Ammonium ion rotation in ammonium perchlorate as studied by infrared spectroscopy

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The infrared spectra of the ND-stretching bands of dilute NH_3D^+ in NH_4ClO_4 are presented. The spectra are studied over the temperature range from 3 K to room temperature. At low temperatures, the NH_3D^+ is preferentially oriented. The extent of the orientation at a given temperature depends on the deuterium concentration and thus on the concentration of NH_3D^+ ions. As the temperature is raised, the various ND-stretching bands collapse due to a variety of dephasing processes. At low temperature, the dephasing process is phonon-assisted tunneling. As the temperature is raised, dephasing is accomplished by interaction among librational states. At still higher temperatures, the bandwidth is due to stochastic motion of the ammonium ions.

I. INTRODUCTION

Vibrational spectroscopy examines molecules in condensed phases on a time scale of 0.1 to 100 ps. This is very much slower than the time scale of x-ray and neutron diffraction methods but much faster than the time scale of low energy inelastic neutron scattering (INS) or magnetic resonance. Vibrational spectroscopy is uniquely suited to examine systems for which the methods which operate on faster time scales give very different results from those which operate on slower time scales. Ammonium perchlorate below room temperature is a much studied example of such a system. In this paper, we report the results of applying our method of studying motion by vibrational spectroscopy[1,2] to rotation of the ammonium ion in ammonium perchlorate in the temperature range from 3 K to room temperature. We find a complicated structure at 3 K. As the temperature is raised "rotation" sets in. At the lower temperatures, the rotational motion involves tunneling of the ammonium ion. At higher temperatures more usual types of rotation occur. Surprisingly, we also find that the orientation of individual NH_3D^+ ions at low temperature is affected by the concentration of deuterium in the crystal.

Ammonium salts provide crystals exhibiting a very wide range of barriers to the rotation of the ammonium ions and a wide variety of order–disorder phase transitions.[3] Ammonium perchlorate is a particularly interesting example of such a salt. It apparently has a very low barrier to rotation of the ammonium ion with no phase transitions at temperatures up to 511 K.[3] At this temperature, the perchlorate groups become disordered. Indeed, the transition temperature is about the same as that in $RbClO_4$ (548 K), indicating that the orientation of the ammonium ions has little influence on the high temperature crystal structure. At lower temperatures, the rotational motion of the ammonium ion in crystalline ammonium perchlorate changes dramatically as a function of temperature. Neutron diffraction studies indicate random orientation of the ammonium ion in the crystal at room temperature.[4] Evidence from measurements of

the total neutron cross section agrees that the ammonium ions are undergoing nearly free rotation at this temperature.[5] The barrier height estimated from a variety of experiments is exceptionally low, with estimates ranging between 0.5 to 1.0 kcal/mol.[6]

As the temperature is lowered, the ammonium ion rotation slowly freezes out. By liquid nitrogen temperatures, the neutron diffraction data can be analyzed in terms of large-amplitude, rigid-body oscillations about fixed equilibrium positions.[7] By 10 K, these oscillations are sufficiently small to produce a well-defined orientation for the ammonium ions. The crystal has an orthorhombic unit cell, space group *Pnma*. In this structure, the ammonium ion sits in a position of C_s symmetry, with four possible hydrogen atom sites. Two of these sites are on a symmetry plane of the crystal cell, and two (degenerate) sites lie off the plane. All of the hydrogens are weakly bonded to the perchlorate environment with $H \cdots O$ distances ranging from 1.9 to 2.1 Å. On the time scale of neutron diffraction, therefore, the motion of the ammonium ion can be thought of as changing in character from small oscillation at the lowest temperatures to nearly free rotation at higher temperatures.

In addition to the thermally activated rotations of the ammonium ion, INS studies have observed tunneling transitions between 0.02 and 0.08 cm^{-1} which occur at the lowest temperatures.[8-10] The work of Prager and Alefeld[8] revealed a complicated splitting of the ground librational state of NH_4ClO_4. Huller[9] has proposed a model which reproduces the proper number of lines in the INS spectrum if the barrier is taken to be equivalent for rotation about three of the four possible threefold axes; this equivalence is not required by the crystal symmetry. Subsequent work[10] has shown that these tunneling levels shift and broaden with increasing temperature due to interaction with the first excited librational state.

NMR studies also exhibit effects due to the tunneling of NH_4^+ and NH_3D^+ ions in ammonium perchlorate. The NMR spectrum of ammonium perchlorate still shows motional averaging at 1 K, and the tunneling frequency is estimated to be from 500 MHz to 50 GHz.[11,12] Relaxation (T_1) measurements at low temperatures show a large

and complicated dependence of T_1 on the crystal orientation.[13] Moreover, additional relaxation is observed when the crystal is doped with NH_3D^+ impurities. This relaxation is attributed to the motion of the deuterium atoms due to tunneling.[14] Calculations have been done for the librational states of partially deuterated ammonium ions. These calculations are based on the inelastic neutron scattering work and thus on information taken from the very lowest part of librational potential well.[15] Introduction of the deuterium breaks the symmetry and thus the partially deuterated ions are sensitive to terms in the potential that do not affect the spectra observable for NH_4^+ and ND_4^+ ions.

