Vol. A42 (1972) ACTA PHYSICA POLONICA No 6

MOLECULAR CONSTANTS OF DIBORON TETRACHLORIDE AND DIBORON TETRAFLUORIDE — GREEN'S FUNCTION ANALYSIS

By K. Ramaswamy, S. Swaminathan and G. Shanmugam

Department of Physics, Annamalai University, Annamalainagar*

(Received March 24, 1972)

The Green function and partitioning techniques are applied to diboron tetrachloride and diboron tetrafluoride. A new set of isotopic rules are formulated. The molecular constants like the potential energy constants, mean amplitudes of vibration, rotational distortion constants and Coriolis coupling constants are calculated.

1. *Introduction*

It has been well established [1–6] that in molecules having high symmetry and different isotopes, the Green function analysis is quite successful in arriving at the exact force field. Since the boron compounds, especially those containing boron-boron bond are abundant in isotopic data, the Green function analysis can be applied to determine the exact force field for these molecules. The present paper deals with the applicability of Green's function analysis to the molecular force field of diboron tetrachloride and diboron tetrafluoride.

Diboron tetrachloride and diboron tetrafluoride have been subjected to a large number of *X*-ray diffraction and electron diffraction and Raman and infrared measurements. Recent electron diffraction measurements of Ryan and Hedberg [7] on B_2Cl_4 and infrared studies of Nimon *et al.*, [8] on B_2Cl_4 and B_2F_4 isolated in a matrix of solid argon at liquid hydrogen temperatures along with the Raman spectra of the two compounds have established the staggered V_d configuration for these molecules. Quantum mechanical calculations [9] on the energy of the potential barrier for B_2Cl_4 are reported to be 1.67 KCal/mol and 1.85 KCal/mol, and 0.003 KCal/mol for B_2F_4.

The vibrational spectral data given by Nimon *et al.*, for B_2Cl_4 and B_2F_4 along with the electron diffraction data of Ryan and Hedberg for B_2Cl_4 and the *X*-ray diffraction data of Trefonas and Lipscomb [10] were used in the present calculations. These are summarized in Table I.

* Address: Department of Physics, Annamalai University, Annamalainagar (P. O.), Tamil Nadu, India.

2. *Isotopic rules for* $X_2Y_4 \rightarrow X_2^iY_4$ *molecules*

In deriving the isotopic rules the well known Green's function analysis was used. X_2Y_4 staggered type molecules belong to $D_{2d}(=V_d)$ point group and have nine distinct normal modes which fall under $3a_1+1b_1+2b_2+3e$ irreducible representations. Of these $1b_1$ is Raman active but has not been observed. However, Gayles and Self [11] suggested the possibility that this mode may have a value of 150 cm^{-1} from the combination bands.

The isotopic rules for the different vibrational species were derived by solving the secular determinant [2]

$$|\varepsilon\omega^2\, G(\omega^2)+I| = 0 \tag{1}$$

where $G(\omega^2)$ is the Green function for the unperturbed molecule, ω the frequency of vibration, I the identity matrix and $\varepsilon = (m^i-m)/m$ (m^i is the mass of the substituted isotopic atom and m is the mass of the original atom). The Green function for the unperturbed molecule is related to the matrix of transformation l between the normal and mass weighted Cartesian coordinates. To obtain l, a set of orthonormalized Cartesian symmetry coordinates S which includes both rotations and translations was constructed. A linear combination of these symmetry coordinates with a proper "mixing parameter" will yield a set of normal coordinates. The main difficulty lies in the determination of the proper combination of symmetry coordinates with suitable mixing parameter to represent the actual normal modes. The choice becomes difficult if there are more than two normal modes of vibration in a single species. For example in the present case there are three normal modes of vibration in a_1 species. There are three possibilities of writing down the normal coordinates: two mixing parameters between the three symmetry modes, or one mixing parameter for any two of the symmetry modes and treating the third one itself as the normal mode or treating all the symmetry coordinates as truly representing the normal modes. Assuming the first possibility the equations were solved with two mixing parameters, which led to imaginary results for the mixing parameters. The proper combination of the symmetry coordinates which gave the real solution for a_1 species is given below.

$$\begin{aligned} Q_1 &= (S_1+aS_2)/\sqrt{1+a^2} \\ Q_2 &= (S_2-aS_1)/\sqrt{1+a^2} \\ Q_3 &= S_3. \end{aligned} \tag{2}$$

The b_1 species, where there is a single torsional vibration, is not considered here. For b_2 species,

$$\begin{aligned} Q_5 &= (S_5+bS_6)/\sqrt{1+b^2} \\ Q_6 &= (S_6-bS_5)/\sqrt{1+b^2} \end{aligned} \tag{3}$$

For e species.

