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Vibrational Analysis of Bidentate Nitrate and Carbonate Complexes[1]

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Normal coordinate calculations have been made for nitrate and carbonate ions, assuming them to act as bidentate metal ligands. Force fields which give satisfactory frequencies for the uncomplexed anions have been perturbed in ways corresponding to metal–oxygen bonding and ligand polarization, and the effects on infrared and Raman frequencies of the ligand have been calculated.

Introduction

It has been customary, during the past several years, to use infrared spectra as a means of determining the structures of coordination complexes. In particular, the question of whether nitrate and carbonate ions coordinate as monodentate or as bidentate ligands has received much attention,[2] but it has become clear that it is not usually possible to decide on the basis of infrared evidence alone which of these forms exists in any given complex. Nevertheless, several workers have been able to show that distinctive trends in frequencies and band splittings are found in a few cases of known bidentate complexes, and a thorough analysis of these systems for information on the ways in which changes in the various molecular parameters affect the observed spectra seemed desirable.

In the calculations presented here, we have determined the spectral effects of variations in several parameters, the most important of which appear to be metal–oxygen bond strength and oxyanion polarization, in order to provide an insight into the detailed mechanism of bidentate complex formation. Both ligand vibrations and metal–oxygen vibrations are examined, particular attention being paid to the exact forms of the normal modes and their dependence on the strength of the complex formation.

Normal Coordinate Calculations

The procedure used was the same as that of the earlier work of this type.[3] The Wilson *F–G* matrix method[4] was used to analyze the normal modes of vibration of the planar bidentate MO_2XO complex. Figure 1 shows the internal coordinates used in our calculations, and from them the following in-plane symmetry coordinates were obtained

$$S_r = (1/\sqrt{2})(r_1 + r_2) \qquad S_\gamma = \Delta\gamma$$
$$S_\rho = \Delta\rho \qquad S_{-r} = (1/\sqrt{2})(r_1 - r_2)$$
$$S_R = (1/\sqrt{2})(R_1 + R_2) \qquad S_{-R} = (1/\sqrt{2})(R_1 - R_2)$$
$$S_\theta = \Delta\theta \qquad S_{-\alpha} = (1/\sqrt{2})(\alpha_1 - \alpha_2)$$
$$S_\beta = (1/\sqrt{2})(\beta_1 + \beta_2) \qquad S_{-\beta} = (1/\sqrt{2})(\beta_1 - \beta_2)$$

The out-of-plane modes of the complex were omitted from our treatment since in the planar molecule these would not be affected by changes in in-plane stretching force constants.

A generalized *G* matrix was set up using molecular parameters whose values were between those for NO_3^- and CO_3^{2-}. The X–O bond lengths and O–X–O interbond angles were all taken as equal: 1.26 A and 120°, respectively. Actual bond lengths are 1.22 A in $NaNO_3$ and 1.29 A in $CaCO_3$.[5] We assumed that changes in stretching force constants would have a more pronounced effect on the vibrational frequencies than changes in molecular geometry, so that the same *G* matrix could be used for all of the calculations. An average mass of 13 amu was used for the ligand central atom. With a metal–oxygen bond distance of 2.0 A, the X–O–M angle was 86° 58′, and the O–M–O angle 66° 4′. The mass of the metal atom was taken as 60 amu, which covers the transition metals from Mn to Zn.

Using this *G* matrix, the simplest set of force constants that could satisfactorily reproduce the experimental frequencies[6] for the uncomplexed anion was found. A modified valence force field with one off-diagonal element fulfilled the task adequately. To reproduce the free-anion frequencies, the calculations were made assuming the C_{2v} symmetry of the complex but using the force constants of the uncomplexed oxyanions. The blocks corresponding to the separate symmetry species in the factored *FG* product matrix then gave identical eigenvalues owing to the artificial separation of the degenerate modes of the free ions. Next, the metal–oxygen stretching force constant was increased from zero, leaving the oxyanion force constants at their values for the free ion. Then, with the metal–oxygen force constant left at zero, the oxyanion bond force constants were changed in such a way that the force constant for the uncoordinated oxygen increased as those for the coordinated oxygens decreased, the sum of the three remaining the same as for the free

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[1] This study was aided by a grant from the Office of Saline Water, U. S. Department of the Interior.

