

GREEN'S FUNCTION ANALYSIS OF THE VIBRATIONS OF DIBORANE

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Green's function analysis of substituted and perturbed molecules was applied to the vibrational study of diborane. A new set of isotopic rules has been formulated. The potential energy constants, mean amplitudes of vibration, rotational distortion constants and the Coriolis coupling constants have been calculated and found to be in agreement with the experimental values.

1. Introduction

Diborane has a peculiar bridged hydrogen structure and is one of the simplest electron-deficient molecules [1]. Because of these unique features, the calculation of the normal vibrations and the potential function is important for a better understanding of its valence structure. The presence of abundant varieties of isotopic species makes it ideal for the application of Green's function analysis [2-5], a method which has been found to be of great use in uniquely fixing the molecular force fields and also to be suitable in obtaining isotopic rules without recourse to the force fields.

The Raman and infrared spectra of diborane and its isotopes have been studied by a large number of workers [6-8]. Recent studies of polarized infrared spectra of single crystals of diborane by Freund and Halford [9] have confirmed the earlier vibrational assignments. Normal coordinate analyses of diborane have been carried out by Bell and Languet-Higgins [10], Venkateswarlu and Radhakrishnan [11] and Sverdlov and Zaitseva [12] using GVFF, Ogawa and Miyazawa [13] using UBFF, and by Adams and Churchill [14] using SVFF. Ogawa and Miyazawa concluded that the UBFF does not adequately represent the molecular force field for diborane and for compounds having a similar bridged structure. Recently, a complete infrared high resolution spectrum of diborane, together with its structure obtained in such a study, and accompanied by rotational distortion

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constants, was reported by Lafferty *et al.* [15]. Electron diffraction results of Bartell and Carroll [16] have also been confirmed by these authors.

The present paper deals with the formulation of isotopic rules, the evaluation of molecular constants like the potential energy constants, mean amplitudes of vibration, rotational distortion constants and the Coriolis coupling constants of X_2Y_6 bridged-type molecules, using Green's function analysis.

2. Isotopic rules for $X_2Y_6 \rightarrow X_2^iY_6$ molecules

Nonplanar bridged X_2Y_6 type molecules belong to D_{2h} point group having eighteen distinct normal vibrational modes which fall into the irreducible representations $4A_g + 1A_u + 2B_{1g} + 3B_{1u} + 2B_{2g} + 2B_{2u} + 1B_{3g} + 3B_{3u}$.

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

$$|\varepsilon\omega^2 G(\omega^2) + I| = 0 \quad (1)$$

where $G(\omega^2)$ is the Green's function of the unperturbed molecule, ω the frequency of vibration, I the identity matrix and

$$\varepsilon = \frac{(m_X^i - m_X)}{m_X}$$

m_X^i is the mass of the substituted atom and m_X is the mass of the original atom. The Green's 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 rotations and translations, was constructed. A linear combination of these symmetry coordinates with proper "mixing parameters" will yield a set of normal coordinates. The main difficulty lies in the determination of the proper combination of symmetry coordinates with the suitable mixing parameters to represent the actual normal modes of vibration in a single species. For example in the A_g species there are four symmetry coordinates and using them we can write a number of sets of normal coordinates. But only one of them will be the "proper and true" set and will give the real solution for this species. This set is as follows:

$$\begin{aligned} Q_1 &= (S_1 + cS_3) \sqrt{1+c^2} \\ Q_2 &= (S_2 + dS_4) \sqrt{1+d^2} \\ Q_3 &= (S_3 - cS_1) \sqrt{1+c^2} \\ Q_4 &= (S_4 - dS_2) \sqrt{1+d^2}. \end{aligned} \quad (2)$$

Even here c and d cannot be solved for independently. Hence as a first approximation one of the values was chosen as unity. Such an approximation gave a very good fit for the various equations involving the sum rule, and the sum of the 2×2 product rule and 3×3 product rule (Eqs (A.2)–(A.4)). In other words these equations gave consistent values for the

mixing parameters. This consistency was observed in both the B_{1u} and B_{3u} species, where there are more than two normal modes.

