

Chapter 5

**STUDY OF VIBRATIONAL SPECTRA OF BENZENE DERIVATIVES
(FLURO BENZENE, C₆H₅F, DEUTERATED BENZENE C₆D₆, AND MONO DEUTERIUM
SUBSTITUTED BENZENE C₆H₅D)**

5.1 The Algebraic Hamiltonian :

According to the general algebraic description for one dimensional degrees of freedom, a dynamically symmetric Hamiltonian operator for n interacting (not necessarily equivalent) oscillators of a polyatomic molecule in terms of Morse anharmonic oscillators by introducing the U(2) algebra for each bonds can be written as (Sen *et al*, 2011; 2012; 2013) :

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j}^n A_{ij} C_{ij} + \sum_{i<j}^n \lambda_{ij} M_{ij}, \quad (5.1)$$

where C_i , C_{ij} and M_{ij} are the invariant algebraic operators. In the local basis the operators C_i are the diagonal matrix with eigenvalues

$$\langle N_i, \nu_i | C_i | N_i, \nu_i \rangle = -4(N_i \nu_i - \nu_i^2) \quad (5.2)$$

The couplings between the bonds are introduced by the operators C_{ij} and M_{ij} , are called Majorana and Casimir operators respectively. The role of the Majorana operators M_{ij} is to introduce off-diagonal couplings between pairs of local modes. In the simplest case of equivalent interacting bonds, the Majorana operator naturally leads to a solution for symmetrized coupled modes, in which the invariance of the Hamiltonian operator, under bond exchange, is explicitly taken into account. A rather appealing feature of this

algebraic model is that such a “symmetrizing” property of the Majorana operator, actually quite a trivial for one for two equal bonds, can readily be extended to any molecular geometry, even a very complex one. The key point is that the basic information characterizing the specific molecular geometry can easily be incorporated by introducing proper linear combinations for Majorana operators.

In purely local limit of N oscillators, these oscillators are somehow correlated with each other through the C_{ij} operators, which account for (diagonal) cross-anharmonicities, represented by the following equation:

$$C_{ij} = C_i - N_{ij} \left(\frac{C_i}{N_i} + \frac{C_j}{N_j} \right), \quad (5.3)$$

where $N_{ij} = N_i + N_j$

Furthermore, following eq. (5.3), it should be noted that one basically subtracts from C_i those terms arising from uncoupled single-oscillator contribution. In the special case of a pair of equivalent oscillators i and j ($N_i = N_j$), the above equation can be replaced by the following matrix elements,

$$\langle v_i v_j | C_{ij} | v_i v_j \rangle = -4(v_i - v_j)^2 \quad (5.4)$$

i.e., the matrix elements do not depend on $N_i(N_j)$. As a result, C_{ij} will account for different contribution throughout different polyads and within the same polyad; the most important aspect of C_{ij} is the dependence of its matrix elements on the product $v_i v_j$.

The quantum numbers v_i correspond to the number of quanta in each oscillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^n v_i. \quad (5.5)$$

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

In Eq. (5.1), the invariant Casimir (C_{ij}) and Majorana (M_{ij}) operators have the following matrix elements (Sen *et al.*, 2013):

$$\left. \begin{aligned}
 \langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle &= -4 \left[(v_i + v_j)(N_i + N_j) - (v_i + v_j)^2 \right] \\
 \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= v_i N_j + v_j N_i - 2v_i v_j \\
 \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -\sqrt{v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)} \\
 \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -\sqrt{v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)}
 \end{aligned} \right\} \quad (5.6)$$

Thus, the eigenvalues of the Hamiltonian can be easily evaluated and provide a description of n coupled anharmonic vibrators.

