Chapter 4

STUDY OF VIBRATIONAL SPECTRA OF MONOMER AND DIMER OF BENZENE USING ALGEBRAIC METHOD

4.1 Construction of model Hamiltonian for Monomer, C_6H_6 and Dimer, $(C_6H_6)_2$:

Using the results of the Lie Algebraic theory of polyatomic molecules (c.f. Chapter-2), in this chapter we calculate the vibrational frequencies of monomer and dimer of benzene.

In Lie algebraic method, the $U(2)$ model is very much successful in explaining the stretching and bending vibrational energies of small and medium size molecules. The algebraic Hamiltonian in the $U(2)$ model can be constructed with the Casimir and Majorana operators and hence able to explain successfully the stretching vibrations of methane. The motivation for the construction of this algebraic model is the isomorphism of the one dimensional Lie algebra $U(2)$ with that of the one dimensional Morse oscillator, which is a good description of a stretching vibration of a molecule (Roosmalen, Dieperink and Iachello, 1982; Roosmalen, Iachello, Levine and Dieperink, 1983b; Roosmalen, Benjamin and Levine, 1984). The eigenstates of the one dimensional Schrodinger equation with Morse potential

$$h(p,x) = \frac{p^2}{2\mu} + D\left[1 - \exp(-\alpha x)\right]^2 \qquad (4.1)$$

can be put into one to one correspondence with the dynamical symmetry $U(2) \supset O(2)$ characterized by the quantum numbers $|N, m\rangle$ with the

provision that one takes only the positive branch of *m*, i.e., *m = N,N - 1, N −
2, ..., 1* or *0* for *N* = odd or even (*N* = integer). Thus the Hamiltonian
corresponding to the Morse potential on the basis of *U*(2) algebra is given
by

$$H = \varepsilon_0 + AC \qquad (4.2)$$

where C is the invariant operator of O(2), with eigenvalues ($m^2 − N^2$). So,
the eigenvalues of H are

$$E = \varepsilon_0 + A(m^2 − N^2) \qquad (4.3)$$

Introducing the vibrational quantum number $v = N − m / 2$, one can write
the eigenvalue as

$$E = \varepsilon_0 - 4A\ Nv - v^2 \ , \ \text{with } v = 0,1,........N/2 \ or \ (N-1)/2 \ (\text{for } N = \text{even or odd}) \qquad (4.4)$$

Since the potential in coordinate can be taken to a good approximation, as
a Morse potential, we can write the Hamiltonian of a polyatomic molecule
in terms of Morse anharmonic oscillators by introducing an algebra *U*(2) for
each coordinate(C-H bonds).

The algebraic model Hamiltonian we consider is thus has the following form
(Sarkar *et al.*,2006;2008)

$$H = A_{CH} \sum_{i=1}^{6} C_i^{CH} + A_{CH}' \sum_{i<j=1}^{6} Cij + \sum_{i<j=1}^{6} \lambda_{ij}' M_{ij} + A_{CC} \sum_{i=1}^{6} C_i^{CC} + A_{CC}' \sum_{i<j=1}^{6} C_{ij} + \sum_{i<j=1}^{6} \lambda_{ij} M_{ij} \qquad (4.5)$$

In the equation (5), C_i is an invariant operator with eigenvalues $4(v_i^2 − N_i v_i)$
and the operator C_{ij} is diagonal with matrix elements.

$$\langle N_i,v_i; N,v_j | C_{ij} | N_i,v_i; N_j,v_j \rangle = 4 \left[\ v_i + v_j \ ^2 - \ v_i + v_j \ \ N_i + N_j \ \right] \qquad (4.6)$$

while the operator M_{ij} has both diagonal and non-diagonal matrix element

$$\langle N_i,v_i; N_j,v_j | M_{ij} | N_i,v_i; N_j,v_j \rangle = \langle N_i v_j + N_j v_i - 2v_i v_j)$$

$$\langle N_i,v_i+1; N_j,v_j-1 | M_{ij} | N_i,v_i; N_j,v_j \rangle = - \left[v_j(v_i+1)(N_i-v_i)(N_j-v_j+1) \right]^{1/2} \qquad (4.7)$$

$$\langle N_i,v_i-1; N_j+1 | M_{ij} | N_i,v_i; N_j,v_j \rangle = - \left[v_i(v_j+1)(N_j-v_j)(N_i-v_i+1) \right]^{1/2}$$

Eq. (4.7) is a generalization of the two-bond model to n bonds (Iachello and
Levine, 1995; Sen *et al*, 2011;2012;2013).