The normal coordinates for the other species were chosen as follows:

A_u species:

$$Q_5 = S_5 \quad (3)$$

B_{1g} species:

$$\begin{aligned} Q_6 &= (S_6 + eS_7)/\sqrt{1+e^2} \\ Q_7 &= (S_7 - eS_6)/\sqrt{1+e^2} \end{aligned} \quad (4)$$

B_{1u} species:

$$\begin{aligned} Q_8 &= (S_8 + fS_9)/\sqrt{1+f^2} \\ Q_9 &= (S_9 - fS_8)/\sqrt{1+f^2} \\ Q_{10} &= S_{10} \end{aligned} \quad (5)$$

B_{2g} species:

$$\begin{aligned} Q_{11} &= (S_{11} + gS_{12})/\sqrt{1+g^2} \\ Q_{12} &= (S_{12} - gS_{11})/\sqrt{1+g^2} \end{aligned} \quad (6)$$

B_{2u} species:

$$\begin{aligned} Q_{13} &= (S_{13} + hS_{14})/\sqrt{1+h^2} \\ Q_{14} &= (S_{14} - hS_{13})/\sqrt{1+h^2} \end{aligned} \quad (7)$$

B_{3g} species:

$$Q_{15} = S_{15} \quad (8)$$

B_{3u} species:

$$\begin{aligned} Q_{16} &= (S_{16} + kS_{18})/\sqrt{1+k^2} \\ Q_{17} &= S_{17} \\ Q_{18} &= (S_{18} - kS_{16})/\sqrt{1+k^2} \end{aligned} \quad (9)$$

where the Q and S terms represent the normal coordinates and the Cartesian symmetry coordinates, respectively, and c , d , e , f , g , h and k are the corresponding mixing parameters of the respective species. The six translational and rotational symmetry coordinates are also normal coordinates.

The frequencies of the isotopically substituted X_2Y_6 molecules 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 equation (1) reduces to

$$\begin{aligned} &\{[\varepsilon\omega^2 G_{11}(\omega^2) + 1]^2 - [\varepsilon\omega^2 G_{14}(\omega^2)]^2\} \{[\varepsilon\omega^2 G_{22}(\omega^2) + 1]^2 - [\varepsilon\omega^2 G_{25}(\omega^2)]^2\} \times \\ &\quad \times \{[\varepsilon\omega^2 G_{33}(\omega^2) + 1]^2 - [\varepsilon\omega^2 G_{36}(\omega^2)]^2\} \end{aligned} \quad (10)$$

after taking into consideration the fact that $G_{11}(\omega^2) = G_{44}(\omega^2)$, $G_{22}(\omega^2) = G_{55}(\omega^2)$, $G_{33}(\omega^2) = G_{66}(\omega^2)$, $G_{14}(\omega^2) = G_{41}(\omega^2)$, $G_{25}(\omega^2) = G_{52}(\omega^2)$, $G_{36}(\omega^2) = G_{63}(\omega^2)$ and all other G_{ij} 's are zero. From equation (10) we get six equations which are independently equal to zero, whose solutions give the frequencies corresponding to the species of the isotopically substituted molecules. The isotopic rules thus obtained are given in the Appendix. The frequencies of the corresponding unidimensional A_u and B_{3g} species were obtained by mass-scaling the corresponding frequencies of the unperturbed molecules by

$$\omega_j^i = \left[\frac{m_x}{m_x^i} \right] \omega_j^2. \quad (11)$$

Vibrational frequencies of Lord and Nielson [6], Lehman *et al.* [7] and Taylor and Emery [8] and the molecular parameters of Lafferty *et al.* [15] presented in Table I, were used in the present calculations.

