The Use of ^{18}O Enrichment to Determine the Mode of Co-ordination in MXO_3 Species *via* Infrared Frequency and Intensity Patterns: the Shape of Matrix-isolated KNO_3

By **Ian R. Beattie, J. Steven Ogden,*** and **David D. Price,** Department of Chemistry, The University, Southampton SO9 5NH

This paper describes a new experimental approach to the problem of determining the mode of co-ordination of $[XO_3]^{n-}$ ions (*e.g.* $[NO_3]^-$, $[CO_3]^{2-}$). Using the nitrate ion as an example, it is shown, *via* line diagrams, that a qualitative distinction between monodentate and bidentate binding should be possible simply by noting the number and relative intensities of isotope bands associated with the highest frequency N–O stretching mode in the i.r. spectrum of the ^{18}O-enriched material. The method is illustrated by reference to the matrix i.r. spectrum of molecular KNO_3, where the initial qualitative conclusion of bidentate co-ordination is confirmed by subsequent force-constant analysis.

TERNARY molecular salts have long been regarded as playing an important role in high-temperature vapour transport, and in particular oxo-species such as Na_2SO_4 have attracted considerable interest in view of their possible importance in corrosion mechanisms. However, there are still very little detailed structural or spectroscopic data for these species, and in many cases, even the grosser features of their shapes are unknown. We are currently studying a range of alkali-metal salt vapours using matrix-isolation techniques, with the basic aim of determining the mode of co-ordination of the cation by oxy-anions such as $[NO_3]^-$, $[ClO_4]^-$, $[SO_4]^{2-}$, or $[PO_4]^{3-}$ using vibrational spectroscopy.

The general problem of distinguishing between mono- and bi-dentate binding in, for example, metal nitrato-complexes, has been extensively reviewed,[1] and the work of Hester and co-workers in particular [2,3] describes how an unequivocal distinction based upon spectroscopic data is theoretically possible if the symmetries of the N–O stretching modes can be correctly assigned. In a C_{2v} bidentate complex MNO_3, the expected order [2] of the N–O stretching modes † is $\nu_{A_1} > \nu_{B_2} > \nu_{A_1}$, and is different from that predicted for an idealised C_{2v} monodentate complex, where $\nu_{B_2} > \nu_{A_1} > \nu_{A_1}$. For both types of complex, the two highest frequency N–O modes ($A_1 + B_2$) correlate with the E' stretching mode in free $[NO_3]^-$ (D_{3h}) and the remaining (A_1) mode correlates with the A_1' breathing mode.

For each type of complex, the three N–O stretching modes are active in both the i.r. and the Raman and in principle a definitive depolarisation study in the Raman should establish the assignments of the A_1 and B_2 modes and hence the type of co-ordination. However, the highest frequency A_1 band derives from a depolarised (E') band in the free ion, and although there may be a significant splitting of this degeneracy in the complex into two well-separated features, the depolarisation ratio of the A_1 component is expected [4] to be only slightly less than the value predicted ($\rho_p = \frac{3}{4}$) for the B_2 component.

The identification of even strongly polarised Raman bands in matrix-isolation studies is regarded as at least difficult by most experimentalists, and we have therefore been interested in developing a new method of distinguishing between mono- and bi-dentate co-ordination in oxy-anion salts. Our approach is based on the use of characteristic isotope frequency and intensity patterns in the i.r. spectrum of the ^{18}O-enriched material, and this paper first outlines the basic model appropriate for MXO_3 species, and secondly uses the model to show that molecular KNO_3 isolated in low-temperature matrices exhibits bidentate binding.

PROCEDURE

In order to illustrate the application of our method, we have carried out a series of general calculations on co-ordinated nitrates based on the approach of Hester and co-workers [2,3] and these involve a number of simplifying assumptions. First, since we shall be concerned exclusively with the stretching region of the i.r. spectrum, we assume that the stretching modes in both free and co-ordinated nitrates are uncoupled from the bending modes. Two stretching force constants are then sufficient to describe the $A_1' + E'$ stretching modes in free (D_{3h}) nitrate, and if K_r and K_{rr} denote the principal and interaction stretching constants respectively, it may then be shown quite generally, for D_{3h} XY_3, that equations (1) and (2) apply. Typical

$$\lambda_{A_1'} = (K_r + 2K_{rr})(1/M_Y) \qquad (1)$$

$$\lambda_{E'} = (K_r - K_{rr})(1/M_Y + 3/2M_X) \qquad (2)$$

values [1] for free $[NO_3]^-$ are taken to be $\nu_{A_1'} = 1\ 050\ cm^{-1}$ and $\nu_{E'} = 1\ 390\ cm^{-1}$, and these equations yield values for K_r and K_{rr} of 7.93 and 1.255 mdyn Å^{-1} respectively.‡

