Reactivity of the $\beta$-AlF$_3$(100) Surface: Defects, Fluorine Mobility and Catalysis of the CCl$_2$F$_2$ Dismutation Reaction

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Abstract

Hybrid exchange density functional theory is used to model defects on the $\beta$-AlF$_3$ (100) surface. The stability of the surface with respect to the diffusion of surface F ions is investigated. It is shown that under typical reaction conditions (600 K) the surface is not kinetically hindered from reaching thermodynamic equilibrium. A reaction mechanism for the catalysis of $2\text{CCl}_2\text{F}_2 \rightarrow \text{CCIF}_3 + \text{CCl}_3\text{F}$ is proposed. The mechanism and corresponding reaction barriers are calculated using a double-ended transition state search method. It is predicted that the processes that determine the overall reaction rate occur at defect sites.
I. INTRODUCTION

There has been much recent interest in the use of aluminium fluoride ($\text{AlF}_3$) as a strong Lewis acid catalyst. High surface area (HS) $\text{AlF}_3$ can now be prepared with a Lewis acidity comparable to those of the widely used Swarts catalysts based on antimony pentafluoride.$^{[12]}$ Such a material is of interest as strong Lewis acid catalysts are used in the large scale production of chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs)$^{[3-6]}$ for a wide range of applications including aerosol propellants, refrigerants and solvents.

The various crystalline forms of $\text{AlF}_3$ consist of arrangements of corner sharing $\text{AlF}_6$ octahedra.$^{[7-9]}$ The thermodynamically stable phase is $\alpha$-$\text{AlF}_3$. The surfaces of $\alpha$-$\text{AlF}_3$ are known to be less catalytically active than the surfaces of the $\beta$ phase, which show moderate catalytic activity, and the amorphous HS materials, which show high catalytic activity.$^{[10]}$ Many experimental studies have been performed to investigate the structure and chemical properties of $\text{AlF}_3$, including solid state NMR$^{[11-13]}$, powder X-ray diffraction$^{[11,12,14-18]}$, infrared spectroscopy$^{[17-19]}$, X-ray photoelectron spectroscopy$^{[11,19,20]}$ and temperature programmed desorption$^{[21]}$. The majority of traditional surface science techniques for determining surface structure require large, pure, crystalline samples. Producing suitable $\text{AlF}_3$ crystals is very difficult. There is, consequently, very little information available on the detailed atomic-scale surface structure of these fluorides.

Ab initio modelling has recently been used to predict the structures and properties of crystalline $\text{AlF}_3$ surfaces.$^{[22,23]}$ It was shown that $\text{AlF}_3$ surfaces are stoichiometric as $\text{AlF}_3$ is a highly ionic material and under typical conditions the Al and F ions remain strictly $\text{Al}^{3+}$ and $\text{F}^{-}$. Under-coordinated Al ions are, therefore, always exposed at the surface. The under-coordinated surface Al ions on $\text{AlF}_3$ are, similarly, predicted to display Lewis acidity and may be responsible for the catalytic nature of $\text{AlF}_3$.$^{[23,24]}$ It has previously been shown that under-coordinated Al ions at the surface of $\eta$-$\text{Al}_2\text{O}_3$ lead to its Lewis acidity.$^{[25]}$ A strong Lewis acid can be characterised by a large $\text{NH}_3$ binding energy and a large blue shift in the stretching frequency of adsorbed CO. The reactivities of under-coordinated Al ions on several $\text{AlF}_3$ surfaces have previously been characterised via the calculation of their $\text{NH}_3$ binding energies and CO stretching frequencies.$^{[21,26]}$ While all sites display at least moderate Lewis acidity, the sites displaying the strongest Lewis acidity consist of under-coordinated Al ions bound to five bidentate F ions.$^{[21,26]}$ It is predicted that such sites will not be exposed
FIG. 1: A side view (left) and a plan view (right) of the β-AlF₃ (100) termination. The Al ions are represented by small spheres and the F ions by large spheres. The rows of surface Al ions run from top to bottom in the plan view (right).

on α-AlF₃. They are, however, predicted to occur on the β-AlF₃ (100) surface which is thought to be exposed in small quantities on β-AlF₃ crystallites.

The β-AlF₃ (100) surface, shown in figure 1, contains two inequivalent rows of ions in which alternate Al ions are under-coordinated. The uppermost row is labelled row A while the lower row is labelled row B. The surface Al ions are all coordinated to five bidentate F ions, and in addition, every alternate Al ion is also coordinated to a monodentate F ion. It is energetically favourable for monodentate F ions to cap every alternate Al ion, as in this way the structure maintains a stoichiometric surface while minimising the electrostatic repulsion between the F ions.

At finite temperatures, however, it is likely that the monodentate F ions are able to diffuse across the surface from one Al ion to another. Assuming a surface consisting of evenly distributed F ions, the movement of one F ion from above one surface Al ion to an adjacent, previously under-coordinated, Al ion will result in two F ions adjacent to one another and two under-coordinated Al ions adjacent to one another. These groupings of monodentate F ions and under-coordinated Al ions can be considered to be defect sites.

