Contribution from the William Ramsay
and Ralph Forster Laboratories, University College,
Gower Street, London W.C.1, United Kingdom

Vibrational and Electronic Spectra of Transition-metal Carbonyl Complexes. II. An Examination of the Significance of Approximate C-O Stretching Force Constants

L. M. Bower and M. H. B. Stiddard

Received June 10, 1967

The value of approximate C-O stretching force constants is considered in the light of their contemporary use. In particular, the approximations inherent in the Cotton-Kraihanzel force field are considered and it is concluded that considerable care must be exercised before making quantitative assertions based on force constants obtained there from.

Introduction

The infrared spectra of transition metal carbonyl complexes contain very strong absorption bands in the region 1800-2000 cm.$^{-1}$ It is normally assumed that these bands are associated principally with C-O stretching vibrations and numerous qualitative and quantitative discussions thereof have been published. For example, a comparison of the infrared spectra of substituted carbonyls $M(CO)_5L$, $M(CO)_4L_2$, and $M(CO)_3L_3$ demonstrates that C-O stretching frequencies decrease with increased substitution in the parent carbonyl and inferences have been drawn about the nature of the carbon-oxygen and metal-carbon bonds.[1] Further, the geometry of a carbonyl complex $M(CO)_xL_y$ has been often inferred from a comparison of the number of bands observed in the C-O stretching region with that predicted by a simple group theoretical treatment.[2,3] Derivatives of the octahedral Group 6 carbonyls have been frequently studied and a useful interpretation of their spectra was proposed by Orgel,[4] who assumed a simple electronic interaction of C-O dipoles. Subsequently, a semi-quantitative treatment has been proposed by Cotton and Kraihanzel,[5] who interpreted a large number of spectral data in terms of C-O stretching force constants. In this treatment, separation of the high frequency C-O stretching modes is achieved by setting equal to zero all force constants governing other vibrations in the complete secular equation for the carbonyl complex. The Cotton-Kraihanzel method has been extensively applied[6-17] and it appears appropriate to attempt an assessment of its merits with two questions particularly in mind.

(i) To what extent do the approximations inherent in the method limit its applications?

(ii) Are there any extra advantages to be gained by calculation of force constants rather than a qualitative discussion of C-O stretching frequencies?

In order to tackle question (i), discussion of a system which has been treated in a reasonably rigorous way is required. We consider first, therefore, the vibrational spectra of the octahedral hexacarbonyls $M(CO)_6$, which have been quantitatively studied by Jones[18-21] and hence, in a comparative way, note the approximations made by Cotton and Kraihanzel. These approximations may be considered under two principal headings: (a) effect of neglect of anharmonicity; (b) effect of high frequency separation.

Anharmonicity. To calculate accurately quadratic force constants, it is necessary to use mechanical frequencies ω, which the molecule would exhibit if there were no anharmonic terms in the potential energy function. Values of mechanical C-O stretching frequencies have been estimated from binary and ternary overtone and combination bands[20] and the neglect of anharmonicity may be expressed in an equation of the type*

$$x_O = x_M - \alpha$$

---

(1) M. Bigorgne and R. Poilblanc, *Bull. Soc. Chim. France*, 1301 (1962).
(2) F. A. Cotton and R. Parish, *J. Chem. Soc.*, 1440 (1960).
(3) M. Bigorgne and A. Zelwer, *Bull. Soc. Chim. France*, 1986 (1960).
(4) L. E. Orgel, *Inorg. Chem.*, 1, 25 (1962).
(5) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, *84*, 4432 (1962).
(6) F. A. Cotton and C. S. Kraihanzel, *Inorg. Chem.*, *2*, 533 (1963).
(7) F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964).
(8) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, *4*, 1328 (1965).
(9) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, *4*, 389 (1965).
(10) A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.*, 3407 (1965).
(11) A. S. Kasenally, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.*, 5343 (1965).
(12) J. Lewis, A. R. Manning and J. R. Miller, *J. Chem. Soc.*, (A), 843 (1966).
(13) A. R. Manning and J. R. Miller, *J. Chem. Soc.*, (A), 1521 (1966).
(14) G. R. Van Heck and W. DeW. Horrocks, *Inorg. Chem.*, 5, 1968 (1966).
(15) L. W. Houk and G. R. Dobson, *Inorg. Chem.*, *5*, 2119 (1966).
(16) W. Jetz, P. B. Simons, J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, *5*, 2217 (1966).
(17) E. W. Abel and I. S. Butler, *Trans. Far. Soc.*, *63*, 45 (1967).
(18) L. H. Jones, *J. Mol. Spectroscopy*, *8*, 105 (1962).
(19) L. H. Jones, *Spectrochim. Acta*, *19*, 329 (1963).
(20) J. M. Smith and L. H. Jones, *J. Mol. Spectroscopy*, *20*, 248 (1966).
(21) L. H. Jones, *Inorg. Chem.*, 6, 1269 (1967).
(*) The term x, equal to λ/μ (where $\lambda/\mu = 0.4038 \times \nu_{CO}^2$ and $1/\mu$ = reduced mass of the CO group in appropriate units) is used throughout in solving the secular equations because it is related directly to the C-O stretching force constants.

