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A probe of the dynamics of NH_4^+ ions in $\text{NH}_4\text{Dy}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ crystals via vibrational spectra

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Received 23 June 1992

Abstract. Infrared spectra of ammonium dysprosium sulphate tetrahydrate ($\text{NH}_4\text{Dy}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) were investigated at $95 < T < 315$ K with a view to understanding the dynamics of NH_4^+ ions in the lattice. The observed vibrational behaviours, i.e. splitting of the vibrational modes, shifts in frequencies, and linewidths of the ammonium vibrations in the lattice, were tested against two vibrational exchange dephasing models. Our results suggest that at $95 < T < 200$ K the behaviour of the ammonium modes is consistent with the Harris–Shelby–Cornelius model, where the high-frequency modes dephase independently via specific low-frequency modes that are undergoing exchange with the thermal bath. The dephasing channels were identified with the librations of the ammonium ions. At $200 < T < 275$ K, vibrational dephasing channels are more complex and can no longer simply be equated with ammonium librational modes, thus suggesting additional motion of the ammonium ions in the lattice. It is also argued that at $200 < T < 275$ K the motion of the NH_4^+ ion in the lattice can best be described as a superposition of large-amplitude reorientational motion and small-amplitude librational fluctuations. Above 275 K, ammonium ions in the lattice almost attain free rotation, thus modulating the intermolecular interactions in the lattice.

1. Introduction

The ammonium lanthanide sulphate tetrahydrates ($\text{NH}_4\text{L}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{L} \equiv \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy}$) and the rubidium lanthanide sulphate tetrahydrates ($\text{RbL}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{L} \equiv \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Er}$) crystallize with a monoclinic structure at room temperature. These crystals have interesting features because: (i) not only are $\text{NH}_4\text{L}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (ALSTH) and $\text{Rb}_4\text{L}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (RLSTH) lattices isostructural within the series but ALSTH and RLSTH lattices are also isostructural with each other, and (ii) all lattices in both series, except ADySTH and RErSTH , undergo a structural phase transition at $T < 300$ K [1–4]. In fact, most of the crystals of the ALSTH and RLSTH series, depending on the lanthanide ion, show multiple structural phase transitions. Because the ALSTH and RLSTH series form a large group of crystals which are isostructural at room temperature [3], yet have unique thermodynamic behaviour at $T < 300$ K, these lattices have the excellent potential of serving as hosts to test various thermodynamic theories or models.

The presence of the structural phase transitions in ALSTH lattices has been ascertained either by specific heat capacity (C_p) [1, 2] or by the electron paramagnetic

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resonance (EPR) [4–6] technique. The results have proven controversial. The EPR measurements of Gd^{3+} doped in ACeSTH and ASmSTH crystals [4–6] suggest three phase transitions in these lattices at $140 < T < 290$ K, while the C_p data indicate only two phase transitions in ACeSTH and ASmSTH [2]. Also, the observed heat capacity anomaly associated with the highest temperature phase transition in ACeSTH and ASmSTH reflects a typical order–disorder λ -shape; while from the EPR measurements [4], it has been claimed that these transitions are of the first order. Besides the aforementioned controversies, the heat capacity data on ALSTH lattices suggest an additional anomaly which manifests itself as a very broad peak at $200 < T < 300$ K [7]. The EPR or heat capacity data fail to provide an adequate explanation for this additional anomaly. Whether this additional peak can be ascribed to some extra degrees of freedom attained by the lattice remains unanswered. Also, whether this additional anomaly has any role in driving the structural transitions in ALSTH needs to be ascertained.

The dynamics in molecular crystals usually are probed with the help of NMR and incoherent neutron scattering techniques. These techniques measure the Fourier transformed orientational autocorrelation function from which information about the dynamics of molecules in condensed phases can be extracted [8]. More recently, vibrational spectroscopy has been applied to the same end [9–13]. This technique is uniquely suited for this study since it operates on a time scale intermediate between that of NMR and diffraction methods. The intramolecular modes of the polyatomic units that are probed by vibrational spectroscopy decay by population relaxation (T_1 processes) and/or vibrational dephasing (T_2 processes). The decay is manifested experimentally in the lineshape, linewidth, and frequency shift of the vibrational band. In condensed phases, the T_1 relaxation processes, which involve a vibrational energy transfer to the thermic bath (i.e. the reservoir), are usually much slower than the phase relaxation (T_2) processes [14, 15]. Hence, they do not contribute significantly to band broadening. Of the T_2 mechanisms, it has been pointed out [10, 11] that the intermolecular energy exchange of low-frequency modes plays an important role in the dephasing of high-frequency vibrations via the anharmonic portion of the vibrational potential. For several systems, the low-frequency exchanging modes are observed to be the torsional modes of the polyatomic units [12, 13, 15]. If such is the case for ALSTH lattices, then a temperature-dependent analysis of the vibrational spectrum will provide information about the molecular motion in different temperature ranges. Therefore, we undertook infrared measurements at $95 < T < 315$ on $NH_4Dy(SO_4)_2 \cdot 4H_2O$ (ADySTH) crystals with a view to ascertaining the dynamics of ammonium ions in the lattice. From the identification of the dephasing modes, information regarding the dynamics of the ammonium ions has been extracted. The choice of ADySTH as the test system over the other isostructural ALSTH lattices was guided by the fact that interpretation of the spectrum would not be hampered by a phase transition that could alter the known room temperature crystal structure.