β-AlF₃ is known to catalyse several halide exchange reactions. One of the simplest is the
dismutation of CCl₂F₂:

\[ 2\text{CCl}_2\text{F}_2 \longrightarrow \text{CCl}_3\text{F} + \text{CClF}_3. \] (1)

Although this and similar reactions are widely used to characterise the catalytic properties of AlF₃ surfaces, the kinetics and mechanisms of these processes are poorly understood. The reaction given in equation (1) proceeds on many alumina and chromia based surfaces. It is known that these surfaces do not just offer adsorption sites for the reactants, but that they are also directly involved in halogenating the reacting CCl₂F₂ molecules. The reaction has been shown to proceed in a non-concerted manner. That is, a sequence of fluorination and chlorination reactions occur at the catalyst surface.

It has previously been shown that HCl can dissociate upon adsorption at the surface of β-AlF₃ and that there is either no energy barrier or a very low energy barrier to the dissociation. It is proposed here that CCl₂F₂ dismutation initially involves dissociation of the molecule upon adsorption. Unlike the dissociation of HCl upon adsorption though, it is expected that there is a significant energy barrier associated with the dissociation of CCl₂F₂ as, in contrast to HCl, CCl₂F₂ is not strongly polar. If the barrier is not insurmountable at elevated temperatures, then it is hypothesised that the dismutation reaction proceeds via a two step process, shown diagrammatically in figure 2. The first step involves the adsorption of a CCl₂F₂ molecule via its Cl atom to an under-coordinated Al ion on the surface. Subsequently, the C-Cl bond dissociates and a new C-F bond with a nearby surface F ion is formed. The newly formed CClF₃ molecule then desorbs, leaving a Cl ion at the surface. The second step of the dismutation reaction involves the adsorption of a second CCl₂F₂ molecule, this time via its F atom. The C-F bond dissociates and a bond is then formed between the C and a previously deposited Cl ion to form a CCl₃F molecule, which can then desorb from the surface. This two step reaction mechanism can be written as

\[ \text{CCl}_2\text{F}_2 + \text{F}_{\text{surf}} \longrightarrow \text{CClF}_3 + \text{Cl}_{\text{surf}} \quad \text{(step 1)} \]  

\[ \text{CCl}_2\text{F}_2 + \text{Cl}_{\text{surf}} \longrightarrow \text{CCl}_3\text{F} + \text{F}_{\text{surf}} \quad \text{(step 2)}. \] (2)

In this paper the β-AlF₃ surface is studied, and defect sites consisting of adjacent under-coordinated Al ions are modelled. These models are used to estimate the concentration of the defect sites at the β-AlF₃ (100) surface. The mobility of the monodentate F ions is studied from calculations of the transition barriers associated with their movement. The
dismutation of CCl$_2$F$_2$, at the $\beta$-AlF$_3$ (100) surface is investigated. The adsorption of CCl$_2$F$_2$ to this surface is initially considered and then the structures and energetics of the transition barriers are calculated for the reactions defined in equations 2 and 3. Reaction pathways and energetics are initially calculated on a defect free surface, and then the influence of two different modelled defect sites on step one of the reaction are considered. The energetics of the calculated pathways are analysed and transition state theory is used to make an estimate of the overall turnover of the dismutation reaction at the $\beta$-AlF$_3$ (100) surface.

II. METHODOLOGY

The density functional theory (DFT) calculations were performed using CRYSTAL and the B3LYP hybrid exchange functional. This functional has been shown to provide a reliable description of geometric and electronic structure and energetics in a wide range of materials. Polarised triple valence Gaussian basis sets were used throughout. Details of the basis sets can be found in the supplementary information. In CRYSTAL, the convergence of the real space summations of the Coulomb and the exchange contributions to the Hamiltonian matrix are controlled by five overlap criteria. The control of these approximations is described in detail elsewhere. The values used in this study are $10^{-8}$, $10^{-8}$, $10^{-8}$, $10^{-8}$ and $10^{-16}$. A shrinking factor of eight was used to define the Pack-Monkhurst
net for sampling in reciprocal space and an atom centred numerical sampling grid consisting of 75 radial points and 974 angular points in the region of chemical interest (referred to in CRYSTAL as an extra large grid) was used to calculate the matrix elements of the DFT potential. This set of tolerances converges the total energy to within \(10^{-4}\) eV per AlF\(_3\) formula unit.

Locally stable structure, whose energies are of interest, were fully optimised using a conjugate gradient algorithm. The structures were considered to be converged when the residual absolute forces along all allowed symmetry directions were below \(1.0 \times 10^{-2}\) eV Å\(^{-1}\). Transition state structures were identified using the nudged elastic band (NEB) algorithm\(^{40,41}\). This algorithm has only recently been implemented in CRYSTAL^42 and the current work represents the first instance of the implementation being used to calculate reaction pathways and barriers for surface catalysed reactions. Transition structures were considered converged when the residual absolute forces along all allowed symmetry directions were below \(2.6 \times 10^{-2}\) eV Å\(^{-1}\). The computational cost of converging to a transition state using the NEB algorithm is very high; consequently, the tolerances used in our CRYSTAL calculations and the thicknesses of our slabs were reduced for these calculations. The values of the five overlap criteria were reduced to \(10^{-6}\), \(10^{-6}\), \(10^{-6}\), \(10^{-6}\) and \(10^{-12}\), a shrinking factor of two was used to define the Pack-Monkhorst net and an atom centred numerical grid consisting of 75 radial points and 434 angular points (referred to in CRYSTAL as a large grid) was used. The slab thicknesses (defined as the vertical distance between the Al ions on row A of the slab) were reduced from 13.8 Å (26 Al ions per \((1\times1)\) slab) to a distance of 10.2 Å (20 Al ions per \((1\times1)\) slab). The effects of these approximations are well controlled and are discussed in section III B.

