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المرحلة الرابعة

Chapter five: Electronic Spectra of Diatomic Molecules

Introduction:-

1-The absorption or emission of electromagnetic radiation in visible and ultraviolet due to transition between electronic energy levels of molecule.

The electronic spectrum appears as absorption bands from or emission band from, and these bands contain large number of spectrum line.

2-The separation between electronic levels is of the order of 10^{-6}cm^{-1} or more. During electronic transitions vibrational and rotational energy changes can also occur.

The analysis of electronic spectrum gives information on the rotational constant and vibrational frequencies of both ground and excited electronic states.

3-Molecules possessing permanent electric dipole moment give pure rotational spectra.

4-Vibrational spectra required a change of dipole moment.

5-Electronic spectra given by all molecules since change in the electrons distribution in molecules are always accompanied by dipole moment change.

Vibrational coarse structure:-

To understand the vibrational coarse structure, we drop the rotational energy term from the expression for total energy

$$\varepsilon_T = \varepsilon_{el} + \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e + \left(v + \frac{1}{2}\right)^3 y_e \bar{\omega}_e + \dots \text{cm}^{-1}$$

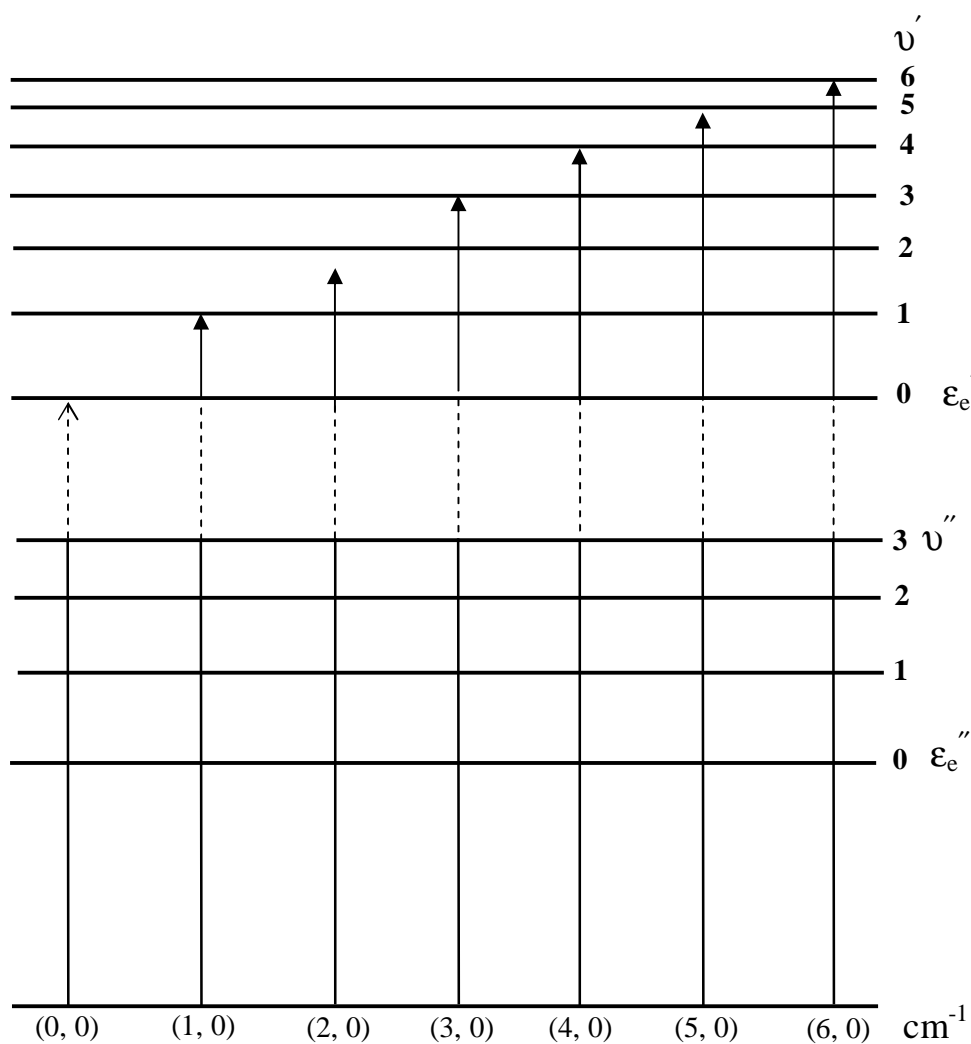
For $v = 0, 1, 2, 3, 4 \dots \dots \dots$. The energy levels corresponding to this equation are shown in the following figure.

