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Temperature-dependent Raman study of ammonium perchlorate single crystals: Evidence for NH_4^+ quantum rotation below 30 K

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We report a detailed temperature-dependent Raman study of oriented single crystals of NH_4ClO_4 and ND_4ClO_4 in the lattice-mode region from 10 to 300 K. Based on the deuterium shift, characteristic changes in bandwidth with temperature, structural information, etc., we have assigned the Raman bands in the lattice-mode region, which provides deeper insight into the dynamics of ammonium ions in the lattice. We have observed temperature-dependent sidebands by ± 19 cm^{-1} (10 K) from the main bands associated with some of the internal and lattice modes of the NH_4^+ ion below 30 K. These spectral features have been explained in terms of a model in which the NH_4^+ ion rotates almost freely about one of the axes coinciding with the N—H(2)...O(1) bond while it performs librational motion about the two perpendicular axes below 30 K.

INTRODUCTION

It is well recognized that the thermal, mechanical, and many other physical properties of solids are strongly influenced by the orientational freedom of molecular groups which, in turn, depend mainly on the height, shape, and symmetry of the potential rotational moment of inertia, and temperature. Molecular groups like CH_4, —CH_3, and ions like NH_4^+ in different solids have been studied extensively by high-resolution inelastic neutron scattering (INS),[1,2] nuclear magnetic resonance (NMR),[3,4] infrared spectroscopy,[5] and many other techniques.[6] Until now, clearly separated and almost free rotational transitions have been observed experimentally only in solid hydrogen,[1,7] solid methane in phase II, and in the rotation of the —CH_3 group in γ-picoline (Ref. 2) at low temperatures using mainly the INS technique. The potential barriers for rotation of molecular groups are very small, and the rotational quantum numbers of the free molecule are good quantum numbers for describing orientational motion in these systems. On the other hand, if the orienting potential is strong in comparison with the rotational constant, the molecular groups perform small angular oscillations (librations) around their equilibrium orientations. In the range of intermediate potential strength, the librational states may split by quantum-mechanical tunneling of molecular ions among the different equilibrium orientations. Since most of these motions have low frequencies, a careful study of the low-frequency Raman spectra may yield valuable information about the dynamics of molecular ions in solids. We report such studies on ammonium perchlorate in this communication.

Ammonium perchlorate has been extensively investigated by various techniques to elucidate the dynamical properties of the cation in the orthorhombic (D_{2h}^{16}) lattice.[8–15(a)] From temperature-dependent Raman study of the linewidth, intensity, and frequency shift of some of the internal and lattice modes, we had shown that NH_4ClO_4 undergoes two phase transformations at 40 and 180 K.[8] As the lattice modes provide a sensitive probe of the crystalline field, proper analysis of the lattice-mode Raman spectra can, in principle, yield a better understanding of molecular dynamics in solids. From the limited data available in the literature, only a qualitative and incomplete analysis of the low-frequency modes of NH_4ClO_4 had previously been attempted by different workers as summarized in Table I. The neutron-diffraction results[14] on NH_4ClO_4 indicate that, below 40 K, the N—H(2)$\cdots$O(1) bond is strong and straight, while the remaining N—H$\cdots$O bonds are bent and weak (for structure and numbering of atoms, see Fig. 1). Many studies[6,8–15(a)] indicate a very low potential barrier for the NH_4^+ (Ref. 14) reorientation in the lattice. Moreover, the structural data indicate one of the three NH_4^+ librational frequencies to be much smaller than the other two. An analysis of the tunnel-split components of the NH_4^+ librational ground state predicts[15(a)] one of the

TABLE I. Assignment of lattice-mode Raman spectra of NH_4ClO_4 by earlier workers at room temperature (RT) and at 12 K.

RT freq. (cm^{-1})	12-K freq. (cm^{-1})	Assign.[a]	Ref.
43		ClO_4^- (LM)	10,11
65		ClO_4^- (LM)	11
68		NH_4^+ (T)	10
152		NH_4^+ (T)	10,11
	35	NH_4^+ (T)	9
	50	NH_4^+ (T)	9
	165	ClO_4^- (LM)	9
	180	NH_4^+ (L)	9

[a] LM denotes lattice modes; T denotes translational modes; L denotes librational modes.

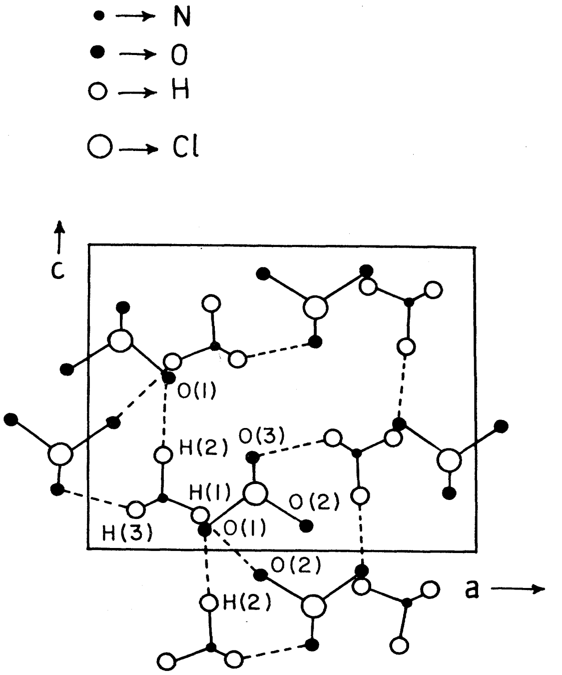

FIG. 1. The crystal structure of ammonium perchlorate projected on the mirror plane *a-c*. The dashed lines joining the oxygen and hydrogen atoms indicate the O $\cdots$ H hydrogen bond (after Ref. 14).

NH_4^+ librational frequencies to be much higher than the other two.

