# **Quadrant II – Transcript and Related Materials**

Programme	:	Bachelor of Science (Third Year)
Subject	:	Physics
Paper Code	:	PYC108
Paper Title	:	DSC: Atomic and Molecular Physics
Unit 6	:	Spectra of Diatomic Molecule
Module Name	:	Fortrat Parabolas and explanation of band
		structure on its basis, Electronic Spectra

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### Notes

**Electronic Spectra** 

### Electronic spectra of diatomic molecule

Electronic band comprises of large number of spectral lines arranged in a particular manner.

Each band in electronic spectrum arises when there is change in electronic energy, vibrational energy and rotational energy. As each electronic state is comprised of vibrational sate and rotational state.

Using Born -Oppenheimer approximation we have

 $E_{Total} = E_{electronic} + E_{vibrational} + E_{rotational}$ 

i.e. electronic, vibrational, rotational energies are completely independent of each other

change in total energy

 $\Delta E_{Total} = \Delta E_{electronic} + \Delta E_{vibrational} + \Delta E_{rotational}$  in joules

$$\begin{split} \Delta \varepsilon_{Total} &= \Delta \varepsilon_{elec} + \Delta \varepsilon_{vib} + \Delta \varepsilon_{rot} \quad in \; cm^{-1} \\ \Delta \varepsilon_{elect} &\approx \; \Delta \varepsilon_{vib} \times 10^3 \approx \Delta \varepsilon_{rot} \times 10^6 \end{split}$$

rotational spectra are shown by molecules possessing a permanent dipole moment and vibrational spectra require a change in dipole during the motion

 $\varepsilon^{\prime\prime} \longrightarrow \varepsilon^{\prime}$  band is observ

$$\bar{v} = \varepsilon_{Total}' - \varepsilon_{Total}'$$

$$\bar{v} = (\varepsilon_{elec}' - \varepsilon_{elec}') + (\varepsilon_{vib}' - \varepsilon_{vib}') + (\varepsilon_{rot}' - \varepsilon_{rot}') - \dots - 1$$

$$\bar{v}_{(v',v'')} = (\varepsilon_{elec}' - \varepsilon_{elec}') + (\varepsilon_{vib}' - \varepsilon_{vib}') - \dots - 2$$
Substitute Equn 2 in Equn 1
$$\bar{v} = \bar{v}_{(v',v'')} + (\varepsilon_{rot}' - \varepsilon_{rot}') \quad in \ cm^{-1} - \dots - 3$$

$$\varepsilon_{rot} = B J(J+1) - \dots - 4$$
Where  $B = \frac{h}{8\pi^2 IC}$ 

Substitute Equn 4 in Equn 3

 $\bar{\mathbf{v}} = \bar{\mathbf{v}}_{(\mathbf{v}',\mathbf{v}'')} + (\varepsilon''_{rot} - \varepsilon'_{rot}) \quad in \ cm^{-1}$ 

 $\bar{\nu}_{spect} = \bar{\boldsymbol{\nu}}_{(\boldsymbol{\nu}',\boldsymbol{\nu}'')} + \Delta \left(BJ(J+1)\right)cm^{-1}$ 

 $ar{m{
u}}_{(m{
u}',m{
u}^")}$  wavenumber of electronic and vibrational transition

Selection rule

$$\Delta J = \pm 1$$

For the state which do not have electronic angular momentum

about internuclear axis

Only P and R branch occur

 $\Delta J = 0, \pm 1$  For the state which have electronic angular momentum about internuclear axis Q along with P and R occurs

$$\bar{\nu}_{spect} = \bar{\nu}_{(\nu',\nu'')} + B'J'(J'+1) - B''J''(J''+1)cm^{-1}$$

The internuclear distance between upper and lower electronic states differ considerably

 $\therefore \varepsilon' > \varepsilon''$  r' > r'' B' < B''  $as \qquad I = \mu r^2$ 