5.2 Structure of Three Derivatives of the Benzene Molecule:

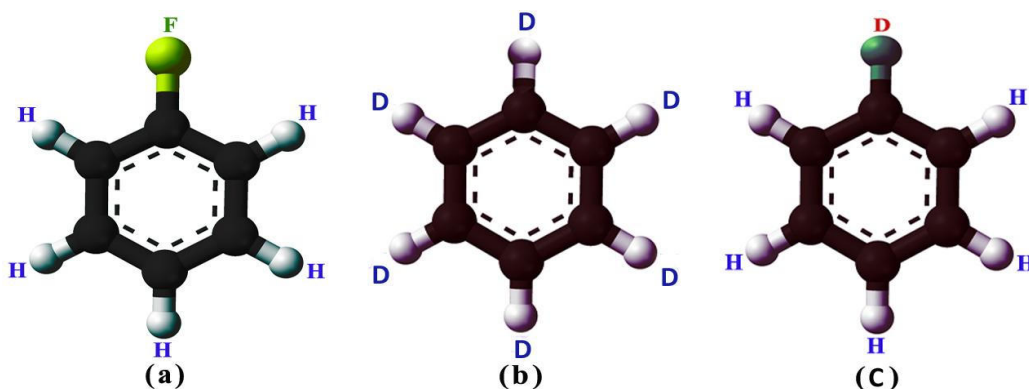


Fig. 5.1 : (a) Partially F-substituted Benzene (Fluorobenzene, C_6H_5F) (b) Deuterated Benzene, C_6D_6 (c) Mono deuterium substituted Benzene, C_6H_5D

5.3 Results and Discussions:

In general, the eigenvalues problem for H must be solved analytically with spectrum generating algebra or dynamical algebra which describes, within a certain approximation, realistic rotation-vibration spectra in one (stretch) and three dimension (stretch and bend). As the dynamical algebra can be incorporated by the language of Lie Algebra and thus after the introduction of $U(2)$ Lie Algebra to describe n stretching bonds, two possible chains of molecular dynamical groups of fluorobenzene are as (Sen *et al.*, 2011, 2013; Oss, 1996):

$$U^1(2) \otimes \dots \otimes U^n(2) \supset O^1(2) \otimes \dots \otimes O^n(2) \supset O(2), \quad (5.7)$$

$$U^1(2) \otimes \dots \otimes U^n(2) \supset U(2) \supset O(2). \quad (5.8)$$

which correspond to local and normal coupling, respectively. The coupling to final $O(2)$ group in the first chain is carried out through different

intermediate couplings $O^j(2)$ and the second chain arises from all the possible couplings of $U^i(2)$ groups to obtain a total $U(2)$ group, which in turn contains the final $O(2)$ group.

To find the vibrational frequencies of fluorobenzene, deuterated and mono deuterium substituted benzene, we use the algebraic parameters A , A' , λ , λ' and N , to study the vibrational spectra of the molecules where N is the vibron number. After considering the common coupled and uncoupled bond-bond interaction in the molecular configuration in case of the molecules and also considering the Majorana couplings, on the basis of the symmetry of the molecules, the numbers of algebraic parameters are reduced to four for Fluorobenzene and to five for other two. In this regard, one should note that this is the unique beauty of the algebraic model where one needs only a fewer parameters to describe the vibrational spectra of a molecule with a good accuracy.

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

$$N_k = \frac{\omega_e}{\omega_e x_e} - k (k=1, 2, \dots) \quad (5.9)$$

Where ω_e and $\omega_e x_e$ are the spectroscopic constants.

For the molecules in normal mode, we can have the values of ω_e and $\omega_e x_e$ from each bond from the study of Nakamoto (Nakamoto, 1997) and that of Huber and Herzberg (Huber and Herzberg, 1979). Using the values of ω_e and $\omega_e x_e$ for each bond, we can have the initial guess for the value of the vibron number N . It may be noted here that in the algebraic approach, there is provision to change (not more than $\pm 20\%$) the value of N to get better accuracy. This is equivalent to change the single-bond anharmonicity according to the specific molecular environment, in which it can be slightly different.

To obtain a starting guess for the parameter A we use the expression for the single-oscillator normal mode which is given as

$$E(v=1) = -4A(N-1). \quad (5.10)$$

Using eq. (5.10), A can be obtained as

$$A = -\frac{E_1}{4(N-1)} \quad (5.11)$$

To obtain the initial guess for λ (for the Fluorobenzene), whose role is to split the initially degenerate local modes, placed here at the common value E . Following the simple Hamiltonian matrix structure (5.12) leads to finding out the corresponding algebraic parameters

$$\begin{pmatrix} -4A(N-1) - 4A'(2N-1) + \lambda N & -\lambda N \\ -\lambda N & -4A(N-1) - 4A'(2N-1) + \lambda N \end{pmatrix} \quad (5.12)$$

