



# The pathway to reorientation in ammonium fluoride

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Received 25 January 2000

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## Abstract

Two alternative transition states for ammonium ion rotation in crystalline  $\text{NH}_4\text{F}$  have been characterised using ab initio calculations. In one all the cations rotate in phase, while in the other the rotating ions are isolated from each other by non-rotated ions. These two transition states are characterised by the cation displacement and changes in the bond lengths and bond angles within the ammonium ion. The pathway for passing over the barrier was investigated by low temperature molecular dynamics runs from each transition state. In both cases the order of events in passing from the ground state to the transition state is first cation displacement towards a neighbouring fluoride ion, secondly, lengthening of the NH bond pointing to this ion, and thirdly, rotation about this bond. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The reorientation of ammonium ions in the solid state is an essential ingredient in the numerous solid-solid phase transitions and other phenomena displayed by ammonium salts. It has been studied for many years by NMR, vibrational spectroscopy, thermodynamics and other techniques. In many salts such reorientations involve making and breaking of hydrogen bonds between the ammonium ion and the anion concerned so that studies of the ammonium ion reorientation are also relevant for understanding hydrogen-bonding.

Classical simulation techniques have been used to study such problems and have been moderately successful in explaining the mechanisms of various phase transitions. However they have generally assumed that the ammonium ion is rigid. It is well

known that NH bond lengths change on hydrogen-bonding, and so it is not surprising that the ion becomes distorted and polarised when it rotates.

In earlier work we studied the energetics of reorientation of ammonium ions in  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{F}$  [6,7] using ab initio calculations. In this Letter we extend our earlier work to include calculations of transition states in which the rotating ions are surrounded by non-rotated ammonium ions and we have studied the pathway for reorientation of  $\text{NH}_4\text{F}$  through these transition states.

## 2. Simulation details

The calculations have been performed using the same methods as in our previous work. We used the finite-electronic temperature method of Alavi et al. [1] (FEMD). In this method, a free energy functional is optimised, yielding at self-consistency the elec-

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tronic free energy. The method uses a density functional with BLYP gradient corrections [2,3]. Troullier–Martins [4] pseudopotentials in the Kleinman–Bylander form [5] were used with  $s$  non-locality for F and N. The present work differs slightly from our previous work in that new pseudopotentials were generated using the BLYP functional so that they were fully consistent with the gradient corrections used. The plane wave cut off was 90 Rydberg and a  $k$  point mesh was used with either  $4 \times 4 \times 2$  points for calculations with a single primitive unit cell or  $2 \times 2 \times 2$  for the quadrupled cell size.

The lattice structure of ammonium fluoride is hexagonal with two formula units per unit cell. In the ground state each ammonium ion is in a site with  $C_{3v}$  symmetry with three equivalent ‘equatorial’ NH bonds and one ‘axial’ one which is parallel to the crystallographic  $c$  axis. There are four neighbouring fluoride ions to which the four NH bonds can be said to hydrogen-bond. The next nearest neighbours are 12 ammonium ions. In the calculations with the ‘all’ rotated transition state a single crystallographic unit cell was used, while in the calculations with ‘1 in 8’ ions rotated the simulation cell used included  $2 \times 2 \times 1$  unit cells with 8 formula units. The purpose of the latter calculation was to get as near as possible to the rotation of a single ion in a sea of non-rotated ions; in this calculation all 12 nearest ammonium ions are not rotated.

The transition states were prepared from the ground state in two steps. First, either both ions in the unit cell or one ion in the extended system was rotated by  $60^\circ$  about the  $c$  axis so that the axial NH group remained hydrogen bonded to a fluoride ion, and secondly the structure was relaxed using the BFGS method subject to symmetry constraints until the energy was a minimum.

Molecular dynamics runs were then started from each of the two transition states with random velocities corresponding to a temperature of 15 K. The trajectories were analysed to determine the path to the ground state as explained in Section 4.

