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Displacement and distortion of the ammonium ion in rotational transition states in ammonium fluoride and ammonium chloride

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Ab initio density functional calculations have been carried out on ammonium fluoride to determine the equilibrium structure and the transition state for rotation of the ammonium ion. The calculated equilibrium geometry agrees satisfactorily with crystallographic data. Optimization of the crystal geometry in the transition state for rotation results in significant distortion and displacement of the ammonium ion within the unit cell. Upon reexamination of the rotational transition states in ammonium chloride, similar distortion and displacement of the ammonium ion are found. The rotation process is similar to a carousel motion, in which the ion moves along the rotation axis and changes shape as it rotates. These results show that rigid ion models for ammonium ion rotational dynamics in crystals are, at best, incomplete. © 1999 American Institute of Physics.
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I. INTRODUCTION

Ammonium halides exhibit rich phase diagrams with many solid–solid phase transitions. In all these phases the ammonium ions rotate at measurable rates, and some phases are orientationally disordered. Understanding the pathways and energetics of ammonium ion rotation in crystals is therefore a key step in understanding the phase transitions. The rotational motion of ammonium ions in crystalline salts has been studied for many years using a variety of experimental and theoretical methods.¹ Smith has reviewed the theory and experiments on the rotational energy levels of the ammonium ion in crystals.²

The most effective experimental techniques are nuclear magnetic resonance and neutron scattering, and these experiments have greatly extended the knowledge derived from thermodynamics and spectroscopy. Existing theoretical models for ammonium ion rotation are based on the assumption (usually implicit) that the ammonium is rigid and does not distort as it rotates. The underlying idea is that the intraionic force constants are large, and the interionic forces small, compared with those that lead to the highly distorted transition states of chemical reactions. In a crystal, the potential energy of interaction between the ion and its surroundings is described in terms of electrostatic and repulsive overlap forces, and can be calculated as a function of orientation provided the ion is rigid.

In an earlier paper³ on ordered crystalline ammonium chloride we showed that *ab initio* calculations are able to give accurate results for many physical properties, such as the lattice parameter, N–H bond length, compressibility, activation energy for rotation, and vibrational frequencies. In

this paper we extend the calculations to ammonium fluoride and allows for ion distortion and displacement, both of which we find to be significant.

Ammonium fluoride, alone among the ammonium halides, crystallizes in the hexagonal wurtzite structure^{4–9} (space group $P6_3mc$, $Z=2$), with a coordination number of 4. In choosing a set of experimental crystallographic parameters with which to compare the calculated results, preference was given to data taken at the lowest temperature, at which thermal motion of the ammonium ion is smallest. The parameters a , c/a , and u determined by van Beek *et al.*⁹ at 120 K, and the N–H bond distances determined by Adrian and Feil⁷ at 77 K, were chosen. These values are listed in Table I.

The fact that ammonium fluoride adopts the wurtzite structure in preference to the CsCl-like structures of the other ammonium halides may be ascribed to an increased degree of hydrogen bonding between the ammonium and fluoride ions compared to other halides. Evidence in support of hydrogen bonding in ammonium fluoride includes the low N–H stretching frequency and high H–N–H bending frequency,¹⁰ and the high activation energy for rotation.¹¹ There are no phase transitions below room temperature, and no orientational disorder of the ammonium ions.

The ¹H and ¹⁹F NMR lines narrow at about 250 K, showing that the ammonium ions rotate fairly rapidly at room temperature. The activation energy for rotation was estimated from the NMR line narrowing to lie in the range 42 ± 4 kJ/mol. Relaxation time measurements by Svare *et al.*¹² gave an activation energy of 39.3 kJ/mol. With the addition of the zero point energy of the 523 cm^{-1} torsional mode,¹⁰ the experimental barrier height is found to be 48.7 kJ/mol.

In this paper we report results of *ab initio* calculations on crystalline ammonium fluoride. The agreement between the

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TABLE I. The calculated and observed unit cell parameters for the equilibrium structure of NH_4F .