where the subscripts O and M refer respectively to observed and mechanical frequencies and α is the anharmonic correction term.

High Frequency Separation. In the Cotton-Kraihanzel method, all force constants governing the low frequency fundamental vibrations are neglected, being considered small compared with those governing the C-O stretching modes. The secular equation is factored to its maximum extent by using symmetry coordinates and the factor corresponding to a given symmetry species is considered in the form

$$|H - Ex_M| = O\ ;\quad H = \frac{FG}{\mu}$$

where F and G are potential and kinetic energy matrices respectively and E is the unit matrix. Assuming the high frequency separation, all of the elements in a factor, other than H_{1i} (subscript 1 refers to C-O stretching and subscript i to all other symmetry coordinates) are equated to zero. Hence an approximation to H_{11} may be expressed in the form

$$x_M = H_{11}' = H_{11} + \beta$$

where β is a correction factor; in the quadratic case, for example, it is dependent upon H_{22} and $H_{12}H_{21}$ since

$$x = \frac{H_{11}H_{22} \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}H_{21}}}{2}$$

For the A_{1g}, E_g, and T_{1u} factors of the secular determinant for $M(CO)_6$

$$H_{11} = K + \gamma$$

where K represents the sum of force constants associated with C-O stretching modes only (F_{CO}; $F'_{CO,CO}$), while γ is a complimentary expression involving MC-CO interaction force constants ($F'_{MC,CO}$), which is equated to zero in the high frequency separation.

In the Cotton-Kraihanzel method, a constant (K′) is obtained from the expression $x_O = K'$, which may now be related to the correction terms α, β and γ by the equation

$$K' = K + \gamma + \beta - \alpha = K - \delta$$

where δ is the total correction term ($= \alpha - \beta - \gamma$).

The Hexacarbonyls. The C-O stretching modes of the hexacarbonyls $M(CO)_6$ have been interpreted by Cotton and Kraihanzel in terms of three force constants: k_1' (C-O stretching constant) and k_c' and k_t' (*cis* and *trans* C-O stretch-stretch interaction constants) which are related to the *observed* frequencies by the equations

$$x_A = k_1' + k_t' + 4k_c'$$
$$x_E = k_1' + k_t' - 2k_c'$$
$$x_T = k_1' — k_t'$$

where subscripts A, E, and T refer to the modes belonging to the A_{1g}, E_g, and T_{1u} species respectively. Hence each force constant, so obtained, is dependent upon two or three of the correction factors δ_A, δ_E, and δ_T. *VIZ.*