None of the combinations with one or two mixing parameters yield real values for the mixing parameter. Hence the symmetry coordinates themselves were taken as the normal coordinates. In the above equations a and b refer to the mixing parameters, S_1, S_2, S_3 *etc.*

are the external symmetry coordinates (given in Appendix A) constructed from group theoretical methods.

The frequencies of the isotopically substitued $X_2^i Y_4$ molecule can be obtained from equation (1) and the perturbation associated with the six rows of the l matrix representing the two X atoms. The resulting determinant is a quadratic polynomial in ω^2. In the present case the determinantal equation (1) takes the form,

$$\{[\varepsilon\omega^2 G_{11}(\omega^2)+1]^2-[\varepsilon\omega^2 G_{15}(\omega^2)]^2\}\{[\varepsilon\omega^2 G_{33}(\omega^2)+1]^2-[\varepsilon\omega^2 G_{36}(\omega^2)]^2\} = 0 \quad (4)$$

taking into consideration that $G_{11}(\omega^2) = G_{22}(\omega^2) = G_{33}(\omega^2) = G_{44}(\omega^2)$,

$$G_{15}(\omega^2) = G_{51}(\omega^2) = G_{24}(\omega^2) = G_{42}(\omega^2),\ G_{33}(\omega^2) = G_{66}(\omega^2) \text{ and } G_{36}(\omega^2) = G_{63}(\omega^2)$$

TABLE I

The observed vibrational frequencies assignments [8] in cm^{-1} and the molecular parameters [9, 10] for B_2Cl_4 and B_2F_4

Vibrational species		$^{10}B_2Cl_4$	$^{11}B_2Cl_4$	$^{10}B_2F_4$	$^{11}B_2F_4$
a_1	ω_1	1177.0	1128.6	1456.6	1398.2
	ω_2	401.9	399.6	676.0	672.4
	ω_3	176.9	176.0	319.8	319.2
b_2	ω_5	750.7	724.9	1187.0	1154.7
	ω_6	289.3	288.2	545.3	541.9
e	ω_7	950.9	912.2	1413.1	1366.3
	ω_8	105.0	105.0	144.0	144.0
	ω_9	540.6	517.9	686.0	657.3

B_2Cl_4	B_2F_4
$R_{B-B} = 1.702$ Å	$R_{B-B} = 1.67$ Å
$r_{B-Cl} = 1.75$ Å	$r_{B-F} = 1.32$ Å
$\hat{\alpha} = Cl\hat{B}Cl = 118.65°$	$\hat{\alpha} = F\hat{B}F = 120°$
$\hat{\varphi} = B\hat{B}Cl = 120.67°$	$\hat{\varphi} = B\hat{B}F = 120°$

and that all other G_{ij} are zero. Solutions of equation (4) give the frequencies of the isotopically substituted molecules. The various isotopic rules derived are given in Appendix B. The values of the various mixing parameters are, for B_2Cl_4, $a = +0.347564$ and $b = -0.431861$ and for B_2F_4, $a = +0.396165$ and $b = -0.609854$.

3. *Potential energy constants*

Using the mixing parameters, the symmetry force constant matrix was obtained from the relation [3]

$$F = \tilde{B}^{-1} A \Lambda \tilde{A} B^{-1} \quad (5)$$

where Λ is a diagonal matrix whose elements Λ_K defined by

$$\Lambda_K = 4\pi^2 C^2 \omega_K^2 \quad (6)$$

Here, C is the velocity of light, ω_K is the vibrational frequency of the K^{th} mode, B is the transformation matrix between the internal and external symmetry coordinates and A is the unitary matrix of the mixing parameters. It is of interest to note here that the quantity BA is equivalent to the L matrix. Thus we determine this quantity purely from the isotopic frequencies without assumptions regarding the force fields. Thus this method has an