The structure of the low energy \(\beta\)-AlF\(_3\) \((100)\) \((1\times1)\) termination was obtained from a previous computational study\(^22\) and is shown in figure 1. The surface contains four Al sites, (two on row A and two on row B) and two monodentate F ions (one on each row) per \((1\times1)\) unit cell. This \((1\times1)\) cell can be represented by \([ \bullet\circ ]\), where the two rows of circles represent rows A and B. The filled circles represent surface F ions above Al ions while the unfilled circles represent under-coordinated Al ions. To obtain accurate energies for the formation of particular defects, calculations must be performed within cells large enough to contain a given defect and a buffer zone in which the F ions are arranged in their thermodynamic equilibrium positions. This removes the effects of defect-defect interactions.
Defects consisting of two adjacent F ions along row A can be calculated within a (5×1) cell. This cell contains two such defects and can be represented by [•◦••••◦•••••◦•◦•◦•◦•◦••]. It is not possible to model a single defect of this type without introducing a second defect due to the periodicity of the system. A similar calculation was performed to calculate the energy associated with two adjacent F ions along row B. To predict the number of double defects, that is the formation of three adjacent F ions on one row and three adjacent under-coordinated Al ions on the other row, surface energies within a (3×1) cell, [◦••◦•◦•◦•◦], were calculated.

The ratio of the number of defect sites (consisting of two or three adjacent F ions) to the total number of monodentate F ions at thermodynamic equilibrium is

\[
\frac{n}{N} = \sum_i \exp\left(\frac{-\Delta E_i}{kT}\right),
\]

where \(n\) and \(N\) are the total number of defect sites and monodentate F ions respectively, \(k\) is the Boltzmann constant, \(T\) is the absolute temperature and \(\Delta E_i\) is the energy difference between the ground state surface and the surface containing a defect of type \(i\). In order to predict the number of defects to an accuracy of 50% at 600 K, the defect energy must be calculated to within an accuracy of 0.02 eV per defect.

The transition state structures and energy barriers for the diffusion of F ions between neighbouring Al ions were calculated using the NEB algorithm. The F ions can either move along the rows in the crystallographic <001> direction or perpendicular to the rows in the <010> direction. Two different mechanisms for the diffusion of F ions were considered. The first mechanism, denoted here as ‘direct’, involves an F ion moving directly from one Al ion to another. The second mechanism, labelled ‘indirect’, involves the concerted motion of two F ions: A monodentate F ion displaces an F ion that is bound between the two adjacent Al ions and then the displaced F ion becomes a monodentate F ion above the second Al ion. The direct mechanism is shown on the left hand side of figures 3 and 4 and the indirect mechanism is shown on the right hand side of these two figures.

Binding energies were calculated for the adsorption of CCl₂F₂ to under-coordinated Al ions on the β-AlF₃ (100) (1×1) surface. Adsorption via both a Cl and an F were considered. In addition adsorption at several different orientations about the molecule’s axis perpendicular to the surface was considered. Calculations were also performed within (2×1) cells to enable an estimate of the binding energies at low coverages. The calculated binding energies (a negative value denotes binding between the surface and molecule) were corrected for basis
set superposition error (BSSE) using the counterpoise scheme\textsuperscript{33}. As the absolute binding energies are relatively small, the corrections for BSSE are significant. The binding energies are quoted before and after BSSE correction and the accuracy of these calculations is discussed in section III C. Transition state structures and energy barriers were calculated using the NEB algorithm for several different end point configurations for the reactions described by equations 2 and 3. BSSE corrections were not been applied to transition state energy barriers because, to a reasonable approximation, the BSSE correction of the initial state and the BSSE correction of the transition state will cancel one another.

III. RESULTS AND DISCUSSION

A. Stable Structures

The calculated defect energies are given in table I along with the predicted ratio of the number of defects to the total number of surface F ions at 300 K and 600 K. The predominant defect consists of two adjacent F ions on row A and two adjacent under-coordinated Al ions on row B \[•••\]. (Note: This diagram represents the local environment of the defect, rather than the (5\times1) cell that was used to calculate the energy of the defect.) The preference for adjacent F ions on row A as opposed to row B may be due to the distorted environment around the Al ions along row A; two of the F ions that neighbour these Al ions are part of a constrained Al-F-Al-F ring (see figure 1). In our previous study\textsuperscript{44} of NH\textsubscript{3} adsorption to this surface we showed that NH\textsubscript{3} binds to Al ions on row A with a binding energy of around -2.0 eV compared to -1.9 eV for Al ions on row B. Analysis of the results presented here suggests that, similarly, the Al ions on row A also bind monodentate F ions more strongly than the Al ions on row B.

