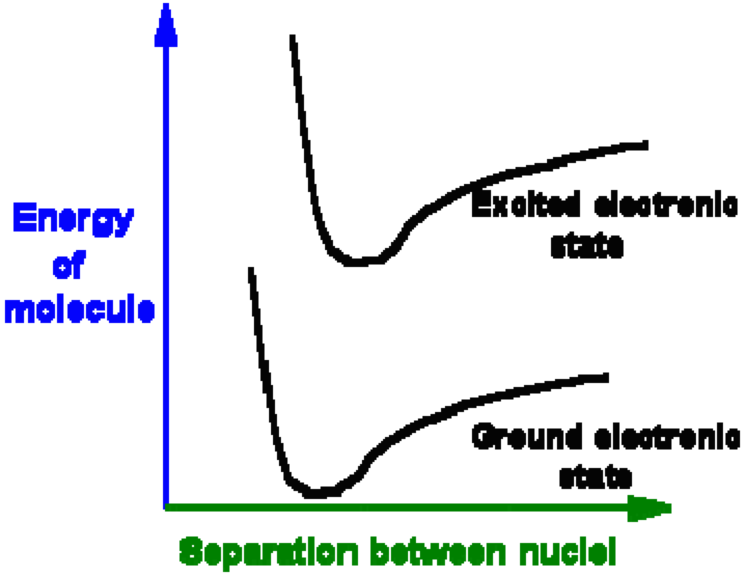
Molecular Spectroscopy.
Born-Oppenheimer Approximation

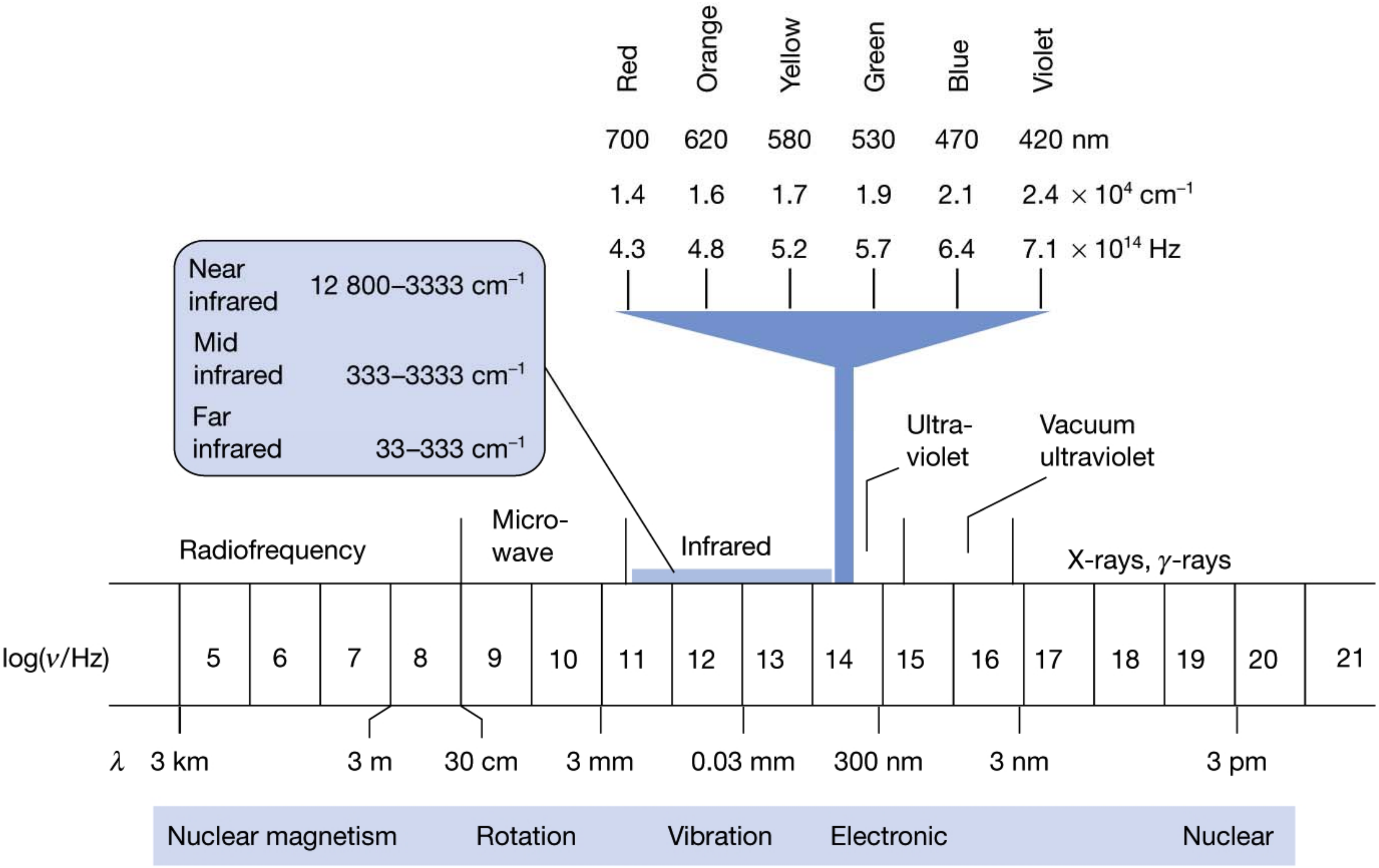
$\Psi_{tot} = \Psi_{el}\,\Psi_{vib}\,\Psi_{rot}$ (Motions are independant)

$E_{tot} = E_{el} + E_{vib} + E_{rot}$ ($E_{el} >> E_{vib} >> E_{rot}$)

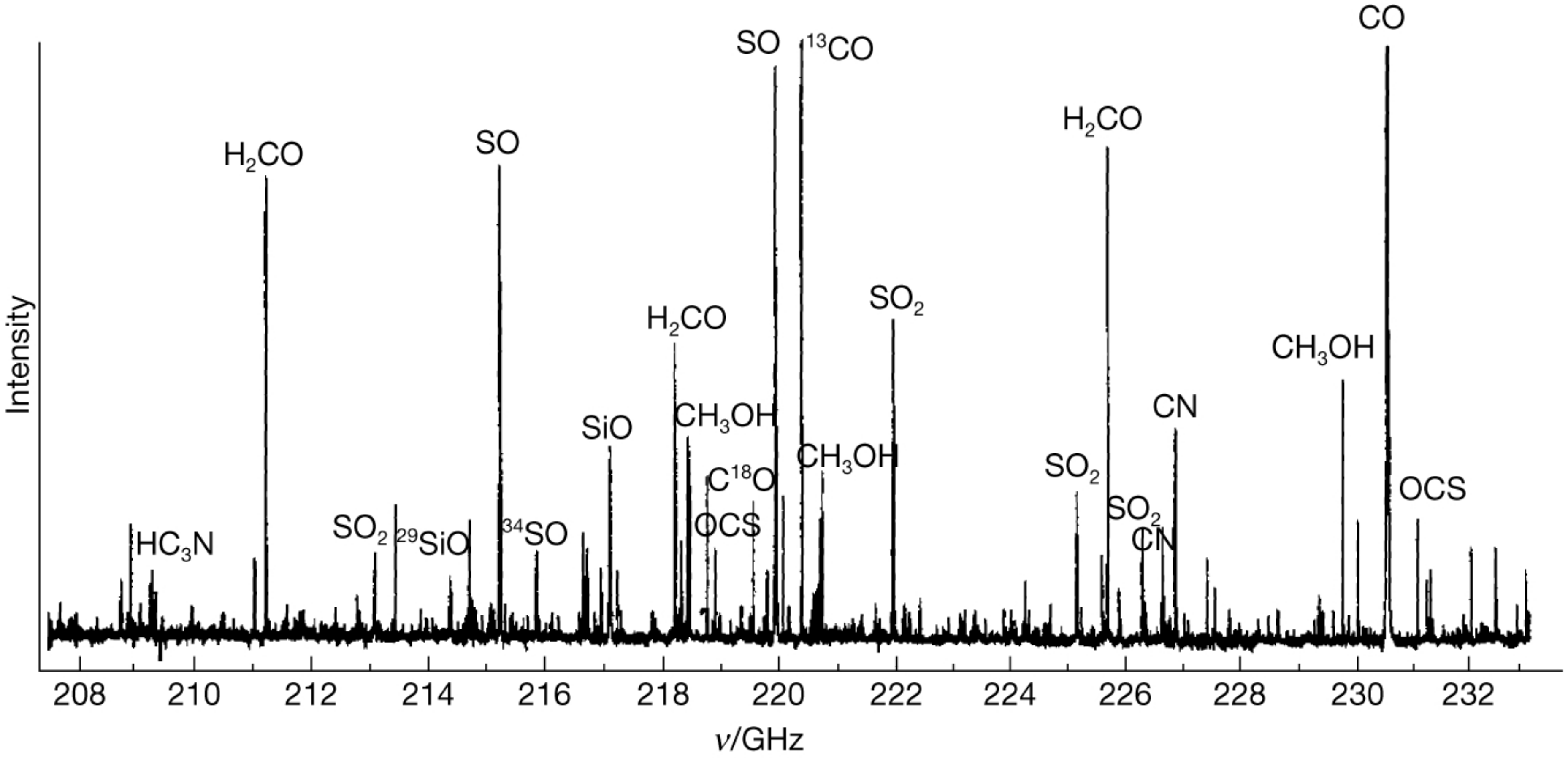
Potential energy curves



Spectral range of rotational, vibrational, and electronical motion



Rotational spectra are in the microwave region



The rotational spectrum of the Orion Nebula identifies molecules in the cloud.

(G. A. Blake *et al., Astrophys. J.* <B>315</B> (1987) 621.)

Rotational Energy (classical)

Classical mechanics, one particle: $E = \frac{I\omega^2}{2}$

where $I = m r^2$ is the moment of inertia

Classical mechanics, arbitrary object: $E = \frac{1}{2} I_A \, \omega_A^2 + \frac{1}{2} I_B \, \omega_B^2 + \frac{1}{2} I_C \, \omega_C^2$

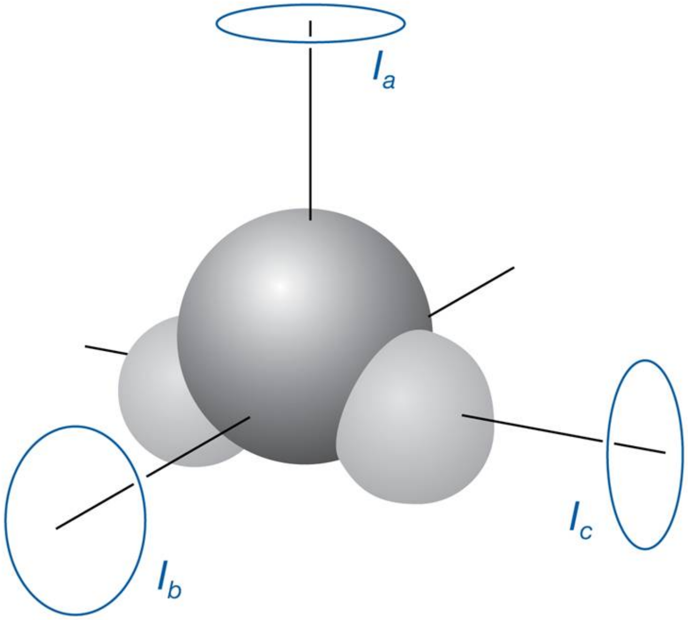
where A, B, and C are principal axes of rotation and $I_A = \sum_i m_i \, r_i^2$

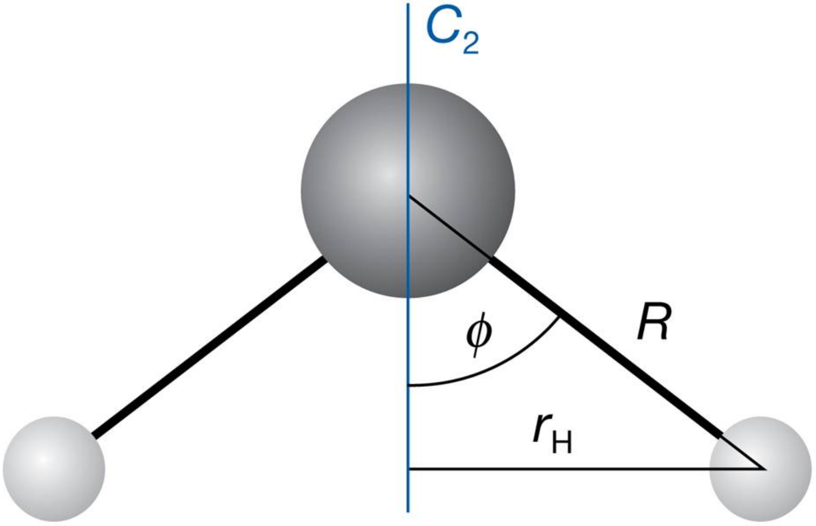
using $J_k = I_k \, \omega_k$ we get: $E = \frac{1}{2} \frac{J_A^2}{I_A} + \frac{1}{2} \frac{J_B^2}{I_B} + \frac{1}{2} \frac{J_C^2}{I_C}$

Moments of Inertia

H_2O

$$I_a = 2\, m_H R^2 \sin^2 \phi$$





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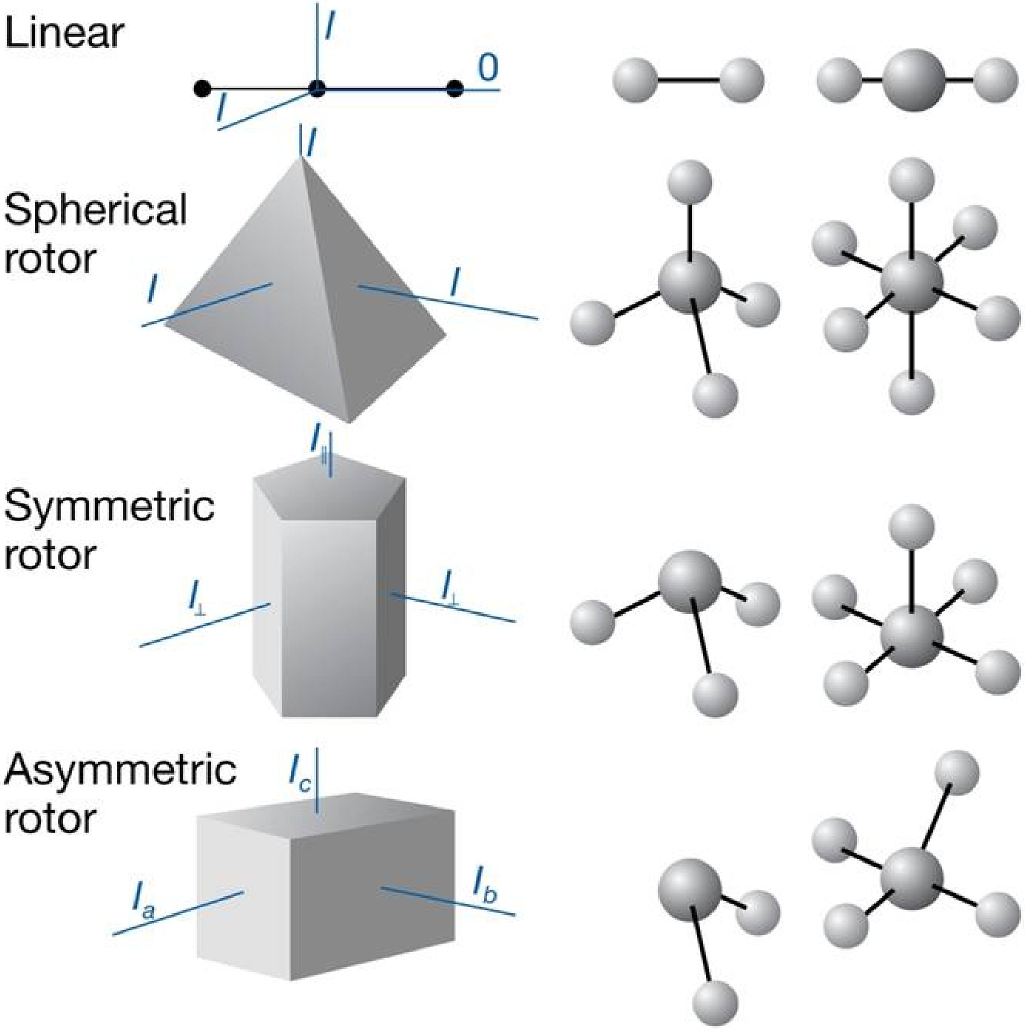
In any molecule there are three General Axes of Inertia. They are perpendicular to each other and cross each other in the Molecular Center of Inertia.

