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# Solid-state studies. Part XXIV: Raman spectral consequences of disorder in the structure of phase II of ammonium nitrate

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## Abstract

The Raman spectra of a wide variety of isotopomeric polycrystalline samples of phase II of ammonium nitrate are explained on a model in which the disorder within the lattice is incorporated within factor-group correlations. This model also provides an explanation for the single crystal Raman data.

## Introduction

It has long been realized that intermolecular vibrational coupling can occur in crystalline materials and, indeed, there are probably few crystals of any complexity in which such coupling is not appreciable in at least one spectral region. More recently, it has been realized that such coupling may occur not only between chemically identical units but also between dissimilar molecules or ions (Kearley et al. 1980; Jayasooriya et al., 1980). Thus, in a recent report on the Raman spectrum of phase IV of ammonium nitrate, we demonstrated that it was necessary to invoke vibrational coupling between the deformation modes of the cation and stretching modes of the anion in order to explain the vibrational spectra in the 1400 $\text{cm}^{-1}$ region (Kearley et al., 1980). The present paper is concerned with an analogous study of phase II (52 to 125°C) of ammonium nitrate. The crystal structures of phases II and IV of ammonium nitrate have certain similarities, and it might be expected that similar phenomena may occur in the 1400 $\text{cm}^{-1}$ spectral region. For phase IV,

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the infrared spectrum was difficult to study in any detail in the 1400 $cm^{-1}$ region; the corresponding IR spectrum of phase II is even less tractable and is excluded from the present discussion.

In phase IV of ammonium nitrate the existence and consequences of coupling between chemically distinct ions (heteroionic coupling) were made manifest by a variety of isotopic substitutions—partial and complete deuteration, with and without $^{15}N$ substitution. It was then found that the intensity and frequency of the "nitrate" peaks were sensitive to the isotopic nature of the ammonium ion and, conversely, "ammonium" peaks were sensitive to isotopic changes at the nitrate ion. Two related concepts emerged from this work. First, strong vibrational coupling between a set of chemical identical ions opposes the vibrational disruption consequent upon isotopic substitution. Thus, in a lattice containing a random array of $NH_4^+$, $NH_3D^+$, and $NH_2D_2^+$, interionic vibrational coupling between the deformation motions of $NH_2$ units persists so that such a lattice may still be regarded as containing an average $NH_4^+$ ion, albeit at a lower concentration than in the fully protonic material. It is therefore reasonable to use factor-group labels to describe the vibrations of such isotopomeric materials. From this follows the second concept—that in this situation vibrational coupling between chemically distinct units only occurs between vibrations of identical factor-group symmetry.

Phase II of ammonium nitrate has been reported as belonging to the $P\bar{4}2_1m$ ($D_{2d}^3$) space group with two formula units in the unit cell (Lucas et al., 1979). Disorder of both cations and anions leads to two orientations for each, related by $\pi/3$ rotations for the nitrate ions or $\pi/2$ rotations of the ammonium ions (Fig. 1) which occupy sites of $C_{2v}$ and $S_4$ symmetries, respectively. The vibrational analysis detailed in the present paper depends crucially on taking account of this disorder. This we do by applying the factor-group method of analysis to each orthogonal disordered structure and investigating the correlations which exist between these factor groups. Essentially, we argue that the nature of any disorder constrains the spectral consequences of the disorder. In particular, our analysis leads to specific spectral predictions which may be compared with experiment. The $P\bar{4}2_1m$ space group leads to the possibility that L.O./T.O. splitting may be observed in the Raman spectrum which would, in the limit, lead to vibrational frequencies which vary with the propagation direction in the crystal and so, in the polycrystalline samples used in the present work, a broadening mechanism. The disorder will also contribute to the breadth of the spectral lines and, indeed, it is found that in phase II the bands are significantly broader than in phase IV. While it may be argued that the disorder in this lattice quenches L.O./T.O. effects (Tang and Torrey, 1977), it should be noted that such effects have been reported as observable in nitrate melts (Devlin et al.,

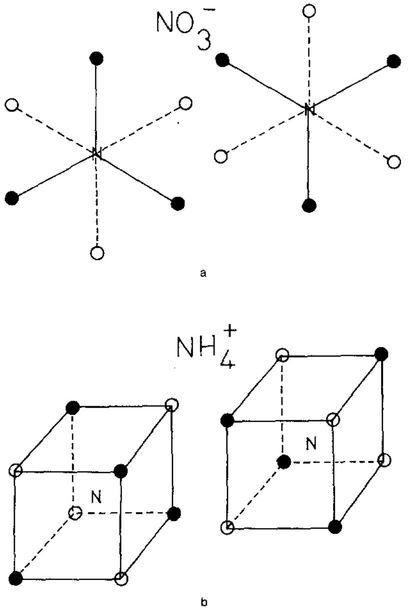

**Fig. 1.** (a) Alternative orientations of the two nitrate ions in the unit cell of phase II of ammonium nitrate where the solid–solid or dashed–dashed lines correspond to the $D_{2d}^3$ space group and the solid–dashed line to the $C_{4v}^2$ space group. (b) alternative orientations of the two ammonium ions where solid–solid or open–open circles lead to the $D_{2d}^3$ space group but solid–open circles give $C_{2v}^8$.