2. Theoretical background

The basic description of the vibrational exchange problem can be given in terms of a zero-order vibrational Hamiltonian H_0 , which describes the energy levels of the fundamentals (A, B) and their interaction with low-frequency exchanging modes (L),

a zero-order reservoir Hamiltonian H_R , and a coupling V between the vibrational system and the reservoir. It has the form

$$H = H_0 + H_R + V. \quad (1)$$

For nearby or overlapping vibrational bands, two models have been successfully used to interpret the temperature dependence of experimentally observed line shapes, HSC exchange [10] and AO exchange [11] (identified by the initials of the researchers who put forth these models). The key difference between these two approaches is the partitioning of the degrees of freedom of the molecule and its surroundings in order to identify the dominant anharmonic interactions responsible for dephasing. In the HSC exchange model, dephasing arises from random modulation of the vibrational frequency caused by intramolecular anharmonic coupling of the vibrational fundamental (A) to low-frequency modes (L) which are undergoing intermolecular energy exchange with the bath. Therefore, for the HSC model

$$H_0 = H_A + H_L$$

and

$$V = H_{AL} + H_{RL} \quad (2)$$

where H_A and H_L represent the unperturbed vibrational mode A and exchange modes L , H_{AL} is the perturbation which couples the A and L modes causing a frequency shift $\delta\omega$, and H_{RL} describes the interaction between the reservoir and the L modes.

In the AO model, two fundamentals, say A and B , that lie close together in frequency (splitting = $\delta\omega$ at $T = 0$ K) are coupled via a low-frequency mode (L) whose thermal excitation results in the vibrational dephasing of modes A and B . For the AO model, the terms in equation (1) have the form

$$H_0 = H_A + H_B + H_L$$

and

$$V = H_{AB} + H_{ABL} \quad (3)$$

where H_A , H_B and H_L represent the unperturbed vibrational modes, A and B , and exchange mode L , which are coupled to each other by H_{ABL} . H_{AB} describes the interaction between modes A and B .

Both exchange theories predict a temperature dependence in the frequency shift and a broadening of the high-frequency fundamentals. Under the assumption of Markovian statistics and in the low-temperature limit, when the thermal occupation of modes L is low

$$\omega(T) = \omega_0 + \omega_{ex}(T) \quad (4)$$

and

$$T_2^{-1}(T) = (T_2^{-1})_0 + T_{ex}^{-1}(T). \quad (5)$$

In equation (4) ω_0 is the frequency of mode A at $T = 0$ K in the HSC model and the mean frequency of modes A and B in the AO model. $(T_2^{-1})_0$, in equation (5), is the vibrational relaxation rate of the vibrational mode (A in the HSC model and A or B in the AO model) at $T = 0$ K. $\omega_{\text{ex}}(T)$ and $T_{\text{ex}}^{-1}(T)$ are the temperature-dependent frequency shift and the linewidth contribution resulting from the dephasing process, respectively. In the case of a single exchange mode L , the explicit expressions obtained for $\omega_{\text{ex}}(T)$ and $T_{\text{ex}}^{-1}(T)$ from the HSC and AO models are summarized in table 1. In both models, the shift and width exhibit an exponential temperature dependence with the same 'activation energy' E_L , which is equal to a quantum of energy of the low-frequency exchanging mode L . In addition, the AO model requires that the two interacting fundamentals A and B display the same activation energy E_L and shift toward each other with increasing temperature. On the other hand, in the HSC model, different high-frequency modes can be selectively dephased by different but specific low-frequency modes, so that E_L for each mode A can be different, and the anharmonic frequency shift $\delta\omega$ can have either a positive or negative value.

Table 1. Exchange models for vibrational dephasing.