### 3. Structure of the transition states and barriers to reorientation.

Table 1 gives the energies and structural information for the two transition states compared with the

Table 1  
Structure and energetics of the transition states

State	Ground	Transition (all)	Transition (1 in 8)
energy/kJ mol <sup>-1</sup>	0	66.3	62.7
distances/Å:			
NH(ax)	1.0472	1.13	1.07
NH(eq)	1.0475	1.02	1.02
NF(ax)	2.698	2.50	2.60
angles/deg:			
ax-N-eq	109.14	111.69	107.16
eq-N-eq	109.82	107.16	108.3

ground state. It is striking that the barriers to reorientation (when expressed as a energy per reorienting molecule) are about 65 kJ/mol, with the barrier to rotating an isolated ion being about 3.6 kJ/mol lower than that for rotating all ions. We note that both the structure and energies reported here differ slightly from those in our previous work [7] using a different pseudopotential. This suggests that there is an uncertainty of  $\pm 3$  kJ/mol in the energies, although we believe that the relative energies of the two transition states are correct.

We showed in our earlier work that the ammonium ions are distorted in the transition state and that the distortion is greatest when all the ions are rotated as opposed to when half are rotated. The results from the ‘1 in 8’ transition state follow this trend. The figures in Table 1 show that the displacement of the ammonium ion towards the axial fluoride is about 0.1 Å instead of 0.2 Å and that the lengthening of the axial NH bond is considerably less than before. It is clear that the environment of the axial fluoride ion has a big effect on the strength of the interaction of the remaining hydrogen bond. If it has all four hydrogen bonds intact (as in the ‘1 in 8’ transition state) then the axial NH bond is less distorted than when the other three hydrogen bonds are broken. This effect was also seen in our earlier work [7] where the unrotated ion whose the axial fluoride had only 1 hydrogen bond in a ‘1 in 2’ transition state was displaced more than the rotated ion whose axial fluoride had four intact hydrogen bonds.

### 4. Pathway to reorientation

Fig. 1 shows the variation of energy with time for the two molecular dynamics runs started from the

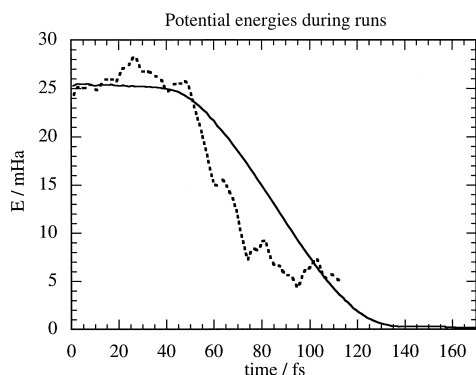


Fig. 1. Variation of energy per rotated molecule in the two molecular dynamics runs at 15 K. The solid line is for the run starting from the 'all rotated' transition state while the dashed line is for the '1 in 8' rotated transition state.

'all rotated' and '1 in 8' transition states relative to the ground state.

At first sight the difference in the energy fluctuations between the two curves may be surprising, but this is accounted for by the difference in the number of degrees of freedom. In the '1 in 8' run there are eight times as many degrees of freedom as in the 'all' run and the thermal kinetic energies per rotating ion are 3.43 mHa and 0.42 mHa respectively. There is a similar difference in the thermal contribution to the potential energy which is shown clearly in the differences in the potential energies of the ground states in these calculations.

These runs were started with random velocities corresponding to a temperature of 15 K, and it is possible that they are not typical of the ensemble of trajectories passing through the transition states. Nevertheless it is instructive to follow the geometry changes during the runs in order to learn something of the pathway over the barrier. Fig. 2 shows various structural quantities as a function of the instantaneous potential energy relative to the ground state. In this figure the direction of the actual trajectories are from right to left as the ground state is on the left of the figure and the transition state on the right. Trajectories for the 'all rotated' transition state are shown by solid lines and those for the '1 in 8' transition state by dashed lines. The changes in the two runs follow each other quite closely.