TABLE I

The observed vibrational frequencies (in cm^{-1}), molecular parameters and the mixing parameters of $^{10}\text{B}_2\text{H}_6$ and $^{11}\text{B}_2\text{H}_6$

Vibrational species		$^{10}\text{B}_2\text{H}_6$	$^{11}\text{B}_2\text{H}_6$	Mixing parameters		
				$^{10}\text{B}_2\text{H}_6$		$^{11}\text{B}_2\text{H}_6$
A_g	ω_1	2537	2524	c	1	1
	ω_2	2110	2104	d	0.414530	-0.319493
	ω_3	1186	1180	e	-4.470116	-0.527442
	ω_4	820	794	f	1.269203	1.558156
A_u	ω_5	829	829	g	0.896218	0.928047
				h	-0.006165	-0.032067
B_{1g}	ω_6	1768	1768	k	-2.464985	2.427116
	ω_7	1044	1035	$\text{B-H}_t = 1.200 \text{ \AA}$ $\text{B-H}_b = 1.320 \text{ \AA}$ $\text{B-B} = 1.762 \text{ \AA}$ $\text{H}_t\hat{\text{B}}\text{H}_t = 121^\circ$ $\text{H}_b\hat{\text{B}}\text{H}_b = 96^\circ 12'$ $\text{H}_t\hat{\text{B}}\text{H}_b = 109^\circ 12' \text{ (calc.)}$		
B_{1u}	ω_8	2625	2612			
	ω_9	950	950			
	ω_{10}	368	368			
B_{2g}	ω_{11}	2640	2591			
	ω_{12}	930	920			
B_{2u}	ω_{13}	1920	1915			
	ω_{14}	977	973			
B_{3g}	ω_{15}	1012	1012			
B_{3u}	ω_{16}	2528	2525			
	ω_{17}	1606	1602			
	ω_{18}	1181	1177			

3. Potential energy constants

From the various isotopic rules that are given in the Appendix, the mixing parameters were calculated and the symmetry force constant matrix was obtained from the relation [4]

$$F = \tilde{B}^{-1} A \Lambda \tilde{A} B^{-1} \quad (12)$$

where Δ is a diagonal matrix whose elements Δ_k are defined by

$$\Delta_k = 4\pi^2 c^2 \omega_k^2 \quad (13)$$

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 Cartesian symmetry coordinates and A is the unitary matrix of the mixing parameters. The symmetry force constant elements obtained are presented in Table II along with the relevant valence constants.

TABLE II
The symmetry force constants and the important valence constants of Diborane¹

Symmetry species	Force constant values	Symmetry species	Force constant values	Valence constants
A_g	$F_{11} = -3.4256$	B_{2g}	$F_{1111} = 3.7809$	$f_a = 3.6004$ $f_b = 1.9367$ $f_R = 2.5853$ $f_\alpha = 0.6296$ $f_\phi = 0.4831$ $f_c = 0.3734$ $f_{aa} = -0.0757$ $f_{bb} = -0.0458$ $f_{\alpha\alpha} = -0.1734$
	$F_{22} = 2.1978$		$F_{1212} = 0.9878$	
	$F_{33} = -0.6782$		$F_{1112} = -1.2431$	
	$F_{44} = 2.5853$	B_{2u}	$F_{1313} = 2.0475$	
	$F_{12} = 0.1245$		$F_{1414} = 0.5685$	
	$F_{13} = -0.4904$		$F_{1314} = 0.4096$	
	$F_{14} = 0.2157$		$F_{1515} = 0.2162$	
	$F_{23} = -0.1868$	B_{3g}	$F_{1616} = 3.6237$	
	$F_{24} = -0.2683$		$F_{1717} = 1.5838$	
	$F_{34} = -0.3235$	B_{3u}	$F_{1818} = 0.5811$	
	$F_{55} = 0.4732$		$F_{1617} = 0.0873$	
	A_u	$F_{66} = 1.9175$	$F_{1618} = 0.4185$	
		$F_{77} = 0.5736$	$F_{1718} = -0.1309$	
	B_{1g}	$F_{67} = -0.4183$		
$F_{88} = 3.5714$				
B_{1u}	$F_{99} = 1.0455$			
	$F_{1010} = 0.3734$			
	$F_{89} = 0.4735$			
	$F_{810} = 0.2736$			
	$F_{910} = 0.6138$			

¹ Bond stretching constants are expressed in mdynes/Å, bending constants in mdynes Å/radian² and the stretch-bend interaction constants are in mdynes/radian.