The lower states are indicated by a (") and the upper by (')

The vibrational levels in the excited state would be more closely spaced than in the ground state.

From the above equation the frequency of a spectral line can be written as

$$\bar{\nu} = (\epsilon_{el}^c - \epsilon_{el}^a) + \left[\left(v^c + \frac{1}{2} \right) \omega_e^c - \left(v^c + \frac{1}{2} \right)^2 \omega_e^c x_e^c \right] - \left[\left(v^a + \frac{1}{2} \right) \omega_e^a - \left(v^a + \frac{1}{2} \right)^2 \omega_e^a x_e^a \right]$$



**The vibrational coarse structure of
electronic absorption from ground state.**

Any transition ($\nu'' \rightarrow \nu'$) has some definite probability. However the situation is simple if the absorption is from the electronic ground state to an excited state, as almost all molecules exist in the lowest vibrational state. Therefore the transitions which are of considerable intensity are those originating from the $\nu''=0$ state, labeled according to their (ν', ν'') values as (0,0), (1,0), (2,0), (3,0). The set of lines corresponding to these transition is called a ν' progression since the value of ν' increases by unity for each line in the set.

The wave number of the (0,0) transition is then.

$$\bar{\nu}_{00} = (\epsilon_{el}^c - \epsilon_{el}^a) + \left[\frac{1}{2} \omega_e^c - \frac{1}{4} \omega_e^c x_e^c \right] - \left[\frac{1}{2} \omega_e^a + \frac{1}{4} \omega_e^a x_e^a \right] \text{ --- (3)}$$

From the above equation (3) one can be determined the vibrational frequency ω_e and an harmonic constant x_e of both ground and excited electronic states of a molecule in addition to separation between the electronic state.

Vibrational analysis of band system:-

In the energy Scale, taking the minimum of the potential energy curve as zero, the vibrational term value $E(\nu)$ is given by

$$E(\nu) = \epsilon_\nu = \left(\nu + \frac{1}{2} \right) \omega_e - \left(\nu + \frac{1}{2} \right)^2 \omega_e x_e + \left(\nu + \frac{1}{2} \right)^3 \omega_e y_e \text{ --- } cm^{-1}$$

In vibration analysis of the spectrum of a band system, the energy of the $\nu=0$ vibrational level is taken as zero. That is in the modified system the vibrational term

$$E(0) = \epsilon_\nu = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \frac{1}{8} \omega_e y_e \text{ --- at } (\nu = 0)$$

Is taken as the zero and modified vibrational term $E_0(v)$. Then

$$\begin{aligned}
 E_0(v) &= v\omega_e^c - v^2\omega_e^c x_e - v\omega_e x_e + v^3\omega_e^c y_e + \frac{3}{2}v^2\omega_e y_e + \frac{3}{4}v\omega_e y_e \\
 &= v\left(\omega_e - \omega_e x_e + \frac{3}{4}\omega_e y_e\right) - v^2\left(\omega_e x_e - \frac{3}{2}\omega_e y_e + \dots\right) + v^3(\omega_e y_e + \dots) \\
 &= v\omega_{e(0)} - \omega_{e(0)} x_{e(0)} v^2 + \omega_{e(0)} y_{e(0)} v^3 \dots \dots \dots \dots \dots \dots (4)
 \end{aligned}$$

Where

$$\omega_{e(0)}^c = \omega_e^c - \omega_e x_e + \frac{3}{4}\omega_e y_e + \dots$$