Parameter	HSC model	AO model ^a
$\delta\omega$	Anharmonic shift of combination level	Spacing between interacting fundamentals in the absence of exchange
τ	Resident lifetime of low-frequency mode L (determined by H_{RL} in equation (2))	Reservoir correlation time for coupling force constant between modes A , B and L (determined by H_{ABL} in equation (3))
Frequency shift (T) $\omega_{\text{ex}}(T)$	$\delta\omega/[1 + (\delta\omega)^2\tau^2]e^{-E_L/kT}$	$A'(\delta\omega)\tau^2/[1 + (\delta\omega)^2\tau^2]e^{-E_L/kT}$
Linewidth (T) $T_{\text{ex}}^{-1}(T)$	$(\delta\omega)^2\tau/[1 + (\delta\omega)^2\tau^2]e^{-E_L/kT}$	$A'\tau/[1 + (\delta\omega)^2\tau^2]e^{-E_L/kT}$

^a A' is a proportionality constant depending on the reduced masses of the normal modes involved and on the magnitudes of the coupling constants determined by H_{AB} and H_{ABL} in equation (3), given in the text.

In the HSC model, the parameters $\delta\omega$ and τ which quantify the strength of the interactions between modes A and L and between mode L and the reservoir, respectively, can be extracted from the temperature-dependent lineshift and linewidth analysis using the expressions in table 1. Only if these interactions are comparable in magnitude, i.e. $\delta\omega \sim 1/\tau$ or $(\delta\omega)\tau \sim 1$, will vibrational exchange by the HSC mechanism be dominant. The experimental evidence for this exchange is the appearance of both temperature-dependent broadening as well as a frequency shift. The ratio of the HSC expressions for $\omega_{\text{ex}}(T)$ and $T_{\text{ex}}^{-1}(T)$, given in table 1, yields the temperature-invariant quantity $(\delta\omega)\tau$. Thus, the behaviour of the ratio of

experimental linewidth to shift with temperature can also be used to determine if HSC exchange is the dominant mechanism for vibrational dephasing.

If the anharmonic shift $\delta\omega$ is not very small, then in the low-temperature limit, two well-defined peaks may be observed in the fundamental vibrational spectrum at $\sim\omega_0$ (the fundamental band) and at $\omega_0 + \delta\omega$ (its hot band), corresponding to the transitions $\langle n_A = 0, n_L = 0 | \rightarrow \langle n_A = 1, n_L = 0 |$ and $\langle n_A = 0, n_L = 1 | \rightarrow \langle n_A = 1, n_L = 1 |$, respectively.

3. Experimental details

Single crystals of $\text{NH}_4\text{Dy}(\text{SO}_4)\cdot 4\text{H}_2\text{O}$ (ADySTH) were grown by isothermal evaporation of an aqueous solution containing ammonium sulphate and dysprosium sulphate octahydrate in a 4:1 ratio. The prismatic crystals are monoclinic with space group $P2_1/c$ and unit cell parameters $a = 0.6512(2)$ nm, $b = 1.811(6)$ nm, $c = 0.8658(7)$ nm, and $\beta = 96.59(4)^\circ$. For temperature-dependent infrared measurements at $95 < T < 315$ K, the ADySTH crystals were milled in fluorocarbon and sandwiched between two KBr optical flats. The sandwiched flats were mounted in a temperature-variable cell that operated on the cold finger principle. The sample temperature was monitored, using two pre-calibrated copper-constantan thermocouples directly mounted against the opposing KBr flats. The sample temperature was varied with the help of a Specac 20121 temperature controller. The sample temperature was accurate to ± 2 K.

The infrared spectra were recorded, using an IBM IR-32 Fourier transform infrared spectrometer in conjunction with the Nicolet PC/IR spectrometer program loaded on a DOS-based DELL 220 computer. One hundred interferograms, acquired at a nominal resolution of 2 cm^{-1} , were signal averaged to obtain each primary spectrum. The usual precaution of keeping the sample-compartment chamber free of water vapours and carbon dioxide was enforced see [16], and references therein.

4. Results and discussion

4.1. Infrared data and analysis

The infrared spectrum of ADySTH in the range 4000 to 1350 cm^{-1} can be ascribed to three characteristic types of modes: the 'internal' modes of the NH_4^+ group, the 'internal' modes of the H_2O molecule, and 'combination' modes of external translational/librational phonons with the internal modes. In this paper, we focus our attention on the spectral features arising from NH_4^+ vibrations, and these are marked in the 295 K spectrum reproduced in figure 1. Based on the observed vibrational bands in ASmSTH [1] and published results on other ammonium lattices [17–19], the 1433 , 2857 , 3065 , and 3270 cm^{-1} bands for ADySTH can be assigned to the asymmetric bend of the ammonium ion (ν_4), its first overtone ($2\nu_4$), the symmetric stretch (ν_1), and asymmetric stretch (ν_3) modes, respectively. The very weak shoulder at 1700 cm^{-1} has been tentatively assigned [17] to the symmetric bending mode (ν_2).

