

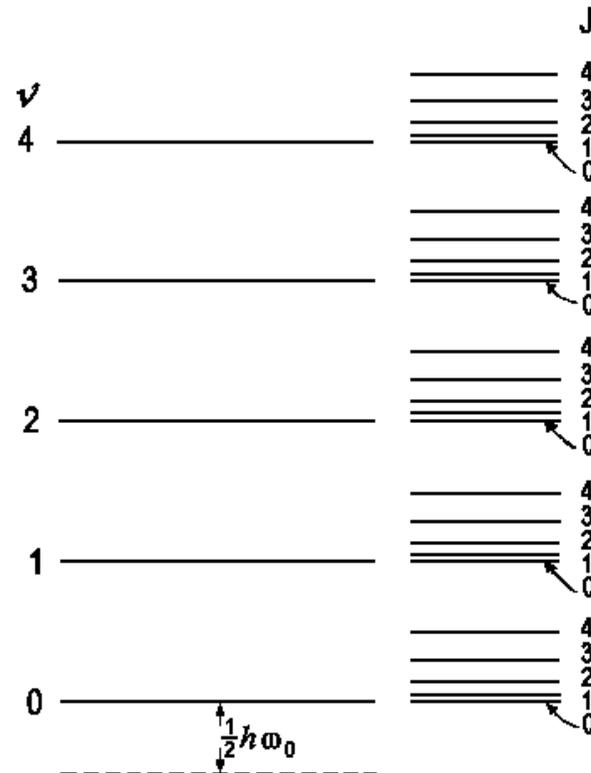
Vibrational-Rotational Spectroscopy

vibrational levels

$$E_v = (v + \frac{1}{2}) h\omega_0$$

rovibrational levels

$$E_r = B \cdot J (J + 1)$$



vibrational levels

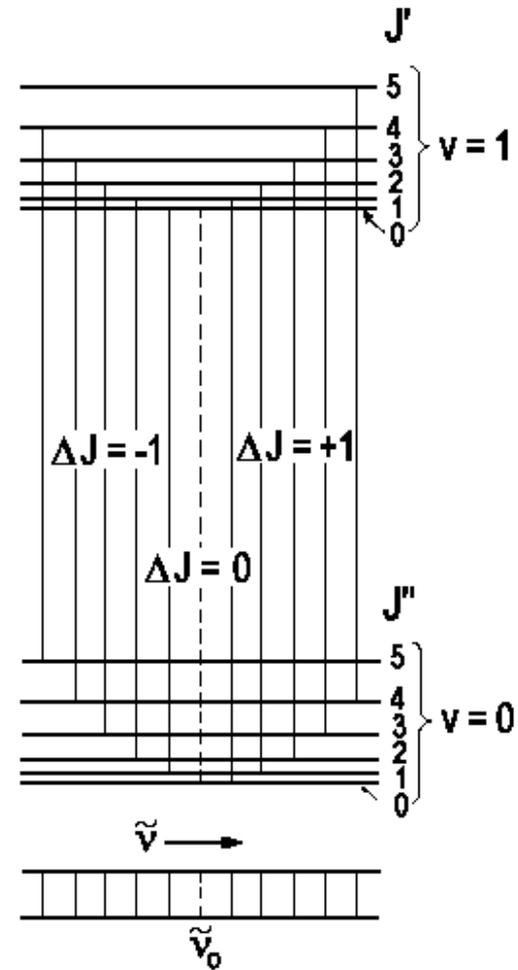
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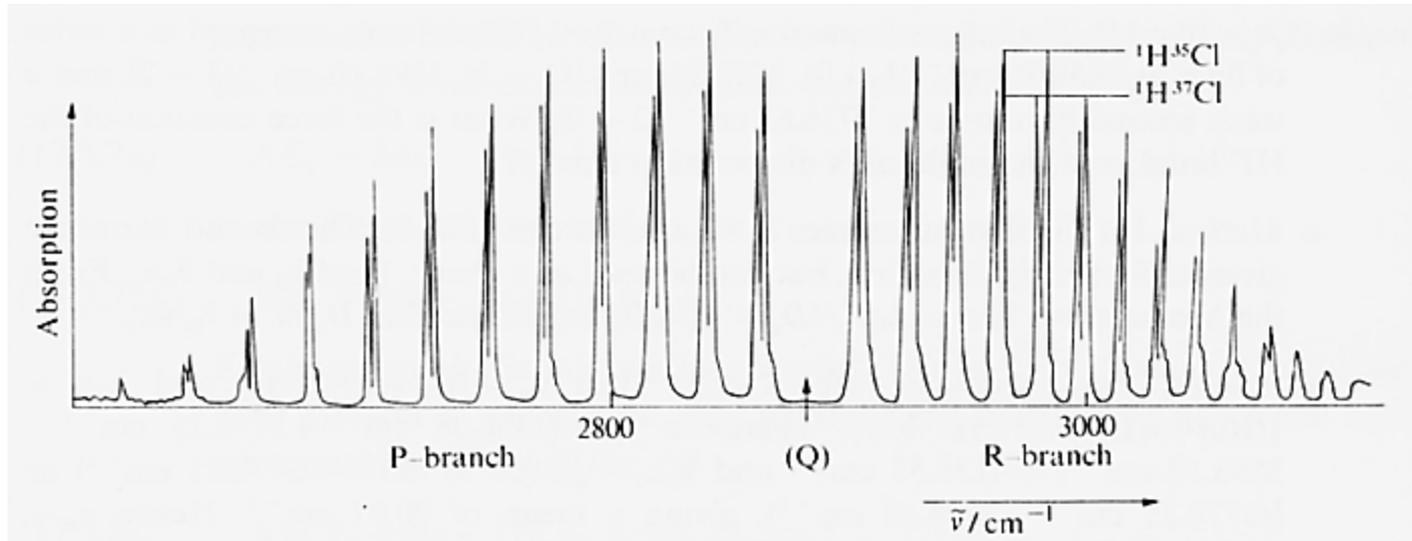
rovibrational levels

