Temperature-dependent Raman study of ammonium perchlorate single crystals: The orientational dynamics of the NH_4^+ ions and phase transitions

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A detailed temperature-dependent study of the Raman spectra of oriented single crystals of NH_4ClO_4 is reported in the spectral regions of lattice modes and internal vibrations of the ClO_4^- and NH_4^+ ions between 10 and 300 K. The internal modes of the ClO_4^- ions show splitting into several components due to site and correlation field effects. The linewidth, frequency shift, and intensities of some of the internal modes of the ClO_4^- and NH_4^+ ions and the frequency shift of a few lattice modes show anomalous temperature dependence around 180 and at 40 K. These anomalies have been explained in terms of phase transformations associated with the changes in hydrogen bonding strength and reorientational freedom of the NH_4^+ ions in the lattice. The low temperature transition at 40 K exhibits a sharp and discontinuous anomaly in some of the spectral parameters measured in this study which is associated with order–disorder-type transition. The measured linewidth of the ν_1' mode in the diagonal scattering configuration can be understood in terms of vibrational dephasing of the ν_1' excited state due to vibrational–librational coupling. The estimated activation energies in the 50–160 K and 10–40 K temperature ranges are found to be 141 and 51 cm^{-1}, respectively, which correspond to the observed NH_4^+ librational frequencies.

I. INTRODUCTION

Ammonium perchlorate is an extensively investigated system below room temperature because of the complicated reorientational motion and other dynamical properties of the ammonium ions in the lattice and possible phase transformations in this system. Earlier studies indicated low rotational barriers ranging from 0.2 to 1 kcal/mol.[1–6] The x-ray[7–9] and neutron diffraction[10,11] studies between 10 and 298 K at selected temperatures have shown that NH_4ClO_4 belongs to an orthorhombic system with centrosymmetric space group P_{nma} (D_{2h}^{16}) having four formula units in an unit cell at all the temperatures without any evidence of a phase transformation. However, the x-ray diffraction studies by Stammler *et al.*[12] indicate that NH_4ClO_4 undergoes a polymorphic phase transformation around 83 K in addition to the well known orthorhombic to cubic transformation at ~517 K. Previous workers have reported anomalous behavior of this system between 10 and 50 K and around 100–110 K by IR studies[13], around 70 K by Raman studies[14], and the 30–40 K and ~200 K by rotational heat capacity measurements[1], and in widely different temperature ranges by magnetic resonance studies.[15–18] These anomalies were tried to be understood qualitatively in terms of ammonium reorientational freedom and/or phase transformations in the system. On the other hand the recent IR data[19] on NH_3D^+ ions in NH_4ClO_4 lattice have been interpreted by assuming a continuous evolution of the rotational motion of the ammonium ion with temperature. Except for a few, most of the earlier studies have been reported at only fixed temperatures or in a limited spectral region and therefore a clear understanding of this system is lacking.

In view of the complicated reorientational motion of the ammonium ion, conflicting reports about possible phase transformations in widely different temperature ranges by different techniques, ambiguity about the possible site and correlation field splittings, etc., we have undertaken a systematic temperature-dependent Raman study of the single crystals of NH_4ClO_4. As the time scale for Raman scattering lies between that for neutron diffraction and magnetic resonance techniques, Raman spectroscopy is uniquely suited to examine the fast reorientational dynamics of the NH_4^+ ions in NH_4ClO_4 lattice. We have observed anomalous changes in frequency shift, linewidth, and intensities of some of the internal modes of the NH_4^+ and ClO_4^- ions and a few lattice modes in NH_4ClO_4 as a function of temperature around 180 and at 40 K. These anomalies arise due to phase transformations within the same space group of the system. From a temperature-dependent linewidth study of the ν_1' (A_g) mode of the NH_4^+ ion in the 10–40 K and 50–160 K temperature ranges, the most significant dephasing process has been established to be a coupling of the NH_4^+ internal vibrational mode with the librational modes.

EXPERIMENTAL

Single crystals of ammonium perchlorate were grown from saturated aqueous solution of analytical grade ammonium perchlorate. The crystals used in the present Raman study were transparent pieces in the form of parallelopipes of ~2 mm × 2 mm × 5 mm dimensions with the longest side as *C* axis. The crystals were polished and oriented properly to record Raman spectra in different polarization geometries.

The Raman spectra were obtained with the help of a SPEX Ramalog 1403 double monochromator coupled with the third monochromator and a cooled photomultiplier tube RCA 31034. A Spectra-Physics model 165 Ar^+ laser operating with a constant output power of ~600 mW at 4880 Å was used as the excitation source. The sample was exposed to a laser power of ~300 mW. The spectrometer control as well as data processing were achieved with the help of a microprocessor based SPEX Datamate system. An Air Pro-

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ducts closed cycle helium cryocooler was used for obtaining the Raman spectra from room temperature down to 10 K. Temperature reading and monitoring were made possible by a precalibrated gold vs Chromel thermocouple in conjunction with a digital temperature controller. The sample was equilibrated at each temperature for at least 30 min. Although the temperatures were controlled to ± 0.5 K or better, the absolute temperature at the sample was estimated to be accurate within ± 3 K due to laser heating, etc. In order to check the reproducibility of the data and to countercheck a possible artifact of crystal imperfections, etc., the experiments were repeated on five different crystals at different temperatures and the results were found to be completely reproducible. The experimental results presented in this paper are for the same crystal at different temperatures between 10 and 300 K. Plasma lines of an Ar^+ ion laser and known CCl_4 lines were used for spectral calibration. Wave number shifts reported here are believed to be accurate to $\pm 0.1\ \mathrm{cm}^{-1}$ while the absolute accuracy of the band positions is within $\pm 0.3\ \mathrm{cm}^{-1}$.

The effect of finite slit width on the experimentally measured linewidth of different vibrational bands was corrected using the following expresssion[20]:

$$\delta_t = \delta_a \left[1 - \left(\frac{S}{\delta_a} \right)^2 \right] \cdots, \qquad (1)$$

where δ_t is the correct full-width at half-maximum (FWHM), δ_a is an apparent linewidth as measured experimentally, and S is the slit width in cm^{-1}. As the spectral slit width was much narrower than the linewidth of vibrational bands even at the lowest temperatures, this formula provides fairly accurate estimates of the true linewidth. A graphical resolution procedure was adopted for the overlapping bands in order to obtain correct linewidth (FWHM) values of those bands. 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. The integrated intensities of different vibrational modes were obtained by measuring the total area of the bands and were corrected for Bose–Einstein population factor.

Room temperature IR spectrum was obtained in Nujol mull media by a Perkin–Elmer model 983 IR spectrometer.