Infrared and Raman studies of ammonium perchlorate have shown definite effects due to ammonium ion rotation, but the explanations have been inconclusive at best. Schutte et al.[16,17] noted large changes in the infrared and Raman spectra of ammonium perchlorate and perdeuterated ammonium perchlorate as a function of temperature due to the onset of rotation or to a possible phase transition at 70 K. Heat capacity studies revealed the onset of rotation, but did not show any phase transitions.[1] A Raman study of the lattice modes also found no evidence for a phase transition near 70 K.[19] Falk et al. examined the spectrum of isotopically dilute NH_3D^+ ions in ammonium perchlorate and found two broadbands at 22 K, below which further splitting was observed.[20]

In this paper, we will first describe the infrared spectrum of isotopically dilute NH_3D^+ ions in ammonium perchlorate from 3 to 200 K. Concentrating on the ND stretching region, the spectra at low temperatures (7 K) show site splittings due to the three distinct deuterium positions in the crystal lattice, plus sum bands with the external motions of the ammonium ion. Moreover, at the lowest temperatures (4 K), the bands from one of the deuterium sites disappear, indicating that the NH_3D^+ ions are partially ordered. Above 10 K, first the site splittings, and subsequently the fundamental and sum bands broaden and collapse in a manner which phenomenologically resembles the temperature dependent collapse of the infrared spectra of water of hydration reported in an earlier paper.[1] The observation of the collapse of the fundamentals and the phonon sum bands at high temperatures requires a slight modification of the Redfield exchange theory previously utilized. We combine our data with that from neutron scattering and diffraction to delineate the various temperature regions in which different models of the rotational motion of the ammonium ion and its coupling to the internal vibrational modes are applicable.

II. EXPERIMENTAL

Crystals of partially deuterated ammonium perchlorate were obtained by recrystallizing reagent grade NH_4ClO_4 from an aqueous solution containing a small amount of HDO. The crystals were then dried and samples were prepared in Nujol or hydrocarbon grease mulls between either calcium fluoride or cesium iodide windows. The concentration ratio of deuterium to hydrogen was estimated from the relative intensities of the infrared stretching bands. Three deuterium concentrations were
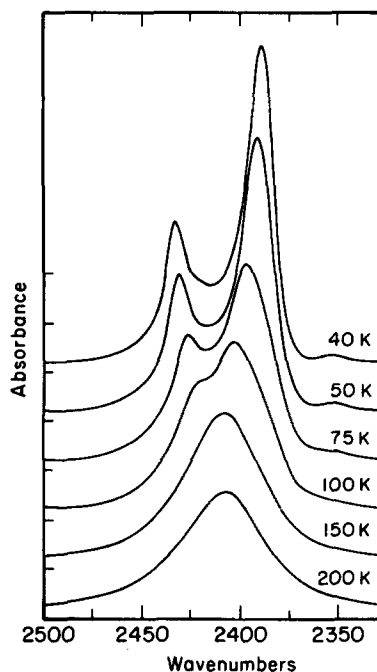

FIG. 1. The infrared spectrum in the ND stretching region of an isotopically dilute sample of NH_3D^+ ions in NH_4ClO_4 as a function of temperature from 40 to 200 K. The deuterium concentration is estimated from relative intensities to be 4 mol %. The spectra in Figs. 1–5 have been redrawn.

studied: 4, 1, and <0.5 mol% D. For convenience these concentrations will be referred to as high, medium, and low, respectively.

The infrared spectra were taken on a model 8000 Nicolet Fourier transform infrared spectrometer. The nominal resolution was $0.5\ cm^{-1}$. The temperature of the sample was held constant to 0.1 K and accurate to ±1 K using the cryostat and controller of Ref. 1 for the spectra between 7 and 200 K. The 4 K spectrum was taken using a modified Hofman Laboratories liquid helium Dewar. Pumping on the liquid helium to achieve a temperature of about 3 K produced no changes in the spectrum.

III. RESULTS AND DISCUSSION

A. Spectra

Above 40 K, the ND stretching regions of the three deuterated NH_4ClO_4 samples were quite similar. Spectra for the high deuterium concentration sample are shown in Fig. 1. Two bands which collapse with increasing temperature are observed, in agreement with the experiments of Falk et al.[20] Below 40 K, these two bands further split into a series of lines whose relative intensity varied with deuterium concentration. The infrared spectra for the three samples from 40 to 7 K are shown in Figs. 2–5.

The fact that the infrared lines were still changing at 7 K prompted us to take spectra of the low deuterium concentration sample at liquid He temperature. The results are shown in Fig. 6 along with the 7 K spectrum of the medium deuterium concentration sample for com
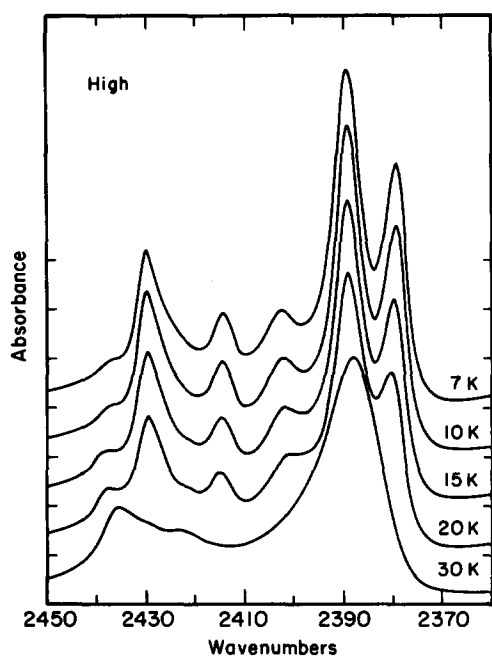
FIG. 2. The ND stretching region of an isotopically dilute sample of NH_2D^+ in NH_4ClO_4 as a function of temperature from 7 to 30 K. 4 mol% deuterium concentration (referred to as "high" in the text).
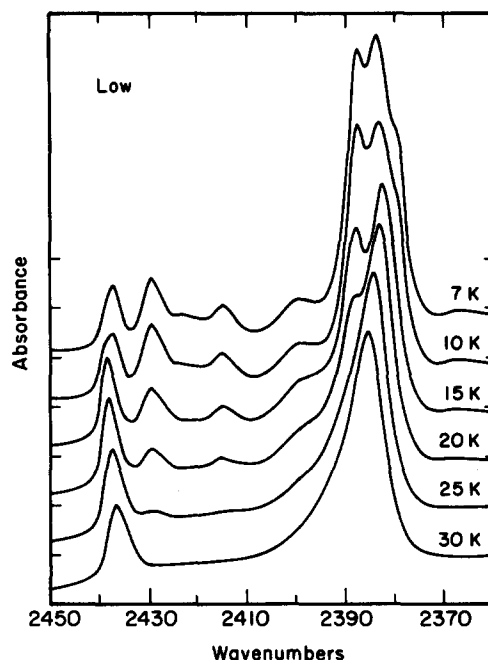