4. Mean amplitudes of vibration

The mean square amplitude (Σ) matrix for the various atom pairs was obtained from Cyvin's relation [17],

$$\Sigma = L\Delta\tilde{L} = BA\Delta\tilde{A}B \quad (14)$$

where Δ is a diagonal matrix with elements

$$\Delta_k = \frac{h}{8\pi^2 c \omega_k} \cot h \left(\frac{hc\omega_k}{2KT} \right). \quad (15)$$

Here h is the Planck constant, c the velocity of light and T the absolute temperature. The relevant mean vibrational amplitude values are given in Table III.

Vibrational mean amplitude quantities in Å

TABLE III

	$^{10}\text{B}_2\text{H}_6$	$^{11}\text{B}_2\text{H}_6$
σ_a	0.0872	0.0843
σ_b	0.1007	0.0994
σ_R	0.0667	0.0634

5. Rotational distortion constants

The values of the τ elements defined by Kivelson and Wilson [18] were determined from the values of the elements of l , and the matrix of transformation between the normal and mass-weighted Cartesian coordinates constructed using the relation

$$l = S\tilde{A}. \quad (16)$$

The explicit relationship between the l elements and the τ elements was determined using the method suggested by Oka and Morino [19] and Alti *et al.* [20]. The obtained values for the rotational distortion constants D_J , D_{JK} and D_K are given in Table IV.

Rotational distortion constants in cm^{-1}

TABLE IV

Molecule	D_J	D_K	D_{JK}
$^{10}\text{B}_2\text{H}_6$	1.2478×10^{-6}	2.3419×10^{-5}	5.7449×10^{-6}
$^{11}\text{B}_2\text{H}_6$	1.0541×10^{-6}	2.4290×10^{-5}	7.1812×10^{-6}

6. Coriolis coupling constants

The values of the Coriolis coupling constants (ζ) were determined from the l matrix using the relation given by Meal and Polo [21] *i. e.*,

$$\zeta^\alpha = lM^\alpha \tilde{l}. \quad (17)$$

The values of these constants for interaction of the vibrations were calculated assuming the B-B axis as the axis of rotation. They are given in Table V.

7. Results and discussion

In this study, the assignment, internal coordinates and symmetry coordinates used are identical with those of Ogawa and Miyazawa. The ω_9 and ω_{15} values are those of Lehman *et al.* It is seen from the Appendix that the isotopic rules obtained are similar to the Teller-Redlich Product Rules and are derived without assuming any force field model.

TABLE V

Coriolis coupling constants

	ζ Elements	$^{10}\text{B}_2\text{H}_6$	$^{11}\text{B}_2\text{H}_6$
$A_g \times B_{3g}$	$\zeta_{1,15}$	-0.3916	-0.3916
	$\zeta_{2,15}$	0.7931	0.7691
	$\zeta_{3,15}$	-0.3916	-0.3916
	$\zeta_{4,15}$	-0.2534	-0.3188
$A_u \times B_{3u}$	$\zeta_{5,16}$	0.9246	0.9266
	$\zeta_{5,18}$	0.3809	0.3759
$B_{1g} \times B_{2g}$	$\zeta_{6,11}$	-0.2482	-0.6349
	$\zeta_{6,12}$	0.4061	-0.7414
	$\zeta_{7,11}$	0.6381	0.2191
	$\zeta_{7,12}$	0.6145	0.0968
$B_{1u} \times B_{2u}$	$\zeta_{8,13}$	0.1098	0.0048
	$\zeta_{8,14}$	-0.6974	-0.7854
	$\zeta_{9,13}$	0.0705	0.0278
	$\zeta_{9,14}$	-0.4476	-0.6188
	$\zeta_{10,13}$	-0.9995	-0.9999
	$\zeta_{10,14}$	-0.0320	-0.0546