It is evident from figure 1 that ν_3 (3270 cm^{-1}) and ν_2 (1700 cm^{-1}) modes of NH_4^+ overlap extensively with the stretching and bending vibrations of H_2O . On the other hand, the ν_1 (3065 cm^{-1}) and $2\nu_4$ (2857 cm^{-1}) ammonium vibrations exhibit

less overlap, while ν_4 (1433 cm^{-1}) is well isolated, allowing a reasonably detailed analysis of its temperature dependence.

At room temperature, the site symmetry of the NH_4^+ ion is C_1 with four equivalent ions in the primitive cell [1]. Since ADySTH does not exhibit any phase transition, according to specific heat capacity measurements [2], the site symmetry and number of equivalent ammonium ions are expected to remain unchanged at low temperatures. The low-symmetry crystalline field will split the triply degenerate ν_4 bending vibration of the tetrahedral molecule into three components [19]. In addition, interactions between internal vibrations of the four ammonium ions in the primitive cell (correlation field effects or resonant exchange between identical oscillators) will result in further splitting. Based on a symmetry-adapted, zone centre, normal coordinate analysis [20], the infrared-active internal modes for NH_4^+ ions in ADySTH are

$$\nu_1(A_u + B_u) + \nu_2(2A_u + 2B_u) + \nu_3(3A_u + 3B_u) + \nu_4(3A_u + 3B_u).$$

Thus, if the resonant exchange of vibrational quanta between identical oscillators is significant, six components should be observed in the ν_4 infrared spectrum.

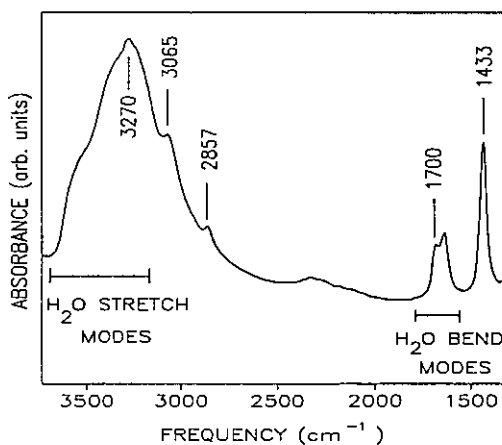


Figure 1. Infrared absorption spectrum of ammonium dysprosium sulphate tetrahydrate at 295 K. The water modes are identified in the figure. The vibrations at 3270, 3065, 2857, 1700, and 1433 cm^{-1} are assigned to ammonium ions (see text).

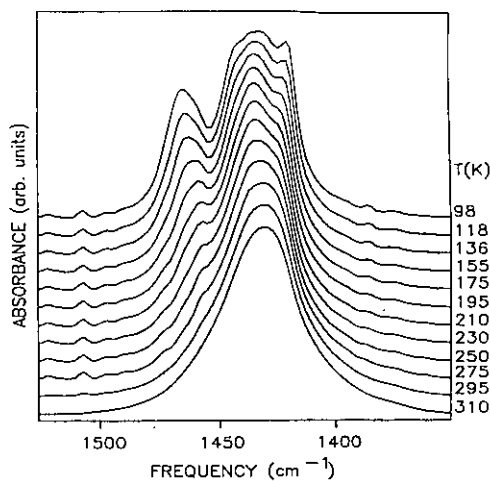


Figure 2. Temperature dependence of the N-H bending mode (ν_4) of ammonium ions in $\text{NH}_4\text{Dy}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The spectra are reproduced at a few selected temperatures.

Figure 2 depicts the effect of temperature on the infrared spectra of ADySTH in the region corresponding to ν_4 . As can be seen from this figure, the ν_4 mode splits at low temperature. However, the overlap in the split vibrations is considerable. Therefore, the ν_4 region was curve resolved, using a computer procedure discussed elsewhere [16]. The curve resolved spectrum at 98 K is reproduced in figure 3. It consists of a main band that has been resolved into three Lorentzian components and a high-frequency shoulder that can be resolved into approximately two components. To a first-order approximation, the correlation field effects ($< 2\text{ cm}^{-1}$) may be

neglected, so that the three components of the main band at 1443, 1432, and 1421 cm^{-1} correspond to the site split components of the triply degenerate ν_4 vibration. In order to assign the shoulder band, we note that its intensity decreases more rapidly relative to the intensity of the main band components (see figure 2). Such an anomalous temperature dependence makes it doubtful if it could be attributed to a fundamental ν_4 absorption. Some contribution to this band could arise from the interaction of a ν_4 vibration with a low-frequency lattice phonon. Such sum bands have been observed in the spectra of other ammonium lattices [21]. We will return to the question of the assignment and character of the shoulder band after analysing the components of the main band.