Classification of the Moments of Inertia



Diatomics, CO_2, N_2O, C_2H_2:
$I_A = I_B$, $I_C = 0$

CH_4, CCl_4: tetrahedral
SF_6: octahedral
$I_A = I_B = I_C = I$

NH_3, CH_3I, C_6H_6:

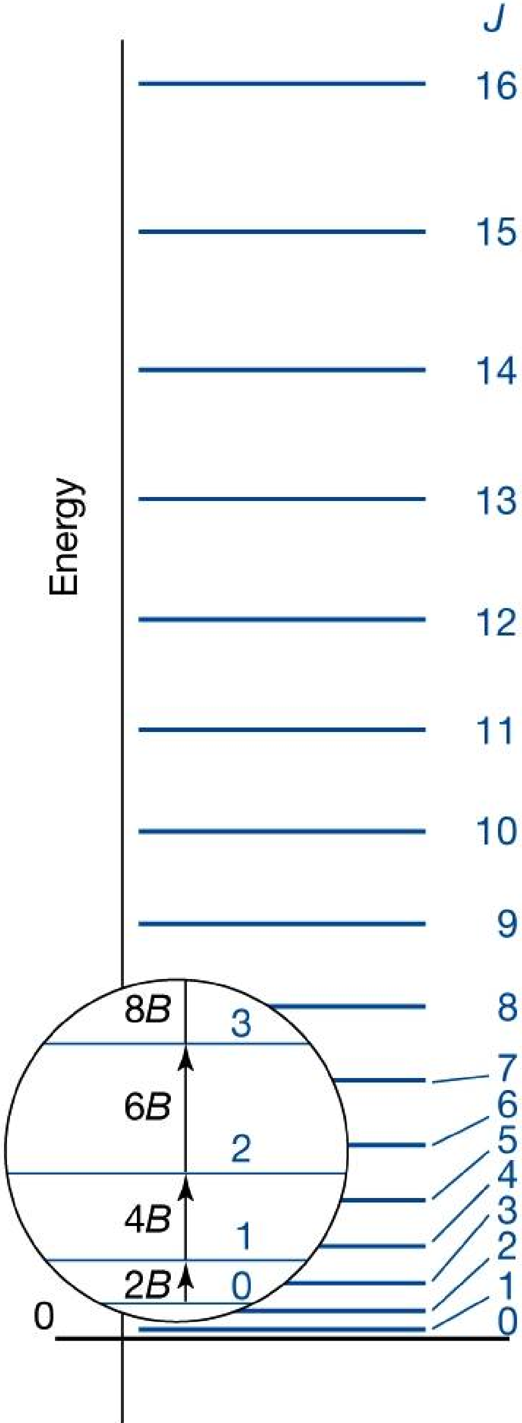
$I_A = I_B = I_{\perp} \neq I_C = I_{\parallel}$

H_2O, NO_2, H_2CO, CH_3OH

$I_A \neq I_B \neq I_C$

Comment: quite often „rotor“ is called „top“. Thus, we have a spherical top, a symmetric top, ….

Spherical Rotor: $I_A = I_B = I_C = I$



$$E = \frac{J_A^2 + J_B^2 + J_C^2}{2I} = \frac{J^2}{2I}$$

in Quantum Mechanics $J^2 \Rightarrow \hbar^2 J(J+1)$ $J=0,1,2,..$

Note that J in Classical Mechanics represents the angular momentum, while in Quantum mechanics it's just a number.

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

Rotational constant $B = \frac{\hbar}{4\pi c I} (cm^{-1})$

$$E_J = 2\pi \hbar c B J(J+1)$$

Rotational term: $F(J) = B J(J+1)$ **cm^{-1}**

Symmetric Rotor: $I_A = I_B = I_\perp$, $I_C = I_\parallel$, $I_\perp \neq I_\parallel$

$I_\perp > I_\parallel$ → prolate rotor, $I_\perp < I_\parallel$ → oblate rotor

$$E = \frac{J_A^2 + J_B^2}{2I_\perp} + \frac{J_C^2}{2I_\parallel} = \frac{\mathbf{J}^2}{2I_\perp} + J_C^2\left(\frac{1}{2I_\parallel} - \frac{1}{2I_\parallel}\right)$$

where $J^2 = J_A^2 + J_B^2 + J_C^2$

In quantum mechanics $J^2 \rightarrow \hbar^2 J(J+1)$ and $J_C \rightarrow \hbar K$

Therefore, the rotational term is given by:

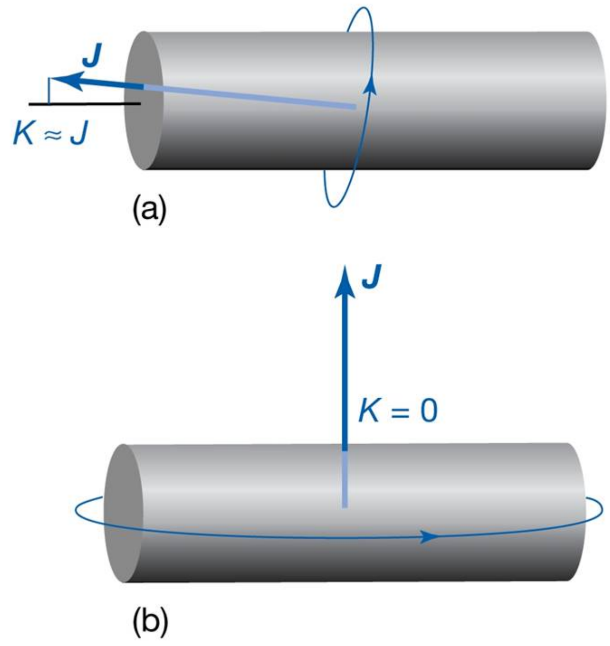
$$F_{JK} = B\,J(J+1) + (A - B)K^2$$

where A and B are two rotational constants:

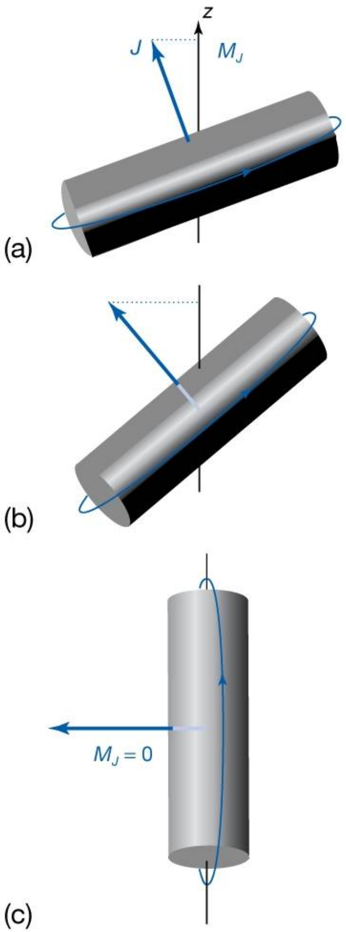
$$A = \frac{\hbar}{4\pi c I_\parallel} \qquad B = \frac{\hbar}{4\pi c I_\perp}$$

Symmetric Rotor: the role of the quantum numbers K and M_J

$F(J) = BJ(J+1) + (A - B)K^2$



The role of the quantum number K



The role of the quantum number M_J

Symmetric Rotor: particular cases

$$|K| \approx J$$

$$F_{J,K} = B \cdot J + A \cdot J^2 \approx A \cdot J^2$$

$$|K| = 0$$

$$F_J = B \cdot J\,(J+1)$$

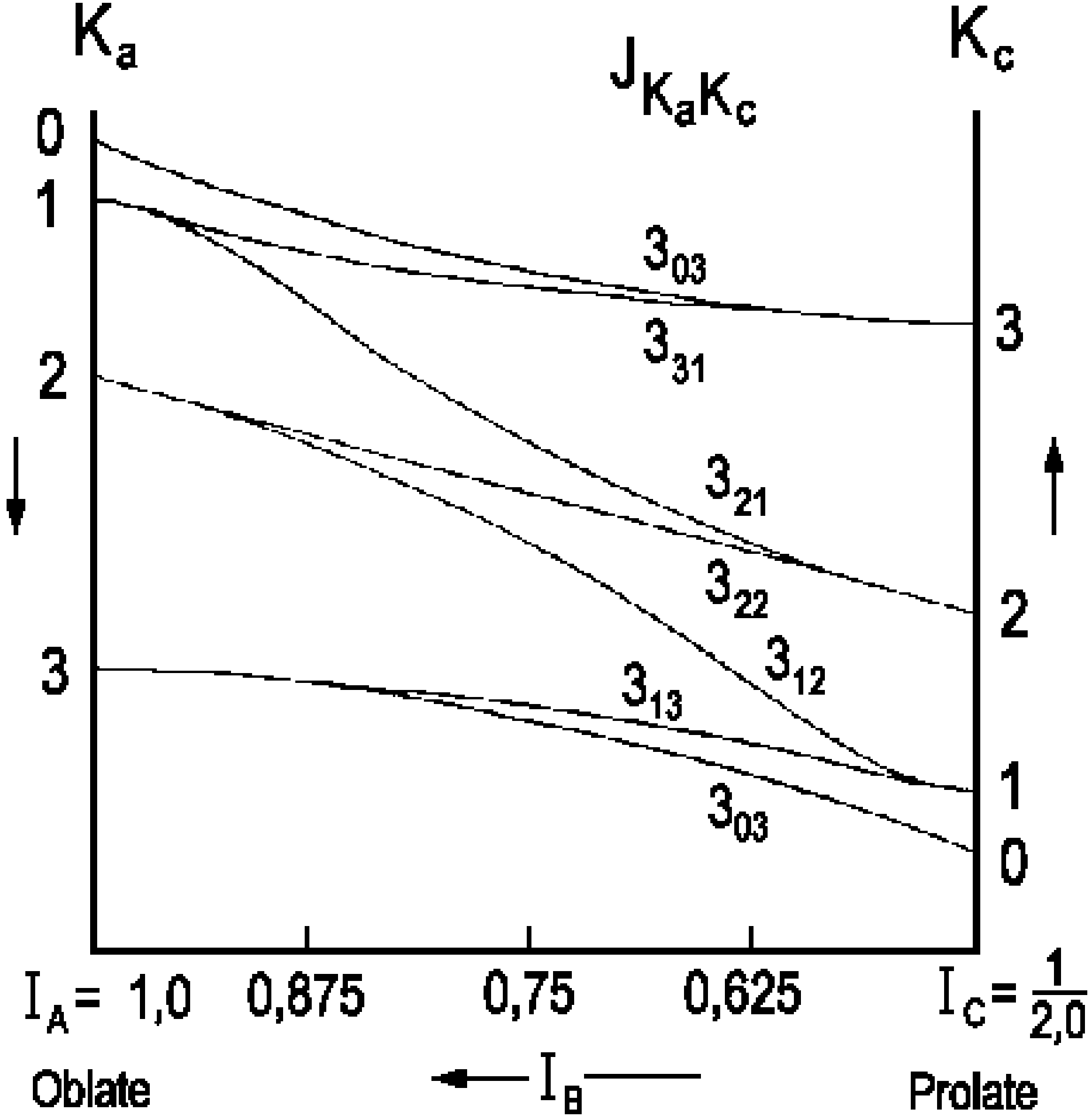
This is the case for diatomic molecules

Elastic Rotor

$$F_J \approx B \cdot J(J+1) - D \cdot J^2(J+1)^2 + \cdots$$

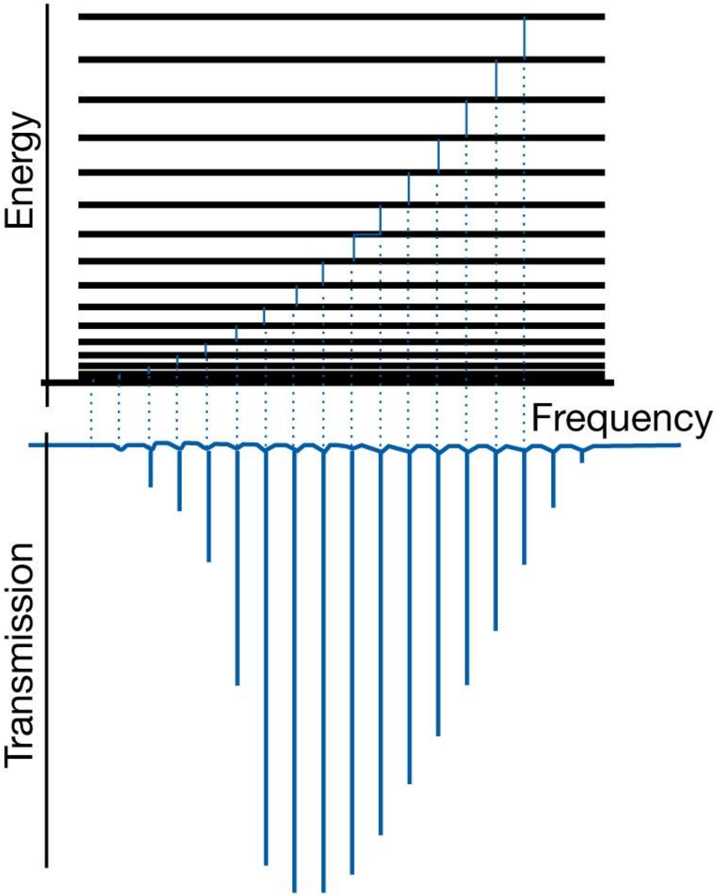
where the constant $D \ll B$. D is called centrifigural distortion constant

Asymmetric Rotor



Rotational Spectrum

The electric dipole moment μ must be nonzero! →
The molecule must be polar → homonuclear diatomic molecules and spherical tops have no rotational spectra



General Selection Rules:

