that this surface will act as a catalyst for many halide exchange reactions. The catalysis of such reactions may require two or more uncapped Al ions to be adjacent to one another. It is, therefore, important to investigate the mobility and distribution of the F ions at the surface before studying the mechanisms by which catalytic processes occur. It is energetically favourable for the monodentate F ions on $\beta$-AlF$_3$(100) to cap every alternate Al ion, as this minimises the electrostatic repulsion between the F ions. The structure of this surface is shown in figure 7.4 in chapter 7. The surface consists of two rows of surface Al ions that run parallel to the $<001>$ direction. In the proceeding
discussions we shall refer to the upper most row as row A and to the other row as row B. The F ions can either move along the rows in the $<001>$ direction or perpendicular to the rows in the $<010>$ direction. In this chapter the diffusion of F ions to adjacent under-coordinated Al sites on the $\beta$-AlF$_3$(100) surface is considered. Transition barriers for the diffusion processes are calculated. In steady state, the distribution of capped and uncapped surface Al ions is determined by the relative energetics of the surface. The energetics of different configurations of capped and uncapped Al ions are also calculated. The occurrence of two or more under-coordinated Al ions that are adjacent to one another results in a surface defect. The relative energetics are used to predict the density of defects on the surface of $\beta$-AlF$_3$(100). These energies are then used, along with the transition barriers, to calculate the rate at which the diffusion of surface F ions occurs.

11.2 Methodology

Transition state structures and energetics were calculated using the nudged elastic band (NEB) algorithm. Calculations were performed within a $(1 \times 1)$ cell. Two different mechanisms for the diffusion of F ions were considered. The first mechanism involves an F ion moving directly from one Al ion to another. The second mechanism involves an F ion diffusing indirectly via the F ion bound between the two adjacent Al ions. These two mechanisms are shown in figures 11.1 and 11.2.

The energies of several slabs consisting of different configurations of capped and uncapped Al ions were calculated from geometry optimisations within $(2 \times 1)$ cells. A model was developed to predict the relative configurational energies as a function of the distribution of the surface F ions. The model was shown to predict the energetics reasonably well, but not accurately enough to enable an estimation of the number of defects that occur at the surface. The energy associated with the isolation of two adjacent Al ions along row A or row B were, hence, obtained from $ab\ initio$ calculations within $(5 \times 1)$ cells and
Table 11.1: Transition and final state energies, relative to the initial structure, for the direct movement of an F ion form row A to row B on the $\beta$-AlF$_3$ (100) surface. The energies are calculated using different slab sizes and different numerical tolerances within the calculations.

<table>
<thead>
<tr>
<th>No. of Al ions in slab</th>
<th>Numerical accuracy</th>
<th>Transition Barrier Energy (eV)</th>
<th>Final Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>High</td>
<td>2.11</td>
<td>1.03</td>
</tr>
<tr>
<td>26</td>
<td>Low</td>
<td>2.07</td>
<td>1.03</td>
</tr>
<tr>
<td>20</td>
<td>Low</td>
<td>2.15</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The number of surface defects was estimated. A kinetic Monte Carlo model was parameterised with the calculated energetics of the surfaces and reaction barriers to predict the rate at which F ions diffuse on the surface and the time it takes for a disordered surface to reach dynamic equilibrium.

11.3 Results and Discussion

11.3.1 Reaction Barriers

Calculation of reaction barriers is computationally very expensive, we therefore considered the effect of using thinner slabs and lower numerical tolerances (see section 3.4.8) on the resultant reaction barriers. The transition barriers for the diffusion of F ions from row A to row B via the direct pathway, using different approximations, are shown in table 11.1. The transition barrier, relative to the initial structure, is reproduced to within 0.05 eV in all approximations. The change in energy between the initial and final structures are calculated less accurately. (However, the calculations performed using thicker slabs can be used for these quantities.) Transition state energies have, therefore, been calculated using thin slabs and low numerical accuracy in all subsequent calculations, while thicker slabs were maintained for initial and final state calculations.

Minimum energy pathways were calculated for the direct and indirect movement of
Table 11.2: The transition structures and energetics for the direct pathway. The bridging 
F ions are labelled \( F_{\text{bri}} \) and the F ions that are moving between Al ions are labelled \( F_{\text{dif}} \).

<table>
<thead>
<tr>
<th>F ion</th>
<th>Direction of diffusion</th>
<th>Energy barrier (eV)</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{Al}_6-\text{Al}_5 )</td>
<td>( \text{Al}<em>6-F</em>{\text{dif}} )</td>
</tr>
<tr>
<td>( F_A )</td>
<td>&lt;010&gt;</td>
<td>2.15</td>
<td>3.14</td>
</tr>
<tr>
<td>( F_B )</td>
<td>&lt;010&gt;</td>
<td>1.11</td>
<td>2.97</td>
</tr>
<tr>
<td>( F_A )</td>
<td>&lt;001&gt;</td>
<td>1.33</td>
<td>3.24</td>
</tr>
<tr>
<td>( F_B )</td>
<td>&lt;001&gt;</td>
<td>1.22</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Table 11.3: The transition structures and energetics for the indirect pathway.

