Chapter 3

STUDY OF VIBRATIONAL SPECTRA OF BENZENE USING LIE ALGEBRAIC METHOD

3.1 Hamiltonian for C-H, C-C bonds of the Molecules:

Our significance lies on the quantization scheme of stretching vibrations in $U(2)$ is rather different from $U(4)$ and implies a complete separation between rotations and vibrations. If this separation applies, one can identify each oscillator by means of an algebra $U(2)$ which leads the general form of Hamiltonian of the concerned molecules, given by

$$\hat{H} = A_{CH}\sum_{i=1}^{6}\hat{C}_i + A'_{CH}\sum_{i<j=1}^{6}\hat{C}_{ij} + \sum_{i<j=1}^{6}\lambda_{ij}M_{ij} + \\ + A_{CC}\sum_{i=7}^{12}\hat{C}_i + A'_{CC}\sum_{i<j=7}^{12}\hat{C}_{ij} + \sum_{i<j=7}^{12}\lambda_{ij}\hat{M}_{ij} \tag{3.1}$$

3.2 Structure of the Benzene Molecule, C_6H_6:

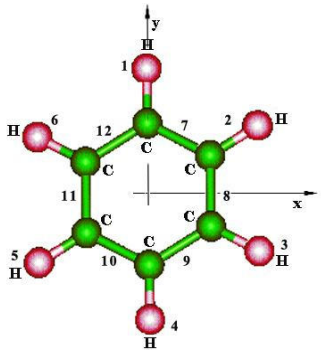

Fig. 3.1: Structure of Benzene Molecule, C_6H_6, Bond numbering (1 to 6) for C-H and (7 to 12) for C-C.

3.3 Symmetry adapted operators of the Benzene Molecule:

In order to do the construction of the symmetry adopted operators and of the Hamiltonian operator of the molecule Benzene, we refer the Fig. 3.1.

By inspection of the figure, one can see that there can be three types of interactions for C-H in Benzene:

1. First-neighbor couplings. [for example, (12,), (23)…];
2. Second-neighbor couplings. [for example, (13), (24)…];
3. Third-neighbor couplings. [for example, (14), (25)……].

The symmetry adopted operators of Benzene with symmetry D_{6h} are those corresponding to these three couplings. That is

$$S^{(I)} = \sum_{i<j=1}^{6} c_{ij}^{/} M_{ij}, \quad S^{(II)} = \sum_{i<j=1}^{6} c_{ij}^{//} M_{ij}, \quad S^{(III)} = \sum_{i<j=1}^{6} c_{ij}^{///} M_{ij}, \tag{3.2}$$

with

$$\begin{aligned}
&c'_{12} = c'_{23} = c'_{34} = c'_{45} = c'_{56} = c'_{16} = 1, \quad c'_{13} = c'_{24} = c'_{35} = c'_{46} = c'_{15} = c'_{26} = 0, \\
&c'_{14} = c'_{25} = c'_{36} = 0; \\
&c''_{12} = c''_{23} = c''_{34} = c''_{45} = c''_{56} = c''_{16} = 0, \quad c''_{13} = c''_{24} = c''_{35} = c''_{46} = c''_{15} = c''_{26} = 1, \\
&c''_{14} = c''_{25} = c''_{36} = 0; \\
&c'''_{12} = c'''_{23} = c'''_{34} = c'''_{45} = c'''_{56} = c'''_{16} = 0, \quad c'''_{13} = c'''_{24} = c'''_{35} = c'''_{46} = c'''_{15} = c'''_{26} = 0, \\
&c'''_{14} = c'''_{25} = c'''_{36} = 1
\end{aligned} \tag{3.3}$$

The total Majorana operator S is the sum

$$S = S^{(I)} + S^{(II)} + S^{(III)}. \tag{3.4}$$

Diagonalization of S produces states that carry representations of S_6, the group of permutations of six objects, while diagonalization of the other operators produces states that transform according to the representations A_{1g}, E_{1u}, E_{2g}, B_{1u}, of D_{6h}. This result can be verified by computing the characters of the representations carried by the eigenstates of $S^{(I)}$, as shown for example in Wilson, Decius and Cross, (1955).