FIG. 4. The same as Fig. 2, but at less than 0.5 mol% deuterium (low).

parison. In addition to the ND stretch, we show the bands due to the ND bend $v_6(e)$ and the antisymmetric hydrogen bend $v_5(e)$ [Figs. 6(b) and 6(c)]. The sharp lines at slightly lower frequency than the NH_3DClO_4 bands are due to NH_3D^+ ions which diffused into the CsI plates. These lines agree with the frequencies previously found for such samples,[21] and served as good markers for the NH_3D^+ bands in the ammonium perchlorate.

B. Assignment

Below 78 K, Choi et al.[7] found that the ammonium rotational motion can be described as a large amplitude libration about an equilibrium position. As stated earlier, the site symmetry for the ammonium ion is C_s. This implies that in the isotopically dilute crystal there are
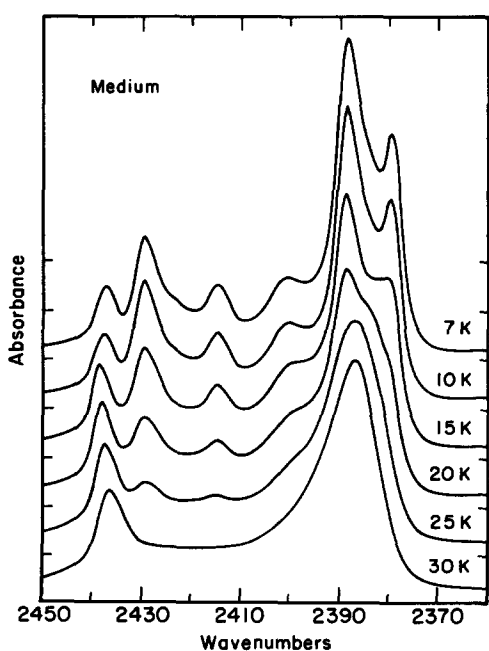

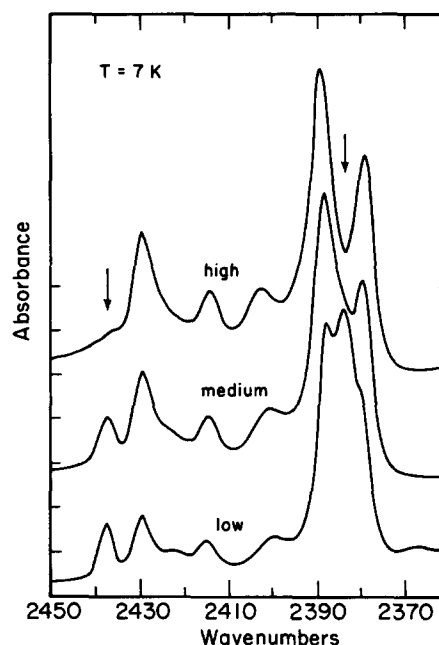FIG. 3. The same as Fig. 2, but at 2 mol% deuterium (medium).

FIG. 5. The ND stretching region of NH_3O^+ in NH_4ClO_4 at 7 K for three different deuterium concentrations (same designations as in Figs. 2–4). The arrows denote the fundamental and librational sum band which are due to the higher energy NH_3D^+ site.
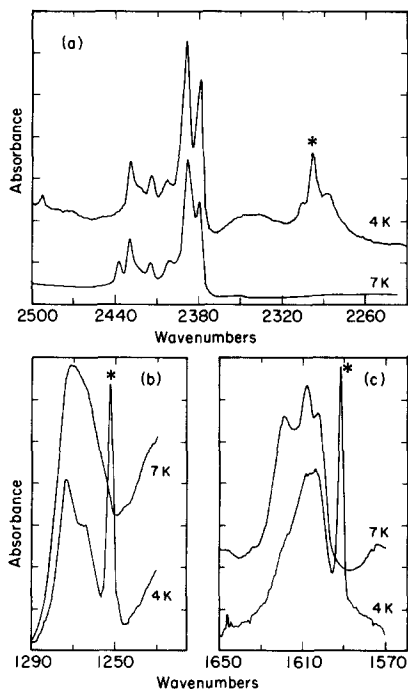
FIG. 6. The 4 K infrared spectrum of NH_3D^+ in NH_4ClO_4 (low deuterium concentration). (a) ND stretching region, (b) ND bend (ν_6), (c) NH bend (ν_5). Bands with an asterisk are from NH_3D^+ ions which have diffused into the CsI plates. For comparison, the 7 K spectra (at medium deuterium concentration) are also displayed.

three distinct orientations for the NH_3D^+ ion, one of which is twofold degenerate. One would therefore expect to see three bands at low temperatures corresponding to a statistical distribution of deuterium atoms in the three sites. The 40 K spectrum (Fig. 1) was previously interpreted in this fashion,[20] assuming that two of the three sites accidentally have the same ND stretching frequency. The appearance of more than three lines at lower temperatures requires a reevaluation of this assignment.

