Configurations of Weak Interactions from Vibrational Perturbations in Tetrahedral XY_4 Molecules or Ions

By **J. Alan Creighton,** Chemical Laboratory, University of Kent at Canterbury, Canterbury CT2 7NH

Approximate methods are described for estimating changes in stretching force constants due to weak interactions involving tetrahedral molecules or ions from the shifts in their vibration frequencies. These methods are used to discuss published vibrational data for the C_{3v} species $Na[Co(CO)_4]$ and $[(H_{15}C_7)_3HN][GaCl_4]$ in solution, which are deduced to be apical ion-pairs from the size of the force-constant changes. Approximate formulae are also given for the stretching frequencies of trigonal-planar XY_3 and octahedral XY_6 molecules for stretching-force-constant perturbations which lower their symmetry to C_{2v} and D_{4h} respectively.

There are many published examples of small changes in the vibration frequencies of molecules or ions due to environmental or other effects, such as complex formation, solvation, crystal site, or matrix effects. Where these effects result in a splitting of bands, vibrational measurements have often been used to deduce the symmetry of the perturbation. However, for a weak interaction which perturbs the force field of the molecule only slightly, the frequencies show an approximately first-order dependence on the force-constant changes. Additional information about the sense of the interaction (for example whether a tetrahedral molecule interacting with another molecule or ion to form a C_{3v} complex interacts apically or facially) may therefore in principle be gained from the sign of the shifts in the individual vibrational bands. This has been exploited for the particular case of the relatively strong interactions of tetrahedral and trigonal-planar oxo-anions acting as ligands with transition-metal atoms in order to determine the mode of binding of these ions from vibrational measurements, following numerical studies of the effects of force-field perturbations on these ions by Hester and his co-workers.[1]

The purpose of this paper is to investigate two approximate methods which may be used in analysing frequency-shift data for the study of rather weaker interactions, where the small frequency shifts are normally not known with sufficient precision to warrant exact treatments. Three tetrahedral XY_4 species, for which frequency shifts consistent with small C_{3v} perturbations in solution have recently been published, are examined as examples. Where measurable frequency shifts can be observed, these methods appear to provide a useful general approach for studying the configuration of weak complexes of small molecules or ions, particularly for solution species for which there is sometimes a shortage of alternative structural methods.

RESULTS AND DISCUSSION

(i) *Neglect only of Bending Vibrations.*—A regular tetrahedral XY_4 molecule has two stretching frequencies $(\nu_1)_0$ and $(\nu_3)_0$ (the zero subscript here denotes the unperturbed molecule), and when the symmetry of the molecule is lowered to C_{3v} the three-fold degeneracy of (ν_3) is partially removed to give two components $\nu_3(a_1)$ and $\nu_3(e)$ in addition to ν_1. The Table reproduces recently published measurements of $(\nu_1)_0$ and $(\nu_3)_0$ for three tetrahedral species in solution, and also the corresponding data ν_1, $\nu_3(a_1)$, and $\nu_3(e)$ for the same species perturbed to C_{3v} symmetry by a weak interaction with another species present in the solutions (the counter ion in two of the examples). The stretching frequencies are seen to show shifts of a few percent as a result of the perturbations, whereas it is found for these and other examples of weakly perturbed species that the shifts in the bending frequencies are very much smaller. In discussing these frequency shifts quantitatively it thus seems a reasonable approximation to disregard bending motions and to assume that the perturbations affect only the force constants concerned with bond stretching. This approximation is made here throughout, and amounts to using the high-frequency separation approximation [2] for the stretching vibrations. Justification for this approximation is given below [see equations (5)—(7) and following discussion] by calculating the very small effect on the stretching-frequency shift of including bending in the calculations for some specific tetrahedral molecules.

Stretching wavenumbers (cm^{-1}) of tetrahedral species weakly perturbed to C_{3v} symmetry in solution

	ν_1	$\nu_3(a_1)$	$\nu_3(e)$	$(\nu_1)_0$	$(\nu_3)_0$	Ref.
$Na[Co(CO)_4]$	2 005	1 857	1 905	2 005	1 889	4
$[(H_{15}C_7)HN]$-$[GaCl_4]$	339	362	383	344	377	*
CBr_4,Cl^-	260	666	675	267	675	3

* Data from R. A. Work and M. L. Good, *Spectrochim. Acta*, 1972, **A28**, 1537.