TABLE II

Symmetry force constants and important valence constants in mdynes/Å

F elements	B_2Cl_4	B_2F_4	Valence constants		
				B_2Cl_4	B_2F_4
F_{11}	3.8701	6.6880	f_R	3.8701	6.6880
F_{22}	4.8612	3.4975	f_r	3.5531	5.5209
F_{33}	0.6606	0.5903	f_α	0.3117	0.6863
F_{12}	−2.7571	−2.8841	f_φ	0.1211	0.3392
F_{13}	0.9003	1.6553	f_{Rr}	−1.3785	−1.4421
F_{23}	−1.3693	−1.6254	$f_{r\alpha}$	−1.1648	−1.6803
F_{55}	3.0954	7.4954			
F_{66}	0.2746	0.4687			
F_{56}	0.0234	−0.3149			
F_{77}	3.1278	5.5454			
F_{88}	0.0863	0.1039			
F_{99}	0.2325	0.3352			
F_{78}	0.0699	0.0721			
F_{79}	0.0419	0.0623			
F_{89}	−0.0823	−0.0887			

added advantage over the various kinematic methods for evaluating the force constants wherein the L matrix is generated purely from the geometry of the molecule. The symmetry force constant elements obtained using equation (5) are presented in Table II along with the important valence constants.

4. *Mean amplitudes of vibrations*

The mean square amplitude matrix (Σ) for the various atom pair was obtained from Cyvin's relation [12]

$$\Sigma = L\Delta\tilde{L} \tag{7}$$

where Δ is a diagonal super matrix with elements,

$$\Delta_K = \frac{h}{8\pi^2 c\omega_K} \cot h \frac{hc\omega_K}{2KT}. \tag{8}$$

Here h is the Planck constant, K the absolute temperature and c the velocity of light. The important mean vibrational amplitude quantities are presented in Table III.

TABLE III

Vibrational mean amplitude quantities in Å

	B_2Cl_4	B_2F_4
σ_R	0.0614	0.0522
σ_r	0.0621	0.0564

5. *Rotational distortion constants*

The rotational distortion parameters for vibration-rotation interaction given by Wilson and Howard [13] and Nielson [14] are

$$\hbar^4 \tau_{\alpha\beta\gamma\delta} = -\frac{K}{I^0_{\alpha\alpha} I^0_{\beta\beta} I^0_{\gamma\gamma} I^0_{\delta\delta}} \sum_i \frac{a_i^{\alpha\beta} a_i^{\gamma\delta}}{\omega_i^2} \qquad (9)$$

where α, β, γ and δ can be in turn x, y or z. If these parameters are expressed in MHZ, the constant K assumes the value 5.7498×10^8, the vibrational frequencies in cm^{-1} and the components of moment of inertia tensor $I^0_{\alpha\alpha}$ evaluated for the ground state and in the centre of mass of the molecule and the coefficients $a_i^{\alpha\beta}$ are expressed in a. m. u. Å^2.

The coefficients $a_i^{\alpha\beta}$ in terms of the l matrix elements and of the equilibrium Cartesian coordinates, α_K, β_K and γ_K takes the form [15]

$$a_i^{\alpha\alpha} = 2 \sum_K m_K^{\frac{1}{2}} (\beta^0_K l^\beta_{Ki} + \gamma^0_K l^\gamma_{Ki}) \qquad (10)$$

$$a_i^{\alpha\beta} = -2 \sum_K m_K^{\frac{1}{2}} \alpha^0_K \beta^0_K (\alpha \neq \beta) \qquad (11)$$

where m_K is the mass of the K^{th} atom. The calculated distortion constants are given in Table IV.

TABLE IV

Rotational distortion constants in KHZ

Molecule	D_J	D_K	D_{JK}
B_2Cl_4	12.1727	46.9129	77.0646
B_2F_4	53.1135	414.7672	786.6440

6. *Coriolis coupling constants*

The values of the Coriolis coupling constants (ζ) for the doubly degenerate species were determined from the l matrix using the relation given by Meal and Polo [16] *i. e.*,

$$\underset{\alpha=x,y,z}{\overset{\alpha}{\zeta}} = l M^\alpha \tilde{l}$$

where α denotes the axis of rotation (here we have considered the axis lying along the B$-$B bond alone) and M is a block diagonal super matrix made up of n identical (3×3)

submatrices, one for each atom. The obtained ζ values were found to obey the sum rule for this type of molecules *i. e.*,

$$\sum_i \zeta_i = \frac{I_z}{2I_x}$$

where I_x and I_z are the moments of inertia along the respective axes. They are given in Table V.