On co-ordination, the equivalence of the three N–O bonds is removed, and we assume that two principal stretching constants, K_1 and K_2, and one general-purpose interaction constant K_{rr}, now constitute the minimum number of force constants which might realistically describe the N–O stretching modes. In both monodentate and bidentate C_{2v} complexes, two of the N–O bonds will remain equivalent, and these are associated with K_2, whilst the unique N–O bond is described by K_1. For bidentate complexes, we anticipate [2] a higher bond-order for the ' free ' N=O linkage, and thus expect $K_2 < K_1$, whereas in monodentate complexes, the reverse would be expected,[3] with $K_1 < K_2$. The final assumption concerning force constants is the use of the artificial, but convenient constraint $2K_2 + K_1 = 3K_r$, and we retain the value of K_{rr} found in free $[NO_3]^-$.

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† Throughout this paper, ν_{B_2} refers to an in-plane antisymmetric mode.

‡ Throughout this paper: 1 dyn = 10^{-5} N.

The only assumption made in the calculation of G matrix elements is that the NO_3 unit remains planar with all ONO angles 120°.

We then compute * all the N–O stretching frequencies in both free and co-ordinated nitrate ions for the isotopically labelled species $N^{16}O_n{}^{18}O_{3-n}$ (n = 0—3), and focus attention on the frequency range 1 250—1 550 cm^{-1}. This region includes the i.r. active E' mode in free $[N^{16}O_3]^-$ and also encompasses the resulting $A_1 + B_2$ modes prominent in the i.r. spectra of the majority of co-ordinated nitrates.[1] Our calculations are displayed as a series of line spectra, spanning a range of different values of K_1 and K_2, and in order to simulate typical spectral results, an attempt has also been made to indicate the relative i.r. band intensities which would be expected for a 50% random distribution of ^{18}O atoms for each particular species in question. The basic assumption made here is that all the frequency components arising from the parent E' mode in a D_{3h} nitrate ion have equal absorbances. Thus in co-ordinated $[N^{16}O_3]^-$, where the E' degeneracy is lifted as a result of inequivalent force constants, the A_1 and B_2 components are taken to have the same intensity, whilst in free $[N^{16}O_2{}^{18}O]^-$, where the degeneracy is removed by inequivalent oxygen masses, the same assumption is made.

When considered separately, each of the above simplifications may be shown to be reasonable, and as indicated below, when considered *collectively*, they also appear to result in a vibrational model which is both simple and qualitatively very useful.

RESULTS AND DISCUSSION

Figure 1 summarises the results of six typical isotope frequency and intensity calculations which range from ' strong ' bidentate binding [Figure 1(*i*)] through ' free ' nitrate [1(*iii*)] to ' strong ' monodentate [1(*vi*)] co-ordination, and show several interesting features. First the ' free ' ion isotope pattern shown in Figure 1(*iii*) is an almost equally spaced quartet characteristic of partial isotopic substitution in the E' stretching mode of a planar XY_3 species. This type of isotope pattern is well documented in matrix-isolation studies on metal trichlorides,[5] and need not be discussed further apart from noting that the 50% ^{18}O-enrichment chosen to illustrate these calculations will give the approximate intensity ratios 5 : 3 : 3 : 5, rather than the 81 : 9 : 27 : 11 ratios appropriate for chlorine isotopes in natural abundance.

In contrast to Figure 1(*iii*), calculations (*ii*) and (*i*), respectively, show the isotope patterns expected for increasing distortion due to bidentate binding. Two groups of bands emerge which may readily be associated with the A_1 and B_2 components of the split E' mode, and even for a relatively small difference between K_1 and K_2, it is clear that under modest resolution the highest-frequency group is predicted to appear essentially as a 1 : 1 doublet on 50% ^{18}O-enrichment. Only under good resolution (*ca.* 2 cm^{-1}) would each component of this doublet reveal a closely spaced 1 : 2 : 1 triplet fine structure.