<table>
<thead>
<tr>
<th>F ion</th>
<th>Direction</th>
<th>Energy barrier (eV)</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{Al}_6-\text{Al}_5 )</td>
<td>( F-F )</td>
</tr>
<tr>
<td>( F_A )</td>
<td>&lt;010&gt;</td>
<td>1.39</td>
<td>4.23</td>
</tr>
<tr>
<td>( F_B )</td>
<td>&lt;010&gt;</td>
<td>1.33</td>
<td>4.21</td>
</tr>
<tr>
<td>( F_A )</td>
<td>&lt;001&gt;</td>
<td>1.00</td>
<td>3.81</td>
</tr>
<tr>
<td>( F_B )</td>
<td>&lt;001&gt;</td>
<td>1.35</td>
<td>3.81</td>
</tr>
</tbody>
</table>

F ions along the <100> and <010> directions within a \((1\times1)\) cell. The transition state 
energies, relative to the lowest energy surface, are given in tables 11.2 and 11.3 for the 
direct and indirect pathways respectively. Selected bond lengths for the transition state 
structures are also given in these tables. It can be seen that in half of the cases considered 
the diffusion occurs indirectly via an intermediate F ion. Structures along the direct and 
indirect reaction pathways for the movement of F ions along row A 
are shown in figure 11.1, similarly structures are shown for the movement of F ions from 
row A to row B in figure 11.2.

The transition structures for the direct pathways (left hand side of figures 11.1 and 
11.2) consist of distorted four member \((-\text{Al}-\text{F}-\text{Al}-\text{F})\) rings. The energy barriers vary considerably for diffusion along the <010> axis, depending on the direction of movement. 
The vertical distance between the capped Al ion in row A and the uncapped Al ion in row
Figure 11.1: The reaction pathways for the diffusion of an F ion along row A (in the <001> direction). The left hand side shows the direct pathway and the right hand side shows the indirect pathway.
Figure 11.2: The reaction pathways for the diffusion of an F ion from row A to row B (in the <010> direction). The left hand side shows the direct pathway and the right hand side shows the indirect pathway.
B is 1.6 Å compared with 0.8 Å between the capped Al ion in row B and the uncapped Al in row A, consequently, it is easier for an F ion to move from row B to row A than it is for movement from row A to row B.

The transition structures for the indirect pathways (right hand side of figures 11.1 and 11.2) consist of two under coordinated Al ions each bound to four bidentate F ions and a monodentate F ion. The bond lengths between the Al and monodentate F ions are around 1.6 Å, which is typical for monodentate F ion bonding. The transition structures and energetics are very similar for each of the different indirect reaction pathways. There is, however, one exception to this, the transition energy for movement along row A is significantly lower at 1.0 eV. Analysis of this transition state structure suggests that it is similar to the other structures and differs only in that the F ions directly below the under-coordinated Al ions are displaced along the <001> direction, distorting the truncated octahedra around the Al ions and reducing the total energy of the system.

In a recent study [99], the dynamics of an AlF₃ surface was studied using polarisable ionic potentials and running molecular dynamics over a time period of ten ps. It was shown, that at temperatures as low as 300K, the surface F ions moved rapidly between Al ions. This suggests a maximum transition barrier of around 0.12 eV, given the assumption that a single F ion switched between Al ions once in ten ps. This contradicts the current findings and highlights the necessity for a higher level of theory to accurately calculate the energetics of bond cleavage and bond formation.

### 11.3.2 Stable Structures

The relative energetics of several different surfaces within a (2x1) cell were considered. Analysis of these results suggests that the relative energetics are dominated by the electrostatic repulsions between neighbouring monodentate F ions and suggests that they may be reproduced by a simple model. Three factors contribute to the energies in the model.
These are the number of adjacent F ions along row A ($F_{AA}$), the number of adjacent F ions along row B ($F_{BB}$) and the number of adjacent F ions where one is on row A and the other on row B ($F_{AB}$). Analysis of our data shows that the relative energetics can be estimated using

$$E = 0.26F_{AA} + 0.50F_{BB} + 0.21F_{AB}$$  \hspace{1cm} (11.1)

The calculated and estimated values for the systems considered are shown in table [11.4]. Overall the fit is good, on average the surface energies are accurate to within 13%. The largest discrepancy occurs when the model over-estimates the surface energy by 0.27 eV, an error of 55%.

The energies are not, however, predicted accurately enough to enable a reliable estimation of the number of defect sites (adjacent under-coordinated Al ion). The fraction of under-coordinated Al sites that are considered defective, is given by

$$n = 2\exp\left(\frac{E_d}{kT}\right)$$  \hspace{1cm} (11.2)

where $E_d$ is the energy associated with the formation of the defect. The factor of two arises as two Al ions are involved in each defect site. To predict the number of defects to an accuracy of 50% at 600K, the defect energy must be calculated to within an accuracy of 0.02 eV. To obtain accurate energies for the formation of adjacent Al along row A a surface consisting of such defects is calculated within a (5x1) cell •◦◦•◦•◦•◦•◦ ◦••◦•◦••◦•. A similar calculation was performed to calculate the energy associated with adjacent under-coordinated Al ions along row B. The resultant defect energies are 0.38 eV and 0.13 eV for the formation of adjacent under-coordinated Al ions along row A and along row B respectively. Therefore, at 600K, approximately 0.14% of the Al ions along row A are predicted to be adjacent to another Al ion, compared with 16% on row B. To predict
Table 11.4: The relative energetics, compared to the stable surface, of a selection of surfaces, calculated within a (2×2) cell. The surfaces are represented by two rows of circles, the top row represents row A and the bottom row, row B. The filled circles represent capped Al ions and the hollow circles represent uncapped Al ions.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Calc. Ene (eV)</th>
<th>$F_{AA}$</th>
<th>$F_{BB}$</th>
<th>$F_{AB}$</th>
<th>Pred. Ene (eV)</th>
<th>$\Delta$ E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>•◦•◦</td>
<td>0.40</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0.42</td>
<td>0.02</td>
</tr>
<tr>
<td>••••</td>
<td>1.06</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1.04</td>
<td>0.02</td>
</tr>
<tr>
<td>•◦•◦</td>
<td>2.05</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>2.00</td>
<td>0.05</td>
</tr>
<tr>
<td>•◦•◦</td>
<td>0.97</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.97</td>
<td>0.00</td>
</tr>
<tr>
<td>••••</td>
<td>1.33</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1.21</td>
<td>0.12</td>
</tr>
<tr>
<td>•◦•◦</td>
<td>0.49</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0.76</td>
<td>0.27</td>
</tr>
<tr>
<td>••••</td>
<td>0.87</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>1.00</td>
<td>0.13</td>
</tr>
<tr>
<td>••••</td>
<td>0.73</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0.73</td>
<td>0.00</td>
</tr>
<tr>
<td>•◦•◦</td>
<td>0.53</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.71</td>
<td>0.18</td>
</tr>
<tr>
<td>••••</td>
<td>1.17</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1.21</td>
<td>0.04</td>
</tr>
<tr>
<td>••••</td>
<td>0.58</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0.47</td>
<td>0.11</td>
</tr>
</tbody>
</table>