For a tetrahedral XY_4 species perturbed to C_{3v} symmetry there are four stretching-force-constant changes in a valence force-field representation. These may be represented as the fractional increases α and γ in the stretching force constant f_r for the unique bond and for the other three bonds, and the fractional increases a and c in the stretch–stretch interaction constant f_{rr} involving the unique bond and involving only the other three bonds respectively. In order to calculate these force-constant changes from the three observed frequency shifts it is necessary to treat the change in one of the force constants, or in a linear combination of the force constants, as a variable parameter. Particularly

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[1] H. Brintzinger and R. E. Hester, *Inorg. Chem.*, 1966, **5**, 980; R. E. Hester and W.E. L. Grossman, *ibid.*, p. 1308.

[2] E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.

convenient for this purpose is the off-diagonal matrix element f_{13} connecting the two $a_1(C_{3v})$ stretching symmetry co-ordinates of the perturbed molecule. Representing these symmetry co-ordinates as in equations (1) and (2), where r_1 to r_4 are bond-length displacements,

$$S_1 = (r_1 + r_2 + r_3 + r_4)/2 \qquad (1)$$

$$S_3(a_1) = (3r_1 - r_2 - r_3 - r_4)/12^{\frac{1}{2}} \qquad (2)$$

f_{13} may be shown to be equal to $3^{\frac{1}{2}}[(\alpha - \gamma)f_r + 2(a - c)f_{rr}]/4$. This function is small for small force-constant perturbations, and plots of α, γ, a, and c against f_{13} for small values of f_{13} on either side of zero thus shows all solutions for the force-constant changes which are consistent with a small perturbation.

The set of stretching-force-constant changes may be conveniently computed as a function of f_{13} by evaluating the other three elements of the perturbed $\mathscr{F}$ matrix as a function of f_{13} using the three stretching frequencies for the perturbed molecule, and also calculating from $(\nu_1)_0$ and $(\nu_3)_0$ the elements of the unperturbed matrix $\mathscr{F}_0$ expressed in the same C_{3v} symmetry co-ordinates. Writing $(\Delta\mathscr{F}) = \mathscr{F} - \mathscr{F}_0$, the matrix of valence force-constant changes is then given by $(\Delta F) = \tilde{U}(\Delta\mathscr{F})U$, where the U matrix must contain both components of the degenerate symmetry co-ordinate $S_3(e) = (2r_2 - r_3 - r_4)/6^{\frac{1}{2}}$, $S_3'(e) = (r_3 - r_4)/2^{\frac{1}{2}}$. The fractional changes in the alternative representation of the Urey–Bradley force field may then be simply calculated from α, γ, a, and c by use of the relations between the Urey–Bradley and valence force constants for tetrahedral molecules. Thus $K\alpha_{\mathrm{UB}} = f_r\alpha - 1{\cdot}9Fa$ and $K\gamma_{\mathrm{UB}} = f_r\gamma - 1{\cdot}9F(a + 2c)/3$, where α_{UB} and γ_{UB} are fractional changes in the Urey–Bradley stretching force constant K for the unique and for the other three bonds respectively. The fractional changes in the Urey–Bradley non-bonded repulsion constant F are equal to the changes a and c in f_{rr} since for the tetrahedral molecules $3f_{rr} = 2{\cdot}1F$.

Figure 1 shows the fractional force-constant changes for $Na[Co(CO)_4]$ and $[(H_{15}C_7)HN][GaCl_4]$ plotted as functions of f_{13}. For both species $|\alpha| > |\gamma|$ unless it is assumed that there are unreasonably large changes in f_{rr}, thus indicating that both these species are apical ion-pairs. The Urey–Bradley force-constant changes for $[(H_{15}C_7)HN][GaCl_4]$ make this conclusion particularly clear since $\gamma_{\mathrm{UB}} \simeq 0$ throughout the whole range of Figure 1. A similar plot for the weakly bound complex ion CBr_4,Cl^- has already been published and suggests that this species is a *facial* complex.[3] The above result for $Na[Co(CO)_4]$ confirms the conclusion of Edgell *et al.*[4] that this is an apical ion-pair, based on qualitative discussion of the sense of the splitting of ν_3.

