

## **Title: Vibrational structure of electronic transition**

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The band spectrum seen in the Ultra-Violet (UV) and visible (VIS) regions of the electromagnetic spectrum can not interpreted as vibrational and rotational spectrum those are discussed in previous lectures.

The frequencies in the UV and visible region are much greater than the vibrational and rotational frequencies.

Thus line spectra seen in the UV and visible region in the atomic transitions are due to the electronic transitions.

Thus the band spectra seen in the UV and visible region in the molecular transitions are possibly due to the electronic transitions.

In the following, we will learn the analysis of the molecular spectra in the UV-VIS region.

We have learnt from the previous lecture-28 that the Schrodinger equation of a diatomic molecule can be written as

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 + V \right) \Psi = E \Psi \quad \dots\dots\dots(31.1)$$

Where first term is the kinetic energy of the nuclei, second term is the kinetic energy of the electrons and  $V$  is the potential and is defined as the sum of electron-electron repulsion, electron-nuclear attraction and nuclear-nuclear repulsion

$$V = \sum_{i>j=1}^n \frac{e^2}{r_{ij}} - \sum_{i=1}^n \frac{Z_A e^2}{r_{iA}} - \sum_{i=1}^n \frac{Z_B e^2}{r_{iB}} + \frac{Z_A Z_B e^2}{R} \quad \dots\dots\dots (31.2)$$

$$= V_{ee} - V_{en} + V_{nn}$$

Using Born-Oppenheimer approximation we can write the total wavefunction

$$\Psi(r, R) = \phi(r, R) \chi(R) \quad \dots\dots\dots(31.3)$$

Where  $\phi(r, R)$  is the electronic wavefunction depends on the electronic coordinate  $r$  and inherently depends on the nuclear coordinate  $R$  and  $\chi(R)$  is nuclear wavefunction.

The electronic energy  $E_e(R)$  can be calculated by fixing the nuclei at  $R$  from

$$\left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 + V(r, R) \right\} \phi(r, R) = E_e(R) \phi(r, R) \quad \dots\dots\dots(31.3)$$

As we have understood that this electronic energy with the nuclear-nuclear repulsion acts as potential energy for the vibrational motion of the molecule. Therefore, the excess of the energy of a non-rotating molecule over the minimum electronic energy must be considered as the vibrational energy. In addition there is a rotational energy of the molecule. Thus the total energy  $E$  of the molecule is the sum of these three energies,

$$E = E_e + E_v + E_R \quad \dots\dots\dots(31.4)$$

If we write equation 31.4 in terms of the wave-number unit then

$$T = T_e + G(\nu) + F(J) \dots\dots\dots(31.5)$$

$$\text{Or, } T = T_e + \omega_e \left( \nu + \frac{1}{2} \right) - \omega_e x_e \left( \nu + \frac{1}{2} \right)^2 + B_v J(J+1) \dots\dots\dots(31.6)$$

$$\text{Where, } G(\nu) = \omega_e \left( \nu + \frac{1}{2} \right) - \omega_e x_e \left( \nu + \frac{1}{2} \right)^2 + \omega_e y_e \left( \nu + \frac{1}{2} \right)^3 \dots\dots\dots(31.6(a))$$

$$\text{And } F(J) = B_v J(J+1)$$

The general graphical representation of two electronic states with their vibrational and rotational levels is given in figure-31.1. In this figure, vibrational and rotational states are also shown for two different electronic states. Here the single prime refers to the final or excited state and double prime is used for the initial or ground state.

