

## Molecules and electronic, vibrational and rotational structure



Max Born  
Nobel 1954



Robert Oppenheimer



Gerhard Herzberg  
Nobel 1971



## Hamiltonian for a molecule

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 + V(\vec{R}, \vec{r})$$

$i$  refers to electrons,  $A$  to nuclei;

Potential energy terms:

$$V(\vec{R}, \vec{r}) = -\sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |\vec{R}_A - \vec{R}_B|} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Assume that the wave function of the system is separable and can be written as:

$$\Psi_{\text{mol}}(\vec{r}_i, \vec{R}_A) = \psi_{\text{el}}(\vec{r}_i; \vec{R}) \chi_{\text{nuc}}(\vec{R})$$

Assumed that the electronic wave function  $\psi_{\text{el}}(\vec{r}_i; \vec{R})$  can be calculated for a particular  $\vec{R}$

Then:  $\nabla_i^2 \psi_{\text{el}}(\vec{r}_i; \vec{R}) \chi_{\text{nuc}}(\vec{R}) = \chi_{\text{nuc}}(\vec{R}) \nabla_i^2 \psi_{\text{el}}(\vec{r}_i; \vec{R})$

$$\nabla_A^2 \psi_{\text{el}} \chi_{\text{nuc}} = \psi_{\text{el}} \nabla_A^2 \chi_{\text{nuc}} + 2(\nabla_A \psi_{\text{el}})(\nabla_A \chi_{\text{nuc}}) + \nabla_A^2 \psi_{\text{el}}$$

Born-Oppenheimer: the derivative of electronic wave function w.r.t nuclear coordinates is small:

$$\nabla_A \psi_{\text{el}} \approx 0$$

Nuclei can be considered stationary. Then:

$$\nabla_A^2 \psi_{\text{el}} \chi_{\text{nuc}} = \psi_{\text{el}} \nabla_A^2 \chi_{\text{nuc}}$$

Separation of variables is possible.

Insert results in the Schrödinger equation:

$$H_{\text{mol}} \psi_{\text{el}} \chi_{\text{nuc}} = E_{\text{mol}} \psi_{\text{el}} \chi_{\text{nuc}}$$



## Separation of variables in the molecular Hamiltonian

$$H\Psi_{\text{mol}} = \chi_{\text{nuc}} \left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \right\} \psi_{\text{el}} +$$

$$\psi_{\text{el}} \left\{ \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|} - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 \right\} \chi_{\text{nuc}} = E_{\text{total}} \Psi_{\text{mol}}$$

The wave function for the electronic part can be written separately and "solved"; consider this as a problem of molecular binding.

$$\left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \right\} \psi_{\text{el}}(\vec{r}_i; \vec{R}) = E_{\text{el}} \psi_{\text{el}}(\vec{r}_i; \vec{R})$$

Solve the electronic problem for each  $R$  and insert result  $E_{\text{el}}$  in wave function.

This yields a wave equation for the nuclear motion:

$$\left\{ -\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|} + E_{\text{el}}(\vec{R}) \right\} \chi_{\text{nuc}} = E_{\text{total}} \chi_{\text{nuc}}$$



## Schrodinger equation for the nuclear motion

The previous analysis yields:

$$\left\{ -\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|} + E_{el}(\vec{R}) \right\} \chi_{\text{nuc}} = E_{\text{total}} \chi_{\text{nuc}}$$

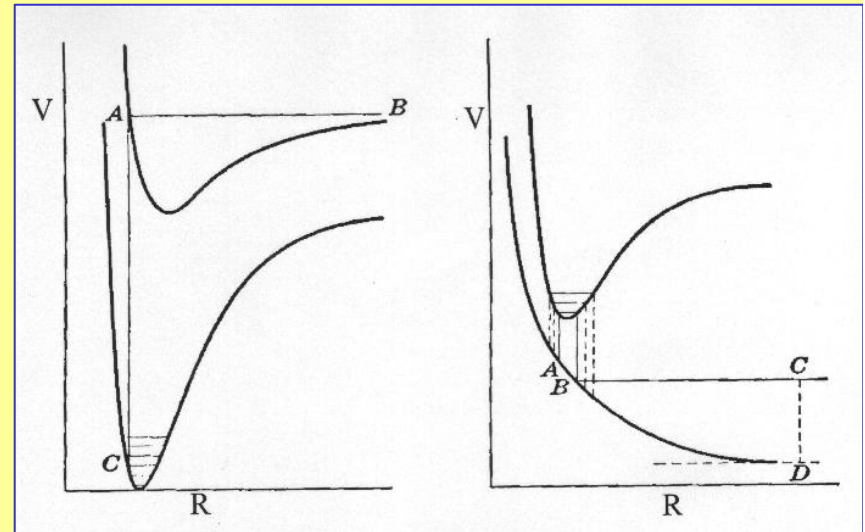
This is a Schrödinger equation with a potential energy:

$$V(\vec{R}) = \underbrace{\sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|}}_{\text{nuclear repulsion}} + \underbrace{E_{el}(\vec{R})}_{\text{chemical binding}}$$

Now try to find solutions to the Hamiltonian for the nuclear motion

$$-\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 \chi_{\text{nuc}}(\vec{R}) + V(\vec{R}) \chi_{\text{nuc}}(\vec{R}) = E \chi_{\text{nuc}}(\vec{R})$$

Typical potential energy curves in molecules



## Quantized motion in a diatomic molecule

Quantummechanical two-particle problem  
Transfer to centre-of-mass system

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

Single-particle Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \Delta_{\vec{R}} \chi_{\text{nuc}}(\vec{R}) + V(\vec{R}) \chi_{\text{nuc}}(\vec{R}) = E \chi_{\text{nuc}}(\vec{R})$$

Consider the similarity and differences  
between this equation and that of the  
H-atom:

- interpretation of the wave function
- shape of the potential

Laplacian:

$$\Delta_{\vec{R}} = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right)$$

$$+ \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial^2}{\partial \phi^2}$$

Angular part is the well-know equation  
with solutions:

Angular momentum operators

Spherical harmonic wave functions !