1970). We have attempted to explain the phenomena reported in this paper by a detailed consideration of several L.O./T.O. models but have been unable to discover any which similtaneously provides as explanation of the single-crystal (Tang and Torrey, 1977) and isotopically enriched material Raman spectra.

## Experimental

Raman spectra were recorded using a Spex 1401 double-beam monochromator and a Spectra-Physics 165 $Ar^+$/Kr laser. The exciting line used was 20490 $cm^{-1}$ and the laser power, measured at the sample, was ca. 30 mW. Photon counting was achieved using an Ortec Photon Counting System 5C1. Spectra were recorded at a sample temperature[1] of 90°C using a modified microscope hot-stage arrangement. Following base-line correction, the spectra were deconvoluted, a least-squares fitting being employed to determine the optimum Gaussian band positions and areas.

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[1] The temperature range of stability of Phase II ammonium nitrate is ca. 80 to 12b°C.

"Analar" grade ammonium nitrate (Hopkin and Williams) was used in this study, deuteration being achieved by recrystallization from the appropriate $H_2O/D_2O$ mixtures. Maximum deuteration (95%) was attained after 15 recrystallizations from $D_2O$ (99 atom %) in a sealed system under reduced pressure. Deuterated samples were sealed in glass tubes immediately after preparation. $NH_4^{15}NO_3$ (97 atom %) was purchased from Prochem B.O.C. Ltd. and deuterated by the above procedure.

## Results and discussion

The vibrations of interest in phase II of ammonium nitrate occurring in the 1400 $cm^{-1}$ region are the antisymmetric stretching mode of the nitrate ion, $\nu_3$, and the antisymmetric deformation mode of the ammonium ion, $\nu_4'$ (primed modes are those to be associated with vibrations of the cation). A correlation between these modes under site and factor groups is given in Fig. 2.

The Raman spectra of protonic and several levels of deuterated and $^{15}NO_3^-$ (97 atom %) substituted ammonium nitrate in phase II are illustrated in Fig. 3a–i, and frequency data for the strong peaks, derived by Gaussian analysis, are collected in Table 1. In contrast to the bands in the 1400 $cm^{-1}$ region, the $2\nu_2$ band at 1664 $cm^{-1}$ is sharp and, as with our treatment of phase IV (Kearley et al., 1980), this band will be used as an internal intensity standard in the present study. The breadth of the bands in the 1400 $cm^{-1}$ region of phase II makes an immediate detailed analysis difficult, although the number of strong bands and their approximate relative intensities are reasonably clear. It was found that bands in the corresponding spectral region of phase IV of ammonium nitrate are Gaussian to within experimental error,

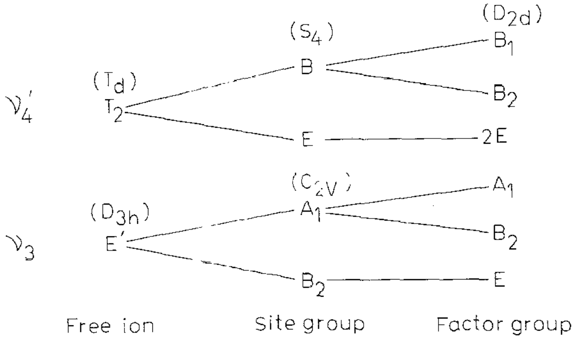

**Fig. 2.** Correlations between free-ion, site-, and factor-group symmetries for the ammonium-ion antisymmetric deformation mode, $\nu_4'$, and the nitrate-ion antisymmetric stretching mode, $\nu_3$, in phase II of ammonium nitrate.