$$E_r = B \cdot J(J + 1)$$

Selection rules:

- 1) The molecule must have a permanent dipole moment;
- 2) $\Delta n = \pm 1; \pm 2, \pm 3...$
- 3) $\Delta J = \pm 1$





http://www.pci.tu-bs.de/aggericke/PC4e/Kap_III/Rot-Vib-Spektren.htm

In Vibrational-Rotational Spectroscopy, we need to find the difference between initial and final state, similarly to any spectroscopic technique:

$$\Delta E = E_{final} - E_{initial} = E_{n_2, J_2} - E_{n_1, J_1}$$

Contribution of rotational energy: $E_{J, M_J} = \frac{\hbar^2}{2\mu} \left\langle \frac{1}{R^2} \right\rangle J(J+1)$

As a first approximation: $\left\langle \frac{1}{R^2} \right\rangle = \frac{1}{R_e^2}; I = \mu R_e^2$

Define rotational constant: $B_e = \frac{h}{8\pi^2 I}$

Then: $E_J / h = B_e J(J+1)$ E is energy in ergs (E/h is energy in hertz)

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$$E_J / h = B_e J(J + 1)$$

However, averaging over the vibrational state shows that rotational constant is not exactly the equilibrium rotational constant, as it depends on the vibrational state

$$E_{n, J} / h = B_n J(J + 1)$$

Where $B_n = B_e - \alpha_e (n + 1/2)$

α_e is the vibration-rotation constant that describes how the vibrational state changes changes the average interatomic distance

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There is one more correction related to the centrifugal distortion:
The effect of rotational on the interatomic distance (or centrifugal distortion)

$$E_J'' / h = -D_c J^2 (J + 1)^2$$

Here D_c (in cm^{-1}) = $\frac{4B_e^3}{\omega_e^2}$ is the centrifugal stretching constant

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Combining all those terms that describe the contribution of rotational energy for a given vibrational level n :

$$E_{n, J} = [B_e - \alpha_e (n + 1/2)] J(J + 1) - D_c J^2 (J + 1)^2$$

or

$$E_{n, J} = B_n J(J + 1) - D_c J^2 (J + 1)^2$$

Thus, remembering the contribution of the electronic and vibrational energy

$$\begin{aligned} E_{n,J} &= E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \\ &= -D_e + \left(n + \frac{1}{2}\right) \hbar \omega_e - \left(n + \frac{1}{2}\right)^2 \hbar x_e \omega_e + \dots \\ &\quad + B_n J(J+1) - D_c J^2 (J+1)^2 \end{aligned}$$