[2] See, for example, (a) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957); (b) B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, 3965 (1958); (c) J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960); (d) K. Buijs and C. J. H. Schutte, *Spectrochim. Acta*, **18**, 307 (1962); (e) B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 5278 (1963); (f) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963); (g) C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

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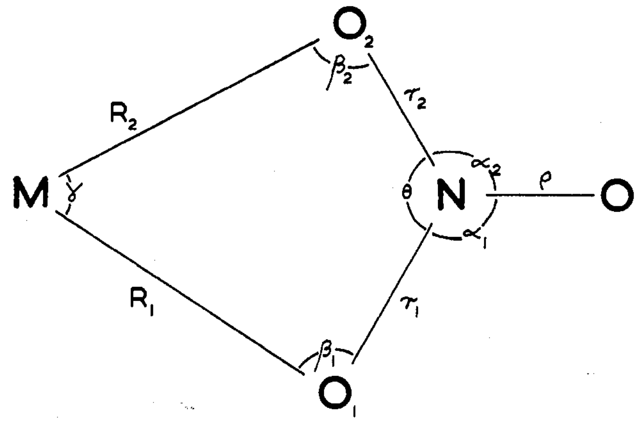

Figure 1.—Internal coordinates of a metal–XO_3 bidentate complex used in normal coordinate analysis.

anion. This situation is believed to represent closely simple polarization of the oxyanion, a view which is strongly supported by the results of Fujita, *et al.*,[7] for the case of the polarized carbonate ion. Finally, the metal–oxygen bond stretching force constant was given a value of 1.0 mdyne/A, and the effect of polarization of the anion bonds was redetermined.

Deformation force constants for the X–O–M and O–M–O angles were set equal to zero throughout, it having been established independently that incorporation of reasonable nonzero values for these force constants produced but small changes in the frequencies discussed. In addition, these changes produced new frequencies in the 500–600-cm^{-1} region. These, of course, are unreasonably high and have not been experimentally observed. Without a more detailed knowledge of charge distributions it is very difficult to predict the direction and reasonable magnitude of changes in the remaining force constants, but, at the suggestion of a referee, we further examined the effects on the various spectral features of changes in F_θ and F_α, the OXO bending force constants, and in the two F_{rr} off-diagonal interaction constants. The bending force constants were varied from the free-ion value of 0.54 mdyne/A over the range 0.22–1.20 mdynes/A, and the interaction constants, from 2.06 mdynes/A over the range 1.34–3.50 mdynes/A. The results of these changes are presented and discussed in the following section.

Results and Discussion

The calculated frequency variations produced by changes in M–O and in X–O (X = N or C) force constants are plotted in Figures 2 and 3.[8] Figure 2 shows clearly the effects of metal binding, without ligand distortion, on the frequencies derived from the A_1' and

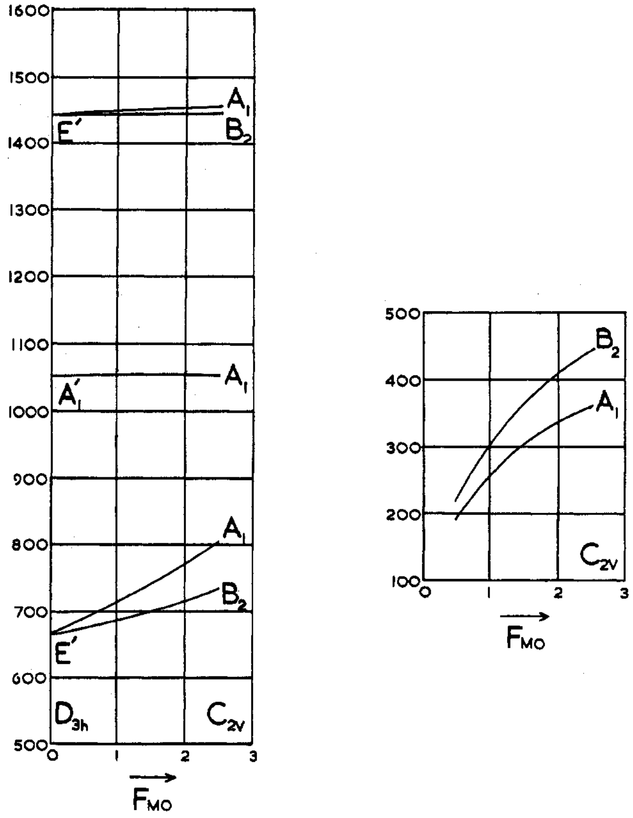

Figure 2.—Frequency variations (in cm^{-1}) resulting from perturbation of an XO_3 oxyanion by bidentate metal bonding (F in mdynes/A): (a) XO_3 frequencies; (b) M–O frequencies.