$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1$$

$\Delta J = 1$ absorption
$\Delta J = -1$ emission

Additional Selection Rule for a symmetric top:

$$\Delta K = 0$$

Transition frequency

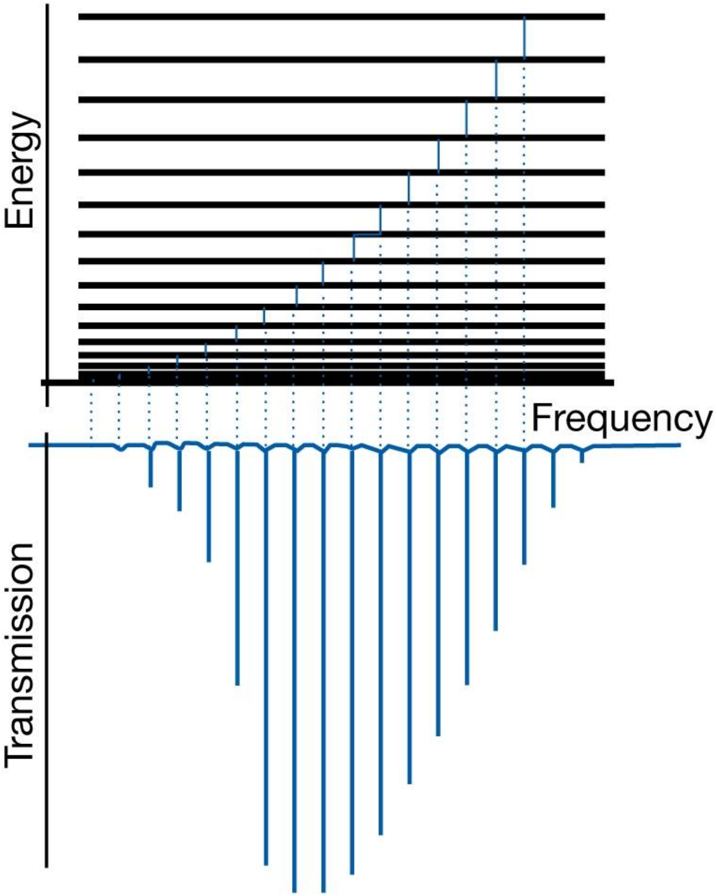
$$\nu(J) = B\cdot(J+1)(J+2) - B\cdot J(J+1) = 2B(J+1)$$

$$\Delta\nu = 2B$$

Usually B ~ 0.1 – 10 cm^{-1} and the corresponding transitions lie in the microwave spectral region

Intensity of the Rotational Spectrum

$$I = C\, g_J\,(N_J - N_{J'}) \left| \langle v', J' M_{J'} | D_Z | v, J, M_J \rangle \right|^2$$

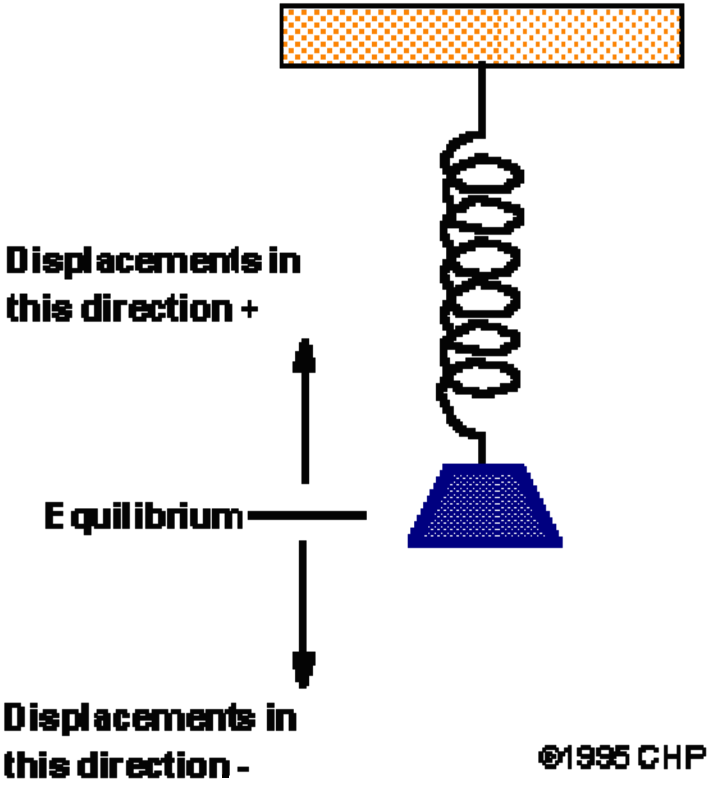


$$N_J = N_0\, e^{-\frac{E_J}{kT}}$$

Where g_J is the degeneracy of the state $|v, J, M_J>$: $g_J = 2J+1$

Vibrational Movement in Molecules. Harmonic Oscillator

Point weight on a spring



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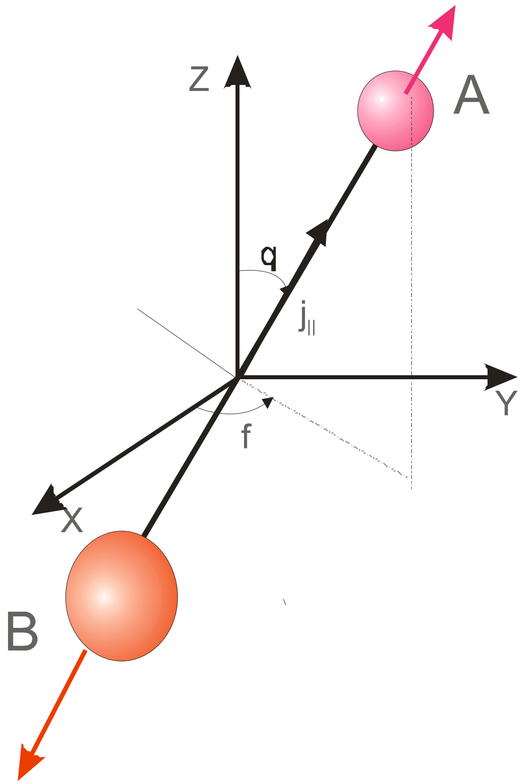
$$F = -k x$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{kx^2}{2}\right)\psi_n(x)=E_n\psi_n(x)$$

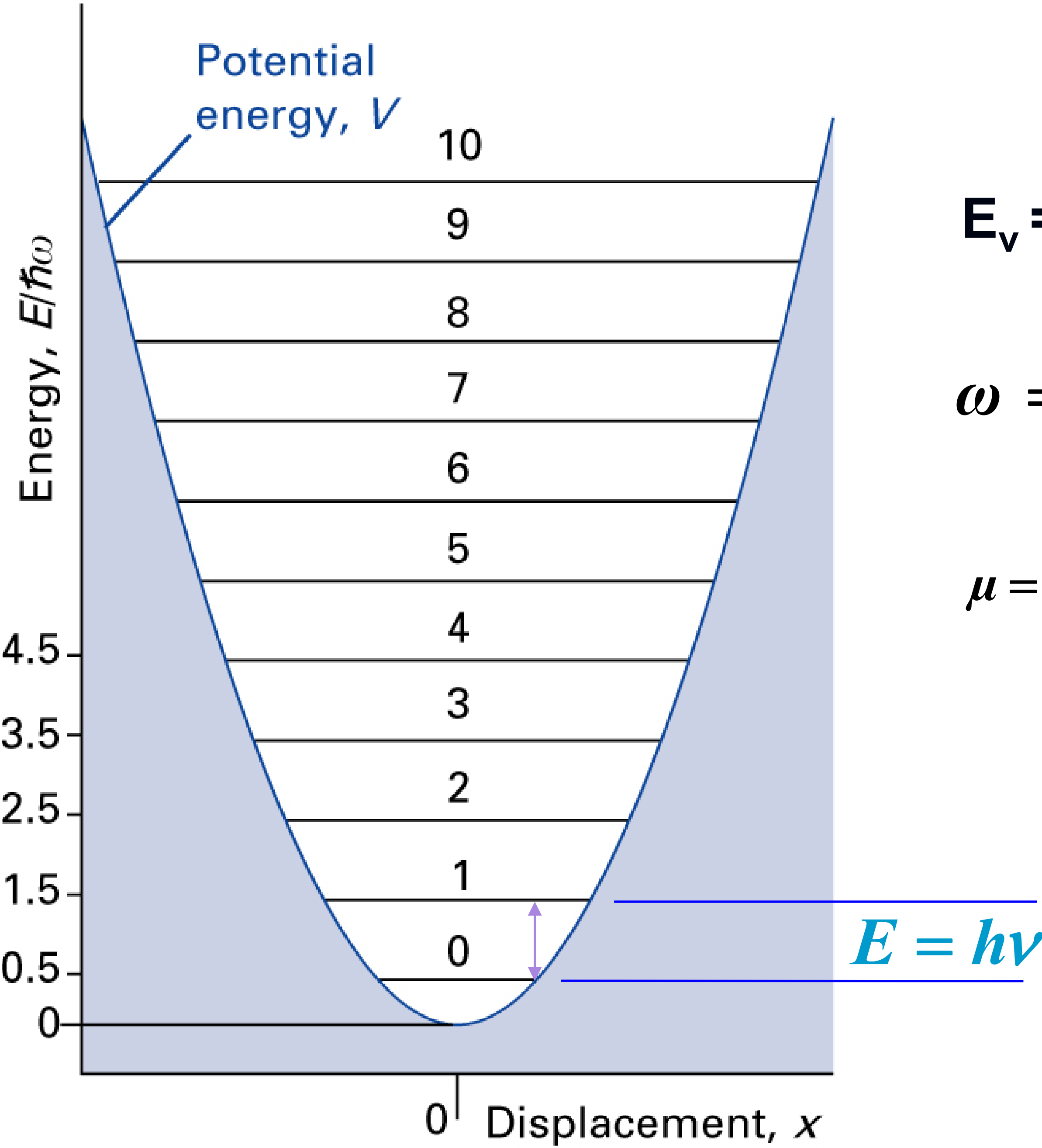
Diatomic molecule



Reduced mass:

$\mu = m_A m_B/(m_A+m_B)$

Diatomic Molecule Energy Levels

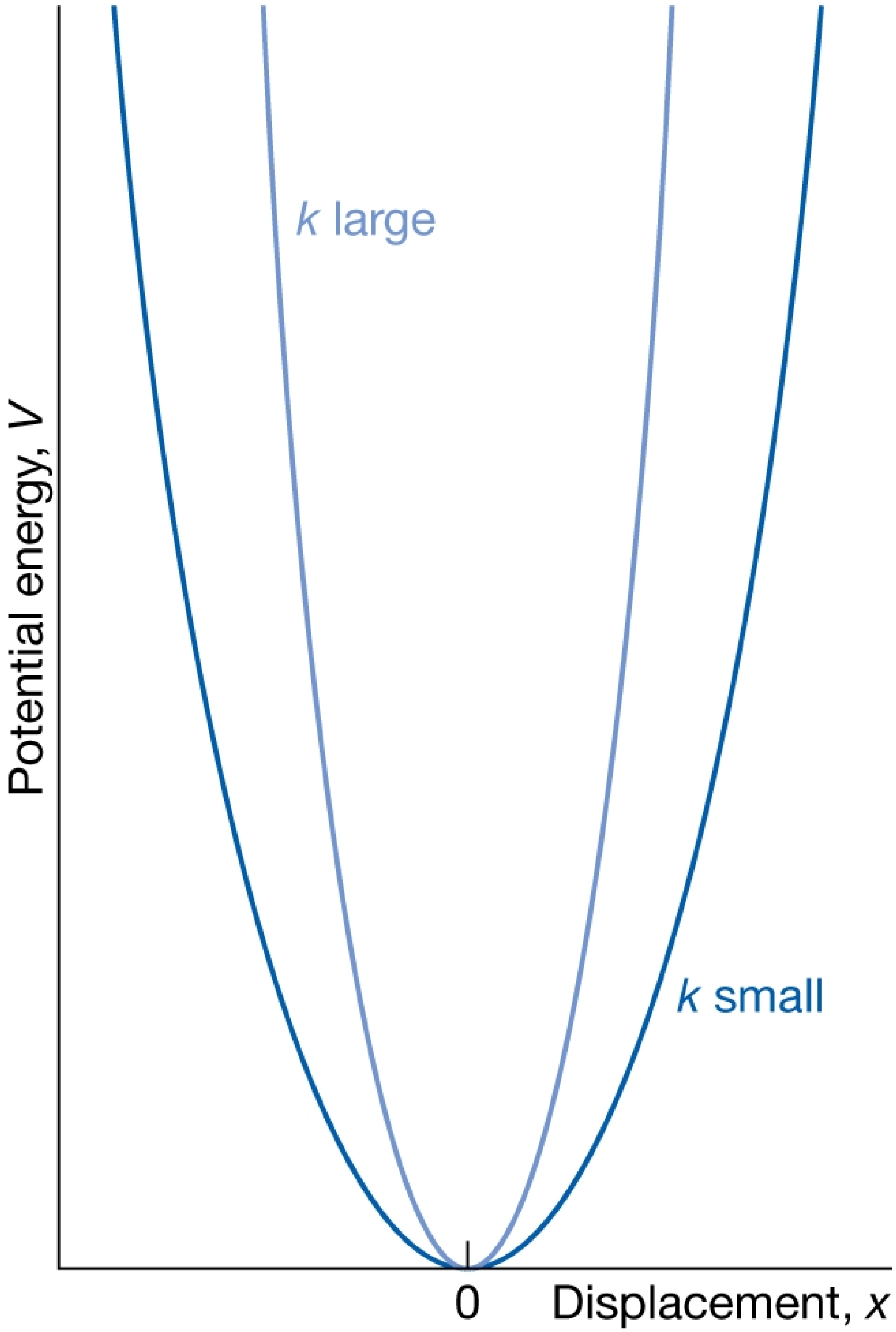


$$E_v = (v + ½)\ \hbar\ \omega, \quad v = 0,1,2,\ldots$$

$$\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_A \cdot m_B}{m_A + m_B}$$

$$E = h\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$



$$\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$$

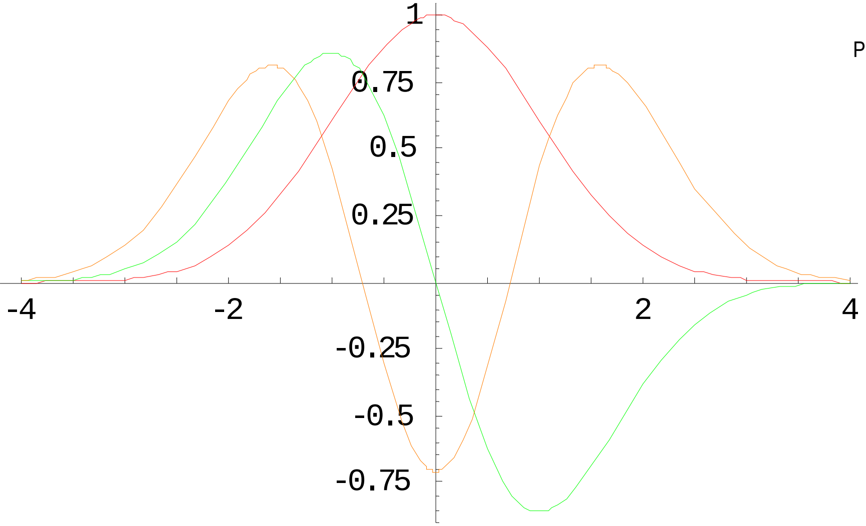
Harmonic Oscillator: the Wavefunctions

$$\psi_v(z) = N_v\, H_v(z)\, e^{-z^2/2}; \qquad z = \frac{x}{\alpha}; \qquad \alpha = \left(\frac{\hbar^2}{\mu k}\right)^{\frac{1}{4}}$$