Molecular guests in ionic alkali halide host crystal are known to exhibit strong sum and difference bands with the translational phonon modes of the host crystal.[22] The ammonium ion (and as seen in the bands in CsI in Fig. 6, NH_3D^+) as a guest is no exception. The same phenomenon occurs for NH_3D^+ guests here in the host NH_4ClO_4 lattice. At low temperatures, only the sum bands will be present. A single crystal Raman study of ammonium percholorate has identified lattice modes at 35 and 51 cm^{-1}.[19] Of course, the sum band frequencies we see may be different, due to anharmonicity and to the relaxation of the $k = 0$ wave vector selection rule that applies to the Raman spectrum for the pure crystal. Preliminary inelastic neutron scattering studies of ammonium perchlorate identified phonon modes at 23 and 48 cm^{-1}.[23,24] There is another set of lattice modes calculated[15] and observed[19] above 100 cm^{-1}. These are often considered to be the librational modes. However, in the noncentrosymmetric crystal of NH_4ClO_4 the translation and libration modes are not strictly separable. The same, of course, is true for the localized external modes

of impurities in an NH_4ClO_4 lattice. Furthermore, there is evidence for the existence of a low frequency "unobserved" librational mode.[19] We will call the two sets of modes we see translations (at about 25 cm^{-1}) and librations (at about 50 cm^{-1}). However, each of these modes undoubtedly contain both rotational and translational character, and we will return to the question of their character after examining the spectra.

If we assume that there are three possible deuterium sites, each giving rise to a fundamental plus two sum bands at approximately 25 and 50 cm^{-1} above the fundamentals, there would be a maximum of nine infrared lines in the ND stretching region at low temperatures. Indeed, we see eight lines in the 7 K spectrum at low and intermediate deuterium concentrations. Thus, we can make assignments to the lines as shown in Fig. 7 and listed in Table I. Note that the lattice modes, particularly the librational mode ν_L, are expected to be very anharmonic and strongly coupled to the internal modes of the ammonium ion. Thus, the ν_L sum frequency need not be the same for the different sites.

The 7 K spectrum at low deuterium concentration shows bands from each of the three sites. Spectra both at lower temperature and at higher deuterium concentration show bands from fewer sites. The 4 K spectrum at low deuterium concentration (Fig. 6) shows bands missing at 2384.5 cm^{-1} in the fundamental region and at 2437 cm^{-1} in the librational sum band region. These two bands must belong to one of the sites which we label "$D3$," and this site must have an energy on the order of 5 K higher than sites $D1$ and $D2$. Surprisingly, a similar spectral change occurs at the fixed temperature of 7 K as the deuterium concentration is increased (Fig. 5). It is the same two bands that disappear, and thus, it is site $D3$ that is raised in energy by increasing
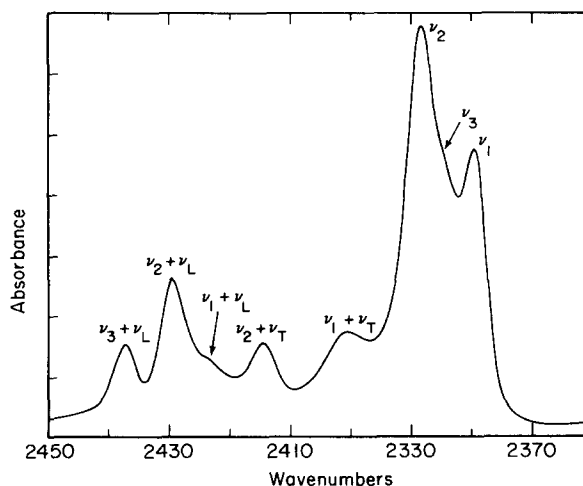

FIG. 7. Assignments in the ND stretching region at 7 K for the medium deuterium concentration sample. We observe fundamentals from the three deuterium sites ν_1, ν_2, and ν_3, two translational bends $\nu_i + \nu_T$, and three librational combination bands $\nu_i + \nu_L$. The ν_3 bands have been assigned by their temperature dependence to site $D3$ (see the text). Bands ν_1 and ν_2 and their associated sum bands belong to sites $D1$ and $D2$. See also Table I.

TABLE I. Low temperature frequencies and assignments in the ND stretching region at NH_4ClO_4.

Infrared band	Frequency (cm^{-1})[a]
Fundamentals[b]	
ν_1	2379.5 ± 0.5
ν_2	2388.2
ν_3	2384.5
Translation sum bands	
$\nu_1 + \nu_T$	2400.4
$\nu_2 + \nu_T$	2414.5
Libration sum bands	
$\nu_1 + \nu_L$	2423.0
$\nu_2 + \nu_L$	2429.1
$\nu_3 + \nu_L$	2437.0

[a]Frequencies taken from the medium deuterium concentration sample.
[b]Fundamentals are labeled 1 to 3 corresponding to the three possible NH_3D^+ orientations. Position 3 is the off-axis degenerate site (see the text); the remaining two positions are arbitrarily labeled 1 and 2.

the deuterium concentration. That site $D3$ still exists, but is raised in energy, is demonstrated by the observation that the $D3$ bands do occur at successively higher temperature for samples of successively higher deuterium concentration. Simplifications also occur in going from 7 to 4 K in the other two observable NH_3D^+ bands [Figs. 6(b) and 6(c)].

Further assignment of the infrared bands requires a knowledge of the relative energies of the three sites for the NH_3D^+ ion. In our previous paper,[1] we found that, in weakly hydrogen-bonded systems, an electrostatic energy calculation for a crystal predicted the correct form of the intermolecular potential for the librational motion. We therefore decided to calculate the electrostatic energy of interaction for the NH_3D^+ ion with the host NH_4ClO_4 lattice in the four possible NH_3D^+ ion orientations in an attempt to reproduce the energy differences observed in the infrared spectrum.