the number of double defects, that is the formation of three adjacent under-coordinated Al ions on one row and three F ions on the other row, surface energies within a (3×1) cell, [•◦◦◦], were calculated. Defect energies of 0.88 eV and 0.38 eV where obtained for three adjacent under-coordinated Al ions along row A and row B respectively. At 600K, approximately 0.000013% of the Al ions along row A will be part of a row of three such ions and along row B this figure will be 0.19%.

11.3.3 Kinetic Monte Carlo Simulations

A kinetic Monte Carlo model is used to simulate the movement of F ions at the $\beta$-AlF$_3$ (100) surface. We consider the dynamics and composition of the surface at 600K as this is a typical temperature at which the catalyst operates. In our kinetic Monte Carlo model the transition barrier associated with the movement of an F ion from its current site to a neighbouring site is calculated as a function of the coordination of the neighbouring Al sites. We have, however, only calculated transition barriers for movement of F ions within
Table 11.5: The values for $E_N$ used in our kinetic Monte Carlo model.

<table>
<thead>
<tr>
<th>F Diffusion Event</th>
<th>$E_N$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Along row A</td>
<td>1.8</td>
</tr>
<tr>
<td>Along row B</td>
<td>2.2</td>
</tr>
<tr>
<td>Between the rows</td>
<td>1.7</td>
</tr>
</tbody>
</table>

a $(1 \times 1)$ cell, consequently, each pathway involves the movement of half of the surface F ions from one site to another. It is therefore necessary to predict the transition barrier for the diffusion of an isolated F ion as a function of the coordination of the neighbouring Al ions. We assume that the transition state energies can be approximated as the sum of the average energy of the surface before and after the diffusion event and a constant, $E_N$. A different value of $E_N$ is used to describe each of the three different types of diffusion event (across row A, across row B and movement between the rows). The transition state energy barrier is hence given by

$$E_{TS} = \frac{1}{2} \Delta E + E_N \quad (11.3)$$

where $\Delta E$ is the difference between the initial and final state energies, $\Delta E$ is positive if the initial state is the most stable state. The values for $E_N$ are obtained from our calculations within a $(1 \times 1)$ cell and are displayed in table 11.5. The value of $E_N$ for movement between the rows can be obtained from two of our calculations; the value obtained from each of these calculations is the same, this supports the use of this model.

Our kinetic Monte Carlo model was run on a grid consisting of 1000 F ions and 1000 vacant sites. Initially the F ions and vacant sites were randomly distributed. The simulation was run 100 times, hence the effective size of the grid was 100,000. This total size was necessary to capture sufficient numbers of rare events. The composition of the surface was recorded every $10^{-5}$ s. The size of the individual grids determines the time-steps using in the simulation; if the grid is too small then the time-step is too large and the
sampling of the surface will be biased by the last diffusion event. The effect of grid-size on the evolution of the surface was carefully analysed and it was shown that a grid-size of 1000 was sufficient.

The number of adjacent uncapped Al ions was counted every $10^{-5}$ s of simulation time. The number of these occurrences, as a percentage of the total number of uncapped Al ions is plotted in figure 11.3. The surface reaches steady state after approximately 0.05 seconds, this suggests, that under catalytic conditions, the surface will always be in dynamic equilibrium. It is predicted from this model that 13% of the uncapped Al ions on row B will neighbour an uncapped Al ion that is also on row B and 1.6% of the uncapped Al ions will neighbour an uncapped Al ion on row A. Several of these pairs of Al ions will also be adjacent to an uncapped Al ion on the alternate row. The energetics of such occurrences were not considered in our estimation of the number of defect sites in section 11.3.2, this is why the defect concentrations differ slightly in the two approaches.

11.4 Conclusions

Two competing mechanisms for the diffusion of fluorine ions at the surface of $\beta$-AlF$_3$ were considered. It was shown that these mechanisms both have similar energetics and it depends on the local environment as to which provides the lowest energy barrier, con-
sequently, both types of mechanism will occur. It was demonstrated, that under typical reaction temperatures (600K), that the surface fluorine ions are mobile at the surface, and that the surface will be in dynamic equilibrium. It is predicted that the majority of the under-coordinated Al ions will be evenly distributed on the surface, however, around 16% of the under-coordinates Al ions will be adjacent to another such Al ion and around 0.06% will be adjacent to two such Al ions. Over 99% of these Al ions will be on row B of the surface.
Chapter 12

Dismutation of CCl\textsubscript{2}F\textsubscript{2} on the $\beta$-AlF\textsubscript{3} (100) Surface