The B-H_i stretching force constant 3.6004 mdynes/Å obtained here compares well with the value of 3.42 mdynes/Å obtained by Bell and Languet-Higgins. Adams and Churchill obtained a value of 3.538 mdynes/Å from their recent normal coordinate treatment. The corresponding stretching force constant obtained from Badger's rule [22] is 3.008 mdynes/Å. The value obtained for the bridge bond stretching is 1.9367 mdynes/Å. Bell and Languet-Higgins report a value of 1.43 mdynes/Å and the values obtained by Adams and Churchill and from Badger's rule are 1.684 mdynes/Å and 1.865 mdynes/Å, respectively. The Bridge bond stretching force constant is 53 per cent of the terminal bond stretching constant and furthermore we find, in agreement with Ogawa and Miyazawa and Adams and Churchill, that there is a substantial force constant corresponding to the B-B bond stretching. The value obtained here for the B-B stretching is 2.5853 mdynes/Å which compares favourably with the value of 2.21 mdynes/Å reported by Bell and Languet-Higgins. The value obtained by Adams and Churchill is 2.511 mdynes/Å. The value of the B-B stretching force constant in B₂Cl₄ and B₂F₄ [23] (3.8701 and 6.6880 mdynes/Å) are consistent with the value of the bond lengths (1.702 and 1.67 Å).

The value of the force constant, 2.5853 mdynes/Å, in B₂H₆ is consistent with a bond length of 1.762 Å and this confirms the possibility of the existence of the B-B bond. The existence of such a bond is in agreement with molecular orbital calculations, which show significant electron density in the region which would be occupied by a B-B bond. This can also be seen from the equality of the boron-boron distance (1.762 Å) and the sum (1.76 Å) of Pauling's tetrahedral covalent radii [24]. The bending constants f_α and f_ϕ are found to be 0.6296 and 0.4831 mdynes Å/radian² which compare well with the values

of Adams and Churchill (0.515 and 0.336 mdyne $\text{\AA}/\text{radian}^2$) respectively. Regarding the interaction constants, the values obtained are $f_{aa} = -0.0757$, $f_{bb} = -0.0458$ mdyne/ \AA and $f_{ax} = -0.1734$ mdyne/radian. All these are negative. The torsional force constant f_τ obtained here is 0.3734 mdyne/ \AA whereas Adams and Churchill have reported a value of 0.042 mdyne/ \AA .

The mean amplitudes of vibration calculated for $^{10}\text{B}_2\text{H}_6$ ($\sigma_{\text{B-H}_t} = 0.0872 \text{\AA}$, $\sigma_{\text{B-H}_b} = 0.1007 \text{\AA}$ and $\sigma_{\text{B-B}} = 0.0607 \text{\AA}$) compare well with the electron diffraction values of Bartel and Carrol. (They have reported a value of 0.0734 for B-H_t, 0.857 \AA for B-H_b and 0.0608 \AA for B-B.) Then using the isotopic rules and treating the $^{11}\text{B}_2\text{H}_6$ as the unperturbed molecule, and $^{10}\text{B}_2\text{H}_6$ as the isotopically substituted perturbed molecule, the mixing parameters have been calculated (Table I) and the calculations repeated for finding the mean amplitudes of vibration, rotational distortion constants and the Coriolis coupling constants. The values obtained for D_J and D_K are $1.2478 \times 10^{-6} \text{cm}^{-1}$ and $2.3419 \times 10^{-5} \text{cm}^{-1}$, which compare well with the values of Lafferty *et al.*, reported from their high resolution infrared study ($D_J = 1.21 \times 10^{-6}$, $D_K = 1.65 \times 10^{-5}$, and $D_{JK} = 1.54 \times 10^{-6}$, for $^{11}\text{B}_2\text{H}_6$, $D_J = 1.17 \times 10^{-6}$, $D_K = 1.97 \times 10^{-5}$ and $D_{JK} = 1.97 \times 10^{-6}$, all in cm^{-1}). However there seems to be a considerable discrepancy between their D_{JK} values and ours. Our values are consistently higher than the reported ones.

Since the moment of inertia about the B-B axis of diborane is so much the smallest, rotation about this axis will cause the largest Coriolis perturbation and so we have considered this axis alone. The coupling constants obtained are given in Table V. Smith and Mills [25] reported the following three elements from their infrared study: $|\zeta_{5,18}| = 0.55$, $|\zeta_{7,12}| = 0.61$ and $|\zeta_{9,14}| < 0.2$, for diborane. Of these $\zeta_{5,18}$ and $\zeta_{7,12}$ compare well with our values and our value for $\zeta_{9,14} = -0.4476$.

