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THE RAMAN SPECTRA OF PHASE III AMMONIUM NITRATE

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The Raman spectrum of phase III ammonium nitrate and isotopomeric materials show that $\delta(NH_2)$ and $\nu(N-O)$ vibrations are coupled together throughout the lattice. This observation may be relevant to both the phase-changes of ammonium nitrate and its explosive properties.

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Final Report: THE RAMAN SPECTRA OF PHASE III AMMONIUM NITRATE

Background

The above grant provided funding which enabled completion of a systematic study of phases II, III and IV of ammonium nitrate. The significance of the work supported by the AFSC is clear in the context of the entire study. The general picture which emerges is presented in the next section; outline details of the phase III studies are then given.

Ammonium Nitrate II, III and IV: an overview

Ammonium nitrate is a safe, cheap, low energy explosive which is also widely used as a nitrogen fertilizer. The phase stable at room temperature is phase IV but above ca 33°C this is metastable with respect to phase III. Above ca 82°C phase II is the stable form. At suitable temperatures direct IV → II transitions occur.

The phase transitions tend to show some considerable hysteresis and are sensitive to the impurity ion and moisture content of the sample as well as its history. Clearly, the presence and freedom of movement (or tying-down) of crystal defects is of significance. However, some phase transitions move through the crystal with extreme rapidity (in one videotaped study, one crystal changed from phase IV to II between successive frames of the videotape).[1] Typically, different crystallites within a sample undergo phase transitions at slightly different temperatures and all may not undergo the same transition (IV → II and III → II can be in competition). Whilst a complete explanation of this behaviour is lacking, it has, at least, been found possible to provide a rationalisation.[1] In this context it may be noted that an intermediate between phases IV and III has been positively established[1] and shown to have a structure rather similar to that of phase II.[2]

1. G.J. Kearley, S.F.A. Kettle and J.S. Ingman. J.Chem.Soc.(Faraday II) In press.

2. G.J. Kearley and S.F.A. Kettle. Angewande Chemie. Submitted for publication.

The speed of movement of the phase boundary mentioned above suggests that there exists a strong motional coupling between the ions in the ammonium nitrate lattice. Such a coupling could, equally, be of importance in affecting its explosive characteristics. This would seem less likely if the coupling occurred only in one phase. It therefore becomes of interest to investigate the nature of vibrational coupling in ammonium nitrate and its phase dependence.

Our studies of the Raman spectra of phase IV ammonium nitrate quickly revealed the existence of a novel vibrational coupling between the ammonium and nitrate ions.[3] Ammonium ion deformation vibrations - $\delta(NH_2)$ - and some nitrate ion band stretching vibrations - $\nu(NO)$ - both occur at ca 1450 cm^{-1}, and there is a wealth of spectral features in this region. However, these features cannot be directly assigned to $\delta(NH_2)$ or $\nu(NO)$. Isotopic modification to either NH_4^+ or NO_3^- affects all bands. These observations demonstrate that the NH_4^+ and NO_3^- vibrators are coupled together. We have termed this phenomenon "heteroionic vibrational coupling".[3] Several detailed partial and complete isotopic substitutions enabled a complete energy level diagram representing this interaction to be constructed for phase IV ammonium nitrate.

Neutron diffraction data show that phase II ammonium nitrate has a crystal structure which is related to that of phase IV and so heteroionic vibrational coupling in the 1400 cm^{-1} region might be expected for phase II. Accordingly, isotopic studies were carried out and showed that this coupling does, indeed, occur. It was, further, possible to infer from the data that the disorder which occurs in phase II is short range - there is little, if any, short range correlation.[4] Phase II is disordered at both ammonium and nitrate sites and so, if heteroionic vibrational coupling occurs in this phase, it seems that it could occur for any phase and the AFSC provided funds which enabled this prediction to be checked for phase III.