## Angular momentum in a molecule

Solution:

$$\vec{N}^2 |N, M\rangle = \hbar^2 N(N+1) |N, M\rangle$$

$$N_z |N, M\rangle = \hbar M |N, M\rangle$$

with

$$N = 0, 1, 2, 3, \dots$$

$$M = -N, -N+1, \dots, N$$

And angular wave function

$$|N, M\rangle = Y_{NM}(\theta, \phi)$$

Hence the wave function of the molecule:

$$\chi_{\text{nuc}}(R, \theta, \phi) = \Xi(R) Y_{NM}(\theta, \phi)$$

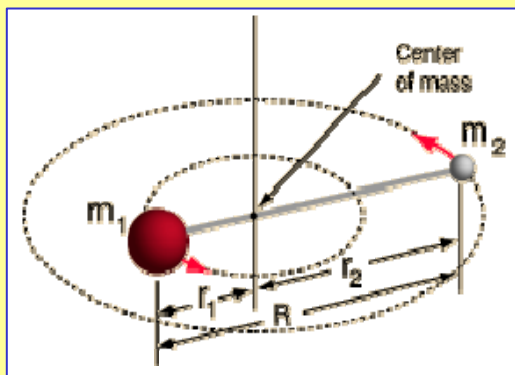
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Reduction of molecular Schrödinger equation

$$\left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \vec{N}^2 + V(R) \right] \chi_{\text{nuc}}(R) = E_{\text{vib,rot}} \chi_{\text{nuc}}(R)$$



## Eigenenergies of a "Rigid Rotor"



Rigid rotor, so it is assumed that  $R = R_e = \text{constant}$

Choose:  $V(R) = V(R_e) = 0$

All derivatives  $\frac{\partial}{\partial R}$  yield zero

Insert in:

$$\left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \vec{N}^2 + V(R) \right] \chi_{\text{nuc}}(R) = E_{\text{vib,rot}} \chi_{\text{nuc}}(R)$$

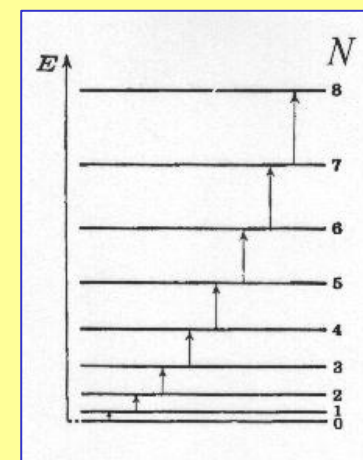
$$\left[ \frac{1}{2\mu R_e^2} \vec{N}^2 \right] \chi_{\text{nuc}}(R) = E_{\text{vib,rot}} \chi_{\text{nuc}}(R)$$

So quantized motion of rotation:  $E_{\text{rot}} = \hbar^2 \frac{N(N+1)}{2\mu R_e^2} = BN(N+1)$

With  $B$  the rotational constant

→ Deduce  $R_e$  from spectroscopy

isotope effect



## Vibrational motion

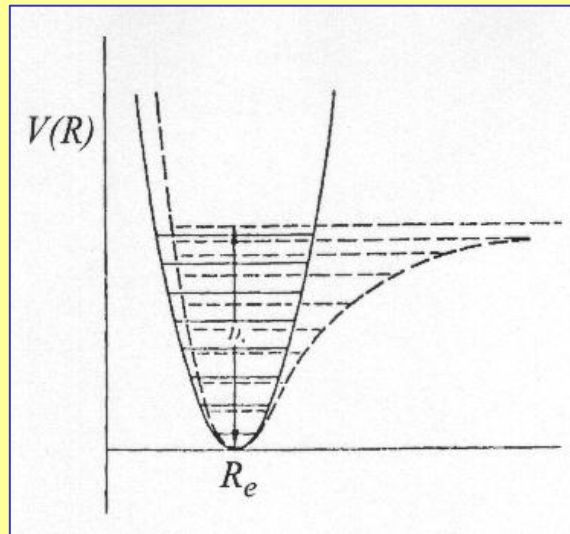
$$\left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \vec{N}^2 + V(R) \right] \chi_{\text{nuc}}(R) = E_{\text{vib,rot}} \chi_{\text{nuc}}(R)$$

Non-rotation:  $N=0$

Insert :

$$\Xi(R) = \frac{Q(R)}{R}$$

$$\longrightarrow \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) \right] Q(R) = E_{\text{vib}} Q(R)$$



Make a Taylor series expansion around  $\rho = R - R_e$

$$V(R) = V(R_e) + \left. \frac{dV}{dR} \right|_{R_e} \rho + \frac{1}{2} \left. \frac{d^2V}{dR^2} \right|_{R_e} \rho^2 + \dots$$

$$V(R_e) = 0 \quad \text{by choice}$$

$$\left. \frac{dV}{dR} \right|_{R_e} = 0 \quad \text{at the bottom of the well}$$

$$\text{Hence: } V(R) = k(R - R_e)^2 \quad \text{harmonic potential}$$





## Vibrational motion

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} + \frac{1}{2} k\rho^2 \right] Q(\rho) = E_{\text{vib}} Q(\rho)$$