***H_v* are the Hermite polynomials:**

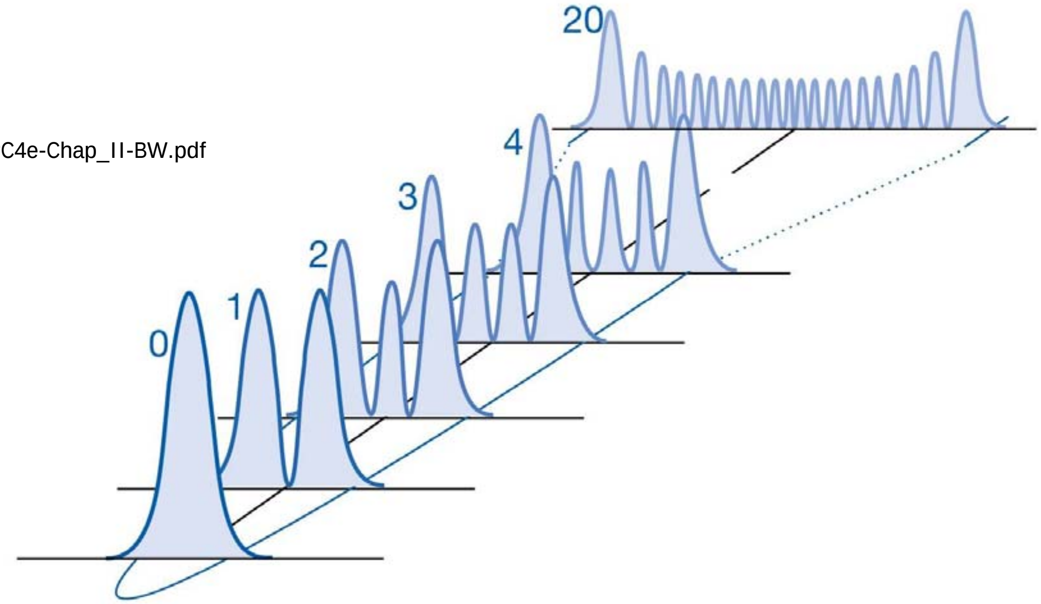
$H_0(z) = 1$, $H_1(z) = 2z$, $H_2(z) = 2z^2 - 2$, $H_3(z) = 8z^2 - 12z$, etc.

v = 2 1 0



ψ(z)

PC4e-Chap_II-BW.pdf

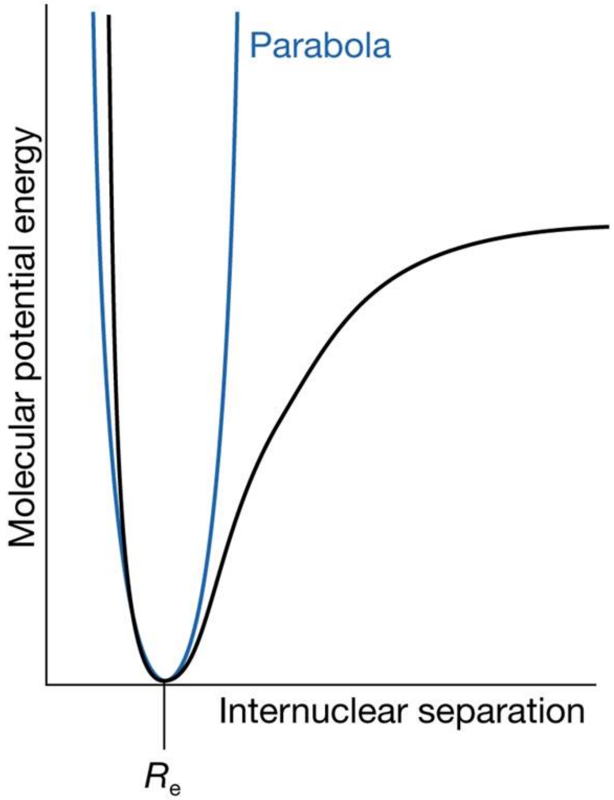


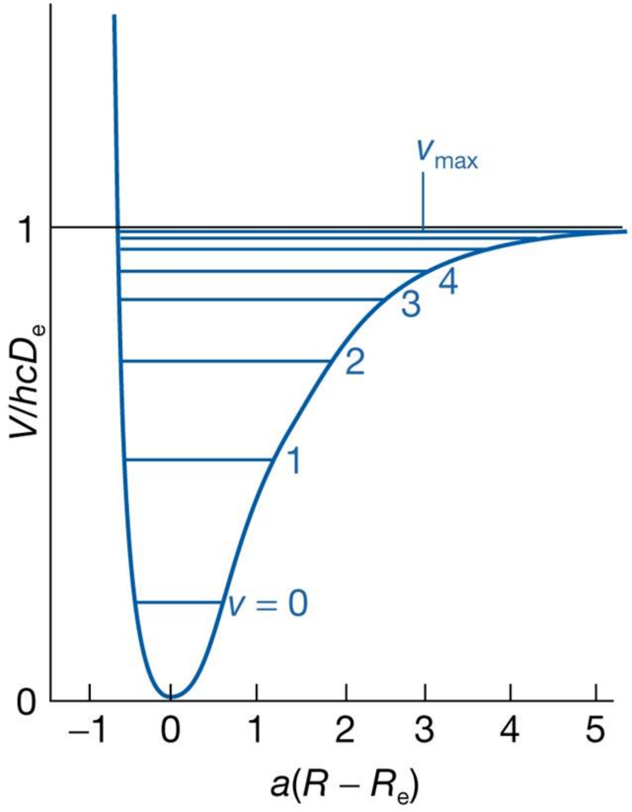
$|\psi|^2$

Vibrational Energy Levels of a Diatomic Molecule

Necessary condition for vibrational transitions:
a molecule must have a permanent dipole moment

Selection rule for harmonic oscillator: $\Delta v = v' - v'' = \pm 1$ → the fundamental line
unharmonic oscillator: $\Delta v = v' - v'' = \pm 2, \pm 3, \pm 4 \ldots$ → harmonics





$E_v = (v+\frac{1}{2})\,\omega_e$, $\omega_e = {}^{1}/_{2\pi c}\,({}^{k}/_{\mu})^{1/2}$ [cm^{-1}]

$E_v = (v + \frac{1}{2})\,\omega_e + (v + \frac{1}{2})^2\,\omega_e{}^2 x_e{}^2 + \cdots$

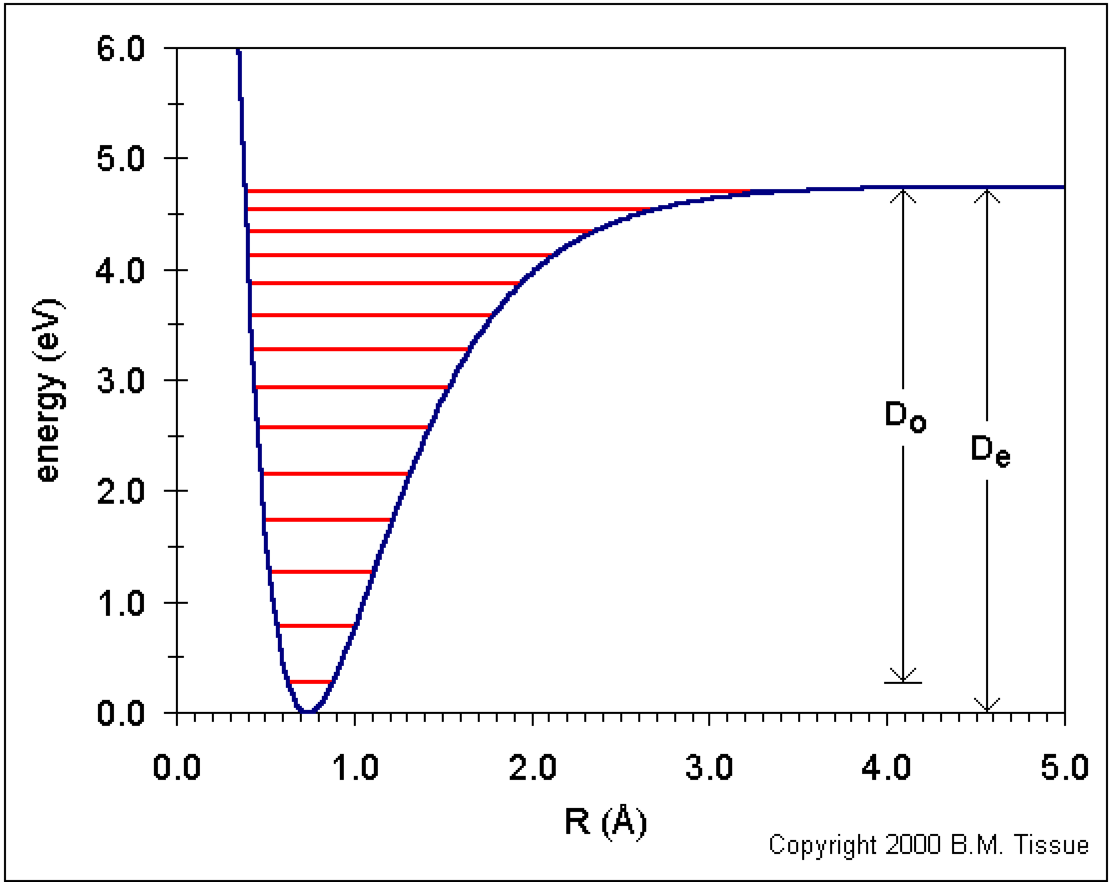
Morse Potential

$$V(R) = D_e\left(1 - 2^{-\beta(R-R_0)}\right)^2$$

$$\beta = \pi \nu_e \sqrt{\frac{2\mu}{D_e}}$$

$E_v = (v + ½)\,\omega_e - (v + ½)^2\,\omega_e^{\,2}\,x_e^{\,2} + (v + ½)^3\,\omega_e^{\,3}\,y_e^{\,3}$ + higher terms, v=0,1,2…

Note: the higher term ($\omega_e^2 x_e^2$) is ***not*** a product, it's just a constant, (the same is true for $\omega_e^3 y_e^3$,…). In same handbooks these constants are defined as: **$\omega_e x_e$, $\omega_e y_e$,…**



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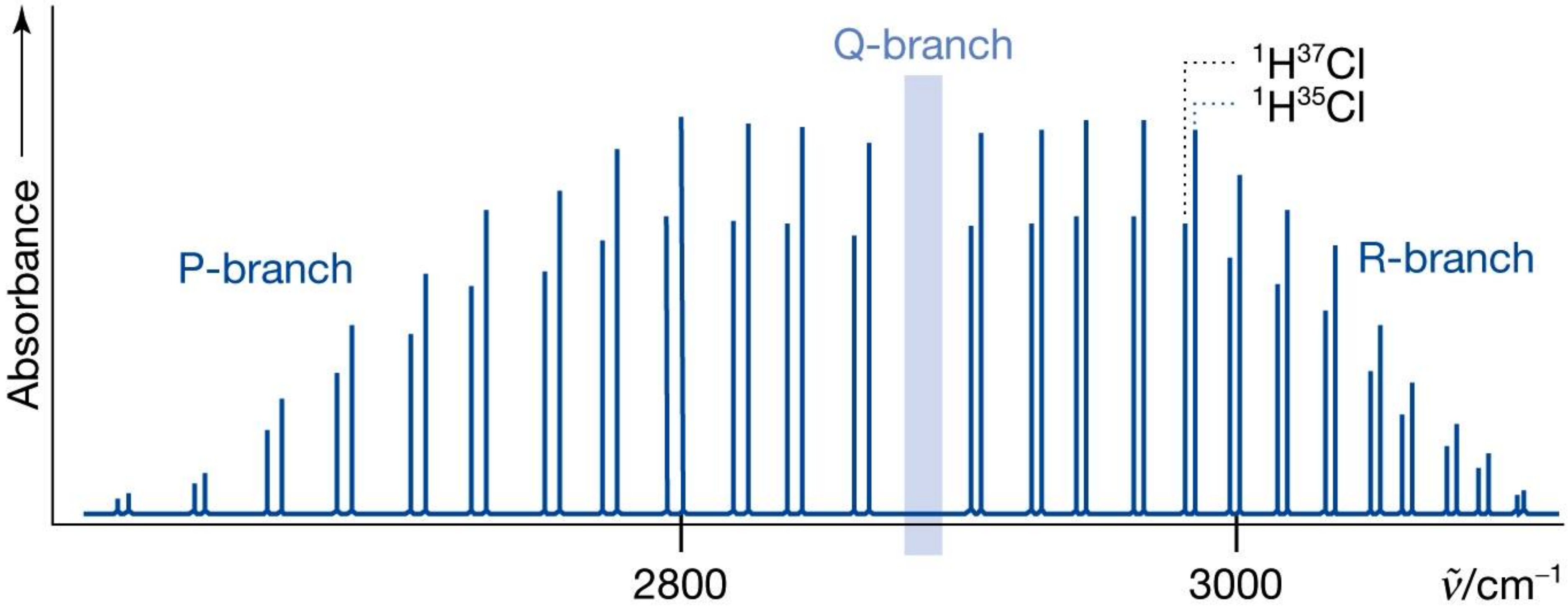
Vibrational–Rotational Transitions

Selection rules for vibrational-rotational transitions: $\Delta J = 0, \pm 1$; $\Delta M_J = 0, \pm 1$

$J' - J = -1 \rightarrow$ P rotational branch, $\Delta S \approx \omega_e - 2 B_v J$

$J' - J = 0 \rightarrow$ Q rotational branch, $\Delta S \approx \omega_e$ (exist only for $K \neq 0$ states)

$J' - J = 1 \rightarrow$ R rotational branch, $\Delta S \approx \omega_e + 2 B_v (J+1)$



$$S(v, J) = G(v) + F(J) = (v + ½)\,\omega_e - (v + ½)^2\,\omega_e^2 x_e^2 + J(J+1)\,B_v - J^2(J+1)^2\,D_v + \cdots$$

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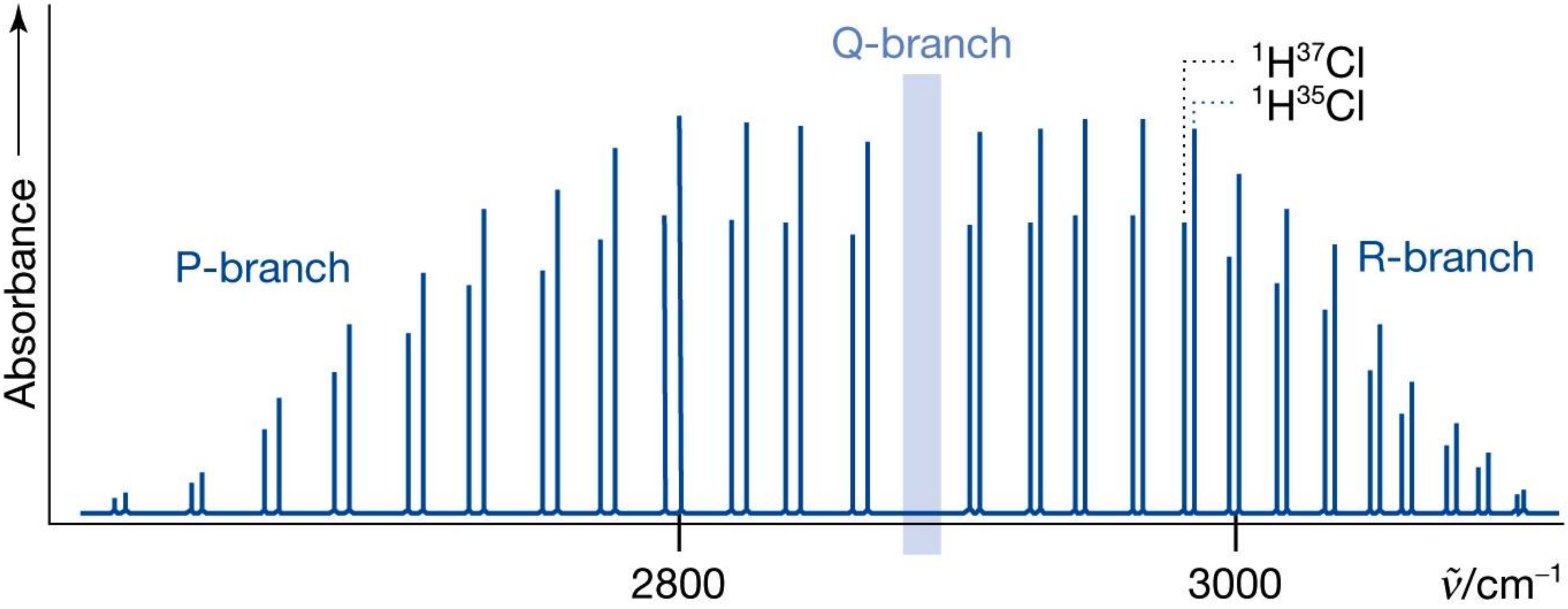
$J' - J = -1 \rightarrow$ P rotational branch, $\Delta S \approx \omega_e - 2 B_v J$