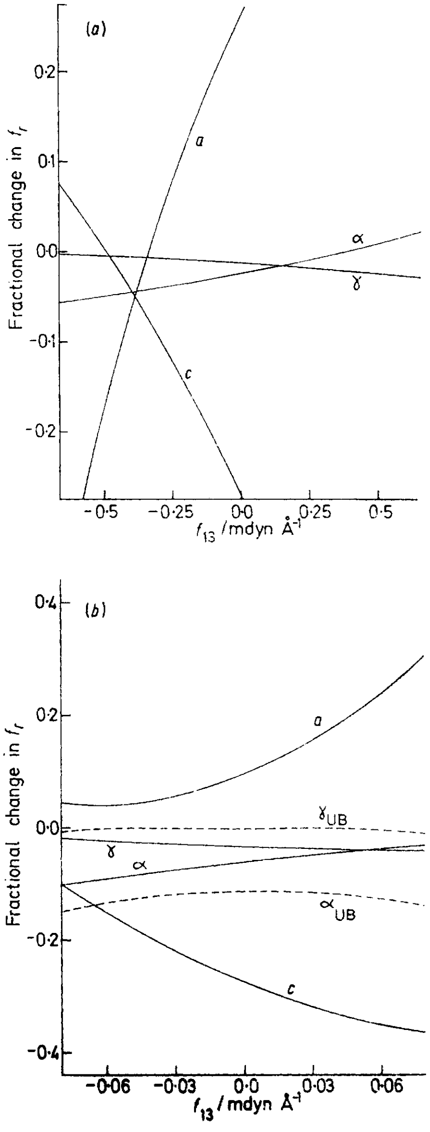

FIGURE 1 Fractional changes in the stretching force constants, f_r (or f_{rr}), of (*a*) $[Co(CO)_4]^-$ and (*b*) $[GaCl_4]^-$ on forming the contact ion-pairs $Na[Co(CO)_4]$ and $[(H_{15}C_7)HN][GaCl_4]$ in solution (see text)

(ii) *First-order Perturbation Method.*—While the above method gives a complete and fairly accurate picture of the stretching-force-constant changes which are consistent with the observed frequency shifts, it is probably not necessary in most cases to know the force-constant changes particularly accurately in order to deduce the sense of the perturbation. Indeed the experimental frequency shifts from which the force-constant changes are calculated are themselves often not known with very high fractional accuracy. A more convenient, though more approximate, first-order perturbation method for estimating the force-constant changes was therefore also investigated, in which it is assumed that the perturbation has a negligible effect on the form of the normal modes. Thus in particular it is assumed that there is a negligible interaction between $\nu_1(a_1)$ and $\nu_3(a_1)$ as a result of the

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[3] J. A. Creighton and K. M. Thomas, *J.C.S. Dalton*, 1972, 2254.

[4] W. F. Edgell and J. Lyford, *J. Amer. Chem. Soc.*, 1971, **93**, 6407.

perturbation, which requires that $(\nu_1)_0$ and $(\nu_3)_0$ are not close together or that the perturbation is not large. These requirements are likely to be approximately met in many cases however, and, since this first-order method also makes clear the importance for some molecules of stretch–stretch interaction constant changes in determining the direction of splitting of ν_3, this method is also given here in some detail.

With the usual notation involving the G and $\mathscr{F}$ matrices and the transformation matrices U and L,[2] the vibration frequencies $(\nu_i)_0$ of the unperturbed molecule are related to the force constants by $\tilde{L}_0\mathscr{F}_0L_0 = \Lambda_0$, in which Λ_0 is a diagonal matrix with elements $(\lambda_i)_0 = 4\pi^2(\nu_i)_0{}^2$. For the perturbed molecule, assuming the normal co-ordinates to be unchanged, equation (3)

$$(\Delta\Lambda) = \tilde{L}_0(\Delta\mathscr{F})L_0 = \tilde{L}_0U(\Delta F)\tilde{U}L_0 \qquad (3)$$

follows. Here the matrix $(\Delta\Lambda)$ has diagonal elements $\Delta\lambda_i = 8\pi^2(\nu_i)_0(\Delta\nu_i)$ which give the first-order corrections $\Delta\nu_i$ to the frequencies, while the off-diagonal elements contribute to higher orders of approximation.[5]