RESULTS AND DISCUSSION

The Raman active modes in the ammonium perchlorate single crystals have been carefully studied in various scattering geometries as a function of temperature to obtain accurate values of frequency shifts, linewidths, and intensity variations. Our room temperature spectra are similar to those reported by Van Rensburg *et al.*,[13] Schutte,[14] and Brill and Goetz.[21] However, we have observed a number of new bands in the lattice mode region in the Raman spectra at 10 K compared to the observation of Rosasco *et al.*[2] We have also observed the splitting of the ν_3 mode of the ClO_4^- ion and the overtones of the same vibration in our room temperature IR spectra. Representative Raman spectra at a few selected temperatures are shown in Figs. 1–4. Figure 5 shows the variation of the different mode frequencies as a function of temperature. The temperature-dependent variation of the linewidth (FWHM) and intensities of different modes are shown in Figs. 6–8.

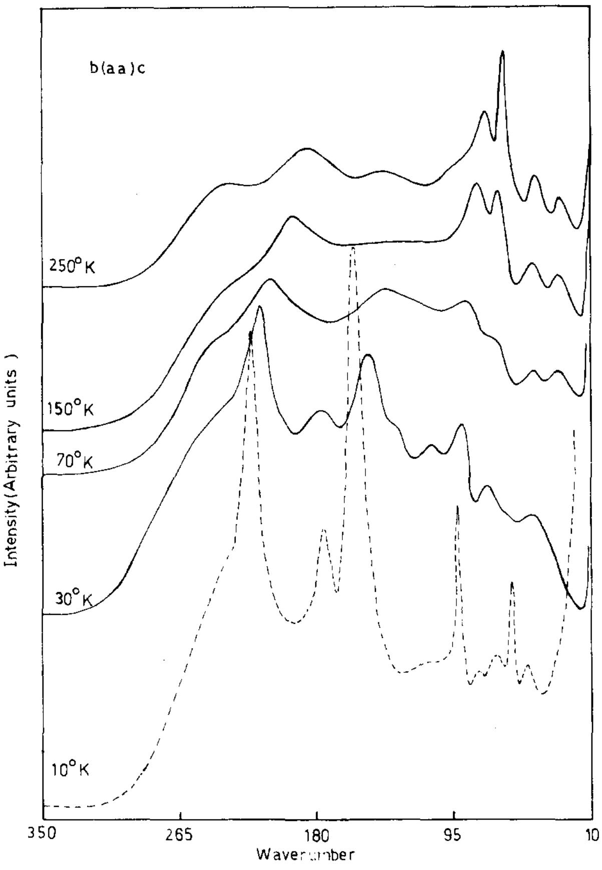

FIG. 1. Temperature-dependent Raman spectra of NH_4ClO_4 single crystal in the $b(aa)c$ scattering geometry (lattice mode region).

Factor group analysis and assignment

Ammonium perchlorate belongs to the orthorhombic system having a centrosymmetric space group D_{2h}^{16} with four formula units per unit cell.[7,10] The NH_4^+ and ClO_4^- ions are located on sites of C_s symmetry. Under the approximation that the Cl–O and N–H bonds are much stronger than the NH_4^+–ClO_4^- interactions, its Raman spectrum may be understood in terms of the "external lattice phonons" and the "internal vibrations" of the NH_4^+ and ClO_4^- ions. Moreover the internal modes in the unit cell can be correlated with the tetrahedral "free ion" vibrations of the NH_4^+ and ClO_4^- ions having symmetry species $\nu_1(A_1)$, $\nu_2(E)$, ν_3, and $\nu_4(F_2)$. With this available information, a group theoretical analysis was carried out. The symmetry classification of the normal modes is given in the correlations of Table I where the internal modes of the NH_4^+ ion are distinguished by a prime from the internal modes of similar nature of the ClO_4^- ion. Only the *gerade* modes of A_g (aa, bb, cc), B_{1g} (ab), B_{2g} (ac), and B_{3g} (bc) symmetries are Raman active in the indicated scattering geometries in parentheses, while only the modes of B_{3u} (a), B_{2u} (b), and B_{1u} (c) symmetries are infrared active. The group theoretical analysis given in Table I predicts that the nondegenerate totally symmetric $\nu_1(A_1)$ stretching

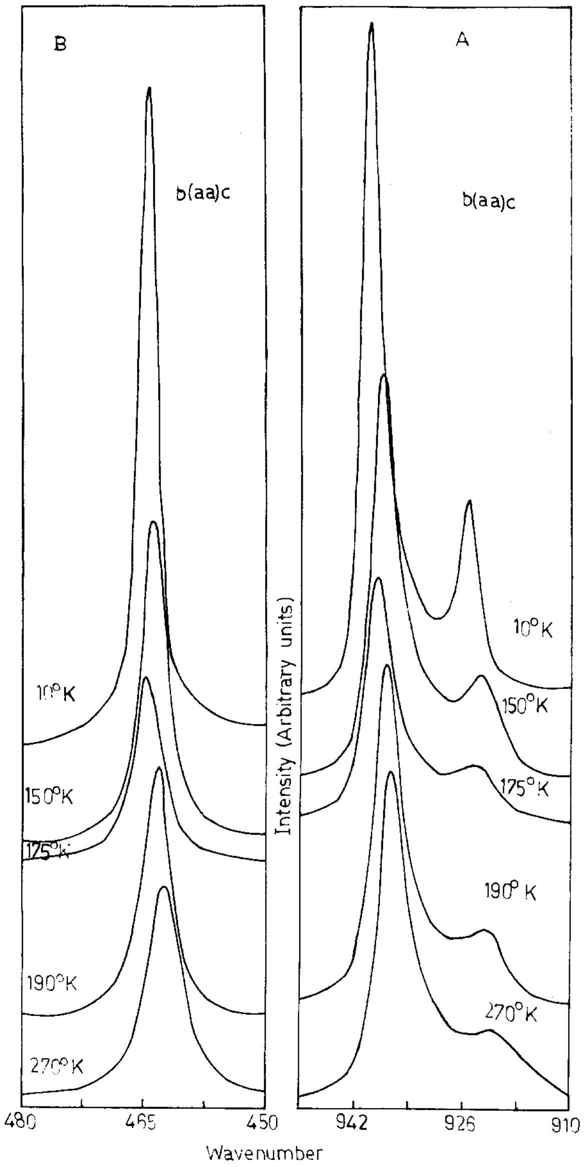

FIG. 2. Temperature-dependent Raman spectra in the $b(aa)c$ scattering geometry for (A)ν_1 and (B)ν_2 vibrational modes of the ClO_4^- ion in NH_4ClO_4 single crystal.