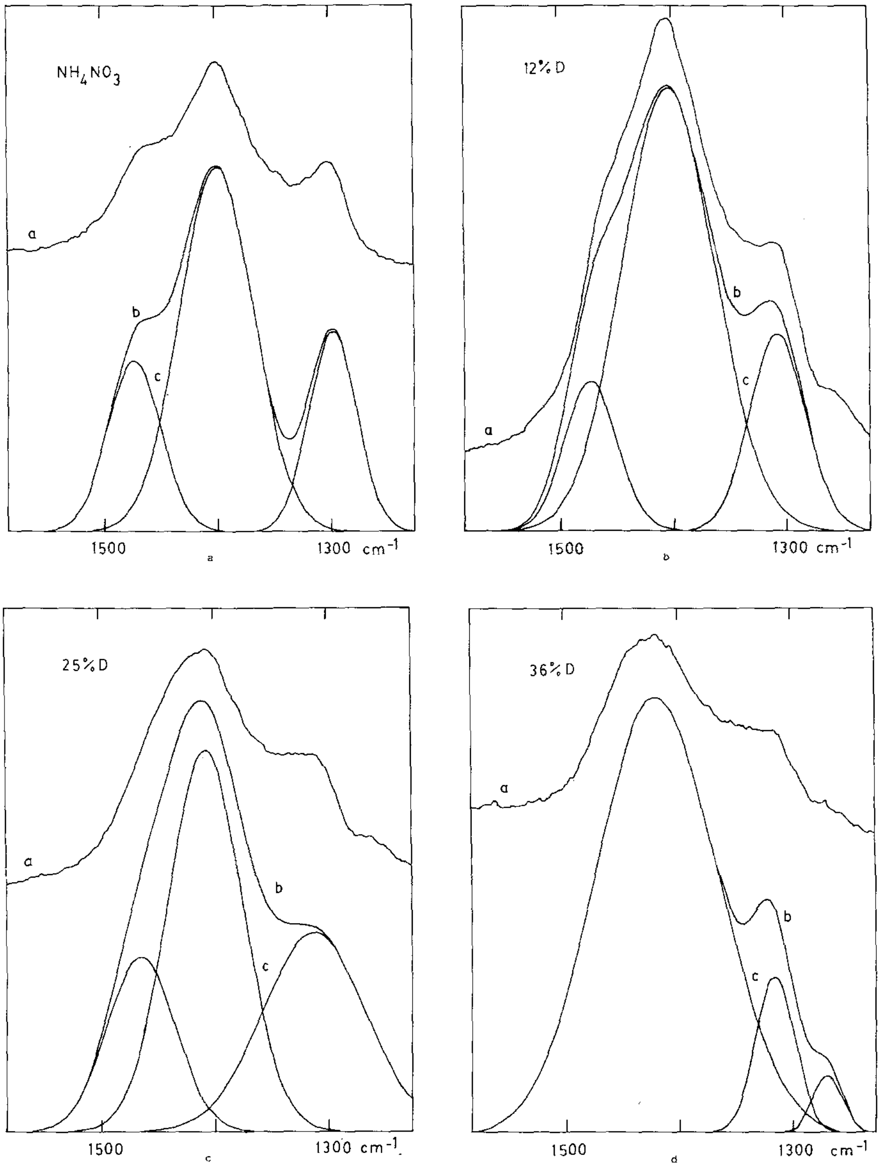

**Fig. 3.** (a–i) Raman spectra of polycrystalline ammonium nitrate recorded at 90° C (phase II) with the isotopic compositions indicated. The letters a, b, and c refer to "raw" spectrum, computed spectrum, and deconvoluted components, respectively.