$$k_1' = k_1 - \frac{1}{6}[\delta_A + 2\delta_E + 3\delta_T]$$

$$k_c' = k_c - \frac{1}{6}[\delta_A - \delta_E]$$

$$k_t' = k_t - \frac{1}{6}[\delta_A + 2\delta_E - 3\delta_T]$$

where k_1, k_c, and k_t are the «true» force constants. Unfortunately, in a system like $M(CO)_6$, it is not possible to calculate absolute force constants since the number of force constants required to define the vibrations of the molecule is in excess of the number of observable fundamental frequencies. Hence, one can only choose a set of force constants which appear to be the most acceptable. In the first place, Jones[18] interrelated a number of interaction constants in a plausible way by use of simple valence theory («resonance interaction valence force field») to obtain a set of satisfactory force constants. More recently, using new anharmonic corrections, he has reported[21] a set of C-O stretching force constants calculated in a different way. Bend-bend and stretch-bend interaction constants are neglected so that the F matrices for the A_{1g}, E_g, and T_{1u} species include eleven valence force constants. Further restrictions were introduced by assuming a range of values for MC-CO stretch-stretch interaction constants so that equations can be solved completely for the remaining eight force constants using eight observed frequencies. In Table I, various K values and force constants for $Mo(CO)_6$ are listed and, if the most recent values of Jones are accepted, δ values are as follows :

$$\delta_A = -0.05 \text{ or } -0.21\ ;\quad \delta_E = -0.11 \text{ or } -0.27;$$
$$\delta_T = 0.53 \text{ or } 0.65.$$

Therefore, in spite of the uncertainy of these values, it is clear that the correction factors cannot be neglected and appear to influence significantly the Cotton-Kraihanzel force constants. In particular, δ values are certainly of similar magnitude to k_c' and k_t'. Indeed, the relative values of k_t' and k_c' must now be considered uncertain. It must be emphasised, however, that *per se* the k values quoted offer no significant advantage over the k′ values but it is unwise to *use* the latter in any *quantitative* descrpition of electron distribution in the hexacarbonyls.[7]

Substituted Hexacarbonyls. If the reasonable assumption is made, that, in octahedral carbonyl complexes, the substituent ligand L acts as a point mass in the vibrating system, then the form of the secular equations for the derivatives *trans* $M(CO)_4L_2$, *cis* $M(CO)_3L_3$, and *cis/trans* $M(CO)_2L_4$ is similar to that for $M(CO)_6$. Thus the limitations in applying the Cotton-

Table I. C-O Stretching Force Constants for $Mo(CO)_6$ (mdyne $Å^{-1}$)

K_{values} A_{1g}	E_g	T_{1u}	k′	k_c'	k_t'	Source
18.23	16.61	16.21	16.68 [a]	0.27 [a]	0.47 [a]	Cotton and Kraihanzel[5]
18.40	18.16	18.00	18.12	0.04	0.12	Jones[18]
18.18	16.50	16.74	16.90 [b]	0.28 [b]	0.16 [b]	Jones[21]
18.02	16.34	16.86	16.88 [b]	0.28 [b]	0.02 [b]	Jones[21]

[a] Should be k′, k_c' and k_t' respectively. [b] Considered by Jones to be the most reasonable.

Kraihanzel method to these systems may be assessed by considering the expression $x_O = K' = K—\delta$ for each stretching mode in a way similar to that outlined above for $M(CO)_6$. For the compounds $M(CO)_6$, *trans* $M(CO)_4L_2$, *cis* $M(CO)_3L_3$, *cis* $M(CO)_2L_4$, and *trans* $M(CO)_2L_4$ respectively, C-O stretching frequencies, assigned by qualitative methods, follow the order $\nu_{A1g} > \nu_{Eg} > \nu_{T1g}$, $\nu_{A1g} > \nu_{B1g} > \nu_{Bu}$, $\nu_{A1} > \nu_E$, $\nu_{A1} > \nu_{B1}$, and $\nu_{A1g} > \nu_{B2u}$, which is consistent with the Cotton-Kraihanzel model. Thus, although a C-O stretching frequency is determined partly by δ values, this consistency suggests that the C-O stretching frequencies are sufficiently separated for any cumulative effect of δ values *not* to alter this order.