[3] G.J. Kearley, S.F.A. Kettle and J.S. Ingman. J.Chem.Phys. 73, 2129 (1980)

[4] G.J. Kearley and S.F.A. Kettle. J.Cryst.& Spect.Research. In press.

Phase III ammonium nitrate

Ammonium nitrate III has a crystal structure which is quite different to those of phases IV and II.[5] In phase III, the ammonium ions are disordered but the nitrate ions are not. The infrared spectrum of phase III consists of very broad bands, particularly in the 1400 cm^{-1} region, so that it is extremely difficult to extract any useful information. The Raman bands in this region are also somewhat broadened but are much more amenable to analysis. Detailed study was made of the Raman spectra of NH_4NO_3, $NH_xD_{4-x}NO_3$, ND_4NO_3, $NH_4{}^{15}NO_3$, $(NH_4)_2{}^{14}NO_3{}^{15}NO_3$, $ND_4{}^{15}NO_3$, $NH_4N^{18}O_3$ and $ND_4N^{18}O_3$ each in phase III. All admitted of a simple 'superposition of spectra of ions' interpretation except in the 1400 cm^{-1} region. Here, again, it was clear that heteroionic vibrational coupling occurs. It also became clear that the ammonium ion disorder in phase III is one in which there is a short-range correlation between ammonium ion positions. A detailed discussion will not be given here; a copy of a paper enumerating the results is appended.

Overview

It is clear that there exists a novel vibrational coupling between ammonium and nitrate ions in ammonium nitrate. This heteroionic vibrational coupling occurs in phases with very different crystal structures and in ordered, disordered and partially ordered lattices. It seems a rather ubiquitous phenomenon. Although the energy of the vibrations involved (*ca* 1400 cm^{-1}) is such that they will have but a small population at room temperature, it is entirely possible that their excitation is of significance in some phase-change and in explosion phenomena.

This latter aspect is particularly interesting in that preliminary work suggests that similar vibrational coupling occurs in a wide variety of materials containing $-NH_2$ and $-NO_2$ groups, many of which are of importance as explosives. Examples are $C(NH.NH_2)_3^+.NO_3$[6] and $C_6(NO_2)_3(NH_2)_3$.[7]

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Solid State Studies Part XXV.

RAMAN SPECTROSCOPIC EVIDENCE FOR SHORT-RANGE ORDER OF AMMONIUM-ION ORIENTATIONS IN THE STRUCTURE OF AMMONIUM NITRATE-III.

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Abstract.

Previously available single-crystal Raman data for ammonium nitrate-III are reinterpreted in the light of recent crystallographic data and the recognition of heteroionic vibrational coupling. Frequency data are presented for ammonium nitrate-III isotopically substituted with $^{15}NO_3^-$ and $N^{18}O_3^-$ in the presence of protonated and deuterated ammonium ions. These data show that the spectra are interpretable in terms of a modified factor-group model and reveal the presence of short-range order of ammonium-ion orientations in phase III.

Introduction.

Ammonium nitrate is known to occur in at least five phases at atmospheric pressure, of which three IV, III and II have been well characterised structurally. Of these the room temperature phase, phase IV, and phase II, stable between 85 and 125°C, have clearly related crystal structures. However, a major quantitative difference between them is that in phase II both ammonium and nitrate ions are orientationally disordered whereas in phase IV both are ordered. In phase III (stable between 32 and 85°C), the nitrate ions are ordered but the ammonium ions disordered. Although the crystallographic work has shown that in both phase II and phase III the ionic disorder takes the form of ions occupying sites with two different orientations, each with a 50% probability, such studies do not readily distinguish between the limits of total disorder and the existence of small domains of local order. It has been recognised that vibrational spectra, which may be sensitive to short-range interactions, provide a method which may distinguish between these limits.(1) The present communication is concerned with the evidence provided by the Raman spectra of ammonium nitrate-III and its isotopomers on the disorder in this material.

