Chapter 4

Calculation of Vibrational Energy Levels of Hydrogenated Buckminsterfullerene (C$_{60}$H$_{60}$)

Using the results of the Lie algebraic theory of Large Polyatomic molecules (c.f. Chapter – 2), in this chapter we calculate the vibrational energy levels of Hydrogenated Buckminsterfullerene (C$_{60}$H$_{60}$).

Results and Discussion

We have used U (2) algebraic model to study the vibrational spectra of the Hydrogenated Buckminsterfullerene (C$_{60}$H$_{60}$) molecule with fewer algebraic parameters [i.e A, A’, λ, λ’ and N (Vibron number)].

A comparison of the experimental and calculated frequencies of stretching vibrations of Hydrogenated Buckminsterfullerene using algebraic model are shown in Table 4.1. Using established norms (Iachello and Levine, 1995; Oss, 1996) the Vibron number N and other algebraic parameters A, λ, λ’ are shown in Table 4.2 for C$_{60}$H$_{60}$. 
4.1. Vibron number:

The vibron number $N$ [total number of bosons, label of the irreducible representation of $U(2)$] is related to the total number of bound states supported by the potential well. Equivalently, it can be put in a one-to-one correspondence with the anharmonicity parameters $x_e$ by means of

$$x_e = \frac{1}{(N + 2)} \quad (4.1)$$

Eq. (4.1) can be re-written as

$$N = \frac{\omega_e}{\omega_e x_e} - 2, \quad \omega_e \rightarrow \text{spectroscopic constant} \quad (4.2)$$

Using the values of $\omega_e$ and $\omega_e x_e$ for the C-H bond (Huber and Herzberg, 1979), from Eq. (4.2) we can have the value of $N$. 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 $\pm 20\%$ of the original value [Eq. (4.1)]. Here we have used the value of $N$ obtained from Eq. (4.2) without any change. It may be noted here that during the calculation of the vibrational frequencies of Hydrogenated Buckminsterfullerene ($C_{60}H_{60}$), the value of $N$ is kept fixed and not used as a free parameter.

4.2. Values of the fitting parameters.

The fitting parameters $A$, $\lambda$, $\lambda'$, $N$ which are used in this study for the vibrational frequencies of Hydrogenated Buckminsterfullerene ($C_{60}H_{60}$) for few stretching vibrational bands are given in the Table 4.2.
To obtain a starting guess for the parameter $A$ we use the expression for the single-oscillator fundamental mode which is given as,

$$E(\nu = 1) = -4A(N - 1)$$ \hfill (4.3)

Using the Eq. (4.3), $A$ can be obtained as,

$$\bar{A} = \frac{\bar{E}}{4(1 - N)}$$ \hfill (4.4)

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

To obtain the initial guess for $\lambda$, whose role is to split the initially degenerate local modes, placed here at the common value $E$, used in Eq. (4.3). Such an estimate is obtained by considering the following simple Hamiltonian matrix structure

$$
\begin{pmatrix}
-4A(N - 1) - 4A(2N - 1) + \lambda N & -\lambda N \\
-\lambda N & -4A(N - 1) - 4A(2N - 1) + \lambda N
\end{pmatrix}
$$ \hfill (4.5)

We can easily find that

$$\lambda \equiv \frac{|E_3 - E_2|}{2N}$$ \hfill (4.6)

and

$$\lambda' \equiv \frac{|E_1 - E_2|}{6N}$$ \hfill (4.7)

To have better result a numerical fitting procedure (in a least-square sense, for example) is required to obtain the parameters $A$, $A'$, $\lambda$, and $\lambda'$ starting from values
as given by Equations (4.4), (4.6) and (4.7). Initial guess for $A'$ may be taken as zero.

4.3 Analysis of the spectra:

Using the model Hamiltonian [Eq. (2.7)] in this study we have calculated the vibrational energy levels of Hydrogenated Buckminsterfullerene ($C_{60}H_{60}$) for few vibrational bands (Table 4.1). From the limited available experimental data in this study we reported RMS deviation for the seven vibrational bands as $2.39 \text{ cm}^{-1}$. We completed the study in single fit. It may be noted here that for two bands deviation is large (above three) but for few others bands we got deviations even less than one. That is why ultimately the RMS deviation is dropped down to $2.39 \text{ cm}^{-1}$.

**Table 4.1**: Vibrational energy (cm$^{-1}$) levels of Hydrogenated Buckminsterfullerene ($C_{60}H_{60}$)

<table>
<thead>
<tr>
<th>Mode/Irrep</th>
<th>Expt.</th>
<th>Calc.</th>
<th>$^a\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{1u}$</td>
<td>880</td>
<td>877.325</td>
<td>2.675</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>1150</td>
<td>1149.932</td>
<td>0.068</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>1425</td>
<td>1425.020</td>
<td>-0.020</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>1610</td>
<td>1609.996</td>
<td>0.004</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>2490</td>
<td>2492.742</td>
<td>-2.742</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>2920</td>
<td>2916.438</td>
<td>3.562</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>3050</td>
<td>3053.547</td>
<td>-3.547</td>
</tr>
</tbody>
</table>

$^a$[ref.(Iijima, 1991)] $^a\Delta$ (Expt.-Calc.) $\Delta$(r.m.s)=2.39 cm$^{-1}$
Table 4.2: The fitting parameters* of $C_{60}H_{60}$ used in the present study

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>N</td>
<td>44</td>
</tr>
<tr>
<td>A</td>
<td>-8.285</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>2.102</td>
</tr>
<tr>
<td>$\lambda'$</td>
<td>-1.042</td>
</tr>
</tbody>
</table>

*All parameters are in cm$^{-1}$ except N, which is dimensionless

4.4 Conclusion:

Using one dimensional Vibron model in this chapter we have calculated vibrational energy levels of $C_{60}H_{60}$. The stretching vibrational spectrum (seven vibrational bands) has been computed with four algebraic parameters. In this study, we have reported the analysis of fundamental vibrations of Hydrogenated Buckminsterfullerene. In the study of vibrational spectra of Hydrogenated Buckminsterfullerene (Table 4.1) we obtain the $\Delta$ (r.m.s) as 2.39 cm$^{-1}$ for the seven vibrational bands. The results are good agreement with experimental data. In the next chapter (Chapter-5) we use the Lie algebraic method for computing vibrational energy of single layered Carbon Nano Tubes.