In view of the low potential barrier, low crystal-field symmetry,[14] and conflicting reports about the orientational freedom of cations, proper analysis of the lattice-mode Raman spectra, a clear identification of the NH_4^+ librational (rotational) and transitional modes in NH_4ClO_4 is extremely important. We therefore undertook a systematic temperature-dependent lattice-mode Raman-spectroscopic study on NH_4ClO_4 and ND_4ClO_4 single crystals. One of the most interesting findings in these studies is an observation of temperature-dependent sum and difference bands separated by $\pm 19\ \mathrm{cm}^{-1}$ (10 K) from the main bands associated with some of the internal and lattice modes of the NH_4^+ ion below 30 K in the Raman spectra of NH_4ClO_4. After comprehensive discussion, we have arrived at the conclusion that the NH_4^+ ion behaves like a one-dimensional free rotator along the N—H(2) $\cdots$ O(1) axis while it librates around the other two perpendicular axes below 30 K. To our knowledge, this is the first observation of clearly separated rotational levels of the NH_4^+ ion in a chemically pure solid by Raman spectroscopy.

EXPERIMENT

Single crystals of ammonium perchlorate were grown from saturated aqueous solutions of analytical-grade material. The deuterated crystals were grown by repeated crystallization (five times) of crystalline NH_4ClO_4 in D_2O. The crystals used in the present study were transparent pieces in the form of parallelepipeds with the longest side as the *c* axis and the smallest side as the *a* axis.

The Raman spectra were measured with a conventional SPEX triple monochromator and a microprocessor-based photon-counting system. A closed-cycle helium cryocooler was used for low-temperature studies. The integrated intensities of the bands were obtained from graphical resolution assuming multi-Lorentzian bands given by the formula

$$I=\sum_n I(\nu_{0n})b_n^2/[b_n^2+(\nu-\nu_{0n})]^2 , \tag{1}$$

where ν_{0n} is peak frequency and b_n is the half-width at half maximum height (HWHM) of the *n*th band. The full width at half maximum (FWHM) so obtained was corrected for finite slit width using the formula[15(b)]

$$(\delta_n)_t=(\delta_n)_a\{1-[s/(\delta_n)_a]^2\} , \tag{2}$$

where $(\delta_n)_t$ is the correct FWHM of the *n*th band. $(\delta_n)_a$ is the apparent FWHM of the *n*th band, and S is the slit width in cm^{-1}. The slit width S in cm^{-1} was measured directly from the FWHM of the plasma lines as the natural width of these lines is very small. Figure 2 depicts a typical result obtained by this procedure in the lattice mode (*aa*) region where we have obtained very good

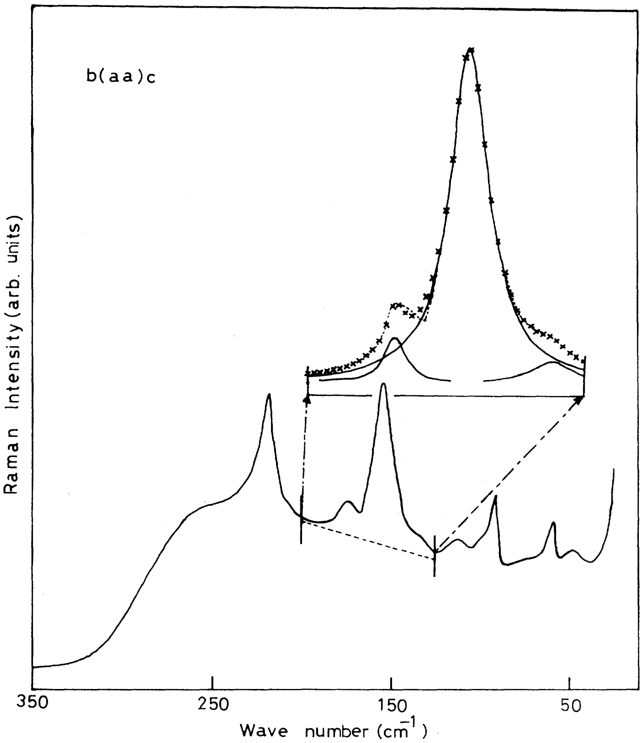

FIG. 2. Observed (dotted curve) and deconvoluted (solid curve) $156\text{-}\mathrm{cm}^{-1}$ NH_4^+ librational band contours as discussed in the text. The point $\times$ is the calculated band contour on the Raman spectra of ammonium perchlorate single crystal at 15 K. The dashed line represents the baseline used for deconvoluting the spectra.

agreement between the observed and deconvoluted intensities. Plasma lines of the argon-ion laser and known CCl_4 lines were used for spectral calibration and the accuracy of the band positions reported in this paper is estimated to be within ± 0.5 cm^{-1}.

FACTOR-GROUP ANALYSIS

In general, the quasirotational (librational) and translational motions of the molecular units in the lattice give rise to coupled modes, which makes a quantitative understanding of the lattice-mode Raman spectra quite difficult. However, the coupling depends on the time scales of the different types of motion and is expected to be significant only if the frequencies of these motions are nearly similar. For the motion of the ammonium and perchlorate ions in these systems, one can start with the first-order approximation that the coupling between the translational and librational motions is not significant due to the unusually low potential barriers governing the librational motion of cations. We shall, therefore, try to analyze the observed spectra in this approximation. Both NH_4ClO_4 and ND_4ClO_4 belong to the D_{2h}^{16} space group and the ammonium as well as the perchlorate ions occupy sites of C_s symmetry ($Z=4$).[14] The external optical modes belong to the F_1 and F_2 types of the T_d symmetry for free ions. These correlate with the different types of C_s site group and the D_{2h} space group as shown in Table II. One would expect a 12-site symmetry split, and a maximum of 24 Raman-active site-split and correlation-field-split components in the lattice-mode region. However, if the correlation field splitting is not large in the lattice-mode region, one would observe bands at approximately the same frequency positions in the A_g (*aa*,*bb*,*cc*) and B_{2g} (*ac*) and the B_{1g} (*ab*) and B_{3g} (*bc*) polarization geometries.