In a previous paper we have presented, and discussed in detail, the vibrational spectra of ammonium nitrate-IV in the 1400 cm^{-1} region.(2) Whereas other spectral regions are relatively straightforward, admitting of a site- or factor-group interpretation, the spectra in the 1400 cm^{-1} region are rather complicated, although ultimately interpretable in terms of the factor group. A detailed analysis of the effects of partial and complete isotopic substitution showed that this complexity originates in an interionic coupling between the $\delta(NH_2)$ modes of the ammonium ion and the $\nu(NO)$ modes of the nitrate, modes which have characteristic frequencies in this spectral region. The techniques of isotopic substitution and dilution have proved generally useful as probes for investigating interionic and intermolecular vibrational coupling, providing small and controllable perturbations to this mixing. Their application to ammonium nitrate-II (3) demonstrated that a factor-group model making explicit allowance for orientational disorder is needed to explain the spectra. The clear implication is that the disorder is such that there is no domain pattern, for if such a pattern existed a phase IV-like factor-group approach would be expected to be applicable. In an ordered structure, heteroionic vibrational coupling occurs between modes of the same factor-group symmetry species, but for disordered structures the selection rules would be expected to be less restrictive. Nevertheless, as we have shown elsewhere (3) they are not totally permissive; in particular, we have explained the fact that there are just two symmetry-distinct spectra which may be obtained in the single-crystal Raman spectra of ammonium nitrate-II.

Single-crystal studies of ammonium nitrate-III present some problems. This phase is not readily prepared directly; rather it is usually prepared from phase IV. Unfortunately, although the IV - III order/disorder transition is between two orthorhombic structures, the crystallographic axes are not preserved. This effect alone would probably cause degradation of the crystallites during thermal cycling but in addition, the ca. 5% volume increase associated with this transition sets up considerable strains within the crystallites which commonly fracture leading to a powdering of the smaple.

Although higher-temperature phases are usually of higher symmetry than lower-temperature phases, the IV - III transition is accompanied by a reduction in the site symmetries of both types of ion from C_{2v} (phase IV) to C_s (phase III) with a doubling of the unit-cell contents from two to four formula units. Presumably these changes arise from an optimisation of hydrogen bonding within the coordination sphere of neighbouring oxygen atoms. The structure of phase IV permits only one oxygen atom from each nitrate ion to participate in strong hydrogen bonding (4).

In phase III however, all N-H...O distances are comprable with all oxygen atoms being similarly involved in hydrogen-bonding. It has been suggested that the IV - III transition leads to an increase in hydrogen-bond strength (5) but a recent Raman study(6) shows that, overall, this is little changed. The more symmetrical pattern of hydrogen bonds in phase III is reflected by the reduced site-splittings of degenerate nitrate-ion modes in the spectrum of this phase compared with that of phase IV, despite the near trigonal geometry of this ion in both phases. For both NH_4^+ and NO_3^- ions the picture of distortions which thus emerges is of ions in phase IV which occupy relatively symmetric sites but which are nonetheless highly distorted, giving way, in phase III, to less symmetric sites which are occupied by ions subject to less severe distortions.

Despite the difficulty of obtaining good single crystals of ammonium nitrate-III, Tang and Torrie(7) have reported a single-crystal Raman study in which they collected polarisation data for phase III using a fragment of crystal obtained by heating a single crystal of phase IV. These authors were aware of the possible problems associated with this procedure and recognised that some 'leakage' between polarisations may be present in their spectra.

The present study aims to reinterpret the single-crystal Raman data recorded by Tang and Torrie in the light of recent crystallographic data and our work on the other phases of ammonium nitrate. This we achieve by supplementing the existing data with the Raman spectra of ammonium nitrate-III isotopically substituted, separately, with $^{15}NO_3^-$ and $N^{18}O_3^-$ in the presence of both protonated and deuterated ammonium ions.

Results and Discussion.