From the above matrix structure, we easily find that

$$\lambda = \frac{E_3 - E_1}{2N} \quad (5.13)$$

and for the hyperfine splitting of the spectrum, the corresponding algebraic parameter is

$$\lambda' = \frac{E_2 - E_1}{6N} \quad (5.14)$$

To achieve the better results, a numerical fitting procedure (in a least-square sense) is required to obtain the parameters A, A', λ and λ' , as given by equations (5.11), (5.13) and (5.14). Initial guess for A' may be taken as zero. For C_6D_6 and C_6H_5D , one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the role of which is to split the degeneracies of local modes and the values of the parameters can be calculated by considering the following matrix structure of the molecules.

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

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

$$\lambda = \frac{E_3 - E_1}{2N} \quad (5.15)$$

and

$$\lambda' = \frac{E_2 - E_1}{6N} \quad (5.16)$$

By using a numerical fitting procedure (in a least square sense) one can adjust the values of the parameters N , A , A' , λ and λ' to fit the experimental result.

The fitting algebraic parameters used in the study of vibrational spectra of Fluorobenzene is given in table 5.1 and those of deuterated an mono deuterium substituted benzene are given in table 5.2, where tables 5.3, 5.4, 5.5 show the calculated frequencies of the three derivatives of benzene with the corresponding deviations considering the different theoretical and experimental values.

Table 5.1: Fitting algebraic parameters of Fluorobenzene (C₆H₅F):

Vibron Number	Algebraic parameters (cm ⁻¹)		
N	A	λ	λ'
50.00	-30.43	0.376	0.05

Table 5.2: Fitting Algebraic parameters of CH, CC and CD bonds of C₆D₆ and C₆H₅D :

Bonds	CH	CC	CD
Vibron Number	53	137	59
Algebraic Parameters (cm ⁻¹)	$A_{CH} = -1.93$	$A_{CC} = -2.38$	$A_{CD} = -1.49$
	$A'_{CH} = -8.2986$	$A'_{CC} = -0.1056$	$A'_{CD} = -0.1932$
	$\lambda = 1.87$	$\lambda = 3.21$	$\lambda = 2.00$
	$\lambda' = 0.61$	$\lambda' = 0.81$	$\lambda' = 0.43$

Table 5.3 : Calculated and experimental normal fundamental frequencies (cm^{-1}) of Fluorobenzene ($\text{C}_6\text{H}_5\text{F}$):

Normal fundamental level	$\bar{\nu}_{obs}$ (Scotoni <i>et al.</i> , 1995, <i>J.Chem.Phys.</i> 103 , 897)	$\bar{\nu}_{cal}$ (Singha <i>et al.</i> , 2014, <i>Polycyclic Aromatic Compound</i> 34 , 1-8)	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	$\frac{ \bar{\nu}_{obs} - \bar{\nu}_{cal} }{\bar{\nu}_{obs}} \times 100\%$
ν_1	3047.9	3048.17	-0.27	0.008%
ν_2	3060.3	3058.15	2.15	0.071%
ν_3	3061.3	3062.25	-0.95	0.031%
ν_4	3067.3	3067.10	0.20	0.001%
ν_5	3069.6	3068.45	1.15	0.037%
ν_6	3070.6	3071.33	-0.73	0.023%
ν_7	3076.0	3075.24	0.76	0.024%
ν_8	3079.1	3078.20	0.90	0.029%
ν_9	3079.4	3079.56	-0.16	0.005%
ν_{10}	3080.1	3081.69	-1.59	0.051%
ν_{11}	3084.9	3083.17	1.73	0.056%
ν_{12}	3090.3	3089.58	-0.72	0.023%
ν_{13}	3094.0	3094.55	-0.55	0.017%
ν_{14}	3104.0	3102.85	1.15	0.037%
ν_{15}	3109.6	3108.22	1.38	0.44%
ν_{16}	3111.0	3112.36	-1.36	0.043%
ν_{17}	3112.1	3113.20	-1.10	0.035%