B. Fluorine Mobility

As the calculation of reaction barriers is computationally expensive, the effect of using thinner slabs and lower numerical tolerances (as discussed in section II) on the computed reaction barriers was considered. The transition energy barriers for the direct diffusion of F ions from row A to row B, using different approximations, are shown in table II. The transition energy barrier is consistent to within 0.05 eV in all approximations.
TABLE I: The defect energies, relative to the defect free surface, associated with two or three adjacent F ions on either row A or row B. The ratio of the number of defect sites to the total number of surface F ions at 300 K and 600 K (calculated using equation 4) is also shown. The diagrams in the first column of the table represent the local environment of the defects, rather than the cells that were used to calculate the defect energies.

<table>
<thead>
<tr>
<th>Description of defect</th>
<th>Defect energy $\Delta E_i$ (eV)</th>
<th>Ratio of (no. of defects):(no. of surface F ions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 adjacent F ions on row A <img src="%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F" alt="●●●●" /></td>
<td>0.13</td>
<td>1:150 (300 K)</td>
</tr>
<tr>
<td>2 adjacent F ions on row B <img src="%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F" alt="●●●●" /></td>
<td>0.38</td>
<td>1:2,400,000 (300 K)</td>
</tr>
<tr>
<td>3 adjacent F ions on row A <img src="%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F" alt="●●●●●●" /></td>
<td>0.38</td>
<td>1:2,400,000 (300 K)</td>
</tr>
<tr>
<td>3 adjacent F ions on row B <img src="%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F%E2%97%8F" alt="●●●●●●" /></td>
<td>0.88</td>
<td>1:6.2×10^{14} (300 K)</td>
</tr>
</tbody>
</table>

TABLE II: Transition state and final state energies, relative to the initial structure, calculated using different slab thicknesses and different levels of numerical accuracy for the direct movement of an F ion from row A to row B on the $\beta$-AlF$_3$ (100) surface.

<table>
<thead>
<tr>
<th>No. of Al ions in slab</th>
<th>Numerical accuracy</th>
<th>Relative transition energy (eV)</th>
<th>Relative final energy, $\Delta E$ (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>

state energies have, therefore, been calculated using thin slabs and lower numerical accuracy in all subsequent NEB calculations.

Approximate minimum energy pathways were calculated for the direct and indirect movement of F ions along the <010> and <001> directions within a (1×1) cell. The transition state energies, relative to the defect free surface, are given in tables III and IV 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 it is energetically favourable for the F ions to move directly from one site to another, while in
TABLE III: The transition state 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 $F_{\text{dif}}$. The subscript on the $Al$ denotes the coordination of the $Al$ ion. The subscript on the $F$ in the first column of the table denotes the row that the $F$ ion is initially on.

<table>
<thead>
<tr>
<th>F ion of diffusion</th>
<th>Energy barrier, $\Delta E^\dagger$ (eV)</th>
<th>Rate constant ($s^{-1}$)</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
<td>600 K</td>
<td>$Al_6$–$Al_5$</td>
</tr>
<tr>
<td>$F_A$ $&lt;010&gt;$</td>
<td>2.15</td>
<td>$5 \times 10^{-24}$</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>$F_B$ $&lt;010&gt;$</td>
<td>1.11</td>
<td>$2 \times 10^{-6}$</td>
<td>$5 \times 10^{3}$</td>
</tr>
<tr>
<td>$F_A$ $&lt;001&gt;$</td>
<td>1.33</td>
<td>$5 \times 10^{-10}$</td>
<td>$7 \times 10^{1}$</td>
</tr>
<tr>
<td>$F_B$ $&lt;001&gt;$</td>
<td>1.22</td>
<td>$3 \times 10^{-8}$</td>
<td>$6 \times 10^{2}$</td>
</tr>
</tbody>
</table>

TABLE IV: The transition state structures and energetics for the indirect pathway. The subscript on the $Al$ denotes the coordination of the $Al$ ion. The subscript on the $F$ in the first column of the table denotes the row that the $F$ ion is initially on.

<table>
<thead>
<tr>
<th>F ion of diffusion</th>
<th>Energy barrier, $\Delta E^\dagger$ (eV)</th>
<th>Rate constant ($s^{-1}$)</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
<td>600 K</td>
<td>$Al_6$–$Al_5$</td>
</tr>
<tr>
<td>$F_A$ $&lt;010&gt;$</td>
<td>1.39</td>
<td>$4 \times 10^{-11}$</td>
<td>$2 \times 10^{1}$</td>
</tr>
<tr>
<td>$F_B$ $&lt;010&gt;$</td>
<td>1.33</td>
<td>$5 \times 10^{-10}$</td>
<td>$7 \times 10^{1}$</td>
</tr>
<tr>
<td>$F_A$ $&lt;001&gt;$</td>
<td>1.00</td>
<td>$2 \times 10^{-4}$</td>
<td>$4 \times 10^{4}$</td>
</tr>
<tr>
<td>$F_B$ $&lt;001&gt;$</td>
<td>1.35</td>
<td>$2 \times 10^{-10}$</td>
<td>$5 \times 10^{1}$</td>
</tr>
</tbody>
</table>

the remaining cases it is favourable for the diffusion to occur 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 3 and structures for the movement of $F$ ions from row $A$ to row $B$ are shown in figure 4.