In the upper part of the figure the distance between the nitrogen in the rotating ammonium ion

from the axial fluoride is plotted. Quite large changes in this distance can occur with small changes of energy near both the ground state (left of figure) and

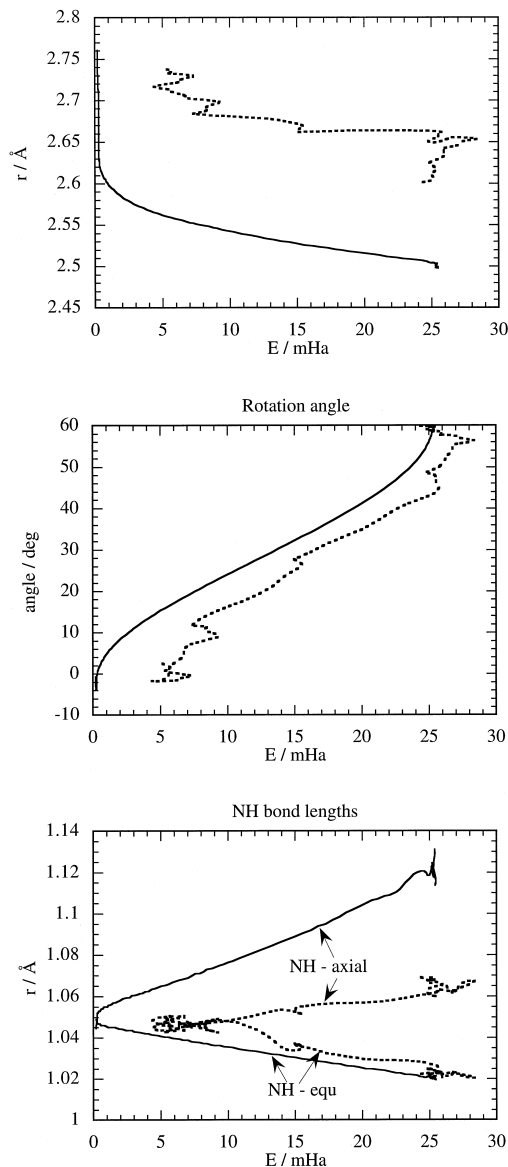


Fig. 2. Variation of structural parameters with energy during molecular dynamics runs. Above: The distance between the rotating ammonium ion and the axial fluoride; middle: the rotation angle; bottom: NH bond lengths. Results from the 'all rotated' transition state are shown by solid lines and those from the '1 in 8' rotated state are shown by the dashed line. Note that the left hand side of the figures corresponds to the ground state and the right hand side to the transition state.

the transition state (right hand side). This reflects the low frequency of the corresponding translational mode in both the ground state and in the transition state. The onset of rotation (middle part) is preceded by the displacement and followed by the changes in the bond lengths (lower part) and the umbrella angle (not shown).

The sequence of events leading to passage from the ground state over the barrier can be found from the data plotted in Fig. 3 for the ‘all’ transition state and Fig. 4 for the 1 in 8 transition state. From these we can follow the pathways for reorientation, which are similar in the two cases. Going from the ground state to the transition state, it is necessary to break the  $C_3$  site symmetry of the ammonium ion, for example through excitation of the relevant librational