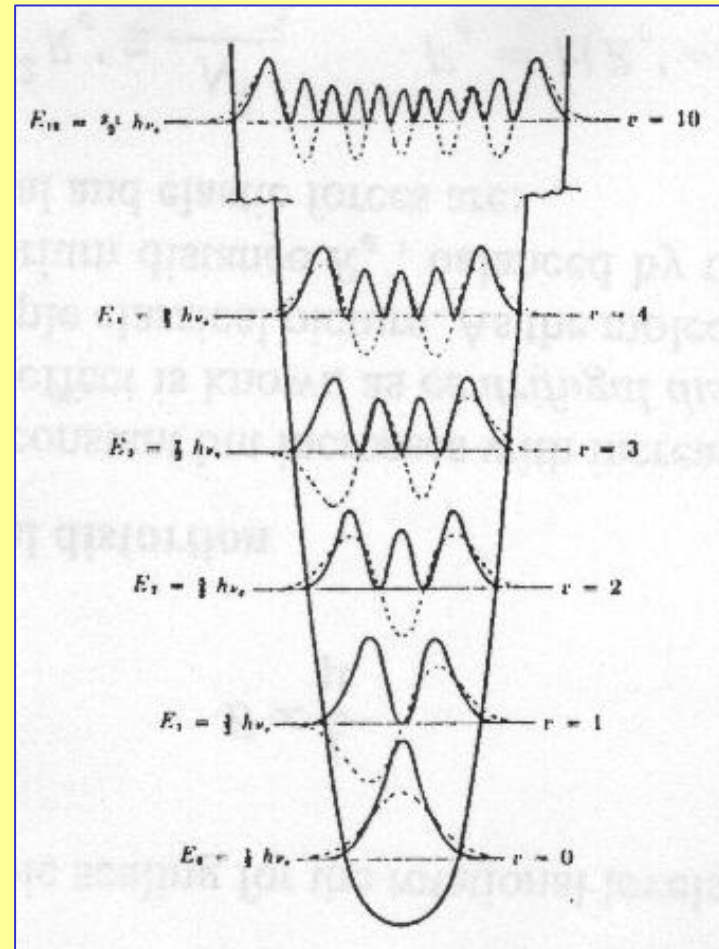
So the wave function of a vibrating molecule resembles the 1-dimensional harmonic oscillator, solutions:

$$Q_v(\rho) = \frac{2^{v/2} \alpha^{1/4}}{\sqrt{v!} \pi^{1/4}} \exp\left[\frac{1}{2} \alpha \rho^2\right] H_v(\sqrt{\alpha} \rho)$$

with:  $\alpha = \frac{\mu \omega_e}{\hbar}$  and  $\omega_e = \sqrt{\frac{k}{\mu}}$

Energy eigenvalues:

$$E_{\text{vib}} = \hbar \omega_e \left( v + \frac{1}{2} \right)$$



## Finer details of the rovibrational motion

Centrifugal distortion:

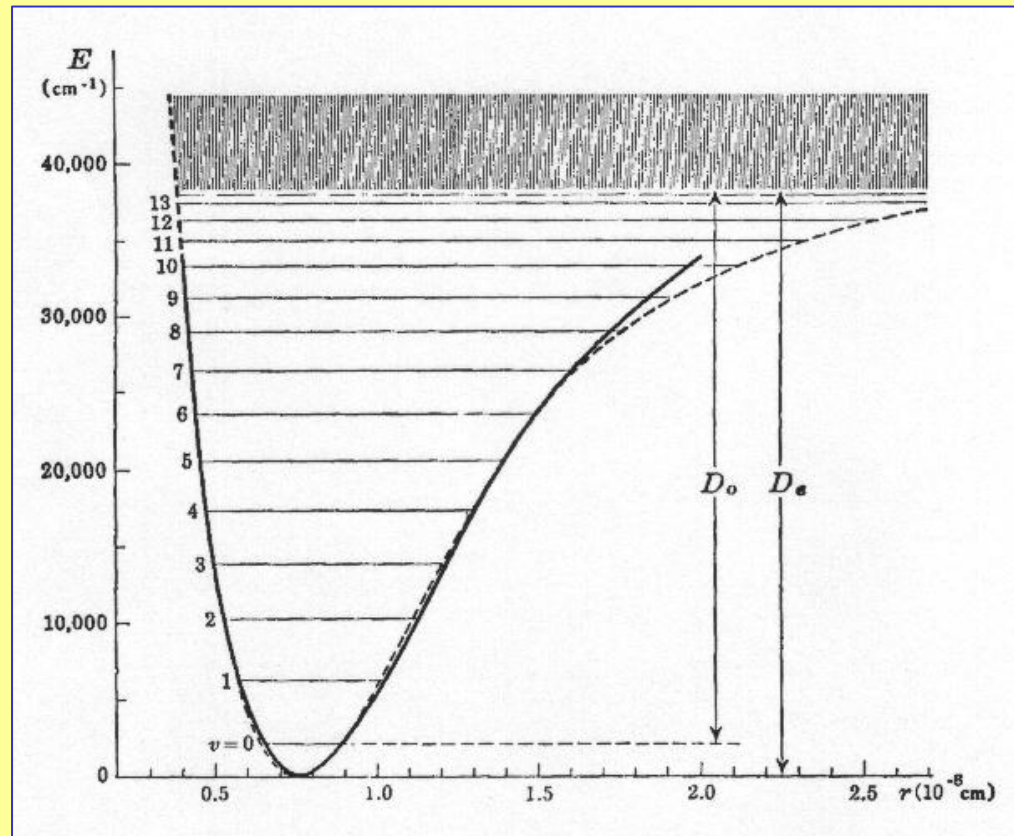
$$E_{\text{rot}} = BN(N+1) - DN^2(N+1)^2$$

Anharmonic vibrational motion

$$E_{\text{vib}} = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \dots$$

Dunham expansion:

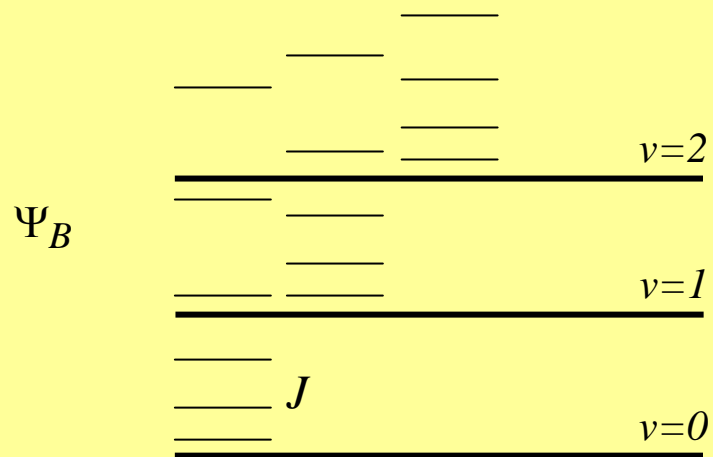
$$E_{vN} = \sum_{k,l} Y_{kl} \left( v + \frac{1}{2} \right)^k N^l (N+1)^l$$