Parameter	Observed	Reference	Calculated (this work)
a	4.4365(3) Å	9	4.4561 Å
c/a	1.6155(1)	9	1.6237
u	0.3777(1)	9	0.3782
N–H _{ax}	1.035(8) Å	7	1.0421 Å
N–H _{eq}	1.045(6) Å	7	1.0424 Å
H _{ax} –N–H _{eq}	109.60(25)°	7	109.3°

calculated and observed equilibrium geometry of NH_4F crystals is good. In the transition state generated by rotating of the ammonium ion as a rigid body, it was found that both the barrier to rotation and the forces on the atoms were very large. In order to reduce the forces, the constraints on the atomic positions (apart from that which defines the transition state) were relaxed. This model of a flexible ammonium ion is consistent with the “molecular mechanics” approach in chemistry, rather than the rigid ammonium ion model used in previous work. When the geometry of the rotated ion is optimized, the ion is found to be distorted from a regular tetrahedron, and displaced from its equilibrium position. The rotational transition state in ammonium chloride has also been reexamined and a similar distortion and displacement were also found. These results show that the dynamics of rotation of the ammonium ion in crystals is more complex than has been thought previously.

II. COMPUTATIONAL METHODS

The method we use is Alavi’s FEMD method^{13–15} in which the Kohn–Sham–Mermin functional¹⁶ is minimized using an iterative diagonalization method. In fact, as the gap between the highest occupied and lowest unoccupied orbitals is large, the use of this method rather than a more standard total energy method such as Car–Parrinello¹⁷ or other density functional total energy method is immaterial. We used the local density approximation with gradient corrections.^{18,19} The electronic orbitals were expanded in a plane wave basis setup to a cutoff of 90.0 Ry, corresponding to approximately 48 474 plane waves. We used the pseudopotential method to obviate the need to include core electrons explicitly. Troullier–Martins pseudopotentials²⁰ in the Kleinman–Bylander form²¹ using s nonlocality for F and N were employed. The pseudopotentials were generated using core radii of 1.4 a.u. for the valence states of N and 1.3 a.u. for the valence states of F. The above cutoff was sufficient to give well-converged results. Calculations were done on a single unit cell of NH_4F containing two formula units with periodic boundary conditions. We used a $4 \times 4 \times 2$ Monkhorst–Pack k -point mesh in order to sample the Brillouin zone adequately.

Calculations were performed with a number of lattice parameters a and c to find the energy minimum with the N–H bond lengths close to the correct values. The nitrogen and hydrogen atoms positions were then optimized with fixed lattice parameters.

In the wurtzite structure, the ammonium ion is surrounded by four fluoride ions forming a nearly regular tetrahedron. Although the site symmetry is C_{3v} , it is close to T_d , and the stable orientation of the ammonium ion in the unit cell will be referred to as the T_d orientation. When an ammonium ion rotates from one stable orientation to another, it passes through an energy maximum corresponding to the transition state. Two modes of rotation of the ammonium ion are possible. One mode is a rotation by 90° about an S_4 axis bisecting two N–H bonds. In this transition state, all N–H bonds point into the spaces between the fluoride ions. The other mode is a rotation by 60° around a C_3 axis lying along an N–H bond. In this transition state, the N–H bond along the rotation axis remains pointing toward a fluoride ion, while the other three bonds point into the spaces between fluoride ions.

There are two inequivalent types of N–H bond: the axial bond parallel to the crystal c axis, and the three equatorial bonds. However, the c/a and u parameters for ammonium fluoride are close to the “ideal” values that yield a regular tetrahedron of fluoride ions around the ammonium ion. Hence, the local site symmetry is very close to T_d , and the distinction between the C_3 rotations about different NH bonds is assumed to be small. Calculations were carried out on both the S_4 and the axial C_3 transition states. In the latter the molecule is rotated about the axial bond parallel to the c axis of the crystal.

The S_4 transition state was obtained from the equilibrium orientation by inverting the four hydrogen atoms at the nitrogen atom. The axial C_3 transition state was obtained from the equilibrium orientation by rotating the ammonium ion through 60° about the z axis. In each transition state, the transformed ions were constrained by requiring one hydrogen atom of the rotated ion to lie in a mirror plane through the nitrogen atom during the optimization of the other atomic coordinates.