#### For Q branch

When 
$$\Delta J = 0$$
  
 $J' - J = 0 \Rightarrow J' = J''$   
 $\bar{\nu}_Q = \bar{\nu}_{(v',v'')} + B'J''(J'' + 1) - B''J''(J'' + 1)cm^{-1}$   
 $\bar{\nu}_Q = \bar{\nu}_{(v',v'')} + B'(J''^2 + J'') - B''(J''^2 + J'')cm^{-1}$   
 $\bar{\nu}_Q = \bar{\nu}_{(v',v'')} + B'J''^2 + B'J'' - B''J^2 + B''J'' cm^{-1}$   
 $\bar{\nu}_Q = \bar{\nu}_{(v',v'')} + (B' - B'')J'' - (B' - B'')J''^2cm^{-1}$ 

#### For P branch

## $\Delta J = -1, J'' = J' + 1$

$$\bar{v}_{P} = \bar{v}_{(v',v'')} + B'J'(J'+1) - B''(J'+1)(J'+1)cm^{-1}$$

$$\bar{v}_{P} = \bar{v}_{(v',v'')} + B'[(J'+1-1)(J'+1)] - B''[(J'+1)(J'+1+1)]cm^{-1}$$

$$\bar{v}_{P} = \bar{v}_{(v',v'')} + B'[(J'+1)^{2} - (J'+1)] - B''[(J'+1)^{2}(J'+1)]cm^{-1}$$

$$\bar{v}_{P} = \bar{v}_{(v',v'')} - (B'+B)(J'+1) + (B'-B'')(J'+1)^{2}cm^{-1}$$

For R branch

$$\Delta J = +1, \quad J' = J'' + 1$$
$$\bar{\nu}_R = \bar{\nu}_{(v',v'')} + (B' + B)(J' + 1) + (B' - B'')(J' + 1)^2 cm^{-1}$$

Combined equation

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + (B'+B)m+(B'-B'')m^2 \ cm^{-1} -----5$$
  
 $m = \pm 1, \pm 2 \dots$ 

+ve for R branch, -ve for P branch

Taking 10% difference between the upper and lower B values  $B^\prime < B^\prime\prime$ 

P branch lines occur on the low wavenumber side of the band origin and the spacing between the lines increases with m

R branch lines occur on the higher wavenumber side of the band origin and the spacing between the lines decreases with m such that lines reach a maximum number and then begin to return to low wavenumbers with increasing spacing

The point where R branch separation decreases to zero is called BAND HEAD

Band is called Red degraded band-intensity fall off points towards the red or low frequency

Rotational fine structure of vibrational electronic transition with 10% difference between B' and B"



B' > B''

Q branch spreads to higher wavenumber

P branch spreads to lower wavenumber

R branch lies on the higher wavenumber side consists of series of lines on the increasing separation

Band head appears in the P branch to low frequency of the origin

Band is called Violet degraded band

**Fortrat** represented fine structure in the Electronic spectra of diatomic molecules by using the equation of a parabola, the **Fortrat** parabola

The **Fortrat diagram** is an important graphical method used in the analysis of molecular spectra

Equn 5 is parabolic equation

$$\begin{split} \bar{v}_{P,R} &= \bar{v}_{(v',v'')} + (B'+B)m+(B'-B'')m^2 \ cm^{-1} ----5 \\ m &= J+1 \ , \ J=0,1,2..... \\ m &= +1,+2,+3 \ ... \ ... \ R \ branch \\ m &= -1,-2,-3 \ ... \ ... \ P \ branch \\ Writing \ parabolic \ equations \ for \ P,R,Q \\ \bar{v}_{P,R} &= \bar{v}_{(v',v'')} + (B'+B)p+(B'-B'')p^2 \ cm^{-1}---6 \\ \bar{v}_Q &= \bar{v}_{(v',v'')} + (B'-B)q+(B'-B'')q^2 \ cm^{-1} - -7 \end{split}$$

Equn 6 and & represents Equn of parabola

p takes positive and negative values,

q takes only positive value

Position of the vertex

Tangent to the parabola makes  $90^{\circ}$  to v axis

$$\frac{\partial \bar{v}_{P,R}}{\partial P} = 0 = (B' + B'') + 2(B' - B'')p = 0$$
$$p = -\frac{B' + B''}{2(B' - B'')}$$

For B'<B" band head occurs at positive region of p values (in R branch)

B'> B" band head occurs in the negative region of p value(P branch)

For 10% difference between B' and B" the band head occurs at  $\text{p}\approx 10$ 



Fortrat Parabola for 10 % difference between B' and B" with B'< B"

Electronic transitions between various states involve radiation in the visible or ultraviolet region as the energies involved are high.