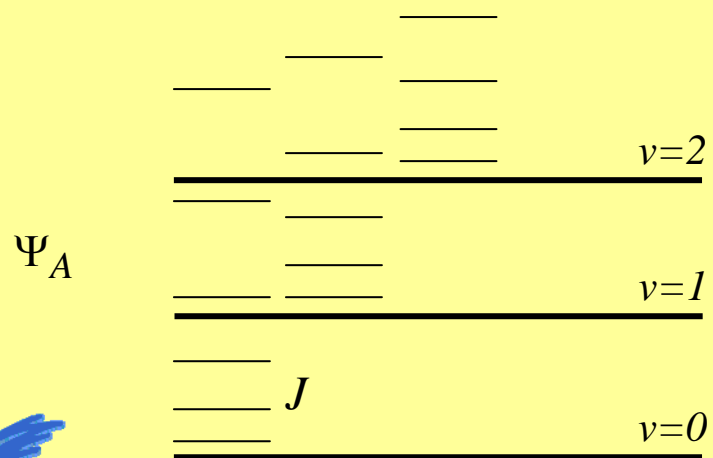
Vibrational energies in the  $\text{H}_2$ -molecule



## Energy levels in a molecule: general structure



Rovibrational  
structure  
superimposed on  
electronic  
structure



## Radiative transitions in molecules

The dipole moment in a molecule:

$$\mu = \mu_e + \mu_N = -\sum_i e\vec{r}_i + \sum_A eZ_A\vec{R}_A$$

In a molecule, there may be a:

- permanent or rotational dipole moment
- vibrational dipole moment

$$\vec{\mu}_N = \vec{\mu}_0 + \left( \frac{d}{dR} \vec{\mu} \right)_{R_e} \rho + \frac{1}{2} \left( \frac{d^2}{dR^2} \vec{\mu} \right) \rho^2$$

In atoms only electronic transitions,  
in molecules transitions within  
electronic state

$$\Psi_{\text{mol}}(\vec{r}_i, \vec{R}_A) = \psi_{\text{el}}(\vec{r}_i; \vec{R}) \psi_{\text{vib}}(\vec{R})$$

Dipole transition between two states

$$\mu_{if} = \int \Psi' \mu \Psi'' d\tau$$

Two different types of transitions

$$\mu_{if} = \int \psi'_{\text{el}} \psi'_{\text{vib}} (\mu_e + \mu_N) \psi''_{\text{el}} \psi''_{\text{vib}} d\tau =$$

$$\int \left( \int \psi'_{\text{el}} \mu_e \psi''_{\text{el}} d\vec{r} \right) \psi'_{\text{vib}} \psi''_{\text{vib}} d\vec{R} +$$

$$\int \psi'_{\text{el}} \psi''_{\text{el}} d\vec{r} \int \psi'_{\text{vib}} \mu_N \psi''_{\text{vib}} d\vec{R}$$

Electronic transitions

Rovibrational transitions



## The Franck-Condon principle for electronic transitions in molecules

1<sup>st</sup> term:

$$\mu_{if} = \int \left( \int \psi'_{el} \mu_e \psi''_{el} d\vec{r} \right) \psi'_{vib} \psi''_{vib} d\vec{R}$$

Only contributions if (parity selection rule)

$$\psi'_{el} \neq \psi''_{el}$$

Franck-Condon approximation:  
The electronic dipole moment independent  
of internuclear separation:

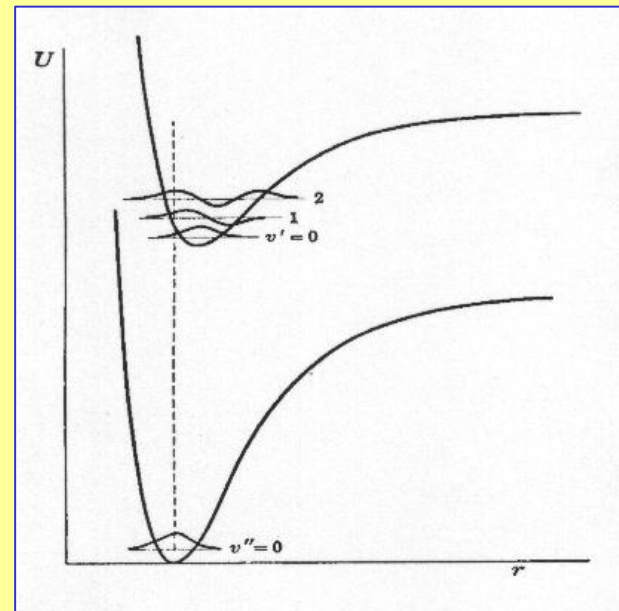
$$\overline{M}_e(R) = \int \psi'_{el} \mu_e \psi''_{el} d\vec{r}$$

Hence

$$\mu_{if} = \overline{M}_e(R) \int \psi'_{vib} \psi''_{vib} d\vec{R}$$

Intensity of electronic transitions

$$I \propto |\mu_{if}|^2 \propto \left| \int \psi'_{vib} \psi''_{vib} d\vec{R} \right|^2 \propto |\langle v' | v'' \rangle|^2$$



Intensity proportional to the square  
of the wave function overlap



## Rotational transitions in molecules

2<sup>nd</sup> term in the transition dipole

$$\mu_{if} = \langle \Psi_{N'M'} | \mu | \Psi_{NM} \rangle$$

Projection of the dipole moment vector on the quantization axis.

