ANHARMONICITY FACTORS AND POTENTIAL ENERGY CONSTANTS OF B_2H_6 AND B_2D_6

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Abstract

The anharmonicity factors of B_2H_6 and B_2D_6 have been calculated using Dennison's method. Using the calculated harmonic wave numbers, the valence force constants have been obtained by the Wilson's F-G matrix method.

Introduction

Several authors[1-6] have studied the structure of diborane and the electron diffraction data of Hedberg and Schomaker[7] have finally established ethylene-like bridge structure for this molecule. The Raman and infra-red spectra of B_2H_6 and B_2D_6 have been studied by Lord and Nielson.[8] Later Venkateswarlu and Thirugnanasambandam[9] have made the normal co-ordinate treatment by the Wilson's F-G matrix method[10] using a very general quadratic potential energy function. They have not taken into account the anharmonicity correction for the frequencies observed.

In this investigation the anharmonicity correction is taken into account and the potential constants for these molecules are evaluated using the harmonic wave-numbers.

Method

The diborane molecule belongs to the D_{2h} point group having eighteen fundamental frequencies falling under eight species $4A_g + 1A_u + 2B_{1g} + 3B_{1u} + 2B_{2g} + 2B_{2u} + 1B_{3g} + 3B_{3u}$. Among the three frequencies under B_{1u} type one frequency at 368 cm.$^{-1}$ in B_2H_6 and 262 cm.$^{-1}$ in B_2D_6 is distinctly different from the others in the sense that it is not an ordinary harmonic vibration. Bell[12] has shown that this belongs to the fourth power vibration. This vibration has not been made use of in the present calculation.

The symmetry co-ordinates used are the same as those used by Venkateswarlu and Thirugnanasambandam. The relation between the valence force constants (f) and the symmetry force constants (F) may be given as $f = \tilde{U}FU$ where f, F are the force constant matrices and U is the matrix formed by the coefficients of the internal co-ordinates in the symmetry co-ordinates. The valence force constants (f) may be equated to the symmetry force constants (F) as given in Table I.

TABLE I

The relation between the valence and symmetry force constants

$f_d = (F_{11} + F_{88} + F_{1111} + F_{1616})/4$

$f_D = (F_{22} + F_{66} + F_{1313} + F_{1717})/4$

$f_R = F_{44}$

D^2 $f_\alpha = (F_{33} + F_{1818})/12$

d^2 $f_\beta = (F_{33} + F_{1818})/12$

Dd $f_\theta = (F_{55} + F_{77} + F_{99} + F_{1212} + F_{1414} + F_{1515})/8 + (F_{33} + F_{1818})/12$

$f_{dd} = (F_{11} - F_{88} - F_{1111} + F_{1616})/4$

$f'_{dd} = (F_{11} - F_{88} + F_{1111} - F_{1616})/4$

$f''_{dd} = (F_{11} + F_{88} - F_{1111} - F_{1616})/4$

$f_{Dd} = (F_{12} + F_{1617})/4 = f_{Dd}'$

$f''_{Dd} = (F_{12} - F_{1617})/4 = f_{Dd}'''$

$f_{DD} = (F_{22} - F_{66} - F_{1313} + f_{1717})/4$

$f'_{DD} = (F_{22} + F_{66} - F_{1313} - F_{1717})/4$

$f''_{DD} = (F_{22} - F_{66} + F_{1313} - F_{1717})/4$

D $f_{D\alpha} = (F_{13} + F_{1618})/2\sqrt{12}$

D $f'_{d\alpha} = (F_{13} - F_{1618})/2\sqrt{12}$

d $f_{d\beta} = -(F_{13} - F_{1618})/2\sqrt{12}$

d $f_{d\beta} = -(F_{13} + F_{1618})/2\sqrt{12}$

D $f_{D\alpha} = (F_{23} + F_{1718})/2\sqrt{12}$

D $f'_{D\alpha} = (F_{23} - F_{1718})/2\sqrt{12}$

d $f_{D\beta} = -(F_{23} - F_{1718})/2\sqrt{12}$

d $f'_{D\beta} = -(F_{23} + F_{1718})/2\sqrt{12}$

D^2 $f_{\alpha\alpha} = (F_{33} - F_{1818})/12$

Db $f_{\alpha\beta} = -(F_{33} - F_{1818})/12$

Dd $f'_{\alpha\beta} = -(F_{33} + F_{1818})/12$

$$d^2 f_{\beta\beta} = (F_{33} - F_{1818})/12$$

$$\sqrt{D}d\, f_{\alpha\theta} = (F_{13} - F_{1618})/2\sqrt{12} + (F_{89} + F_{1112})/2\sqrt{8}$$