The transition state structures for the direct pathways (left hand side of figures 3 and 4) consist of distorted four member (-$Al$-$F$-$Al$-$F$-) rings. The energy barriers vary considerably for diffusion along the $<010>$ direction, depending on whether the $F$ ions are moving from
FIG. 3: 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. The structures shown between the end points and transition states represent geometries along the minimum energy pathway. The Al ions are represented by small spheres and the F ions by large spheres.

row A to row B or from row B to row A. This asymmetry is related to the different geometry of the two sites. The vertical distance between the fully-coordinated Al ion in row A and the under-coordinated Al ion in row B is 1.6 Å compared with 0.8 Å between the fully-coordinated Al ion in row B and the under-coordinated Al in row A; consequently, it is easier for an F ion to move from row B to row A than to move from row A to row B.

The transition state structures for the indirect pathways (right hand side of figures 3 and 4) consist of two under-coordinated Al ions each bound to four bidentate F ions and a
FIG. 4: 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. The structures shown between the end points and transition states represent geometries along the minimum energy pathway. The Al ions are represented by small spheres and the F ions by large spheres.

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 state structures and energetics are generally very similar for each of the different indirect reaction pathways. The exception is that the transition state energy for movement along row A is significantly lower (1.0 eV). Analysis of this transition state structure suggests that it differs from other
transition state structures 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.

The rate constants, $k_i$, for the diffusion of F ions were estimated using harmonic transition state theory,

$$k_i = f \frac{kT}{h} \exp \left( -\frac{\Delta E_i^\dagger}{kT} \right)$$

where $\Delta E_i^\dagger$ is the transition state energy barrier. $f$ is the ratio of the vibrational partition functions of the transition and initial states, where the quantity for the transition state does not include the reactive mode. This value is approximated to unity, as to a first approximation, the partition functions of the initial and transition states are of the same order of magnitude, hence the ratio of the two is close to one. The reaction rates vary linearly with this factor, compared with exponentially with the energy barrier, hence, this is an appropriate approximation. The resulting rate constants at 300 K and 600 K for each of the pathways are given in tables III and IV. At 300 K the surface F ions are predicted to be effectively immobile. At 600 K, however, the F ions are predicted to move rapidly: On a scale of several hops every ms for F ions diffusing from row A to row B. It is, therefore, predicted that at 600 K the kinetic barriers associated with the diffusion processes will not hinder the surface from achieving its thermodynamically stable phase.

C. Molecular Adsorption of CCl$_2$F$_2$

Various geometries for the adsorption of CCl$_2$F$_2$ on the (defect free) $\beta$-AlF$_3$ (100) surface were considered. These include adsorption via the molecule’s F or Cl atoms to Al ions on either row A or row B of the surface. The CCl$_2$F$_2$ molecules were adsorbed in a number of different orientations about the Al-(Cl,F)-C axis and the largest binding energies, as a function of orientation, are shown in table V. Structures consisting of CCl$_2$F$_2$ adsorbed F down and Cl down on row A are shown in figure 5. In the case of adsorption via the Cl atom a second adsorption geometry, in which the molecule is rotated by approximately 180° about the axis perpendicular to the surface, is also shown (figure 5c). This geometry is used in section III D as the starting point for the NEB pathway that involves the formation of CClF$_3$ on row B as the C atom is significantly closer to the F ion on row B compared to the
TABLE V: 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) (1×1) surface.

<table>
<thead>
<tr>
<th>Adsorption ion</th>
<th>Site of adsorption</th>
<th>No BSSE correction</th>
<th>With BSSE correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>row A</td>
<td>-0.19</td>
<td>-0.08</td>
</tr>
<tr>
<td>F</td>
<td>row B</td>
<td>-0.18</td>
<td>-0.08</td>
</tr>
<tr>
<td>Cl</td>
<td>row A</td>
<td>-0.13</td>
<td>-0.03</td>
</tr>
<tr>
<td>Cl</td>
<td>row B</td>
<td>-0.14</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

FIG. 5: Adsorption of CCl$_2$F$_2$ on row A of the β-AlF$_3$(100) surface. (a) Adsorption via an F atom. (b) and (c) Adsorption via a Cl atom. The displayed binding energies have not been corrected for BSSE.

structure shown in figure 5b.

The adsorption energies are relatively small: For comparison NH$_3$ binds with a binding energy of up to -2.0 eV. We have previously shown that the binding energy of molecules to the surface is dominated by electrostatic interactions. Analysis of the Mulliken population of isolated molecules shows that the halide atoms of CCl$_2$F$_2$ are much less negatively charged than the N atom in NH$_3$, this may explain why CCl$_2$F$_2$ only binds weakly to the surface. In addition, there is electrostatic repulsion between the neighbouring surface F ions and the CCl$_2$F$_2$ molecules and also inter-molecular repulsion between neighbouring CCl$_2$F$_2$.
molecules, both of which reduce the magnitude of the binding energy.

To estimate the effect of the repulsion between CCl$_2$F$_2$ molecules and F ions, the adsorption of CCl$_2$F$_2$ on row A when all of the monodentate F ions were on row B was calculated as the distances between the CCl$_2$F$_2$ and monodentate F ions are increased in this geometry. The molecule was found to bind significantly more strongly than when the monodentate F ions were distributed between both rows. The resulting binding energy was around 0.2 eV stronger ( -0.38 eV or -0.25 eV after correction for BSSE). To estimate the repulsion between neighbouring CCl$_2$F$_2$ molecules, calculations were performed at a quarter monolayer coverage in a (2×1) cell. It was found that CCl$_2$F$_2$ binds more strongly, by around 0.04 eV, when the coverage was decreased from a half monolayer to a quarter monolayer (The minimum distance between neighbouring CCl$_2$F$_2$ molecules is increased from 5.3 Å to 9.3 Å.).