The highest-frequency (A_1) mode in bidentate co-ordination thus gives rise to a total of six bands on ^{18}O enrichment. These arise from the terminal N–O modes in the six different isotopic species; (*a*) $M^{16}O^{16}ON^{16}O$, (*b*) $M^{16}O^{18}ON^{16}O$, (*c*) $M^{18}O^{18}ON^{16}O$, (*d*) $M^{16}O^{16}ON^{18}O$, (*e*) $M^{16}O^{18}ON^{18}O$, and (*f*) $M^{18}O^{18}ON^{18}O$. For 50% ^{18}O enrichment, these are present in the relative proportions 1 : 2 : 1 : 1 : 2 : 1 and their individual contributions to this isotopic pattern are shown in Figure 1(*i*).

The frequency splitting of the basic (abc)–(def) doublet is predicted to be *ca.* 25 cm^{-1}, and it thus bears a strong resemblance to the simple doublet which would be predicted for a single terminal N=O mode completely uncoupled from all other vibrations in the molecule. This similarity arises not because coupling is weak or non-existent (in fact it is quite appreciable, as previously demonstrated by Hester and Grossman,[2] and also by these calculations) but because coupling between this mode and the other stretching modes is essentially the same from one isotope modification to the next; *i.e.* there is little differential coupling. This in turn arises basically because the ^{16}O–^{18}O frequency shifts are relatively small compared with the frequency separation between the fundamentals.

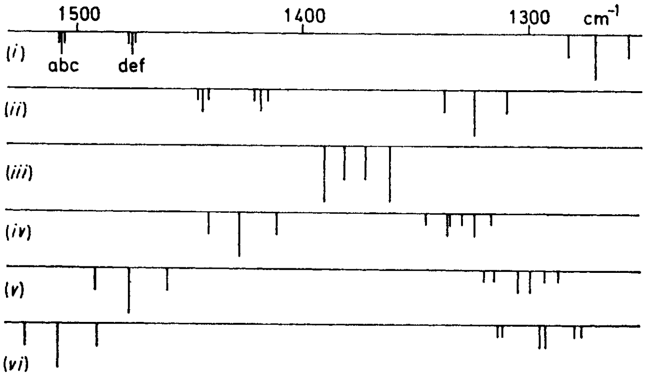

FIGURE 1 Calculated i.r. frequency and intensity patterns (1 250—1 550 cm^{-1}) for 50% ^{18}O-enriched nitrates; (*i*) C_{2v} bidentate: $K_1 = 9.93$, $K_2 = 6.93$, $K_{rr} = 1.225$ mdyn Å^{-1}; (*ii*) C_{2v} bidentate: $K_1 = 8.93$, $K_2 = 7.43$, $K_{rr} = 1.225$ mdyn Å^{-1}; (*iii*) D_{3h} ' free ' ion: $K_1 = K_2 = 7.93$, $K_{rr} = 1.225$ mdyn Å^{-1}; (*iv*) C_{2v} monodentate: $K_1 = 6.93$, $K_2 = 8.43$, $K_{rr} = 1.225$ mdyn Å^{-1}; (*v*) C_{2v} monodentate: $K_1 = 5.93$, $K_2 = 8.93$, $K_{rr} = 1.225$ mdyn Å^{-1}; and (*vi*) C_{2i} monodentate: $K_1 = 5.26$, $K_2 = 9.26$, $K_{rr} = 1.225$ mdyn Å^{-1}

Calculations (*iv*)—(*vi*) show the corresponding patterns expected for increasing monodentate binding. The highest frequency group is now predicted as a 1 : 2 : 1 triplet on 50% ^{18}O-enrichment, with an overall splitting of *ca.* 30 cm^{-1}. For this antisymmetric motion of the terminal N^nO^mO group, our calculations predict band superposition for molecule species $M^{16}ON^nO^mO$ and $M^{18}ON^nO^mO$, and the triplet structure is thus due to the three possible types of terminal groups: $N^{16}O_2$, $N^{16}O^{18}O$, and $N^{18}O_2$.

These results therefore provide a very clear distinction between these two modes of co-ordination. In ^{18}O-enriched bidentate complexes, the highest frequency band

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* Calculations were carried out using programs based on the standard Wilson–GF method.

should appear essentially as a well-spaced doublet each component of which should show triplet fine structure. In contrast, the highest frequency band in a monodentate complex should appear as a basic triplet. The relative intensities of the doublet or triplet components will, of course, depend on the extent of ^{18}O-enrichment, and quite generally, it may be shown that for an atom ratio $^{16}O : ^{18}O$ of $n : 1$, the relative intensities of the triplet in the monodentate complex should be $n^2 : 2n : 1$. In the bidentate case, the basic high-frequency doublet should be in the ratio $n : 1$, and the triplet fine structure within each component should be $n^2 : 2n : 1$.