From Table I, it is seen that the values of the mixing parameters of $^{10}\text{B}_2\text{H}_6$ and $^{11}\text{B}_2\text{H}_6$ are very nearly equal except for the values of e and h corresponding to the B_{1g} and B_{2u} species. Since the molecular constants are very sensitive to the mixing parameters, the trend observed in the Coriolis coupling constants of $^{10}\text{B}_2\text{H}_6$ and $^{11}\text{B}_2\text{H}_6$ involving B_{1g} and B_{2u} species can be studied.

In conclusion it may be pointed out that Green's function analysis yields a complete set of molecular constants within reasonable accuracy and that the molecular force field for diborane and other bridged structure molecules will be well represented by the Green's function procedure. Application of the method to similar bridged structures is in progress.

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APPENDIX

Isotopic rules for $X_2Y_6 \rightarrow X_2^iY_6$ molecules

A_g species

$$\omega_1^{i2} \omega_2^{i2} \omega_3^{i2} \omega_4^{i2} = \frac{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2}{(1 + \epsilon)} \quad (\text{A.1})$$

$$\begin{aligned} & \omega_1^2 \omega_2^2 (\omega_3^2 + \omega_4^2) + \omega_3^2 \omega_4^2 (\omega_1^2 + \omega_2^2)] = \\ & \frac{\varepsilon m_X C^2 \omega_1^2 \omega_3^2 (\omega_2^2 + d^2 \omega_4^2) + 2\varepsilon m_Y D^2 \omega_2^2 \omega_4^2 (c^2 \omega_1^2 + \omega_3^2) +}{C^2 D^2 d_2^2 (1 + \varepsilon)} \\ & \quad + C^2 D^2 d_2^2 \omega_1^2 \omega_2^2 (\omega_3^2 + \omega_4^2) + \omega_3^2 \omega_4^2 (\omega_1^2 + \omega_2^2) \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} & \omega_1^2 (\omega_2^2 + \omega_3^2 + \omega_4^2) + \omega_2^2 (\omega_3^2 + \omega_4^2) + \omega_3^2 \omega_4^2] = \\ & \frac{\varepsilon m_X C^2 [(\omega_1^2 + \omega_3^2) (\omega_2^2 + d^2 \omega_4^2) + D^2 \omega_1^2 \omega_3^2] + 2\varepsilon m_Y D^2 [(\omega_2^2 + \omega_4^2) (c^2 \omega_1^2 + \omega_3^2) +}{C^2 D^2 d_2^2 (1 + \varepsilon)} \\ & \quad + C^2 \omega_2^2 \omega_4^2] + C^2 D^2 d_2^2 [\omega_1^2 (\omega_2^2 + \omega_3^2 + \omega_4^2) + \omega_2^2 (\omega_3^2 + \omega_4^2) + \omega_3^2 \omega_4^2] \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} & \omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2 = \\ & \frac{\varepsilon m_X C^2 [D^2 (\omega_1^2 + \omega_3^2) + \omega_2^2 + d^2 \omega_4^2] + 2\varepsilon m_Y D^2 [C^2 (\omega_2^2 + \omega_4^2) + \omega_3^2 + c^2 \omega_1^2] +}{C^2 D^2 d_2^2 (1 + \varepsilon)} \\ & \quad + C^2 D^2 d_2^2 (\omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2) \end{aligned} \quad (\text{A.4})$$

where $d_2^2 = (m_X + 2m_Y)$, $C^2 = (1 + c^2)$, $D^2 = (1 + d^2)$ and c and d are the mixing parameters.