RESULTS AND DISCUSSION

The Raman spectrum of NH_4ClO_4 exhibits drastic temperature dependence and we have shown that it undergoes two phase transitions at 40 and 180 K within the same space group.[8] Here we shall be mainly concerned with the lattice-mode region and dynamics of cations. The lattice-mode Raman spectra of NH_4ClO_4 and ND_4ClO_4 single crystals in various scattering geometries at room temperature and 10 K are shown in Figs. 3 and 4. Before going into details, we shall briefly summarize (a) the variation of the Raman spectral parameters with temperature, and (b) the observed effects of deuteration.

(a) We have observed three distinct types of variations in the Raman spectra as a function of temperature.

(i) All the bands except the 70- and 168-cm^{-1} (B_{1g},B_{3g}) and 65.4-cm^{-1} (B_{2g}) ones observed at room temperature could be traced down to 10 K.

(ii) The low-temperature (10 K) bands at 196 cm^{-1} (B_{1g},B_{3g}), 156 cm^{-1} (A_g,B_{2g}), 113 cm^{-1} (B_{1g},B_{2g},B_{3g}), 48 cm^{-1} (B_{1g},B_{3g}), and 33 cm^{-1} (B_{2g}), on the other hand, could be traced only up to 40–70 K.

(The above two groups of bands have been identified as lattice modes for the purpose of assignment and have been listed in Table III.)

(iii) We have observed sidebands due to quasi-one-dimensional rotation of the NH_4^+ ion separated by ± 19 cm^{-1} (10-K value, Fig. 5) from the NH_4^+ vibrational and lattice modes up to 30 K. Below 15 K the spectral pattern in the (80–160)-cm^{-1} (B_{1g},B_{2g},B_{3g}) and (50–85)-cm^{-1} (A_g) frequency ranges show complicated splittings (Fig. 4). The observed multiplet structure in the (80–130)-cm^{-1} (B_{1g},B_{2g},B_{3g}) range has been qualitatively understood in terms of tunnel-split components of the excited NH_4^+ librational states. The remaining structure has not been understood properly at this stage. The frequencies of these bands are given in Table IV.

(b) We have observed the following effects upon deuteration.

(i) At room temperature, the 179-cm^{-1} (A_g) band of the NH_4^+ ion shows a frequency shift, while other bands do not shift upon deuteration.

(ii) At temperatures below 120 K, the positions of all the observed bands in the lattice region of the deuterated system are different than those for the hydrogenated system. The bands assignable to the librational and translational modes of the cation, however, show the expected deuteration shift.

(iii) In contrast to the hydrogenated system, neither side bands nor low-temperature tunnel splitting of the

TABLE II. Correlation of the lattice modes of NH_4ClO_4 and ND_4ClO_4 in the (10–300)-K temperature range.

ClO_4^- (NH_4^+) ion T_d symmetry	C_s site symmetry	D_{2h}^{16} space group
F_2 NH_4^+ (ClO_4^-)[a] Translation	$2A'$	$2A_g$,$2B_{1u}$ $2B_{2g}$,$2B_{3u}$
	A''	B_{1g}, A_u[b] B_{3g},B_{2u}
F_1 NH_4^+ (ClO_4^-) Libration	A'	A_g,B_{1u} B_{2g},B_{3u}
	$2A''$	$2B_{1g}$,$2A_u$[b] $2B_{3g}$,$2B_{2u}$

[a] $1B_{1u}$, $1B_{2u}$, and $1B_{3u}$ components of the translational modes correspond to the acoustic modes.
[b] Inactive.

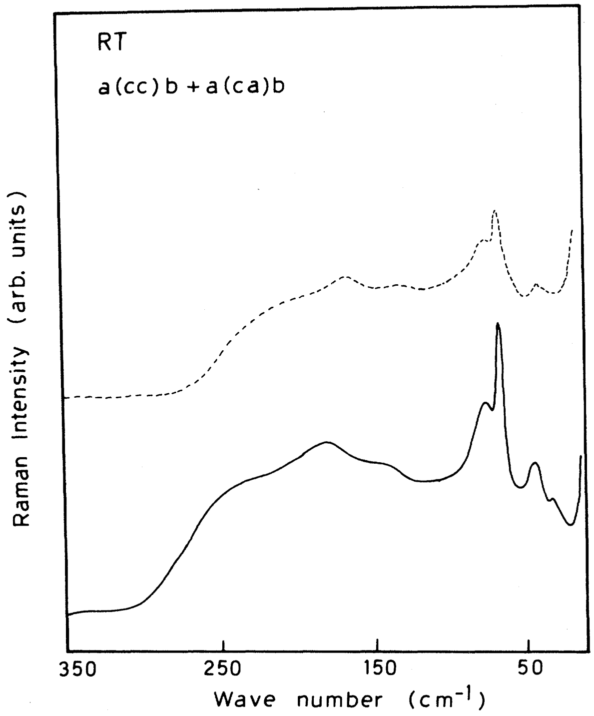

FIG. 3. The polarized lattice-mode Raman spectra of NH_4ClO_4 (solid curve) and ND_4ClO_4 (dashed curve) single crystals at room temperature in the $a(cc)b + a(ca)b$ polarization geometries.

$ND_4{}^+$ vibrational or lattice modes could be observed.

In order to identify the origin of the observed sidebands associated with the $NH_4{}^+$ vibrational and lattice modes, we shall first assign the observed lattice modes in the Raman spectra of NH_4ClO_4 and ND_4ClO_4 single crystals.

LATTICE MODES DUE TO THE $ClO_4{}^-$ ANION

Based on the characteristic fast increase in the linewidth of the librational modes compared to the translational modes of $NH_4{}^+$ ions with temperature, expected deuteration shift, similarity of the temperature dependence of the respective modes in the hydrogenated and deuterated systems, and polarization characteristics, comparison with the lattice modes of the $ClO_4{}^-$ ion in $NaClO_4$,[16] etc., we have assigned the observed Raman bands in the lattice-mode region to the NH_4ClO_4 systems. The $ClO_4{}^-$ ions are distorted from their regular tetrahedral structure and are localized in the lattice below room temperature.[8] The lattice modes of the $ClO_4{}^-$ ions are therefore expected to give sharp and relatively stronger bands in the Raman spectra of these compounds. The $ClO_4{}^-$ lattice modes were therefore assigned on the basis of deuteration insensitivity, relatively sharp nature of these bands, and in analogy with the assignments in $KClO_4$ (Ref. 17) and $NaClO_4$ (Ref. 16) single crystals. The results are summarized in Table III.