The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain .where below each group we have used quantum numbers characterizing the eigenvalues of the corresponding invariant operator N is the number of bosons related to stretching physical modes. The quantum numbers v_i correspond to the number of quanta in each oscillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{n} v_i \qquad (4.8)$$

For a particular polyad, the total vibrational quantum number is always conserved. The inclusion of M_{ij} in the local Hamiltonian operator cannot affect the conservation rule. In eq. (4.5), C_i is an invariant operator of uncoupled bond with eigenvalues $4\ v_i^2 - N_i v_i$ and the operator C_{ij} for coupled bonds are diagonal with matrix elements given by Eq. (4.6)

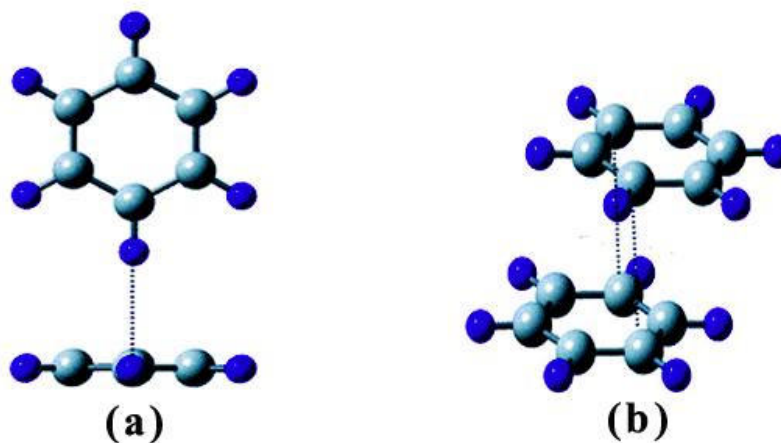**4.2   Structure of the Molecules:**

Fig. 4.1:   Structure of the Benzene Dimer: (a) T-shape and (b) Parallel displaced arrangement.

4.3   Results and discussions:

In this work we use the algebraic parameters i.e. *A, A', λ, λ'* and *N*, to study the vibrational spectra of Benzene molecules where *N* is the vibron number.

The values of Vibron number (N) can be determined by the relation (Oss, 1996),

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \qquad (i = 1, 2........) \qquad (4.9)$$

Where ω_e and $\omega_e x_e$ are the spectroscopic constants of polyatomic molecules of stretching interaction of the molecule considered (Nakamoto, 1997; Huber and Herzberg, 1979). This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than ±20% of the original value [Eq. (4.9)]. It may be noted that during the calculation of the vibrational frequencies of methane, the value of N is kept fixed and not used as free parameter. To obtain a starting guess for the parameter A we use the expression for the single-oscillator fundamental mode which is given as,

$$E(v-1) = -4A(N-1) \qquad (4.10)$$

Using the relation (4.10), A can be obtained as,

$$A = -\frac{E_1}{4(N-1)} \qquad (4.11)$$

To obtain an initial guess for the parameter λ whose role is to split the initially degenerate local modes is obtained by considering the relation (Oss, 1996; Sen et al, 2011; 2012; 2013)

$$\lambda = \frac{E_3 - E_1}{2N} \qquad (4.12)$$

and

$$\lambda' = \frac{E_2 - E_1}{6N} \qquad (4.13)$$

The value of these parameters can be calculated by considering the following general matrix structure of the molecules

$$\begin{pmatrix} -4A(N-1) - 4A'(2N-1) + \lambda N & -\lambda N \\ -\lambda N & -4A(N-1) - 4A'(2N-1) + \lambda N \end{pmatrix} \qquad (4.14)$$

To have better results a numerical fitting procedure (in a least-square sense) is required to obtain the parameters A, A', λ and λ' starting from the values as given by Eq. (4.11) , Eq. (4.12) and Eq. (4.13). Initial guess for A' may be taken as zero.