mode and the doubly degenerate symmetric bending mode $\nu_2(E)$ of the free ion should split into two and four Raman active components, respectively, whereas the triply degenerate assymetric stretch $\nu_3(F_2)$ and the asymmetric deformation mode $\nu_4(F_2)$ of each of the free ions should split into six Raman active components in the ammonium perchlorate lattice. We have assigned the observed Raman peaks in different polarization geometries at 10 K in NH_4ClO_4 in analogy with the assignment of the internal modes of the ClO_4^- group in $KClO_4$ single crystals,[22] and other existing Raman assignments on ammonium perchlorate.[2,18,21,23] The band assignment is given in Table II along with the IR data at room temperature. It is clear from Table II that, except for one component of the ν_3 mode, all other predicted modes of the ClO_4^- ion have been observed experimentally in our Raman studies. It is interesting to observe from Table II that the overall static and dynamic field splitting is maximum for the ν_3 vibrational mode of the ClO_4^- ion in conformity with the highly polar nature of this mode. The overall static and dynamic field splittings of all the internal modes ν_1, ν_2, ν_3, and ν_4 of the ClO_4^- group are 1.5, 2.2, 69.2, and 17.8 cm^{-1}, respectively, at 10 K.

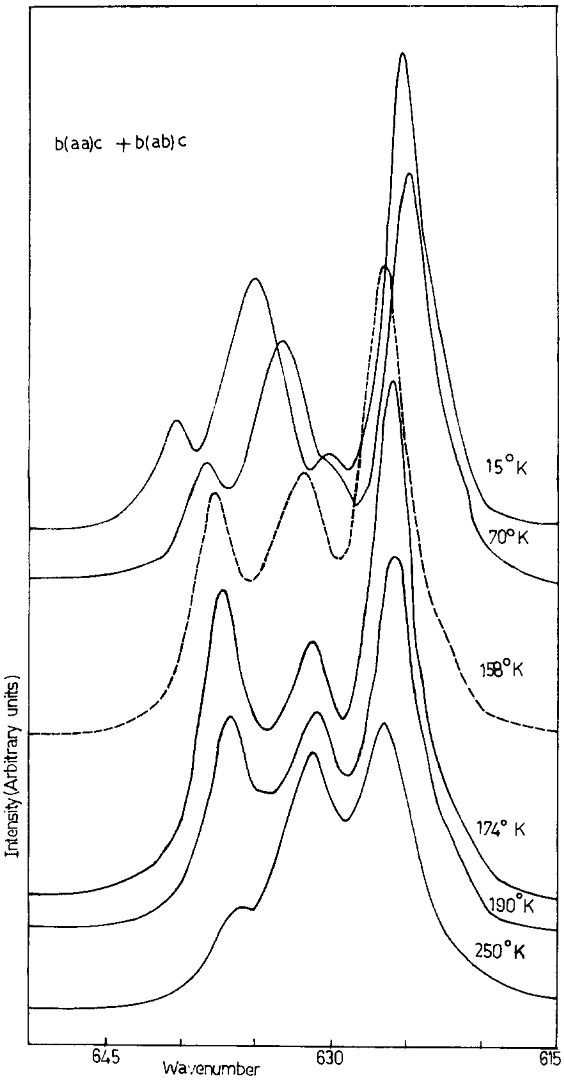

FIG. 3. Temperature-dependent Raman spectra in the $b(aa)c + b(ab)c$ scattering geometries for the ν_4 vibrational mode of the ClO_4^- ion in NH_4ClO_4.

Temperature dependence of Raman spectra: Evidence for phase transformation

Our careful Raman studies of the frequency shift, linewidth (FWHM), and integrated intensities of some internal modes of the NH_4^+ and ClO_4^- ions and a few lattice modes over the 10–300 K temperature range (Figs. 5–8) show definite discontinuities and anomalous behavior around 180 and 40 K. Our experimental observations are contrary to the suggestions by many earlier workers[19,24] that the rotational/reorientational motion of the NH_4^+ ions evolve in a continuous and regular manner with temperature in the NH_4ClO_4 lattice. As the spectral changes take place in

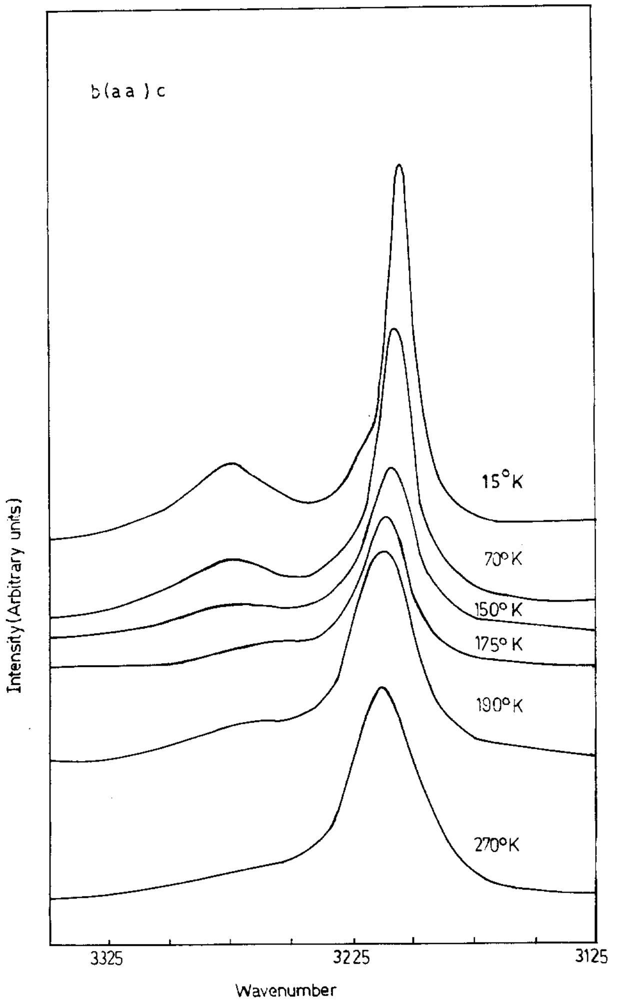

FIG. 4. Temperature-dependent Raman spectra for the ν_1' and ν_3' modes of the NH_4^+ ion in the $b(aa)c$ scattering geometry.

almost the entire temperature range, we shall first discuss the spectral anomalies between the 190–160 K temperature range and at 40 K.

When the temperature of the system is raised in narrow steps from 10 K, we observe the following spectral anomalies at 40 K.