The model we used was the simple point charge model of Ref. 1. The perchlorate ions were treated as having a $+3e$ charge on the chlorine atom and four $-1e$ charges on the oxygen atoms; the ammonium ion consisted of a $-1e$ charge on the nitrogen and four $+0.5e$ charges on the hydrogen atoms. The interatomic distances and unit cell dimensions were taken from the neutron diffraction data of Ref. 7 at 10 K, except that the lengths of the NH (and ND) bonds were all standardized at 1 Å. This latter precaution was taken to keep the center of charge of the ammonium ions on the nitrogen.

To model the orientational forces on the NH_3D^+ ions in this simplified calculation, a normal ammonium ion was modified to have an additional dipole moment in the direction of the ND bond by putting an additional positive charge on the deuterium and an additional negative charge on the

nitrogen. Introduction of this dipole mimics the asymmetry of the NH_3D^+ due to three effects: (1) The center of NH_3D^+ is no longer at the center of charge and thus the ion does have a dipole moment. (2) Introduction of the deuterium leads to small changes in the electronic structure (as in CH_3D). (3) The effective N–D bond length is shorter than the NH bond length leading to an ion with asymmetric short range interactions with its neighbors. All of these effects have the symmetry (though not the range) of a simple dipole moment. Furthermore, each of these effects can couple the orientations of NH_3D^+ ions together. The dipoles can couple directly or via polarization of the intermediate ClO_4^- ions. Only the direct charge forces are summed in our calculation, so that the results can be taken only as a qualitative guide.

The electrostatic energy of interaction was calculated directly by summing over successive shells of unit cells of approximately equal distance away from the NH_3D^+ ion (i. e., a shell consisted of all cells with the same r where $r = |x| + |y| + |z|$ for a cell $xa + yb + zc$ away; x, y, z are whole numbers and a, b, and c are lattice vectors). Two checks were performed on the energy calculation to insure that there were no boundary or convergence errors. First, since the NH_3D^+ ion is not in the center of the unit cell, the direct calculation does not automatically preserve the symmetry of the two degenerate NH_3D^+ ion orientations. The number of unit cells included in the calculation was therefore increased until the energies for the two equivalent NH_3D^+ orientations had sufficiently converged.

The second check was to calculate the electrostatic energy of interaction by a completely different method, a Bertaut calculation in reciprocal space.[1,25] The energy for an ammonium perchlorate crystal with a single NH_3D^+ ion (in a given orientation) in every cell was calculated, and then the electrostatic energy for the lattice of the NH_3D^+ dipoles alone was subtracted from that number. The difference should be just the electrostatic energy of interaction between the dipole lattice and the host lattice, eliminating the dipole–dipole effects. The energy differences calculated by this method were identical to those calculated in direct space.

The energies for the three deuterium positions are shown (Fig. 8) as functions of the shell size of the direct calculation. The energy scale in the figure is arbitrary, depending on the size of the dipole on the NH_3D^+ ion. The doubly degenerate sites, $D3$, have the highest energy, and we can assign the higher energy infrared bands to these two off-axis NH_3D^+ orientations. This assignment explains the fact that the bands of the higher energy site gain intensity steadily (Figs. 2–4), eventually surpassing the intensities of the bands of the other two orientations. If we assume that the intrinsic intensities of the bands for each site are approximately equal, this large increase in intensity with temperature can only occur if it is the doubly degenerate site which has the higher energy.

These energy calculations should only be used to qualitatively order the energies of the NH_3D^+ orientations. The infrared spectra indicate that the energy difference
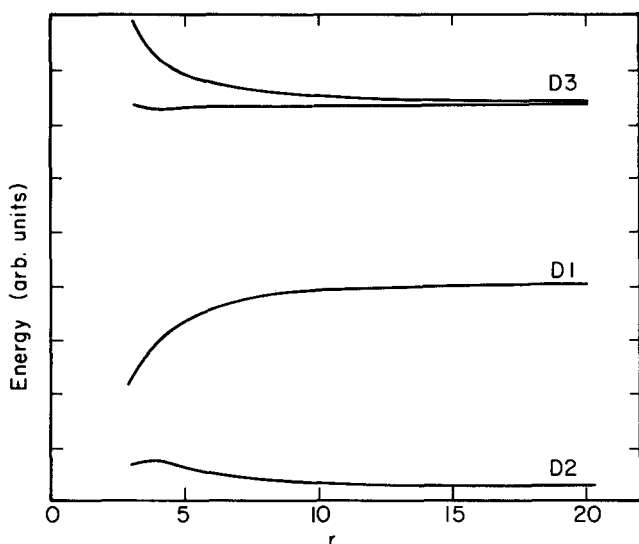
FIG. 8. The electrostatic energy of interaction between an NH_3D^+ ion and the surrounding NH_4ClO_4 lattice. r^3 is a rough estimate of the number of unit cells included in the calculation (see the text). The three possible deuterium sites are labeled D1, D2, and D3, with the latter being doubly degenerate. The energy scale is arbitrary. Convergence in the calculation is determined by the convergence of the energy calculated for the two D3 sites, which are equivalent in the crystal, but are not constrained to be so in the calculation.

between the two lower energy deuterium positions D1 and D2, is not as great as the electrostatic energy calculations predict, since the relative intensities of the D_1 and D_2 bands do not noticeably change as a function of temperature.

The Bertaut calculation with the dipole–dipole (NH_3D^+–NH_3D^+) interaction left in gives a qualitative indication of the concentration-dependent orientation of the NH_3D^+ ions. The energy levels were calculated in order of increasing energy as D3, D2, and D1. This is opposite to the order given by the calculation without the dipole–dipole interaction and disagrees with the experimental observation that the D3 site becomes less populated as the concentration of deuterium increases at constant temperature. The calculation does serve to show that the orientation of the NH_3D^+ ions can be affected by coupling the ions via a dipole moment. However, the Bertaut calculation with one NH_3D^+ in the same position in each unit cell is not a good model for the random placement of NH_3D^+ in the real crystal containing a low concentration of deuterium atoms.