Ammonium nitrate-III is reported as belonging to the Pnma (D_{2h}^{16}) space group with $Z = 4$ (8). The nitrate-ion sublattice is ordered but there are two alternative orientations for the ammonium ion which have been assumed to be populated with equal probability. Both types of ion occupy sites of C_s symmetry. There is no ambiguity associated with the assignment of the major part of the Raman spectrum of phase III, although a detailed analysis of the ν(NH) vibrations in the 3000 cm^{-1} region has not yet proved possible owing to extensive Fermi resonance of these with combination modes (9). In the 1400 cm^{-1} region however, heteroionic vibrational coupling occurs between $\delta(NH_2)$ and ν(NO) modes so that an isotopic substitution affects most spectral bands. We have therefore confined our study to these modes and this spectral region. A correlation between free-ion, site- and factor-group symmetries is given in Figure 1 for the antisymmetric stretching mode of the nitrate ion, ν_3, and the antisymmetric deformation mode of the ammonium ion, ν_4'. Throughout this work primed modes designate those which are to be associated with vibrations of the ammonium ion.

All of the spectra that we report were obtained from polycrystalline samples. The single-crystal data of Tang and Torrie are therefore of key importance to us in that they provide the symmetry labels which are needed for a detailed discussion. On the other hand, the single-crystal spectra contain little indication of the parentage of features in the 1400 cm^{-1} region. This information is provided by our isotopic studies. For example, the only modes persisting in the 1400 cm^{-1} region of the spectrum of a fully deuterated sample are to be associated with nitrate modes; the spectra of partially deuterated samples indicate the correlation with features in the protonic material. Our work and that of Tang and Torrie are thus interwoven; it is simplest to proceed by first reviewing the single-crystal data but at the same time to anticipate some of the conclusions derived from our spectra of isotopomeric materials.

Table 1 shows that a single-crystal Raman spectrum of the 1400 cm^{-1} region should show three bands of A_g symmetry, two of B_{1g}, two of B_{3g} and three of B_{2g}. In accord with these expectations Tang and Torrie found that the spectra for B_{1g} and B_{3g} polarisations each contain two peaks, in agreement with the factor-group predictions. However, for the B_{2g} polarisation there are again two peaks, in contrast to the three predicted. The Raman spectral bands in the 1400 cm^{-1} region are all very broad and it is not to be expected that two proximate bands of the same symmetry species would necessarily be resolved. We therefore assume a coincidence of two 'ammonium' features. Tang and Torrie's A_g spectrum contains at least five peaks in contrast with the three predicted by a factor-group analysis. We note that the rather weak feature at 1360 cm^{-1} in the A_g spectrum corresponds to a strong peak in the B_{2g} spectrum and it seems likely that this feature arises from 'break-through' between polarisations. Our isotopic studies showed that the peak at 1417 cm^{-1} in the A_g spectrum is entirely consistent with its assignment to $2\nu_4$, that is, as an overtone of the fundamental appearing in the Raman and infrared spectra of NH_4NO_3-III at 716 cm^{-1}. We conclude, then, that the A_g spectrum is also in accord with the factor-group predictions.

The Raman spectra of isotopomers of ammonium nitrate-III are shown in Figure 2 and approximate band frequencies are given in Table 1. All spectra show a band, unusually sharp, above 1600 cm^{-1} which, as in phases IV and II, is assigned as $2\nu_2$. It is to be noted that its behaviour on isotopic substitution in the NO_3^- group is consistent with this. The level of ^{18}O substitution was 70 atom% accounting for the greater breadth of this band in these samples. There is a further broad band in this spectral region for our spectra of NH_4^+ nitrates-III. A similar band, usually very sharp, is common in other ammonium salts, although very weak in ammonium nitrate-IV and II, and is assigned as the symmetric $\delta(NH_2)$ mode, ν_2'. On deuteration it drops below the spectral region under study, falling to ca. 1170 cm^{-1}.