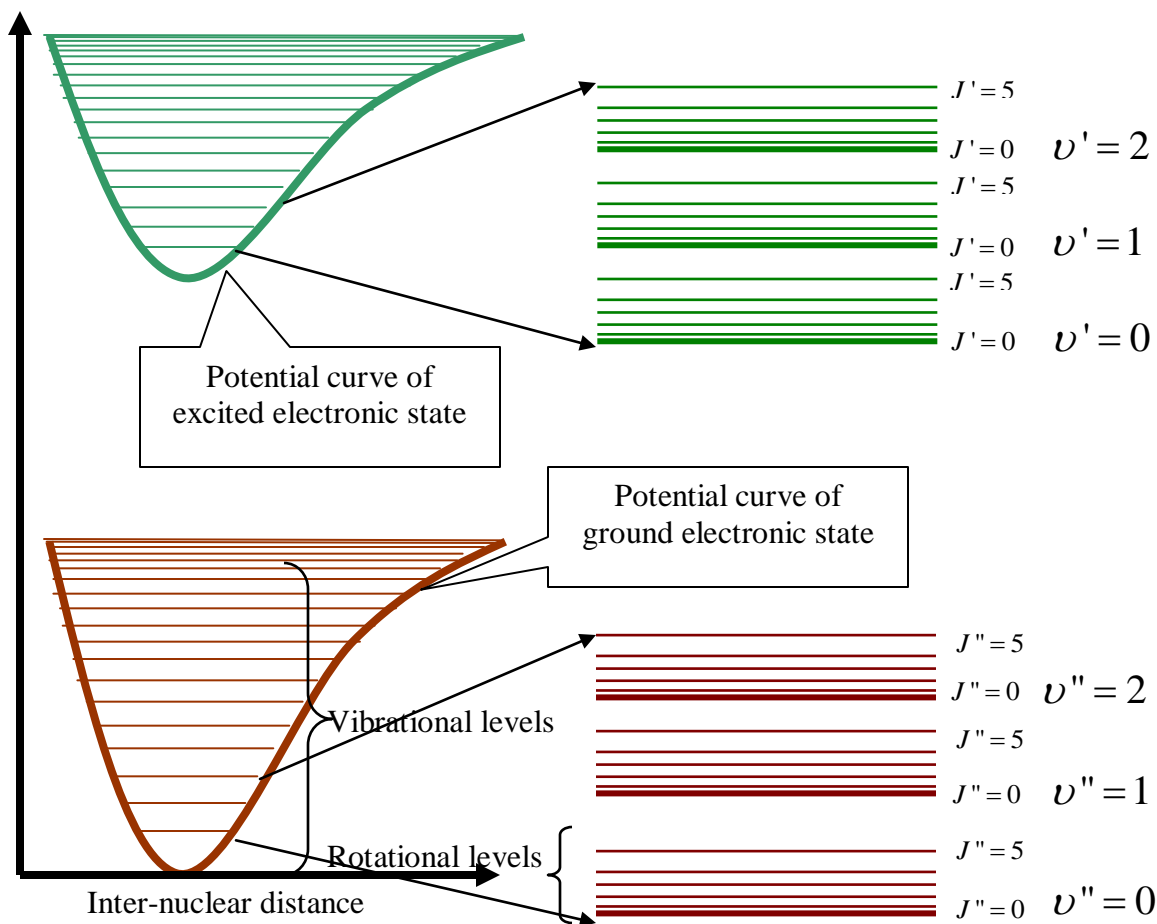
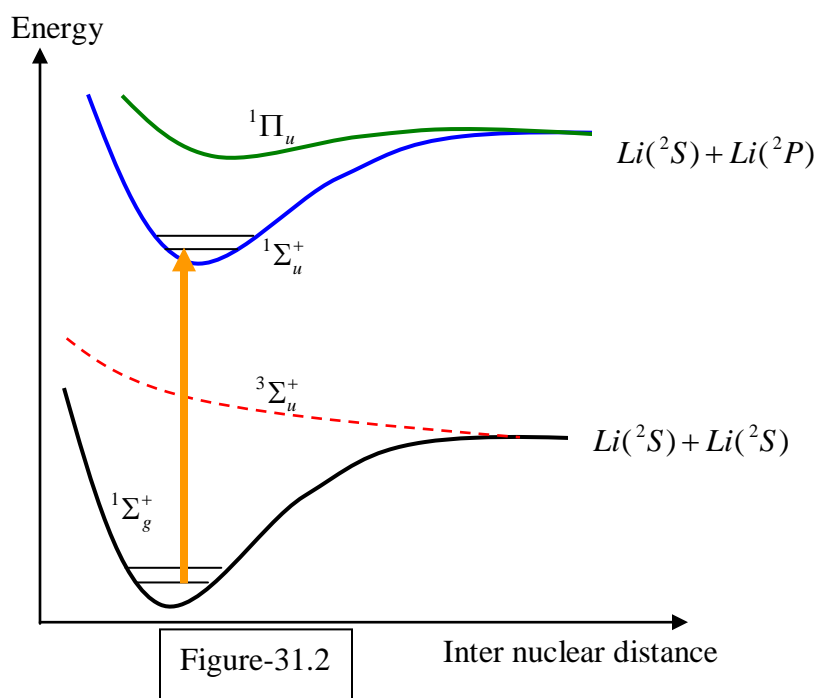


Figure-31.1

The potential energy curve of different electronic states of  $Li_2$  molecule is shown in figure-31.2. We will learn the nomenclature of these electronic states in next lectures. The vertical arrow designates the electronic transitions between the two electronic states. These transitions consist of vibrational as well as rotational transitions between these electronic states.

Thus, a closer look into these electronic transitions provides information about the vibrational and rotational structure of the electronic transitions. This depends on the resolution of the observed spectrum. Now we will focus our attention to these structures.



Note: The electronic transitions are always drawn by vertical line on the potential curve. The meaning is that the electronic transitions occur much faster than the nuclear motion. So during the transition the inter-nuclear distance remains same.