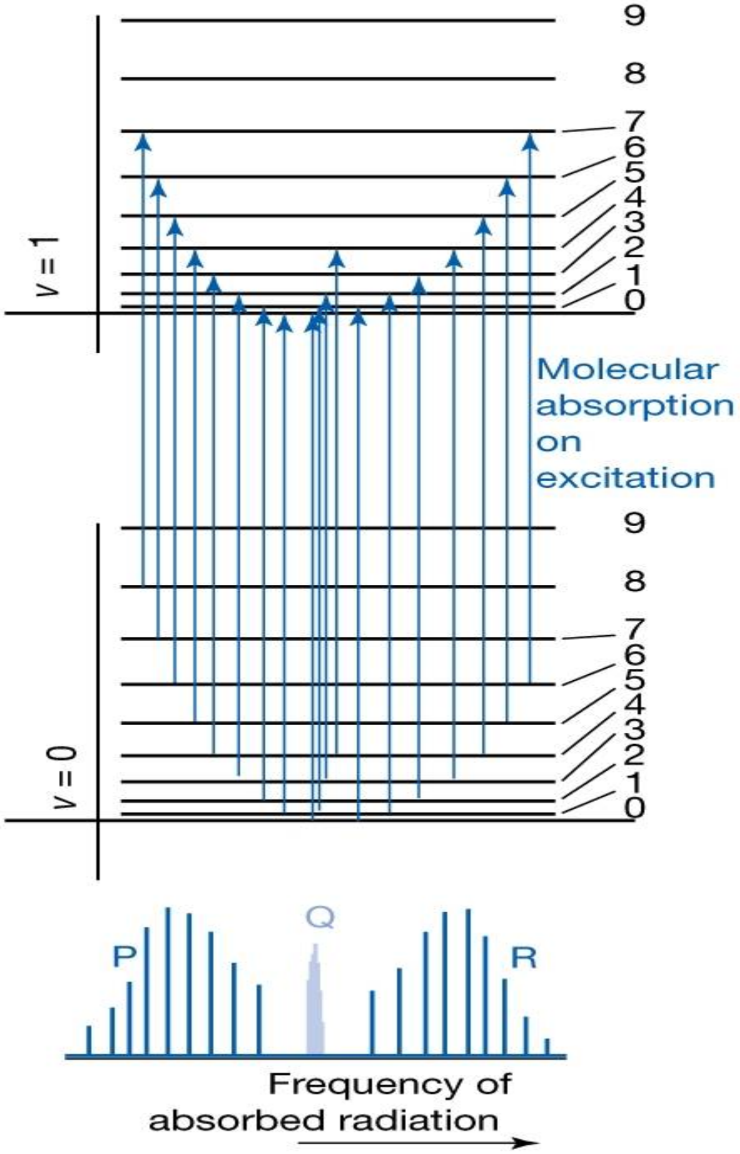
$J' - J = 0 \rightarrow$ Q rotational branch, $\Delta S \approx \omega e$ (exist only for $K \neq 0$ states)

$J' - J = 1 \rightarrow$ R rotational branch, $\Delta S \approx \omega e + 2 Bv (J+1)$



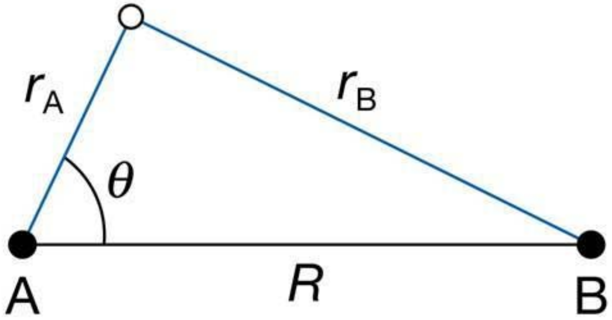
$S(v, J) = G(v) + F(J) = (v + ½)\,\omega_e - (v + ½)^2\,\omega_e^2 x_e^2 + J(J+1)\,B_v - J^2(J+1)^2\,D_v + \cdots$

Vibrational–Rotational Transitions



Molecular energy and wave function: H_2^+ ion

Coordinate system



Schrödinger equation: $H\Psi = E\Psi$

Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\Delta \qquad \hat{V} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right)$$

Secular equation:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

$\alpha = \langle \Psi_A | H | \Psi_A \rangle = \langle \Psi_B | H | \Psi_B \rangle$ **Coulomb Integral**

$\beta = \langle \Psi_A | H | \Psi_B \rangle = \langle \Psi_B | H | \Psi_A \rangle$ **Exchange Integral**

$S = \langle \Psi_A | \Psi_B \rangle$ **Overlap Integral**

Zero-order wavefunctions

$$\Psi_A = \frac{e^{-r_A/a_0}}{\left(\pi a_0^3\right)^{1/2}} \qquad \Psi_B = \frac{e^{-r_B/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

Molecular wavefunction

$$\Psi = c_A\Psi_A + c_B\Psi_B$$

H_2^+ ion: Solutions

Energies

$$E_1 = \frac{\alpha + \beta}{1 + S}$$

$$E_2 = \frac{\alpha - \beta}{1 - S}$$

$$\alpha < 0$$

$$\beta \le 0$$

Wavefunctions: σ molecular orbitals

$$\Psi_+ = N\left[\Psi_A(r_A) + \Psi_B(r_B)\right]$$

Bonding Molecular Orbital

$$\Psi_- = N\left[\Psi_A(r_A) - \Psi_B(r_B)\right]$$

Antibonding Molecular Orbital

$$\Psi_A = \frac{e^{-r_A/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

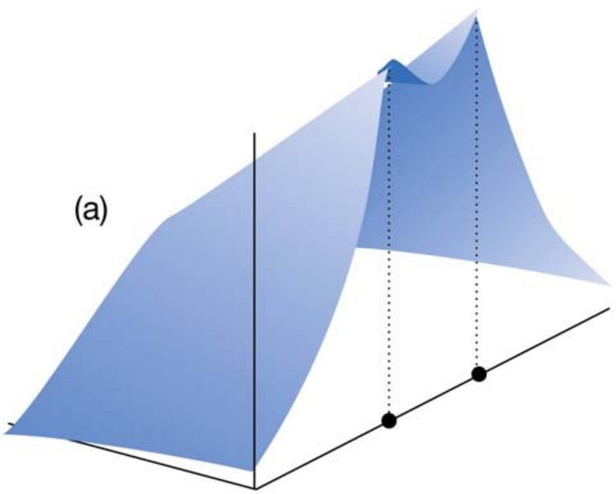
$$\Psi_B = \frac{e^{-r_B/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

$$N = \frac{1}{\left[2(1+S)\right]^{1/2}}$$

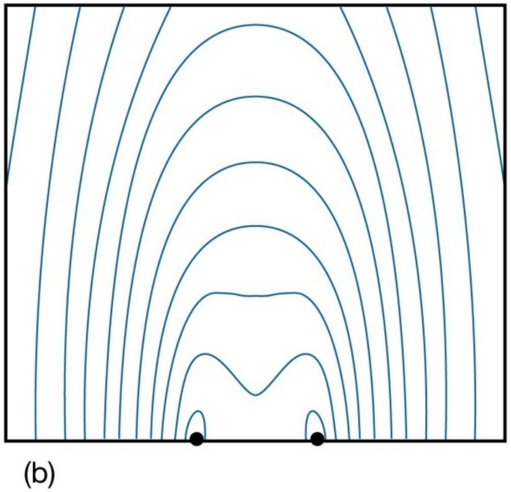
Normalization Factor

H_2^+ ion: Bonding Orbital

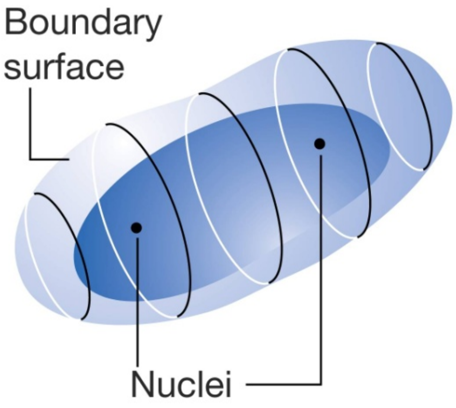
Bonding σ orbital: $\Psi_+ = N\left[\Psi_A(r_A) + \Psi_B(r_B)\right]$



Amplitude representation



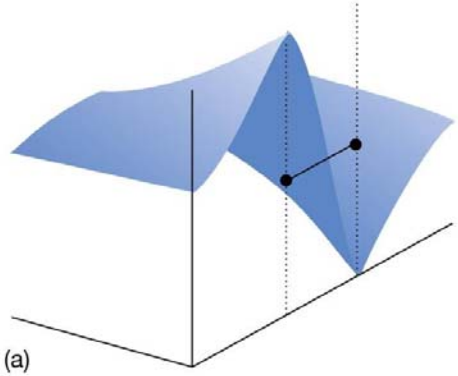
Contour plot representation



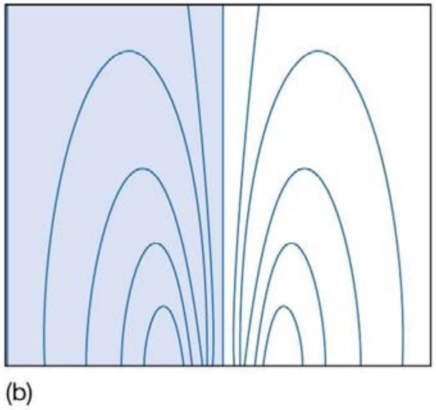
Three-dimensional sketch

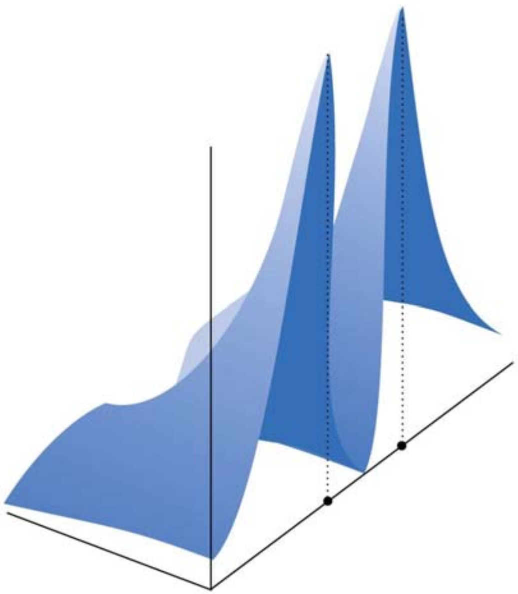
H_2^+ ion: Antibonding Orbital

Antibonding σ^* orbital: $\Psi_- = N\left[\Psi_A(r_{A1}) - \Psi_B(r_{B1})\right]$



Amplitude representation

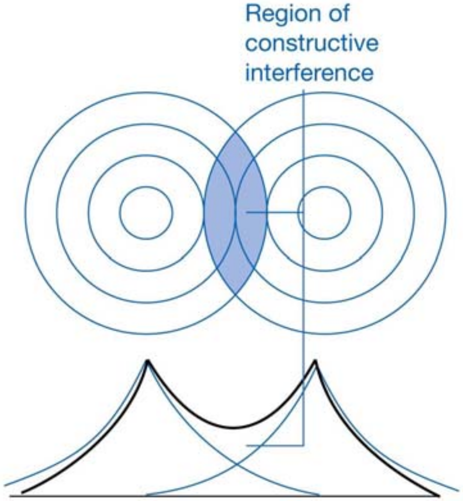




Electron density: $|\Psi_-|^2$

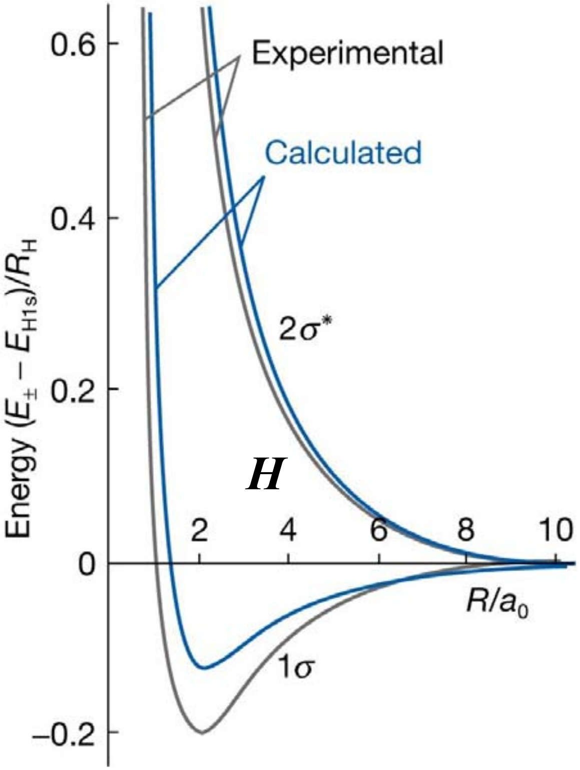
Contour plot representation

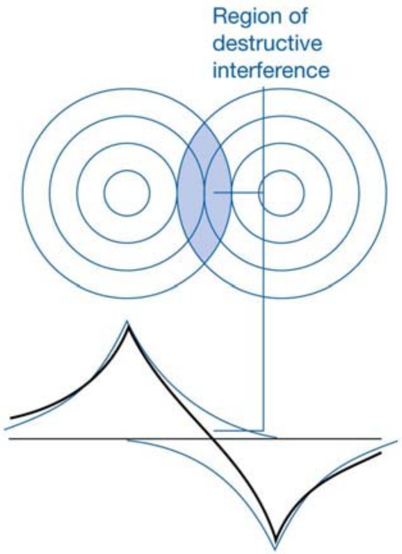
H_2^+ ion: complete description



$1\sigma_g$ orbital

$E_g = (\alpha+\beta)/(1+S)$





$2\sigma_u^*$ orbital

$E_u = (\alpha-\beta)/(1-S)$

The σ orbitals have cylindrical symmetry with respect to the molecular axis

Linear Combination of Atomic Orbitals (LCAO): Homonuclear Diatomic Molecules

$$\Psi(q) = \sum_i c_i \phi_i(q)$$

Each molecular orbital is presented as a linear combination of atomic orbitals of an appropriate symmetry

