FORCE CONSTANTS IN THE POTENTIAL ENERGY OF A VIBRATING MOLECULE

(Determination of the Maximum Number by a Group Theoretical Method)

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1. INTRODUCTION

The potential energy $V$ of a molecule, consisting of $n$ atoms and performing small vibrations about its equilibrium configuration, can be expressed as a quadratic form in the $3n$ cartesian displacements ($x_i; i = 1$ to $3n$) of the atoms with constant coefficients as in (1).

$$2V = \sum_{i,j=1}^{3n} b_{ij} x_i x_j. \tag{1}$$

In the above expression, $b_{ij} = b_{ji}$. Since the potential energy does not depend on bodily translations and rotations of the molecule, a new set of $3n - 6$ orthogonal co-ordinates ($S_i$) which may be called internal co-ordinates, which are linear combinations of the cartesian displacements and are orthogonal to the translational and rotational modes of motion can be formed. The potential energy, in this new set of co-ordinates, will have the form

$$2V = \sum_{i,j=1}^{3n-6} F_{ij} S_i S_j. \tag{2}$$

In the above expression, $F_{ij} = F_{ji}$. It follows that there can be $\frac{1}{2} (3n - 6) (3n - 5)$ independent constants in the potential energy expression of a completely unsymmetrical molecule composed of $n$ atoms. Such a case is regarded as possessing only one element of symmetry, namely the identity operation. The presence of other symmetry elements in the molecule results in further relations between $(F_{ij})$.

The application of symmetry operations belonging to the point group appropriate to a molecule transform the set of internal co-ordinates and transformation matrices which connect the old and new sets of internal co-ordinates form a reducible representation of the point group under consideration. When this representation $\Gamma$ is completely reduced, it consists of a number of irreducible representations $\Gamma_i$, a fact which may be symbolically written as in (3).
S. BHAGAVANTAM AND P. V. PANTULU

\[ \Gamma = \sum_i n_i \Gamma_i \]  

(3)

\( n_i \) is the number of times the \( i \)-th irreducible representation occurs in the completely reduced representation. It is easy to show that for a molecule whose symmetry results in the completely reduced representation having a structure given by (3), the maximum number of independent constants required for writing out the potential energy is given by (4).

\[ \sum_i \frac{1}{2} n_i (n_i + 1) \]  

(4)

The present available method for evaluating (4) in respect of a particular molecule consists in determining the structure of the completely reduced representation, which involves the determination of \( n_i \) for all \( i \). \( n_i \) is given by formula (5) (Bhagavantam and Venkatarayudu, 1963).

\[ n_i = \frac{1}{N} \sum_{\rho} h_{\rho} X_{\rho} (R) X_i (R) \]  

(5)

where

- \( N \) is the order of the group.
- \( h_{\rho} \) is the number of elements in the \( \rho \)-th class.
- \( X_{\rho} (R) \) is the character of the group element \( R \) belonging to \( \rho \)-th class in the reducible representation.
- \( X_i (R) \) is the character of same \( R \) in the \( i \)-th irreducible representation.

Thus, this method requires a knowledge of the complete character table of the group and the determination of \( n_i \) for each irreducible representation.

2. DESCRIPTION OF A NEW METHOD

The purpose of this paper is to present a more elegant method of deriving the same result. It is an adaptation of the method suggested by Bhagavantam (1942) for obtaining the maximum number of independent constants required to describe a physical property of a crystal of given symmetry.

From the potential energy expression (2), it is evident that \( (F_{ij}) \) transform like the products of the components of a \( 3n - 6 \) dimensional vector \( (S_1, S_2, \ldots, S_{3n-6}) \) amongst themselves, i.e., as a symmetric tensor of rank 2 which consists of \( \frac{1}{2} (3n - 6) (3n - 5) \) components. The transformation properties of \( (F_{ij}) \) under the set of symmetry operations of the point group