The work of Tang and Torrie shows that there are several features contained within the broad band between 1400 and 1500 cm^{-1} in NH_4NO_3-III. Comparison with the spectra of its isotopomers shows that not all of these bands disappear on deuteration, notwithstanding the fact that the factor-group model indicates that they are probably largely of ammonium-ion parentage. The data are explained if one peak at ca. 1420 cm^{-1} is assigned as the nitrate-ion in-plane deformation overtone $2\nu_4$. It is to be noted that we have already invoked this overtone to explain the A_g single-crystal data. Another general feature emerges from a comparison of the spectra in Figure 2. The strong 'nitrate' peaks at ca. 1400 cm^{-1} are invariably at a higher frequency in the spectra of the ND_4^+ salts than in the corresponding NH_4^+. This is conclusive evidence that the vibrations of NH_4^+ and NO_3^- are coupled together. That is, just as in phases IV and II, heteroionic vibrational coupling occurs in this spectral region. The existence of heteroionic coupling indicates that the vibrations are delocalized; that is, that a factor-group model is appropriate. A check on this is provided by the partial isotopic substitution when the one-mode (when the factor-group model is appropriate) or two mode (calling for a site model) nature of the vibrations is made apparent. We have carried out such studies and it is clear that all features arising between 1300 and 1500 cm^{-1} are one-mode in nature. Despite the breadth of the spectral bands this conclusion is clear; in this context samples containing equal proportions of two isotopomers were most indicative. It is to be noted that only for the A_g spectrum did the single-crystal Raman data indicate the necessity for a factor-group model of ammonium-ion vibrations. An alternative to the isotopomer probe which we have used is a comparison between infrared and Raman spectra. Unfortunately, the infrared spectra contain only broad, strong and almost featureless absorptions so that such a comparison is not possible.

Figure 2 shows that in most spectra there are shoulders on the strong peaks some of which appear to move, on isotopic substitution, in an unexpected way. For example, low-frequency shoulders occur on the strong ca 1400 cm^{-1} band in NH_4NO_3, $NH_4{}^{15}NO_3$ and $NH_4N^{18}O_3$ but high-frequency shoulders appear for the corresponding deuterated species. Fortunately, these peaks may be characterised by appeal to the single-crystal Raman data. Because of this complexity, it is simplest to proceed by presenting our explanation of the data.

Figure 3 contains energy level and correlation data for the various isotopic species. For NH_4NO_3 the symmetry species shown are those given by the single-crystal data. Several points immediately emerge from this Figure. First the considerable effects of heteroionic coupling as seen in the effects of deuteration. Secondly, the $2\nu_4$ overtone is involved in Fermi resonance with the other A_g fundamentals. It is not possible to determine the uncoupled frequency of $2\nu_4$ from our spectra but ν_4 is found at 716 cm^{-1} in all the $^{14}NO_3{}^-$ and $^{15}NO_3{}^-$ salts but at ca. 699 cm^{-1} in the Raman spectrum of $NH_4{}^{14}N^{18}O_3$. This 699 cm^{-1} peak is broadened because the enrichment is only 70 atom% and shows an isotopic splitting; clearly it is two-mode in nature. It is interesting that the overtone is one-mode in nature. Examples of the converse situation are known(10).

The low-frequency shoulder on the ca. 1400 cm^{-1} peak in protonic samples, known to be of A_g symmetry from the single-crystal studies, moves under the ca. 1400 cm^{-1} peak on deuteration. Because of the simultaneous appearance of high-frequency shoulders on this band it could be argued that this A_g feature moves through it and reappears above. However, this would imply considerable heteroionic coupling, because a shift of ca. 80 cm^{-1} would be required, and in all probability a marked change in intensity. On these grounds we have excluded this interpretation. Similarly, if heteroionic coupling were dominant it is possible that the levels at ca. 1400 cm^{-1} in deuterated samples in Figure 3 would correlate with 'ammonium' levels' at *ca.* 1450 cm^{-1} rather than as shown. This correlation is excluded by the spectra of partially deuterated samples. The actual correlations between the B_{1g}, B_{2g} and B_{3g} levels in protonic and deuterated samples is not strictly determined because of the absence of single-crystal data on deuterated samples. In Figure 3 we have assumed that the effects of site splitting of the nitrate modes are greater than those of intermolecular vibrational coupling; this assumption, which is consistent with all our data, could be tested if well resolved infrared spectra were available. The argument which we found decisive is that of intensities; polycrystalline and single-crystal data indicate that the 1360 cm^{-1} B_{2g} mode is the strongest band in this spectral region of NH_4NO_3. Unless there is a major redistribution of intensity - and there is no evidence for this - then its position in the spectra of the deuterated samples is essentially the frequency of the strongest peak.