12.1 Introduction

$\beta$-AlF\textsubscript{3} is known to catalyse several halide exchange reactions. One of the simplest of these reactions is

\begin{equation}
2\text{CCl}_2\text{F}_2 \rightarrow \text{CCl}_3\text{F} + \text{CCIF}_3
\end{equation}

(12.1)

In this chapter we shall attempt to understand the mechanism by which this reaction proceeds on the $\beta$-AlF\textsubscript{3} (100) surface. Although reactions such as this one are often used to characterise the catalytic properties of AlF\textsubscript{3} surfaces, the kinetics of these reactions and the mechanisms by which they proceed are poorly understood. It is known, however, that $\beta$-AlF\textsubscript{3} does not just offer adsorption sites for the reactants, but that it is directly involved in the dismutation of CCl\textsubscript{2}F\textsubscript{2} \cite{120, 121, 122, 123, 124, 125}. The reaction is thought to proceed in a non-concerted manner; that is, a sequence of fluorination and chlorination reactions occur at the catalyst surface \cite{126}.  

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In chapter 10 we showed that HCl can dissociate upon adsorption at the surface of $\beta$-AlF$_3$ and that there is either no energy barrier or a very low energy barrier to the dissociation. We propose that adsorption and dissociation of CCl$_2$F$_2$ could occur in an analogous manner. We would, however, expect there to be a significant energy barrier associated with the dissociation of the CCl$_2$F$_2$ molecule as, unlike HCl, CCl$_2$F$_2$ is not strongly polar. If the barrier is not insurmountable at elevated temperatures, then reaction 12.1 could proceed via a two step process. The first step would involve the adsorption of a CCl$_2$F$_2$ molecule via its Cl ion to an under-coordinated Al ion and the subsequent dissociation of the C-Cl bond and the formation of a C-F bond with a nearby surface F ion. The newly formed CClF$_3$ molecule could then desorb, leaving a Cl ion at the surface. The second step of the reaction would involve the adsorption of a second CCl$_2$F$_2$ molecule, this time via its F ion. The C-F bond is broken and a bond is formed between the C and the Cl ion previously left behind at the surface to form a CCl$_3$F molecule, which can then desorb from the surface. This two step reaction mechanism can be written as

$$\text{CCl}_2\text{F}_2 + \text{F}_{\text{surf}} \rightarrow \text{CClF}_3 + \text{Cl}_{\text{surf}}$$  \hspace{1cm} (12.2)

$$\text{CCl}_2\text{F}_2 + \text{Cl}_{\text{surf}} \rightarrow \text{CCl}_3\text{F} + \text{F}_{\text{surf}}$$  \hspace{1cm} (12.3)

In this chapter we consider the energetics of this proposed reaction pathway. We start by considering the adsorption of CCl$_2$F$_2$, CCl$_3$F and CClF$_3$ molecules to the $\beta$-AlF$_3$ (100) surface. We then calculate the structure and energetics of the transition barriers for these reactions. The energetics of these pathways are analysed and used to predict the overall turnover of reaction 12.1 at the $\beta$-AlF$_3$ (100) surface.
12.2 Methodology

Energies were calculated for the adsorption of CCl$_2$F$_2$, CCl$_3$F and CClF$_3$ at half mono-
layer adsorption to under-coordinated Al ions on the $\beta$-AlF$_3$ within a (1×1) cell; the
minimum distance between adjacent CFC molecules was 5.3 Å. In each case several dif-
f erent orientations of the CFC molecule were considered. In addition, a small number of
calculations were performed within (2×1) cells to enable an estimate on the binding ener-
gies at very low coverages. Transition state structures and energy barriers were calculated
using the nudged elastic band (NEB) algorithm for several possible reaction pathways
described by equations 12.2 and 12.3. All NEB calculations were performed using thin
slabs and low numerical tolerances (see sections 3.4.8 and 11.3.1). The calculated bind-
ing energies were corrected for BSSE using the counterpoise scheme [5]. The absolute
binding energies were relatively small, consequently the correction for BSSE was signifi-
cant. The binding energies are quoted before and after BSSE correction and the accuracy
of these calculations are discussed in section 12.3.

12.3 Results and Discussion

12.3.1 Adsorption of CCl$_2$F$_2$

Various geometries for the adsorption of CCl$_2$F$_2$ on the $\beta$-AlF$_3$ (100) were considered.
These included adsorption via the molecule’s F and Cl ions to Al ions on both row A and
row B of $\beta$-AlF$_3$ (100). The CCl$_2$F$_2$ molecules were adsorbed in a number of different
orientations and the largest binding energies, as a function of orientation, are shown in
table 12.1. Structures consisting of CCl$_2$F$_2$ adsorbed F down and Cl down on row A
are shown in figure 12.1. In the case of adsorption via the Cl ion a second adsorption
geometry, in which the molecule is rotated by approximately 180° is also shown.

The adsorption energies are relatively small. Analysis of the Millikan populations
Table 12.1: The binding energies (with and without corrections for BSSE) for CCl$_2$F$_2$ adsorbed at half monolayer coverage on the β-AlF$_3$ (100) surface.