C. Temperature dependence

Having assigned the ND stretching bands in the infrared spectrum, we can now describe their temperature dependence. First of all, we assume that the hydrogen and deuterium atoms are mobile on the time scale of the experiments at all temperatures. This means that we always see spectra arising from an equilibrium distribution of ammonium ions. The evolution with temperature of the rotational motion is continuous, but we will arbitrarily consider four regimes in which

certain theories or pictures of this motion are applicable. We will also discuss the results of other spectroscopies in each temperature region.

The motional averaging processes which are occurring in ammonium perchlorate can best be explained in terms of the energy level diagram for the NH_3D^+ ion drawn in Fig. 9. We have included in the diagram the first two librational levels of the ground vibrational state and first three levels of the first excited level. In this simplified picture, we consider only one external mode (the libration). Additional energy levels can be included to illustrate the processes that affect the translational bands.

Three classes of energy levels are shown schematically in Fig. 9: site splittings which are about 10 K or 8 cm^{-1} in magnitude, librational energy levels which are 50 cm^{-1} magnitude, and the ND stretching levels of 2400 cm^{-1} magnitude. The doubly degenerate site, D3, is higher in energy for all deuterium concentrations.

1. Very low temperatures (<5 K)

At these temperatures, the NH_3D^+ ions are partially ordered, i.e., one of the three possible orientations of the N–D bond, D3, is not populated in the crystal. Several lines in the infrared spectrum due to this deuterium site are gone (see Fig. 6). The only motions which the NH_3D^+ ions undergo are small-amplitude librations and tunneling between the two remaining possible orientations. This tunneling has been observed for NH_4^+ ions in the form of tunneling splittings in the neutron scattering experiments, and for NH_3D^+ impurities in NMR
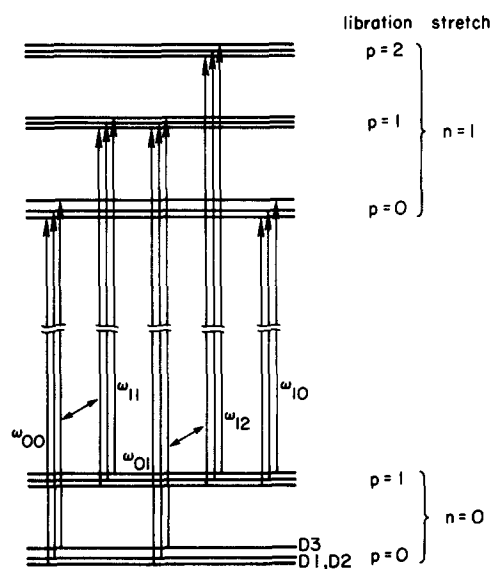

FIG. 9. Energy level scheme for an isolated NH_3D^+ ion in ammonium perchlorate. The ground vibrational state for the N–D stretch ($n = 0$), and the two lowest librational levels ($p = 0$ and $p = 1$) are shown along with the site (D1, D2, and D3) splittings due to the crystal lattice. The $n = 1$ vibrational level with its lowest three librational levels is also depicted. Possible infrared transitions are drawn in. The stretching frequency is about 2400 cm^{-1}, the librational frequency about 50 cm^{-1} and the site splittings, less than 10 cm^{-1}.

relaxation measurements of the host lattice. Note that since the neutron scattering is for NH_4^+, rather than NH_3D^+, quantitative comparison with our results is difficult. The small amplitude nature of the librations of the ions manifests itself as sharp lines in the Raman spectrum of the lattice modes (with well-defined factor group splittings) and as well-defined thermal ellipsoids about fixed hydrogen sites in the neutron diffraction data.

2. Low temperature (5–30 K)

At very low temperatures (Fig. 6) we see four bands due to the fundamental ω_{00}, and the libration sum band ω_{01} from sites D_1 and D_2 (Fig. 9). There are also two translation sum bands which are not included in the energy level diagram. As the temperature is raised, the bands arising from site $D3$ grow in (Fig. 6). Since these bands achieve a substantial intensity by 7 K, $D3$ must have have an energy about 7 K or 4 cm^{-1} above that of the $D1$ and $D2$ sites. Since we did our experiments at 3 and 4 K and those at 7 K and above in different crystals, we did not take experiments at very small temperature intervals in this range. Thus the presence of a phase transition or other anomaly is not ruled out. Be that as it may, by 10 or 15 K, the structure due to the three discrete sites begins to collapse and by 30 K, only two bands are seen in the spectrum (Figs. 2–4). The two bands are the fundamental at about 2385 cm^{-1} and the librational sum band at about 2437 cm^{-1}. The barrier to the rotation of the NH_3D^+ is estimated to be 150 cm^{-1} or higher. This makes the collapse of the site split bands by a process involving site hopping impossible. Instead the bands must average via a phonon-assisted tunneling mechanism.[26-28] We envision the process by which the bands collapse as one in which a T_2 or pure dephasing process results by rapid motion of the system among the tunneling energy levels.