Since there are two ammonium ions per unit cell in the wurtzite structure, it is possible to rotate either one or both ions in the unit cell, and this was done for the axial C_3 transition state. This is a method of approximating the case of a single ammonium ion rotating in a crystal otherwise at equilibrium, though there are still interactions between alternating layers of rotated and nonrotated ammonium ions.

III. THE EQUILIBRIUM STRUCTURE OF NH_4F

Table I summarizes the calculated unit cell parameters of the equilibrium structure of ammonium fluoride crystal, together with the experimental values derived from diffraction experiments. The calculated results are in good agreement with the experimental crystallographic data. The calculated unit cell length a and the c/a ratio agree with experiment within about one percent. The calculated u parameter is slightly greater than the “ideal” value of $\frac{3}{8}$, consistent with the experimental results of Morosin,⁶ Adrian and Feil,⁷ and van Beek *et al.*⁹ By contrast, Lawson *et al.*⁸ obtained a value slightly less than $\frac{3}{8}$ in a neutron diffraction study of ND_4F . The calculated values of the two independent N–H bond lengths, 1.0424 and 1.0421 Å, do not differ significantly, and

lie between the experimental values of 1.035(8) and 1.045(6) Å, obtained from a combined low-temperature x-ray and neutron diffraction study of NH_4F .⁷ The shorter bond length of 1.025 Å obtained by Lawson *et al.*⁸ may be due to thermal motion since the measurements were carried out near room temperature. The lengthening of the N–H bond in NH_4F relative to the bond lengths in NH_4Cl (1.032 Å)³ and in NH_4ReO_4 (1.025 Å)²² is consistent with the presence of hydrogen bonding in the fluoride.

Figure 1 shows a graph of the valence electron density along the N–H··F direction (bold line), together with the corresponding graph of valence electron density along the N–H··Cl direction in NH_4Cl (dashed line). The pseudopotential keeps the valence electrons away from the nuclei of the nitrogen and fluorine atoms, and so there is a minimum in the calculated electron density at these sites. The hydrogen atom can be identified by a shoulder at about 1.0 Å from the nitrogen nucleus. The minimum in the calculated electron density between the ammonium ion and the fluoride ion is 0.044 a.u. (electrons bohr⁻³). This compares well with the analysis of x-ray diffraction data by van Beek *et al.*,⁹ who reported the electron density at the two bond critical points in NH_4F as 0.032 a.u. and 0.030 a.u.

Alavi *et al.*³ found that the minimum value of the calculated valence electron density between the ammonium ion and the chloride ion in NH_4Cl was 0.026 a.u. In both these crystals the minimum values of the electron density in the region between the hydrogen atom and the halide ion are low. It is hard to argue, on the basis of the calculated electron densities in the hydrogen bond region, that there are hydrogen bonds in the fluoride but not the chloride, although the vibrational spectra suggests that this is the case.²³ We believe that the electron density does not provide a good criterion for the existence or otherwise of hydrogen bonds.

IV. THE TRANSITION STATES IN NH_4F

When the ammonium ion was rotated as a rigid body from the equilibrium orientation to the axial C_3 transition

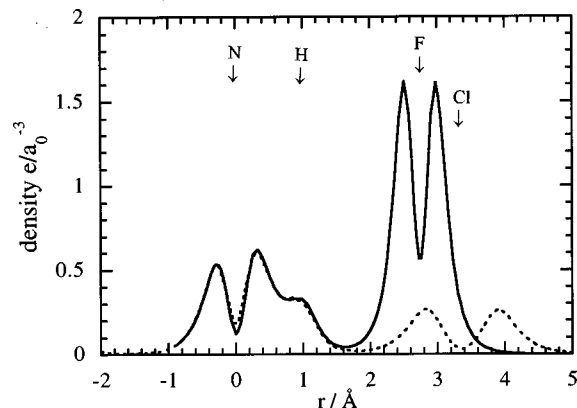


FIG. 1. The valence electron density along the N–H··X directions with the ammonium ions in their equilibrium orientation in NH_4F (full line) and NH_4Cl (dotted line). The N atom is at $r=0$. The position of the hydrogen atom corresponds to the shoulder centered near 1 Å. The minima in the electron density at the nuclei of the heavy atoms are a consequence of the pseudopotential method.