<table>
<thead>
<tr>
<th>Adsorption ion</th>
<th>Site of adsorption</th>
<th>Binding Energy (eV) No BSSE</th>
<th>BSSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>A</td>
<td>-0.19</td>
<td>-0.08</td>
</tr>
<tr>
<td>F</td>
<td>B</td>
<td>-0.18</td>
<td>-0.08</td>
</tr>
<tr>
<td>Cl</td>
<td>A</td>
<td>-0.13</td>
<td>-0.03</td>
</tr>
<tr>
<td>Cl</td>
<td>B</td>
<td>-0.14</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

Figure 12.1: Adsorption of CCl$_2$F$_2$ on row A of the β-AlF$_3$(100) surface. (a) Adsorption via an F ion. (b) Adsorption via a Cl ion. (c) Adsorption via a Cl ion. The binding energies, without corrections for BSSE, at half monolayer coverage are also given.
on the CCl$_2$F$_2$ molecule before and after adsorption shows that there is effectively no charge transfer between the molecule and the surface, hence, one can conclude that the adsorption is predominately due to electrostatic effects. The binding energy of NH$_3$, discussed in chapter 8, was shown to also be dominated by electrostatics. The Mulliken charge on the N ion in NH$_3$ is around 0.8 |e|, the charge on the F and Cl ions in CCl$_2$F$_2$, when they bind to the surface, are 0.3 |e| and 0.1|e| respectively. This explains, at least in part, the weakness of the bond between the surface and the CCl$_2$F$_2$ molecule. In addition, there will be electrostatic repulsion between the surface F ions and the adsorbed CCl$_2$F$_2$. To estimate the effect of this repulsion the adsorption of CCl$_2$F$_2$ on row A when all of the monodentate F ions are on row B was calculated. The molecule bound significantly more strongly than when the monodentate F ions were split between both rows. The resultant binding energy was -0.38 eV (-0.25 eV after correction for BSSE). This suggests that the binding energy is significantly weakened by the presence of nearby surface F ions. In addition, tests were performed at a quarter monolayer coverage on a (2×1) cell. It was shown that CCl$_2$F$_2$ bound more strongly, by around 0.04 eV, when the coverage was decreased from a half monolayer to a quarter monolayer.

The corrections for BSSE are approximately 0.1 eV, although this is a typical correction for BSSE, it is a large fraction of the binding energies. This suggests that the structures are unlikely to be fully optimised to their BSSE corrected minimum energy structure. It is, therefore, difficult to estimate the true binding energy for these systems; the BSSE corrected value is likely to be an under-estimate of the true binding energy. We shall therefore assume that the binding energies lie somewhere between the BSSE uncorrected and corrected values. The binding energy for the adsorption of CCl$_2$F$_2$, via its F ion, to within the nearest 0.05 eV, is estimated to be -0.15 eV if two F ions occur either side of the adsorbed molecule and -0.35 eV in the presence of no nearest neighbours. Similarly, the binding energies for adsorption via the Cl ion can be approximated as -0.10 eV and -0.30 eV.
12.3.2 Adsorption of CClF$_3$ and CCl$_3$F

The first step of our proposed reaction mechanism involves the cleavage of the C-Cl bond of an adsorbed CCl$_2$F$_2$ molecule and the formation of an C-F bond with a nearby monodentate F ion to form CClF$_3$. Adsorption of CClF$_3$ on a partially chlorinated $\beta$-AlF$_3$ (100) surface has therefore been considered. Two of these structures are shown in figure 12.2 and the largest binding energies, as a function of CClF$_3$ orientation, are shown in table 12.2.

The second step of the proposed reaction mechanism involves a CCl$_2$F$_2$ molecule reacting with a nearby monodentate Cl ion to form an adsorbed CCl$_3$F on the surface. The structures and energetics of this system have been considered. The binding energies of the optimised structures are shown in table 12.3. Two of these structures are shown in figure 12.3. As for the adsorption of CCl$_2$F$_2$, the corrections for BSSE are large relative to the binding energies. The true binding energy is likely to occur somewhere between the corrected and uncorrected BSSE binding energies. The binding energies for adsorption of CClF$_3$ and CCl$_3$F are significantly reduced when monodentate halide ions are close to the adsorbed molecule.
Figure 12.3: Adsorption of CCl$_3$F on row B of the $\beta$-AlF$_3$(100) surface. (a) F ions on rows A and B. (b) F ions all on row A. The binding energies, without corrections for BSSE, at half monolayer coverage are also given.

Table 12.2: The binding energies (with and without corrections for BSSE) for the adsorption of CClF$_3$, via its F ion, on a partially chlorinated $\beta$-AlF$_3$ (100) surface

<table>
<thead>
<tr>
<th>Site</th>
<th>Cl ion</th>
<th>F ion</th>
<th>No BSSE</th>
<th>BSSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>row A</td>
<td>row A</td>
<td>row B</td>
<td>-0.17</td>
<td>-0.05</td>
</tr>
<tr>
<td>row A</td>
<td>row B</td>
<td>row A</td>
<td>-0.32</td>
<td>-0.21</td>
</tr>
<tr>
<td>row B</td>
<td>row B</td>
<td>row A</td>
<td>-0.16</td>
<td>-0.06</td>
</tr>
<tr>
<td>row B</td>
<td>row A</td>
<td>row B</td>
<td>-0.34</td>
<td>-0.25</td>
</tr>
</tbody>
</table>

Table 12.3: The binding energies (with and without corrections for BSSE) for the adsorption of CCl$_3$F, via its Cl ion, on the $\beta$-AlF$_3$ (100) surface

<table>
<thead>
<tr>
<th>Site</th>
<th>F ion</th>
<th>F ion</th>
<th>No BSSE</th>
<th>BSSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>row A</td>
<td>row B</td>
<td>row B</td>
<td>-0.36</td>
<td>-0.24</td>
</tr>
<tr>
<td>row A</td>
<td>row A</td>
<td>row B</td>
<td>-0.21</td>
<td>-0.08</td>
</tr>
<tr>
<td>row B</td>
<td>row A</td>
<td>row A</td>
<td>-0.30</td>
<td>-0.19</td>
</tr>
<tr>
<td>row B</td>
<td>row A</td>
<td>row B</td>
<td>-0.23</td>
<td>-0.10</td>
</tr>
</tbody>
</table>
12.3.3 Reaction mechanisms and barriers

Minimum energy paths and transition energies were calculated for the transfer of CFC molecules along row A, along row B and between the rows for both steps of the reaction. The results from these calculations are summarised in tables [12.4] and [12.5]. The lowest transition energies for each step of the reaction occur when the CFC molecules move between rows.