## Vibrational structure of electronic transitions

Using equation-31.5, the wavenumbers of the spectral lines between two electronic states are given by,

$$\bar{\nu} = T'_{final} - T''_{initial} = (T'_e - T''_e) + (G(\nu') - G(\nu'')) + (F(J') - F(J'')) \dots\dots\dots(31.7)$$

Here,  $T''_{initial}$  and  $T'_{final}$  are the term values of the initial and final states respectively. If the final state is the excited electronic state and initial state is the ground state, then this is known as electronic absorption. If the transition is from excited electronic state to ground or other lower electronic state then it is known as emission. Here the single prime refers to the final state and double prime is used for the initial state.

So, from equation 31.7, we can write that the transition energy (in  $\text{cm}^{-1}$ ) is the sum of three (electronic, vibrational and rotational) transition energies.

$$\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v + \bar{\nu}_r$$

Note that, for an electronic transition  $\bar{\nu}_e$  is constant and the high resolution of this spectrum will give the structure arising from the vibrational and rotational energies between these two electronic states.

For the time being, let us consider that rotational features are much smaller and hence let us neglect the rotational part. Thus, the coarse structure of the electronic transition is known as vibrational structure.

Substituting the values of  $G(\nu)$  from equation-31.6(a) in equation-31.7, we get

$$\begin{aligned} \bar{\nu} = \bar{\nu}_e + & \left[ \omega'_e \left( \nu' + \frac{1}{2} \right) - \omega'_e x'_e \left( \nu' + \frac{1}{2} \right)^2 + \omega'_e y'_e \left( \nu' + \frac{1}{2} \right)^3 + \dots \right] \\ & - \left[ \omega''_e \left( \nu'' + \frac{1}{2} \right) - \omega''_e x''_e \left( \nu'' + \frac{1}{2} \right)^2 + \omega''_e y''_e \left( \nu'' + \frac{1}{2} \right)^3 + \dots \right] \dots\dots\dots(31.8) \end{aligned}$$

In actual vibration analysis, however, a modified form of equation-31.8 is employed. Equation-31.8 refers to the vibrational energy terms to the minimum of the potential energy curve where  $G(\nu) = 0$ . In a modified form, the vibrational energies are measure with respect to the ground vibrational level i.e. vibrational level with  $\nu = 0$ . The vibrational term corresponding to this  $\nu = 0$  level can be obtained from equation-31.6(a) as:

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \frac{1}{8}\omega_e y_e + \dots \dots \dots (31.9)$$

The new vibrational energy term values are then measured with respect to this  $G(0)$  value, which, is chosen as new zero level and the corresponding vibrational term values are represented by the symbol  $G_0(\nu)$  and may be expressed as a function of vibrational quantum number  $\nu$  as follows:

$$G_0(\nu) = \omega_0 \nu - \omega_0 x_0 \nu^2 + \omega_0 y_0 \nu^3 \dots \dots \dots (31.10)$$

Equations (31.6(a)), (31.9) and (31.10) are related by:

$$G(\nu) = G_0(\nu) + G(0) \quad \text{or} \quad G_0(\nu) = G(\nu) - G(0) \dots \dots \dots (31.11)$$

Equation 31.8 may be written with  $(\nu'')$  for the lower electronic state and with  $(\nu')$  for the upper electronic state.

$$\bar{\nu}(\nu', \nu'') = \bar{\nu}_0 + (\omega'_0 \nu' - \omega'_0 x'_0 \nu'^2 + \omega'_0 y'_0 \nu'^3 + \dots) - (\omega''_0 \nu'' - \omega''_0 x''_0 \nu''^2 + \omega''_0 y''_0 \nu''^3 + \dots) \quad (31.12)$$

Here  $\bar{\nu}_{00}$  is the transition from  $\nu'' = 0$  to  $\nu' = 0$  and is known as origin of the transition.

Where,

$$\bar{\nu}_{00} = \bar{\nu}_e + \left( \frac{1}{2}\omega'_e - \frac{1}{4}\omega'_e x'_e + \frac{1}{8}\omega'_e y'_e + \dots \right) - \left( \frac{1}{2}\omega''_e - \frac{1}{4}\omega''_e x''_e + \frac{1}{8}\omega''_e y''_e + \dots \right) \dots \dots \dots (31.13)$$

The transformation is done with the relations

$$\omega_0 = \omega_e - \omega_e x_e + \frac{3}{4}\omega_e y_e + \dots$$

$$\omega_0 x_0 = \omega_e x_e - \frac{3}{2}\omega_e y_e + \dots$$

$$\omega_0 y_0 = \omega_e y_e + \dots$$

The coefficients  $\omega_0 y_0$  and  $\omega_e y_e$  are very small and can be neglected. Using (") for lower state and (') for upper state the above relations for two electronic states are:

$$\omega_0'' = \omega_e'' - \omega_e'' x_e'' \quad \omega_0' = \omega_e' - \omega_e' x_e'$$

$$\omega_0'' x_0'' = \omega_e'' x_e'' \quad \omega_0' x_0' = \omega_e' x_e'$$

These equations give the relations between two types of vibrational constants.