(i) The frequencies of the lattice modes at 42, 72, and 150 cm^{-1} (300 K values) show sharp discontinuity and change of slope at 40 K. In going from 10 to 40 K, the frequencies of the first two bands remain almost constant, while the frequency of the 150 cm^{-1} mode changes at a faster rate (Fig. 5). The intensities of these bands also show drastic variations at 40 K (Fig. 1).

(ii) The frequency and linewidth of the ν_1' and the frequency of the ν_3' mode of the NH_4^+ ion show a sharp change of slope at 40 K (Figs. 5 and 6).

(iii) The linewidth of the ν_1 (ClO_4^-) mode shows a change of slope at 40 K. The separation within the correlation field split pairs of the site symmetry split components of the ν_4 mode decreases rapidly from 10 upto 40 K (Fig. 5).

On increasing the temperature from 40 K in narrow steps, we have observed the following spectral anomalies in the 160–190 K temperature range.

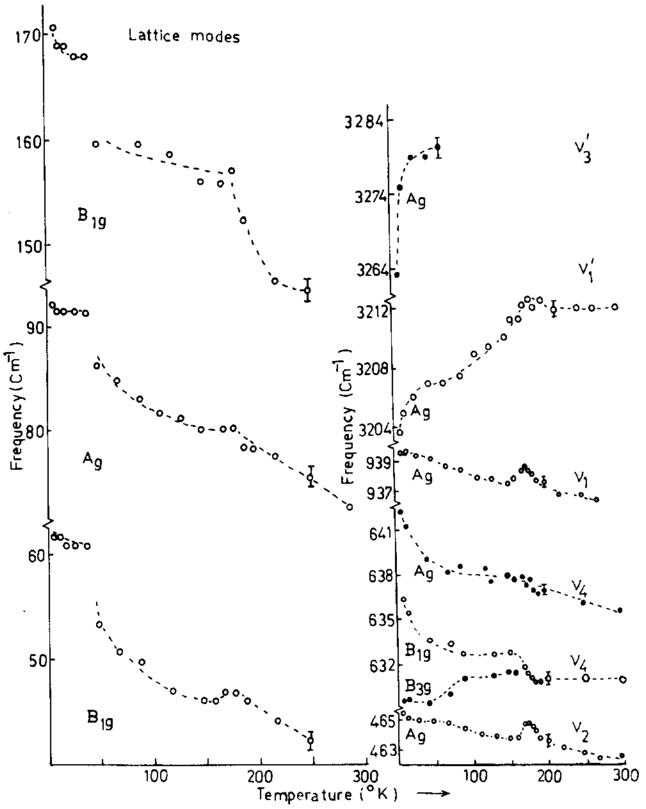

FIG. 5. Variation of some vibrational mode frequencies in NH_4ClO_4 with temperature. Dashed line through the experimental points is drawn as a guide to the eye.

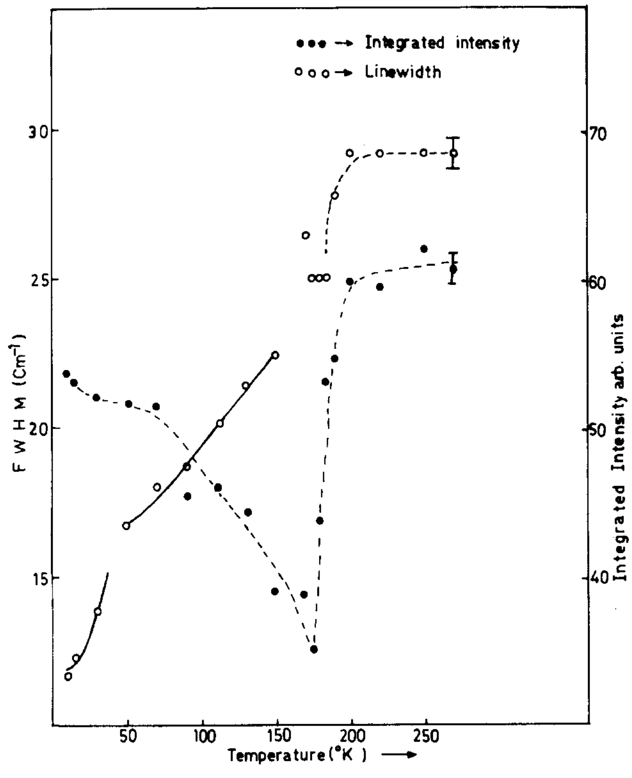

FIG. 6. Variation of the linewidth and integrated intensities of the ν_1' mode of the NH_4^+ ion as a function of temperature. Dashed line through the experimental points is drawn as a guide to the eye while the solid line represents the theoretical fit according to expression (3) of the text.

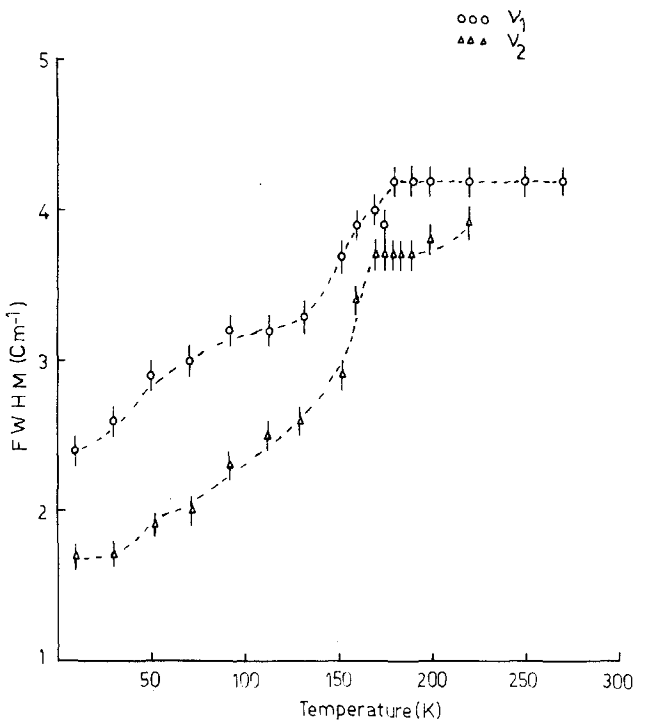

FIG. 7. Variation of the linewidth of the ν_1 and ν_2 modes of the ClO_4^- ions as a function of temperature. Dashed line through the experimental points is drawn as a guide to the eye.