$$\omega_{e(0)} x_{e(0)} = \omega_e x_e - \frac{3}{4}\omega_e y_e + \dots$$

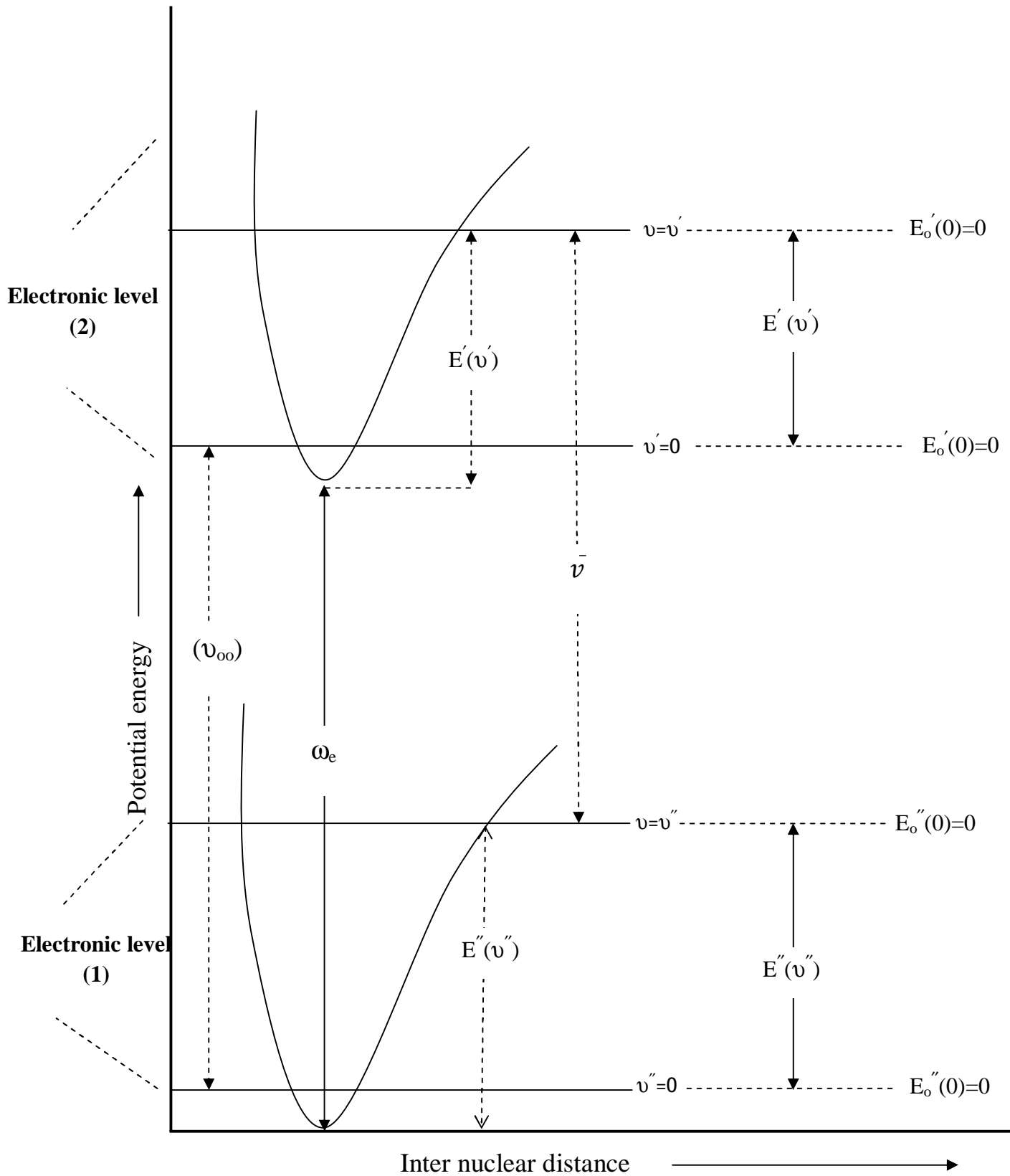
$$\omega_{e(0)} y_{e(0)} = \omega_e y_e + \dots$$

In the modified from the wave number of a spectral line can be written from eq. (2).

$$\bar{\nu} = \omega_{e00} + E_0^c(v^c) - E_0^a(v^a)$$

Where ω_{e00} is the wave number of the (0,0) band ω_e get,

$$\bar{\nu} = \bar{\nu}_{00} + E_0^c(v^c) - E_0^a(v^a)$$



The wave number separation of two vibration levels in an electronic state given by $E_o(v+1) - E_o(v)$ and is called the first difference denoted by $\Delta E\left(v + \frac{1}{2}\right)$ and using equation (4)

$$\Delta E\left(v + \frac{1}{2}\right) = \omega_{e(0)}^c - \omega_{e(0)} x_{e(0)} - 2\omega_e x_o v$$