TABLE V

Coriolis coupling constants

	Molecule	
	B_2Cl_4	B_2F_4
ζ_8	0.2559	0.1935
ζ_9	0.0156	0.0191
$\sum_i \zeta_i$	0.2715	0.2126
$\frac{I_z}{2I_x}$	0.2715	0.2126

7. *Results and discussion*

It is seen from the Appendix B that the isotopic rules obtained here essentially reduce to those of Redlich-Teller product rules and that these rules are derived independently without assuming the force field model. The fact that the mixing parameter (which is the most important factor in the present calculation) is able to reproduce all the molecular constants within reasonable limits shows the validity of the method used in the analysis of the force field for the molecule under consideration.

Nimon *et al.* carried out a normal coordinate analysis for these molecules using two Urey-Bradley-type force fields and have found that the GUBFF is satisfactory for both molecules whereas UBFF is adequate for B_2Cl_4 only. This has led them to conclude that there exists a strong interaction along the coordinates connecting the X type atoms on opposite ends of the molecules while such interaction is small in B_2Cl_4. However, the present force field analysis yields a uniform result for all the molecules. Thus we may conclude that the Green function analysis yields a suitable and probably the reliable force field for these molecules.

It may be noted that the values of the force constants obtained here are considerably higher than the ones reported by Nimon *et al.* This might be due to the different procedures used in the evaluation of the F matrix elements. As has been pointed out earlier, the advantage of the Green function analysis lies in generating the force field without any assumptions. Hence no restrictions were imposed on the off diagonal elements. Perhaps this may be the reason for the difference in the values of F matrix elements. From the results given in Table II the following points may be noted. The value of the B$-$B stretching force constant is 6.688 mdynes/Å in B_2F_4 and 3.870 mdynes/Å in B_2Cl_4. The value of B$-$B stretching constant 3.870 md/Å in B_2Cl_4 compares well with the value of Nimon *et al.* The value for B−B stretching constant in B_2F_4 appears to be high compared to Nimon *et al*'s, value (4.21 mdynes/Å). Cyvin [17] reports a value of 6.29 for B−F stretch and 3.05 mdynes/Å for B−B stretch. This might be due to the fact that Cyvin has used 624 cm^{-1} as the vibrational frequency corresponding B−B stretch as reported by Gayles and Self [11] while Nimon *et al.*, have established 1380 cm^{-1} as representing the B−B stretching mode. The isotope shifts obtained are also consistent with this assignment. Since there is a considerable difference in the frequencies of B−B stretch in B_2Cl_4 and B_2F_4, it is probable that the value of f_{BB} is considerably higher in B_2F_4 than in B_2Cl_4. There is also a considerable difference in the B−B bond length values (1.67 Å in B_2F_4 and 1.702 Å in B_2Cl_4). As such it is expected that B−B stretch in B_2F_4 should be higher than in B_2Cl_4 as has been found in the present case. However, no such marked change has been noted by Nimon *et al.* Our f_{BB} is also in good agreement with the value of 3.4 mdynes/Å in B_2Cl_4 and 3.5 mdynes/Å in B_2 molecule reported by Becher and Schnöckel [18]. The high value in B_2F_4 may be due to the high electronegativity and reactivity of fluorine atom.

The BF stretching force constant of 5.52 mdynes/Å and BCl stretching force constant 3.55 mdynes/Å compares favourably with the value of 6.13 mdynes/Å and 3.36 mdynes/Å reported by Nimon *et al.* The values of the bending force constants f_α and f_φ are quite small and are in the expected range of values. However, the values of f_{Rr} and $f_{r\alpha}$ representing the interaction between the B−B and B−*X* bonds and B−*X* and *XBX* angles are high, greater in B_2F_4 than in B_2Cl_4. They are also negative.