The Hamiltonian operator that preserves the symmetry of the molecules can now be constructed. Since all the bonds in **Fig. 3.1** are equivalent, the most general lowest order Hamiltonian for C-H stretching vibrations of C_6H_6 is

$$H = E_0 + A_{CH} C + A'_{CH} C' + \lambda_{CH}^{(I)} S^{(I)} + \lambda_{HH}^{(II)} S^{(II)} + \lambda_{HH}^{(III)} S^{(III)} \tag{3.5}$$

where

$$C = \sum_{i=1}^{6} C_i, \quad C' = \sum_{i<j=1}^{6} C'_{ij} \tag{3.6}$$

In addition, since all bonds are equivalent, the vibron numbers N_i must be all equal, $N_i = N_{CH}$. Thus, the symmetry of the molecule imposes the following conditions on the co-efficients in Eq. (2.30):

$$\begin{aligned} &N_i = N_{CH}, \ \ \mathrm{A}_i = A_{CH}, \ \ \mathrm{A}_{ij} = A'_{CH}, \\ &\lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{45} = \lambda_{56} = \lambda_{61} = \lambda_{CH}^{(I)}, \\ &\lambda_{13} = \lambda_{24} = \lambda_{35} = \lambda_{46} = \lambda_{15} = \lambda_{26} = \lambda_{CH}^{(II)}, \\ &\lambda_{14} = \lambda_{25} = \lambda_{36} = \lambda_{CH}^{(III)} \end{aligned} \tag{3.7}$$

C–H stretching vibrations of C_6H_6 are therefore characterized by five quantities A_{CH}, A'_{CH}, $\lambda_{CH}^{(I)}, \lambda_{CH}^{(II)}$ *and* $\lambda_{CH}^{(III)}$.

Similarly, for C-C stretching vibrations of benzene, we can characterize five similar parameters. Thus, the Majorana terms remove the degeneracies of the local modes and bring the behavior of the molecule towards the normal limit, precisely in the same way as in tri- or tetratomic molecules.

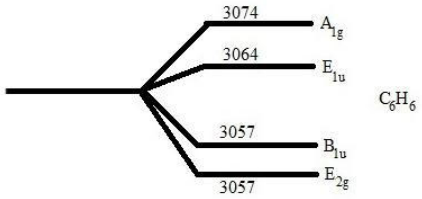

Fig. 3.2: Splitting of the local C-H modes in C_6H_6

3.4 Results and Discussions:

In the algebraic theory, we introduce the vibron number N which is directly related to the anharmonicity of local C-H, C-C stretching bonds. The quantum number v_i corresponds to number of quanta in each oscillator, while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{n} v_i \tag{3.8}$$

For a particular polyad, total vibrational quantum number is always conserved.

The value of the vibron number N for C-H and C-C can be calculated by the following relation (Wulfman, 1973).

$$N = \frac{\omega_e}{\omega_e x_e} - 1 \tag{3.9}$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants (Nakamoto, 1997; Huber and Herzberg, 1979) of polyatomic molecules of stretching interaction of the molecule considered. The value of N has to be taken as the initial guess. Depending on the specific molecular structure one can expect a change of 20% of the value of N.

The value of the parameter *A* can be obtained from the single oscillator fundamental mode as

$$E(v=1) = -4A(N-1) \tag{3.10}$$

Lastly, one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the role of which is to degenerate the local modes and the value of the parameters can be calculated by considering the following matrix structure of the molecule

$$\begin{pmatrix} -4A(N-1)-4A'(2N-1) \\ +3(\lambda+\lambda')N & -\lambda N & -\lambda N & -\lambda N \\ -\lambda N & -4A(N-1)-4A'(2N-1) \\ & +3(\lambda+\lambda')N & -\lambda N & -\lambda N \\ -\lambda N & -\lambda N & -4A(N-1)-4A'(2N-1) \\ & & +3(\lambda+\lambda')N & -\lambda N \\ -\lambda N & -\lambda N & -\lambda N & -4A(N-1)-4A'(2N-1) \\ & & & +3(\lambda+\lambda')N \end{pmatrix} \tag{3.11}$$

To obtain an initial guess for the parameter λ and λ/, we comprise the following relations from the above matrix equation, (Oss, 1996)

$$\lambda = \frac{E_3 - E_1}{2N} \tag{3.12}$$

and

$$\lambda' = \frac{E_2 - E_1}{6N} \tag{3.13}$$

λ// is neglected due to lack of experimental data

3.5 Values of the fitting parameters:

The fitting parameters A, $A^{/}$, λ, $\lambda^{/}$ and N which are used in this study for the vibrational frequencies of Benzene are given in Table 3.1,

Table 3.1. Fitting algebraic parameters for C-H, C-C bonds of Benzene (C_6H_6).