As a means of reducing the number of C-O stretching force constants in appropriate systems, Cotton and Kraihanzel[5] suggest that k_c' and k_t' should be related by the ratio $k_t':k_c' = 2:1$, their suggestion being based on the symmetry properties of the atomic d_π orbitals of the metal. Even if k_c' and k_t' were genuine stretch-stretch interaction constants, it is unlikely that this simplification would be generally acceptable, but with the interference of δ values this ratio may be quite invalid. In Table II some ratios are quoted for carbonyl complexes from whose spectra both k_c' and k_t' may be calculated. Clearly the ratio differs significantly from 2, although the divergence is considerably less than might be anticipated. It is noteworthy that previously the justification of the ratio 2 has been assumed in terms of the coincidence of observed and calculated frequencies. This is not necessarily a sensitive criterion, however, as may be illustrated for the compound *trans* $Ph_3SnMn(CO)_4P(OPh)_3$. Inspection of Figure 1 illustrates that a range of ratios of $k_t':k_c'$ varying between 1.9 and 2.5 leads to calculated values of ν_{B1} tolerably close (± 5 cm^{-1}) to the observed value of 2003 $cm.^{-1}$

Table II. Cotton-Kraihanzel C-O Stretching Force Constants (mdyne $Å^{-1}$)

	$M(CO)_6$ [a]			*trans* $Ph_3SnMn(CO)_4L$ [b]			*trans* $Mo(CO)_4L_2$ [b]	
	M=Cr	M=Mo	M=W	L=$P(OPh)_3$	L=PPh_3	L=PBu_3	L=$P(OMe)_3$	L=PBu_3
k′	16.63	16.68	16.58	16.18	15.88	15.79	15.46	14.91
k_c'	0.26	0.27	0.30	0.22	0.26	0.28	0.31	0.32
k_t'	0.46	0.47	0.47	0.46	0.48	0.46	0.59	0.64
k_t'/k_c'	1.80	1.74	1.57	2.09	1.86	1.61	1.92	2.03

[a] Cotton and Kraihanzel.[5] [b] Bower and Stiddard, unpublished data.

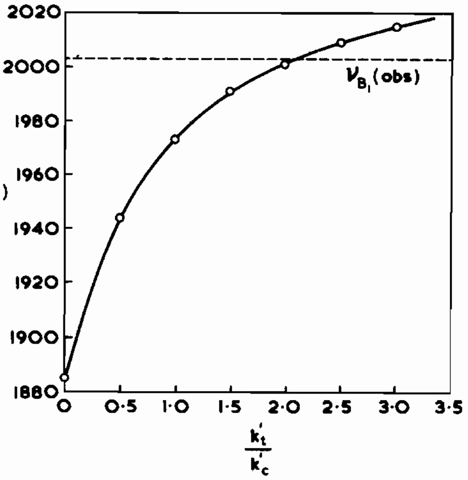


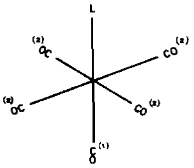
Figure 1. Relationship between calculated frequency ν_{B_1} and the chosen ratio k_t'/k_c' for the compound $Ph_3Sn\text{-}Mn(CO)_4\text{-}P(OPh)_3$: $\nu_{A_1} = 2057$; $\nu_{B_1} = 2003$; $\nu_E = 1973$ cm^{-1}.

It is necessary to enquire into those circumstances under which the Cotton-Kraihanzel treatment is most likely to be relevant. For the related series of derivatives of the type *cis* $M(CO)_3L_3$, trends in C-O stretching force constants are consistent with general suppositions about metal-ligand bonding. Further, a correlation has been recognised between the C-O stretching force constant k′ and the interaction force constant k_i'.[7] This implies that variations of these force constants resulting from a change in electron distribution on changing the substituent ligand L are more important than unknown variations in δ values; it may not be an unreasonable assumption that δ values are comparable for isostructural molecules. It is unwise, however, to give these data any quantitative significance (e.g. a relationship with π-bond order[7]) especially when the force constants do not change substantially. On the other hand, the interpretation of a series of related spectra in terms of electron distribution can be effected quite readily, if one so chooses, by a qualitative discussion of C-O stretching frequencies only,[22] without recourse to the use of C-O stretching force constants.