From Table III it is seen that the calculated values of mean amplitudes of vibration of B_2Cl_4 [σ_{BB} = 0.0614 Å, σ_{B-Cl} = 0.621 Å] compare well with the electron diffraction values of Ryan and Hedberg [σ_{BB} = 0.05 Å, σ_{B-Cl} = 0.0562 Å]. The values of the B−Cl and B−F distances and the corresponding force constants compare favourably with BCl_3 and BF_3 values. The corresponding B−B distance and the f_{BB} are not much different from the values found in boron hydrides. (In B_2H_6, R_{B-B} = 1.762 Å and f_{BB} = = 2.5853 mdynes/Å) [20]. The B−Cl and B−F distances compare well with the sum of the radii (r_{Cl} = 1.035 and r_B = 0.81 and r_F = 0.72 and r_B = 0.81) [19] so that one would expect a normal B−B bond equal to twice its radius sum (1.62 Å) instead of a bond characteristic of electron and orbital defficient compounds, as suggested by Ryan and Hedberg [7]. This is probably due to the fact that the utilization of the fourth stable boron orbital for partial double bond formation with chlorine is less complete. In such a case the residual positive charges on the boron atoms arising from the partial ionic character of the B−Cl bonds would, by mutual repulsion tend to lengthen the B−B bond. In the case of B_2F_4 also the same conditions exist. Perhaps this may be the reason for the large negative values for the f_{Rr} and $f_{r\alpha}$ interaction constants.

The rotational distortion constants obtained for these molecules are presented in Table IV. As is expected the values obtained for B_2F_4 are higher than those for B_2Cl_4. All the calculated values of the Coriolis coupling constants are found to satisfy the ζ sum rule for these molecules as shown in Table V.

One of the authors (G. S.) is greteful to the University Grants Commisions, Government of India, New Delhi, for the financial assistance by the award of a Junior Research Fellowship.

APPENDIX A[1]

S	S_1	S_2	S_3	S_5	S_6	S_{7a}	S_{8a}	S_{9a}	S_{7b}	S_{8b}	S_{9b}
X_1	0	0	0	0	0	0	$-P/M$	$\frac{Q}{2N}$	0	$-P/M$	$\frac{Q}{2N}$
Y_1	0	0	$-1/2$	0	$1/2$	$-S\sqrt{m_X}/2K$	$\frac{(P-m_XI_Xc)}{M}$	$\frac{m_Y\sqrt{m_X}rc}{N}$	$-S\sqrt{m_X}/2K$	$\frac{-(P-m_XI_Xc)}{M}$	$\frac{-m_Y\sqrt{m_X}rc}{N}$
Z_1	0	$1/2$	0	$\sqrt{m_X}/2d_1$	0	$-C\sqrt{m_X}/2K$	$\frac{S[I_Xd_1^2-2m_XK^2r^2]}{M}$	0	$-C\sqrt{m_X}/2K$	$\frac{-S[I_Xd_1^2-2m_YK^2r^2]}{M}$	0
X_2	0	0	0	0	0	0	$-\frac{P}{M}$	$\frac{Q}{2N}$	0	$-\frac{P}{M}$	$\frac{Q}{2N}$
Y_2	0	0	$1/2$	0	$-1/2$	$-S\sqrt{m_X}/2K$	$\frac{[P-m_XI_Xc]}{M}$	$\frac{m_Y\sqrt{m_X}rc}{N}$	$-S\sqrt{m_X}/2K$	$\frac{-[P-m_XI_Xc]}{M}$	$\frac{-m_Y\sqrt{m_X}rc}{N}$
Z_2	0	$1/2$	0	$\sqrt{m_X}/2d_1$	0	$C\sqrt{m_X}/2K$	$\frac{-S[I_Xd_1^2-2m_YK^2r^2]}{M}$	0	$C\sqrt{m_X}/2K$	$\frac{S[I_Xd_1^2-2m_YK^2r^2]}{M}$	0
X_3	0	0	$1/2$	0	$1/2$	$-S\sqrt{m_X}/2K$	$\frac{[P-m_XI_Xc]}{M}$	$\frac{m_Y\sqrt{m_X}rc}{N}$	$S\sqrt{m_X}/2K$	$\frac{[P-m_XI_Xc]}{M}$	$\frac{m_Y\sqrt{m_X}rc}{N}$
Y_3	0	0	0	0	0	0	$-\frac{P}{M}$	$\frac{Q}{2N}$	0	$\frac{P}{M}$	$-\frac{Q}{2N}$
Z_3	0	$-1/2$	0	$\sqrt{m_X}/2d_1$	0	$-C\sqrt{m_X}/2K$	S [illegible] $-2m_YK^2r^2]$ / M	0	$C\sqrt{m_X}/2K$	$\frac{S[I_Xd_1^2-2m_YK^2r^2]}{M}$	0
X_4	0	0	$-1/2$	0	$-1/2$	$-S\sqrt{m_X}/2K$	$\frac{[P-m_XI_Xc]}{M}$	$\frac{m_Y\sqrt{m_X}rc}{N}$	$S\sqrt{m_X}/2K$	$\frac{[P-m_XI_Xc]}{M}$	$\frac{m_Y\sqrt{m_X}rc}{N}$