The second difference $\Delta E^2\left(v + \frac{1}{2}\right)$ defined by

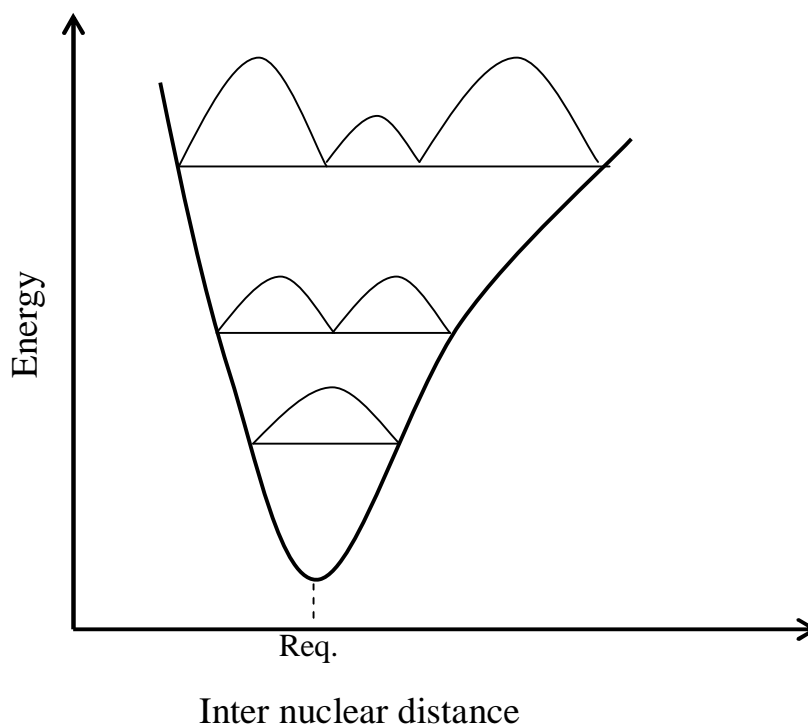
$$\Delta E^2\left(v + \frac{1}{2}\right) = \Delta E\left(v + 1 \frac{1}{2}\right) - \Delta E\left(v + \frac{1}{2}\right)$$

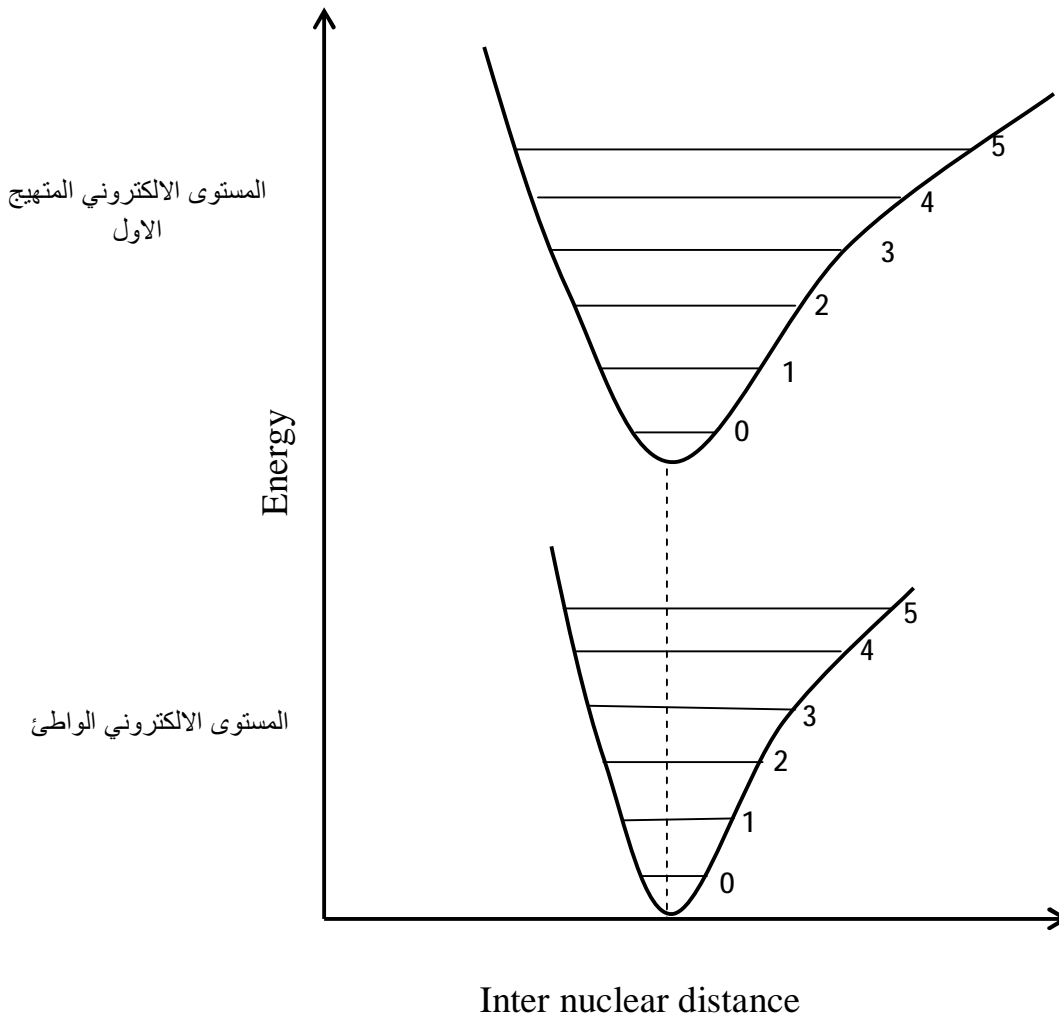
And
$$\Delta E^2 = -2\omega_{e(0)} x_{e(0)} = -2\nu_o x_o$$