The correction for BSSE to the binding energies is approximately 0.1 eV, although this is a typical correction for BSSE, it is a large proportion of the total calculated binding energies. This implies that the geometries are unlikely to be fully optimised to their BSSE corrected minimum energy structures. Furthermore, as the counterpoise scheme yields an upper bound on the magnitude of the BSSE, the BSSE corrected energies are likely to be less negative than the true binding energies. It is, therefore, reasonable to assume that the binding energies lie between the BSSE corrected and uncorrected values presented.

To obtain estimates of the binding energies of CCl$_2$F$_2$ to under-coordinated Al ions on the (defect free) β-AlF$_3$ (100) surface at low coverages, the following approximations have been made in the light of the preceding discussions. The average binding energy, at half monolayer coverage, before and after corrections for BSSE has been used. The overall binding energy is extrapolated to the dilute limit by reducing its magnitude by 0.05 eV to account for intermolecular repulsion. The repulsion between a CCl$_2$F$_2$ molecule and an adjacent monodentate F ions is estimated to be 0.1 eV. At defect sites, when the molecule is adsorbed to an under-coordinated Al ion that has either one or no neighbouring F ions (as opposed to two on the defect free surface), the binding energy is, therefore, increased in magnitude by 0.1 eV per missing F ion. Applying these approximations, the computed binding energy is -0.15 eV, -0.25 eV and -0.35 eV for a CCl$_2$F$_2$ adsorbed via its Cl atom when it is neighbouring two, one and zero F ions respectively. Similarly, the binding energy is -0.20, -0.30 or -0.40 eV when the molecule is bound via its F atom, depending on the
number of neighbouring F ions. Given the approximations made here, the resultant binding energies have been quoted to the nearest 0.05 eV.

D. Reaction mechanisms and barriers

Minimum energy paths and transition state energy barriers were calculated for movement of the CFC molecule along row A, along row B and between the rows on the defect free $\beta$-AlF$_3$ (100) surface for both steps of the reaction (defined by equations 2 and 3). The results from these calculations are summarised in tables VI and VII. The lowest transition state barriers for each step of the reaction occur when the molecule moves between rows.

The lowest energy pathways found for the first and second steps of the reaction are shown in figures 6 and 7 respectively. The first step involves the adsorption of a CCl$_2$F$_2$ molecule to row A (figure 5c) followed by the cleavage of the C-Cl bond and the formation of a CClF$_3$ molecule adsorbed on row B. The transition state barrier associated with this mechanism is 1.48 eV. The pathway for the second step involves the adsorption of a CCl$_2$F$_2$ molecule to an Al on row A of a partially chlorinated surface and the subsequent formation of a CCl$_3$F molecule on row B. The transition state barrier associated with this mechanism is appreciably lower, at 0.89 eV. There are many similarities between the transition state structures of both of these reactions, although the distribution of the surface F and Cl ions differs between the two structures: The surface F ions are distributed amongst the rows for the first step of the reaction but are all on row A for the second step. This suggests that the energy barriers may depend on the initial positions of the surface F and Cl ions.

The reaction pathways for the formation of a CClF$_3$ molecule on row A (step 1) were calculated after adsorption of a CCl$_2$F$_2$ molecule at defect sites that consisted of either two or three adjacent under-coordinated Al ions on row B ([••○••••] and [••○••••••]). In section III A the structures and energies of these defects where calculated within (3×1) and (5×1) cells, respectively. It is, currently, prohibitively expensive to run NEB calculations on such large cells. The defect consisting of two adjacent Al ions was, therefore, modelled within a (2×1) cell [•••••]. In this cell the CCl$_2$F$_2$ is adsorbed to an Al ion that neighbours one under-coordinated Al ion and one fully-coordinated Al ion. The transition state energy barrier for this reaction was calculated to be 1.22 eV. The defect consisting of three adjacent under-coordinated Al ions was modelled within a (1×1) cell where all the F ions were adsorbed to
TABLE VI: The computed energetics and geometries of the transition states for the reaction $\text{CCl}_2\text{F}_2 + \text{F}_{\text{surf}} \rightarrow \text{CCIF}_3 + \text{Cl}_{\text{surf}}$ on the defect free $\beta$-$\text{AlF}_3$ (100) surface.

<table>
<thead>
<tr>
<th>CCl$_2$F$_2$ adsorption site</th>
<th>CCIF$_3$ adsorption site</th>
<th>Energy barrier, $\Delta E^\ddagger$ (eV)</th>
<th>Al–Cl (Å)</th>
<th>Al–F (Å)</th>
<th>C–Cl (Å)</th>
<th>C–F (Å)</th>
<th>F–C–Cl (degrees)</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>
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<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 VII: The computed energetics and geometries of the transition states for the reaction $\text{CCl}_2\text{F}_2 + \text{Cl}_{\text{surf}} \rightarrow \text{CCl}_3\text{F} + \text{F}_{\text{surf}}$ on the defect free $\beta$-$\text{AlF}_3$ (100) surface.