For rotation take the permanent dipole.

$$\vec{\mu} = \mu_0 \begin{bmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{bmatrix} \propto \mu_0 Y_{1m}$$

$$\mu_{if} \propto \mu_0 \int \int Y_{N'M'} Y_{1m} Y_{NM} d\Omega$$

$$\propto \begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N' & 1 & N \\ M' & m & M \end{pmatrix}$$

→ Selection rules

$$\Delta N = \pm 1$$

$$\Delta M = 0, \pm 1$$

Purely rotational spectra

Level energies:

$$F_v = B_v N(N+1) - D_v N^2(N+1)^2$$

Transition frequencies:

$$\begin{aligned} \nu &= F_v(N') - F_v(N'') = \\ &B_v [N'(N'+1) - N''(N''+1)] \\ &- D_v [N'^2(N'+1)^2 - N''^2(N''+1)^2] \end{aligned}$$

Ground state with  $N''$  and excited  $N'$

Absorption in rotational ladder:  $N' = N'' + 1$

$$\nu_{\text{abs}} = 2B_v(N''+1) - 4D_v(N''+1)^3$$

spacing between lines  $\sim 2B$



## Rotational spectrum in a diatomic molecule

Ground state with  $N''$  and excited  $N'$   
Absorption in rotational ladder:  $N' = N'' + 1$

$$\nu_{\text{abs}} = 2B_v(N''+1) - 4D_v(N''+1)^3$$

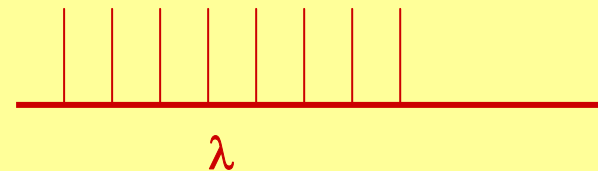
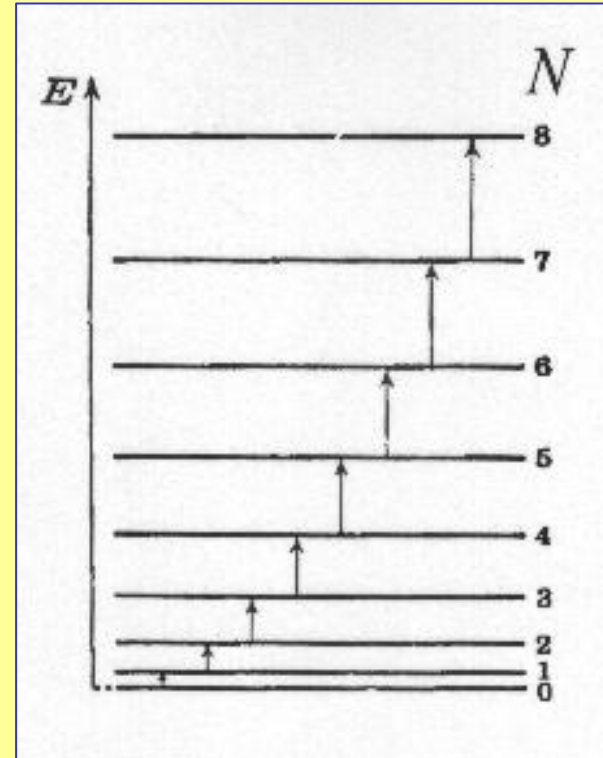
spacing between lines  $\sim 2B$

In an absorption spectrum: R-lines  
In an emission spectrum: P-lines

Homonuclear molecule

$$\mu_N = \sum_A eZ_A \vec{R}_A = eZ_A (\vec{R}_A - \vec{R}_A) = 0$$

For permanent dipole  
No rotational spectrum



## Vibrational transitions in molecules

2<sup>nd</sup> term in the transition dipole

$$\mu_{if} = \int \psi'_{el} \psi''_{el} d\vec{r} \int \psi'_{vib} \mu_N \psi''_{vib} d\vec{R}$$

Within a certain electronic state:

$$\psi'_{el} = \psi''_{el} \longrightarrow \int \psi'_{el} \psi''_{el} d\vec{r} = 1$$

Line intensity:

$$\mu_{if} = \langle v' | \mu_{vib} | v'' \rangle$$

Permanent and induced dipole moments;

$$\vec{\mu}_N = \vec{\mu}_0 + \left( \frac{d}{dR} \vec{\mu} \right)_{R_e} \rho + \frac{1}{2} \left( \frac{d^2}{dR^2} \vec{\mu} \right) \rho^2$$

Permanent dipole does not produce a vibrational spectrum

$$\mu_{if} = \langle v' | \mu_0 | v'' \rangle = \mu_0 \langle v' | v'' \rangle = 0$$

Wave functions for one electronic state are orthogonal.

$$\mu_{if} = \langle v' | \left( \frac{d}{dR} \vec{\mu} \right)_{R_e} \rho | v'' \rangle \propto \langle v' | \rho | v'' \rangle$$

Dipole moment should vary with Displacement  $\rightarrow$  vibrational spectrum





## Vibrational transitions in molecules

Permanent and induced dipole moments;

$$\mu_{if} = \langle v' | \mu_{\text{vib}} | v'' \rangle = \langle v' | a\rho + b\rho^2 | v'' \rangle$$

First order: the vibrating dipole moment

$$\mu_{if} = \langle v' | \mu_{\text{vib}} | v'' \rangle \propto \langle v' | \rho | v'' \rangle$$

Homonuclear molecule

$$\mu_N = \sum_A eZ_A \vec{R}_A = eZ_A (\vec{R}_A - \vec{R}_A) = 0$$

For all derivatives

No vibrational dipole spectrum

In the harmonic oscillator approximation;

$$\langle n | \rho | k \rangle = \int Q_n(\rho) \rho Q_k(\rho) d\rho = \sqrt{\frac{\hbar}{\mu\omega}} \left[ \sqrt{\frac{n}{2}} \delta_{k,n-1} + \sqrt{\frac{n+1}{2}} \delta_{k,n+1} \right]$$

Selection rules:  $\Delta v = v' - v = \pm 1$

Higher order transitions (overtones) from:

- anharmonicity in potential
- induced dipole moments



## Rovibrational spectra in a diatomic molecule

Level energies:

$$T = G(v) + F_v(N)$$

with:

$$F_v = B_v N(N+1) - D_v N^2 (N+1)^2$$

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$$

Transitions from  
 $v''$  (ground) to  $v'$  (excited)

$$\sigma(v'-v'') = \sigma_0 + F_{v'}(N') - F_{v''}(N'')$$

with

$$\sigma_0 = G(v') - G(v'')$$

the band origin; the rotationless  
transition (not always visible)

Transitions

R-branch ( $N' = N'' + 1$ ) - neglect  $D$

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

For  $B_{v'} = B_{v''}$

$$\sigma_R = \sigma_0 + 2B_{v'}(N+1)$$

P-branch ( $N' = N'' - 1$ ) - neglect  $D$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$