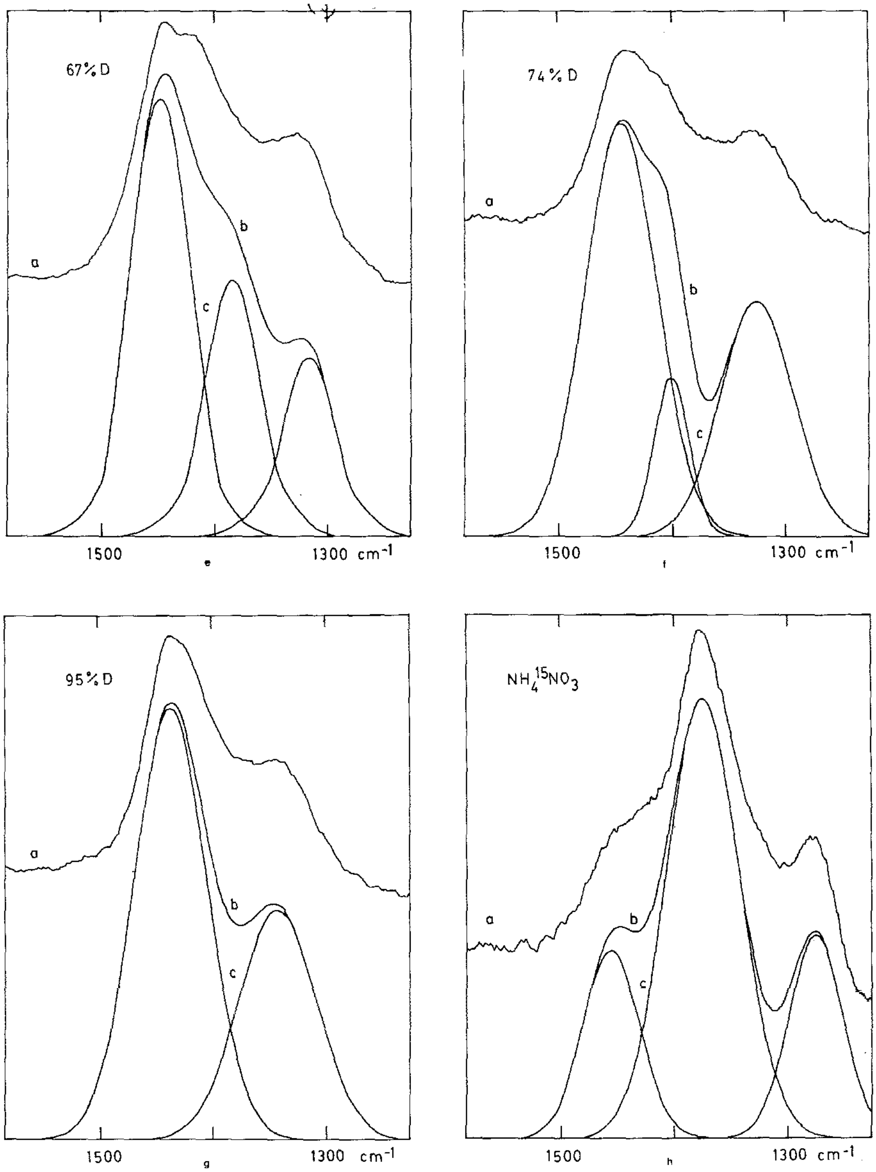

**Fig. 3.** Continued.

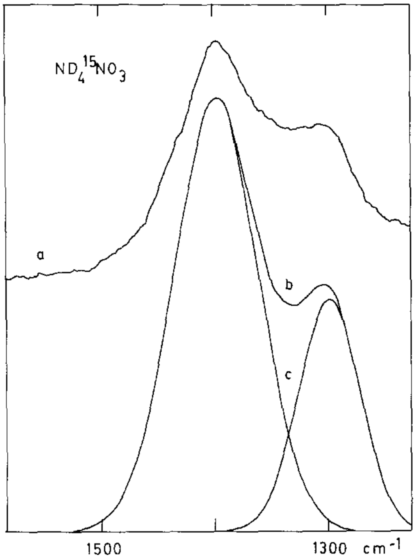

Fig. 3. Continued.

and so a Gaussian analysis of the spectra shown in Fig. 3a–i was carried out, within the constraint that the number of peaks and their relative intensities (using the overtone of $\nu_2$ as a reference) were in accord with those given by superficial analysis of the "raw" spectra.

In general this procedure aided the interpretation of the spectra, but its limitations became evident to us. Whereas in some spectra four bands are evident (e.g., Fig. 3b), we found that a Gaussian analysis with four peaks ignored the low-frequency $NH_3D^+$ feature at 1255 $cm^{-1}$, a feature being added in the 1360 $cm^{-1}$ region. We therefore constrained the number of peaks fitted in each spectrum to three. The 67% D spectrum provided an exception; it was not well fitted, and we therefore report frequencies estimated from the spectrum itself. It is noticeable that the half-widths of some peaks vary, particularly at intermediate levels of deuteration. This variation presumably reflects changes in the abundance of particular vibrators and also in their ability to couple effectively with their neighbors.

The factor-group method predicts that the molecular $\nu$ (N–O) $E'$ mode gives rise to $A_1 + B_2 + E$ components in the crystal; similarly, the $\delta(NH_2)$ $T_2$ mode of the ammonium ion gives rise to $B_1 + B_2 + 2E$. These predictions may immediately be tested by the single-crystal study reported by Tang and Torrie (1977). In the 1400 $cm^{-1}$ region three peaks of $A_1$ polarization were observed in contrast to the one predicted by the above analysis. Three $B_2$ peaks were observed compared with the two expected, and, further, $A_1$ and $B_2$ spectra

**Table 1.** Assignments, frequency, and intensity data for the Raman spectral features arising in the 1400 $cm^{-1}$ region of phase II of ammonium nitrate (frequency and intensity data derived by Gaussian analysis)

| | $\bar{\nu}$ ($cm^{-1}$) | $\Delta\nu_{1/2}$ ($cm^{-1}$) | Integrated area (%) | Total area ($2\nu_2$ = 1) |
|---|---|---|---|---|
| $NH_4^{14}NO_3$ | $\nu_4'$ 1470 | 27.6 | 19 | 17 |
| | $\nu_3$ 1398 | 38.2 | 59 | |
| | $\nu_3$ 1294 | 24.8 | 22 | |
| 12% D | $\nu_4'$ 1472 | 32.7 | 14 | 23 |
| | $\nu_3$ 1402 | 57.1 | 68 | |
| | $\nu_3$ 1308 | 34.8 | 18 | |
| 25% D | $\nu_4'$ 1464 | 34.7 | 18 | 21 |
| | $\nu_3$ 1406 | 38.4 | 50 | |
| | $\nu_3$ 1310 | 52.3 | 32 | |
| 36% D | $\nu_4' + \nu_3$ 1418 | 63.0 | 86 | 18 |
| | $\nu_3$ 1314 | 21.1 | 11 | |
| | $\nu_4'(NH_3D)_3$ 1268 | 16.7 | 3 | |
| 67% D[a] | $\nu_3$ 1446 | 34.0 | 49 | 18 |
| | $\nu_4'$ 1420 | 32.2 | 29 | |
| | $\nu_3$ 1320 | 32.2 | 22 | |
| 74% D | $\nu_3$ 1442 | 37.0 | 56 | 20 |
| | $\nu_4'$ 1398 | 18.2 | 11 | |
| | $\nu_3$ 1324 | 37.4 | 33 | |
| 95% D | $\nu_3$ 1436 | 37.7 | 64 | 17 |
| | $\nu_3$ 1342 | 40.3 | 36 | |
| $NH_4^{15}NO_3$ | $\nu_4'$ 1454 | 29.1 | 20 | 19 |
| | $\nu_3$ 1374 | 37.7 | 60 | |
| | $\nu_3$ 1274 | 29.1 | 20 | |
| $ND_4^{15}NO_3$ | $\nu_3$ 1396 | 43.2 | 72 | 19 |
| | $\nu_3$ 1296 | 32.0 | 28 | |