Symmetry of one-electron molecular orbitals

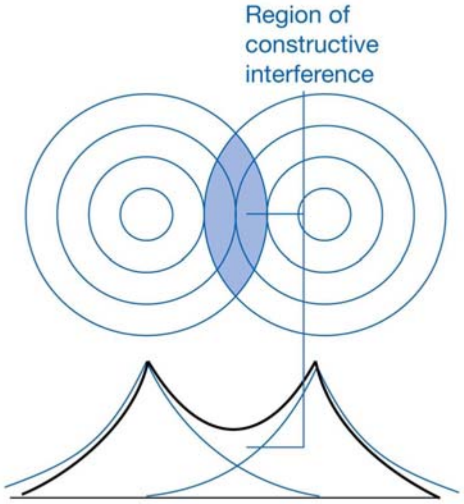
1. Electron axial angular momentum: $l_z = \pm \lambda \hbar$

λ	= 0,	1,	2,	3, …
Orbital	σ,	π,	δ,	ϕ, …

2. Inversion of the electron wave function in the molecular center of symmetry:

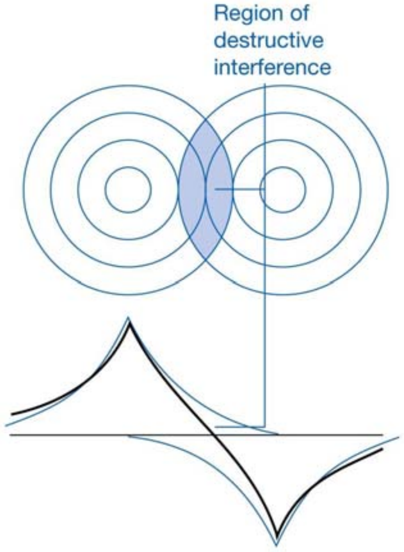
gerade

σ_g



ungerade

σ_u



Aufbau Principles

With the one-electron orbitals established, we can deduce the ground state configuration of a multi-electron molecule by adding an appropriate number of electrons to the orbitals following the Aufbau principles:

- **Electrons occupy different orbitals approximately in the order of their energies**

- **Only two electrons can occupy any non-degenerate orbital**

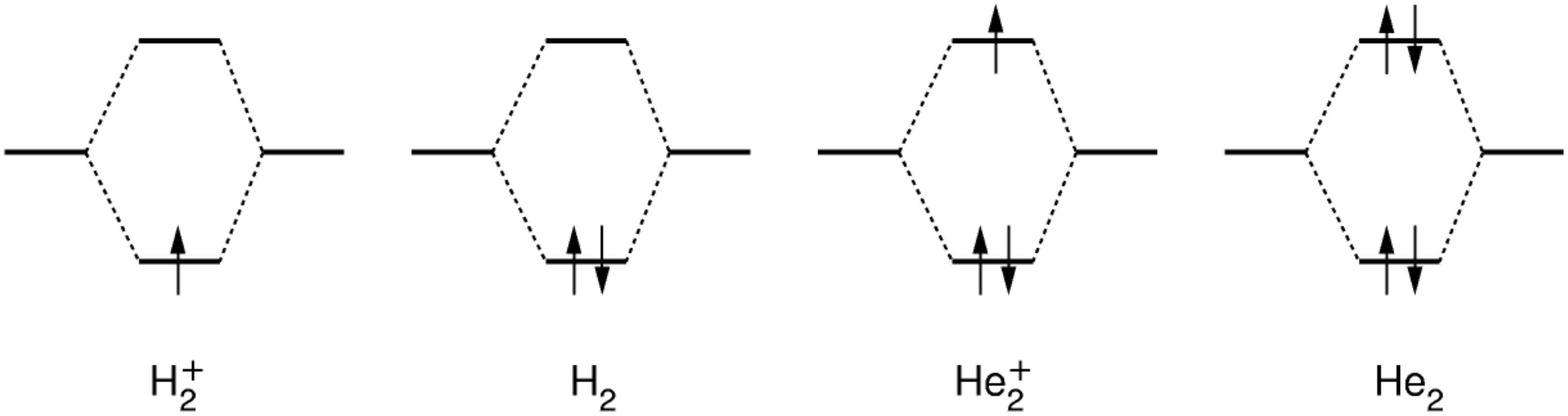
- **An atom, or a molecule in its ground state adopts a configuration with the greatest number of unpaired electrons (Hund's maximum multiplicity rule)**

Wolfgang Ernst Pauli

Nobelpreis 1945

* 25. April 1900 in Wien
\+ 15. Dez. 1958 in Zürich

Orbital Energy Level Diagrams for Period 1 Diatomic Molecules



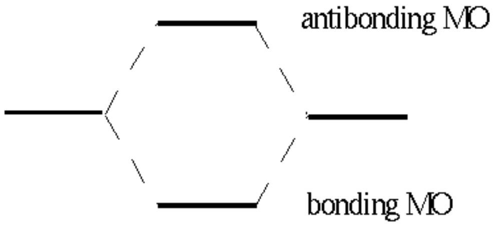
Configuration: $1\sigma_g$ $\quad 1\sigma_g^2$ $\quad 1\sigma_g^2\,1\sigma_u^*$ $\quad 1\sigma_g^2\,1\sigma_u^{*2}$

$$\sigma_g = N_g\,(\Phi_A + \Phi_B) \qquad \sigma^*_u = N_u\,(\Phi_A - \Phi_B)$$

where Φ_A, Φ_B are atomic 1s orbitals

H_2: $\Psi_g \approx \sigma_g(1)\,\sigma_g(2)$

He_2: $\Psi_g \approx \sigma_g(1)\,\sigma_g(2)\,\sigma^*_u(3)\,\sigma^*_u(4)$



Bonding Order

A measure of the net bonding in a diatomic molecule is its bond order, b:

$$b = \frac{1}{2}(n - n^*)$$

where n is the number of electrons in the bonding orbitals and n^* is the number of electrons in the antibonding orbitals.

Examples:

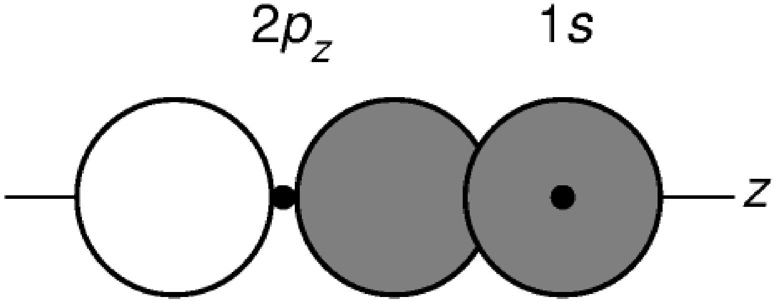
- **H_2 $b = 1$, a single bond H -- H,**
- **He_2 $b = 0$, no bond at all.**

Period 2 Diatomic Molecules: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, Ne_2

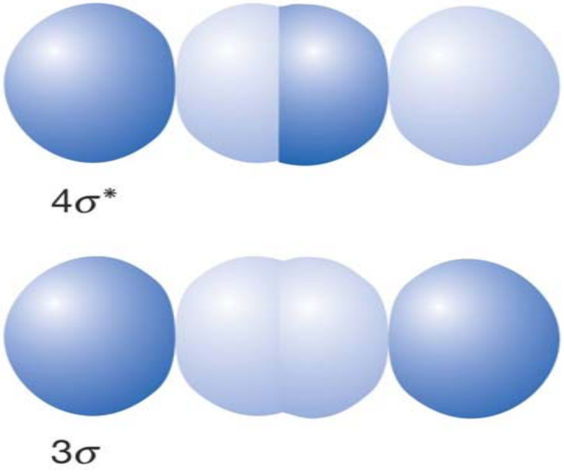
All these atomic orbitals have cylindrical symmetry with respect to the molecular axis and can interact with each other

s + s

p_z + s



p_z + p_z

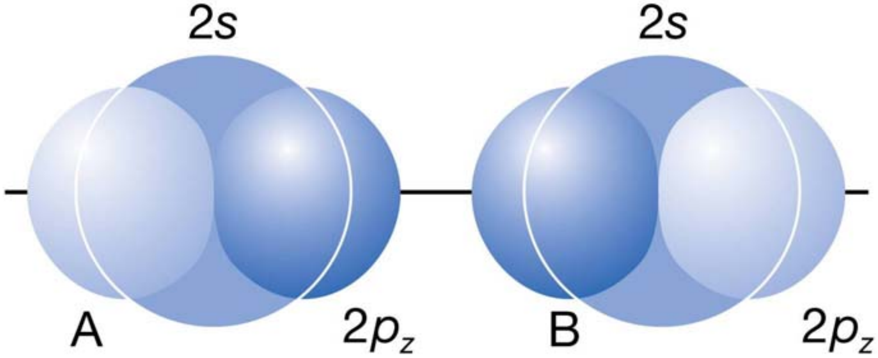


Period 2 Diatomic Molecules: σ orbitals

In general: $\Psi_\sigma = C_{A2s}\,\Phi_{A2s} + C_{B2s}\,\Phi_{B2s} + C_{A2pz}\,\Phi_{A2pz} + C_{B2pz}\,\Phi_{B2pz}$

Let us assume that **Z** axis is parallel to the internuclear axis **R**

Only 2s and 2p$_z$ atomic orbitals can interact producing molecular σ orbitals.

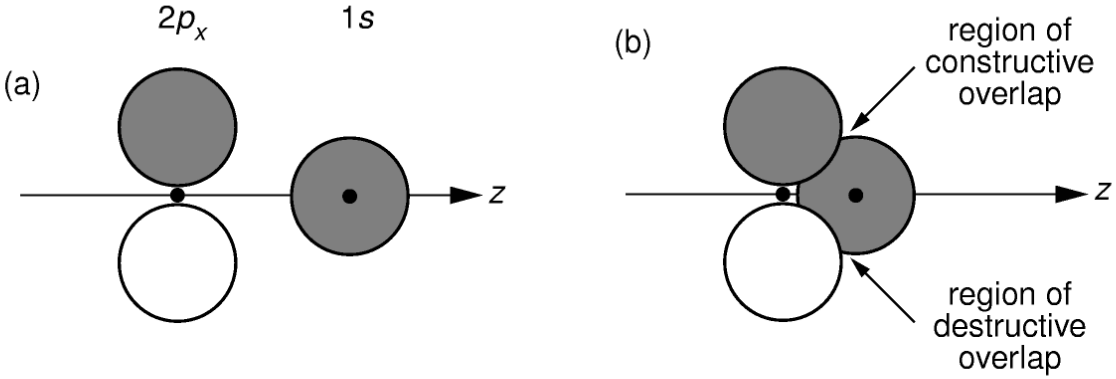


Sometimes, the 2s and 2p$_z$ orbitals can be treated separately, as they distinctly different energies. Then, two 2s orbitals of the two atoms overlap with each other giving a pare of σ_g and σ_u* molecular orbitals and two 2p$_z$ orbitals overlap with each other giving another pair of σ_g and σ_u* molecular orbitals.

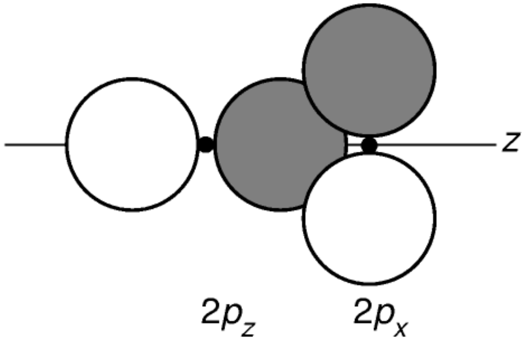
Period 2 Diatomic Molecules: σ and π orbitals

These atomic orbitals have different symmetry and cannot interact with each other

$s + p_x$

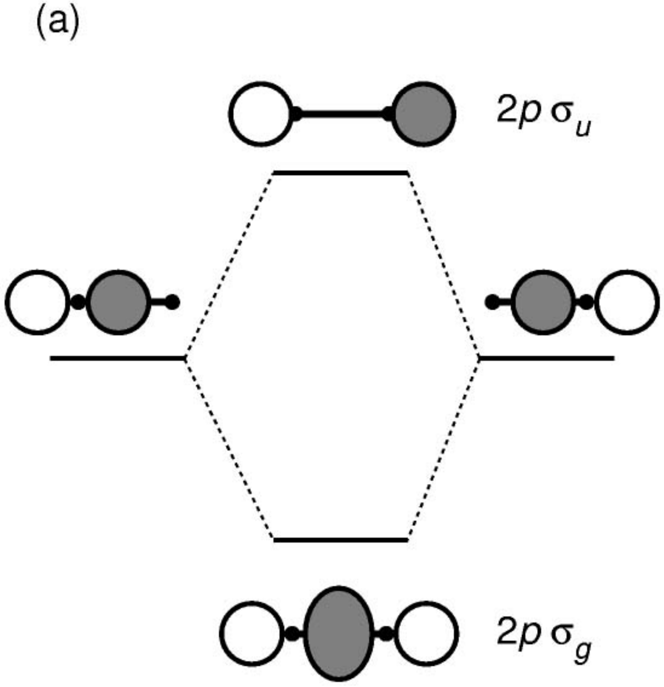


$p_z + p_x$

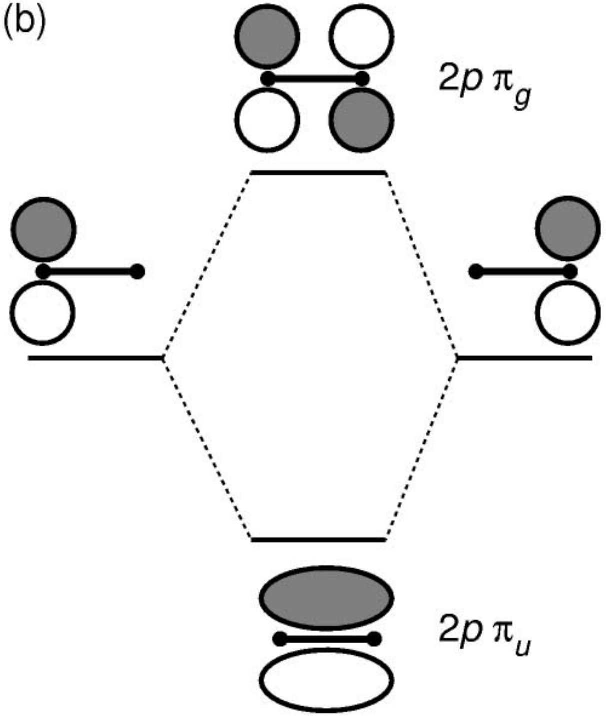


Period 2 Diatomic Molecules: π orbitals

$2p_x$ and $2p_y$ orbitals of both atoms oriented to the same side can produce bonding π_u and antibonding π_g* molecular orbitals. The $\pi 2p_x$ and $\pi 2p_y$ orbitals have the same energy, thus π_u and π_g* orbitals can be populated by the maximum four electrons.