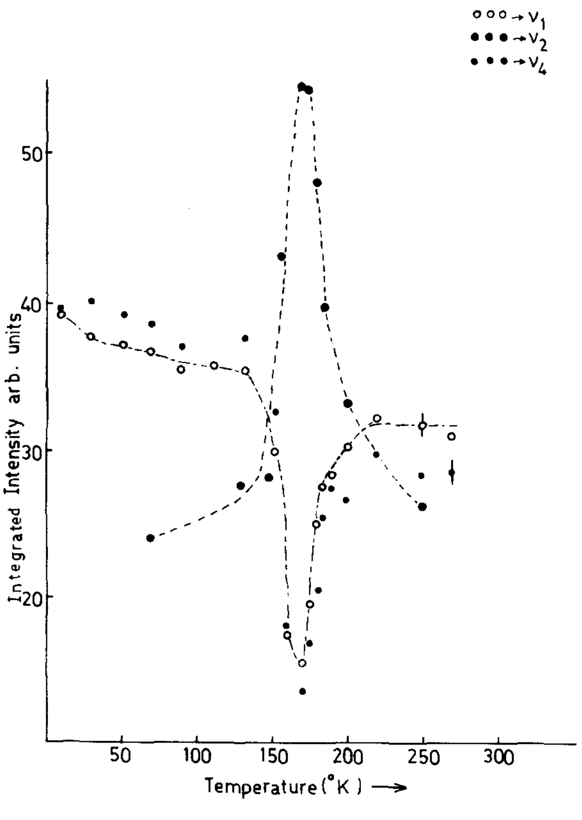

FIG. 8. Temperature induced variation of induced Raman intensity of the ν_1, ν_2, and ν_4 (637 cm^{-1}, 300 K) modes of the ClO_4^- ion in NH_4ClO_4 single crystal. Dashed lines through the experimental points is drawn as a guide to the eye.

(i) The frequencies of the ν_1, ν_2, and $2\nu_2$ modes of the ClO_4^- ion increase and peak at 180 K while the frequencies of all the six factor-group split components of the $\nu_4(ClO_4^-)$ mode show a sudden change of slope at 180 K. The band positions of the $\nu_1'(NH_4^+)$ mode and lattice modes at 42, 72, and 150 cm^{-1} (300 K values) also show a sudden change of slope around 180 K (Fig. 5).

(ii) The linewidth of the $\nu_1'(NH_4^+)$, ν_1, and ν_2 (ClO_4^-) modes show sudden change of slope around 180 K (Figs. 6 and 7).

(iii) The integrated intensities of the $\nu_1'(NH_4^+)$, decrease from 150 to 180 K and then increase steeply up to ~200 K, showing pronounced minima at 180 K (Fig. 6). There is a sudden redistribution of Raman intensities among the factor-group split components of the ν_4 mode of the ClO_4^- ions showing pronounced extrema at 180 K (Figs. 3 and 8).

These anomalous spectral changes around 40 and 180 K cannot be explained in terms of models assuming continuous change in the orientational or rotational freedom of the NH_4^+ and/or ClO_4^- ions, or a continuous and smooth variation of the overall relaxation mechanism as a function of temperature. Our experimental measurements in different spectral regions clearly establish anomalous changes in this system at 40 and 180 K and strongly suggest the existence of phase transformations at these temperatures. These conclusions are supported by the rotational heat capacity[1] measurements, where anomalies in the 30–40 K and at ~200 K temperature regions were detected. The observed Raman features associated with ClO_4^- ions in different scattering geometries at 10, 40, 180 K and other temperatures can be understood in terms of group theoretical predictions and strongly suggest that the space group of the NH_4ClO_4 and the site symmetry of the ions remain the same in the entire temperature range of 10–300 K. Hence the phase transformations take place within the same (D_{2h}) space group of the system.

For proper understanding of the evolution of spectral features as a function of temperature, one has to take into account the various relaxation processes and the changes in the lattice parameters. Let us first consider the variation of lattice parameters. If we plot the measured lattice parameters for NH_4ClO_4[10,13] at 10, 78, 120, and 298 K temperatures (Fig. 9), it is clear that the *a* and *c* axes decrease while the *b* axis increases in going from 78 to 10 K. As no experimental data is available between 298 and 120 K, the exact variation of the lattice parameters is not known in this temperature range. However, the lattice parameters in the analogous systems like NH_4IO_4,[25] NH_4ReO_4,[26] and NH_4BF_4[27] are known to pass through their extremum values around 200 K and the last two systems are also known to have a diffused peak centered around 200 K in the rotational heat capacity data.[28,29] The observation of a diffused peak around 200 K in the temperature-dependent rotational heat capacity data of NH_4ClO_4, the decreasing trend of lattice parameters at 120 K compared to 78 and 298 K, and the observed increase in the frequency shift of vibrational modes around 180 K strongly suggest that the lattice parameters in NH_4ClO_4 should pass through their minimum values

TABLE I. Correlation of the vibrational modes of NH_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
ν_1	A_1	A'	A_g, B_{1u}
			B_{2g}, B_{3u}
		A'	A_g, B_{1u}
ν_2	E		B_{2g}, B_{3u}
		A''	B_{1g}, A_u[a]
			B_{3g}, B_{2u}
		$2A'$	$2A_g, 2B_{1u}$
ν_3/ν_4	F_2		$2B_{2g}, 2B_{3u}$
and NH_4^+ ClO_4^-		A''	B_{1g}, A_u[a]
translation[b]			B_{3g}, B_{2u}
		A'	A_g, B_{1u}
NH_4^+/ClO_4^-	F_1		B_{2g}, B_{3u}
librations		$2A''$	$2B_{1g}, 2A_u$[a]
			$2B_{3g}, 2B_{2u}$

[a] Inactive.

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

around 180 K as indicated in Fig. 9. This apparent decrease of lattice parameters around 180 K is expected to modify the mode frequencies but leaving the linewidths more or less unaffected. As mentioned earlier, linewidths of several modes show drastic changes at 40 and 180 K thereby indicating that other dynamical processes contribute significantly to the observed linewidth of the vibrational modes and a brief discussion of some important processes is given here.

It is well recognized that a number of physical processes contribute to a given line shape and a relaxation mechanism of an excited vibrational state may be studied by measurement of the linewidth of the corresponding Raman bands. The main physical processes contributing to a line shape are population lifetime relaxation of the excited vibrational state, reorientational motion of molecular ions, and anharmonic interactions. The relative importance of each process depends on a particular system. Within the approximation that the vibrational and rotational motions are statistically

TABLE II. Assignment of the observed vibrational modes in NH_4ClO_4 single crystal at room temperature and 10 K.