**Vibrational progressions :** In figure 31.3(a), the group of transitions are originating from the same vibrational state of the upper level  $\nu' = 0, \nu' = 1, \nu' = 2, \dots$  and terminating to the different vibrational levels  $\nu''$  of the lower state. This is known as  $\nu''$ -progression.

On the other hand, in figure 31.3(b), the group of transitions are originating from the same vibrational state of the lower level  $\nu'' = 0, \nu'' = 1, \nu'' = 2, \dots$  and terminating to the different vibrational levels  $\nu'$  of the upper state. This is known as  $\nu'$ -progression.

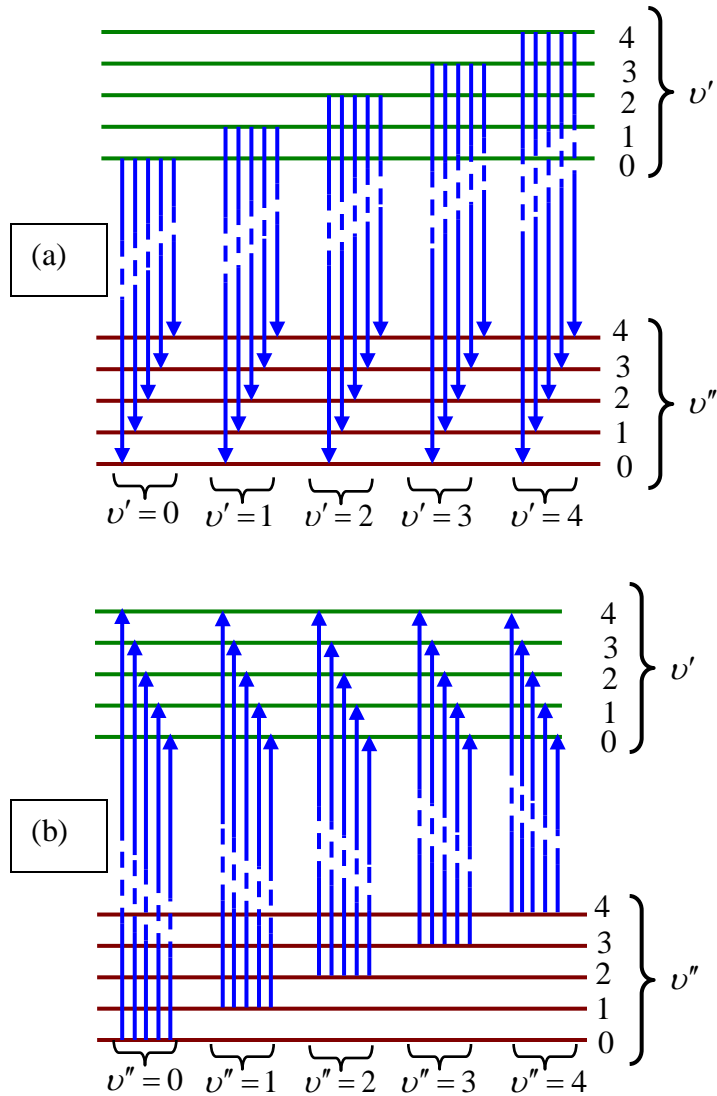


Figure 31.3

Sometimes, the transitions for a particular vibrational mode is defined as  $\nu_{\nu''}^{\nu'}$ . In figure-31.4, several transitions between the two vibrational levels of different electronic states are shown.