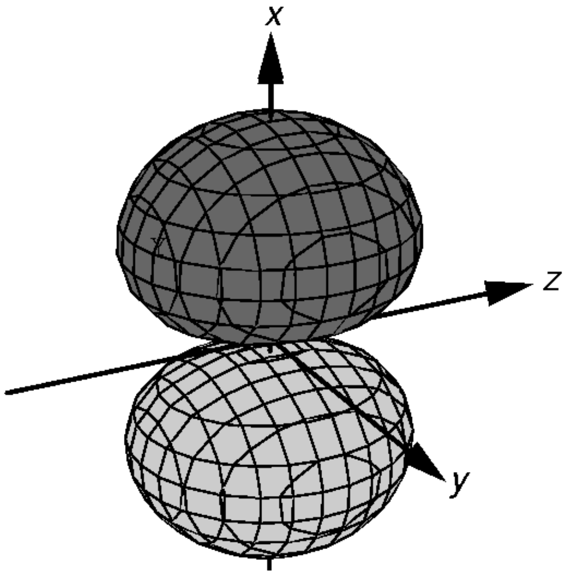


σ orbitals

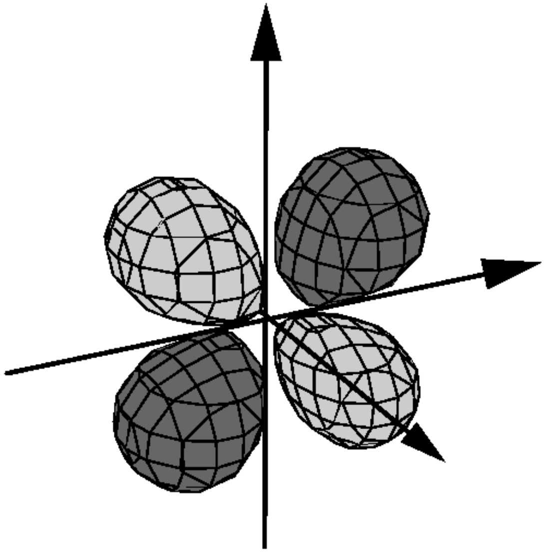


π orbitals

Parity of the π orbitals



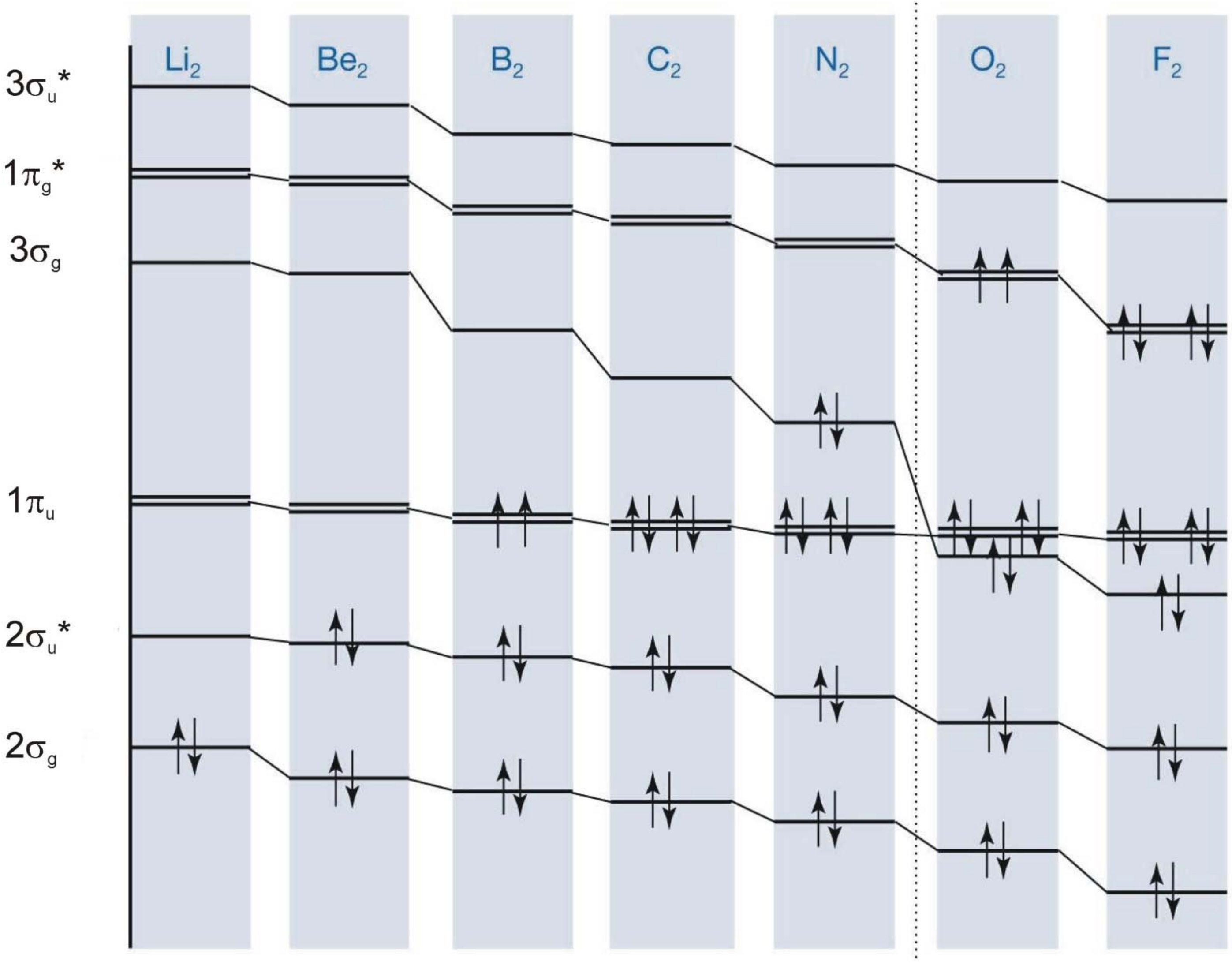
$2p\,\pi_u$ bonding MO



$2p\,\pi_g$ anti-bonding MO

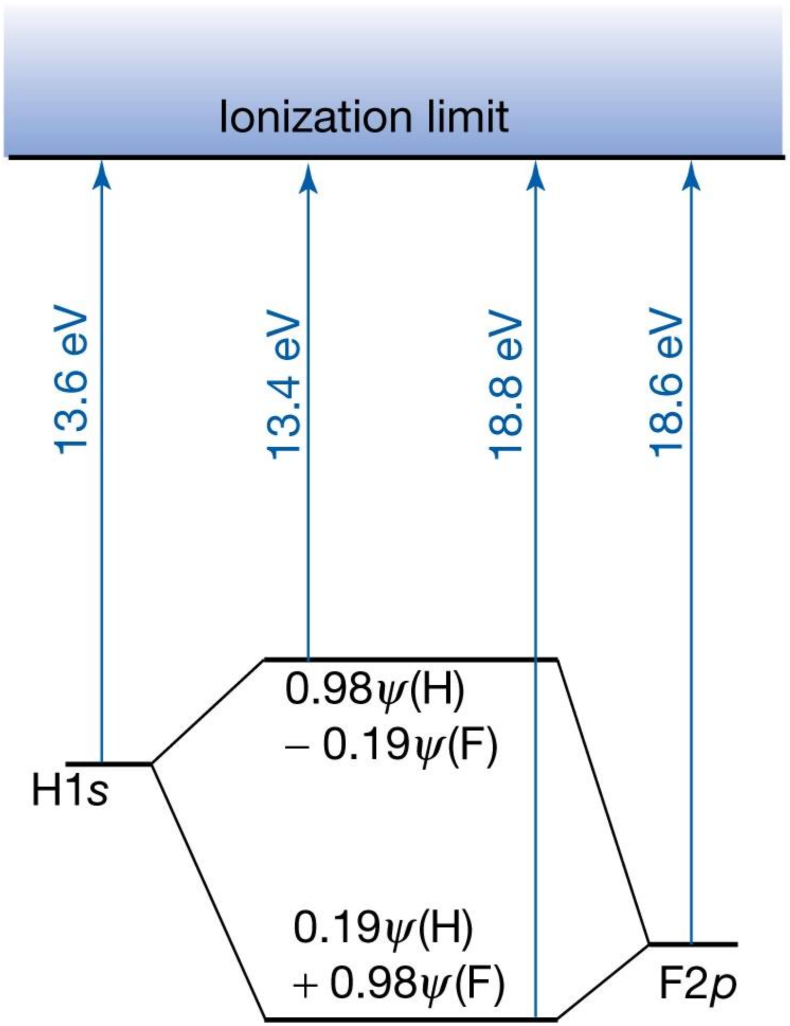
That is, the bonding π orbitals are ungerade (u), while the antibonding π orbitals are gerade (g) with respect to the inversion of all electronic coordinates in the molecular center of symmetry

Electron Structure of the Period 2 Homonuclear Diatomic Molecules



Heteronuclear Diatomic Molecules: Polar Bonding

One-electron energy levels in HF



The one-electron wavefunction can still be written as linear combination of atomic orbitals (LCAO):

$$\Psi = c_H\Phi_H + c_F\,\Phi_F$$

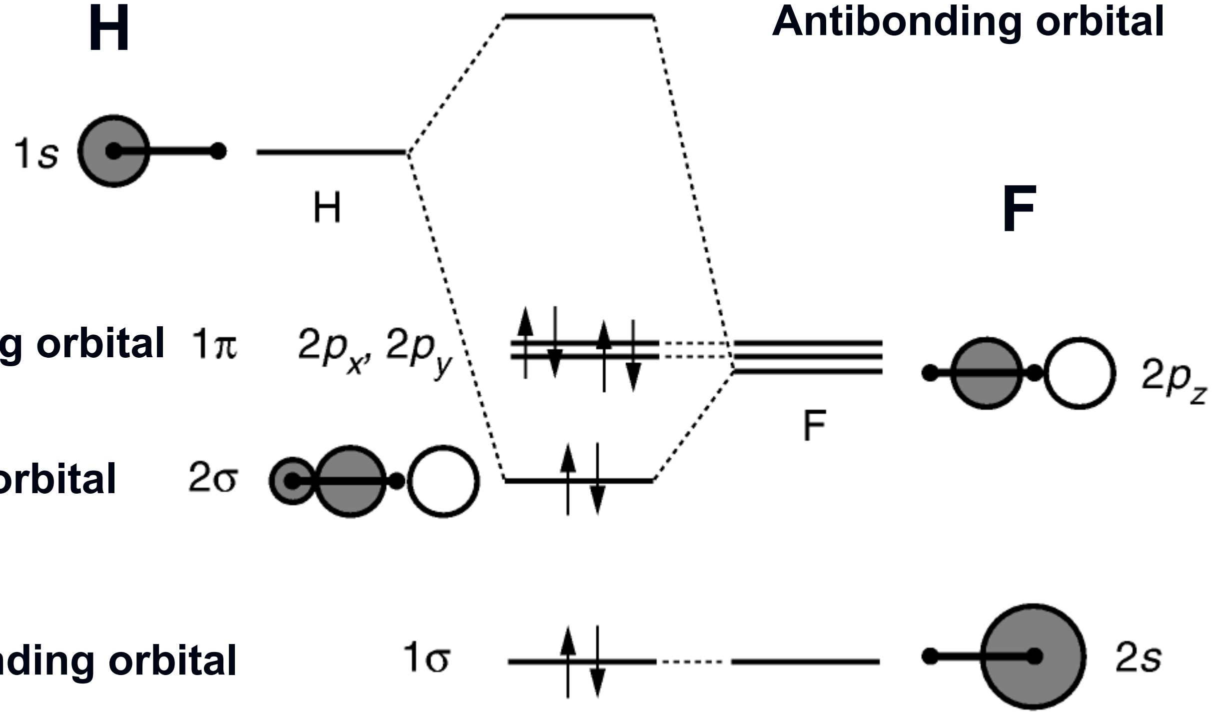
Aufbau principles

1. **The energies of the interacting atomic orbitals Φ_H and Φ_F must be close to each other**
2. **The symmetry of the interacting atomic orbitals must be the same**
3. **The overlap of the atomic orbitals Φ_H and Φ_F must be large.**

In case of HF, $|c_H|^2 < |c_F|^2$, which results in the polar bonding and manifests itself in the nonzero value of the molecular electric dipole moment.

Heteronuclear diatomic molecules : HF

Details on the molecular bonding energies and molecular wavefunctions:



H

Antibonding orbital

F

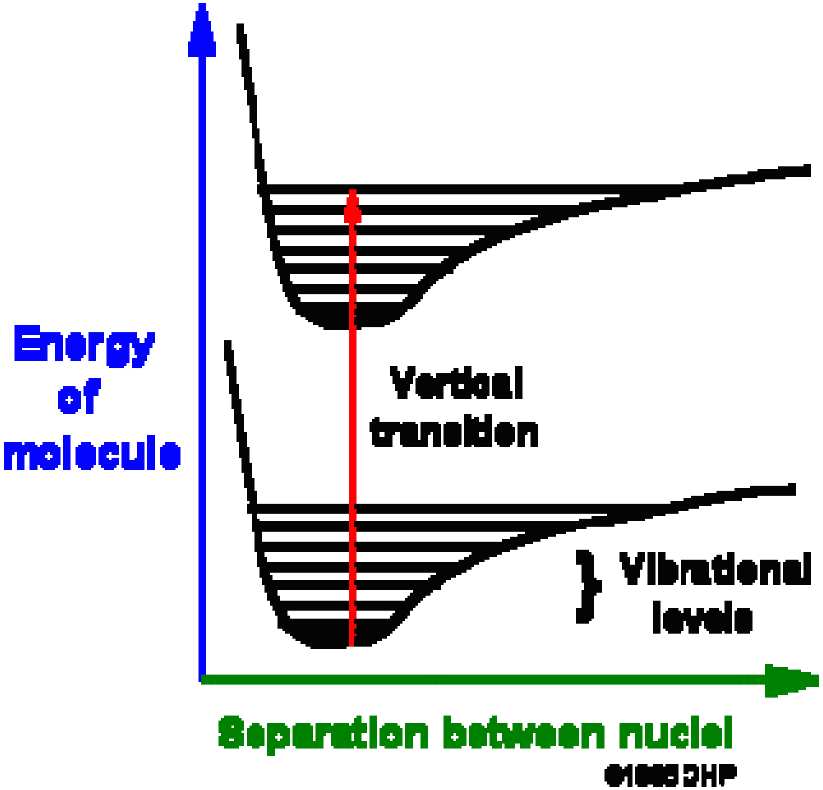
Nonbonding orbital

Bonding orbital

Nonbonding orbital

Electron configuration: $(1\sigma)^2\,(2\sigma)^2\,(1\pi)^4$: $^1\Sigma$

Born-Oppenheimer Approximation: Electronic transitions in molecules



Transition probability

$$W_{k\leftarrow 0} \propto \left|\langle k|\mu_z|0\rangle\right|^2 E_z^2$$

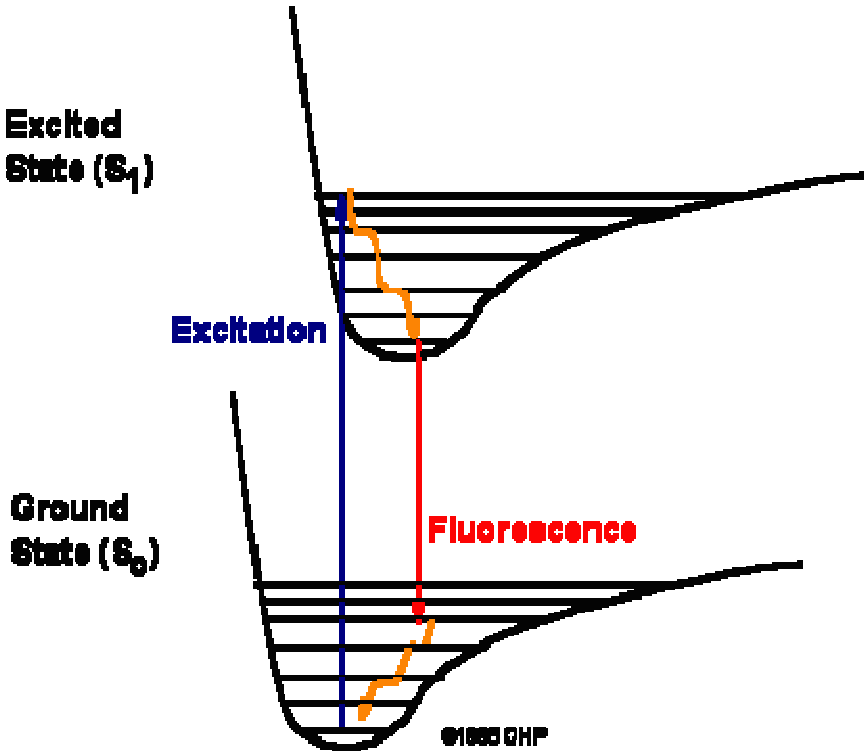
$$\langle k|\mu_z|0\rangle = \int \Psi_k^* \, \mu_z \Psi_0 \, dq$$