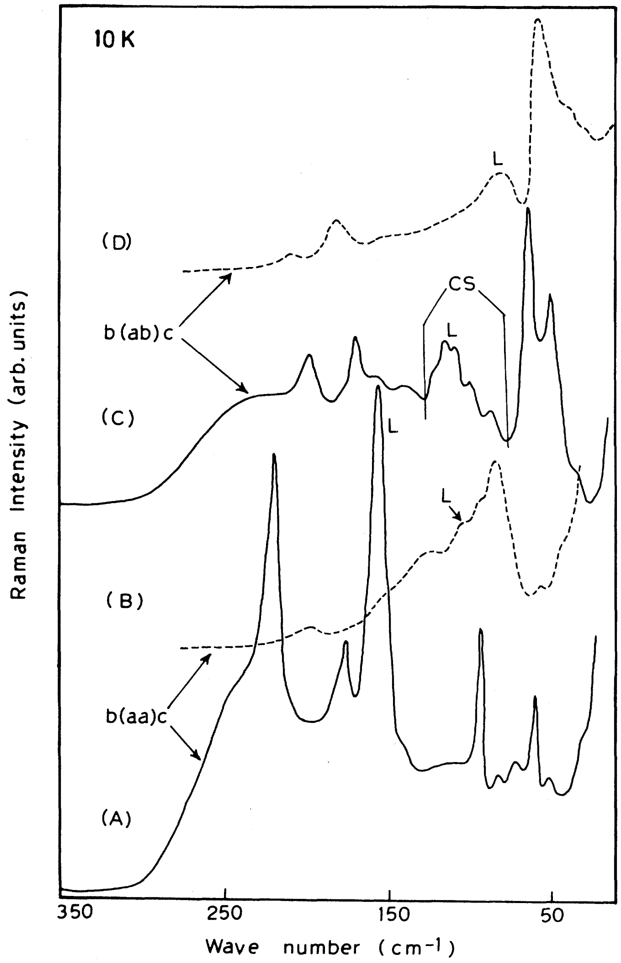

FIG. 4. The polarized lattice-mode Raman spectra of ammonium perchlorate (solid curve, labeled *A* and *C*) and deuterated ammonium perchlorate (dashed curve, labeled *B* and *D*) at 10 K. The different polarization geometries are shown in the figure. *L* represents ammonium librations, while CS is the complicated structure as discussed in the text.

LATTICE MODES OF THE $NH_4{}^+$ CATION

Substitution of deuterium in place of hydrogen in the $NH_4{}^+$ ion would affect the frequencies of the $NH_4{}^+$ lattice modes considerably. The ratios of the librational and translational mode frequencies in the hydrogenated and deuterated salts is expected to be $\sqrt{2}:1$ and 1.1:1, respectively.[10]

The 113- and 156-cm^{-1} (10 K) bands have been unambiguously assigned as $NH_4{}^+$ librational modes as they decrease by factors of 0.71 and 0.66, respectively, in the Raman spectra of ND_4ClO_4. From the known structural data,[14] the ratio of the force constants of different $NH_4{}^+$ librations can be calculated using the following expression:[18]

$$\phi_i \propto K_i^{-0.25} \ , \tag{3}$$

TABLE III. Assignment of the observed lattice modes in NH_4ClO_4 as discussed in the text at some selected temperatures. Entries within parentheses are for ND_4ClO_4 at the respective temperatures. (s denotes strong, m denotes medium, ms denotes medium strong, w denotes weak, vw denotes very weak, wb denotes weak broad, vwb denotes very weak broad, sh denotes shoulder, L denotes libration, T denotes translation.)

		Temperature (K)						
	Symmetry	10	70	150	200	RT		
	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	Assignment
A_g	(57)	60 m	50 w	47 w	47 w	42 w	(42)	ClO_4^-
		68 vw	71 wb	67.3 w	67.3 m	65.5 s	(65)	ClO_4^-
	(85)	91.3 ms	87 wb	80.2 w	80.2 m	73 m	(77)	ClO_4^-
	(95)							NH_4^- (L)
	(105)	156.0 s	140 wb					NH_4^+ (L)
	(128)							ND_3H^+ (L)?
	(202)	218.8 s	207.7 wb	194.8 w	194.8 w	179 w	(163)	NH_4^+ (T)
B_{1g}	(42)	48 s						NH_4^+ (T)
	(60)	65 s	50.6 w	43.3 w		42 w	(42)	ClO_4^-
				72.8 w		70 w	(70)	ClO_4^- (L)
	(79)	113 m	126.4 vwb					NH_4^- (L)
	(155)	167 w	150 wb	153.2 wb		145 sh	(147)	NH_4^+ (L)
	(185)	196 w				168 wb	(168)	ClO_4^- (L)
B_{2g}	(26)	33 m						NH_4^+ (T)
	(60)	62 vw	48 w	47 w	47 m	42.3 s	(42)	ClO_4^-
			71 w	71 w	69.1 w	65.4 w	(65)	ClO_4^-
	(85)	112 mb	107 vwb					NH_4^+ (L)
	(105)	156 w						NH_4^+ (L)
	(128)							ND_3H^+ (L)
	(155,170)	171 w	160 w	156 wb	152.3 wb	146 wb	(163)	ClO_4^-
	(203)	218 w						NH_4^+ (T)
	(26)							NH_4^+ (T)
B_{3g}	(42)	48 s						NH_4^+ (T)
	(60)	64 s	43 wb	41.4 w		42 w	(42)	ClO_4^+
			70.0 wb	78.4 w		70 w		ClO_4^-
	(85)	112 w	98.7 wb				(147)	NH_4^+ (L)
	(155)	167 w	167 wb	168 w		145 sh	(147)	ClO_4^-
	(185)	196 w				168 w	(168)	ClO_4^-