RT			10 K	
Raman (cm^{-1})	IR (cm^{-1})	Assignment	Raman (cm^{-1})	Symmetry
3267.0	3268.0	ν_3' NH_4^+	3263.5	$A_g + B_{1g}$
3212.5	···	ν_1' NH_4^+	3203.7	A_g
···	2170.0		···	
···	2055.0	$2\nu_3/\nu_3 + \nu_1ClO_4^-$	···	
···	2010.0		···	
1410.0	1410.0	ν_4' NH_4^+	1414.0	$A_g + B_{1g}$
1133.0	1134.0		1138.1	B_{1g}
1109.0	1110.0		1117.0	B_{2g}
1078.0	1078.0	$\nu_3ClO_4^-$	1104.9	B_{2g}
			1072.0	A_g
			1068.9	B_{3g}
937.0	937.0	$\nu_1ClO_4^-$	941.2	B_{2g}
922.0	···	$2\nu_2$ ClO_4^-	939.7	A_g
			924.9	A_g
			642.3	A_g
			640.7	B_{2g}
627.0	627.0		636.2	B_{1g}
632.0	sh[a]	$\nu_4ClO_4^-$	629.6	B_{3g}
			625.0	A_g
637.0	637.0	$\nu_4{}^{37}ClO_4^-$	624.5	B_{2g}
			621.3	A_g
			466.5	B_{3g}
			465.0	A_g
463.0	···	ν_2 ClO_4^-	465.0	B_{1g}
			464.3	B_{2g}

[a] Shoulder.

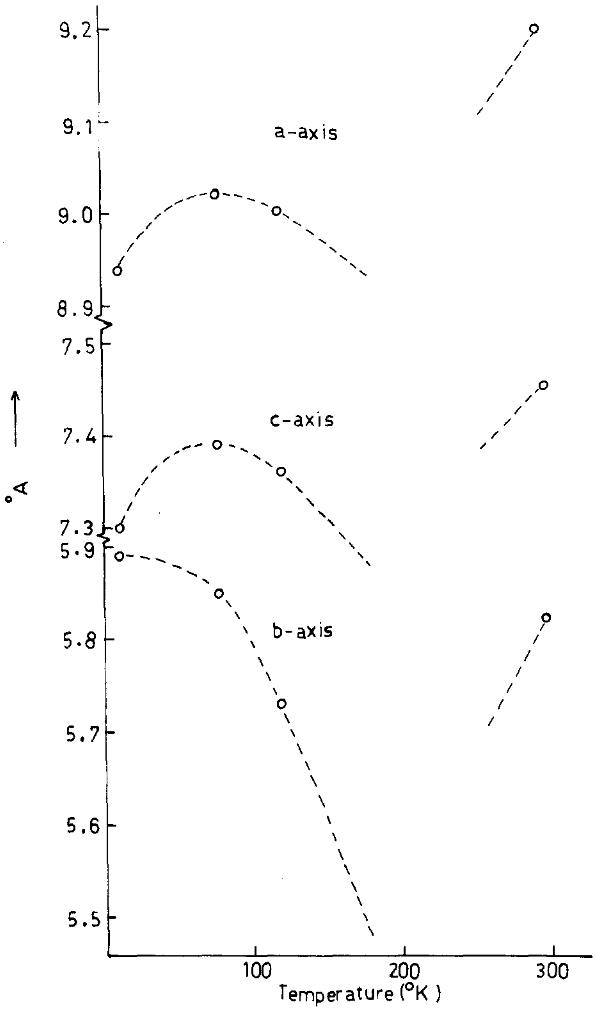

FIG. 9. Variation of the lattice parameters of NH_4ClO_4 as a function of temperature. For details see the text.

independent, it is possible to separate the line broadening contribution due to reorientational motion resulting in the loss of phase coherence and this contributes to the anisotropic part of the Raman scattering (off-diagonal Raman tensor) while other intrinsic vibrational relaxation processes contribute to the isotropic Raman scattering (diagonal components of the polarizability tensor). The angular jumps due to reorientation of the molecular ion from one configuration to the equivalent one make an exponentially varying contribution to the linewidth given by an expression[30]

$$\Gamma_{\text{reorient}} = B_R e^{-U_R/k_BT} \dots, \tag{2}$$

where B_R is the usual prefactor and U_R is the activation energy required for reorientation.

However our linewidth measurement corresponds to only the $A_g(aa)$ components resulting from diagonal scattering and the symmetric Lorentzian line shape rules out the possibility for any significant contribution of reorientational process to the linewidth of the ν_1' mode and suggests that the temperature evolution of the linewidth must be associated with some other physical processes.

The NH_4^+ and ClO_4^- ions in NH_4ClO_4 lattice are bound mainly by hydrogen bonds, which are known to be strongly anharmonic. Anharmonicity can contribute to the temperature-dependent relaxation of an excited vibrational state in two ways. First, anharmonicity gives rise to the thermal expansion of the lattice which results in homogeneous displacement of molecular ions in crystals with a change in temperature leading to a frequency shift but not line broadening. Secondly, anharmonicity also leads to thermal fluctuations in the solid which produce random variations in the crystal potential and hence coupling between different vibrations. This leads to both frequency shift and line broadening and contributes to the band shapes by the following mechanisms.

The excited vibrational state may decay into a number of phonons according to symmetry selection rules and conservation laws due to cubic and quartic terms in the potential energy function. Since the vibrational energy of the stretching modes of an NH_4^+ ion is much larger than kT below 300 K, such processes are not expected to contribute any significant temperature dependence to the linewidth of the NH_4^+ internal modes but may be important for the ClO_4^- ion deformation and lattice modes. The other process of pure vibrational dephasing of the excited vibrational state takes place via the quartic terms in the potential energy function. This can be visualized as an elastic scattering process between the excited vibrational state and some other state which creates a fluctuation in the energy of the excitation thus adding a loss in phase coherence. The excited vibrational state relaxes via coupling between internal vibrational and external rotational–translational degrees of freedom. This process is generated by a large variety of inter- and intramolecular forces including dipole–dipole van der Waals interaction between ions (dispersive forces), dynamic polarization effects introduced during vibration, short-range repulsion, centrifugal, and Coriolis forces, etc. Vibrational relaxation originates either in dephasing of molecular vibrations (analogous to the T_2-type spin–spin relaxation in NMR), or in depopulation of vibrational levels due to inelastic collisions (T_1-type spin-lattice relaxation), or sometimes a combination of the two processes. The pure vibrational dephasing of an excited state due to exchange demodulation (observation of a symmetric Lorentzian line shape indicates that diagonal terms in the quartic component of the potential are important) leads to an Arrhenius-type dependence of linewidth on temperature[31]

$$\Gamma(T) = A + B e^{-U/kT} \dots, \tag{3}$$

where A is a measure of the decay of the excited state via an inelastic three phonon process, while the constant B is related to the inelastic decay of the low frequency lattice mode of energy $U = \hbar\omega_L$ coupling with the interal mode. This process is expected to be important if the energy of the coupling lattice mode $\hbar\omega_L \simeq kT$ at the range of temperatures studied.