$$\sqrt{D}d\, f'_{\alpha\theta} = (F_{13} - F_{1618})/2\sqrt{12} - (F_{89} + F_{1112})/2\sqrt{8}$$

$$\sqrt{D}d\, f''_{\alpha\theta} = (F_{13} + F_{1618})/2\sqrt{12} - (F_{89} - F_{1112})/2\sqrt{8}$$

$$\sqrt{D}d\, f'''_{\alpha\theta} = (F_{13} + F_{1618})/2\sqrt{12} + (F_{89} - F_{1112})/2\sqrt{8}$$

$$\sqrt{D}d\, f_{\nu\theta} = (F_{23} - F_{1718})/2\sqrt{12} + (F_{67} + F_{1314})/2\sqrt{8}$$

$$\sqrt{D}d\, f'_{\nu\theta} = (F_{23} - F_{1718})/2\sqrt{12} - (F_{67} + F_{1314})/2\sqrt{8}$$

$$\sqrt{D}d\, f''_{\nu\theta} = (F_{23} + F_{1718})/2\sqrt{12} + (F_{67} - F_{1314})/2\sqrt{8}$$

$$\sqrt{D}d\, f'''_{\nu\theta} = (F_{23} + F_{1718})/2\sqrt{12} - (F_{67} - F_{1314})/2\sqrt{8}$$

$$Dd\, f_{\alpha\theta} = (F_{33} - F_{1818})/12$$

$$Dd\, f'_{\alpha\theta} = (F_{33} + F_{1818})/12$$

$$Dd\, f_{\beta\theta} = -(F_{33} + F_{1818})/12$$

$$Dd\, f'_{\beta\theta} = -(F_{33} - F_{1818})/12$$

$$Dd\, f_{\theta\theta} = -(F_{55} - F_{77} + F_{99} + F_{1212} - F_{1414} + F_{1515})/8 + (F_{33} + F_{1818})/12$$

$$Dd\, f'_{\theta\theta} = -(F_{55} + F_{77} - F_{99} - F_{1212} + F_{1414} + F_{1515})/8 + (F_{33} + F_{1818})/12$$

$$Dd\, f''_{\theta\theta} = (F_{55} - F_{77} - F_{99} - F_{1212} - F_{1414} + F_{1515})/8 + (F_{33} + F_{1818})/12$$

$$Dd\, f'''_{\theta\theta} = -(F_{55} - F_{77} + F_{99} - F_{1212} + F_{1414} - F_{1515})/8 + (F_{33} - F_{1818})/12$$

$$Dd\, f''''_{\theta\theta} = (F_{55} + F_{77} + F_{99} - F_{1212} - F_{1414} - F_{1515})/8 + (F_{33} - F_{1818})/12$$

$$Dd\, f'''''_{\theta\theta} = (F_{55} - F_{77} - F_{99} + F_{1212} + F_{1414} - F_{1515})/8 + (F_{33} - F_{1818})/12$$

$$Dd\, f''''''_{\theta\theta} = -(F_{55} + F_{77} - F_{99} + F_{1212} - F_{1414} - F_{1515})/8 + (F_{33} - F_{1818})/12$$

$$f_{\alpha\kappa} = F_{14}/2$$

$$f_{\nu\kappa} = F_{24}/2$$

$$D\, f_{\kappa\alpha} = F_{34}/\sqrt{12}$$

$$d\, f_{\kappa\beta} = -F_{34}/\sqrt{12}$$

$$\sqrt{D}d\, f_{\kappa\theta} = F_{34}/\sqrt{12}$$

Anharmonicity Factors

Considering a pair of molecules X_2H_6 and X_2D_6, the anharmonicity factors X_{ii} may be calculated making use of Dennison's rule[11] which states that if ω_i and ω_i^* are the harmonic wave-numbers of hydrated and deuterated molecules respectively and ν_i and ν_i^* are the observed fundamentals then

$$\omega_i = \nu_i\ (1 + x_{ii})$$

and

$$\omega_i^* = \nu_i^*\ [1 + x_{ii}\ (\nu_i^*/\nu_i)]$$

ω_i/ω_i^* can also be expressed as the ratio of the kinetic energy matrices. Thus the anharmonicity factor x_{ii} can be calculated, the other data being known. The vibrational spectral data and the calculated anharmonicity factors are presented in Table II.