B_{1g} species

$$\omega_6^2 \omega_7^2 = \frac{\omega_6^2 \omega_7^2 (2I_X + \varepsilon m_X R^2) d_3^2 d_4^2}{4\varepsilon I_X m_Y [m_X R^2 b^2 S_{\beta/2}^2 d_4^2 + (R + 2a C_{\alpha/2})^2 d_3^2] + (2I_X + \varepsilon m_X R^2) d_3^2 d_4^2} \quad (\text{A.5})$$

$$\begin{aligned} & \omega_6^2 + \omega_7^2 = \\ & \frac{4\varepsilon I_X m_Y [\{(R + 2a C_{\alpha/2}) d_3 - e \sqrt{m_X R b S_{\beta/2} d_4}\}^2 \omega_6^2 + \{\sqrt{m_X R b S_{\beta/2} d_4} +}{4\varepsilon I_X m_Y [m_X R^2 b^2 S_{\beta/2}^2 d_4^2 + (R + 2a C_{\alpha/2})^2 d_3^2] + (2I_X + \varepsilon m_X R^2) d_3^2 d_4^2} \\ & \quad + e(R + 2a C_{\alpha/2}) d_3\}^2 \omega_7^2 + (2I_X + \varepsilon m_X R^2) E^2 d_3^2 d_4^2 (\omega_6^2 + \omega_7^2)] \end{aligned} \quad (\text{A.6})$$

where R , a and b are respectively the $X-X$, $X-Y_t$ and $X-Y_b$ bond distances. I_X is the moment of inertia along the X axis whose value $= [m_Y (R + 2a C_{\alpha/2})^2 + 2m_Y b^2 S_{\beta/2}^2 + m_X R^2 / 2]$, $d_3 = [2I_X (I_X - 2m_Y b^2 S_{\beta/2}^2)]^{1/2}$, $d_4 = [2(I_Y - 4m_Y a^2 S_{\alpha/2}^2)]^{1/2}$ with $I_Y = [4m_Y a^2 S_{\alpha/2}^2 + m_Y (R + 2a C_{\alpha/2})^2 + m_X R^2 / 2]$ i.e., the moment of inertia along Y axis, $S_{\alpha/2}$ and $C_{\alpha/2}$ stand for $\sin \alpha/2$ and $\cos \alpha/2$ and $S_{\beta/2}$ and $C_{\beta/2}$ stand for $\sin \beta/2$ and $\cos \beta/2$. Here α and β are the $Y_t X Y_t$ and $Y_b X Y_b$ angles. $E^2 = (1 + e^2)$ and e is the mixing parameter.

B_{1u} species

$$\omega_8^2 \omega_9^2 \omega_{10}^2 = \frac{\omega_8^2 \omega_9^2 \omega_{10}^2 (2\varepsilon m_X + d_1^2)}{d_1^2 (1 + \varepsilon)} \quad (\text{A.7})$$

$$\begin{aligned} & \omega_8^i \omega_9^i + \omega_9^i \omega_{10}^i + \omega_8^i \omega_{10}^i = \\ & = \frac{2\epsilon m_X m_Y F^2 \omega_8^2 \omega_9^2 + 2\epsilon m_Y d_1^2 (f^2 \omega_9^2 \omega_{10}^2 + \omega_8^2 \omega_{10}^2) + (2\epsilon m_X + d_1^2) d_2^2 F^2 [\omega_8^2 \omega_9^2 + \omega_9^2 \omega_{10}^2 + \omega_8^2 \omega_{10}^2]}{F^2 d_1^2 d_2^2 (1 + \epsilon)} \end{aligned} \quad (\text{A.8})$$

$$\begin{aligned} & \omega_8^i + \omega_9^i + \omega_{10}^i = \\ & \frac{2\epsilon m_X m_Y F^2 (\omega_8^2 + \omega_9^2) + 2\epsilon m_Y d_1^2 [f^2 (\omega_9^2 + \omega_{10}^2) + (\omega_8^2 + \omega_{10}^2)] + (2\epsilon m_X + d_1^2) d_2^2 F^2 [\omega_8^2 + \omega_9^2 + \omega_{10}^2]}{F^2 d_1^2 d_2^2 (1 + \epsilon)} \end{aligned} \quad (\text{A.9})$$

where $d_1^2 = (2m_X + 6m_Y)$, $F^2 = (1 + f^2)$ and f is the mixing parameter.