For  $B_{v'} = B_{v''}$

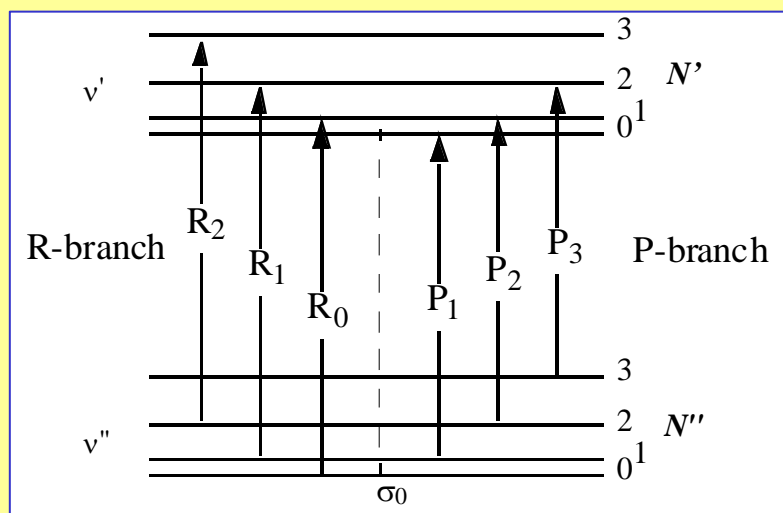
$$\sigma_R = \sigma_0 + 2B_{v'}(N+1)$$



## Rovibrational spectra

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$



More precisely spacing between lines:

$$\sigma_R(N+1) - \sigma_R(N) \approx 3B_{v'} - B_{v''} < 2B_{v'}$$

$$\sigma_P(N+1) - \sigma_P(N) \approx B_{v'} + B_{v''} > 2B_{v'}$$

If, as usual:  $B_{v'} < B_{v''}$

Rotational constant in excited state is smaller.



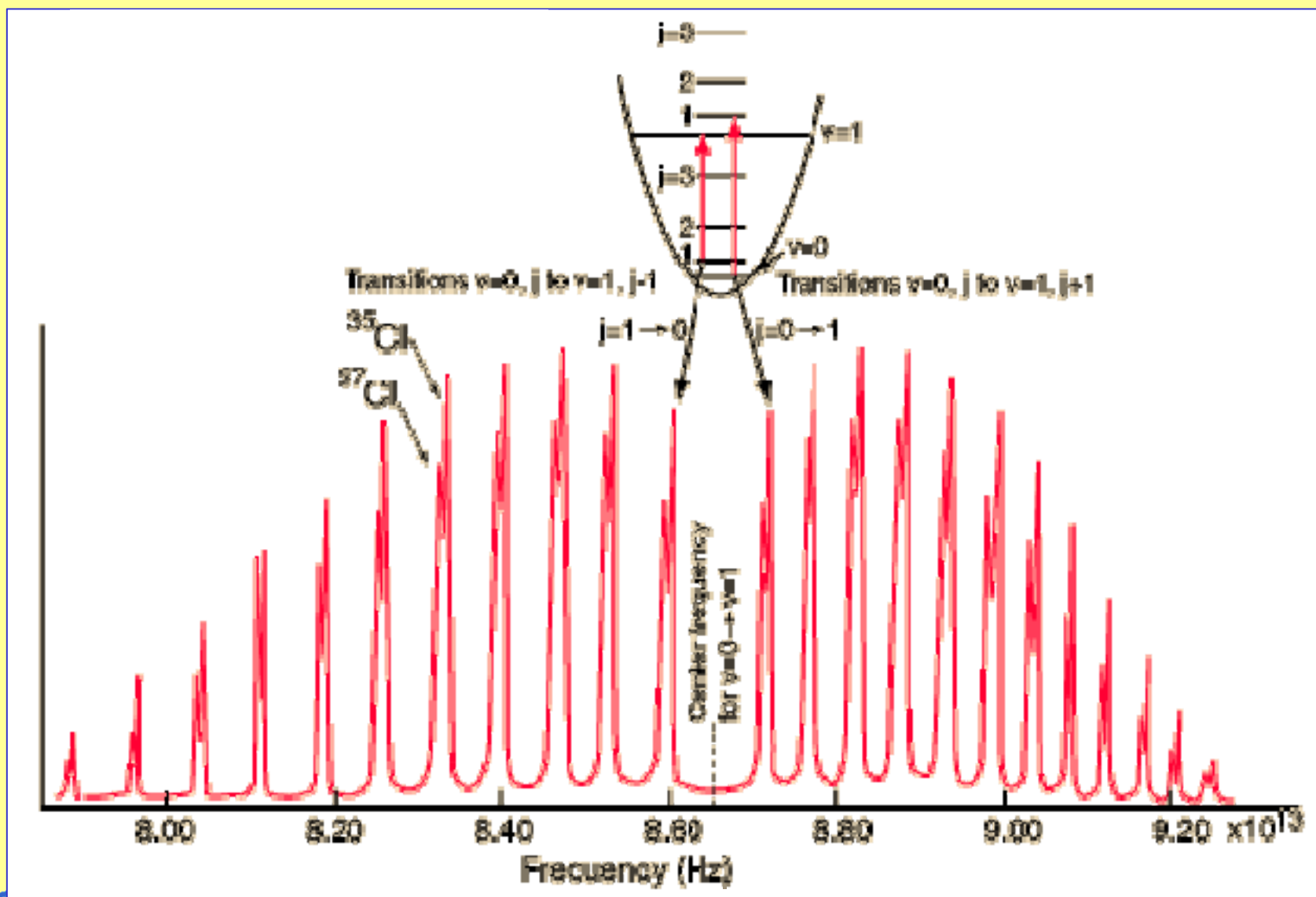
Spacing in P branch is larger  
Band head formation in R-branch