The other spectroscopies have also observed temperature-dependent phenomena in this temperature region which are presumably due to phonon-assisted tunneling, but so far no theory that explains the observations is available. The inelastic neutron spectrum shows the transitions among the tunneling energy levels directly.[10,27] The bands due to these transitions shift in a complicated way between low temperature and 40 K. In the same temperature, the width of the bands increases with an activation energy of about 177 cm^{-1}. The 177 cm^{-1} is higher than the frequency of the librations. At higher temperatures, the INS bands become too broad to observe. The Raman-active lattice modes show a similar rapid increase in width between 18 and 82 K.[19] The variation of T_1 relaxation in the NMR is also a rapid function of temperature.[13] Neutron diffraction shows large thermal ellipsoids for the libration of the ammonium ion even at 10 K.[7]

3. Intermediate temperature (30–150 K)

Above 30 K, the infrared bands from the different sites have merged into single peaks, and therefore, we no longer distinguish between these sites in discussing the spectra. The spectrum has collapsed to two bands (Fig. 1), the fundamental at about 2390 cm^{-1} and the li-
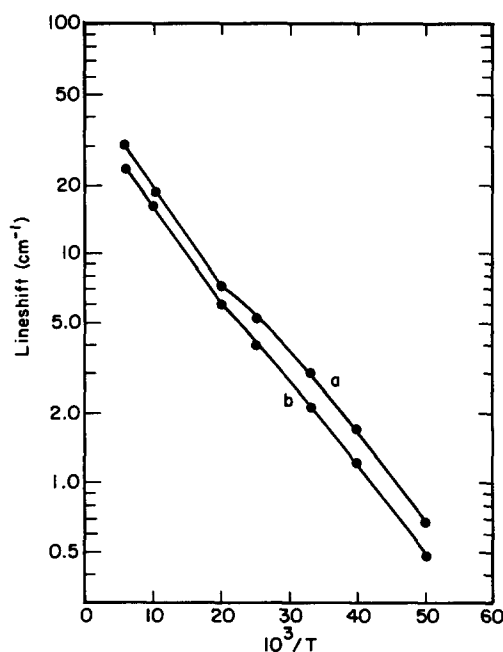

FIG. 10. The observed line shifts of the fundamental (a) and the librational sum band (b) of the NH_3D^+, ND-stretching band in ammonium perchlorate plotted semilogarithmically vs $1/T$.

brational sum band at about 2430 cm^{-1}. The translational sum bands have broadened to the point at which they cannot be identified.

The logarithm of the line shifts of the two bands are plotted vs $1/T$ in Fig. 10. The near-exponential behavior of the line shifts suggests that the collapse can be explained in terms of a simple dephasing model for the ND stretching vibration. For our model we will use the vibration-libration Hamiltonian from our previous paper.[1] The Hamiltonian can be broken into three parts:

$$H_{TOT} = H_V + H_L + H_{LV} , \tag{1}$$

$$H_V | \psi_n(q) \rangle = (T_V + \tfrac{1}{2} m\omega_0^2 q^2) | \psi_n \rangle = \hbar\omega_0(n + \tfrac{1}{2}) | \psi_n \rangle , \tag{2}$$

$$H_L | \phi_p(\theta) \rangle = (T_L + V_L) | \phi_p \rangle = \epsilon_p | \phi_p \rangle , \tag{3}$$

$$H_{LV} = m\omega_0 \delta\omega(\theta) q^2 . \tag{4}$$

Here H_V is the Hamiltonian for the N–D stretching motion with coordinate q, harmonic frequency ω_0, effective mass m and eigenfunctions ψ_n. H_L refers to the librational motion with eigenfunctions ϕ_p and eigenvalues ϵ_p. H_{LV} is the coupling term which is proportional to a frequency shift $\delta\omega(\theta)$, where θ is the librational coordinate. T and V are kinetic and potential energies, respectively. If H_{LV} is small compared to H_V and H_L, the eigenvalues of H_{TOT} are approximately given by[1]

$$E_{n,p} = \epsilon_p + \hbar\omega_0(n + \tfrac{1}{2}) + \hbar\langle\delta\omega\rangle_p(n + \tfrac{1}{2}) , \tag{5}$$

where

$$\langle\delta\omega\rangle_p = \langle\phi_p|\delta\omega(\theta)|\phi_p\rangle .$$

Equations (1)–(5) are identical to those used in our model of $NaClO_4 \cdot H_2O$,[1] except that the librational potential V_L is not the same. In addition, we are interested not only in the fundamental vibration $\omega_{p,p}$ (Fig. 9) but also

in the sum and difference bands $\omega_{p,p+1}$ and $\omega_{p,p-1}$. In general, the frequency $\omega_{pp'}$ is given by

$$\omega_{pp'} = \omega_0 + \tfrac{3}{2}\langle \delta\omega \rangle_{p'} - \tfrac{1}{2}\langle \delta\omega \rangle_p + \Omega_{p'} - \Omega_p , \qquad (6)$$

where

$$\Omega_p \equiv \frac{\epsilon_p - \epsilon_0}{\hbar} .$$

We can now return to a discussion of the energy level diagram in Fig. 9, remembering that we can ignore the site splittings of the librational levels. At the lowest temperatures, only ω_{00} and ω_{01}, the fundamental and the phonon sum band, are observed. As the crystal is heated, the ions are occasionally excited to the next highest librational state $(p=1)$. This occasional excitation leads to a dephasing of the two vibrational bands. In principle, we should include the coupling of ω_{00} and ω_{01} to each of the three new bands, ω_{11}, ω_{12}, and ω_{10}. However, to first order we need only consider exchange dephasing processes of near resonant transitions.[29] Therefore as a first approximation, we can say that ω_{00} will interact exclusively with ω_{11}, and ω_{01} will interact exclusively with ω_{12}. The remaining band ω_{10} will contribute to the line shape only through its isolated absorption. This band could be the low frequency shoulder at about 2390 cm^{-1} in the 100 K spectrum (Fig. 1). As the temperature increases, the fundamental, sum and difference bands become closer in energy, and the various dephasing cross terms which we have ignored will eventually contribute to the line shape.