TABLE II. Rotational transition states in NH_4F .

The “ax” and “eq” directions are referred to in the crystal c axis.					
Interatomic distances (Å) and angles					
Orientation	Energy (kJ/mol)	H–N–H		N–H	N–F
T_d	0	109.3°	ax:	1.042	2.736
			eq:	1.042	2.720
Flexible model with all ions rotated					
C_3	69.0	108.7°	ax:	1.187	2.469
			eq:	1.017	2.818
S_4	131.3	109.6°	ax:	1.014	2.740
			eq:	1.012	2.718
Flexible model with alternate ions rotated					
C_3	74.2				
Rotated ion:		110.0°	ax:	1.064	2.626
			eq:	1.016	2.757
Unrotated ion:		109.5°	ax:	1.070	2.610
			eq:	1.038	2.763

state, the calculated energy barrier for C_3 rotation was found to be 82 kJ mol⁻¹. This value is considerably larger than the experimental value, 48.7 kJ/mol.¹¹ More importantly, the calculated forces on the atoms in the transition state were very large, and in order to reduce the forces the ammonium ion was permitted to relax its geometry. The resulting energy barriers, bond lengths and interatomic distances for this flexible ion model are shown in Table II and Fig. 2.

The energy barrier for rotation about the S_4 axis is much higher than for C_3 rotation, and hence this mode of rotation can be ignored in practice. The N–H bond lengths in the S_4 transition state shorten considerably.

Figure 2 shows the calculated changes in geometry between the ground state and the axial C_3 transition state, when all ammonium ions rotate simultaneously. The equatorial N–H bonds shorten from 1.042 Å in the equilibrium orientation to 1.016 Å in the C_3 orientation. The axial N–H bond in the rotated ion lengthens from 1.042 to 1.187 Å, if all ions rotate, or 1.064 Å in the more realistic case, when only alternate ions rotate. At the same time, the nitrogen atoms move along the c axis of the crystal toward the neighboring fluoride ions. If all ions are rotated, the nitrogen atoms shift

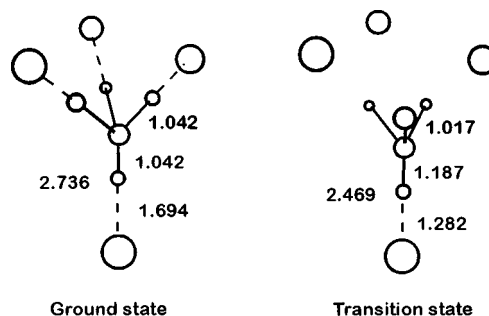


FIG. 2. Changes in the local geometry in ammonium fluoride as the ammonium ion rotates. The left-hand side of the diagram shows the bond lengths in the ground state; the right-hand side shows the situation during simultaneous rotation of all ammonium ions about the C_3 axis. The figures to the right of each picture are, respectively, the equatorial N–H bond length, the axial N–H bond length, and the H··F distance; the figure on the left is the total N··F distance.

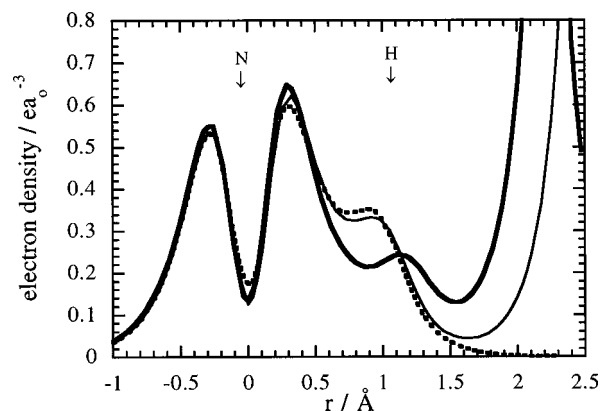


FIG. 3. The valence electron density along the N-H directions in NH_4F . Thin full line: equilibrium orientation. Heavy full line: the $\text{N-H}_{\text{ax}} \cdots \text{F}$ direction in the C_3 transition state with all ions rotated. Note the lengthening of the N-H bond, the shortening of the distance between the N and F atoms, and the increased electron density between the H and F atoms. Dotted line: the N-H_{eq} direction in the C_3 transition state with all ions rotated. Note the shortening of the N-H bond.

by 0.27 Å; if only alternate ions rotate, nitrogen atoms in the rotated and unrotated ions shift by 0.110 and 0.126 Å, respectively.