[a] Frequencies quoted for this sample were estimated from the "raw" spectrum (see text).

were essentially superimposable—both in the spectral region and all in others studies (Tang and Torrey, 1977). We regard as a major outcome of the present work that these rather remarkable observations are explained by our analysis.

Additional problems became evident from a study of the isotopomeric spectral data we obtained but for which explanations are given by our analysis. In our previous study (Kearley, 1980) of phase IV of ammonium nitrate, we found that almost all of the intensity in the 1400 $cm^{-1}$ of the Raman spectrum originated in the nitrate-ion vibrations (using $2\nu_2$ as an internal intensity standard); inspection of the intensity data collected in Table 1 reveals that this is also the case for this spectral region of phase II of ammonium nitrate. The Wolkenstein model (Wolkenstein, 1941), when applied to the nitrate ions within the unit cell, predicts the following approximate relative peak intensities:

$$A_1 = 3, \qquad B_2 = 2 \qquad E = 3$$

It is clear then that one of the strongest peaks in the 1400 $cm^{-1}$ region—the $A_1$ factor-group mode derived from the nitrate-ion vibration—should be in-sensitive to deuteration because there is no ammonium-ion vibration with which it can couple. This is not observed, all peaks in this spectral region being deuteration sensitive.

Application of the Wolkenstein model (Wolkenstein, 1941) to the ammonium-ion vibrations leads to the following approximate relative peak intensities:

$$B_1 = 0, \qquad B_2 = 2, \qquad E = 3$$

Of these, only $B_2$ and $E$ can steal intensity from the nitrate modes and so a maximum of six peaks seems likely to have significant intensity ($A_1 + 2B_2 + 3E$). Only two $E$ peaks are clearly evident in the single-crystal Raman and these are each close to $A_1/B_2$ common features. One further feature is $A_1/B_2$ common. Recognizing the inherent breadth of all these peaks in a polycrystalline sample, analysis of only three features is evidently appropriate and, as indicated above, was all that could be justified. This band near-coincidence pattern is explained by the present analysis.

Before detailing our explanation of these observations, it is appropriate to discuss our spectral observations in some detail and to highlight one pertinent result. Whereas there are two peaks at 1398 and 1470 $cm^{-1}$ in $NH_4NO_3$ (Fig. 3a), only one persists, at 1436 $cm^{-1}$, in $ND_4NO_3$ (Fig. 3g). It seems evident that the difference is due to the disappearance of ammonium-ion deformation modes from this frequency region. Because on progressive deuteration (Fig. 3b–3g) the 1398 $cm^{-1}$ peak rises smoothly to 1436 $cm^{-1}$ while the 1470 $cm^{-1}$ peak gradually shifts and loses intensity, it appears that the latter peak is an "ammonium" entity. A possible explanation for this observation is that in the low symmetry of a partially deuterated crystal, there could be a mixing of the $A_1$ nitrate mode with vibrations of $NH_nD_{4-n}^+$ species. However, the observation that there is no frequency in the 1400 $cm^{-1}$ region common to both $NH_4NO_3$ and $ND_4NO_3$ excludes this.

Our explanation for these phenomena derives from a consideration of the disorder present in the lattice which we represent by the use of a modified factor-group model in which the correlation between alternative disordered structures is of key importance. We therefore consider this disorder in more detail, dealing first with the nitrate anions. The $P\bar{4}2_1m$ space group requires that the unit cell contain a pair of nitrate groups represented only by solid lines for both (Fig. 1a) or dashed lines for both. However, because each nitrate group has equal probability of adopting the orientations represented by solid or dashed lines in Fig. 1a, equally possible arrangements of nitrate anions are the dashed–solid line representations. These two latter arrangements are not compatible with the $P\bar{4}2_1m$ space group. Rather, they lead to the space group $P4bm$ ($C_{4v}^2$) quite accurately. Because of the nitrate group disorder, neither the $P\bar{4}2_1m$ nor the $P4bm$ space groups correctly describe the arrangement of nitrate ions in the lattice. Either is equally good (or bad) in this respect. $P\bar{4}2_1m$

is the space group in which a structural analysis was carried out because one arrangement of the disordered ammonium ions also subtends this lattice (see Fig. 1b). In our analysis of the vibrations of the nitrate groups we recognize this complementary between $P\bar{4}2_1m$ and $P4bm$ by taking the factor groups isomorphic to $D_{2d}$ and $C_{4v}$ as equally appropriate to describe the vibrations of the nitrate lattice. The point groups $C_{4v}$ and $D_{2d}$ are isomorphic and, further, a given polarizibility tensor element transforms under identical symmetry labels in the two groups. Thus, a single-crystal Raman measurement which gives a $B_2$ spectrum for a $D_{2d}^3$ crystal would also give a $B_2$ spectrum for a $C_{4v}^2$ crystal.