TABLE II

Spectral data, harmonic wave-numbers and anharmonicity factors for B_2H_6 and B_2D_6

Type	B_2H_6			B_2D_6		
	Observed frequencies cm.$^{-1}$	Harmonic wave-numbers cm.$^{-1}$	x_{ii}	Observed frequencies cm.$^{-1}$	Harmonic wave-numbers cm.$^{-1}$	x_{ii}
A_g ..	2524	2663·57	0·0553	1860	1933·84	0·0397
	2104	2220·35	0·0553	1511	1570·98	0·0397
	1180	1245·25	0·0553	929	965·88	0·0397
	794	837·91	0·0553	726	754·82	0·0397
A_u ..	829	858·43	0·0355	592	607·04	0·0254
B_{1g} ..	1768	1826·16	0·0329	1273	1303·17	0·0237
	1035	1069·05	0·0329	870	890·62	0·0237
B_{1u} ..	2612	2759·58	0·0565	1999	2082·76	0·0419
	950	1003·68	0·0565	705	734·54	0·0419
B_{2g} ..	2591	2716·40	0·0484	1980	2053·26	0·0370
	920	964·53	0·0484	740	767·38	0·0370
B_{2u} ..	1915	2042·73	0·0667	1465	1538·10	0·0499
	973	1037·90	0·0667	728	764·33	0·0499
B_{3g} ..	1015	1079·25	0·0633	730	763·80	0·0463
B_{3u} ..	2525	2692·15	0·0662	1845	1934·30	0·0484
	1602	1708·05	0·0662	1205	1263·32	0·0484
	1177	1254·92	0·0662	881	923·64	0·0484

RESULTS AND DISCUSSION

The secular equations have been framed using the harmonic wave-numbers. By solving those equations, the symmetry force constants have

been evaluated. From the relations given in Table I, the valence force constants are calculated and given in Table III along with the values obtained by Venkateswarlu and Thirugnanasambandam.

TABLE III

Potential constants of B_2H_6 and B_2D_6 (10^5 dynes cm.$^{-1}$)

Potential constant	Present investigation	Venkateswarlu and P. T. Sambandam
f_d	2·7158	3·474
f_D	1·4790	1·837
f_K	1·9000	2·910
f_α	0·2463	0·219
f_β	0·3111	0·350
f_θ	0·7464	0·357
f_{dd}	−1·3842	−0·074
f'_{dd}	0·0632	..
f''_{dd}	0·1132	..
f_{DD}	0·6709	0·152
f'_{DD}	−0·0085	0·093
f''_{DD}	−0·1415	0·192
f_{Dd}	0·0518	0·200
f'_{Dd}	0·0518	..
f''_{Dd}	−0·0018	..
f'''_{Dd}	0·0018	..
$f_{d\alpha}$	0·0118	..
$f'_{d\alpha}$	−0·0097	..
$f_{D\alpha}$	0·0303	0·313
$f'_{D\alpha}$	−0·0087	..
$f_{d\beta}$	0·0097	0·008
$f'_{d\beta}$	−0·0118	..
$f_{D\beta}$	0·0098	..
$f'_{D\beta}$	−0·0340	..
$f_{\alpha\alpha}$	0·0534	..

TABLE III—(*Contd.*)

Potential constant	Present investigation	Venkateswarlu and P. T. Sambandam
$f_{\beta\beta}$	0·0674	..
$f_{\alpha\beta}$	—0·0600	..
$f'_{\alpha\beta}$	—0·2769	..
$f_{\alpha\theta}$	0·0600	—0·051
$f'_{\alpha\theta}$	0·2769	..
$f_{\beta\theta}$	—0·2769	..
$f'_{\beta\theta}$	—0·0600	..
$f_{\delta\theta}$	0·3130	0·046
$f'_{\delta\theta}$	—0·3336	..
$f''_{\delta\theta}$	0·0238	..
$f'''_{\delta\theta}$	0·0014	..
$f_{D\theta}$	0·0526	0·104
$f'_{D\theta}$	0·0631	..
$f''_{D\theta}$	0·0321	..
$f'''_{D\theta}$	0·0321	..
$f_{\theta\theta}$	0·2977	0·044
$f'_{\theta\theta}$	0·1209	0·053
$f''_{\theta\theta}$	—0·0572	0·046
$f'''_{\theta\theta}$	—0·0033	..
$f''''_{\theta\theta}$	0·0157	..
$f'''''_{\theta\theta}$	0·1227	..
$f''''''_{\theta\theta}$	0·1050	..
$f_{R\delta}$	0·0050	..
f_{RD}	0·0050	..
$f_{R\alpha}$	0·0022	..
$f_{R\beta}$	0·0022	..
$f_{R\theta}$	0·0023	..

From Table II it can be seen that the anharmonicity correction ranges between two and seven per cent. The evaluation has been made by making use of symmetry matrix method and a large number of force constants has been evaluated. Since the secular equations for hydrated and deuterated molecules have been combined, a unique set of force constants has been obtained. Comparing the values of the present investigation with that of Venkateswarlu and Thirugnanasambandam, there is a considerable variation in the values of the stretching, bending and all other interaction force constants.

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