Spacing between R(0) and P(1) is  $4B$

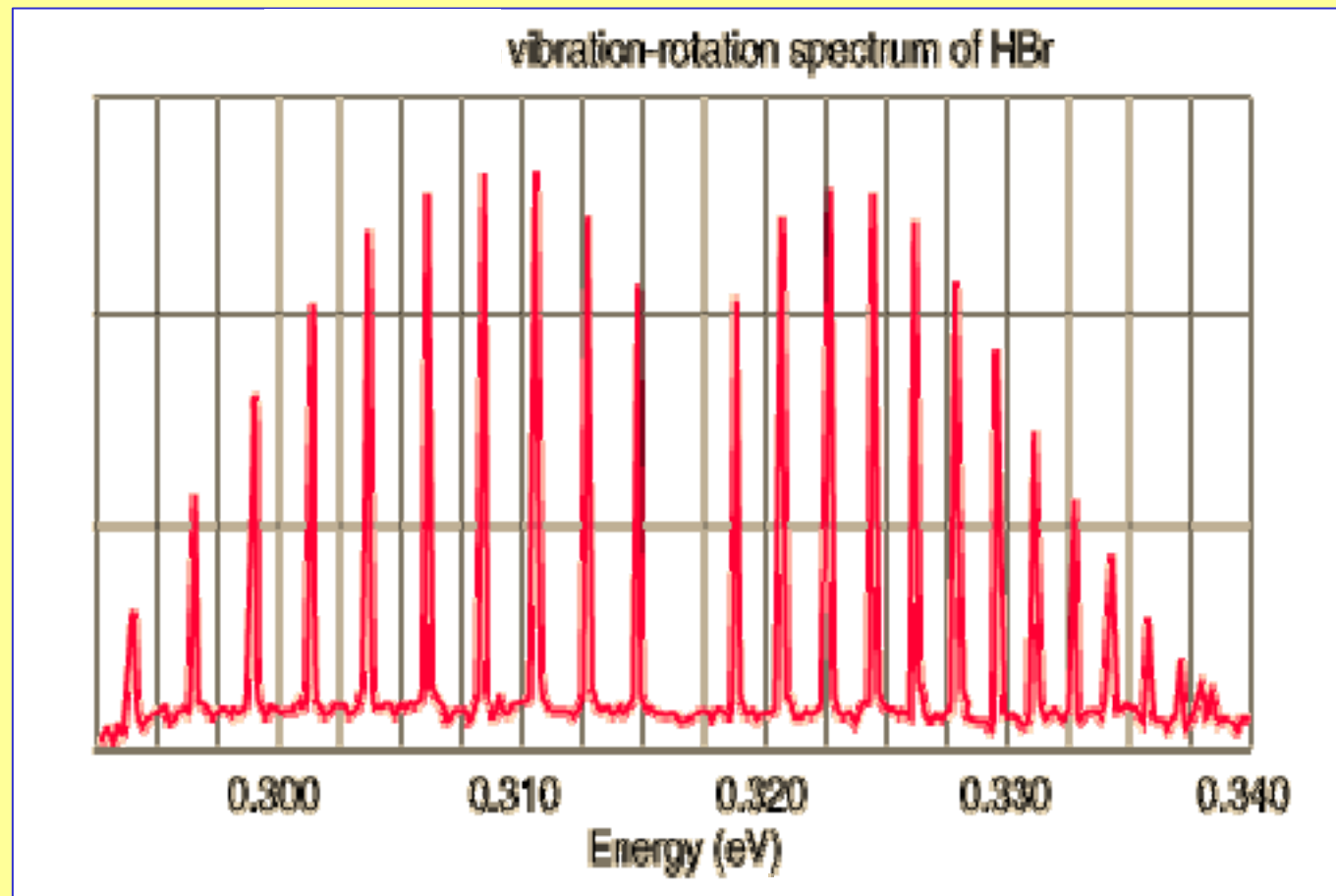
"band gap"



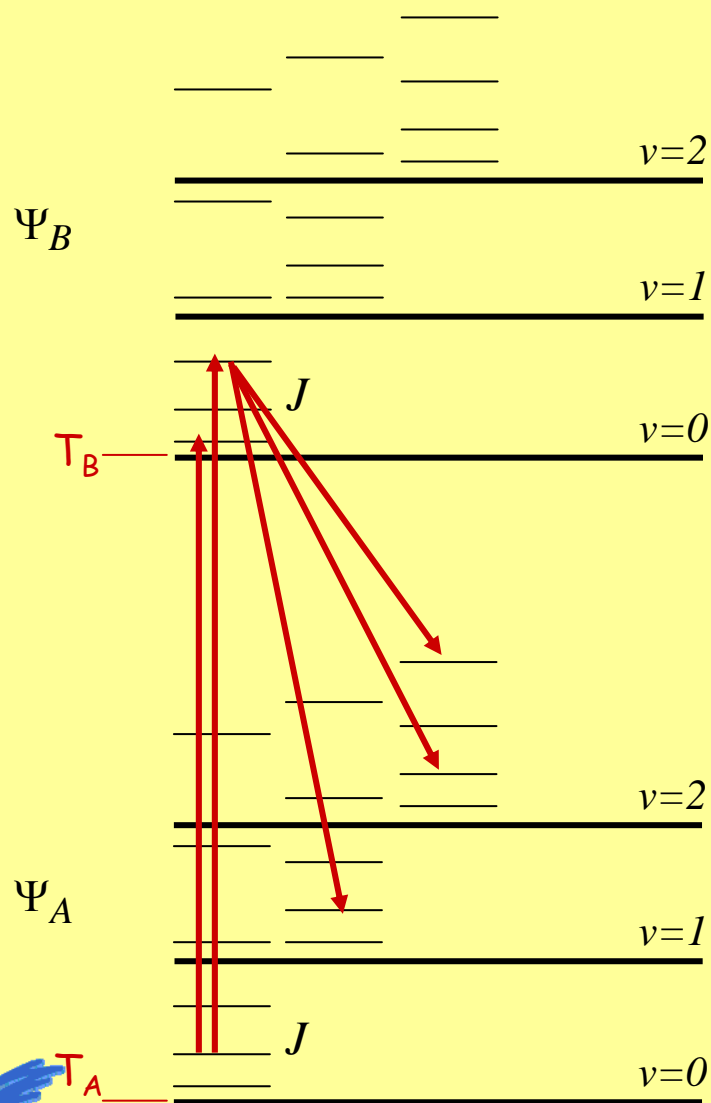
Example: rovibrational spectrum of HCl; fundamental vibration