The unsymmetrized force-constant perturbation matrix (ΔF) has diagonal elements αf_r and γf_r and off-diagonal elements af_{rr} and cf_{rr} for a C_{3v} perturbation of a tetrahedral XY_4 molecule. Also required to evaluate $(\Delta\Lambda)$ are the elements of the matrix L_0. These are found by means of the standard relation [2] $L\tilde{L} = G$. For the XY_4 molecule perturbed to C_{3v} symmetry only the L_0 matrix elements l_{11} and l_{33} are required which respectively relate the two stretching symmetry co-ordinates S_1 and S_3 to the normal co-ordinates associated with ν_1 and ν_3. With S_1 and S_3 chosen as above [equations (1) and (2)], $l_{11} = \mu_Y{}^{\frac{1}{2}}$ where μ_Y is the reciprocal of the mass of atom Y. However, l_{33} is not uniquely defined since there is also a bending symmetry co-ordinate S_4 in the same tetrahedral symmetry class as S_3. I thus write for this symmetry class $L_0 = L_cC$, where L_c is a matrix chosen arbitrarily provided that it satisfies $L_c\tilde{L}_c = G$ and C is an orthogonal matrix.[6] It is convenient to choose L_c such that it defines the normal co-ordinate associated with ν_3 as pure stretching; L_0 then has the form (4) where $p = (\mu_Y + \frac{4}{3}\mu_X)^{\frac{1}{2}} = g_{33}{}^{\frac{1}{2}}$, $q = g_{43}/g_{33}{}^{\frac{1}{2}}$, $s = (g_{44} - g_{34}{}^2/g_{33})^{\frac{1}{2}}$, and g_{33}, *etc.*,

$$L_0 = \begin{bmatrix} p & 0 \\ q & s \end{bmatrix} \begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix} \qquad (4)$$

refer to appropriate elements of the G matrix. Here ϕ is a mixing parameter equal to zero if ν_3 involves purely bond stretching and to $\pi/2$ if ν_4 is pure stretching. Thus $l_{33} = (\mu_Y + \frac{4}{3}\mu_X)^{\frac{1}{2}}\cos\phi$. From (3), equations (5)—(7) are now found for the first-order corrections to λ_i.

$$\Delta\lambda_1 = \tfrac{1}{4}[(\alpha + 3\gamma)f_r + 6(a + c)f_{rr}]\mu_Y \qquad (5)$$

$$\Delta\lambda_3(a_1) = \tfrac{1}{4}[(3\alpha + \gamma)f_r - 2(3a - c)f_{rr}](\mu_Y + \tfrac{4}{3}\mu_X)\cos^2\phi \qquad (6)$$

$$\Delta\lambda_3(e) = (\gamma f_r - cf_{rr})(\mu_Y + \tfrac{4}{3}\mu_X)\cos^2\phi \qquad (7)$$

$\cos^2\phi$ is in fact very nearly unity for many XY_4 molecules, as illustrated by the following values of $\cos^2\phi$ calculated from published L matrices:[7] CCl_4, 0·9840; $SiCl_4$, 0·9960; $GeCl_4$, 0·9997; $GeBr_4$, 0·9855; and $SnBr_4$, 0·9573. Neglect of the bending contribution to ν_3 (setting $\cos^2\phi = 1$) therefore normally has a very small effect on the calculated stretching-frequency shifts, thus justifying the neglect of bending in the earlier treatment [method (i)], and this approximation is now again made here, dropping $\cos^2\phi$ from (5)—(7) above.

The expressions (5)—(7) reduce to a particularly simple form if it is assumed that the fractional changes in the stretch–stretch interaction force constants are equal to the mean of the fractional changes in the stretching force constants of the two bonds involved, *i.e.* $a = \frac{1}{2}(\alpha + \gamma)$ and $c = \gamma$. Then using also $(\lambda_1)_0 = (f_r + 3f_{rr})\mu_Y$ and $(\lambda_3)_0 \simeq (f_r - f_{rr})(\mu_Y + \frac{4}{3}\mu_X)$, the frequency shifts are given by equations (8)—(10). Analogous approximate expressions for the frequency shifts

$$\Delta\nu_1 = (\nu_1)_0\,(\alpha + 3\gamma)/8 \qquad (8)$$

$$\Delta\nu_3(a_1) = (\nu_3)_0(3\alpha + \gamma)/8 \qquad (9)$$

$$\Delta\nu_3(e) = (\nu_3)_0\gamma/2 \qquad (10)$$

which accompany a C_{2v} perturbation of a tetrahedral XY_4 molecule are (11)—(14), while for a C_{2v} perturbation

$$\Delta\nu_1 = (\nu_1)_0(\beta + \beta')/4 \qquad (11)$$

$$\Delta\nu_3(a_1) = (\nu_3)_0(\beta + \beta')/4 \qquad (12)$$

$$\Delta\nu_3(b_1) = (\nu_3)_0\beta/2 \qquad (13)$$

$$\Delta\nu_3(b_2) = (\nu_3)_0\beta'/2 \qquad (14)$$

of a trigonal-planar XY_3 molecule (15)—(17) are obtained and, for a D_{4h} perturbation of an octahedral