Each transition appears as a series of different rotational and vibrational states in each electronic state.

Whenever there is a change in the dipole moment of the molecule, there is always a change in the electronic configuration.

As a result, all molecules exhibit electronic spectra. This implies that homopolar diatomic molecules like  $H_2$ ,  $N_2$  ... which neither show the rotational nor the vibrational spectra as their electric dipole moment is always zero, this shows that the electronic spectra which

possess rotational and vibrational fine structure. As a result, one can determine the moment of inertia and force constant in such molecules.

The probability of locating the oscillator is maximum at the center for v = 0 state and it is maximum at or near both ends of the range of motion for all other states v = 1, v = 2 ...

Those transitions are favourable that connects an initial configuration of highest probability with the final state of highest probability. And these transitions are brightest.

The other transitions which occur are of lesser probability and are weaker.

The electronic transitions in a diatomic molecule occur when v = 0,  $R = R_0$  (center of range of motion)

For v > 0, R is either extreme of the range.

As R do not change effectively during an electronic transition (Franck Condon Principle) the transition is shown as a vertical line .

The curve of potential energy against intermolecular distance for the electronic ground state and first excited state of diatomic molecule is represented in the diagram.

For each of the state, the vibrational energy levels are shown as v = 0,1,2,3 ... Superimposed on these levels the graph of the corresponding harmonic oscillator probability density  $|\psi|^2$ 

For v = 0,  $|\psi|^2$  is maximum at the center and for the higher values of v, the maxima occur at the ends of the range of motion.

Only those transitions are favoured which connect an initial state of high probability density with a final state of high probability density. That is the electronic transitions in a diatomic molecule are more likely to occur when the distance between the nuclei is at the center of the range for v = 0 and at either of the extreme ends.

There is no selection rule for  $\Delta v$  and the transition occurs in accordance with Franck-Condon Principle

Case 1

The upper electronic state has the same internuclear distance as the lower electronic states. As per the Frank Condon Principle a transition occurs vertically. If vibrationally and electronically the molecule is initially in the ground state ( $\mathcal{E}' \ and \ v'$ ) then the most probable transition is to ( $\mathcal{E}' \ and \ v''=0$ ). The line which joins v'=0 to v''=0 is the strongest line. There is some chance that the transition may end over to the  $v''=1.2 \dots ...$  states. These are diminished intensity lines.



Case 2

Fig. shows the transition from v = 0 to v = 1 of the upper state. It takes place as ,  $|\psi|^2$  is maximum at the end of the motion for v = 1 .the other transition to v = 2,3,4 .... lead to weak lines.



### Case 3

Fig shows the transition which is most likely to dissociate a molecule. As the vertical lines from v' = 0 of the lower state intersects the upper curve at a point where no bound state is

possible. The other transition to the bound state give rise to weak lines. The spectrum consists of several weak lines followed by a continuum with no line structure.



Internuclear distances

Predissociation

If two excited states intersect, one of them has a minima and usual set of vibrational levels and other has no minima and is unstable.

If the transition from v'' = 0 ends at any of the level a, b, c, e, f no dissociation of molecule will occur but if it ends at 'd' level there is possibility of the molecule shifting to unbound state at higher R end of vibration leading to dissociation.

If there was no unbound state then this transition would have not lead to dissociation.

This phenomenon is called predissociation. It implies the dissociation of a molecule in a state at an energy less than the dissociation energy corresponding to that state.