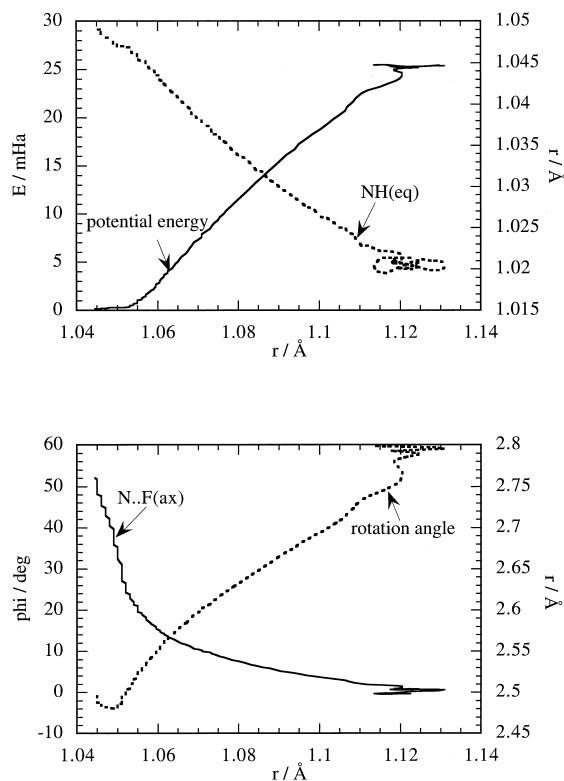


Fig. 3. Variation of energy and structural parameters during the molecular dynamics runs. Values of energy, NH equatorial bond length (above) and rotation angle and N-F distance (below) are plotted against the axial NH bond length which has been used as a reaction coordinate. In these figures the ground state is on the left and the transition state on the right.

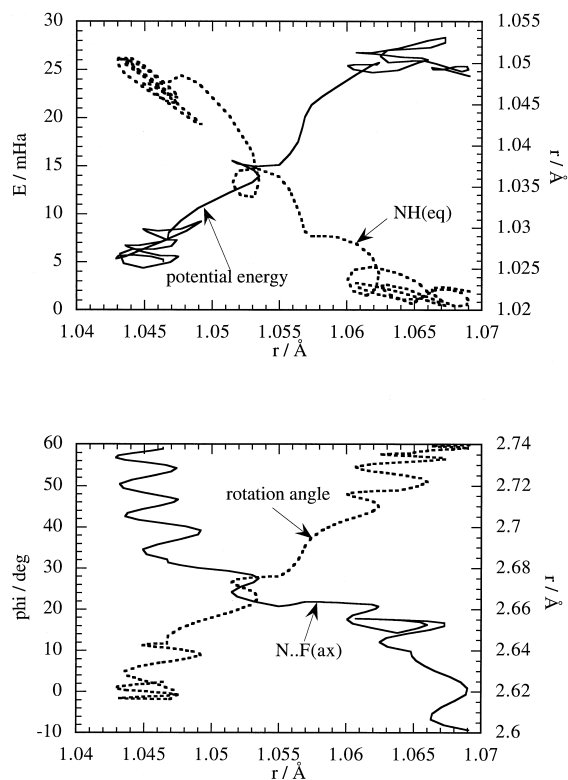


Fig. 4. As Fig. 3, but for reorientation via the ‘1 in 8’ transition state

mode. It is also necessary for the ammonium ion to move towards the axial fluoride and it appears that this is the initial step both for moving towards the barrier towards the transition state and for crossing the barrier. The relevant translational phonon has a low frequency and high amplitude and is surely anharmonic. In these figures we have used the length of the axial NH bond as a reaction coordinate. As the reaction starts (the ground state is on the left of these figures) the NF distance decreases rapidly as the ammonium ion moves towards the fluoride ion. When it has moved a significant distance and the NH bond has begun to stretch, the molecule starts to rotate and the potential energy rises.

In both cases the ammonium ion spends about 40 fs in the vicinity of the transition state before it finds the pathway to the ground state. This suggests that the barrier region is broad and rather flat. The trajectories shown take about one-third of a picosecond to traverse the barrier from one minimum to the next.

## 5. Conclusions

In this study we have shown that the pathway to reorientation involves the relative translation of the ammonium ion relative to the hydrogen-bonded fluoride, the rotation of the ion and changes in internal angles and bond lengths. In the trajectories examined the first step was a large excursion of the ammonium ion towards the fluoride ion which remains hydrogen-bonded, followed by the onset of rotation. Finally internal changes of bond lengths and bond angles within the ammonium follow.

## Acknowledgements

We acknowledge financial support from EPSRC (grants GR/K20651 and GR/L08427), the IFI (grant

to the Irish Centre for Colloids and Biomaterials), and the Natural Sciences and Engineering Research Council of Canada. The calculations were carried out at the Irish Supercomputer Centre.

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