$$\Delta\nu_1 = (\nu_1)_0(\alpha + 2\beta)/6 \qquad (15)$$

$$\Delta\nu_3(a_1) = (\nu_3)_0(2\alpha + \beta)/6 \qquad (16)$$

$$\Delta\nu_3(b_2) = (\nu_3)_0\beta/2 \qquad (17)$$

XY_6 molecule, (18)—(22). In these relations α, β, γ, and δ denote fractional increases in the stretching

$$\Delta\nu_1 = (\nu_1)_0(\beta + 2\delta)/6 \qquad (18)$$

$$\Delta\nu_2(a_{1g}) = (\nu_2)_0(2\beta + \delta)/6 \qquad (19)$$

$$\Delta\nu_2(b_{1g}) = (\nu_2)_0\delta/2 \qquad (20)$$

$$\Delta\nu_3(a_{2u}) = (\nu_3)_0\beta/2 \qquad (21)$$

$$\Delta\nu_3(e_u) = (\nu_3)_0\delta/2 \qquad (22)$$

force constants of a unique bond, or of two, three, or four symmetrically equivalent bonds respectively. The fractional changes in the stretch–stretch interaction constants are in each case taken to be equal

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[5] C. D. Needham and J. Overend, *Spectrochim. Acta*, 1965, **21**, 417.

[6] G. Strey, *J. Mol. Spectroscopy*, 1967, **24**, 87.

[7] G. W. Chantry and L. A. Woodward, *Trans. Faraday Soc.*, 1960, **56**, 1110.

to the mean of the fractional changes in the stretching force constants of the two bonds involved.

To illustrate the accuracy of these approximate expressions, Figure 2 shows the wavenumbers of GeCl$_4$ calculated from (8)—(10) with $\alpha = -3\gamma$, compared with those derived by solution of the full vibrational secular equation from the force constants of Chantry and Woodward.[7] The frequencies ν_1 and ν_3 of GeCl$_4$ are not widely spaced so that there is a fairly strong interaction between ν_1 and $\nu_3(a_1)$ in the perturbed molecule, and it is in these frequencies that equations (8)—(10) show the greatest error, particularly for negative values of α. However, all the wavenumbers are reproduced to within 1·5 cm^{-1} of their exact values for $\alpha = 0{\cdot}05$ and to within 4·5 cm^{-1} for $\alpha = 0{\cdot}1$.

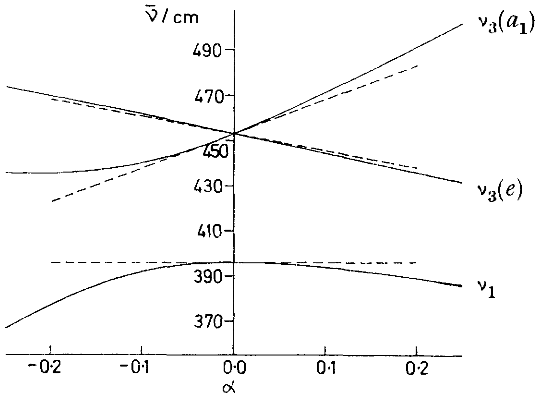

FIGURE 2 Stretching wavenumbers of GeCl$_4$ perturbed to C_{3v} symmetry, calculated from (8)—(10) with $\alpha = -3\gamma$ (— — — —) compared with those from solution of the full vibrational secular equation (——)