In either structure the shortest interatomic separation between nitrate groups is ca. 3 Å. We therefore consider that the vibrational coupling between nitrate groups will be approximated by the dipole–dipole model, remembering that the molecular $E'$ mode, from which all the nitrate features we are discussing derive, is strongly infrared active. To a first approximation, we would expect that vibrations in which dipoles are in phase in the two nitrate ions in the unit cell would oscillate at about the same frequency in $D_{2d}^3$ and $C_{4v}^2$. Similarly, the out-of-phase vibrations will have comparable energies. This is illustrated in Fig. 4 where we show both $D_{2d}^3$ and $C_{4v}^2$ arrangements of the nitrate groups and their $A_1$ and $B_2$ vibrations. The vibration which corresponds to an in-phase arrangement of molecular dipole moment changes is of $B_2$ symmetry in $D_{2d}^3$ and $A_1$ in $C_{4v}^2$. Correspondingly, the out-of-phase combinations are of $A_1(D_{2d}^3)$ and $B_2(C_{4v}^2)$ symmetries. An interplay between $A_1$ and $B_2$ symmetry labels is evident and has to be seen in the context of the comments of the previous paragraph on tensor element transformations and which may be summarized by noting that the coordinate axis $z$ transforms as

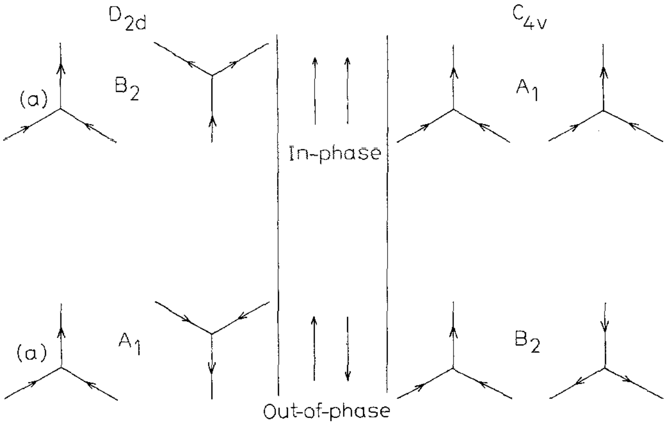

**Fig. 4.** An illustration of the correspondence between antisymmetric stretching vibrations of two nitrate anions in the alternative arrangements afforded by disorder in the structure of phase II of ammonium nitrate. The central arrows indicate the alternative dipole arrangements.

Table 2. Correlation between $\nu_4'$ and $\nu_3$ components under $D_{2d}$ and $C_{2v}$ point groups

| | $D_{2d}$ | | $C_{2v}$ | |
|---|---|---|---|---|
| | Representation | Coordinate axis | Representation | Coordinate axis |
| $\nu_3$ | $A_1$ | | $A_1$ | $z$ |
| | $B_2$ | $z$ | $A_1$ | $z$ |
| | $E$ | $x,y$ | $B_1+B_2$ | $x,y$ |
| $\nu_4'$ | $B_1$ | | $A_2$ | |
| | $B_2$ | $z$ | $A_1$ | $z$ |
| | $E$ | $x,y$ | $B_1+B_2$ | $x,y$ |

$A_1$ in $C_{4v}$ but as $B_2$ in $D_{2d}$. It is evident that, as a consequence of these arguments, we would expect similar $A_1$ and $B_2$ single-crystal Raman spectra which is precisely what was observed by Tang and Torrie (1977).

A corresponding argument may be developed for the ammonium ions, although since the ammonium-ion vibrations obtain intensity in large measure by coupling with and stealing from the nitrate modes, disorder of the ammonium ions is likely to be less important spectrally. The alternative arrangements of ammonium ions are implicit in Fig. 1b. The first of these in which the hydrogens of both ammonium ions are represented by either all solid or all open circles is the $D_{2d}^3$ lattice in which the crystal structure was refined. The second in which the hydrogens of one ammonium ion are represented by solid circles and the other by open circles is rather accurately *Pba*2 ($C_{2v}^8$). The correlations between vibrations in $D_{2d}^3$ and $C_{2v}^8$ are given in Table 2. The detailed arguments are similar to those detailed above for the nitrate-ion disorder, *mutatis mutandis*, both in the context of vibrational frequencies and transformation of tensor elements. Thus, a $B_2(D_{2d}^3)$ vibration is expected to have about the same energy as an $A_1(C_{2v}^8)$; both transform as $z$. The essence of our discussion concerns the nitrate-anion disorder and is thus unaltered by the inclusion of the ammonium ion vibrations.