The lengthening of the axial N-H bond in the transition state is equivalent to a partial transfer of a proton from the ammonium ion to the fluoride ion. Complete proton transfer in the transition state would lead to a molecular complex $\text{H}_3\text{N} \cdots \text{HF}$ within the crystal. The calculations of Carroll and Bader²⁴ on the $\text{H}_3\text{N} \cdots \text{HF}$ complex showed that, in the gas phase, the complex consists of two uncharged molecules, not two ions. When the ion in the crystal rotates, three of the four hydrogen bonds are broken. The fourth hydrogen bond pulls the entire ammonium ion toward the fluoride ion and the corresponding hydrogen atom moves away from the nitrogen atom toward the fluorine atom. Although proton transfer in the crystal is not complete, the calculated axial N···F distance in the axial C_3 rotational transition state in the crystal is smaller than the corresponding distance in the gas phase complex, 2.755 Å.²⁴

The calculated values for the barrier for axial C_3 rotation are larger than the experimental value of 48.7 kJ mol⁻¹ based on NMR and IR data. A comparison of the calculated barrier when all ions rotate (69.0 kJ/mol) with the barrier when only alternate ions rotate (74.2 kJ/mol) shows that the effect of interaction between neighboring ammonium ions is significant. The barrier height is higher by about 7% when only alternate ions rotate. This suggests that simultaneous rotation of adjacent ions is energetically favored. When only alternate ions rotate, the axial N-H bond length increases a little more and the displacement is larger, in the unrotated ion than in the rotated ion.

Figure 3 compares the electron density along the $\text{N-H} \cdots \text{F}$ directions in the ground state and the C_3 transition state. It clearly shows a change in the bonding. As the proton forming the $\text{N-H} \cdots \text{F}$ hydrogen bond moves toward the fluoride ion and away from the nitrogen atom and the N···F distance simultaneously decreases, there is a large increase of electron density in the hydrogen bonded region (to 0.128

TABLE III. Rotational transition states in NH_4Cl .

Orientation	Interatomic distances (Å) and angles			
	Energy (kJ/mol)	H-N-H	N-H	N-Cl
T_d	0	109.5°	1.032	3.369
Rigid model with all ions rotated				
S_4	29	109.5°	1.032	3.369
C_3	35.5	109.5°	1.032	3.369
Flexible model with all ions rotated				
S_4	27.1	107.7°	1.023	3.369
C_3	27.1	107.5°	on axis: 1.047	3.087
			off axis: 1.021	3.473

a.u.). This can be interpreted as being the result of increased covalency in the $\text{H} \cdots \text{F}$ region of the hydrogen bond.

V. THE TRANSITION STATES IN NH_4Cl

With these new results in mind, the previous calculations³ of the energy barriers for rotation in ammonium chloride were repeated, but with the ammonium ion allowed to move and distort. The chloride ion is a much weaker base than the fluoride ion, which suggests that the distortion should be less than in ammonium fluoride, but still might be appreciable.

There are two possible rotation modes in ammonium chloride, corresponding to the C_3 and S_4 axes of the ammonium ion. The previous calculation³ showed that, with all ions rotated, the barrier for S_4 rotation is 29 kJ mol⁻¹ and the barrier for C_3 rotation is 35.5 kJ mol⁻¹. The conclusion from these calculations that S_4 rotation is energetically preferred is not without difficulties. First, quasielastic neutron scattering experiments²⁵ show that the activation energies for S_4 and C_3 rotations are approximately equal, and that, in the ordered phase, S_4 rotations are slower than C_3 rotations. Second, 90° rotations about S_4 axes lead to disordering of the ordered phase at low temperatures as the two possible configurations of the ammonium ion are interchanged. The only way that order in the low-temperature phase could be maintained with 90° rotations is for each rotation “event” to consist of two or more consecutive rotations.²⁶ Rotation about a C_3 axis does not lead to interchange of configurations and so maintains orientational order in the crystal.