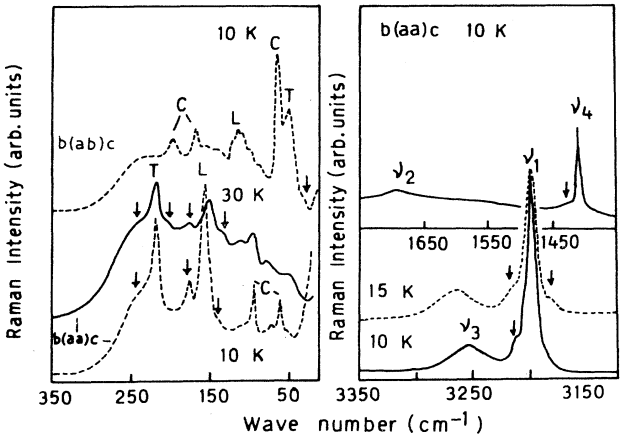

FIG. 5. Representative Raman spectra of ammonium perchlorate in the lattice-mode region and in the regions of internal modes of the ammonium ion at a few selected temperature. *L* and *T* indicate the ammonium librational and translational modes, respectively, while *C* represents perchlorate lattice modes. The arrows indicate the rotational sidebands as discussed in the text.

where ϕ_i's are the librational amplitudes and K_i's are the corresponding force constants. The ratio of the two high-frequency librational force constants for the NH_4^+ ion in NH_4ClO_4 comes out to be 11:18 using known structural data and expression (3). The ratio of the observed bands at 113 and 156 cm^{-1} associated with the NH_4^+ librational frequencies is 113:156–11:16, which is in excellent agreement with the structural data. One of the librational frequencies extracted from the NMR activation energy[12] turns out to be 140±18 cm^{-1} and is close to the observed librational mode at 156 cm^{-1} (10 K). The 113-cm^{-1} band corresponds to the observations of Rosasco *et al.*,[9] but the extremely feeble and broad background (Fig. 1, Ref. 9) centered around 180 cm^{-1} had been misinterpreted by these authors as an NH_4^+ librational mode. This is mainly due to the fact that NH_4ClO_4 is a strong proton conductor[19,20] and therefore a depolarized, featureless background is typical of this system due to translational motion of the proton. The observation of a similar depolarized background in the Raman spectra of NH_4ClO_4 in the lattice-mode region (170–250 cm^{-1}) therefore strongly supports our contention.

TABLE IV. Unidentifiable observed modes in NH_4ClO_4 (10 K). (w denotes weak, vw denotes very weak.)

Symmetry A_g	B_{1g} Frequency (cm^{-1})	B_{2g}	B_{3g}
50.7 vw	86.4 w	81.3 w	85.1 vw
82.1 w	97.5 w	96.2 vw	102.0 w
104.0 vw	107.5 w	123.6 vw	120.0 w
	121.2 w		
	138.4 vw		
	156.0 vw		

The assignment of the 156-cm^{-1} mode as the NH_4^+ librational mode and its correlation to the 105-cm^{-1} band in the deuterated system merits further discussion as the band observed around 155 cm^{-1} in the deuterated spectrum has been associated with the ClO_4^- motion by earlier workers.[9] In view of their close frequencies it is indeed tempting to correlate the 156-cm^{-1} (NH_4ClO_4) and 155-cm^{-1} (ND_4ClO_4) bands with a ClO_4^- mode. This view, however, is not tenable for the following reasons.

(1) In the hydrogenated system the 156-cm^{-1} band is observed in the (*aa*) and (*ac*) scattering geometries, whereas in the deuterated system this band is observed in the off-diagonal scattering geometries only (Fig. 4).

(2) The 156-cm^{-1} band shows a strong temperature dependence and softens upon increasing the temperature from 10 to 30 K. The 155-cm^{-1} band in the deuterated salt, on the other hand, is temperature independent in the same temperature range.

Correlation of the 156-cm^{-1} band of the hydrogenated salt with the 105-cm^{-1} band in the deuterated salt, however, is free from the above discrepancies, as it is observed in the expected scattering geometries and shows similar temperature dependence as the 156-cm^{-1} band in NH_4ClO_4.

The 48- and 218-cm^{-1} bands (10 K) show a deuterium shift by a factor of 0.91 and have been identified as originating predominantly from NH_4^+ translational modes. This is consistent with the observation of Rosasco *et al.*, and the inelastic neutron peak[21] at 48 cm^{-1} also corresponds to our observation. The 33-cm^{-1} band observed in the (*ac*) polarization geometry of the hydrogenated salt has been correlated with the 26-cm^{-1} band in the deuterated system. This band has been correlated with the NH_4^+ translational mode and no band has been observed in the INS spectrum[21] around 33 cm^{-1}. The larger deuterium shift of 0.79 for this band indicates some form of coupling of this mode with the librational motion of the cation because of its low frequency.[22,23]

At higher temperatures, only one band at 178 cm^{-1} (room temperature) shows a definite deuterium shift of 0.9 and is therefore assigned as an NH_4^+ translational mode. This is consistent with the fact that the NH_4^+ (ND_4^+) ions are rotating almost freely at room temperature and retain their tetrahedral structure.[8] The librational motion of a tetrahedral group belongs to the F_1 symmetry and is inactive in the ir and Raman spectra. We may point out here that although the 33- and 48-cm^{-1} bands were reported by Rosasco *et al.*[9] also and assigned as NH_4^+ translational modes, their symmetry assignment is erroneous. From the results given in Table III, it is clear that at low temperatures we have observed and assigned the site-split and correlation-field-split components of the NH_4^+ (ND_4^+) librational and translational modes consistent with the structural data[14] and group theoretical predictions.