The lowest energy path for the first step of the reaction involves the adsorption of a CCl$_2$F$_2$ molecule at an A site (figure 12.1c) followed by the cleavage of the C-Cl bond and the formation of a CClF$_3$ molecule adsorbed on row B (figure 12.2b). The second step involves the adsorption of a CCl$_2$F$_2$ molecule to an Al on row A on a partially chlorinated surface and the subsequent formation of a CCl$_3$F molecule on row B (figure 12.3b). The lowest energy pathways for each of these steps are shown in figures [12.4] and [12.5]. The lowest energy paths for both steps of the reaction mechanism involve the movement of a CFC molecule from one row to the other row, as opposed to movement along a single row. The transition structures for both reactions, shown in figures [12.4] and [12.5], are quite similar. The main difference is that one of the monodentate halide ions bound to the C atom is a Cl in one case and an F in the other case. The transition energy barrier for the first mechanism is around 66% larger than the barrier for the second mechanism. The distribution of the surface F and Cl ions differs between the two transition structures. This suggests that the energy barriers may be determined by the position of the neighbouring Cl and F ions.

An alternate reaction pathway for the formation of a CClF$_3$ molecule has been calculated, this time all the surface F ions are initially on row A and the CCl$_2$F$_2$ molecule is adsorbed on row B. The energy barrier for this reaction is 1.04 eV, significantly lower than the previously calculated barrier of 1.48 eV. The surface is, however, much less likely to be in this initial state. In chapter [11] we calculated the occurrence of local defect regions.
Table 12.4: The resultant geometries and energetics of the transition states for the reaction $\text{CCl}_2\text{F}_2 + \text{F}_{\text{surf}} \rightarrow \text{CClF}_3 + \text{Cl}_{\text{surf}}$. The transition state energy barrier (TS Energy) is relative to the reactants.

<table>
<thead>
<tr>
<th>CCl$_2$F$_2$ ads. site</th>
<th>CClF$_3$ ads. site</th>
<th>TS Energy (eV)</th>
<th>Al–Cl (Å)</th>
<th>Al–F (Å)</th>
<th>C–Cl (Å)</th>
<th>C–F (Å)</th>
<th>$\angle$ F–C–Cl (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>row A</td>
<td>row A</td>
<td>1.67</td>
<td>2.29</td>
<td>1.72</td>
<td>2.82</td>
<td>2.32</td>
<td>118</td>
</tr>
<tr>
<td>row B</td>
<td>row B</td>
<td>1.72</td>
<td>2.28</td>
<td>1.71</td>
<td>3.00</td>
<td>2.50</td>
<td>101</td>
</tr>
<tr>
<td>row A</td>
<td>row B</td>
<td>1.67</td>
<td>2.25</td>
<td>1.71</td>
<td>3.12</td>
<td>2.82</td>
<td>81</td>
</tr>
<tr>
<td>row B</td>
<td>row A</td>
<td>1.48</td>
<td>2.25</td>
<td>1.69</td>
<td>3.26</td>
<td>3.24</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 12.5: The resultant geometries and energetics of the transition states for the reaction $\text{CCl}_2\text{F}_2 + \text{Cl}_{\text{surf}} \rightarrow \text{CCl}_3\text{F} + \text{F}_{\text{surf}}$. The transition state energy barrier (TS Energy) is relative to the reactants.

<table>
<thead>
<tr>
<th>CCl$_2$F$_2$ ads. site</th>
<th>CClF$_3$ ads. site</th>
<th>TS Energy (eV)</th>
<th>Al–Cl (Å)</th>
<th>Al–F (Å)</th>
<th>C–Cl (Å)</th>
<th>C–F (Å)</th>
<th>$\angle$ F–C–Cl (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>row A</td>
<td>row A</td>
<td>1.09</td>
<td>2.27</td>
<td>1.71</td>
<td>3.21</td>
<td>2.72</td>
<td>72</td>
</tr>
<tr>
<td>row B</td>
<td>row B</td>
<td>1.10</td>
<td>2.28</td>
<td>1.70</td>
<td>3.13</td>
<td>2.82</td>
<td>70</td>
</tr>
<tr>
<td>row A</td>
<td>row B</td>
<td>0.89</td>
<td>2.24</td>
<td>1.71</td>
<td>3.61</td>
<td>2.84</td>
<td>74</td>
</tr>
<tr>
<td>row B</td>
<td>row A</td>
<td>0.99</td>
<td>2.22</td>
<td>1.71</td>
<td>3.61</td>
<td>2.87</td>
<td>78</td>
</tr>
</tbody>
</table>

such as a row of three F ions on row A opposite three under-coordinated Al ions on row B. In section 12.3.4 we shall use the defect concentrations, calculated in chapter 11, to estimate the turnover rate for the formation of CClF$_3$.