Example: rovibrational spectrum of HBr; fundamental vibration



## Rovibronic spectra



Vibrations  $\rightarrow$  governed by the Franck-Condon principle

Rotations  $\rightarrow$  governed by angular momentum selection rules

Transition frequencies

$$\nu = T' - T''$$

$$T' = T_B + G'(v') + F_v'(N')$$

$$T'' = T_A + G''(v'') + F_v''(N'')$$

R and P branches can be defined in the same way

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$



## Band head structures and Fortrat diagram

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$

Define:

$m = N + 1$       for the R-branch

$m = -N$         for the P-branch

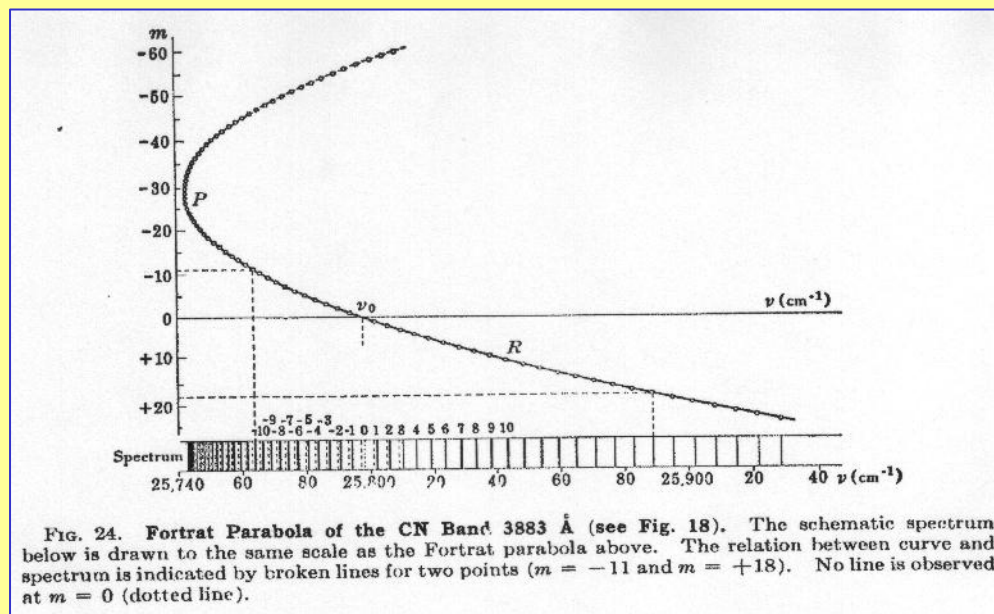
then for both branches:

$$\sigma = \sigma_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

if:  $B_{v'} < B_{v''}$

$$\sigma = \sigma_0 + \alpha m - \beta m^2$$

A parabola represents both branches



- no line for  $m=0$  ; band gap
- there is always a band head, in one branch



## Population distributions; vibrations

Probability of finding a molecule in a vibrational quantum state:

$$P(v) = \frac{e^{-E(v)/kT}}{\sum_v e^{-E(v)/kT}}$$

$$= \frac{1}{Z} e^{\frac{-\omega_e(v+1/2)}{kT}}$$



Boltzmann distribution

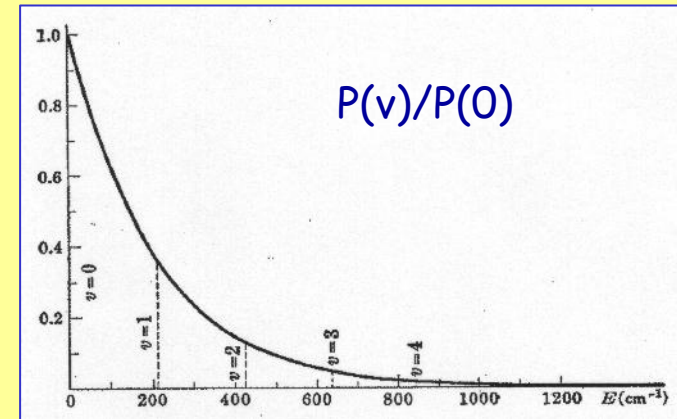


TABLE 14. RATIO OF THE NUMBER OF MOLECULES IN THE FIRST TO THAT IN THE ZEROth VIBRATIONAL LEVEL FOR 300° K. AND 1000° K.

Gas	$\Delta G_{1/2} (\text{cm}^{-1})$	$e^{-\Delta G_{1/2} hc / kT}$	
		For 300° K.	For 1000° K.
H <sub>2</sub>	4160.2	$2.16 \times 10^{-9}$	$2.51 \times 10^{-3}$
HCl	2885.9	$9.77 \times 10^{-7}$	$1.57 \times 10^{-2}$
N <sub>2</sub>	2330.7	$1.40 \times 10^{-5}$	$3.50 \times 10^{-2}$
CO	2143.2	$3.43 \times 10^{-5}$	$4.58 \times 10^{-2}$
O <sub>2</sub>	1556.4	$5.74 \times 10^{-4}$	$1.07 \times 10^{-1}$
S <sub>2</sub>	721.6	$3.14 \times 10^{-2}$	$3.54 \times 10^{-1}$
Cl <sub>2</sub>	556.9	$6.92 \times 10^{-2}$	$4.49 \times 10^{-1}$
I <sub>2</sub>	213.2	$3.60 \times 10^{-1}$	$7.36 \times 10^{-1}$

Note: not always thermodynamic equilibrium





## Population distributions; rotational states in a diatomic molecule

Probability of finding a molecule  
in a rotational quantum state:

$$P(J) = \frac{(2J+1)e^{-E_{\text{rot}}/kT}}{\sum_{J'} (2J'+1)e^{-E_{\text{rot}}/kT}}$$
$$= \frac{1}{Z_{\text{rot}}} (2J+1)e^{-BJ(J+1)+DJ^2(J+1)^2}$$

Find optimum via

$$\frac{dP(J)}{dJ} = 0$$