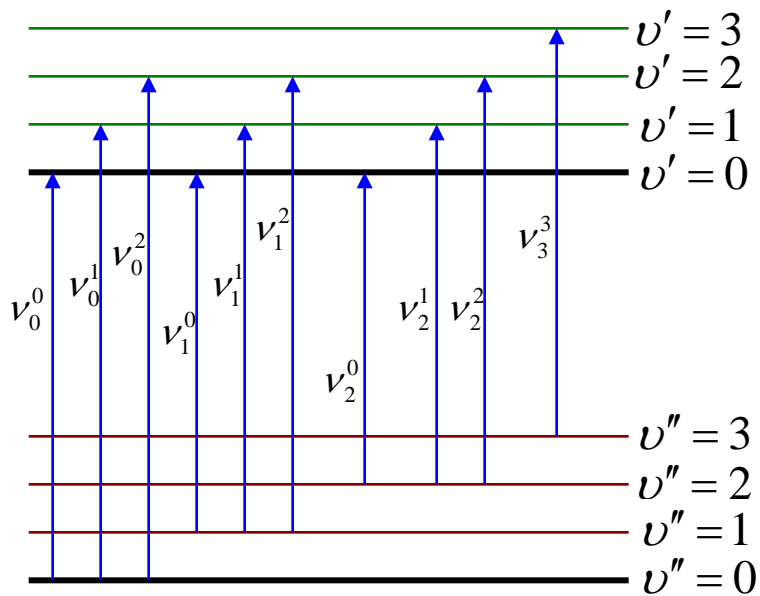


Figure-31.4

Now, the potential energy curve of a particular electronic state along with vibrational levels is shown in figure-31.5. If we analyze the vibrational levels we can get the information about the bond dissociation energy of that molecule. The dissociation energy is the required energy  $D_0$  for which the vibrational transition will be on the top of the potential energy curve as shown in figure-31.5. The difference between the successive vibrational levels will be zero. Let us say that the vibrational quantum no. is  $\nu_D$ . Then

$$\frac{\delta}{\delta \nu} G_0(\nu) = \omega_0 - 2\omega_0 x_0 \nu_D = 0.$$

$$\text{So } \nu_D = \frac{\omega_0}{2\omega_0 x_0}.$$

$$D_0 = G_0(\nu_D) = \omega_0 \nu_D - \omega_0 x_0 \nu_D^2$$

$$= \frac{\omega_0^2}{4\omega_0 x_0} \dots\dots\dots(31.14)$$

Thus if the  $\omega_0$  and  $\omega_0 x_0$  are known for a particular electronic state the bond dissociation energy can be calculated.

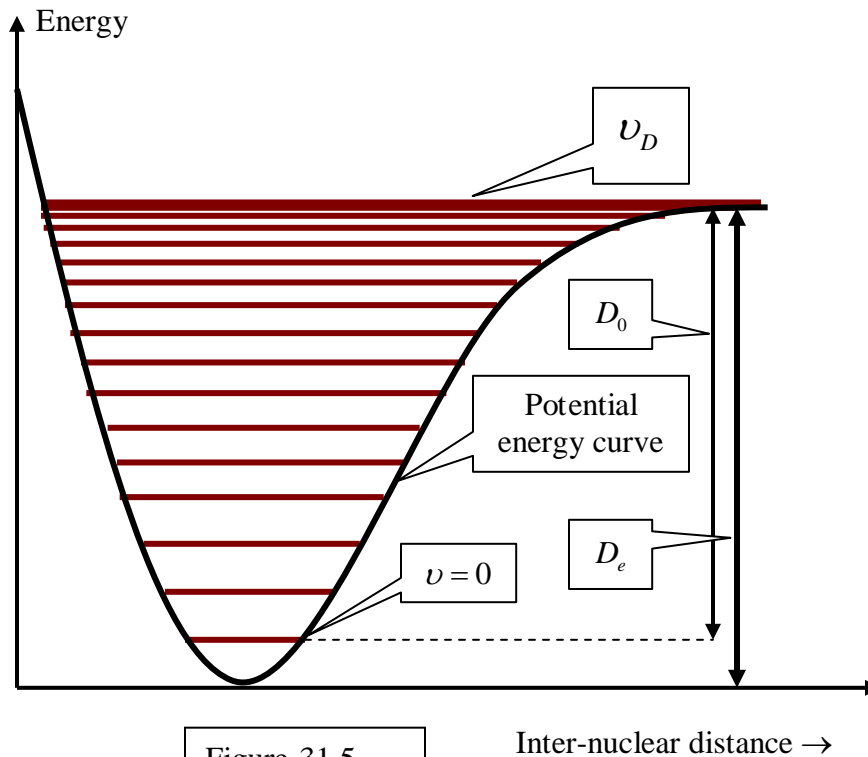
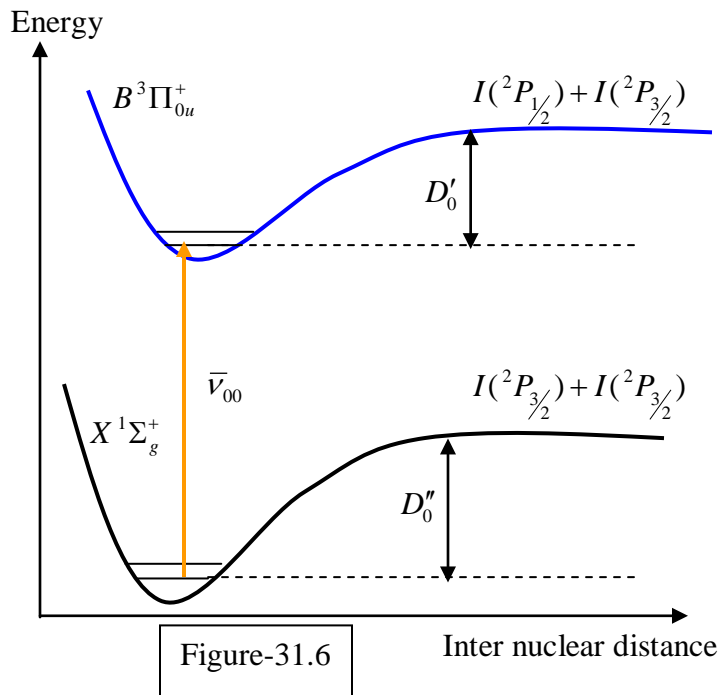


Figure-31.5

Vibrational structure analysis of the Iodine absorption spectrum.