The extent to which this approach may be applied to real systems is illustrated by a re-examination of the i.r. spectrum of matrix-isolated KNO_3.

Matrix-isolation Studies on KNO_3.—*Introduction.* The matrix isolation experiments reported by Devlin and co-workers[6] have demonstrated conclusively that monomeric KNO_3 can be isolated and studied in low-temperature inert-gas matrices. In particular, they identified four fundamentals for KNO_3 in argon at 1 462, 1 291, 1 031, and 830 cm^{-1}, and assigned these to a *monodentate* structure $K^{16}ON^{16}O_2$. For the idealised C_{2v} model, the symmetries of these bands are B_2 (1 462 cm^{-1}), A_1 (1 291 and 1 031 cm^{-1}), and B_1 (830 cm^{-1}). The three highest-frequency bands are N–O stretching modes, and the 830 cm^{-1} band is the out-of-plane NO_3 deformation.

However, these experiments were unable to distinguish unequivocally between monodentate and bidentate binding, and very recently, it has been suggested[7] from calculations that in the related molecule $LiNO_3$ bidentate binding would lead to a lower-energy configuration than monodentate. ^{18}O-Enriched KNO_3 is readily available (Prochem) and it therefore seemed worthwhile to apply the simple theoretical model described above to this problem in an attempt to distinguish *experimentally* between these two possibilities.

Our initial results on the i.r. spectrum of matrix-isolated $KN^{16}O_3$ in argon at 10 K were very similar to those reported by Devlin and co-workers.[6] Four corresponding monomer bands were noted at 1 460.5, 1 293.1, 1 031.1, and 827.5 cm^{-1}, and a fifth, weaker feature was also observed at 721.0 cm^{-1}. This band is close to the E' bending mode in free $[NO_3]^-$ (*ca.* 715 cm^{-1}) and although not discussed by Devlin, seems to be present in his spectra. The two high-frequency bands are approximately equal in intensity, and considerably stronger than the third N–O stretching mode at *ca.* 1 031 cm^{-1}, indicating that the assumption made earlier concerning equal intensity distribution between the components of the split E' mode is borne out experimentally. A typical spectrum of these two N–O stretching modes is shown in Figure 2(*i*).

^{18}O-*Isotope spectra.* The general effect of ^{18}O-enrichment on these modes is shown in Figure 2(*ii*). Here, a sample of 20.3% ^{18}O-enriched KNO_3 has been heated to *ca.* 380 °C in a Pyrex sample tube, and the vapour condensed to 10 K in a large excess of argon. The general experimental details concerning our matrix-isolation system are described elsewhere.[5] Under low resolution, the highest-frequency fundamental at *ca.* 1 460 cm^{-1} now appears as a basic doublet, each component of which shows fine structure, whilst the 1 293 cm^{-1} band gives rise to a clearly defined triplet. For 20.3% ^{18}O-enrichment, our bidentate model predicts a basic high-frequency doublet, with an intensity ratio of *ca.* 4 : 1 ($^{16}O : ^{18}O$) each component showing triplet fine structure of *ca.* 16 : 8 : 1.

Even under low resolution, therefore, this spectrum points very strongly towards the *bidentate* binding model, and this conclusion is supported by the relatively simple triplet observed for the second-highest fundamental at *ca.* 1 300 cm^{-1}. Assuming idealised C_{2v} symmetry, we therefore re-assign the $KN^{16}O_3$ fundamentals as 1 460.5 A_1, 1 293.1 B_2, and 1 031.1 cm^{-1} A_1. The out-of-plane mode at *ca.* 830 cm^{-1} remains B_1 and the weak feature at 721.0 cm^{-1} we arbitrarily assign to the B_2 component of the E' bend.

