Vibrational Analysis of band system– Deslandres Table

- In the energy scale, taking the minimum of the potential energy curve as zero, the vibrational term value E(v) is given by,

$E(V) = \mathcal{E}_v = [v+1/2]v_e - [v+1/2]^2 v_e x_e + [v+1/2]^3 v_e y_e + \ldots\ldots \text{ cm}^{-1}$

In vibration analysis of the spectrum of a band system, the energy of the v=0 vibrational level is taken zero.

$E(0) = ½\, V_e - 1/4\, V_e X_e + 1/8\, V_e Y_e$

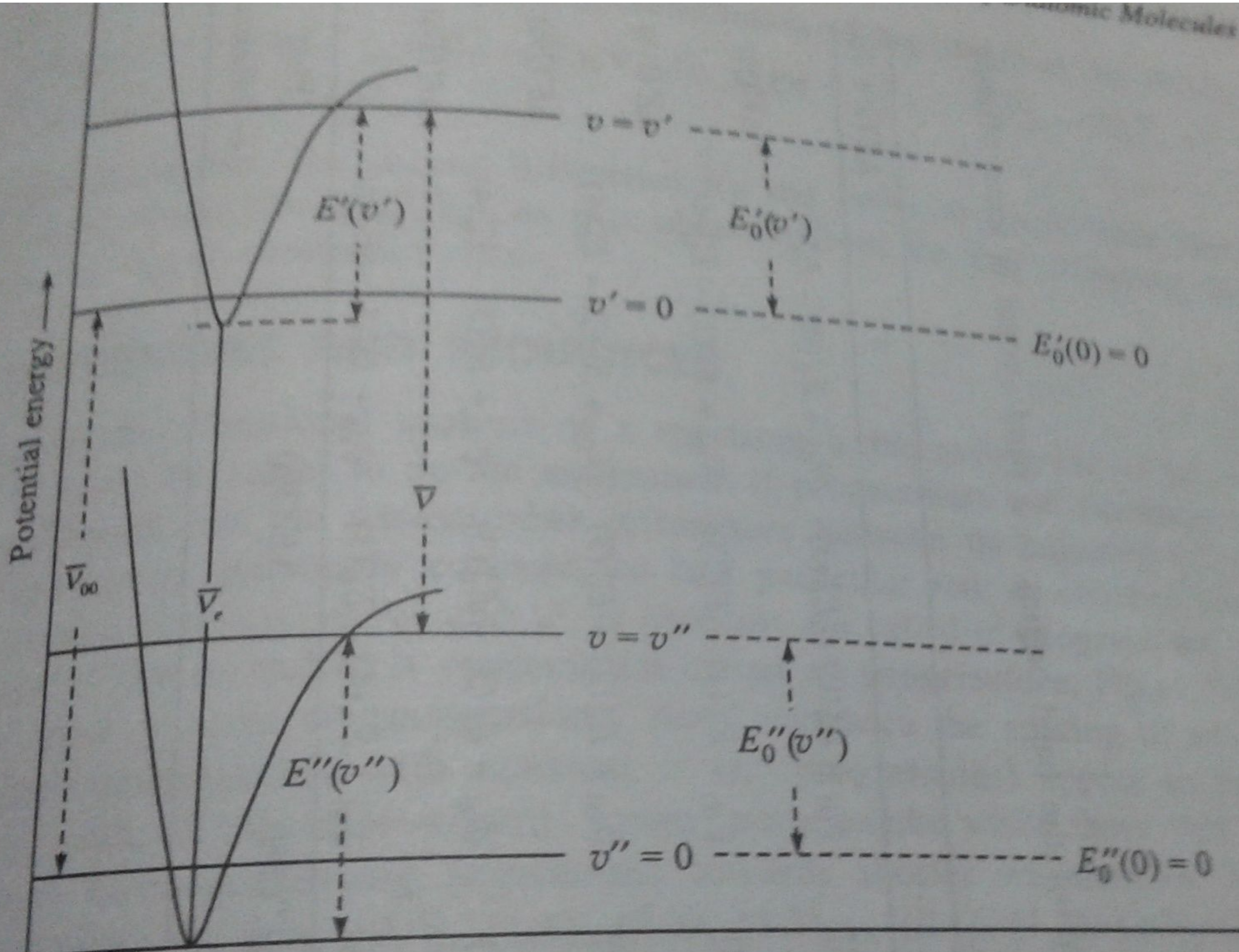

Figure 9.2 Symbols used in the vibrational analysis of a band system.

CONT

- To get information from the observed spectrum the assignment of the values to the band in a band system as to be done first.
- The wave number of each of the band are then arranged in the form of table referred to the deslandres.
- The experimentally observed wave number of each band is entered the wave number separation of two successive vibrational level in an electronic state is given by $E_0 (v+1) - E_o(v)$ and is called the first difference
- The second difference $\Delta^2 E(v+1)$ defined by

Table 9.1 Arrangements of the wavenumbers [(based on Eq. (9.10)] of the band origins in a band system in terms of their (v', v'') values

v' \ v''	0	1	2	3	4	$\Delta E'(v+½)$
0	$\bar{\nu}_{00} + E'_0(0) - E''_0(0)$	$\bar{\nu}_{00} + E'_0(0) - E''_0(1)$	$\bar{\nu}_{00} + E'_0(0) - E''_0(2)$	$\bar{\nu}_{00} + E'_0(0) - E''_0(3)$	$\bar{\nu}_{00} + E'_0(0) - E''_0(4)$	$\Delta E'(½)$
1	$\bar{\nu}_{00} + E'_0(1) - E''_0(0)$	$\bar{\nu}_{00} + E'_0(1) - E''_0(1)$	$\bar{\nu}_{00} + E'_0(1) - E''_0(2)$	$\bar{\nu}_{00} + E'_0(1) - E''_0(3)$	$\bar{\nu}_{00} + E'_0(1) - E''_0(4)$	$\Delta E'(1½)$
2	$\bar{\nu}_{00} + E'_0(2) - E''_0(0)$	$\bar{\nu}_{00} + E'_0(2) - E''_0(1)$	$\bar{\nu}_{00} + E'_0(2) - E''_0(2)$	$\bar{\nu}_{00} + E'_0(2) - E''_0(3)$	$\bar{\nu}_{00} + E'_0(2) - E''_0(4)$	$\Delta E'(2½)$
3	$\bar{\nu}_{00} + E'_0(3) - E''_0(0)$	$\bar{\nu}_{00} + E'_0(3) - E''_0(1)$	$\bar{\nu}_{00} + E'_0(3) - E''_0(2)$	$\bar{\nu}_{00} + E'_0(3) - E''_0(3)$	$\bar{\nu}_{00} + E'_0(3) - E''_0(4)$	$\Delta E'(3½)$
4	$\bar{\nu}_{00} + E'_0(4) - E''_0(0)$	$\bar{\nu}_{00} + E'_0(4) - E''_0(1)$	$\bar{\nu}_{00} + E'_0(4) - E''_0(2)$	$\bar{\nu}_{00} + E'_0(4) - E''_0(3)$	$\bar{\nu}_{00} + E'_0(4) - E''_0(4)$	↑
$\Delta E''(v+½)$	$\Delta E''(½)$	$\Delta E''(1½)$	$\Delta E''(2½)$	$\Delta E''(3½)$		First ← Difference

cont

- If the analysis is correct the second difference for the lower electronic state should also lead to the same value for -2x0 v''0 as that obtained from the first difference similar is the case for the upper electronic state.