The results in Table III show that the first of these difficulties is resolved if the ammonium ion is permitted to distort. The energy barrier for S_4 rotation drops from 29 to 27.1 kJ mol⁻¹, and that for C_3 rotation drops by a much larger amount from 35.5 to 27.1 kJ mol⁻¹. The equality of the energy barriers for the two modes of rotation is probably coincidental. Note that these results are for simultaneous rotation of all ammonium ions. The lengthening of the N-H bond along the rotation axis in the C_3 transition state is small, but the displacement of the ammonium ion is considerable, approximately 0.3 Å toward the chloride ion situated on the rotation axis. This is comparable to the displacement in ammonium fluoride. In both the C_3 and S_4 transition states, the N-H bonds that are removed from the neighborhood of chloride ions shorten considerably, to about 1.02 Å.

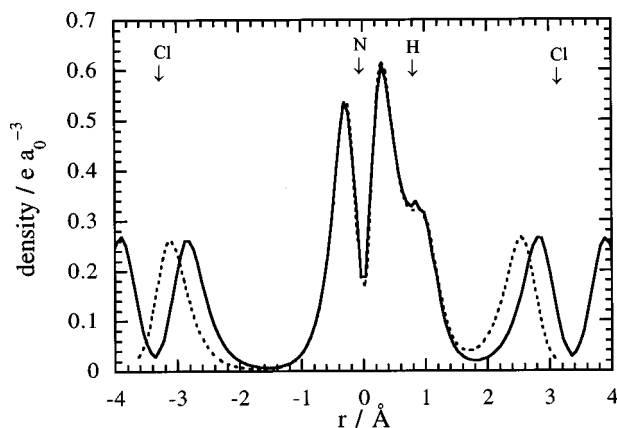


FIG. 4. The valence electron density along the N-H...Cl directions in NH_4Cl . Full line: equilibrium orientation. Dotted line: C_3 transition state. The N atom is at $r=0$ for both curves, and the N-H bond along the rotation axis points to the right. For the transition state curve (dotted line), note the displacement of the ammonium ion, relative to the chlorine atoms, in the N-H...Cl direction, and the increased electron density between the H and Cl atoms.

Howard and Legon studied the $\text{H}_3\text{N}\cdots\text{HCl}$ complex in the gas phase by microwave spectroscopy,²⁷ and showed that the complex consists of a pair of molecules rather than a pair of ions. The calculated axial N...Cl distance in the rotational transition state in the crystal, 3.087 Å, is smaller than the corresponding distance in the gas phase complex, 3.136 Å.²⁷

Figure 4 shows the electron density along the N-H...Cl directions in both the ground state and the axial C_3 transition state. The shift of the ammonium toward one chloride is clearly seen. Although there is an increase in the minimum electron density along the N-H...Cl direction, it is much less than observed in the corresponding ammonium fluoride transition state (compare Fig. 3), and we deduce that there is not significant covalency in this case.

VI. CONCLUSIONS

The main conclusion is that, in crystals, the ammonium ion moves and distorts as it passes through the rotational transition state. The calculated transition state geometry indicates partial transfer of a proton to the fluoride ion. A similar though smaller displacement and distortion is found in ammonium chloride, and the calculated barriers for S_4 and C_3 rotation are equal. The motion is similar to that of a carousel: the ammonium ion shifts along the rotation axis, and changes its shape, as it passes through the transition state at the top of the potential barrier.

Distortion of an ammonium ion interacting with its surroundings has been demonstrated previously by Kassab *et al.*,²⁸ who carried out quantum chemical calculations on a cluster containing an ammonium ion and a number of water molecules. Their objective was to calculate the energy barrier and transition state geometry for rotation of the ion in an aqueous solution. In unsymmetrical surroundings, the ammonium ion was shown to distort appreciably. Thus, the present work is in a sense an extension of the chemical concept of the transition state into the crystalline state.