Comparison of Fig. 4 and 5 shows that those vibrations which transform as $E$ in $D_{2d}^3$ also transform as $E$ in $C_{4v}^2$ and as $B_1 + B_2$ in $C_{2v}^8$; the intersection with the $A_1/B_2$ ($D_{2d}$, $C_{4v}$, $C_{2v}$) vibrations considered above is empty. Accordingly our analysis predicts $E$-mode single-crystal Raman spectra which are quite distinct from the $A_1/B_2$; this prediction is in agreement with the experimental results reported by Tang and Torrie (1977).

This model provides, retrospectively, some justification for the approach we have used in this analysis. If we consider the array of molecular vibrational dipoles in the lattice (such as in Fig. 4 and 5), then this array is described by a translationally invariant lattice. That is, we expect $k = 0$ to be appropriate to an analysis. It is when the details of molecular orientation are added that an ambiguity arises because two arrangements of each pair of ions within the unit cell are equally probable. In our model, therefore, we have given these two

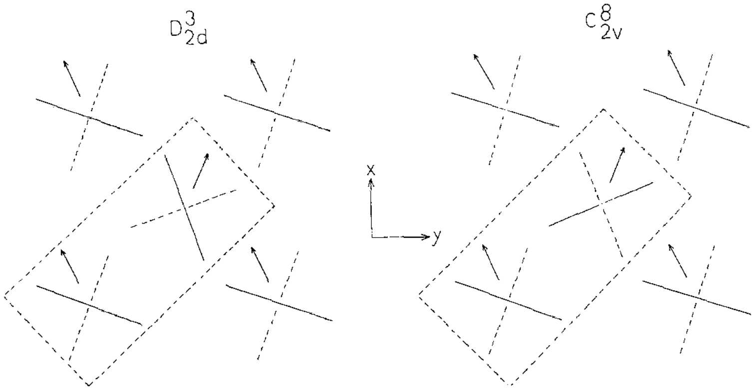

**Fig. 5.** An illustration (schematic only) of the alternative "ammonium" sublattices due to the disordered crystal structure of phase II of ammonium nitrate. Arrows indicate the correlation between one component of the $E\,(D^3_{2d})$ vibration for the alternative space groups $D^3_{2d}$ and $C^8_{2v}$. The ions within the dashed-line box correspond to those illustrated in Fig. 1b.

arrangements equal weight; we note that in the limit of molecular translational invariance our model reduces, correctly, to that of the appropriate point group.

A discussion of the spectral effects of deuteration requires that we unify our treatments of nitrate- and ammonium-ion disorder. This is because the Raman band intensities originate in vibrations of the former ion but the effects of deuteration originate in vibrations of the latter. This unification requires a common space group. Comparison of the space groups $D^3_{2d}$, $C^2_{4v}$, and $C^8_{2v}$ shows that the maximal common subgroup is $C^1_2$ ($P_2$) and it is in this group that we shall work. Vectors oriented along the $z$ axes in $D_{2d}$, $C_{4v}$, or $C_{2v}$ transform as $A$ in $C_2$ whereas $x$ or $y$ oriented vectors transform as $B$ in $C_2$. We conclude that these are the only distinctions which persist in $C_2$. There are two conclusions which emerge. First, all Raman bands in the 1400 cm$^{-1}$ region would be expected to be deuterium sensitive, as observed. Secondly, we would expect the distinction between, for example, $A_1/B_2$ and $E$ nitrate modes in $D_{2d}/C_{4v}$ to persist in $C_2$. However, detailed consideration of the spectra of partially deuterated samples reveals a further complexity. This is evident from the behavior of the peak at 1398 cm$^{-1}$ in the protonic sample which, on progressive deuteration, moves to 1446 cm$^{-1}$ in the 67% D sample whereafter it reverses its dependence on deuteration, occurring at 1436 cm$^{-1}$ in the 95% D sample. It seems that the peak at 1294 cm$^{-1}$ in the protonic sample, which occurs at 1342 cm$^{-1}$ in the fully deuterated, also has an irregular frequency behavior as revealed on progressive deuteration. In view of the difficulty in assigning frequencies accurately, the small decrease in frequency of the high-frequency $\nu_3$ component at high levels of deuteration (67–95% D) may be subject to some question. However, this small decrease in frequency of this peak at high levels of deuteration is in marked contrast to the steep increase in frequency observed at lower deuteration levels (0–67% D), and a plateau, at least, is indicated.