Conclusions.

The analysis presented above shows that notwithstanding the presence of heteroionic coupling, the 1400 cm^{-1} region of the Raman spectrum of ammonium nitrate-III is understandable in terms of a factor-group model. Taken in conjunction with the analysis of other internal vibrations in this phase we conclude that the disorder of ammonium ions has no effect on the spectra. If there were any such effect we would expect that it would be most manifest in the 1400 cm^{-1} region for here degenerate ammonium-ion vibrations couple with degenerate nitrate-ion vibrations; if the ammonium ions were disordered against the ordered nitrate-ion backbone these vibrational interactions would surely have spectral consequences. We conclude therefore, that in ammonium nitrate-III there is a local ordering of ammonium ions with ordered domains extending over a few unit cells, at least. The overall picture which emerges is of phase IV containing ordered nitrate and ammonium ions, of phase III containing ordered nitrate and locally ordered ammonium ions and phase II containing locally disordered nitrate and ammonium ions.

This picture enables us to reflect on the IV - III phase transition, a transition of considerable technical importance. The ordered arrangement of nitrate ions in phase IV is very different to that in phase III; thus, in the former the planes of nitrate groups are coplanar; in the latter they subtend two almost perpendicular sets of planes. The present study adds the information that the transition is from a locally (and extensively) ordered phase IV to a locally ordered phase III. The required rearrangements are such that it does not seem likely that a direct IV - III transition will be facile. It is interesting that there is X-ray evidence for a transient phase, similar to phase II, intermediate between phases IV and III(11) and recently we have been able to record this phase photographically(12). The picture of local disorder in phase II which we have presented elsewhere(3) makes a similar structure particularly attractive for the intermediate, the disorder implying relatively low potential energy barriers for rearrangement of ammonium and nitrate ions.

Acknowledgement

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Experimental.

Raman spectra were recorded using a Spex 1401 double monochromator and an Ortec Photon Counting System 5C1. A Spectra-Physics Ar^+/Kr laser was employed and the power of the exciting line, at 20490 cm^{-1}, was ca. 30 mW measured at the sample. Polycrystalline samples were sealed in capilliary tubes and stored for several weeks at a temperature of 45°C prior to use. During the period of measurement samples were maintained at 45°C by the use of a modified microscope hot-stage arrangement. Confirmation that specimens were indeed in phase III was achieved by reference to the lattice-mode region of the Raman spectrum.

"Analar" grade ammonium nitrate (Hopkin and Williams) was used in this study. Maximum deuteration (95%+) was achieved by repeated recrystallisation of samples from D_2O (99 atom%) in a sealed system under reduced pressure. $NH_4{}^{15}NO_3$ (97 atom%) and $NH_4N^{18}O_3$ were purchased from Prochem B.O.C. Ltd. and deuterated by the procedure given above.

Caption to Table.

Frequency data and assignments for the Raman spectral features arising in the 1400 cm^{-1} region for ammonium nitrate-III

Captions to Figures.

Figure 1. Correlation between 'free ion', site- and factor-group symmetries for the antisymmetric deformation mode of the ammonium ion, ν_4', and the antisymmetric stretching mode of the nitrate ion, ν_3.