In order to explain the temperature dependence of different spectral parameters and dynamics of phase transformations in NH_4ClO_4, we shall divide the discussion into three subsections, viz. high temperature range (300–180 K), intermediate temperature range (180–40 K), and low temperature range (40 K and below).

High temperature range (300–180 K)

The observation of distinct components of the ν_3 and ν_4 (ClO_4^-, F_2) modes in both the IR and Raman spectra at the same frequencies and the appearance of the ν_1(ClO_4^-) mode in the IR spectrum clearly demonstrates that the ClO_4^- ions are distorted and the observed components of the ν_3 and ν_4 modes originate from site symmetry splitting. However, the observation of single bands corresponding to the ν_3' and ν_4' modes in the IR and all the ν_1', ν_2', ν_3', and ν_4' (NH_4^+) modes in the Raman spectrum strongly suggests that the NH_4^+ ions retain a very nearly tetrahedral structure in this temperature range. From the crystal structure data[10] on NH_4ClO_4, it is known that the NH_4^+ ions are surrounded by seven ClO_4^- groups and the ClO_4^- groups are surrounded by seven NH_4^+ groups. Moreover, the comparable value of the linewidth of the ν_2 (ClO_4^-) deformation mode (4.7 cm^{-1}, 270 K) to that of the symmetric stretching ν_1 (ClO_4^-) linewidth (4.2 cm^{-1}, 270 K) indicate that the reorientational contribution to the ν_2 width is negligibly small and hence, the ClO_4^- groups can be taken to be rigid as far as the time scale of measurement is concerned. These observations indicate that the NH_4^+ ions must be reorienting very fast around random molecular axes, thereby averaging out the effect of the crystal field of lower symmetry around it. From the strong IR activity of the ν_4 (ClO_4^-) mode, a measurable correlation field splitting was expected. Although bands were slightly broad at these temperatures, we should have obtained bandhead positions corresponding to the factor-group split components in different polarization geometries even if the components were separated by 0.3 cm^{-1}. As no such splitting was observed in our polarized Raman spectra in the high temperature range, it can be inferred that the correlation field splitting is less than 0.3 cm^{-1}. This, in turn, implies that (a) the resonance coupling of different ClO_4^- groups in the unit cell is insignificant, and/or (b) the crystalline field due to ClO_4^- ions cannot polarize the intermediate NH_4^+ ions (because of very fast reorientation), thereby contributing negligibly to the correlation-field splitting due to coupling of the ClO_4^- groups through polarization of the intermediate NH_4^+ ions.

The nearly constant ν_1' (NH_4^+) linewidth (*aa* geometry) from 190 to 300 K (Fig. 6) rules out the coupling of this mode with librational or other low frequency modes, as this type of interaction is expected to increase the ν_1' linewidth with the increase in temperature. The absence of NH_4^+ librational modes in the Raman spectra in the lattice mode region also supports this view.

Intermediate temperature range (180–40 K)

A comparison of our temperature-dependent frequency shift data and the extrapolated lattice parameters from 300 to 160 K (Fig. 9) indicates that the temperature induced frequency shifts of the vibrational modes is mainly a result of the variation of the lattice parameters. However, the variation of lattice parameters alone appears inadequate to explain the temperature evolution of spectral parameters below 160 K (Figs. 5 and 9).

The rapid decrease of NH_4^+ ν_1' frequency, increase in the ν_2 deformation mode frequencies of ClO_4^- ions and the lattice mode frequencies from 160 to 40 K suggest the formation of hydrogen bonds in this temperature range. The apparent contradictory behavior of increase in the ν_1(ClO_4^-) mode frequency with the formation of hydrogen bonding may be understood in tems of Fermi resonance of ν_1 and $2\nu_2$ modes of the ClO_4^- ion. Our contention is also supported by the presence of similar bands in the Raman spectra[32] of $KClO_4$ where ν_1 and $2\nu_2$ modes are observed at 941.0 and 921.5 cm^{-1}, respectively.

The formation of hydrogen bonds, in turn, is expected to distort the NH_4^+ ion, restrict its reorientational freedom, and also modify the components of induced polarizability along specific directions. The distortion of the NH_4^+ tetrahedra is reflected in the appearance of the ν_1' (NH_4^+) mode in the IR spectrum[13] in this temperature range and by the observation of correlation field splitting in the site symmetry split ν_4(ClO_4^-) components. A rearrangement among the components of the induced polarizability explains the behavior of integrated intensities as depicted in Figs. 6 and 8. However, the sharp dips in the intensity vs temperature curves for some of the modes in the 190–160 K temperature range indicate anomalous behavior of the system. We believe that these anomalies are associated with orientational rearrangement of the ions resulting from the combined effect of changes in the short-range repulsion between the oxygen atoms (separated by less than the sum of their ionic radii) of the cluster of six oxygens around O(2)[10] atom along with the temperature-induced changes in the lattice parameters.

We have observed the NH_4^+ librational mode around 140 cm^{-1} at 50 and 70 K, identified from deuterium shift. This mode broadens rapidly and could not be identified from the background in the 90–160 K temperature range. This observation indicates the presence of very fast relaxation processes and may be correlated with almost instantaneous threefold NH_4^+ reorientations around the N–H bonds in accordance with the QNS[5] results in the 66–150 K temperature range ($\tau_{78\,K} = 9.5$ ps, $\tau_{150\,K} = 1.8$ ps). It is therefore logical to conclude that the reorientation of the NH_4^+ ions is the dominant mechanism for broadening of the ammonium librational modes.

For understanding the linewidth data of the ν_1' mode, we note that the NH_4^+ librations are very anharmonic (librational amplitude is $\sim 30°$ at 78 K[10]) and energies of some of the observed librational modes in this temperature range are comparable to kT. Therefore, the vibrational–librational coupling is expected to contribute significantly to the ν_1' linewidth. As mentioned earlier, expression (3) gives the temperature dependence of the linewidth arising from the aforementioned mechanism. A least square fit of the ν_1' linewidth data to expression (3) was carried out on the smoothly varying part of the curve in the 50–160 K temperature range. We achieved a very good fit with the parameters as given in Table III. The extracted value of the activation energy of 141 cm^{-1} compares well with the observed 0–1 ammonium librational mode at 140 cm^{-1} at 70 K. The value of the decay time of this librational state is extracted to be $\tau = 4.6 \times 10^{-13}$ s. The fast decay of the librational state is responsible for rapid broadening of the NH_4^+ librational

TABLE III. Different parameters which give the best fit to the linewidth of the ν_1' (NH_4^+) mode in the 50–160 K and 10–40 K temperature ranges as per expression (3).