Of particular significance for the quantitative structural applications of equations (8)—(22) is the observation from Figure 2 that is it only for fairly strong perturbations that $\nu_3(a_1)$ and $\nu_3(e)$ cross. Use of (8)—(10) thus leads to the same conclusion about which component of ν_3 has the higher frequency for a small C_{3v} perturbation as do more exact treatments which take account of the vibrational interaction of ν_1 and $\nu_3(a_1)$. The following general conclusions may thus be drawn from (8)—(22) for small perturbations which result in a weakening of the most affected bonds (the force-constant changes for these bonds are then negative), providing (see below) that the perturbation does not result in large changes in the interaction force constant f_{rr}. (*a*) For a C_{3v} perturbation of a tetrahedral XY$_4$ molecule, $\nu_3(a_1) < \nu_3(e)$ indicates $\alpha < \gamma$ and this order of frequencies is thus consistent with an apical interaction. This result has been demonstrated numerically for the particular case of co-ordinated SO$_4^{2-}$ ions by Brintzinger and Hester.[1] (*b*) For a small C_{2v} perturbation of a tetrahedral XY$_4$ molecule, $\nu_3(a_1)$ lies between $\nu_3(b_1)$ and $\nu_3(b_2)$, as has been shown by Decius *et al.*[8] for SO$_4^{2-}$ ions at crystal sites of C_{2v} symmetry. (*c*) For a C_{2v} perturbation of a planar-trigonal XY$_3$ species, $\nu_3(a_1) < \nu_3(b_2)$ indicates $\alpha < \beta$ and is thus consistent with an apical interaction, whereas $\nu_3(a_1) > \nu_3(e)$ indicates an edge-on interaction. This rule has been used in several studies of co-ordinated nitrate ions,[9] and was demonstrated numerically for NO$_3^-$ and CO$_3^{2-}$ ions by Hester and Grossman.[1] (*d*) For a D_{4h} perturbation of an octahedral XY$_6$ species, $\nu_2(a_{1g})$ and $\nu_3(a_{2u})$ are more sensitive to changes in the axial bonds while $\nu_2(b_{1g})$ and $\nu_3(e_u)$ respond mainly to changes in the equatorial bonds, and for an axial elongation ($\beta < \delta$) it is found that $\nu_2(a_{1g}) < \nu_2(b_{1g})$ and $\nu_3(a_{2u}) < \nu_3(e_u)$ whereas for an axial bond shortening this order of frequencies is reversed.

The conclusion (*a*) above, together with the wavenumbers in the Table, show that Na[Co(CO)$_4$] and [(H$_{15}$C$_7$)HN][GaCl$_4$] are apical ion-pairs, in agreement with the results reached by the more detailed analysis of method (i). For CBr$_4$,Cl$^-$ however the order of frequencies $\nu_3(a_1) < \nu_3(e)$ suggests an apical complex, whereas it was concluded from the more complete analysis that this is a *facial* complex.[3] It is clear that the source of this disagreement lies in the more approximate treatment leading to (8)—(10), and it points out the importance which large changes in the stretch–stretch interaction constant f_{rr} can have in determining the direction of splitting of ν_3. Thus in deriving (8)—(10) the fractional changes in f_{rr} were assumed to be the mean of the changes in f_r for the two interacting bonds, whereas in the complete analysis of method (i) there was no constraint on f_{rr}. The equations (5)—(7), which also result from the perturbation treatment, do not however contain any constraint on f_{rr}, and examination shows that for $\lambda_3(a_1) < \lambda_3(e)$ it is necessary that $\alpha f_r - 2af_{rr} < \gamma f_r - 2cf_{rr}$. This inequality is satisfied by $\alpha < \gamma$ and $a < c$ (apical co-ordination) if the terms in f_r are dominant, but also by $\alpha > \gamma$ and $a > c$ (*facial* co-ordination) if those in f_{rr} are dominant. It is thus possible for ν_3 to split in the opposite sense from that predicted by (8)—(10) if f_{rr} is large and also sensitive to the perturbation. This appears to be the case for CBr$_4$ interacting with chloride ions, the large value of f_{rr} (or equivalently of the Urey–Bradley non-bonded repulsion constant F) of CBr$_4$ being due to steric crowding in this molecule,[10] and the high sensitivity of f_{rr} to the perturbation by Cl$^-$ ions possibly being a consequence of the high polarizability of the bromine atoms in CBr$_4$. It is clear that in cases where large changes in f_{rr} occur, conclusions about the sense of the perturbation, based simply on the direction of splitting of a degenerate stretching vibration, must be made with caution.

In conclusion, vibrational frequency shifts can be used to gain qualitative structural information on weak asymmetric perturbations of small molecules or ions, as previous less-general studies have indicated.[1,4] Pro-

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[8] J. C. Decius, E. H. Coker, and G. L. Brenna, *Spectrochim. Acta*, 1963, **19**, 1281.

[9] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[10] T. Simanouti, *Pure Appl. Chem.*, 1963, **7**, 131.

vided the perturbation is small and the changes in the stretch–stretch interaction force constant f_{rr} are not large, the approximate expressions (8)—(22) provide a convenient way of making structural deductions from the direction of the splitting of degenerate vibrations. For molecules or ions where the changes in f_{rr} are large however, a more general method [(i)] is given, which uses all the stretching frequencies to calculate the changes in all the stretching force constants, and in which the only significant approximation is the neglect of bending vibrations.

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