ANHARMONICITY FACTORS AND POTENTIAL ENERGY CONSTANTS OF B₂H₆ AND B₂D₆

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ABSTRACT

The anharmonicity factors of B₂H₆ and B₂D₆ 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 authors¹–⁶ have studied the structure of diborane and the electron diffraction data of Hedberg and Schomaker⁷ have finally established ethylene-like bridge structure for this molecule. The Raman and infra-red spectra of B₂H₆ and B₂D₆ have been studied by Lord and Nielson.⁸ Later Venkateswarlu and Thirugnanasambandam⁹ have made the normal co-ordinate treatment by the Wilson’s F-G matrix method¹⁰ 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 D₂h point group having eighteen fundamental frequencies falling under eight species 4A₁g + 1A₁u + 2B₁g + 3B₁u + 2B₂g + 2B₂u + 1B₃g + 3B₃u. Among the three frequencies under B₁u type one frequency at 368 cm⁻¹ in B₂H₆ and 262 cm⁻¹ in B₂D₆ is distinctly different from the others in the sense that it is not an ordinary harmonic vibration. Bell¹¹ 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

\[
\begin{align*}
    s_a &= (F_{11} + F_{68} + F_{1111} + F_{1616})/4 \\
    s_d &= (F_{22} + F_{66} + F_{1313} + F_{1717})/4 \\
    s_r &= F_{44} \\
    D^2 f_a &= (F_{33} + F_{1818})/12 \\
    d^2 f_\beta &= (F_{33} + F_{1818})/12 \\
    Dd f_\theta &= (F_{55} + F_{77} + F_{99} + F_{1212} + F_{1414} + F_{1515})/8 + (F_{33} + F_{1818})/12 \\
    f_{aa} &= (F_{11} - F_{88} - F_{1111} + F_{1616})/4 \\
    f'_{aa} &= (F_{11} - F_{88} + F_{1111} - F_{1616})/4 \\
    f''_{aa} &= (F_{11} + F_{88} - F_{1111} - F_{1616})/4 \\
    f_{dd} &= (F_{12} + F_{1617})/4 = f_{dd}' \\
    f''_{dd} &= (F_{12} - F_{1617})/4 = f_{dd}'' \\
    f_{bd} &= (F_{22} - F_{66} - F_{1313} + F_{1717})/4 \\
    f'_{bd} &= (F_{22} + F_{66} - F_{1313} - F_{1717})/4 \\
    f''_{bd} &= (F_{22} - F_{66} + F_{1313} - F_{1717})/4 \\
    D s_{\alpha\alpha} &= (F_{13} + F_{1616})/2 \sqrt{12} \\
    D s_{\alpha\alpha}' &= (F_{13} - F_{1616})/2 \sqrt{12} \\
    d s_{\alpha\beta} &= - (F_{18} - F_{1616})/2 \sqrt{12} \\
    d s'_{\alpha\beta} &= - (F_{18} + F_{1616})/2 \sqrt{12} \\
    D f_{\beta\alpha} &= (F_{23} + F_{1718})/2 \sqrt{12} \\
    D f'_{\beta\alpha} &= (F_{23} - F_{1718})/2 \sqrt{12} \\
    d f_{\alpha\beta} &= - (F_{23} - F_{1718})/2 \sqrt{12} \\
    d f'_{\alpha\beta} &= - (F_{23} + F_{1718})/2 \sqrt{12} \\
    D^2 f_{aa} &= (F_{33} - F_{1818})/12 \\
    Db f_{\alpha\beta} &= - (F_{33} - F_{1818})/12 \\
    Dd f'_{\alpha\beta} &= - (F_{33} + F_{1818})/12
\end{align*}
\]