12.3.4 Analysing the Kinetics of the Reaction

The small binding energies associated with adsorption of the CFC molecules implies the overall coverage of the surface will be very low under typical conditions. In equilibrium, the rate of desorption of molecules from the surface will be equal to their rate of adsorption. The ratio of the rate of adsorption to the rate of desorption is approximately

$$\frac{r_{\text{ads}}}{r_{\text{des}}} = \exp\left(\frac{\Delta \mu - E_{\text{ads}}}{k_B T}\right)$$

(12.4)
Figure 12.4: A low energy pathway for $\text{CCl}_2\text{F}_2 + \text{F}_{\text{surf}} \rightarrow \text{CClF}_3 + \text{Cl}_{\text{surf}}$ (reaction 12.2).

where $\Delta \mu$ is the change in the Gibbs free energy per molecule between the gas phase and the adsorbed phase and $E_{\text{ads}}$ is the binding energy of the molecule to the surface. This approximation neglects any change in the Gibbs free energy of the surface induced by adsorption, which has previously been shown to be very small [81]. The chemical potential per molecule of an ideal gas is given by

$$\mu_{\text{gas}} = -k_B T \ln \left[ \left( \frac{2\pi m_i k_B T}{\hbar^2} \right)^{\frac{3}{2}} \frac{k_B T}{p_i} \right]$$  \hspace{1cm} (12.5)$$

The chemical potential of a gas such as $\text{CCl}_2\text{F}_2$ also contains terms due to the internal degrees of freedom of the molecule. It can be assumed that these terms will be dominated by the vibrational degrees of freedom, which will only change by a small amount after adsorption. $\Delta \mu$ in equation [12.4] can, therefore, be written in terms of the chemical potential of an ideal gas. Using this approximation, $\Delta \mu = -0.46 \text{ eV}$ at 300K and $-1.01 \text{ eV}$ at
Figure 12.5: A low energy pathway for $\text{CCl}_2\text{F}_2 + \text{Cl}_{\text{surf}} \rightarrow \text{CCl}_3\text{F} + \text{F}_{\text{surf}}$ (reaction 12.3).
600K for CCl$_2$F$_2$.

The binding energy of CCl$_2$F$_2$, at low coverages, is around 0.15 eV for adsorption via its Cl ion (see section 12.3.1). At 600K approximately one in every $3 \times 10^7$ of the under-coordinated Al ions will be covered by a CCl$_2$F$_2$ molecule that has adsorbed via its Cl ion. The rate constant is given by

$$r = \nu_0\exp\left(-\frac{\Delta E}{RT}\right)$$

Assuming a reaction barrier, $\Delta E$, of 1.48 eV the rate constant is 40 s$^{-1}$. The overall turnover is hence $1 \times 10^{-6}$ s$^{-1}$ per Al site. If the reaction proceeds at a site where all the local monodentate F ions are adsorbed to Al ions on row A, the corresponding transition barrier to the formation of CClF$_3$ is 1.04 eV. The rate constant for this reaction is $2 \times 10^5$ s$^{-1}$. It is energetically unfavourable for the F ions to all adsorb to row A. In chapter 11 we showed that only one in 1600 under-coordinated Al ions on the surface will be surrounded by an under-coordinated Al ion on either side of it and opposite three F ions. CCl$_2$F$_2$ adsorbs with a binding energy of -0.35 eV. The overall turnover for this reaction pathway is approximately $2 \times 10^{-4}$ s$^{-1}$ per Al site, approximately 200 times greater than for the reaction pathway with a barrier of 1.48 eV.

The second step of the reaction (equation 12.3) involves the formation of a CCl$_3$F molecule. The minimum energy barrier for this reaction is 0.89 eV. The turnover at 600K is 0.3 s$^{-1}$ per Al site, hence it is is 1500 times greater than that of the first step. The first step of the overall dismutation reaction is therefore predicted to be the rate limiting step.

Experimental data suggests that the turnover rate per Al site is much higher than predicted from our calculations. A typical reaction in the laboratory involves passing a flow of CCl$_2$F$_2$, usually mixed with helium, through a micro-reactor filled with the AlF$_3$ material and analysing the gas as it exits the reactor [37]. A typical reactor might contain around 20 mg of the catalyst. The gas typically consists of a 3:1 ratio of He to CCl$_3$F$_2$ and
a typical flow rate of the gases would be 100 cm$^3$ min$^{-1}$. The residence time of the flow of gas through the reactor is around 1 second. Therefore, the number of CCl$_2$F$_2$ molecules passing through the reactor per second is approximately $5.6 \times 10^{18}$ at 600K. Assuming a catalyst of surface area of 20 m$^2$g$^{-1}$ with two under-coordinated Al ions per nm$^2$ and that 4% of these are Al ions are reactive then this corresponds to around $3 \times 10^{16}$ active Al sites in the reactor. The overall turnover is therefore of the order of one hundred molecules per second per Al site as opposed to a turnover of $2 \times 10^{-4}$ s$^{-1}$ per Al site, predicted from our calculations.

The errors in our calculated turnovers rates are likely to be quite large as they are very sensitive to the accuracy of the transition energy barrier. For instance, a 20% over prediction of the transition energy barrier leads to an under-estimate of the turnover rate by a factor of 400. We have also shown that the rate limiting step of the reaction occurs at a defect site consisting of a row of three F ions on row A opposite three under-coordinated Al ions on row B of the surface. It is hence, possible that the reaction actually proceeds via a defect site that we have not considered, such as where two adjacent F ions are opposite two under-coordinated Al ions. Therefore, although our calculations predict a turnover rate that is several orders of magnitude smaller than the experimental rate, this does not necessarily mean that the proposed reaction mechanism is incorrect. In the absence of detailed experimental data the mechanism that we have suggested remains the most likely candidate for the dismutation of CCl$_2$F$_2$ on $\beta$-AlF$_3$.