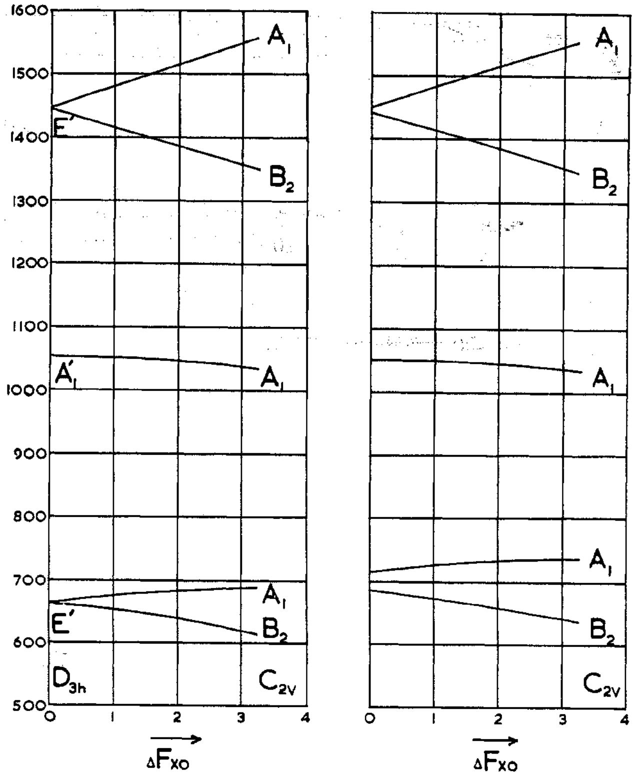

Figure 3.—Frequency variations (in cm^{-1}) resulting from perturbation of an XO_3 oxyanion by both polarization and metal bonding (F in mdynes/A): (a) polarization only; (b) polarization and M–O bonding.

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(7) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

(8) Complete details on the force constant programs used in all these calculations have been set out in tabular form and deposited as Document No. 8913 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

E′ modes of the free oxyanion and also shows the variation of the metal–oxygen frequencies. Figure 3 shows the frequency changes produced by oxyanion polarization, both with and without metal binding. Table I contains sets of normalized eigenvectors associated with some of the frequencies plotted in Figures 2 and 3. These give the contributions of the various symmetry coordinates to each normal mode and show that the nature of the modes is severely modified by the perturbations imposed. The modes selected for display in Table I are merely typical of the three types of perturbation used in this study, it being thought unnecessary to give all of our eigenvector results. It can be seen that the assignments of complex frequencies to the various symmetry species are unambiguously contained in the compositions of the eigenvectors. Both metal binding and oxyanion polarization are seen to cause splitting of the D_{3h} E′ modes into an upper A_1 symmetric component and a lower B_2 antisymmetric component.

The eigenvectors also show how misleading it is to describe these modes, as is often done, as simple X═O stretching, or symmetric or asymmetric XO_2 stretching, etc. Such oversimplified descriptions applied to the highest frequency "X═O symmetric stretching mode," and the next highest "XO_2 asymmetric stretching mode," of the polarized XO_3 lead to the expectation that the frequency usually called free O–X stretch (A_1) should increase at twice the rate of decrease of the asymmetric XO_2 stretching frequency (B_2). This follows from the fact that our polarization procedure causes the free O–X bond force constant to change at twice the rate of a bound O–X force constant. However, Figure 3 shows that this expectation is not consistent with our calculated frequency values for these A_1 and B_2 modes, and the eigenvectors given in Table I show that the expectation is completely unreasonable since it is apparent that each of these modes is, in fact, a complex admixture of several different types of molecular motion.