Figure 2. Raman spectra of polycrystalline ammonium nitrate-III with the isotopic compositions indicated recorded at a sample temperature of 45°C.

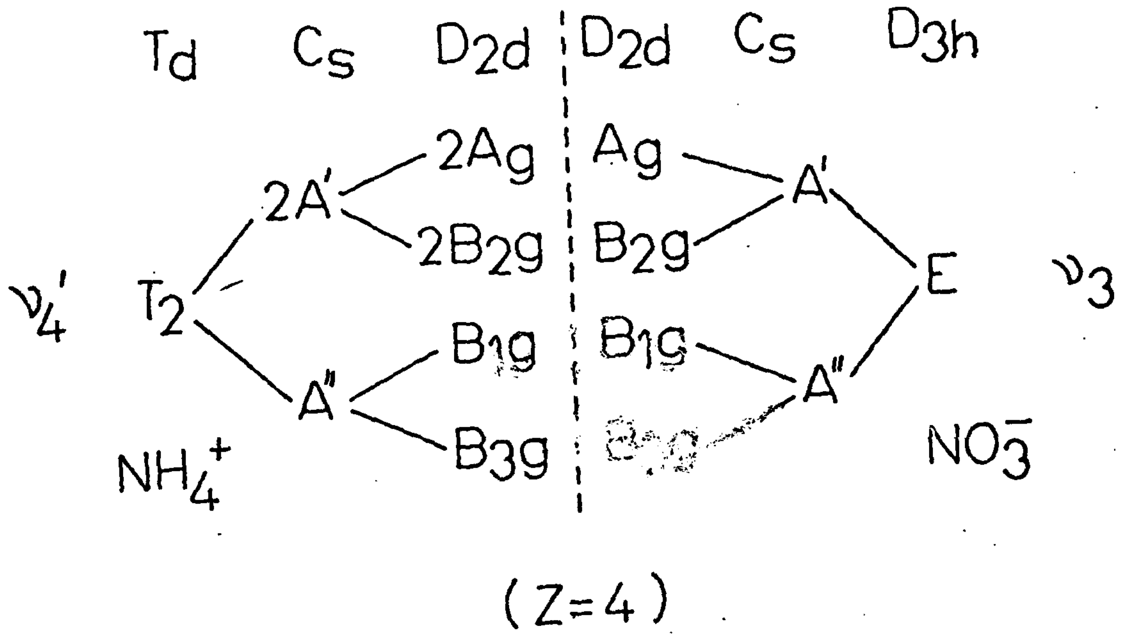
Figure 3. Energy-level diagram correlating the isotopic composition of ammonium nitrate-III with heteroionic coupling effects. The frequency axis is approximate only. The levels denoted by a, b, c, etc for the ^{18}O and ^{15}N samples are tentatively assigned to symmetry species in the same sequence as those for NH_4NO_3.

	(cm^{-1}) $NH_4NO_3$$^+$	(cm^{-1}) ND_4NO_3	(cm^{-1}) $NH_4N^{18}O_3$	(cm^{-1}) $ND_4N^{18}O_3$	(cm^{-1}) $NH_4{}^{15}NO_3$	(cm^{-1}) $ND_4{}^{15}NO_3$
ν_3 A_g	1328	1378	1315	1370	1295	1340
ν_3 B_{2g}	1360		1348		1330	
ν_3 B_{1g},B_{3g}	1356	1405		1392		1380
$2\nu_4$ A_g	1417	1420	1400	1405	1415	1418
ν_4' A_g,$2B_{2g}$	1440		1450		1450	
$\nu_4'$$A_g$,$B_{1g}$,$B_{3g}$	1460					