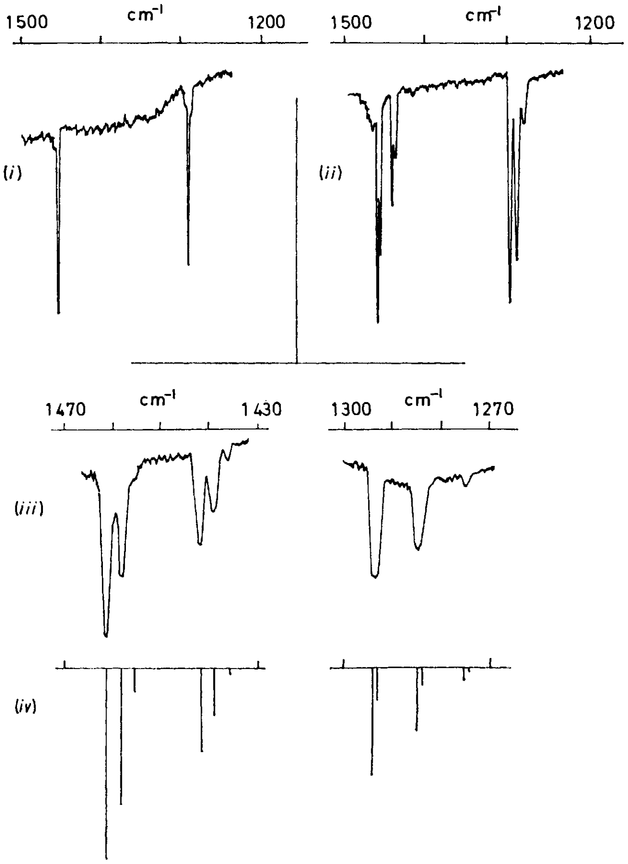


FIGURE 2 Observed and calculated i.r. spectra (cm^{-1}) for KNO_3 isolated in low-temperature argon matrices: (*i*) low-resolution spectrum of $KN^{16}O_3$ (1 200—1 500 cm^{-1}); (*ii*) spectrum of KNO_3 with 20.3% ^{18}O-enrichment; (*iii*) high-resolution spectrum of (*ii*); (*iv*) spectrum calculated for (*iii*) using parameters in the Table

High-resolution studies were carried out on the two most intense stretching modes, and Figure 2(*iii*) shows the patterns obtained. The higher frequency ' doublet ' is seen to split into five distinct components with a possible unresolved shoulder at *ca.* 1 456 cm^{-1}, whilst the lower-frequency triplet shows no further resolvable fine structure. The frequencies of all these components, together with the other fundamentals of $KN^{16}O_3$ observed in this work, are listed in the Table.

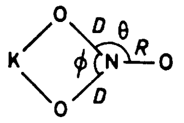
Spectral interpretation. Two stages of calculation were then carried out in an attempt to fit these isotope patterns quantitatively within experimental error using the C_{2v} bidentate model. The first approach was based on the simple recipe described above. Using only the three observed N–O stretching frequencies (1 460.5, 1 293.1, and 1 031.1 cm^{-1}) the force constant parameters $K_1 = 9.29$, $K_2 = 7.06$, and $K_{rr} = 1.26$ mdyn Å^{-1} were obtained and these parameters were then used to generate an isotope line diagram similar to those in Figure 1(*i*) and (*ii*) appropriate for 20% ^{18}O-enrichment. The overall appearance of the resulting pattern was very similar to our observed spectrum, but the isotope frequency fit was well outside experimental error. Thus, whereas the observed separation of the high-frequency ' doublet ' is *ca.* 20 cm^{-1}, this calculation predicted *ca.* 28 cm^{-1}. Our simple force field was therefore modified in basically two ways. Two (rather than one) stretch–stretch interaction constants were employed to allow for different interactions between bridge and terminal N–O bonds, and the existence of the in-plane NO_3 bending modes was acknowledged by including one principal bending constant and two stretch–bend interactions whilst at the same time introducing the observed bending mode at 721.0 cm^{-1} as an additional constraint. No account was taken of cation motion, and all three ONO angles were held fixed at 120°. The line diagram in Figure 2(*iv*) and the accompanying data in the Table show the results of one of several closely similar sets of solutions which match the observed isotope fine structure to within *ca.* 1 cm^{-1}. This Table also indicates our assignment for each individual isotope band, and the agreement between the observed and calculated spectra provides very strong quantitative evidence in favour of the bidentate structure.