Figure 2 shows that the effect of metal binding without oxyanion polarization is only very small for the highest frequency X–O bond stretching modes but is quite marked with the OXO angle deformation modes. Moreover, in contrast to the monodentate cases studied,[3] both the symmetric and the antisymmetric modes are affected, and in a noticeably nonlinear manner. Our eigenvector analysis shows the nonlinearity to be due to a coupling of M–O stretching motion with OXO angle deformation motion, a coupling

TABLE I

NORMALIZED EIGENVECTORS FOR SOME NORMAL MODES, Q_r, OF XO_3 OXYANIONS PERTURBED BY POLARIZATION AND METAL BINDING (MODES LABELED 7, 1, AND 2 ARE CONVENTIONALLY NAMED AS XO_3 STRETCHING MODES, 8 AND 3 ARE THE XO_3 DEFORMATION MODES, AND 9 AND 4 ARE MO STRETCHES)

	$Q_7^{B_2}$	$Q_1^{A_1}$	$Q_2^{A_1}$	$Q_8^{B_2}$	$Q_3^{A_1}$	$Q_9^{B_2}$	$Q_4^{A_1}$
Free Ion							
S_r	0	−0.5101	0.8166	0	−0.5015		
S_ρ	0	0.7213	0.5772	0	0.7104		
S_R	0	0	0	0	0		
S_θ	0	−0.4685	0	0	−0.4939		
S_β	0	0	0	0	0		
S_γ	0	0	0	0	0		
S_{-r}	0.9175	0	0	0.9072	0		
S_{-R}	0	0	0	0	0		
$S_{-\alpha}$	0.3976	0	0	−0.4206	0		
$S_{-\beta}$	0	0	0	0	0		
M–O Bonding with F_{MO} = 1.00 mdyne/A							
S_r	0	−0.5063	0.8182	0	−0.4796	0	−0.2743
S_ρ	0	0.7196	0.5749	0	0.7127	0	0.3216
S_R	0	0.04428	0.004837	0	−0.2407	0	0.8412
S_θ	0	0.4773	0	0	−0.4518	0	−0.3372
S_β	0	0	0	0	0	0	0
S_γ	0	0	0	0	0	0	0
S_{-r}	0.9166	0	0	0.8981	0	−0.3152	0
S_{-R}	−0.02446	0	0	0.1699	0	0.9289	0
$S_{-\alpha}$	0.3991	0	0	−0.4055	0	0.1944	0
$S_{-\beta}$	0	0	0	0	0	0	0
M–O Bonding + Polarization with F_{MO} = 1.00 mdyne/A and ΔF_{XO} = 2.80 mdynes/A							
S_r	0	−0.1685	0.7922	0	0.6406	0	−0.2778
S_ρ	0	0.9234	0.6040	0	−0.5703	0	0.3137
S_R	0	0.02868	−0.01263	0	0.2287	0	0.8435
S_θ	0	0.3437	−0.08649	0	0.4606	0	−0.3361
S_β	0	0	0	0	0	0	0
S_γ	0	0	0	0	0	0	0
S_{-r}	0.8579	0	0	0.9058	0	−0.3268	0
S_{-R}	−0.03655	0	0	0.1900	0	0.9242	0
$S_{-\alpha}$	0.5125	0	0	−0.3788	0	0.1976	0
$S_{-\beta}$	0	0	0	0	0	0	0

which was not found when only a single M–O bond formation was considered. Significantly higher M–O stretching frequencies are responsible for this coupling in the bidentate case. For example, a metal–oxygen bond stretching force constant of 2.0 mdynes/A gave an M–O frequency of 321 cm^{-1} for monodentate coordination,[3] but for bidentate coordination symmetric and asymmetric metal–oxygen frequencies are 341 and 413 cm^{-1}, respectively. These predicted trends agree well with the complex carbonate frequencies reported by Fujita, *et al.*,[7] for mono- and bidentate coordination and support Topping's[9] recent prediction that metal–oxygen frequencies provide a useful indication of complex type.

The most marked effect of oxyanion polarization is seen from Figure 3 to be a large splitting of the components of the D_{3h} E′ asymmetric stretching mode, with the symmetric A_1 component moving to higher frequencies as the asymmetric B_2 component moves down. This is in direct contrast to the monodentate C_{2v} case, where the frequency shifts were reversed in direction. This reversal has been qualitatively predicted by Addison and Logan[10] and Amos, Hoyle, and Sutton,[11] who have suggested that the polarization of the XO_3 lines in the Raman spectrum of a complex should be a most positive means of assigning the type of coordination. For bidentate or bridging ligands, the frequency usually labeled free O–X stretch should be the highest frequency in the spectrum, and since it is a symmetric mode, it should be Raman polarized. In contrast to this, the highest frequency in the monodentate NO_3^- spectrum has been assigned[12] to an asymmetric mode. This band should be depolarized in the Raman spectrum, and this has, in fact, been found to be the case in solutions of calcium nitrate[13] and indium nitrate.[14] In the bidentate case, Amos, *et al.*,[11] have verified that the highest frequency in the spectrum of titanium(IV) nitrate is Raman polarized. The crystal structure of this compound is known from X-ray diffraction measurements,[15] and the nitrate groups in the crystal are acting as bidentate ligands. Similar Raman polarization evidence is available for bidentate nitrate coordination in the liquid complex $Th(NO_3)_4 \cdot 2TBP$.[16]