B_{2g} species

$$\begin{aligned} \omega_{11}^i \omega_{12}^i &= \frac{\omega_{11}^2 \omega_{12}^2 (\epsilon m_X R^2 + 2I_Y) d_4^2}{[8\epsilon m_X m_Y R^2 a^2 S_{\alpha/2}^2 + 4\epsilon m_Y I_Y (R + 2a C_{\alpha/2})^2 + (\epsilon m_X R^2 + 2I_Y) d_4^2]} \quad (\text{A.10}) \\ \omega_{11}^i + \omega_{12}^i &= \\ & \frac{4\epsilon m_Y [\{\sqrt{I_Y} (R + 2a C_{\alpha/2}) - g \sqrt{2m_X} R a S_{\alpha/2}\}^2 \omega_{11}^2 + \{\sqrt{2m_X} R a S_{\alpha/2} + g(R + 2a C_{\alpha/2}) \sqrt{I_Y}\}^2 \omega_{12}^2] + (\epsilon m_X R^2 + 2I_Y) d_4^2 G^2 (\omega_{11}^2 + \omega_{12}^2)}{[8\epsilon m_X m_Y R^2 a^2 S_{\alpha/2}^2 + 4\epsilon m_Y I_Y (R + 2a C_{\alpha/2})^2 + (\epsilon m_X R^2 + 2I_Y) d_4^2] G^2} \end{aligned} \quad (\text{A.11})$$

where $G^2 = (1 + g^2)$ and g is the mixing parameter.

B_{2u} species

$$\begin{aligned} \omega_{13}^i \omega_{14}^i &= \frac{\omega_{13}^2 \omega_{14}^2 (\epsilon m_X R^2 + 2I_X) d_1^2}{[12\epsilon m_Y I_X + (\epsilon m_X R^2 + 2I_X) d_1^2]} \quad (\text{A.12}) \\ \omega_{13}^i + \omega_{14}^i &= \\ & = \frac{4\epsilon m_Y I_X \{(d_1 - h \sqrt{m_X})^2 \omega_{13}^2 + (\sqrt{m_X} + h d_1)^2 \omega_{14}^2\} + (\epsilon m_X R^2 + 2I_X) H^2 d_1^2 d_2^2 (\omega_{13}^2 + \omega_{14}^2)}{[12\epsilon m_Y I_X + (\epsilon m_X R^2 + 2I_X) d_1^2] d_2^2 H^2} \end{aligned} \quad (\text{A.13})$$

where $H^2 = (1 + h^2)$ and h is the mixing parameter.

B_{3u} species

$$\begin{aligned} \omega_{16}^i \omega_{17}^i \omega_{18}^i &= \frac{\omega_{16}^2 \omega_{17}^2 \omega_{18}^2 (2\epsilon m_X + d_1^2)}{d_1^2 (1 + \epsilon)} \quad (\text{A.14}) \\ \omega_{16}^i \omega_{17}^i + \omega_{17}^i \omega_{18}^i + \omega_{16}^i \omega_{18}^i &= \end{aligned}$$

$$= \frac{2\epsilon m_Y d_1^2 (k^2 \omega_{16}^2 \omega_{17}^2 + \omega_{17}^2 \omega_{18}^2) + 2\epsilon m_X m_Y K^2 \omega_{16}^2 \omega_{18}^2 + (2\epsilon m_X + d_1^2) d_2^2 K^2 (\omega_{16}^2 \omega_{17}^2 + \omega_{18}^2 \omega_{17}^2 + \omega_{16}^2 \omega_{18}^2)}{d_1^2 d_2^2 (1 + \epsilon)} \quad (\text{A.15})$$

$$\omega_{16}^{i2} + \omega_{17}^{i2} + \omega_{18}^{i2} = \frac{2\epsilon m_Y d_1^2 [k^2 (\omega_{16}^2 + \omega_{17}^2) + (\omega_{17}^2 + \omega_{18}^2)] + 2\epsilon m_X m_Y K^2 (\omega_{16}^2 + \omega_{18}^2) + (2\epsilon m_X + d_1^2) d_2^2 K^2 (\omega_{16}^2 + \omega_{17}^2 + \omega_{18}^2)}{d_1^2 d_2^2 K^2 (1 + \epsilon)} \quad (\text{A.16})$$

where $K^2 = (1+k^2)$ and k in the mixing parameter.

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