$$\Delta(\text{r.m.s.}) = 1.126 \text{ cm}^{-1}$$

Table 5.4 : Calculated and observed fundamental frequencies (cm^{-1}) of C_6D_6

Mode (Wilson No.)	Symmetry	$\bar{\nu}_{obs}$ (Siebert <i>et al.</i> , 1984 <i>J.Chem.Phys</i> . 81,1115)	$\bar{\nu}_{cal}$ (Singha <i>et al.</i> , 2014, <i>Quantum Matter</i> 3, 1-6)	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	Mode Character
1	A ₁	945.0	947.2	-2.2	Breathing
3	A ₂	1059.0	1061.8	-2.8	C-C-H (D) Wagg
12	B ₁	970.0	978.0	-8.0	C-C-C Trigonal Bend
14	B ₂	1282.0	1282.4	-0.4	C-C Stretch
15	B ₂	824.0	528.8	-1.8	C-C-H (D) Trigonal Wagg
6	E ₂	580.0	581.2	-1.2	C-C-C Bend
8	E ₂	1557.0	1556.0	1.0	C-C Stretch
9	E ₂	869.0	878.8	-9.8	C-C-H (D) Wagg
18	E ₁	814.0	810.4	3.6	C-C-H (D) Wagg
19	E ₁	1333.0	1344.0	-11.0	C-C Stretch
11	A ₂	496.0	497.4	-1.4	C-C-H (D) Wagg
4	B ₂	599.0	596.6	-2.4	C-C-C Puckering
5	B ₂	829.0	830.3	-1.3	C-C-H (D) Trigonal Wagg
10	E ₁	660.0	665.0	-5.0	C-C-H (D) Wagg
16	E ₂	345.0	345.2	-0.2	C-C-C Bend
17	E ₂	787.0	779.6	7.4	C-C-H (D) Wagg

$$\Delta(\text{r.m.s.}) = 5.011 \text{ cm}^{-1}$$

Table 5.5 : Calculated and observed fundamental frequencies (cm^{-1}) of $\text{C}_6\text{H}_5\text{D}$

Mode (Wilson No.)	Symmetry	$\bar{\nu}_{obs}$ (Snell <i>et al.</i> , 1997, Chem.Phys. 225,107)	$\bar{\nu}_{cal}$ (Singha <i>et al.</i> , 2014, Quantum Matter 3, 1-6)	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	Mode Character
16	A ₂	401.0	402.4	-1.4	C-C-C out of plane bending
11	B ₁	596.7	596.4	0.3	C-H out of plane bending
6	A ₁	600.0	600.4	-0.4	C-C-C in-plane bending
4	B ₁	692.6	693.8	-1.2	C-C-C puckering
10	A ₂	834.4	837.9	0.5	C-H out of plane bending
17	B ₁	919.7	916.3	3.4	C-H out of plane bending
1	A ₁	971.8	966.7	5.1	Ring breathing
5	B ₁	983.0	985.3	-2.3	C-H out of plane bending
12	A ₁	992.1	1003.1	-11.0	C-C-C trigonal bending
18	A ₁	1028.6	1025.5	3.1	C-C Stretching
15	B ₂	1163.3	1165.5	-2.2	C-H in plane bending
9	A ₁	1176.1	1176.7	-0.6	C-H in plane bending
14	B ₂	1292.6	1285.9	6.7	C-C stretching
3	B ₂	1329.7	1325.0	4.7	C-H in plane bending
19	A ₁	1470.7	1473.5	-2.8	C-H in plane bending
8	A ₁	1599.7	1599.5	0.2	C-C stretching
13	A ₁	2271.9	2270.5	1.4	C-D stretching
2	A ₁	3053.8	3057.8	-4.0	C-H stretching
7	A ₁	3071.8	3069.2	2.6	C-H stretching
20	A ₁	3090.8	3091.4	-0.6	C-H stretching

$$\Delta(\text{r.m.s.}) = 3.759 \text{ cm}^{-1}$$

5.4 Analysis of spectra:

Here we present the study of the vibrational spectra of benzene derivatives, fluorobenzene, deuterated and mono deuterium substituted benzene using Lie-algebraic method. In this chapter, we have reported the RMS deviations for fluorobenzene, deuterated and mono deuterium substituted benzene for several fundamental frequencies, which are 1.126 cm^{-1} and 3.759 cm^{-1} respectively. These are in good agreement with the observed data.