EVIDENCE FOR ONE-DIMENSIONAL NH_4^+ QUANTUM ROTATION BELOW 30 K

As pointed out earlier, the most surprising observation in our studies is that many vibrational modes associated with the NH_4^+ ion show temperature-dependent sidebands on the high- and low-frequency sides of the central bands. The frequency separation of these side bands increases from 19 ± 0.5 cm^{-1} at 10 K to 22.2 ± 0.5 cm^{-1} at 30 K. The vibrational modes of the ClO_4^- ion, on the other hand, do not show any such structure. In this section we shall focus our attention on understanding the nature of these sidebands. The various possible explanations for the appearance of these sidebands can be conceived in terms of the site and correlation-field splittings, inequivalent NH_4^+ sites in the lattice, combination tones involving the NH_4^+ modes with an unobserved low frequency (~19 cm^{-1}) lattice mode, free rotation of the cation, excited librational state splitting, or one-dimensional (hindered) rotation of the NH_4^+ ion in the lattice. Proper identification of the nature of the observed excitations shall be crucial for understanding the dynamical aspects of the system.

The site and correlation-field splittings of the vibrational modes in a unit cell depend on the degree of distortion of the ion(s) occupying sites of lower symmetry and the induced dipole moment generated during a particular mode of vibration of the molecular species in the unit cell. Therefore the strongly ir-active asymmetric stretching and deformation modes of the cation would be expected to show a much larger splitting compared to the very weakly ir-active symmetric stretching or bending modes in the low-temperature Raman spectra of NH_4ClO_4. The constant frequency separation of the sidebands from all the NH_4^+ vibrational modes thus rules out the possibility of understanding the observed satellite bands as originating from site or correlation-field splittings. Similarly, from the absence of any possible inequivalent sites to accommodate the cations in the *Pnma* space group of NH_4ClO_4 at 10 K, and the absence of similar structure in the low-temperature ir spectra,[24] we must conclude that the sidebands cannot originate from inequivalent cation sites in the lattice. For the site-split or correlation-field-split components as well as for the NH_4^+ ions occupying inequivalent sites, the energies of the NH_4^+ vibrational modes are much larger than kT below 30 K and therefore the intensities of the sidebands are expected to be temperature independent. The strong temperature dependence of the sidebands, the structural data,[14] and other spectroscopic data[24,4] support our contention.

If one attempts to explain the sidebands as combination tones of an unobserved low-frequency lattice mode with the NH_4^+ vibrations, the following serious discrepancies are encountered.

(1) The assumed lattice mode at ~19 cm^{-1} in the Einstein-oscillator approximation would contribute 1.1 cal mol^{-1} K^{-1} to the heat capacity at 10 K, while the experimental value[6] is only 0.543 cal mol^{-1} K^{-1}.

(2) For a 19-cm^{-1} (10 K) NH_4^+ or ClO_4^- lattice mode in NH_4ClO_4, a corresponding mode is expected in the ND_4ClO_4 spectra. No band in the (13–20)-cm^{-1} range was observed either in the lattice-mode region or in combination with the reasonably strong N—D symmetric-stretching mode in the Raman spectra of ND_4ClO_4.

(3) For the 19-cm^{-1} lattice mode, the intensity ratio of the difference and sum tones would be given by $\exp(-\hbar\omega/kT)$ at all temperatures. This expression gives a theoretical value of 0.402 at 30 K, while the experimental value is ~1.

(4) The intensity of the difference-tone band is proportional to $1/[\exp(\hbar\omega/kT)-1]$. Thus the difference-tone intensity should increase 3.5 times in going from 15 to 30 K, while experimentally only a nearly twofold intensity increase has been observed for many difference bands involving 19-cm^{-1} excitation.

At low temperatures the excited librational states in many systems[25] are known to split considerably (2–10 cm^{-1}) due to quantum-mechanical tunneling of ions, while the translational and internal modes show only a very small splitting (~0.5 cm^{-1}). The observed satellite bands separated by ±19 cm^{-1} (10 K) with the internal and external modes of the NH_4^+ ion conclusively show that these bands cannot be explained in terms of excited librational state splittings either. This view is supported by the observation of a complicated multiplet structure ($\Delta\nu\sim5$ cm^{-1}) associated only with the 113-cm^{-1} NH_4^+ librational mode (Fig. 4). Most likely this structure arises from excited librational state splitting due to rotational tunneling of the cation as the hindering barrier is expected to be low for such a low-frequency librational mode. However, in view of the strong temperature dependence of this multiplet, possible interference from combination or overtones of several low-frequency lattice modes, etc., an unambiguous assignment of this multplet is not possible at this stage.

The inadequacy of the possibilities considered so far in explaining the observed sidebands, the small frequency separation, the observation of only two out of the three expected NH_4^+ librations, and structural data of NH_4ClO_4 at 10 K (Ref. 14) suggest that the cations may be rotating almost freely around the strongly hydrogen bonded $N—H(2)\cdots O(1)$ bond making an angle of 84.17° with the *a* axis in the *ac* plane while it librates around the two axes perpendicular to the $N—H(2)\cdots O(1)$ bond. We shall attempt to explain the observed spectral features in terms of this model. The rotational problem, therefore, reduces to that of a plane rotor which can be described by Schrödinger equation of the form

$$-\hbar^2 d^2\psi/2I d\phi^2+V(\phi)\psi=E\psi\ . \tag{4}$$

As $V(\phi)\rightarrow0$, the rotational energy is simply given by $F=AK^2$, where K is the one-dimensional rotational quantum number. The selection rules for the vibration-rotation Raman spectra are $\Delta v=\pm1$ and $\Delta K=0,\pm2$ for the diagonal scattering geometries and $\Delta v=\pm1$ and $\Delta K=\pm2$ for the off-diagonal scattering geometries.[26] However, $\Delta K=0$ transitions may also become allowed in the off-diagonal scattering geometries as the cation performs librational motions around the two perpendicular axes.[27]