Although the magnitude of the splitting of these highest frequency stretching modes for a given amount of oxyanion polarization is higher for the bidentate case, nevertheless our simple calculations fail to reproduce the exceptionally high frequencies reported for several bidentate nitrate groups, though it is clear that they could readily be made to do so by further increasing the ΔF_{XO} values. It follows that complexes such as tin(IV) nitrate,[2g] titanium(IV) nitrate,[7] and the thorium nitrate–TBP complex,[16] which give frequencies as high as 1630, 1650, and 1625 cm^{-1}, respectively, must be highly covalent in character, with extremely polarized NO_3 groups. Logan and Simpson[17] have pointed out that there are other known bidentate nitrate complexes whose maximum absorption is well below 1570 cm^{-1} and monodentates with frequencies as high as 1550 cm^{-1}, confirming that the high-frequency criterion for bidentate complexation is an unreliable one.

Our calculations predict only small shifts to lower frequency for the $\nu_2(A_1)$ symmetric stretching mode, even when strong polarization and metal binding are present. For example, Figure 3 shows a $\nu_2(A_1)$ shift of but 16 cm^{-1} accompanies a 205-cm^{-1} splitting of the high-frequency stretching modes. This prediction is in good accord with the observed spectra from bidentate cobalt(III) carbonate complexes[7] where the splitting of the high-frequency modes ranges from 303 to 379 cm^{-1}, while the $\nu_2(A_1)$ symmetric stretching frequencies observed vary only 33 cm^{-1} from the free CO_3^{2-} ion value. A splitting of 260 cm^{-1} in the spectrum of the bidentate nitrate in $Rb(UO_2(NO_3)_3)$ is likewise accompanied by a mere 27-cm^{-1} lowering in the $\nu_2(A_1)$ frequency,[9] though a lowering of 67 cm^{-1} is reported[2g] for the Sn(IV) complex with a splitting of the N–O stretching modes of 375 cm^{-1}.

This latter complex also is unusual in giving a large downward shift of 130 cm^{-1} in its out-of-plane deformation frequency, indicative of a nonplanar configuration in the SnO_2NO unit. The rubidium uranyl nitrate out-of-plane mode is shifted only 28 cm^{-1} down from the free-ion value of 831 cm^{-1}, and the cobalt(III) carbonate out-of-plane bending is virtually unaffected by complexing. It is known from X-ray crystallographic analysis[15] that in the Ti(IV) complex four nitrate groups are coordinated in bidentate fashion to the titanium atom. It can be assumed that the Sn(IV) complex has a similar structure, so that coupling of the various modes between several nitrate ligands could give rise to the unusual features in this spectrum. The C_{2v} model used does not take account of such couplings, and a normal coordinate analysis based on the D_{2d} point group would be necessary in order to assign the lines in this spectrum properly.

The discussion so far has been limited to results from our simplest calculations, *i.e.*, those in which M–O and X–O bond stretching force constants only were varied. However, for the sake of completeness we investigated the less likely situation in which metal ion complexation caused large changes in OXO bending force constants and in our F_{rr} interaction constants.

Using our basic set of force constants with $\Delta F_{XO} = 0$ and $F_{MO} = 1.00$, the following changes were made: the off-diagonal interaction constant, F_{rr}, between the two X–O bonds connected to the metal atom was in-

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creased from 2.06 to 3.50 mdynes/A, while the interaction constant between the free X–O bond and the bound ones was left unchanged at 2.06 mdynes/A. Next, the F_{rr} between the two bound X–O bonds was increased and simultaneously the free–bound F_{rr} was decreased in such a way as to keep the sum of the three force constants constant, a procedure exactly analogous to the polarization of the stretching force constants described above. Thirdly, with the F_{rr} back at their original value, the angle deformation force constant for the bound O–X–bound O angle, F_θ, was increased from 0.54 to 1.20 mdynes/A, while that for the other two O–X–O angles, F_α, remained set at 0.54 mdyne/A. Then F_θ was increased and F_α was decreased, so that the sum $F_\theta + 2F_\alpha$ remained constant, and, finally, a bond force constant polarization was chosen ($\Delta F_{XO} = 1.90$) and one set from each of the above calculations was repeated.