<table>
<thead>
<tr>
<th>CCl$_2$F$_2$ adsorption site</th>
<th>CCl$_3$F adsorption site</th>
<th>Energy barrier, $\Delta E^\ddagger$ (eV)</th>
<th>Al–Cl (Å)</th>
<th>Al–F (Å)</th>
<th>C–Cl (Å)</th>
<th>C–F (Å)</th>
<th>F–C–Cl (degrees)</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>
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<tr>
<td>row B</td>
<td>row B</td>
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<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>

row A. The transition state energy barrier for this reaction was calculated to be 1.04 eV. In the following section the energy barriers, the number of defect sites and the binding energies of the adsorbed molecules are used to predict the kinetics of the overall reaction.

E. Analysing the Reaction Kinetics

The small binding energies associated with adsorption of CCl$_2$F$_2$ imply that the overall coverage of the surface will be very low under typical reaction conditions (i.e. at temperatures of around 600 K). In equilibrium the chemical potential of a gas phase CCl$_2$F$_2$ molecule and an adsorbed CCl$_2$F$_2$ molecule must be equal to one another:\textsuperscript{45}

$$\mu_{\text{gas}} = \mu_{\text{ads}}.$$  \hfill (6)
The lowest energy pathway for the reaction $\text{CCl}_2\text{F}_2 + \text{F}_{\text{surf}} \rightarrow \text{CClF}_3 + \text{Cl}_{\text{surf}}$ (equation 2) on the defect free $\beta$-AlF$_3$ (100) (1×1) surface. The reaction coordinate is the cumulative minimised distance between images along the pathway.

The chemical potential of an adsorbed molecule is given by

$$\mu_{\text{ads}} = kT \ln \left[ \frac{\theta}{1 - \theta} \cdot \frac{1}{q} \right],$$  

where $\theta$ is the fraction of the surface sites that are covered by an adsorbed molecule. The single particle partition function, $q$, is given by

$$q = \exp \left( \frac{-E_{\text{ads}}}{kT} \right) \cdot q_{\text{vib}},$$  

where $q_{\text{vib}}$ is the vibrational partition function of the adsorbed molecule. The chemical potential of an ideal gas is given by

$$\mu_{\text{ideal gas}} = -kT \ln \left[ \left( \frac{2\pi m_i kT}{\hbar^2} \right)^{\frac{3}{2}} \frac{kT}{p_i} \right],$$
FIG. 7: The lowest energy pathway for the reaction $CCl_2F_2 + Cl_{surf} \rightarrow CCl_3F + F_{surf}$ (equation 3) on the defect free $\beta$-AlF$_3$ (100) (1×1) surface. The reaction coordinate is the cumulative minimised distance between images along the pathway.

where $m_i$ is the mass of the gas molecule, $h$ is the Planck constant and $p_i$ is the partial pressure of the gas. The chemical potential of a gas such as CCl$_2$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. To a good approximation, therefore, the errors associated with setting the chemical potential of CCl$_2$F$_2$ to that of an ideal gas and $q_{vib}$ in equation 8 to unity will cancel, hence

$$
\mu_{CCl_2F_2} = kT \left[ \ln \frac{\theta}{1 - \theta} + \frac{E_{ads}}{kT} \right],
$$

(10)

and therefore,

$$
\frac{\theta}{1 - \theta} = \exp \left( \frac{\mu_{CCl_2F_2} - E_{ads}}{kT} \right),
$$

(11)
The binding energy of CCl$_2$F$_2$, at low coverages, to the defect free surface is around -0.15 eV for adsorption via a Cl atom (see section III C). Using equation 9, $\mu = -1.01$ eV at 600 K for CCl$_2$F$_2$ at standard pressure. It is, therefore, estimated that at 600 K approximately one in every $3 \times 10^7$ of the under-coordinated Al ions will be covered by a CCl$_2$F$_2$ molecule adsorbed via its Cl ion. Approximately 83% of the under-coordinated Al ions on this surface will be in a defect free region (1 in 6 [17%] of the monodentate F ions are involved in defects consisting of two adjacent monodentate F ions [table I]). Assuming a reaction barrier, $\Delta E^\ddagger$, of 1.48 eV and a value of one for the ratio between the transition and initial state vibrational partition functions, the reaction rate constant is 5 s$^{-1}$. The overall turnover is $(0.83 \times 5)/(3 \times 10^7) = 1 \times 10^{-7}$ s$^{-1}$ per Al site. The rate constant and associated data for this reaction pathway are summarised in table VII. Data for analogous reaction pathways at both defect sites (two and three adjacent under-coordinated Al ions) are also displayed as are data for the reaction pathway of step two of the reaction at a defect free surface. Step one of the reaction is predicted to occur predominately at defect sites on the surface of $\beta$-AlF$_3$(100).

When the surface and the reactants are in dynamic equilibrium the number of Cl ions on the surface remains constant, hence, the turnover rates of step one and step two of the reaction will be equal. The rate constant for the second step of the reaction is significantly greater than that of the first step, hence, the number of Cl ions present on the surface will be very small (as the turnover rate of step two is proportional to the amount of Cl present). The overall rate for the reaction, to a very good approximation, will be determined by the rate of step one of the reaction. Step one of the dismutation reaction is, therefore, the rate limiting step. It is possible that the turnover of the second step could be even greater at defect sites, but as this step is not rate limiting we have not investigated such possibilities.