4.2. Vibrational dephasing ($T < 200$ K)

As can be seen from figure 2, the three fundamentals in the main band broaden and collapse together with increasing temperature. Similar behaviour has been noted for the N-D, O-H, and C-H vibrations in systems containing ammonium [22], water [12], and methyl [10] groups and is characteristic of bands undergoing vibrational dephasing via exchange. Thus, we attempted an analysis based on this hypothesis. The curve resolved data were fitted to the expressions for the frequency shift and temperature-dependent broadening given in table 1 to extract the exchange theory parameters and also to determine the temperature range of applicability of the model. Of the three main bands, the fundamental at 1421 cm^{-1} merges at a relatively higher temperature than the other two. Therefore, its frequency could be determined with the least error by the curve resolution procedure. Due to severe overlap, the linewidth of the 1421 cm^{-1} band could accurately be determined at $95 < T < 200$ K. For the remaining two fundamentals, only the frequency shifts of the 1432 cm^{-1} band could be measured with reasonable certainty. The values of the frequencies (ω_0) and linewidths ($(T_2^{-1})_0$), i.e. in the absence of exchange, were estimated from the observed asymptotic behaviour shown in figure 4.

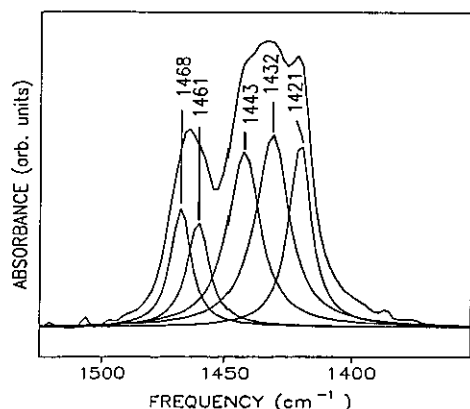


Figure 3. Asymmetric H-N-H bending spectrum of ammonium ions in $\text{NH}_4\text{Dy}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 98 K. Individual peaks have Lorentzian lineshapes and were obtained by a curve fitting computer procedure [16].

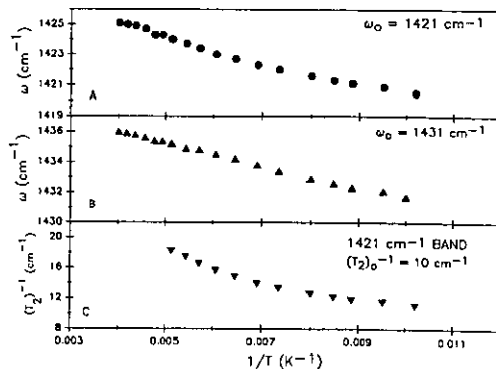


Figure 4. Temperature dependence of frequencies of (A) 1421 cm^{-1} and (B) 1431 cm^{-1} bands and of the (C) linewidth of the 1421 cm^{-1} band showing asymptotic behaviour at low temperatures.

Semilogarithmic plots of the frequency shifts versus $1/T$ are depicted in figure 5. The shifts scale linearly with $1/T$ below 200 K, yielding activation energies $E_L = 414 \pm 30 \text{ cm}^{-1}$ for the 1421 cm^{-1} band and $E_L = 364 \pm 25 \text{ cm}^{-1}$ for the 1432 cm^{-1} band. At $T > 200 \text{ K}$, the frequency shifts for both bands show a deviation from the straight line fits.

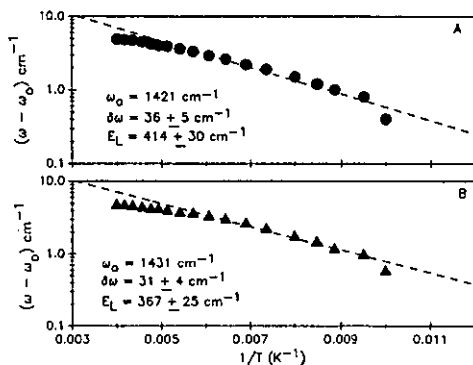


Figure 5. Semilogarithmic dependence of the frequencies of (A) 1421 cm^{-1} band and (B) 1431 cm^{-1} band on $1/T$. Broken curve represents a linear least-squares fit for $T < 20 \text{ K}$.