Bonds	C-H	C-C
Vibron Number	N_{CH} = 43	N_{CC} = 137
Algebraic parameters (cm^{-1})	A_{CH} = -1.93 A'_{CH} = -8.2986 λ = 1.87 λ' = 0.61	A_{CC} = -2.38 A'_{CC} = -0.1056 λ = 3.21 λ' = 0.81

3.6 Analysis of the vibrational spectra of Benzene (C_6H_6):

A comparison of the observed vibrational frequency of Benzene (Goodman *et al*.,1991) and those calculated (Singha *et al*., 2014) using the algebraic model is shown in Table 3.2. Using the model Hamiltonian in this study we calculated the vibrational frequencies of Benzene for few vibrational bands.

The results of our study (Table 3.2) shows that r.m.s deviation obtained for the vibrational frequency of Benzene using algebraic model is 5.751cm^{-1} which is near to the experimental accuracy.

Table 3.2: Calculated and observed harmonic and fundamental frequencies [cm^{-1}] of Benzene (C_6H_6):

Mode [Wilson No.]	Symmetry	$\overline{\nu}_{obs}$ (Goodman *et al* 1991) *J.Phys.Chem.* **95,** 9044	$\overline{\nu}_{cal}$ (Singha *et al* 2014, *Quantum Matter*, **3**, 1-6)	$\overline{\nu}_{obs}$ - $\overline{\nu}_{cal}$	Mode Character
1	A_1	993.1	995.4	-2.3	Breathing
2	A_1	3073.9	3069.8	4.1	C-H stretch in-phase
3	A_2	1350.0	1338.7	11.3	C-H bend in-phase
12	B_1	1010.0	1002.7	7.3	C-C-C trigonal bend
13	B_1	3057.0	3055.2	1.8	C-H trigonal stretch
14	B_2	1309.4	1309.5	-0.1	C-C stretch
15	B_2	1149.7	1137.1	12.6	C-H trigonal bend
6	E_2	608.1	608.3	-0.2	C-C-C bend
7	E_2	3056.7	3047.9	8.8	C-H stretch
8	E_2	1601.0	1600.2	0.8	C-C stretch
9	E_2	1177.8	1167.8	10.0	C-H bend
18	E_1	1038.3	1033.4	4.9	C-H bend
19	E_1	1484.0	1480.4	3.6	C-C stretch
20	E_1	3064.4	3062.5	1.9	C-H stretch

11	A_2	674.0	675.5	-1.5	C-H wagg. in-phase
4	B_2	707.0	704.7	2.3	C-C-C-C puckering
5	B_2	990.0	988.1	1.9	C-H trigonal wagg
10	E_1	847.1	839.1	8.0	C-H wagg
16	E_2	398.0	399.4	-1.4	C-C-C-C torsion
17	E_2	967.0	966.2	0.8	C-H wagg

Δ (r.m.s.) =5.751cm^{-1}

Here we present the study of the vibrational spectra of benzene, C_6H_6 using the Lie algebraic method. Results of our study (Table 3.2) shows that the r.m.s deviation obtained for the vibrational spectra of benzene using the algebraic model Hamiltonian is 5.751 cm^{-1} for the twenty vibrational fundamental frequencies is near to the experimental accuracy. r.m.s deviation reported by us is much less than the r.m.s deviation calculated from the observed values

(Goodman *et al.* 1991). More interestingly, the hurdles of complicated integrations in the solution of coupled differential Schrödinger equations of polyatomic molecules can be avoided by making use of this algebraic model. Thus it can be concluded that U(2) algebraic method is one of the successful alternative theoretical approaches to explore the previously unknown vibrational states of polyatomic molecules.