TABLE

Vibrational frequencies (cm^{-1}) of isotopically-labelled KNO_3 species isolated in argon matrices at 10 K

Observed			Assignment
Ref. 6	This work [a]	Calculated [b]	(C_{2v} bidentate structure)
1 462	1 460.5	1 460.5	$K^{16}O^{16}ON^{16}O$ (A_1)
	1 457.3	1 457.7	$K^{16}O^{18}ON^{16}O$
		1 454.8	$K^{18}O^{18}ON^{16}O$
	1 441.1	1 441.4	$K^{16}O^{16}ON^{18}O$
	1 438.6	1 438.0	$K^{16}O^{18}ON^{18}O$
	1 435.5	1 434.4	$K^{18}O^{18}ON^{18}O$
1 291	1 293.1	1 293.2	$K^{16}O^{16}ON^{16}O$ (B_2)
		1 292.1	$K^{16}O^{16}ON^{18}O$
	1 284.2	1 284.2	$K^{16}O^{18}ON^{16}O$
		1 282.9	$K^{16}O^{18}ON^{18}O$
	1 274.1	1 274.5	$K^{18}O^{18}ON^{16}O$
		1 273.2	$K^{18}O^{18}ON^{18}O$
1 031	1 031.1	1 031.1	$K^{16}O^{16}ON^{16}O$ (A_1)
830	827.5		$K^{16}O^{16}ON^{16}O$ (B_1)
	721.0	721.0	$K^{16}O^{16}ON^{16}O$ (B_2)

[a] Frequency accuracy ±0.3 cm^{-1}. [b] The following parameters were used in these calculations



with $D = 1.4$ Å
$R = 1.12$ Å
$\theta = \phi = 120°$

$F_R = 9.26$ mdyn Å^{-1}
$F_D = 6.72(5)$ mdyn Å^{-1}
$F_{RD} = 1.11$ mdyn Å^{-1}
$F_{DD} = 0.95$ mdyn Å^{-1}
$F_\theta = F_\phi = 1.54$ mdyn Å rad^{-2}
$F_{R\theta} = 1.21$ mdyn rad^{-1}
$F_{D\theta} = 0.76$ mdyn rad^{-1}

Conclusions.—Two main conclusions may be drawn from this work. First, ^{18}O-isotope substitution shows that in matrix-isolated KNO_3, the oxy-anion acts as a bidentate ligand. This mode of co-ordination is presumably also favoured in the vapour phase, and these results therefore provide an interesting comparison with the shape recently predicted for $LiNO_3$.[8] More significantly, however, our calculated line diagrams indicate that the mode of co-ordination in MXO_3 species may readily be inferred simply by noting the ^{16}O–^{18}O frequency and intensity pattern in the X–O stretching region without recourse to detailed calculation. If this generalisation is correct, it is necessary to examine briefly the extent to which some of the more important assumptions made in our simple model might affect the picture.

From a chemical point of view, the arbitrary imposition of C_{2v} symmetry on these species constitutes a significant simplification, as distortions from this geometry are well documented in MNO_3 complexes. The first type of distortion we may envisage is a departure from overall planarity to give a mono- or bi-dentate species in which two of the X–O bonds remain equivalent. This type of distortion would not affect the qualitative appearance of our line diagrams. A second type of distortion leads to a situation in which no two X–O bonds remain equivalent by symmetry. For monodentate XO_3, this might be achieved by a non-linear $\mathrm{M}\overset{\mathrm{O}}{\diagup\;\diagdown}\mathrm{X}$ linkage, and in the bidentate case, by inequivalent M–O bonds. For this type of distortion both modes of co-ordination will lead to *eight* distinct isotopic species, and for 50% ^{18}O-enrichment, the principal effect on the line diagrams, for small distortions, will be to split the central component of each 1 : 2 : 1 triplet into a doublet to give a local pattern of 1 : 1 : 1 : 1. Our spectra for matrix-isolated KNO_3 show no evidence for this type of distortion.

From the point of view of the vibrational analysis, the most serious omission in the simple model is probably the neglect of coupling with bending modes. This is expected to be most important when the common central atom has a low mass relative to oxygen since coupling *via* off-diagonal *G*-matrix elements will then be most significant. However, the nitrate example chosen here, where X is one of the lightest atoms possible, shows very good qualitative agreement between the observed spectrum and the simple bidentate line diagrams. Only when a quantitative frequency fit was attempted was it necessary to introduce interaction with the bending modes. For a heavier central atom (*e.g.* X=P) the simple force field calculations should yield an even better prediction.

We therefore believe that this approach will prove a very helpful diagnostic method for determining co-ordination type and that it will prove useful not only in the characterisation of high-temperature vapours, using matrix-isolation methods, but also for more familiar solid complexes containing carbonato- or nitrato-ligands where a distinction should still be possible despite greater band widths.

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