Y_4	0	0	0	0	0	0	$-\frac{P}{M}$	$\frac{Q}{2N}$	0	$\frac{P}{M}$	$-\frac{Q}{2N}$
Z_4	0	$-1/2$	0	$\sqrt{m_X}/2d_1$	0	$C\sqrt{m_X}/2K$	$\frac{-S[I_X d_1^2-2m_Y K^2 r^2}{M}$	0	$-C\sqrt{m_X}/2K$	$\frac{-S[I_X d_1^2-2m_Y K^2 r^2]}{M}$	0
X_5	0	0	0	0	0	0	$\frac{-\sqrt{m_X m_Y} K^2 Rr}{M}$	$-\frac{T}{N}$	0	$\frac{-\sqrt{m_X m_Y} K^2 Rr}{M}$	$-\frac{T}{N}$
Y_5	0	0	0	0	0	$S\sqrt{m_Y}/K$	$\frac{\sqrt{m_X m_Y}\,[2I_X c+RrK^2]}{M}$	$\frac{m_X\sqrt{m_Y} rc}{N}$	$S\sqrt{m_Y}/K$	$\frac{-\sqrt{m_X m_Y}\,[2I_X c+RrK^2]}{M}$	$\frac{-m_X\sqrt{m_Y} rc}{N}$
Z_5	$1/\sqrt{2}$	0	0	$-\sqrt{m_Y} d_1$	0	0	0	0	0	0	0
X_6	0	0	0	0	0	$S\sqrt{m_Y}/K$	$\frac{\sqrt{m_X m_Y}\,[2I_X c+RrK^2]}{M}$	$\frac{m_X\sqrt{m_Y} rc}{N}$	$-S\sqrt{m_Y}/K$	$\frac{\sqrt{m_X m_Y}\,[2I_X c+RrK^2]}{M}$	$\frac{m_X\sqrt{m_Y} rc}{N}$
Y_6	0	0	0	0	0	0	$\frac{-\sqrt{m_X m_Y} K^2 Rr}{M}$	$-\frac{T}{N}$	0	$\frac{\sqrt{m_X m_Y} K^2 Rr}{M}$	$\frac{T}{N}$
Z_6	$-1/\sqrt{2}$	0	0	$-\sqrt{m_Y}/d_1$	0	0	0	0	0	0	0

[1] $d_1=\sqrt{(m_X+2m_Y)}$; $K=\sqrt{(m_X+2m_Y S^2)}$; $P=m_Y K^2 r(R+2rc)$; $I_X=I_Y=\left\{m_Y\,[(R+2rc)^2+2r^2S^2]+m_X\frac{R^2}{2}\right\}$ $M=2K\sqrt{I_X(I_X d_1^2-2m_Y K^2 r^2)}$; $N=\sqrt{d_1^2[m_X^2R^2+4m_Y\{m_X(R+rc)^2+m_Y(R+2rc)^2\}]}$; $Q=\sqrt{m_X}[Rd_1^2+2m_Y rc]$; and $T=\sqrt{m_Y}[(R+rc)\,d_1^2+2m_Y rc]$.

m_X and m_Y are the respective atomic masses. R and r are the internuclear distances of the $X-X$ and $X-Y$ atoms respectively and $\dot{S}$ and c stand for sin $\alpha/2$ and cos $\alpha/2$.

APPENDIX B

Isotopic rules for $X_2Y_4 \rightarrow X_2^iY_4$ molecules

a_1 Species:

$$\omega_1^{i2}+\omega_2^{i2} = \frac{A^2(\omega_1^2+\omega_2^2)+(a^2\omega_1^2+\omega_2^2)}{A^2(1+\varepsilon)}$$

$$\omega_1^{i2}\omega_2^{i2} = \frac{\omega_1^2\omega_2^2}{(1+\varepsilon)}$$

$$\omega_3^{i2} = \frac{\omega_3^2}{(1+\varepsilon)} \quad \text{where} \quad A^2 = (1+a^2).$$

b_2 Species:

$$\omega_5^{i2}+\omega_6^{i2} = \frac{2m_y(b^2\omega_5^2+\omega_6^2)+B^2(d_1^2+\varepsilon m_x)(\omega_5^2+\omega_6^2)}{B^2d_1^2(1+\varepsilon)}$$

$$\omega_5^{i2}\omega_6^{i2} = \omega_5^2\omega_6^2\frac{(\varepsilon m_x+d_i^2)}{(1+\varepsilon)d_1^2} \quad \text{where} \quad B^2 = (1+b^2).$$

e Species:

$$(\omega_7^{i2}+\omega_8^{i2}+\omega_9^{i2}) = \frac{[E_1(\omega_7^2+\omega_8^2+\omega_9^2)+E_2(\omega_7^2+\omega_8^2)+E_3(\omega_8^2+\omega_9^2)+E_4(\omega_7^2+\omega_9^2)]}{(E_1+E_2+E_3+E_4)}$$

$$(\omega_7^{i2}\omega_8^{i2}+\omega_8^{i2}\omega_9^{i2}+\omega_7^{i2}\omega_9^{i2}) = \frac{[E_1(\omega_7^2\omega_8^2+\omega_8^2\omega_9^2+\omega_7^2\omega_9^2)+E_2\omega_7^2\omega_8^2+E_3\omega_8^2\omega_9^2+E_4\omega_7^2\omega_9^2]}{(E_1+E_2+E_3+E_4)}$$

$$\omega_7^{i2}\omega_8^{i2}\omega_9^{i2} = \frac{E_1\omega_7^2\omega_8^2\omega_9^2}{(E_1+E_2+E_3+E_4)}$$

where

$$E_1 = (\varepsilon m_x^2+d_1^2)\,K^2M^2N^2,$$

$$E_2 = 2m_x^2m_yd_1^2r^2c^2K^2M^2,$$

$$E_3 = 2m_yd_1^2S^2M^2N^2$$

$$E_4 = 2m_xm_yd_1^2K^2N^2$$

and

$$\varepsilon = (m_x^i-m_x)/m_x.$$

REFERENCES

[1] R. E. De Wames, T. Wolfram, *J. Chem. Phys.*, **40**, 853 (1964).
[2] C. D. Bass, L. Lynds, T. Wolfram, R. E. De Wames, *J. Chem. Phys.*, **40**, 3611 (1964).
[3] T. Wolfram, C. D. Bass, R. E. De Wames, L. Lynds, *Bull. Chem. Soc. Japan*, **39**, 201 (1966).

[4] T. Wolfram, R. E. De Wames, *Bull. Chem. Soc. Japan*, **33**, 207 (1966).
[5] K. Ramaswamy, S. Swaminathan, *Austral. J. Chem.*, **22**, 291 (1969).
[6] K. Ramaswamy, G. Shanmugam, *Acta Phys. Polon.*, **A41**, 3 (1972).
[7] R. Ryan, K. Hedberg, *J. Chem. Phys.*, **50**, 4986 (1969).
[8] L. A. Nimon, K. S. Seshadri, R. C. Taylor, David White, *J. Chem. Phys.*, **53**, 2416 (1970).
[9] E. B. Moore, Jr., *Theor. Chim. Acta*, **7**, 144 (1967).
[10] L. Trefonas, W. N. Lipscomb, *J. Chem. Phys.*, **28**, 54 (1958).
[11] J. N. Gayles, J. Self, *J. Chem. Phys.*, **40**, 3530 (1964).
[12] S. J. Cyvin, *Spectrochim. Acta*, **15**, 828 (1959).
[13] E. B. Wilson, Jr, J. B. Howard, *J. Chem. Phys.*, **4**, 260 (1936).
[14] H. H. Nielson, *Rev. Mod. Phys.*, **23**, 90 (1951).
[15] G. De Alti, V. Galasso, G. Costa, *Spectrochim. Acta*, **21**, 649 (1965).
[16] J. H. Meal, S. R. Polo, *J. Chem. Phys.*, **24**, 1119 (1956).
[17] S. J. Cyvin, *Z. Anorg. allg. chem.*, **378**, 117 (1970).
[18] Von H. J. Becher, H. G. Schnöckel, *Z. Anorg. allg. chem.*, **379**, 136 (1970).
[19] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York 1960.
[20] K. Ramaswamy, G. Shanmugam, to be published.