If a continuous radiation in the visible region is passed through cell containing Iodine vapor, a band spectrum can be recorded using a spectrometer arising from absorption by iodine molecules ( $I_2$ ). This is an electronic transition between the ground  $B^3\Pi_{0u}^+$  and the excited  $X^1\Sigma_g^+$  electronic state as shown in the figure-31.6. The  $\nu''=0$  to  $\nu'=0$  is known as the origin transition and will have the lowest frequency (highest  $\lambda$ ) and can be located near 6200Å. The other discrete band extends up to about 5000 Å in the place green region beyond which a continuum can be observed. Since the molecules are at room temperature, the  $\nu''=0$  is the most populated and most of the observed bands are due to transitions for  $\nu''=0$  to  $\nu'=0,1,2,3,\dots\dots$



## Experimental set up :

The experimental set up is shown in figure-31.7(a) and the observed spectrum is shown in figure -31.7 (b).

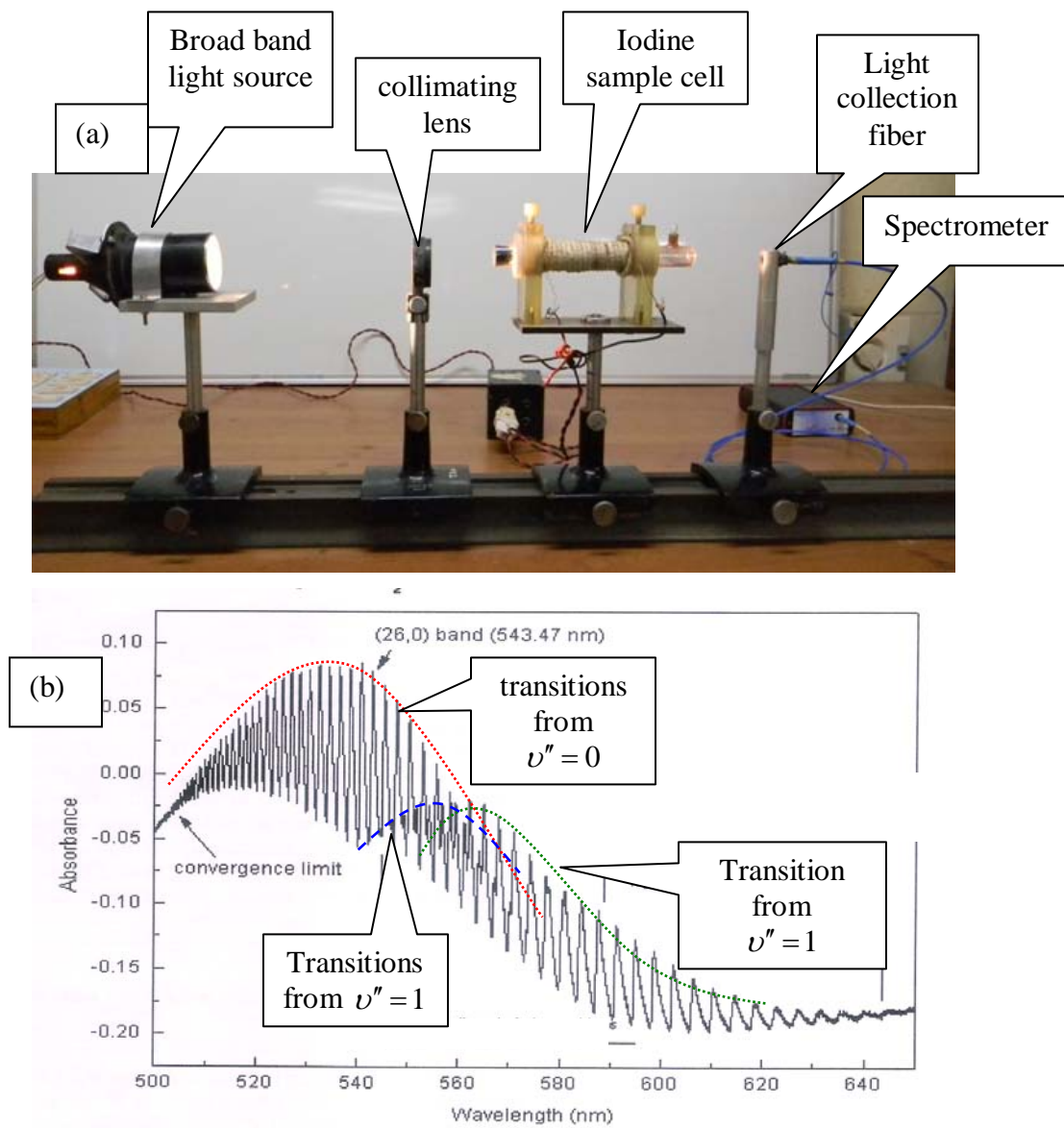


Figure-31.7

## Observations from the spectrum:

1. Each small hump, or peak such as the (26,0) band labeled on the spectrum, corresponds to a transition between two vibrational levels corresponding to two different electronic states and is called a band.
2. Each band is comprised of several hundred lines, each of which involves different upper and lower rotational quantum numbers as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the band head.
3. There are three series of bands. The higher energy side (lower in wavelength) bands are from  $\nu'' = 0$  to  $\nu' = 0, 1, 2, 3, \dots$
4. This series shows a convergence i.e. the transitions extend up to the vibrational level at top of the potential curve.
5. Since the spectrum is taken at the room temperature, the higher vibrational levels of the ground electronic state are also populated. The middle series is from  $\nu'' = 1$  and the higher wavelength series is from  $\nu'' = 2$ .

## CALCULATION OF VIBRATIONAL CONSTANTS:

As discussed earlier that in a given electronic state the difference between two successive vibrational states (with quantum number  $\nu$  and, and in units of  $\text{cm}^{-1}$ ) is given by:

$$\Delta G_{\nu+1/2} = G(\nu+1) - G(\nu) = G_0(\nu+1) - G_0(\nu)$$

substituting from equation 31.10 and simplifying we get:

$$\Delta G_{\nu+1/2} = \omega_e - 2\omega_e x_e (\nu+1) = \omega_0 - \omega_0 x_0 (2\nu+1) \dots\dots\dots(31.15)$$