---

(22) E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

For derivatives $M(CO)_5L$, *cis* $M(CO)_4L_2$ and *trans* $M(CO)_3L_3$ there are two C-O stretching modes of species. A_1. Thus, the form of the secular equation differs from that of $M(CO)_6$ and additional considerations are necessary. For example, for the compound $M(CO)_5L$, examination of the matrix elements of the A_1 factor which are governed by C-O stretching co-ordinates only readily demonstrates that besides the coupling between C-O stretching and other modes, the possibility of coupling between the two A_1 C-O stretching modes must be considered. Thus a new correction term δ' for the A_1 species may be used in order to include this carbonyl-carbonyl coupling and a further restriction is placed on the quantitative interpretation of approximate force constants. Assuming the high frequency separation, the A_1 factor for $M(CO)_5L$ becomes



$$\begin{bmatrix} k_1'-x & 2k_d' \\ 2k_d' & k_2'+k_t'+2k_c'-x \end{bmatrix} = 0$$

where k_1' and k_2' refer to carbonyl groups *trans* and *cis* to L respectively. k_d', k_c', and k_t' are stretch-stretch interaction constants between CO(1)-CO(2), CO(2)-CO(2) (*cis*) and CO(2)-CO(2) (*trans*) respectively. Hence *five* force constants are involved, but only *four* fundamental C-O stretching vibrations may be observed (symmetry species $2A_1+B_1+E$)—or in most cases onl the three infrared active frequencies are known. In order to overcome this problem, Cotton and Kraihanzel introduced the restrictions $k_2' > k_1'$, $k_t' = 2k_c'$ and $k_c' = k_d'$ from valence considerations.[5] The relationship between interaction constants is clearly unsatisfactory[12,15] especially since the intervention of the correction factors δ and δ' must be considered also. In any case, a consideration of the spectrum of the compound Ph_3Sn-$Re(CO)_5$, for example, readily illustrates that internally consistent results may be obtained by assuming a range of relationships between k′ values. In Figure 2, a range of chosen values of k_t'/k_c' are plotted against the calculated values of k_1', k_2' and k_d'/k_c'. There seems no good reason, therefore, to choose arbitrarily that set of force constants dictated by either of the two Cotton-Kraihanzel relationships between the interaction constants. The situation is still less satisfactory when k_t', k_c', and k_d' have to be combined into a generalised interaction constant k_i'. Under these circumstances, there is no justification for the assumption that force constants have even comparative value.[10,11,16] For example, the interpretation[16] of the spectra of compounds of the type $Mn(CO)_5L$ and $Re(CO)_5L$, where L is another metal system (e.g. Ph_3Sn-), in terms of π-donor or acceptor properties of L must be regarded as a dubious exercise, especially when the force constants do not vary by a great deal.

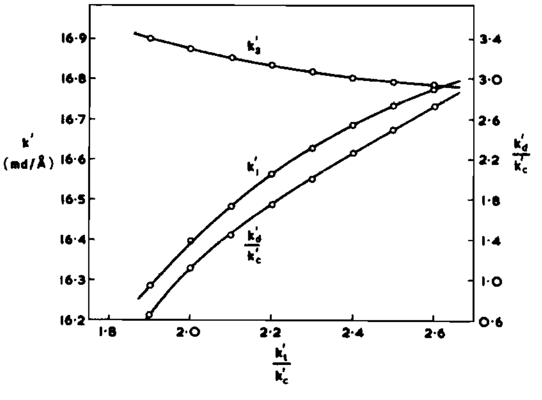


Figure 2. Relationship between calculated force constants and the chosen ratio k_t'/k_c' for the compound Ph_3Sn-$Mn(CO)_5$. $\nu_{A_1(2)} = 2116$; $\nu_{B_1} = 2044$; $\nu_E = 2013$; $\nu_{A_1(1)} = 2003$ cm^{-1}.

Care must be exercised also in the use of force constant calculations as a justification for a specific assignment, particularly when frequencies are close;[5,6,17] under these conditions, the influence of δ and δ' values must be large. In Figure 3, for example, it is demonstrated that two alternative assignments of the spectrum of the compound $W(CO)_4$(Diphos), (Diphos = 1,2-bis-diphenylphosphinoethane), are equally acceptable.[15] Thus, although setting $k_t' = 2k_c'$ and $k_c' = k_d'$ leads to imaginary roots for the assignment $\nu_{A_1(1)} < \nu_{B_1}$, it is indicated that, assuming some flexibility in the ratio $k_t' : k_c' : k_d'$, neither assignment can be eliminated. A similar situation obtains with respect to the assignment of the spectrum of *trans* $Mo(CO)_3$ $[P(OEt)_3]_3$ (see Figure 4). Solution of the secular equations leads to two sets of force constants for each assignment. In the first case ($\nu_{A_1(2)} > \nu_{B_1} > \nu_{A_1(1)}$) one set is not represented since k_t' is negative, but in the other case ($\nu_{A_1(2)} > \nu_{A_1(1)} > \nu_{B_1}$) both sets are included. In general, therefore, Cotton-Kraihanzel force constant calculations make only a limited contribution to the solution of assignment problems extra to that using qualitative ideas about the nature of the symmetry co-ordinates. Where appropriate, comparison of infrared and Raman data constitutes much more convincing evidence.[23]