Direct observation of the predicted distortion and displacement of the ammonium ion in the transition state in crystalline ammonium fluoride is likely to be difficult. However, there are two pieces of experimental evidence that may be relevant. The first is the observation of dielectric relaxation in pure ammonium iodide, indicating an effective dipole moment of 1.4 Debye, and a positive coupling between ions in the Curie-Weiss analysis.²⁹ Lynden-Bell and Michel have interpreted this in terms of distorted and displaced ammonium ions.³⁰

The second piece of evidence is based upon observations of tunneling dynamics in ammonium salts.³¹

The calculated effective mass for rotation of the ammonium ion was found to be much larger than that of the bare ammonium ion, and it was concluded that ammonium ion rotation involves more than simply moving the hydrogens atoms in circles.

ACKNOWLEDGMENTS

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- ¹N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Clarendon, Oxford, 1978).
- ²D. Smith, *Chem. Rev.* **94**, 1567 (1994).
- ³A. Alavi, R. M. Lynden-Bell, P. A. Willis, I. P. Swainson, and R. J. C. Brown, *Can. J. Chem.* (in press).
- ⁴W. Zachariasen, *Z. Phys. Chem. (Leipzig)* **127**, 218 (1927).
- ⁵B. Morosin and J. E. Schirber, *J. Chem. Phys.* **42**, 1389 (1965).
- ⁶B. Morosin, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **26**, 1635 (1970).
- ⁷H. W. W. Adrian and D. Feil, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **25**, 438 (1969).
- ⁸A. C. Lawson, R. B. Roof, J. D. Jorgensen, B. Morosin, and J. E. Schirber, *Acta Crystallogr., Sect. B: Struct. Sci.* **45**, 212 (1989).
- ⁹C. G. van Beek, J. Overeen, J. R. Ruble, and B. M. Craven, *Can. J. Chem.* **74**, 943 (1996).
- ¹⁰R. C. Plumb and D. F. Hornig, *J. Chem. Phys.* **23**, 947 (1955).
- ¹¹L. E. Drain, *Discuss. Faraday Soc.* **19**, 200 (1955).
- ¹²I. Svare, G. Thorkildsen, and K. Otnes, *J. Phys. C* **12**, 2177 (1977).
- ¹³P. L. Silvestrelli, A. Alavi, M. Parrinello, and D. Frenkel, *Phys. Rev. Lett.* **77**, 3149 (1996).
- ¹⁴A. Alavi, *Proceedings of the Conference on Monte Carlo and Molecular Dynamics of Condensed Matter Systems*, SIF, Bologna, Italy, 1996, edited by K. Binder and G. Ciccotti (SIF, Bologna, 1996), Vol. 49, p. 651.
- ¹⁵A. Alavi, J. Kohanoff, M. Parrinello, and D. Frenkel, *Phys. Rev. Lett.* **73**, 2599 (1994).
- ¹⁶N. D. Mermin, *Phys. Rev.* **137**, A1441 (1965).
- ¹⁷R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ¹⁸A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ¹⁹C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ²⁰N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ²¹L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ²²I. P. Swainson and R. J. C. Brown, *Acta Crystallogr., Sect. B: Struct. Sci.* **53**, 76 (1997).
- ²³R. J. C. Brown, *J. Mol. Struct.* **345**, 77 (1995).
- ²⁴M. T. Carroll and R. F. W. Bader, *Mol. Phys.* **65**, 695 (1988).
- ²⁵J. Töpler, D. R. Richter, and T. Springer, *J. Chem. Phys.* **69**, 3170 (1978).
- ²⁶R. W. Gerling and A. Hüller, *J. Chem. Phys.* **78**, 446 (1983).
- ²⁷N. W. Howard and A. C. Legon, *J. Chem. Phys.* **88**, 4694 (1988).
- ²⁸E. Kassab, E. M. Evleth, and Z. D. Hamou-Tahra, *J. Am. Chem. Soc.* **112**, 103 (1990).
- ²⁹I. Fehst, R. Böhmer, W. Ott, A. Loidl, S. Haussühl and C. Bostoen, *Phys. Rev. Lett.* **64**, 3139 (1990).
- ³⁰R. M. Lynden-Bell and K. H. Michel, *Rev. Mod. Phys.* **66**, 721 (1994).
- ³¹W. Burrows and H. L. Strauss, *J. Chem. Phys.* **99**, 5668 (1993).