Experimental data suggests that the turnover rate per Al site is much higher than that predicted from our calculations. In a recent experiment a micro-reactor was used to investigate the dismutation of CCl$_2$F$_2$ over a $\beta$-AlF$_3$ catalyst. The micro-reactor was filled with around 20 mg of the $\beta$-AlF$_3$ material and a gas consisting of a 3:1 ratio of He to CCl$_2$F$_2$ was passed through the micro-reactor at a rate of 100 cm$^3$ min$^{-1}$. The residence time of the gas through the reactor was around one second, during which time approximately 33% of the reactant underwent a dismutation reaction at 663 K. This corresponds to $1 \times 10^{18}$ CCl$_2$F$_2$ molecules undergoing the dismutation reaction per second. If it is assumed that the
TABLE VIII: The turnover rates and associated data for several reaction pathways at 600 K. The fractions of sites available are calculated from data in table I and the values for the CCl$_2$F$_2$ binding energies are discussed in section III C. The turnover for step two is calculated assuming that there is always a surface Cl ion available for the reaction.

<table>
<thead>
<tr>
<th>Description of pathway</th>
<th>Fraction of Sites</th>
<th>CCl$_2$F$_2$ binding energy (eV)</th>
<th>Fraction of sites covered</th>
<th>Energy barrier, $\Delta E^\ddagger$ (eV)</th>
<th>Rate constant, $k$ (s$^{-1}$)</th>
<th>Turnover (molecules s$^{-1}$ per Al site)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 (defect free)</td>
<td>0.83</td>
<td>-0.15</td>
<td>$3 \times 10^{-8}$</td>
<td>1.48</td>
<td>$5 \times 10^0$</td>
<td>$1 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
| Step 1 ([\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ld…
turnover is $2 \times 10^{-3}$ s$^{-1}$, which is still very low.

Calculating reaction rates from transition state theory is well known to be a very difficult problem, especially for large complex systems such as the one studied in this paper. Accurate determination of the potential energy surface is required. There may be many accessible pathways that contribute significantly to the overall rate constant. There are, also, a number of failings of transition state theory. The effects of quantum tunnelling are not included, although for high barriers this effect is very small. It does not include the effects of dynamical recrossings of the transition state, that is, it assumes that every barrier crossing event proceeds directly to the products, and hence the rate constant may be over-estimated.

In our work, there is a very large discrepancy between the experimental turnover and the turnover predicted from our proposed reaction pathway. These errors may be due to inaccurate representations of the potential energy surface and the failings of transition state theory. It has been shown in this paper, however, that relatively subtle differences in the local geometry of the AlF$_3$ surface can dramatically influence the energy barrier of a given reaction. For instance the transition state energy for the indirect diffusion of F ions was around 1.3 eV for three of the four pathways considered but 1.0 eV for the other pathway (section III B). Defect sites could contribute to, or even dominate, the overall reaction rate. For example, a fluorine vacancy in the first few layers of the surface could have a dramatic effect on the reactivity of a local catalytic Al site. It is, therefore, possible that the reaction could proceed via the reaction mechanism that we have proposed but at a defective site that we have not considered. The sensitivity of reaction rates to small changes in geometry could also explain why HS-AlF$_3$ shows significantly greater catalytic activity than $\beta$-AlF$_3$. HS-AlF$_3$ is thought to contain a significant number of Al ions in distorted environments; some of these sites may significantly reduce the energy barrier of a given reaction mechanism.

IV. CONCLUSIONS

In this paper the distribution of monodentate F ions on the $\beta$-AlF$_3$ (100) surface was calculated. The diffusion of these F ions across the surface was then considered. Adsorption of CCl$_2$F$_2$ to the $\beta$-AlF$_3$ surface was investigated and possible reaction pathways for the dismutation of $2\text{CCl}_2\text{F}_2 \rightarrow \text{CCIF}_3 + \text{CCl}_3\text{F}$ were calculated.
It was predicted that the majority of the monodentate F ions on the surface of $\beta$-AlF$_3$ (100) are evenly distributed. At 600 K, however, 17% of the F ions on the surface are predicted to be adjacent to another such F ion and around 0.06% will be adjacent to two such F ions. Over 99% of these groupings of F ions will be on row A of the surface.

Two competing mechanisms for the diffusion of F ions across the surface of $\beta$-AlF$_3$ were considered. It was shown that these mechanisms both have similar energetics and that the local environment determines which one provides the lowest energy barrier. Consequently, both types of mechanism are predicted to occur. It was demonstrated that, under typical reaction temperatures (600 K), the surface F ions are mobile, moving between Al ions on a timescale of several hops per ms. The surface will, therefore, be in thermodynamic equilibrium on the experimental timescale.

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) was proposed. This mechanism involves the participation of surface F ions and occurs via a two step process. Analysis of the reaction barriers suggests that this reaction could plausibly occur on the $\beta$-AlF$_3$ (100) at elevated temperatures, although not with the rate constants observed experimentally. The processes that contribute most significantly to the overall turnover are the reactions corresponding to equation 2 occurring at defect sites. This demonstrates the extent to which a small change to the local structure of the surface can dramatically increase the rate of a reaction. Due to the huge number of possible defects that could occur at a surface it is prohibitively expensive computationally to consider all such possibilities. The sensitivity of the reaction barrier to local geometric structure may, however, 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.

V. ACKNOWLEDGEMENTS

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