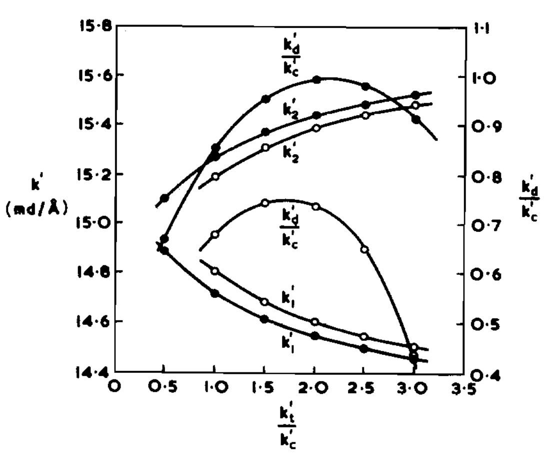


Figure 3. Calculated force constants using two alternative assignments of the spectrum of $W(CO)_4$(Diphos).[7]
Assignment I (●): $\nu_{A_1(2)} > \nu_{B_1} > \nu_{A_1(1)} > \nu_{B_2}$
Assignment II (○): $\nu_{A_1(2)} > \nu_{A_1(1)} > \nu_{B_1} > \nu_{B_2}$

---

(23) R. Poilblanc and M. Bigorgne, *J. Organometal. Chem.*, *5*, 93 (1966).

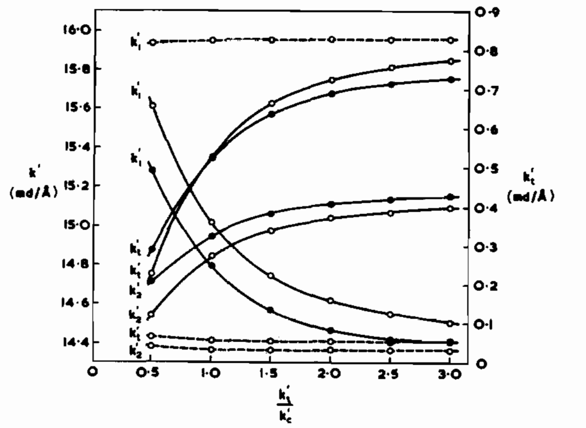


Figure 4. Calculated force constants using two alternative assignments of the spectrum of *trans* $Mo(CO)_3[P(OEt)_3]_3$.[23]
Assignment I (●): $\nu_{A_1(2)} > \nu_{B_1} > \nu_{A_1(1)}$
Assignment II (○): $\nu_{A_1(2)} > \nu_{A_1(1)} > \nu_{B_1}$

Conclusion

The following incomplete answers to questions (i) and (ii) of the *Introduction* are respectfully offered.

(i) In certain circumstances, the Cotton-Kraihanzel model is an acceptable framework within which observed C-O stretching frequencies may be discussed. However, the quantitative significance of approximate force constants has been overemphasised. For example, where «chemical» implications have been deduced, they must be examined with considerable caution, since even in structurally related compounds, C-O stretching force constants do not necessarily have any comparative significance.

(ii) Occasionally, Cotton-Kraihanzel force constant calculations aid assignment, but frequently there is no apparent advantage in carrying out such calculations, which may represent no more than a transformation of data from one form to another. If a qualitative description of the electron distribution in carbonyl complexes is thought to be a meaningful exercise, the former can be effected as readily using observed frequencies as a basis rather than using calculated force constants.

Acknowledgements. We are indebted to the Science Research Council for a maintenance award to L.M.B.