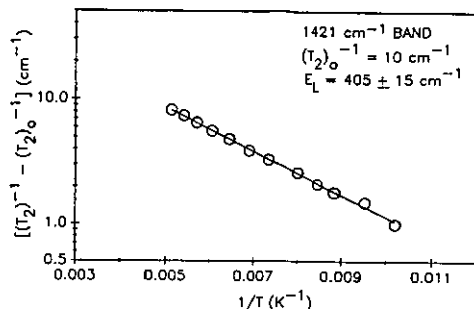


Figure 6. Semilogarithmic plot of linewidth of 1421 cm^{-1} band versus $1/T$. The full line represents a linear least-squares fit to the data.

The temperature dependence of the linewidth of the 1421 cm^{-1} band also exhibits an exponential behaviour, as seen from figure 6, with an activation energy $E_L = 405 \pm 15 \text{ cm}^{-1}$. The errors in the extrapolated low-temperature asymptotic values have been incorporated in the errors specified for the derived parameters. Both the shift and width of the 1421 cm^{-1} band behave exponentially as a function of inverse temperature with the same activation energy, within experimental error, in the range $98 \leq T < 200 \text{ K}$. This evidence implies that the corresponding H-N-H bending fundamental is undergoing vibrational dephasing via an exchange mode L with an activation energy of $410 \pm 30 \text{ cm}^{-1}$ at $T < 200 \text{ K}$. Of the two exchange mechanisms discussed in section 2, the AO model [11] requires the 1421 cm^{-1} fundamental (A) to be interacting with a second fundamental (B) (of close frequency), both of which must have the same activation energy E_L . Since the activation energy of the 1432 cm^{-1} band is nearly equal to (within error) that of the 1421 cm^{-1} band, this band can correspond to fundamental B. However, within the framework of the simplified AO model, if the 1421 cm^{-1} and 1432 cm^{-1} fundamentals interact, they are expected to shift toward each other with increasing temperature. Figure 4 clearly shows that both bands shift toward higher frequency. The two bands, i.e. 1421 and 1432 cm^{-1} bands, appear to be dephasing independently. This observation suggests that the HSC exchange [10] is the dominant mechanism for dephasing. Also, the ratio of the experimental linewidth to shift for the 1421 cm^{-1} fundamental, displayed in figure 7, is constant within error. This experimental behaviour again supports our argument that the vibrational exchange process is dominated by only one exchange mode.

From the least-squares fit in figure 5, the anharmonic frequency shifts $\delta\omega$ were determined to be $36 \pm 5 \text{ cm}^{-1}$ for the 1421 cm^{-1} band and $31 \pm 4 \text{ cm}^{-1}$ for the

1432 cm^{-1} band. These anharmonic shifts are comparable to those observed for the C-H stretch vibrations in durene [10]. The corresponding hot bands ($\omega_0 + \delta\omega$) are expected to occur at $\sim 1456 \text{ cm}^{-1}$ and $\sim 1462 \text{ cm}^{-1}$, respectively. From figures 3 and 4, the two components of the shoulder band in the fundamental bending spectrum have been approximately resolved at 1468 and 1456 cm^{-1} . This is in reasonably good agreement with the expected hot band frequencies, considering that the shoulder band includes contributions from overlapping lattice phonon sum bands. Also, the hot band intensity of the 1421 cm^{-1} mode is expected to be less than that of the 1432 cm^{-1} mode at low T , i.e. inversely proportional to the excitation energies of the exchanging modes. This is the case as observed in figure 3. Thus, in addition to phonon sum modes, some contribution to the shoulder band in the region of the H-N-H ν_4 absorption can be assigned to transitions between anharmonically shifted combination levels of the 1421 cm^{-1} and 1432 cm^{-1} fundamentals with their specific exchange modes (i.e. hot bands). The observation of these 'hot bands' supports the view that HSC exchange is the dominant mechanism for vibrational dephasing of the 1421 cm^{-1} and 1432 cm^{-1} fundamentals at $T < 200 \text{ K}$.

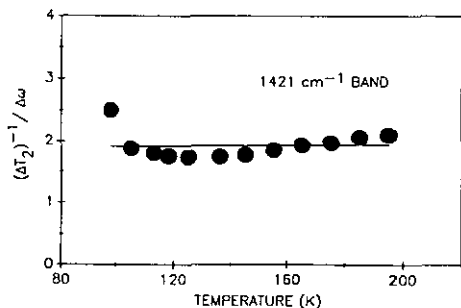


Figure 7. This graph reproduces the experimentally observed ratio of linewidth to frequency shift for the 1421 cm^{-1} band. The full line represents a linear least-squares fit to the data and has a slope ~ 0 .

