ANHARMONICITY FACTORS AND POTENTIAL ENERGY CONSTANTS OF B$_2$H$_6$ AND B$_2$D$_6$

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Abstract

The anharmonicity factors of B$_2$H$_6$ and B$_2$D$_6$ 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$_2$H$_6$ and B$_2$D$_6$ have been studied by Lord and Nielsen.$^8$ 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$_2$H$_6$ and 262 cm$^{-1}$ in B$_2$D$_6$ is distinctly different from the others in the sense that it is not an ordinary harmonic vibration. Bell$^{11}$ 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 \( f = UFU \) 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*

\[
\begin{align*}
\hat{f}_d &= (F_{11} + F_{88} + F_{1111} + F_{1616})/4 \\
\hat{f}_v &= (F_{22} + F_{66} + F_{1313} + F_{1717})/4 \\
\hat{f}_r &= F_{44} \\
D^2 \hat{f}_a &= (F_{33} + F_{1818})/12 \\
d^2 \hat{f}_\beta &= (F_{33} + F_{1818})/12 \\
Dd \hat{f}_\theta &= (F_{35} + F_{77} + F_{99} + F_{1212} + F_{1414} + F_{1515})/8 + (F_{33} + F_{1818})/12 \\
\hat{f}_{dd} &= (F_{11} - F_{88} - F_{1111} + F_{1616})/4 \\
\hat{f}_{dd'} &= (F_{11} - F_{88} + F_{1111} + F_{1616})/4 \\
\hat{f}_{dd''} &= (F_{11} + F_{88} - F_{1111} - F_{1616})/4 \\
\hat{f}_{dd} &= (F_{12} + F_{1617})/4 = \hat{f}_{dd'} \\
\hat{f}_{dd''} &= (F_{12} - F_{1617})/4 = \hat{f}_{dd'''} \\
\hat{f}_{dd} &= (F_{22} - F_{66} - F_{1313} + F_{1717})/4 \\
\hat{f}_{dd'} &= (F_{22} + F_{66} - F_{1313} - F_{1717})/4 \\
\hat{f}_{dd''} &= (F_{22} - F_{66} + F_{1313} - F_{1717})/4 \\
D \hat{f}_{aa} &= (F_{13} + F_{1818})/2 \sqrt{12} \\
D \hat{f}_{a'a} &= (F_{13} - F_{1616})/2 \sqrt{12} \\
d \hat{f}_{a'a} &= - (F_{13} - F_{1616})/2 \sqrt{12} \\
d \hat{f}_{a'a} &= - (F_{13} + F_{1616})/2 \sqrt{12} \\
D \hat{f}_{aa} &= (F_{23} + F_{1718})/2 \sqrt{12} \\
D \hat{f}_{a'a} &= (F_{23} - F_{1718})/2 \sqrt{12} \\
d \hat{f}_{a'a} &= - (F_{23} - F_{1718})/2 \sqrt{12} \\
d \hat{f}_{a'a} &= - (F_{23} + F_{1718})/2 \sqrt{12} \\
D^2 \hat{f}_{aa} &= (F_{33} + F_{1818})/12 \\
Db \hat{f}_{a'a} &= - (F_{33} - F_{1818})/12 \\
Dd \hat{f}_{a'a} &= - (F_{33} + F_{1818})/12
\end{align*}
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