We interpret these behaviors as a manifestation of an effective non-crossing rule. This explanation is detailed in Fig. 6. On the left-hand side of this figure $\nu_4'$ "ammonium" frequencies, which are the highest in this frequency region, are shown together with site- and alternative factor-group effects. "Nitrate" $\nu_3$ frequencies are shown on the right-hand side of this figure and, again, site- and alternative factor-group effects are illustrated. By treating the "ammonium" and "nitrate" sublattices in isolation, the central part of Fig. 6 takes account of the symmetry of both sublattices (and their disorder) in addition to interactions between the chemically distinct species. Progressive deuteration would probably lead to a smooth decrease in frequency of the $\nu_4'$ components (as the "average" $NH_4^+$ ions become more dilute and so correlation effects become smaller; it is to be remembered that the "free ion" frequency of $\nu_4'$ is ca. 1400 cm$^{-1}$). In practice, the factor-group derivatives of $\nu_4'$ encounter the nitrate modes, leading to further mixing, energy-level repulsion, and the observed pattern of frequency shifts, with the $\nu_3$ vibrations increasing in frequency until heteroionic coupling effects are almost absent (at 95% D). Such crossing of levels of the same symmetry does not occur in phase IV (Kearley et al., 1980). This is because in phase IV the $\nu_4'$ factor-group components interleave those of the "nitrate" $\nu_3$ and, consequently, only smooth frequency movements on progressive deuteration were observed. An additional factor which has to be recognized is the lower maximal symmetry

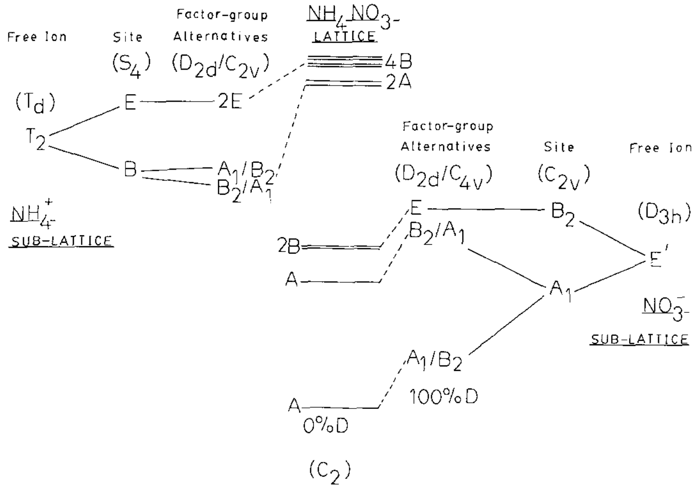

**Fig. 6.** Correlation between free-ion, site, disorder, and heteroionic coupling effects for the antisymmetric deformation mode of the ammonium ion, $\nu_4'$, and the antisymmetric mode of the nitrate ion, $\nu_3$, in the 1400 cm$^{-1}$ Raman spectral region.

of phase II ($C_2$) which admits of fewer symmetry distinctions and thus makes crossing more probable. Further, it is to be noted that one component of the "ammonium" $\nu_2'$ molecular $E$ mode at ca. 1680 cm$^{-1}$ ($NH_4NO_3$) transforms under the $A_1$ representation of the $D_{2d}$ factor group and, while the frequency separation between this mode and $\nu_3$ ($A_1$) at 1294 cm$^{-1}$ makes appreciable heteroionic coupling unlikely, the frequency separation in the deuterated analogue is ca. 140 cm$^{-1}$ and coupling may become more significant.

The above interpretation, and hence Fig. 6, is endorsed by the general downward shift, without any major changes in spectral appearance, of all spectral features in the spectra of $NH_4{}^{15}NO_3$ and $ND_4{}^{15}NO_3$ (Fig. 3h and 3i, respectively) compared with the spectra of the $^{14}NO_3^-$ ion analogues.

## Conclusions

In this paper we have presented an analysis of the vibrational spectrum of a locally disordered crystal. In explaining the experimental data it was not convenient to digress at length on the implications of our treatment. Germane to our discussion are the effects of homo- and heteroionic vibrational coupling. In our study of phase IV of ammonium nitrate it became clear that these couplings oppose the disruptive effects of random isotopic substitution. The analysis presented in this paper shows that they also oppose the effects of crystal disorder. Thus, colloquially, we may say that a $\nu_3$ vibration of a nitrate ion will couple with the corresponding vibration of a neighboring nitrate ion no matter which way up the latter finds itself. In this situation, the appropriate symmetry to consider is that subtended by the vibrational tensors—here vectors—rather than the idealized atomic arrangements. However, the latter determine the lattice and so we proceed by investigating the correlations between the tensor components of the alternative lattices. As an alternative, we could have worked in the maximal subgroup of $D_{2d}$ and $C_{4c}$, that is, work in $C_2$ for the nitrate—a procedure which would have had the advantage of providing unique symmetry labels for the nitrate vibrations. However, the connection between the alternative nitrate lattices ($D_{2d}^3$, $C_{4v}^2$) would have been less evident. We therefore preferred to reserve this alternative treatment for the interpretation of the effects of deuteration where "nitrate" and "ammonium" disordered lattices had to be considered simultaneously and to work in $C_2$.

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