

CHAPTER - 11

An Algebraic Approach for Computing Vibrational Spectra of Triatomic Molecule

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Abstract

In this chapter, we have applied Lie algebraic method [U(2) Lie algebra framework] to calculate the vibrational frequencies of triatomic molecule, Hydrogen Sulphide (H₂S). The calculated vibrational frequencies by Lie algebraic method are compared with existing experimental data.

Key words: *Vibrational spectra, Lie algebraic method, Hydrogen Sulphide*

INTRODUCTION

Lie algebraic theory can be defined as the framework that studies the problems in mathematics and molecular physics. In the last part of the 19th century, Marius Sophus Lie proposed Lie algebras. On the other hand, these methods have been useful in the study of the problems in the beginning portion of the 20th century, after the evaluation of quantum mechanics. This is because quantum mechanics make use of commutators $[x, p_x] = i\hbar$, where $[x, p_x] = x p_x - p_x x$ which is the commutator of x and p_x (linear momentum operator in x direction) and

$\hbar = h/2\pi$, where h is the Planck's constant, which are the significant ingredients of Lie algebras. The framework of the Lie algebraic method has been used to trace the Heisenberg formulation of quantum mechanics [1, 2, 3, 4]. The efficient development of Lie algebraic technique to physical systems (spectrum algebras) was introduced by Iachello and Arima in their pioneer work of spectra of atomic nuclei (interacting Boson model) [5, 6, 7, 8]. Iachello (1981) presented Lie algebraic method (vibron model) for the study of vibrational spectra of molecules [9]. This method is based on the second quantization of the Schrodinger wave equation with a 3-Dimensional Morse potential function and is described as ro-vibration spectra of diatomic molecules [10]. This method was improved in consequent works to study ro-vibrational spectra of polyatomic molecules [11, 12, 13, 14, 15, 22, 23, 24, 25]. Significant interest has focused on the progress of two coupled 1-Dimensional oscillators [16] and its generalization to many coupled 1-Dimensional oscillators [17, 18]. This is given a complete framework to analyze bending vibrational modes in linear molecules [19].

Lie algebraic method for H₂S

The Lie algebraic method is based on the isomorphism of U(2) Lie algebra and the 1-Dimensional Morse oscillator, whose eigenstates may be connected with U(2) \supset O(2) states $|N, m\rangle$. Two U(2) Lie algebras are introduced (U₁(2) and U₂(2)) to describe stretching bonds (S-H) respectively in H₂S. The H₂S can be described by two chains of the molecular dynamical group as given below.

$$\begin{array}{l}
 \text{Chain(I):} \quad U_1(2) \otimes U_2(2) \supset O_1(2) \otimes O_2(2) \supset O_{12}(2) \\
 \quad \quad \quad \downarrow \quad \quad \downarrow \quad \quad \downarrow \quad \quad \downarrow \quad \quad \downarrow \\
 \quad \quad \quad N_1 \quad N_2 \quad n \quad m \quad n+m \\
 \text{Chain(II):} \quad U_1(2) \otimes U_2(2) \supset U_{12}(2) \supset O_{12}(2) \\
 \quad \quad \quad \downarrow \quad \quad \downarrow \quad \quad \quad \quad \downarrow \\
 \quad \quad \quad N_1 \quad N_2 \quad \quad \quad v_1 + v_2
 \end{array}$$

Here chain (I) and chain (II) illustrate local coupling and normal coupling respectively. Quantum numbers in the chain (I) corresponding to various algebras are indicated by n, m and in the chain (II) are v₁, v₂. Vibron numbers N₁ and N₂ are corresponding to the number of bound states of two oscillators and these are constants for the system. It is also noted that n + m = v₁ + v₂ is a conserved quantity. The bending vibrations can be assigned with algebra U₃(2)

to be combined with the algebra $U_1(2) \otimes U_2(2)$ associate with the interacting stretching vibrations.