From this, we get for  $\nu = 0, 1, 2, 3, \dots$  etc:

$\nu$	$\nu+1$	$\Delta G_{\nu+1/2}$
0	1	$\Delta G_{1/2} = \omega_e - 2\omega_e x_e = \omega_0 - \omega_0 x_0$
1	2	$\Delta G_{3/2} = \omega_e - 4\omega_e x_e = \omega_0 - 3\omega_0 x_0$
2	3	$\Delta G_{5/2} = \omega_e - 6\omega_e x_e = \omega_0 - 5\omega_0 x_0$

For iodine, we will concentrate the only vibrational bands for the excited electronic state and the transitions originating from  $\nu'' = 0$ .

Then for the upper electronic state,

$$\Delta G_{\nu+1/2} = \omega'_e - 2\omega'_e x'_e = \omega'_0 - \omega'_0 x'_0 \dots\dots\dots(31.16)$$

where  $\Delta G_{\nu+1/2}$  is the difference (in cm-1) between two vibrational levels with  $\nu' = 0$  and  $\nu' = 1$  in the upper electronic state and is called the first vibrational quantum of the upper electronic state. Further, the difference between two successive vibrational quanta gives approximately the constant second difference,  $\Delta^2 G$  as seen

$$\Delta G_{(\nu+1)+1/2} - \Delta G_{\nu+1/2} = \Delta^2 G_{\nu+1} = -2\omega_e x_e = -2\omega_0 x_0 = \text{constant} \dots\dots\dots(31.17)$$

All the observed vibrational bands originating from  $\nu'' = 0$  are given in table-31.1.

Table 31.1

Observed vibrational bands in iodine absorption spectrum

Serial NO.	Quantum Number $\nu'$	Wavelength nm	Wave No. $1/\lambda$ $\text{cm}^{-1}$	$\Delta G_{\nu'+1/2}$ $= G_0(\nu'+1) - G_0(\nu')$
1	16	571.02	17512.52	96.07
2	17	567.87	17609.66	97.14
3	18	564.72	17707.89	98.22
4	19	561.72	17802.46	94.57
5	20	558.72	17898.05	95.59
6	21	555.95	17987.23	89.18
7	22	553.32	18072.72	85.49
8	23	550.77	18156.4	83.67
9	24	548.22	18240.85	84.45
10	25	545.82	18321.06	80.21
11	26	543.57	18396.89	75.84
12	27	541.24	18476.09	79.19
13	28	539.07	18550.47	74.37
14	29	536.97	18623.01	72.55
15	30	534.94	18693.69	70.67
16	31	532.99	18762.08	68.39
17	32	531.12	18828.14	66.06
18	33	529.32	18892.16	64.03
19	34	527.52	18956.63	64.46
20	35	525.79	19019	62.37
21	36	524.22	19075.96	56.96
22	37	522.64	19133.63	57.67
23	38	521.07	19191.28	57.65
24	39	519.64	19244.09	52.81
25	40	518.22	19296.82	52.73
26	41	516.87	19347.22	50.40
27	42	515.67	19392.25	45.02
28	43	514.47	19437.48	45.23
29	44	513.34	19480.27	42.79
30	45	512.44	19514.48	34.21
31	46	511.32	19557.22	42.74
32	47	510.34	19594.78	37.55
33	48	509.37	19632.09	37.31
34	49	508.54	19664.14	32.04
35	50	507.72	19695.9	31.75
36	51	506.97	19725.03	29.14
37	52	506.22	19754.26	29.22