12.4 Conclusions

We have proposed a reaction mechanism for the dismutation of CCl$_2$F$_2$ to form CCl$_3$F and CClF$_3$ on the surface of $\beta$-AlF$_3$ (100). Our mechanism involves the participation of surface F ions and occurs in a two step process. Calculations of the relevant reaction barriers suggests that this reaction could plausibly occur on the $\beta$-AlF$_3$ (100) at elevated
temperatures.

We have proposed that the rate limiting step of the reaction predominately occurs at a defect site. This demonstrates the extent to which a small change to the local structure of the surface can dramatically increase the rate of a reaction. This may, furthermore, explain why HS-AlF$_3$ is highly reactive; it may be that only a relatively small number of defect sites are responsible for its high catalytic activity. On many surfaces it is thought that such defect sites would poison quickly and not act as highly active catalytic sites. On AlF$_3$, however, we have shown that the CFC reactants only bind weakly to the active sites, hence it is unlikely to poison any defect site. It is, however, still possible that highly defective sites could be poisoned by other molecules such as H$_2$O.
Chapter 13

Conclusions

In this project a recently developed thermodynamic formulism has been used to characterise materials in a realistic reaction environment. We have gained new insights into the relationships between the composition, structure and chemical properties of AlCl$_3$ and AlF$_3$ surfaces.

We have shown that the surface of crystalline AlCl$_3$ is not Lewis acidic. This contradicts the commonly held assumption that AlCl$_3$ is always a strong Lewis acidic material.

AlF$_3$ is a highly ionic material. The Al and F ions remain strictly Al$^{3+}$ and F$^-$, hence, under typical conditions AlF$_3$ surfaces are stoichiometric. Under-coordinated Al ions are, consequently, always exposed at the surface. These Al ions are either coordinated to four or five F ions. It has been suggested that the most reactive Al ions are four-fold coordinated. We have characterised the reactivity of the under coordinated Al ions on several surfaces via the calculation of their NH$_3$ binding energies. Our results show that four-fold Al ions are the least reactive type of under-coordinated Al ions. We suggest that this is because the coordination geometries exert a strong influence on the reactivity of the Al ions. The four-fold Al ions form stable tetrahedral structures, while the 5-fold Al ions are in a distorted and truncated octahedral environment. The most reactive surface Al ions are bound to five bidentate F ions and are truncated octahedra. The surface displaying this
type of Al site is not predicted to be exposed on crystalline \( \alpha \)-AlF\(_3\) samples, however, it is predicted to occur in small quantities on \( \beta \) crystallites. We speculate that such sites occur in higher quantities on high surface area materials. This result may explain the different reactivity of \( \alpha \)-, \( \beta \)- and HS-AlF\(_3\).

The structure and composition of the (01\(\overline{1}\)2) and (0001) terminations of \( \alpha \)-AlF\(_3\) were calculated as a function of HF and H\(_2\)O chemical potentials. The phase diagrams for the two surfaces showed many similarities. Under standard atmospheric conditions the surfaces were predicted to adsorb water above under-coordinated Al ions. To expose the under-coordinated Al ions it was shown that the surfaces must be heated and put under low H\(_2\)O partial pressure and high HF partial pressure. Although phase diagrams for the \( \beta \)-AlF\(_3\) surfaces were not calculated, it is predicted that they would be similar to the phase diagrams of the \( \alpha \) surfaces.

The phase diagram for the (01\(\overline{1}\)2) termination contains phase boundaries between the structures derived from the (1\(\times\)1) and the (\(\sqrt{2} \times \sqrt{2}\)) surfaces. The (1\(\times\)1) 3F termination consists of very strong Lewis acid sites, however it is only thermodynamically stable when its Lewis acid sites are saturated by HF or H\(_2\)O. This suggests that to obtain catalytically active AlF\(_3\) it is necessary to desorb these molecules at a temperature below that at which the surface reconstructs to form the inactive (\(\sqrt{2} \times \sqrt{2}\)) phase. The sol-gel process used to obtain catalytically active HS-AlF\(_3\) satisfies this condition [8,101].

The strength of Lewis acid sites on clean and hydroxylated AlF\(_3\) surfaces were characterised from calculations of the frequency shifts of CO upon adsorption. This study supported the results obtained from calculations of NH\(_3\) adsorption; the strongest Lewis acid sites consist of Al ions bound to five bidentate F ions. We have shown that partial hydroxylation of the surface significantly weakens the Lewis acidity of the under-coordinated Al ions. The strength of the strongest type of Al site is reduced to the strength of the majority of sites found on crystalline \( \alpha \)- and \( \beta \)-AlF\(_3\) surfaces.

Analysis of the adsorption of NH\(_3\) and CCl\(_2\)F\(_2\) to the surfaces of AlF\(_3\) reveals that the
binding energy is predominately due to the interaction of the molecules with the large electrostatic potential above the under-coordinated Al ions. Lewis acidity is commonly associated with the donation of electrons from the base to the acid. This result shows that for AlF$_3$ this is not an accurate description of the interaction.

Our detailed understanding of AlF$_3$ surfaces finally enabled us to suggest the mechanism by which the dismutation of CCl$_2$F$_2$ occurs on $\beta$-AlF$_3$. The mechanism that we propose is a two step process; the first step involves the fluorination of a CCl$_2$F$_2$ molecule and a chlorination of the AlF$_3$ surface. The second step involves the chlorination of a CCl$_2$F$_2$ molecule and a fluorination of the surface.

Overall the project has made significant progress towards development of a new conceptual framework for understanding the chemical reactivity of high surface area AlF$_3$ structures. This conceptual framework will underpin efforts to design better AlF$_3$ based catalysts. The project also provides a firm basis for the investigation of a wide variety of other ionic catalysts.
Bibliography


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