Frank condon principle:-

((An electronic transition takes place so rapidly that a vibrating molecule does not change its inter nuclear distance appreciably during the transition))

((اي ان الانتقال الالكتروني يحدث في وقت اسرع من الوقت اللازم للانتقال الاهتزازي وحدث تغير في المسافة بين الذرات والجزيئات.))





Rotational fine structure of electronic – vibration spectrum:-

$$\epsilon_t^c = \epsilon_{el}^c + \epsilon_v^c + B^c J^c(J^c + 1) \quad cm^{-1} \quad J^c = 0,1,2,3 \dots$$

$$\epsilon_t^\alpha = \epsilon_{el}^\alpha + \epsilon_v^\alpha + B^\alpha J^\alpha(J^\alpha + 1) \quad cm^{-1} \quad J^\alpha = 0,1,2,3 \dots$$

Then the frequencies of the transition are

$$\bar{\nu} = (\epsilon_{el}^c - \epsilon_{el}^\alpha) + (\epsilon_v^c - \epsilon_v^\alpha) + B^c J^c(J^c + 1) - B^\alpha J^\alpha(J^\alpha + 1)$$

Replacing the first two terms by $(\bar{\nu}_{\nu^c\nu^\alpha})$ the wave number of an electronic vibrational transition

$$\bar{\nu} = \bar{\nu}_{\nu^c\nu^\alpha} + B^c J^c(J^c + 1) - B^\alpha J^\alpha(J^\alpha + 1)$$

$\bar{\nu}_{\nu^c\nu^\alpha}$ could be any one of the (0,0), (1,0), (2,0) -----

The selection rule for J depends on the type of electronic transition.

Transition for which both the upper and lower states have no electronic angular momentum about the inter nuclear axis the selection rule is $\Delta J = \pm 1$.

This leads to the presence of both P and R branches for all transitions

$$\Delta J = 0, \pm 1, \pm 2$$

with the restriction that a state with $J=0$ cannot undergo a transition to a $J=0$ state.

That is $J=0 \rightarrow J=0$ in such cases Q branch will also be there in addition to P and R branches.

We shall now consider the rotational contribution in equation (5) in detail for P branch $\Delta J = -1$ or $J' - J'' = -1$.

The rotational contribution:-

$$B^c J^c(J^c + 1) - B^\alpha J^\alpha(J^\alpha + 1) = B^c(J^\alpha - J)J^\alpha - B^\alpha J^\alpha(J^\alpha + 1)$$

$$= -(B^c + B^\alpha)J^\alpha + (B^c - B^\alpha)J^{\alpha 2} \quad cm^{-1} \quad J^\alpha = 1, 2, 3, 4 \dots$$

$$\bar{\nu}_p = \bar{\nu}_{\nu^c\nu^\alpha} - (B^c + B^\alpha)(J^c + 1) + (B^c - B^\alpha)(J^c + 1)^2 \dots \dots (6)$$

$$J^c = 0, 1, 2, 3, 4 \dots$$

As the lowest value of $J' = 1$ for P branch, there will not be any spectral line at $\bar{\nu}_{\nu^c\nu^\alpha}$ for R branch $\Delta J = +1$ $J' - J'' = +1$.

$$\bar{\nu}_R = \bar{\nu}_{\nu^c \nu^\alpha} + (B^c + B^\alpha)(J^c + 1) + (B^c - B^\alpha)(J^\alpha + 1)^2 \dots \dots (7)$$

$$J^\alpha = 0, 1, 2, 3, 4 \dots \dots$$

For Q branch

$$\Delta J=0 \quad \text{or} \quad J' = J''$$

$$\bar{\nu}_Q = \bar{\nu}_{\nu^c \nu^\alpha} + (B^c - B^\alpha)J^{\alpha^2} + (B^c - B^\alpha)J^\alpha \quad J^\alpha = 1, 2, 3, 4 \dots \dots$$

J^α cannot be zero as that would mean a transition from $J=0$ state to another $J=0$. There will be no spectral line at $\bar{\nu}_{\nu^c \nu^\alpha}$ in the red Q branches.