In order to analyze the observed spectra, one must take into account the influence of nuclear spin on rotational transitions. This point has been discussed in detail by Vedder and Hornig.[5(a),5(b)] For the rotation of the ion around the N—H(2) $\cdots$ O(1) axis, only three protons change their positions. From detailed considerations of the spin of the fourth proton, Vedder and Hornig[5(a)] have shown that in this situation the population of the $K=0$ level should increase with a decrease in temperature, leading to a concomitant increase in the $K=0\rightarrow0$ and $K=0\rightarrow2$ transition intensities. Using the proposed energy-level scheme (Fig. 6) based on this model, the strong central bands would correspond to the $\Delta v=1$. $\Delta K=0$ transitions, while the $\Delta v=1$, $\Delta K=\pm2$ transitions are expected to give rise to sidebands separated by 23.6 cm^{-1} from the central bands. Our experimental results can be explained in this framework. However, the observed separation of $\pm19\ \text{cm}^{-1}$ (10 K) for the sidebands is smaller than the planar-rotor predictions. This is believed to be due to the presence of a weak hindering potential originating from the interaction of the molecular unit with all other atoms and ions in the lattice. If a threefold cosine-type hindering potential is assumed, then the $\Delta K=\pm2$ transition energies are expected to be higher than the corresponding free-rotor energies (Fig. 3, Ref. 2), which is contrary to our observation. Therefore the possibility of a threefold barrier hindering the motion of the NH_4^+ ion about the N—H(2) $\cdots$ O(1) axis can be definitely ruled out. This is also supported from the structural data[14] and the complex surrounding of the rapidly interchanging protons where only the H(1) atom is surrounded by a hemispherical umbrella of six oxygen atoms. Although our results can be explained by assuming a sixfold barrier[2] of moderate height of $\sim110\ \text{cm}^{-1}$, limited experimental data and the absence of any literature evidence for such a potential makes it highly speculative. In view of this, a quantitative estimate of the potential height and its shape is not feasible at this stage. However, the comparable value of the $K=0\rightarrow2$ transition energy (19 cm^{-1}, 10 K) with the planar-rotator energy (23.6 cm^{-1}) and a comparison of our data with those for the CH_4 in phase II (Ref. 1) allow the observed sidebands to be interpreted as combination tones with the one-dimensional hindered NH_4^+ rotational states in a very weak hindering potential. This view is strongly supported from the following facts.

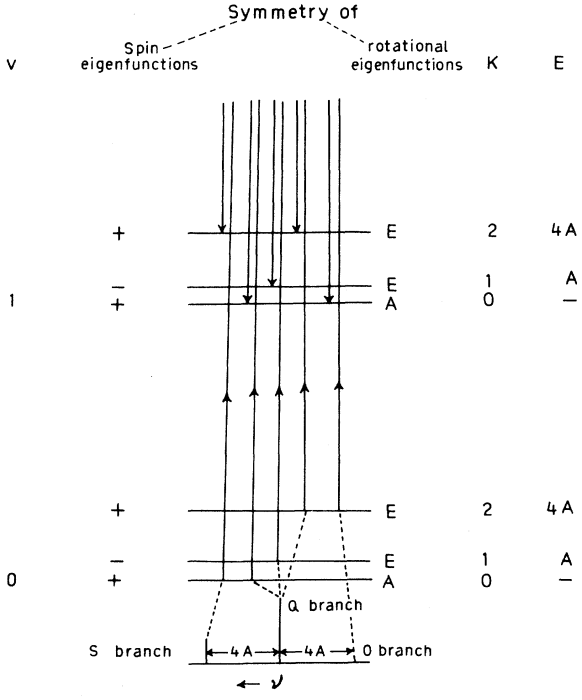

FIG. 6. Vibration-rotation energy-level scheme for the totally symmetric (A_g) ammonium vibrational modes. Different allowed transitions in the Raman scattering are indicated by vertical lines. "A" under energy (E) is the rotational constant.

(1) The decrease of the intensity of the $\Delta v=1$, $\Delta K=-2$ transition with increasing temperature is as expected for a rotational transition.[26,27]

(2) The observed nearly twofold increase in the intensity of the low-frequency sidebands associated with the N—H stretching and the 156-cm^{-1} librational mode for an increase in temperature from 15 to 30 K matches very well with the predicted intensity increase (2.0 times) for the $K=2\rightarrow0$ transition based on the model of one-dimensional rotation of the NH_4^+ ion without spin equilibration.

(3) The rotational heat capacity is a very sensitive function of the potential barrier. The calculated rotational heat capacity of the NH_4^+ ions in tetrahedral, trigonal, and orthorhombic fields show a hump around 30–40 K if and only if there is a free rotation around a N—H bond.[28,29] This anomaly disappears for barrier heights more than 200 $\text{cal}\,\text{mol}^{-1}$ hindering the threefold rotation. The calculated rotational heat capacity in the (30–40)-K temperature range is 1.15 $\text{cal}\,\text{mol}^{-1}\,\text{deg}^{-1}$ when the ion is freely rotating around a N—H bond. Thus the observation of a hump in the rotational heat capacity of NH_4ClO_4 in the (30–40)-K temperature range and the magnitude of rotational heat capacity of ~1.17 $\text{cal}\,\text{mol}^{-1}\,\text{deg}^{-1}$ in the same temperature region strongly support our conclusions.

(4) The observed INS peak[23,30] at 23 cm^{-1} can be consistently understood in terms of the $K=0\rightarrow2$ rotational transitions of the cation as this band cannot be assigned to any lattice modes of the NH_4^+ ion for reasons given earlier.

(5) The existing NMR results can also be understood in terms of the proposed model. For the motion of the NH_4^+ ion taking place at time scales of the order of 10^{-13} s, the NMR technique cannot probe this motion because of its slow time scale. Fast reorientation of the NH_4^+ ion would, however, modify the NMR signals in the following ways.