Temperature range K	A cm^{-1}	B cm^{-1}	U cm^{-1}
50–160 K	16.36	23.0	141.0
10– 40 K	11.89	22.02	51.0

modes in the Raman spectra of lattice mode region above 70 K.

Low temperature range (40–10 K)

As mentioned earlier, the spectral changes, especially the frequency shifts of some lattice modes and the NH_4^+ stretching modes, observed at 40 K are characteristic of disorder–order-type phase transformations similar to those observed in ammonium halides[33] at the disorder–order transitions. As some of the modes associated with both the NH_4^+ and ClO_4^- ions show drastic anomalies at 40 K, the phase transformation at the temperature involves the ordering of both the ions. The unit cell volume of NH_4ClO_4 decreases from 40 to 10 K (Fig. 9) and therefore the vibrational mode frequencies of the ions are expected to increase from 40 K to lower temperatures. However, we have observed a rapid decrease in the frequencies of the ν_1' and ν_3' modes of the NH_4^+ ion and an increase in the ν_2 bending mode frequency of the ClO_4^- ion which cannot be explained in terms of lattice contraction itself. These observations along with structural data at 10 K[10] strongly suggest an increase in the hydrogen bonding strength from 40 to 10 K and also indicate that the hydrogen bonding pattern with one straight and strong hydrogen bond and three bent hydrogen bonds at 10 K remains more or less the same up to 40 K. These conclusions are also supported by the observation of a fast increase in the intensity of the ν_1' mode in the infrared spectra[13] below 50 K. A direct consequence of this hydrogen bonding pattern below 40 K is a more favorable threefold NH_4^+ reorientation around the strongest and straight hydrogen bond. This motion is facilitated by the presence of a nearly hemispherical umbrella of six oxygen atoms providing a rather uniform environment for the motion of the H(1) hydrogen atom.[10] This is in agreement with the conclusions arrived at from the rotational heat capacity data.[1]

Coming to the ν_1' (NH_4^+) linewidth we find that in the low temperature range the width also decreases rapidly and nonlinearly in going from 40 to 10 K. For similar arguments advanced in the discussion of ν_1' linewidth in the intermediate range (librational amplitude ~21° at 10 K[10]), we carried out a least square fitting of the ν_1' linewidth data to expression (3) and obtained a very good fit with the the parameters given in Table III. It turns out that the vibrational–librational coupling is again the dominant mechanism for relaxation of the ν_1' vibrational state in this temperature range but the librational mode taking part in this coupling is centered around 50 cm^{-1}. The high frequency librational mode at 156 cm^{-1} (10 K) which is responsible for the vibrational dephasing of the ν_1' mode in the intermediate temperature range (180–40 K) does not contribute much to the linewidth in the low temperature range (below 40 K) justifying the conclusion that $\hbar\omega_L \simeq kT$ for getting a significant contribution to the linewidth from vibrational–librational coupling. We have observed a NH_4^+ librational mode in our Raman spectra at 48 cm^{-1} (10 K), a similar mode was also identified in the inelastic neutron scattering studies by Prager *et al.*[34]

SUMMARY AND FURTHER DISCUSSION

From our detailed temperature-dependent Raman studies on NH_4ClO_4 single crystals over the 10–300 K temperature range, we have identified two phase transformations in this system at 180 and 40 K. The 180 K phase transformation appears to be associated with the orientational rearrangement of the ions with the temperature induced changes in lattice parameters and short-range repulsive forces. On the other hand the phase transformation at 40 K is of disorder–order-type transition resulting from ordering of both the NH_4^+ and ClO_4^- ions due to changes in the hydrogen bonding pattern which restrict the NH_4^+ reorientational freedom. Earlier reports on possible phase transformations in this system at ~70 K and 100–110 K are incorrect, mainly because of insufficient experimental data. From a temperature-dependent Raman study of the $\nu_4(ClO_4^-)$ multiplet in polycrystalline NH_4ClO_4 Schutte[14] found a gradual shift in the position of the high frequency component starting at 70 K and explained it as due to either a phase transformation or a marked change in NH_4^+ reorientational freedom, at 70 K. Our more detailed studies on all the components of the $\nu_4(ClO_4^-)$ mode along with many other bands and lattice modes, in particular, clearly rule out the possibility of any anomaly at 70 K and establish a phase transition at 40 K. Regarding the other suspected phase transition at 100–110 K, van Rensburg *et al.*[13] based their conclusion on the disappearance of the ν_1' NH_4^+ mode in the IR spectra at ~120 K on heating. However, a closer examination of Fig. 4 of their work shows clear shoulder is present in their 120 K spectra due to ν_1' mode. Therefore their conclusions about the 100–110 K phase transformation are inconsistent and it appears that the shoulder might be disappearing at a somewhat higher temperature. Moreover, none of the these speculated phase transformations by these workers are in agreement with heat capacity data.

Comparing our spectral data in the internal and lattice mode regions with the QNS,[5] heat capacity,[1] and structural data,[10,13] the evolution of the dynamics of the NH_4^+ ion can be summarized as follows: in the high temperature range (300–190 K), the NH_4^+ ions are almost freely rotating around random molecular axes without significant hydrogen bonding. As the temperature is lowered below 170 K, formation of weak and nearly equivalent hydrogen bonds results in restricted reorientation of the NH_4^+ ions around the four N–H bonds. This trend continues until around 40 K where the hydrogen bonding pattern changes drastically, further restricting the NH_4^+ ion reorientational freedom. The NH_4^+ ion reorients rather easily around the threefold axis passing through the strongest hydrogen bonded N–H bond compared to the motions along other molecular axes.

From the study of temperature-dependent ν_1' linewidth (aa) as the NH_4^+ ion, it is concluded that the reoreintational contribution is negligible while the librational–vibrational coupling contributes significantly in the vibrational dephasing of the excited vibrational level. It turned out that the high frequency (140 cm^{-1}) NH_4^+ libration couples to the ν_1' mode in the intermediate temperature range (180–50 K), a coupling of the low frequency (~ 50 cm^{-1}) NH_4^+ librational mode with the ν_1' mode providing dominant contribution to the linewidth in the low temperature range (below 40 K).

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