From equation 31.15, we have  $\Delta G_{v+1/2} = \omega_0 - \omega_0 x_0 - 2\omega_0 x_0 v$ . So we can plot the  $\Delta G_{v+1/2}$  versus  $v$  and fit it with a linear function. From the fitting of the graph we get the vibrational constants  $\omega_0 - \omega_0 x_0$  and  $-2\omega_0 x_0$  from the intercept and the slope of the line as shown in figure -31.8

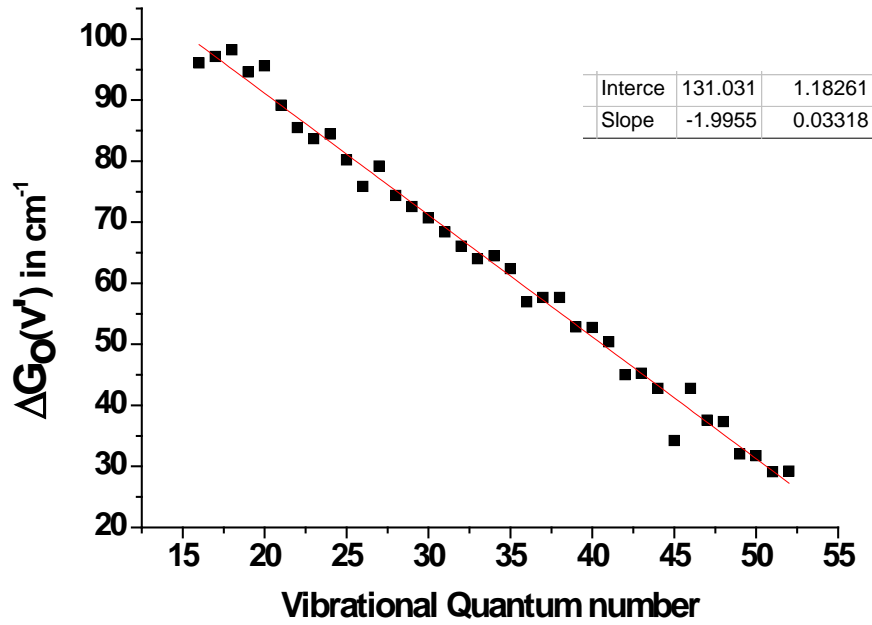


Figure-31.8

$$\text{Slope} = -2\omega'_o x'_o = -1.9955$$

$$\omega'_o x'_o = 0.998 \text{ cm}^{-1}$$

$$\text{And, Intercept} = \omega'_0 - 2\omega'_o x'_o = 131.031$$

$$\omega'_0 = 131.031 + 1.996$$

$$= 133.027 \text{ cm}^{-1}$$

$$\text{Now the dissociation energy in the upper state } D'_0 = \frac{\omega_0^2}{4\omega_0 x_0} = 4432.9 \text{ cm}^{-1}$$

## Recap

In this lecture,

1. we have understood the electronic transitions of diatomic molecules
2. The vibrational transitions between the two electronic states give the vibrational structure of the electronic transitions
3. The vibrational constants of the two electronic states can be calculated by analyzing the vibrational transitions.
4. The  $\nu'' = 0$  to  $\nu' = 0$  is known as the origin transition and will have the lowest frequency (highest  $\lambda$ )
5. The group of transitions are originating from the same vibrational state of the lower level  $\nu'' = 0, \nu'' = 1, \nu'' = 2, \dots$  and terminating to the different vibrational levels  $\nu'$  of the upper state. This is known as  $\nu'$ -progression.
6. The group of transitions are originating from the same vibrational state of the upper level  $\nu' = 0, \nu' = 1, \nu' = 2, \dots$  and terminating to the different vibrational levels  $\nu''$  of the lower state. This is known as  $\nu''$ -progression.
7. There are three series of bands in the absorption of iodine molecule. The higher energy side (lower in wavelength) bands are from  $\nu'' = 0$  to  $\nu' = 0, 1, 2, 3, \dots$ .
8. This series shows a convergence i.e. the transitions extend up to the vibrational level at top of the potential curve.
9. Since the spectrum is taken at the room temperature, the higher vibrational levels of the ground electronic state are also populated. The middle series is from  $\nu'' = 1$  and the higher wavelength series is from  $\nu'' = 2$ .