(a) The spin-spin relaxation time T_1 decreases with decreasing temperature because of the fast motion of the NH_4^+ group, causing relaxation via spin-rotational interaction. (b) The average second-moment value associated with the intramolecular dipolar coupling within the F-type, almost freely rotating, NH_4^+ ion should be consistent with the theoretical value ($\sim10\ \text{G}^2$) corresponding to the freely rotating F-type NH_4^+ ion. (c) The fast reori-

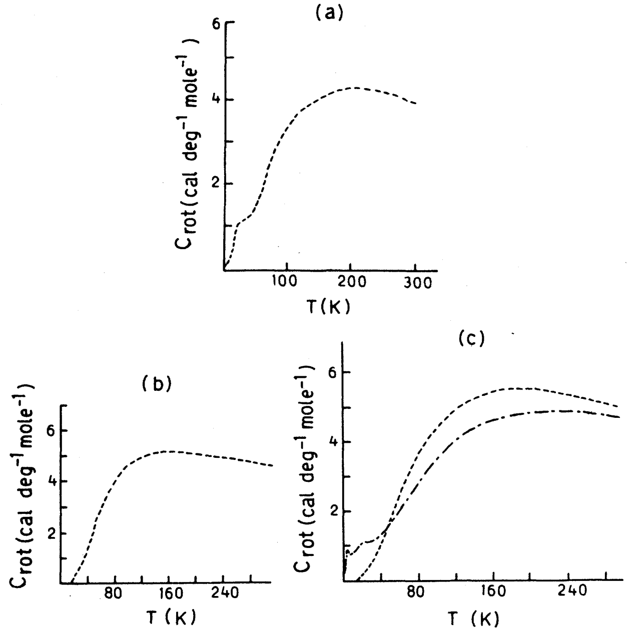

FIG. 7. The rotational heat capacity of the ammonium ion in (a) ammonium perchlorate (experimental result, Ref. 6), (b) an orthorhombic crystalline field for a ground-state splitting of 0.15 cm^{-1} (Ref. 28), and (c) a trigonal crystalline field for a ground-state splitting of 0.094 cm^{-1} (dashed line) and the change in the temperature dependence of heat capacity in the presence of a threefold rotation in a trigonal crystalline field (dashed-dotted curve, Ref. 29).

entation of the $NH_4{}^+$ ion is expected to retard the process of spin equilibration, leading to very high spin conversion time, as found for CH_4 in phase II.[1]

The absence of spin conversion up to 1.7 K for 12 h,[31] the observation of line narrowing in the NMR spectra with decreasing temperature,[4,12,31] and the experimental average value of the second moment $[M_2(F)]$ of 11.1 ± 0.5 G^2 therefore suggest the presence of a very fast reorientation of the $NH_4{}^+$ ions in the lattice. Although the interpretation of our Raman-spectroscopic results is in very good agreement with the structural,[14] NMR, quasielastic-neutron-scattering,[13] and heat-capacity results,[6] our conclusions are at variance with the interpretation[18] of the observed ground-state splitting in the INS spectrum. The observed INS spectrum had been explained by assuming that only 120° tunneling is important. When the magnitude of the tunneling overlap integrals is extracted from the experimental data, it is found that the four 120° tunneling matrix elements are $h_1=-0.035$, $h_2=h_3=-1.317$, and $h_4=-1.410$. This indicates that one of the four N—H rotation axes is a hard rotation axis, whereas the remaining three are soft rotation axes. Using the experimentally obtained librational amplitudes of the threefold librations of the $NH_4{}^+$ ions in NH_4ClO_4, the ratio of the librational force constants and the barrier heights can be found in the harmonic approximation using expression (3). The ratio of the threefold librational force constants came out approximately 5:1:2:2, indicating that one of the rotational axes is very soft and two axes are hard, while the fourth rotational axis is very hard. The structural data, therefore, are at variance with the interpretation of the INS results. The estimated barrier heights from the librational amplitudes turn out to be $\sim$0.2 kcal mol^{-1} for the very soft axis and $\sim$1 kcal mol^{-1} for the hardest rotational axis.[14] The barrier heights from Huller's model, on the other hand, come out to be 2 kcal mol^{-1} around the hard axis and $\sim$1 kcal mol^{-1} around the soft axes.[15(a)] As shown in Fig. 7, the calculated rotational heat capacity of the $NH_4{}^+$ ion from the observed A-E ground-state tunnel splitting of 0.1 cm^{-1} in a trigonal or orthorhombic field is in very poor agreement with the experimental results. Huller's model[18] also fails to take into account the 180° tunneling which is likely to be important as the barrier height is expected to be $\sim$1 kcal mol^{-1} for the librational motion corresponding to the observed librational modes at 156 and 113 cm^{-1}. On the basis of the above discussion, it emerges that the interpretation of the observed INS spectrum is not correct.

CONCLUSIONS

From the detailed temperature-dependent Raman studies on NH_4ClO_4 and ND_4ClO_4 single crystals, we have been able to assign the observed Raman bands in the lattice-mode region of these systems. Our analysis is fully compatible with the known crystal-structure data and group-theoretical predictions. From the observed sum and difference bands separated by ±19 cm^{-1}, we have concluded that the $NH_4{}^+$ ion performs an almost free one-dimensional rotation about the strong and straight N—H(2) $\cdots$ O(1) axis, while it librates around the other two perpendicular axes. A threefold cosine potential hindering the rotation of the $NH_4{}^+$ ion can be ruled out and the hindering potential may be more complicated.

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(1961). (b) The total nuclear spin of all the four protons ($S = 2, 1, 0$) would predict three types of ammonium ions corresponding to the three nuclear-spin functions at room temperature. Whether there is spin equilibration or not in going to lower temperatures, one would not observe combination bands of rotational levels of a freely rotating NH_4^+ ion with the totally symmetric N—H stretching mode as only the $\Delta J = 0$ transitions would be allowed for a spherical top molecule. Moreover, three-dimensional free rotation of the NH_4^+ ions would require a fairly uniform distribution of hydrogen nuclei on a spherical surface rather than discrete positions with different hydrogen bonding strengths for these nuclei in the lattice. Therefore, free rotation of the NH_4^+ ions in the lattice at low temperatures can be ruled out.

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