Comparison of the results obtained with frequencies reported in ref 2g, 7, and 17 shows, however, that none of these approximations is satisfactory. The first, increase of bound F_{rr}, gives values for ν_1, ν_3, and ν_8 that are all too low, even at the highest value of F_{rr} used, which is nearly 75% higher than the value found for the free XO_3 anion. In addition, ν_2 is shifted slightly ($\sim$15–40 cm^{-1}) in the wrong direction. The second approximation, polarization of the bond interaction force constants, gives too small a splitting of ν_1 and ν_7 and too large a splitting of ν_3 and ν_8. It also gives too low a value for ν_8 by as much as 100 cm^{-1}. The change in F_θ alone does not give a large enough splitting of ν_1–ν_7 for a reasonable ν_3–ν_8 splitting. Moreover, ν_7 is 100–160 cm^{-1} high. When the bond deformation force constants are polarized, we find that in order to get the ν_1–ν_7 splitting to the right order of magnitude, it is necessary to use force constants which give much too large a splitting of ν_3 and ν_8. Also ν_8 is too low.

When each of these changes, in turn, is imposed upon a force field where the bond force constants have been polarized by an amount $\Delta F_{XO} = 1.90$, the results are as follows: a change in the bound F_{rr}, which gives a reasonable ν_1–ν_7 splitting, shifts ν_2 by 50 cm^{-1} in the wrong direction and gives much too large (by 180 cm^{-1}) a splitting for ν_3 and ν_8. Simultaneous change in the bound–bound and free–bound F_{rr} gives only slightly better results: no shift in ν_2, correct splitting of ν_1 and ν_7, but too large a splitting of ν_3 and ν_8, with ν_8 100–200 cm^{-1} too low. Changing F_θ to get a reasonable value for the ν_1–ν_7 splitting makes both ν_1 and ν_7 60–100 cm^{-1} too high and also results in a ν_3–ν_8 splitting which is about 60 cm^{-1} too large. Changing F_θ and F_α gives, again, too large a ν_3–ν_8 splitting, with ν_8 100–150 cm^{-1} too low.

We feel that this rather detailed analysis of what we consider are all the reasonable possibilities for change in our approach is necessary to demonstrate the utility of the simple bond polarization approximation. Not only does it reproduce experimental frequencies more closely, but it does so using what seems to be the most realistic approximation. Changing other force constants, however, necessitates assumptions about electronic distributions in the molecules which are not justified in the light of our present knowledge. Moreover, the value of such a simple force field in spectrum diagnosis and assignment is lost as soon as it is complicated by such little-understood factors.

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The Preparation and Properties of Some Ternary Nitrides of Strontium and Barium with Rhenium and Osmium

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Ternary nitrides of rhenium are formed by heating mixtures of strontium or barium nitride with metallic rhenium in pure nitrogen at atmospheric pressures. Under these conditions, osmium gives a ternary nitride only with barium. The isotypic compounds $Sr_9Re_3N_{10}$, $Ba_9Re_3N_{10}$, and $Ba_9Os_3N_{10}$ appear to be orthorhombic. They are all good conductors of electricity and are readily hydrolyzed. The magnetic properties suggest strong interaction between the transition metal ions. In the Ba–Re–N and Sr–Re–N systems, there exist thermally unstable compounds in which the rhenium has a higher oxidation state and the ratio of alkali metal to rhenium is higher than 3. The compound $Sr_{27}Re_5N_{28}$ has a cubic structure related to that of sodium chloride. The proposed structure is derived on the basis of ordered nitrogen vacancies. The rhenium atoms are distributed over the cation sites in such a way that no nitrogen is common to two rheniums. The magnetic susceptibility of this compound is temperature independent from 77 to 300°K. No intermediate phases were observed in the Ba–Os–N system.

Among the ternary oxides of the transition metals, there are notable differences between those formed with small cations such as lithium and magnesium and those obtained with the larger cations of groups I and II. The former often yield phases based on the sodium chloride, spinel, ilmenite, or olivine structures whereas