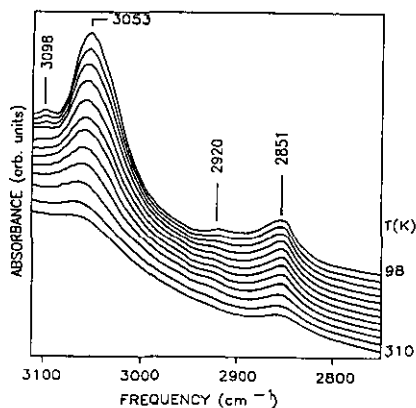


Figure 8. Effect of temperature on the infrared absorption spectra of $\text{NH}_4\text{Dy}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ depicting the behaviour of N-H stretch (ν_1) and N-H-N bend overtone ($2\nu_4$) of ammonium ions at a few selected temperatures. The top-most curve is the spectrum at 98 K and the subsequent curves are at 118, 136, 155, 175, 195, 210, 230, 250, 275, 295, and 310 K.

The temperature dependence of the spectra in the region of the N-H stretch (ν_1) and asymmetric bend overtone ($2\nu_4$) modes is shown in figure 8. The ν_3 band at 3053 cm^{-1} broadens and shifts to higher frequencies with increasing temperature. This behaviour is typical of a vibrational mode that is dephasing by the HSC exchange mechanism, i.e. via coupling to a low-frequency mode which is exchanging its energy with the bath [10]. From a similar analysis for the 3053 cm^{-1} band, as described earlier for the ν_4 fundamentals, the exchange parameters were ascertained from the exponential behaviour of the frequency shift shown in figure 9. The excitation energy of the exchange mode $E_L = 390 \pm 17 \text{ cm}^{-1}$, and the anharmonic frequency shift $\delta\omega = 47 \pm 5 \text{ cm}^{-1}$. The calculated hot band frequency $\omega_0 + \delta\omega$ (3099 cm^{-1}) is in

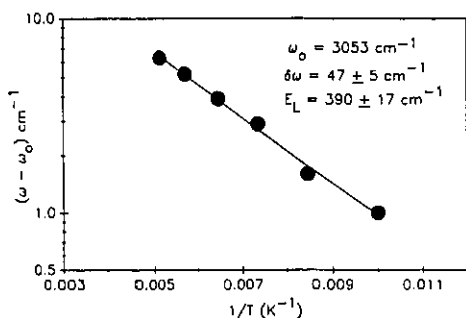


Figure 9. Semilogarithmic graph of the observed frequency shift versus $1/T$ for the 3053 cm^{-1} band. The full line represents a linear least-squares fit to the data.

excellent agreement with the observed band at 3098 cm^{-1} in the 98 K spectrum (see figure 8).

The intensity of the overtone band ($2\nu_4$) at 2851 cm^{-1} is too low (see figure 8) and the overlap with the O–H stretch vibration of water too severe to allow an accurate analysis of its temperature dependence. However, it is worth noting that this band is also accompanied by a shoulder ($\sim 2920\text{ cm}^{-1}$). The separation between the overtone and shoulder bands ($\sim 70\text{ cm}^{-1}$) is in good agreement with $2\delta\omega$ (for the 1421 cm^{-1} band) = 72 cm^{-1} , suggesting that this shoulder, too, may be a hot band.

The ammonium vibrational bands observed in the $T = 98\text{ K}$ spectrum of ADySTH and the exchange parameters extracted from their temperature-dependent analysis at $98 \leq T < 200\text{ K}$ are summarized in table 2. Each fundamental vibration is perturbed by an exchange process dominated by one exchange mode. Based on the HSC model, the dephasing channel is physically determined by the degree of overlap between the RMS amplitudes of the normal coordinates of the vibration fundamental and the low-frequency mode, suggesting a steric interaction between the moving atoms of the modes in question. Consequently, the exchange modes are most probably a librational motion of the ammonium group in the ADySTH lattice, about the various symmetry axes [11–13]. The frequencies of the exchange modes ν_L , which are equal to the activation energies E_L for dephasing of the fundamentals as listed in table 2, are comparable to the torsional frequencies observed in ammonium halides [20]. This suggests fairly strong hydrogen bonding in the ADySTH lattice at $T < 200\text{ K}$. At room temperature, the ammonium ion in isostructural $\text{NH}_4\text{Sm}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ has four close contacts corresponding to the four N–H– \cdots O hydrogen bonds [1, 3]. Three of the oxygens belong to sulphate groups and only one to water. The strength and the asymmetry in hydrogen bonding are expected to become more pronounced at lower temperatures. This would lead to nondegenerate librational frequencies for the ammonium ion about the different symmetry axes. The observed distribution in activation energies, listed in table 2, suggests that the vibrational fundamentals undergo dephasing via anharmonic coupling to the specific librational modes at $T < 200\text{ K}$.