Since we have limited ourselves to the lowest two levels, we can consider the two exchanging systems in Fig. 9 to be separate two-state "hot band" dephasing systems such as those described by the low temperature limit of the Redfield theory[1] and other similar models.[31,32] For such systems, the line shifts have been shown to be exponential in behavior vs $1/T$:

$$\Delta\omega_a(T) = (\omega_{11} - \omega_{00})\exp(-\hbar\langle \Omega_1 \rangle/kT) , \qquad (7)$$

$$\Delta\omega_b(T) = (\omega_{12} - \omega_{01})\exp(-\hbar\langle \Omega_1 \rangle/kT) , \qquad (8)$$

where $\langle \Omega_1 \rangle = \Omega_1 + \tfrac{1}{2}(\omega_{11} - \omega_{00})$ and $\Delta\omega_a$ and $\Delta\omega_b$ refer to the line shifts of the fundamental and sum band, respectively. The slopes of the lines plotted in Fig. 10 give an energy splitting of 55 cm^{-1}, which is close to the 50 cm^{-1} that we obtain for the frequency of the librational mode from the position of the sum bands. Unfortunately, the high temperature intercepts of the line shifts in Fig. 10 lead to frequency shifts ($\omega_{11} - \omega_{00}$ and $\omega_{12} - \omega_{01}$) which are inconsistently large (~ 40 cm^{-1}). It is, of course, not surprising that this theory gives anomalous results at high temperatures.[33]

III. SUMMARY AND FURTHER DISCUSSION

We have studied the infrared spectrum of ammonium perchlorate lightly doped with deuterium over the temperature range from about 3 K to room temperature. Over this temperature range, ammonium perchlorate exists in one crystal form, but the N–D stretching bands show a rich and unexpected variety of dynamic phenomena. The deuterium atom can occupy any of four positions, two of which are degenerate. At very low deu-

terium concentrations, 0.5 mol% or less, three distinct N–D stretching bands attest to the existence of the three types of sites. The temperature dependence of the intensity of these bands show that the three types of orientation differ in energy by 5 to 10 K.

At somewhat higher deuterium concentrations, the spectrum changes due to an increase in the energy differences among the three orientations. The orientation dependence of the interaction of the NH$_3$D$^+$ ions with the rest of the ammonium perchlorate lattice is qualitatively modeled by electrostatic calculations which assign a dipole moment to the NH$_3$D$^+$ ions. The change in the orientation with increasing deuterium concentration should then be modeled by the dipole–dipole interactions among the NH$_3$D$^+$ ions. Our calculations of these interactions for realistic distributions of NH$_3$D$^+$ ions in the lattice will be worthwhile when more detailed measurements of the temperature and concentration dependence of the orientation become available. Although, we cannot explain the interaction in detail, we note that it is well known that the transition temperatures of order–disorder transitions involving hydrogen atoms shift upon deuteration.[3] For example, the phase transition in KH$_2$PO$_4$ shifts almost 100 K upon deuteration and the two phase transitions of NH$_4$Cl shift 5 to 8 K.

The orientational energy of a single NH$_3$D$^+$ in a NH$_4$ClO$_4$ lattice must depend on the shifts in zero point energies of all the vibrations with orientation. The accounting for the effects of all the vibrations is difficult to do; see, for example, the discussion of the simpler case of the partially deuterated methyl rotator in toluene.[34] The orientation dependence on NH$_3$D$^+$ ion concentration deserves further study. We intend to pursue this both by studying other crystals and by going to lower temperatures. Since the orientation of the ion at low temperatures is markedly dependent on the deuterium concentration, it is probably necessary to study the entire temperature range without having to change samples or cryostats.

At higher temperatures, from about 7 to 30 K, the bands due to the different orientations of the NH$_3$D$^+$ merge. This merging is due to rapid dephasing due to exchange. The exchange must occur by phonon-assisted tunneling. It would be desirable to further demonstrate the existence of phonon assisted tunneling by showing that the rate of exchange varies as a low power of the temperature and that it varies in a predictable way with isotopic substitution.[27,28] However, we have not been able to resolve the bands sufficiently in this temperature regime to obtain the temperature dependence. Furthermore, the effects of isotopic substitution on the tunneling levels are profound and mask the simple isotope effects that would provide a test of the tunneling hypothesis.

As the temperature is further increased, the first librational level at about 50 cm^{-1} becomes populated. This provides a new dephasing mechanism which explains the behavior of the spectrum in the 30 to 150 K range. We see a set of sum bands with a spacing of about 50 cm^{-1} and the rate of shift of the bands with temperature gives an energy of 55 cm^{-1}. This has led us to consider that there is only one external mode with

an energy of about 50 cm^{-1} which participates in a significant way in the phenomena we observe, and we consider this mode to be a libration. The other set of sum bands at about 25 cm^{-1}, we have assigned as translation. There are many more modes of both the NH$_3$D$^+$ and of the host lattice to be accounted for but our simple description suffices to explain our observations. Furthermore, the various dephasing mechanisms may be significant in overlapping temperature ranges. Indeed, study of the CHD$_2$ bands of toluene led to the conclusion that both the tunneling mechanisms and librational fluctuations contribute to relaxation.[34]

In the highest temperature range, we see only one band. The width and position of this band is probably best explained by a model which considers stochastic interactions with many of the surrounding molecules. Formal equations of this sort are discussed for toluene.[34] However, the most promising approach to these complex interactions may be by molecular dynamics simulations of a portion of the solid, or at a bit simpler level, by Brownian dynamic simulations.[33]

The absence of phonon sum bands in the vibrational spectra of solids composed of small molecules has long been used as an indication of rotational motion. Our experiments provide a basis for a more precise discussion of the meaning of these sum bands. In particular, the absence of observable phonon bands may only indicate that there is one or more types of rapid relaxation of the phonons which either "wash out" or collapse the phonon bands.

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