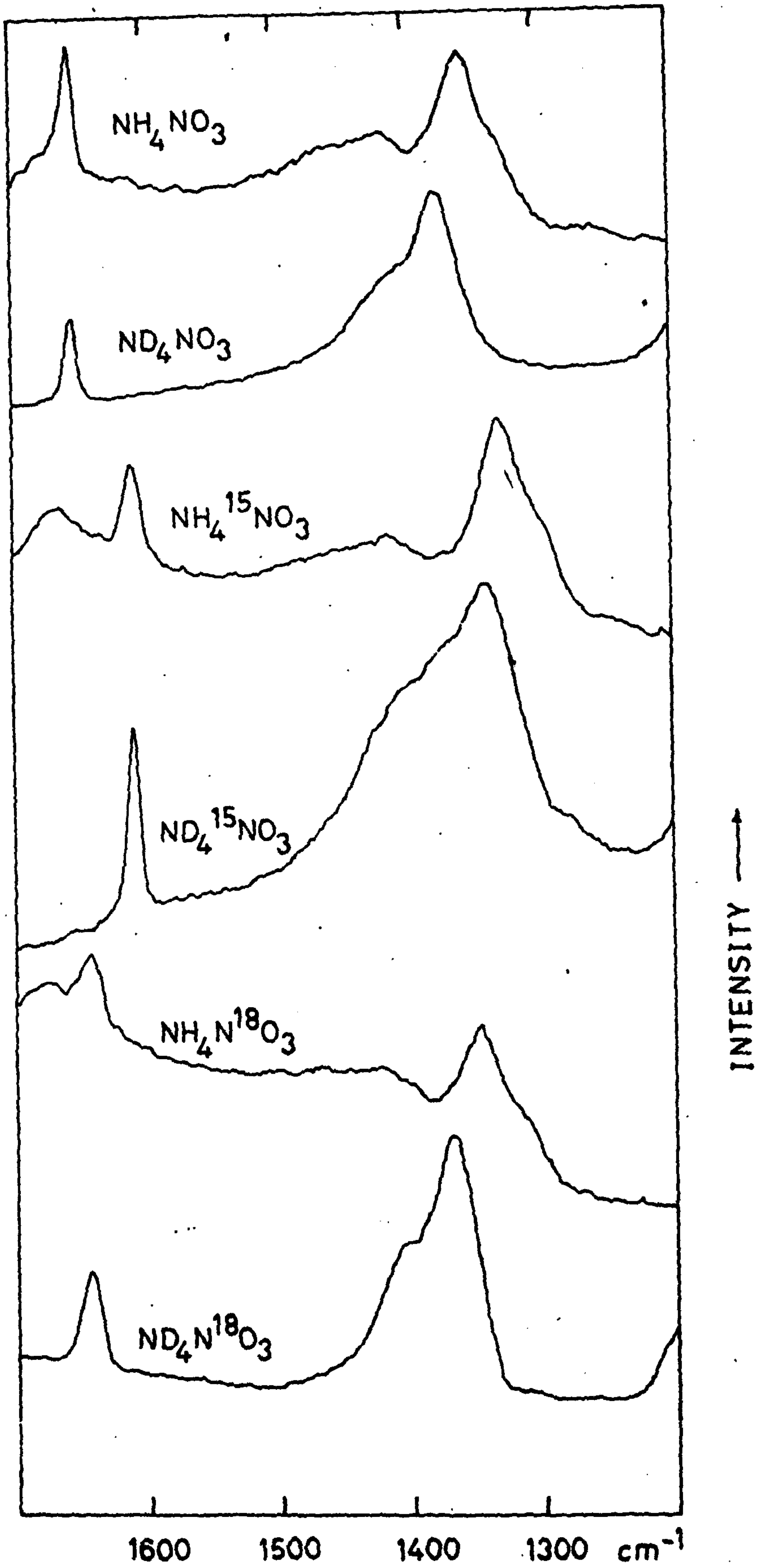
$^+$Single-crystal frequency data from Ref.7.

Kearley and Kettle Table 1.

Kearley and Kettle Figure 1.



Kearley and Kettle Figure 2.



Kearley and Kettle Figure 3.