4.3. Motion of ammonium ions at $T > 200\text{ K}$

For $T > 200\text{ K}$ the behaviour of the 1421 cm^{-1} and 1432 cm^{-1} fundamentals is different from that observed at lower temperatures. This follows from the earlier noted deviations in the frequency shifts of these bands from the low-temperature exponential trends (see figure 5). Considering the physical basis for dephasing, we think it is reasonable to suppose that the phase relaxation of the vibrational modes

Table 2. Summary of the vibrational analysis of ammonium ions in ammonium dysprosium sulphate tetrahydrate. — implies undetermined for reasons explained in the text.

Observed fundamental frequency (cm^{-1})	Assignment	Activation energy E_L (cm^{-1})		Anharmonic shift $\delta\omega$ (cm^{-1})	$\omega_0 + \delta\omega$ (cm^{-1})	Observed shoulder frequency (cm^{-1})
		Lineshift	Linewidth			
1421	ν_4	414 ± 30	405 ± 15	36 ± 5	1456	1461
1432	ν_4	367 ± 25	—	31 ± 4	1462	1468
1443	ν_4	—	—	—	—	—
2851	$2\nu_4$	—	—	72^a	2923	2920
3053	ν_1	390 ± 17	—	47 ± 5	3099	3098

^a $2\delta\omega$ value for the 1421 cm^{-1} fundamental.

continues to be connected, in some way, with the anharmonic coupling between the H–N–H bending modes and the ammonium ion torsional motion. However, as the temperature increases, the torsional potential $V(\theta)$ can no longer be assumed independent of temperature as argued for the HSC exchange model. The potential barrier must fluctuate under the thermal excitation of the phonon reservoir. This results in the appearance of jumps of the ammonium ions from one equilibrium position to another. Such large-amplitude reorientation of the ammonium ions will offer a possible channel for vibrational dephasing. In addition, the now overdamped torsional modes represent fluctuation motions about the equilibrium configurations, constituting a non-negligible complementary phase relaxation process. Such librational fluctuations of the CHD_2 groups in toluene are observed to contribute significantly to the dephasing of the C–H stretching fundamentals [23]. Thus, in view of the complex torsional motion of the ammonium ions, akin to that of a restricted rotor, the slope of the frequency shift curves at $200 \text{ K} < T \leq 250 \text{ K}$. Therefore, the motion of ammonium ions can no longer be simply equated to the ammonium librational frequencies [24].

At still higher temperatures, i.e. $T > 275 \text{ K}$, a single band is observed in the ν_4 absorption spectra of ADySTH (figure 2). Qualitatively, this implies that the torsional motion of the ammonium ions appears to have almost completely averaged out the asymmetric environment of the protons, indicating that the ions must be approaching free rotation [25]. In view of our infrared results, which suggest that the onset of disordering in the orientation of the ammonium ions is gradual, we therefore do not believe the phase transitions in ALSTH are driven by ammonium ions.

5. Conclusions

From detailed vibrational analysis of $\text{NH}_4\text{Dy}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at $95 < T < 315 \text{ K}$, it is argued that the motion of ammonium ions in the lattice can be identified with three distinct temperature regimes, i.e. low ($95 < T < 200 \text{ K}$), intermediate ($200 < T < 275 \text{ K}$), and high ($275 < T < 315 \text{ K}$).

(i) In the low-temperature regime, the behaviour of H–N–H asymmetric bend and N–H symmetric stretch modes, as a function of temperature, indicates that exchange via anharmonic coupling to ammonium librational modes is the dominant vibrational dephasing mechanism. The appearance of hot bands due to transitions between anharmonically shifted combination levels further supports this view. Therefore,

it is concluded that the ammonium ions are undergoing well defined librations at $95 < T < 200$ K.

(ii) In the intermediate-temperature regime, the vibrational dephasing channels, though linked to the torsional motion of the ammonium ions, can no longer be equated to ammonium librations. It is therefore concluded that the molecular motion of the ammonium ions at $200 < T < 275$ K is complex, probably a superposition of large-amplitude reorientational motion and small-amplitude librational fluctuations.

(iii) In the high-temperature regime, the vibrational results suggest that ammonium ions attain almost free rotation at $T > 275$ K.

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