The Hamiltonian in the case of stretching vibrations for the H_2S is of the form

$$H = E_0 + \sum_{i=1}^2 A_i C_i + \sum_{i<j}^2 A_{ij} C_{ij} + \sum_{i<j}^2 \lambda_{ij} M_{ij}.$$

Here i vary from 1 to 2 for two stretching bonds.

$$H = E_0 + A_1 C_1 + A_2 C_2 + A_{12} C_{12} + \lambda_{12} M_{12}. \quad \dots \textbf{(I)}$$

Where A_1, A_2, A_{12} and λ_{12} are algebraic parameters, which are determined by spectroscopic data. The local stretching vibrations are denoted by v_1 and v_3 , while v_2 denotes bending vibrations for H_2S . The Hamiltonian in the equation (I) can be diagonalized to get predicated energy levels. Where in the equation (I), C_i is an invariant operator of the uncoupled bond with eigenvalues $-4(N_i v_i - v_i^2)$ and the operator C_{ij} coupled bonds with matrix elements

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right]. \quad \dots \textbf{(II(a))}$$

The Majorana operator M_{ij} in the equation (I) is used to define local mode interactions in pairs and contains both diagonal and non-diagonal matrix elements given by

$$\begin{aligned} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= (N_i v_j + N_j v_i - 2v_i v_j) \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= - \left[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1) \right]^{1/2} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= - \left[v_i (v_j + 1)(N_j - v_j)(N_i - v_i + 1) \right]^{1/2}. \end{aligned} \quad \dots \textbf{(II(b))}$$

The Majorana operator M_{ij} annihilate one quantum of vibration in bond i and create one in bond j , or vice versa.

RESULTS AND DISCUSSION

The parameters for stretching bonds of the water molecule in equations (I) and (II) as $N_i = N$, $A_i = A$, $A_{ij} = A_{12}$, $\lambda_{ij} = \lambda_{12}$ ($i = 1, 2$). The parameters λ_{ij} illustrate the interactions between stretching bonds (λ_{12}). The vibron number N_i for stretching bonds of H_2S will be calculated by the following relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, i = 1, 2.$$

Here ω_e and $\omega_e x_e$ are the spectroscopic constants. For the H_2S in stretching mode, we got the values of ω_e and $\omega_e x_e$ for the S-H bond from the work of Nakamoto [20]. Using numerical values of ω_e and $\omega_e x_e$ for the bond S-H as the initial guess for the value of the vibron number N_i , it can be understood from the literature that in the algebraic method, there is some condition to change (not be larger than $\pm 20\%$ of the original value) the value of N_i to get better results.

The initial guess value for the parameter A is obtained by using the energy equation for the single-oscillator fundamental mode, which is given as,

$$E(v=1) = -4A(N-1). \quad \dots \text{(III)}$$

Using the equation (III), \bar{A} can be evaluated as,

$$\bar{A} = \frac{\bar{E}}{4(1-N)}. \quad \dots \text{(IV)}$$

Where \bar{A} and \bar{E} are the average values of the algebraic parameters A 's and E 's.

To find an initial guess value for λ , whose role is to split the initially degenerate local modes is obtained by the relation,

$$\lambda \cong \frac{|E_1 - E_2|}{3N}. \quad \dots \text{(V)}$$

In order to get more accurate results, a numerical fitting procedure (in a least square sense, for example) is used to get the parameters A , λ starting from values as given by equations (IV) and (V). The initial guess for A_{12} may be taken as zero. Vibrational frequencies of a H_2S are calculated using the Hamiltonian expression (Lie algebraic method) in fundamental mode and are given in the table (1). The fitting parameters for a H_2S are presented in the table (2)

Table 1. The experimental and calculated vibrational frequencies (in cm^{-1}) of H_2S

$(\mathbf{v}_1 \mathbf{v}_2 \mathbf{v}_3)$	Experimental [21]	Calculated
(1 0 0)	2614.41	2613.17
(2 0 0)	5144.99	5143.416
(3 0 0)	7576.38	7575.28
(4 0 0)	9911.02	9910.22
(5 0 0)	12149.02	12150.074
(6 0 0)	-	14294.8464
(7 0 0)	-	14013.706

Table 2. Algebraic parameters for H_2S [21]

Stretching parameters
$N_1 = N_2 = N = 56$
$A_1 = A_2 = A = -11.892$
$A_{12} = 0.0069$
$\lambda_{12} = 0.125$

CONCLUSION

In the table (1), the calculated values by Lie algebraic method are compared with experimental vibrational frequencies (stretching) of H_2S and we observed that these calculated values are in close agreement with the experimental values.

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