The fitting algebraic parameters used in the study of vibrational spectra of benzene monomer and dimers are given in Table 4.1, whereas Table 4.2 and Table 4.3 show the comparison of the database of the theoretical DFT (Chandrasekaran, Biennier, Arunan, Talbi and George, 2011) and that of algebraic values.

Table 4.1 : Fitting algebraic parameters (*A*, λ , λ′ all are in cm^{-1} whereas *N* is dimensionless):

Molecule	Vibron Number	Stretching algebraic parameters		
	N	*A*	*λ*	*λ′*
Benzene Monomer	44	-18	0.275	0.030
Benzene Dimer	43	-18	0.183	0.026

Table 4.2: Vibrational frequencies (cm^{-1}) of Benzene Monomer:

Vibrational Mode (Wilson numbering)	Benzene Monomer		
	$\overline{v}_{DFT}$ (Chandrasekaran *et al.*, 2011, *J.Phys.Chem.*, A **115,** 11263)	$\overline{v}_{ALG}$ (Singha *et al.*, 2013, *Polycyclic Aromatic Compounds* (in Press)	$\Delta = \overline{v}_{DFT} - \overline{v}_{ALG}$
$V_{13}(B_{1u})$	3071.1	3071.0	0.1
$V_{20}(E_{1u})$	3095.4	3095.0	0.4
	3095.7	3097.2	-1.5
$V_7(E_{2g})$	3079.0	3078.8	0.2
	3079.4	3081.3	-1.9
$V_2 (A_{1g})$	3105.8	3106.2	-0.4

Δ (r.m.s.) = 1.019 cm^{-1}

Table 4.3: Vibrational frequencies (cm^{-1}) of T shaped and Parallel Displaced (PD) Benzene Dimer:

Vibrational mode (Wilson numbering)	Benzene Dimer (TS)			Benzene Dimer (PD)		
	$\overline{v}_{DFT}$ (Chandrasekaran *et al.*, 2011)	$\overline{v}_{ALG}$ (Singha *et al.*, 2013, Polycyclic Aromatic Compounds (in Press)	$\Delta\overline{v}_{DFT}-\overline{v}_{ALG}$	$\overline{v}_{DFT}$ (Chandrasekaran *et al.*, 2011)	$\overline{v}_{ALG}$ (Singha *et al.*, 2013, Polycyclic Aromatic Compounds (in Press)	$\Delta\overline{v}_{DFT}-\overline{v}_{ALG}$
$V_{13}(B_{1u})$	3069.6	3069.0	0.6	3069.9	3070.1	-0.2
$V_{20}(E_{1u})$	3097.7	3093.2	4.5	3095.5	3093.8	1.7
	3103.2	3103.1	0.1	3096.6	3096.5	0.1
$V_7(E_{2g})$	3076.9	3075.8	0.9	3078.7	3078.8	-0.1
	3085.6	3085.0	0.6	3081.6	3080.9	0.7
$V_2 (A_{1g})$	3130.0	3131.4	-1.4	3107.7	3109.3	-1.6
	Δ (r.m.s.) = 1.990 cm^{-1}			Δ (r.m.s.) = 2.449 cm^{-1}		

4.4   **Analysis of the spectra:**

Here we present the study of vibrational spectra of monomer and dimer of benzene using Lie algebraic method. In this chapter, the stretching vibrational spectra (four fundamental frequencies) has been computed with four parameters. We have reported the analysis of fundamental vibrations of monomer and dimer of benzene. The results are good agreement with the experimental data. In this study of vibrational spectra of benzene monomer(table-4.2), benzene dimer (TS and PD)(table-4.3), we obtain Δ(R.M.S) as 1.019cm^{-1}, 1.990 cm^{-1} and 2.449cm^{-1} respectively for four fundamental frequencies.These are in good agreement with the observed experimental values.