Chapter 5

Calculation of Vibrational Energy Levels of Carbon Nano Tubes

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 Carbon Nano Tubes.

Results and Discussion

A comparison of the experimental and calculated frequencies of stretching vibrations of Carbon Nano Tubes using algebraic model are shown in Table 5.1. Using established norms (Iachello and Levine, 1995; Oss, 1996) the vibron number \( N \) and other algebraic parameters \( A, \lambda, \lambda' \) are shown in Table 5.2 for Carbon Nano Tubes.

5.1 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

$$x_e = \frac{1}{(N + 2)} \quad (5.1)$$

Eq. (5.1) can be re-written as

$$N = \frac{\omega_e}{\omega_e x_e} - 2, \quad \omega_e \rightarrow \text{spectroscopic constant} \quad (5.2)$$

Using the values of $\omega_e$ and $\omega_e x_e$ for the C-C bond (Huber and Herzberg, 1979), from Eq. (5.2) 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 ± 20% of the original value [Eq. (5.1)]. It may be noted here that during the calculation of the vibrational frequencies of Carbon Nano Tubes, the value of N is kept fixed and not used as free parameter.

### 5.2 Values of the fitting parameters:

The fitting parameters $A$, $\lambda$, $\lambda'$, $N$ which are used in this study for the vibrational frequencies of Carbon Nano Tubes for four stretching vibrational bands are given in the Table 5.1.

To obtain a starting guess for the parameter $A$ we use the expression for the single-oscillator fundamental mode which is given as,
\[ E(\nu = 1) = -4A(N - 1) \]  

Using the Eq. (5.3), A can be obtained as,

\[ \bar{A} = \frac{\bar{E}}{4(1-N)} \]  

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.(5.3). Such an estimate is obtained by considering the simple matrix structure we can easily find that

\[ \lambda \approx \frac{|E_3 - E_2|}{2N} \]  

and

\[ \lambda' \approx \frac{|E_1 - E_2|}{6N} \]  

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 (5.4), (5.5) and (5.6). Initial guess for A’ may be taken as zero.
Table 5.1: Vibrational energy (cm\(^{-1}\)) levels of single layered Carbon Nano Tubes

<table>
<thead>
<tr>
<th>Modes</th>
<th>* Expt.</th>
<th>Cal.</th>
<th>(\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{2u})</td>
<td>839</td>
<td>834.368</td>
<td>4.632</td>
</tr>
<tr>
<td>(A_{2u})</td>
<td>873</td>
<td>876.265</td>
<td>-3.265</td>
</tr>
<tr>
<td>(E_{1u})</td>
<td>1564</td>
<td>1567.735</td>
<td>-3.735</td>
</tr>
<tr>
<td>(E_{1u})</td>
<td>1590</td>
<td>1586.046</td>
<td>3.954</td>
</tr>
</tbody>
</table>

* [ref.(Sbai et al., 2006)]  \(\Delta = \text{Expt.}-\text{Cal.}\)  \(\Delta (r.m.s) = 3.93 \text{cm}^{-1}\)

Table 5.2: The fitting parameters* of Carbon Nano Tubes used in the present study

| \(N\) | 140 |
| \(A\) | -2.324 |
| \(\lambda\) | 0.785 |
| \(\lambda'\) | -0.842 |

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

5.3 Conclusion:

With the four algebraic parameters, we have reported the fundamental vibrational energy levels of single layered Carbon Nano Tubes; which have a very good accuracy with respect to the observed energy levels. In this study, we have reported the RMS deviation [i.e \(\Delta (r.m.s)\)] for Carbon Nano Tubes for four vibrational bands which are in good agreement with experimental data. In the study of the vibrational spectra of Carbon Nano Tubes for four vibrational bands (Table 5.1), we obtain the \(\Delta (r.m.s)\) as 3.93 cm\(^{-1}\).