in general

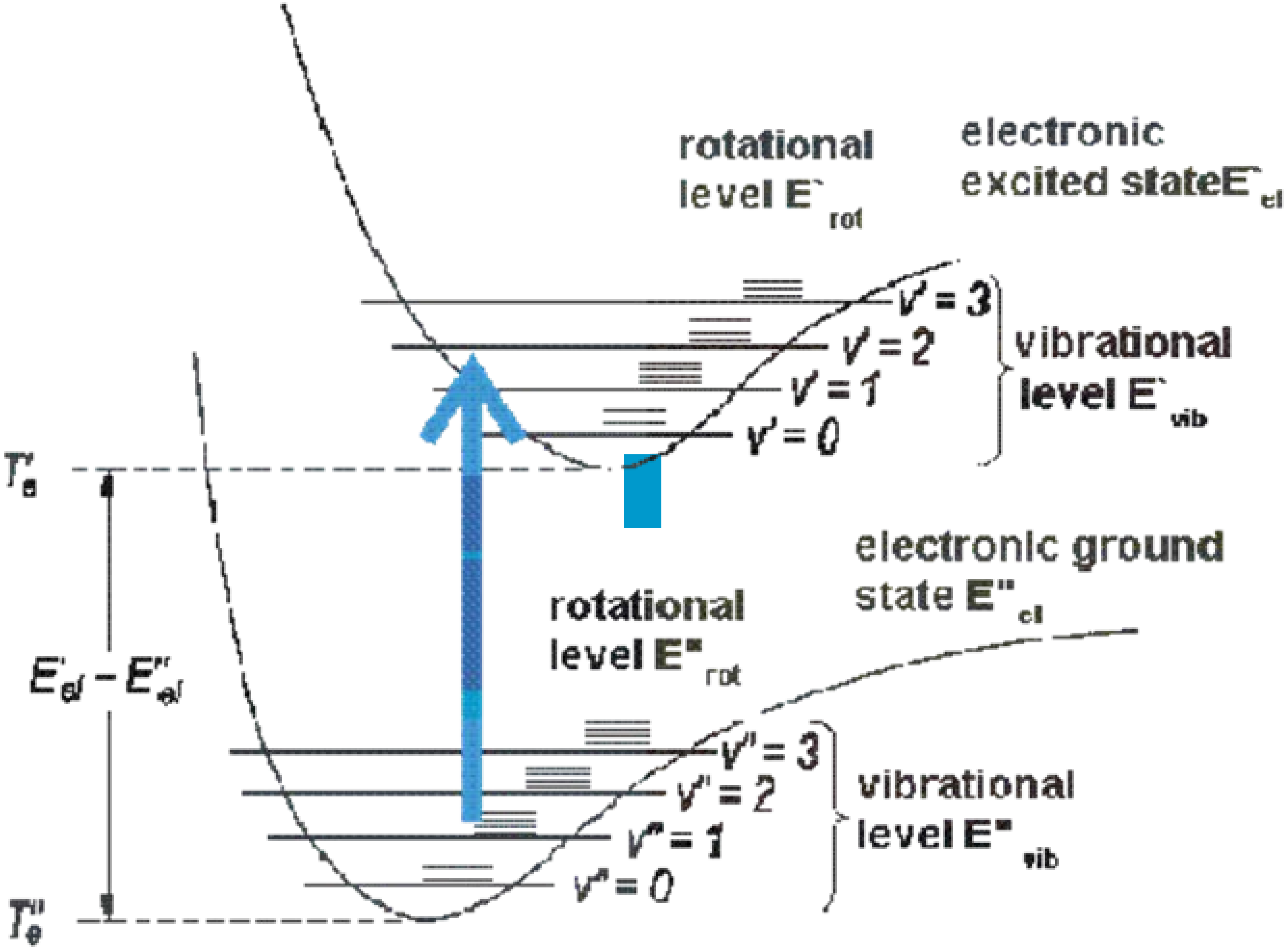
$$\vec{\mu} = \sum_i q_i \, \vec{r}_i$$

$$E_2 - E_1 = h\nu, \quad \lambda = {}^{c}/\nu$$

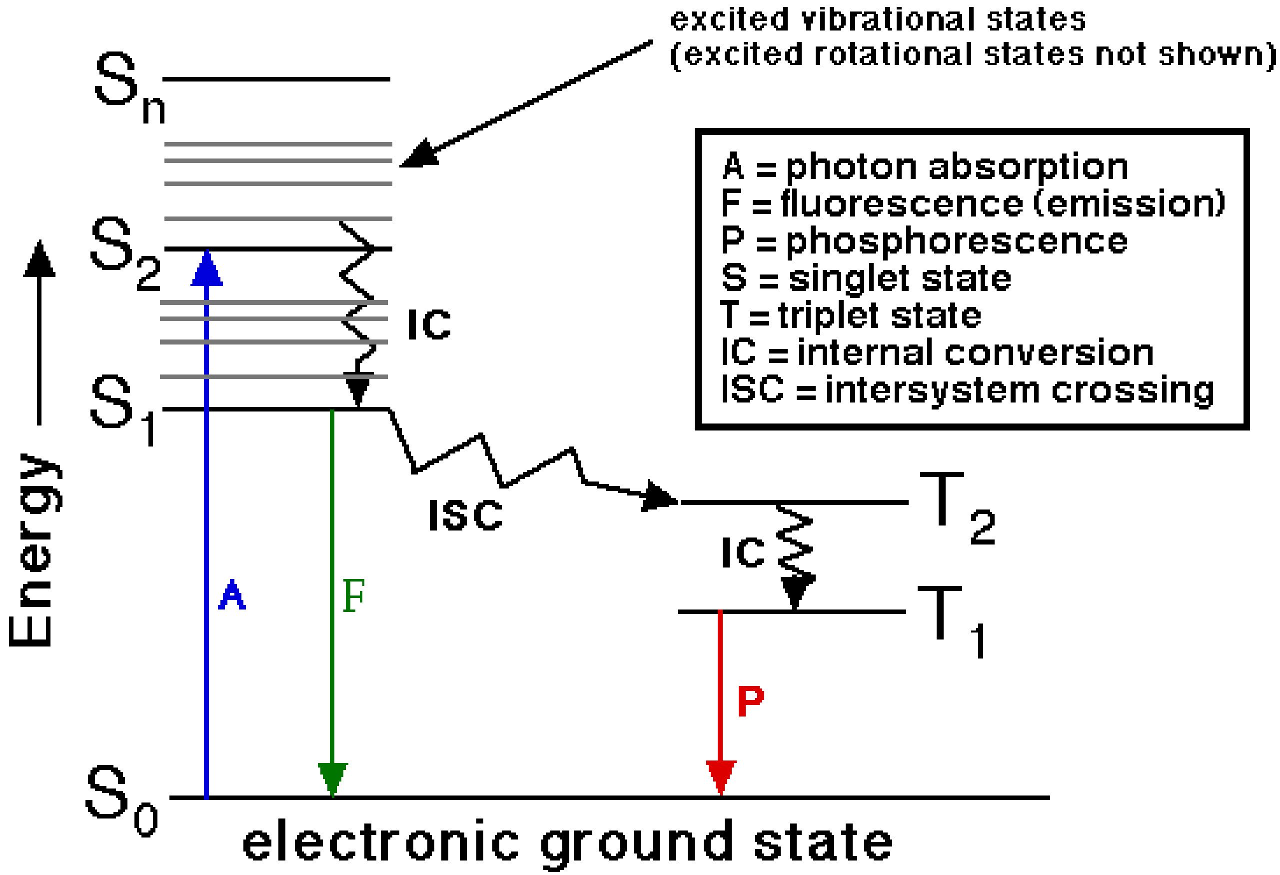
Molecular Fluorescence Spectroscopy



Electronic Transitions



Jablonski Diagram



excited vibrational states
(excited rotational states not shown)

A = photon absorption
F = fluorescence (emission)
P = phosphorescence
S = singlet state
T = triplet state
IC = internal conversion
ISC = intersystem crossing

Electronic Transitions: transition frequency

$$E = E_{el} + E_{vib} + E_{rot}$$

Energy: $\omega = T_e + \omega_e\,(v+½) + B_v J(J+1)$,

where T_e is the minimum of the potential curve

Wave function: $\Psi = \Psi_n^{el}\,\Psi_v^{vib}\,\Psi_J^{rot}$

Transition frequency:

$$\Delta\omega = T_e' - T_e'' + \omega_e'\,(v'+½) - \omega_e''\,(v''+½) + B_v'\;J'(J'+1) - B_v''\;J''(J''+1)$$
$$= \omega_{el} + \omega_{vib} + \omega_{rot}$$

Usually: $\omega_{el} \gg \omega_{vib} \gg \omega_{rot}$

Quantum numbers of electronic states for diatomic molecules

1. **Λ** projection of the electronic orbital angular momentum **L** onto the internuclear axis
2. **S** total electron spin
3. **Σ** projection of the electron spin **S** onto the internuclear axis
4. **Ω = Λ + Σ** projection of the total angular momentum **J** onto the internuclear axis
5. **σ = ±1,** index of reflection of the electronic wave function in the plain (only for Ω =0 states)
6. **g, u** inversion of the electron wavefunction in the molecular center (only for homonuclear mol.)

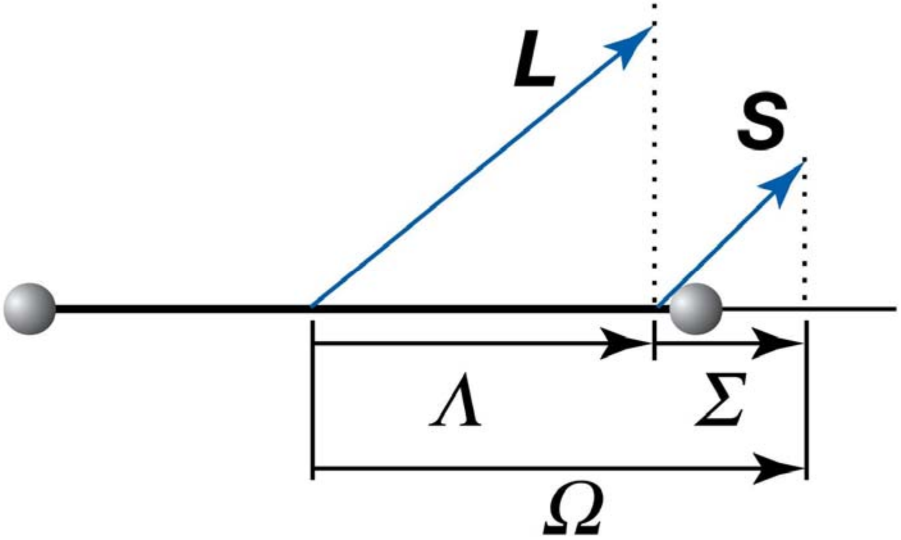
Usually electronic states are written as: $^{2S+1}\Lambda_{\Omega}$, or $^{2S+1}\Lambda_{\Omega}^{\sigma}$, or $^{2S+1}\Lambda_{g,u}$

ALSO:

The states with **Λ=0,1,2** are written: **Σ, Π, Λ** states, respectively.

The states with **S=0** are named **singlets**

The states with **S=1** are named **triplets**



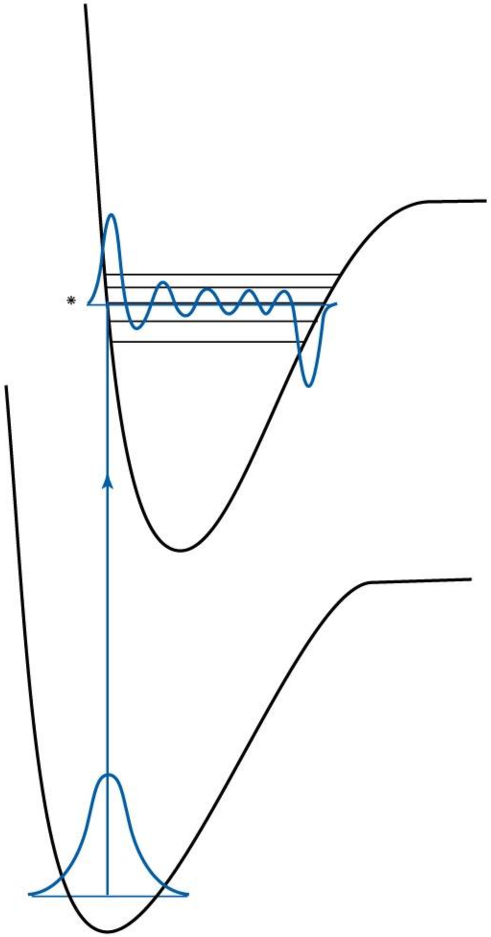
Selection rules for electronic transitions in diatomic molecules

Allowed transitions	**Examples**
$\Delta\Lambda = 0, \pm 1$	$\Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Pi,$ $\Sigma \leftrightarrow \Pi, \Delta \leftrightarrow \Pi$
$\Delta S = 0$	${}^1\Sigma \leftrightarrow {}^1\Sigma, {}^3\Pi \leftrightarrow {}^3\Pi,$ ${}^3\Sigma \leftrightarrow {}^3\Pi, {}^1\Delta \leftrightarrow {}^1\Pi$
$+ \leftrightarrow +$	$\Sigma^+ \leftrightarrow \Sigma^+$
$- \leftrightarrow -$	$\Sigma^- \leftrightarrow \Sigma^-$
$g \leftrightarrow u$	$\Sigma_g^+ \leftrightarrow \Sigma_u^+, \Sigma_g \leftrightarrow \Pi_u$

Selection rules for rotational quantum number J in electronic transitions

Electronic transition	Allowed transitions	Name
$\Sigma \leftrightarrow \Sigma$	$\Delta J = 1$	R-branch
	$\Delta J = -1$	P-branch
All others	$\Delta J = 1$	R-branch
	$\Delta J = 0$	Q-branch
	$\Delta J = -1$	P-branch

Electronic Transitions: Franck-Condon factors



No selection rule for the vibrational quantum number *v* in electronic transitions:

$$v' - v = \text{any integer.}$$

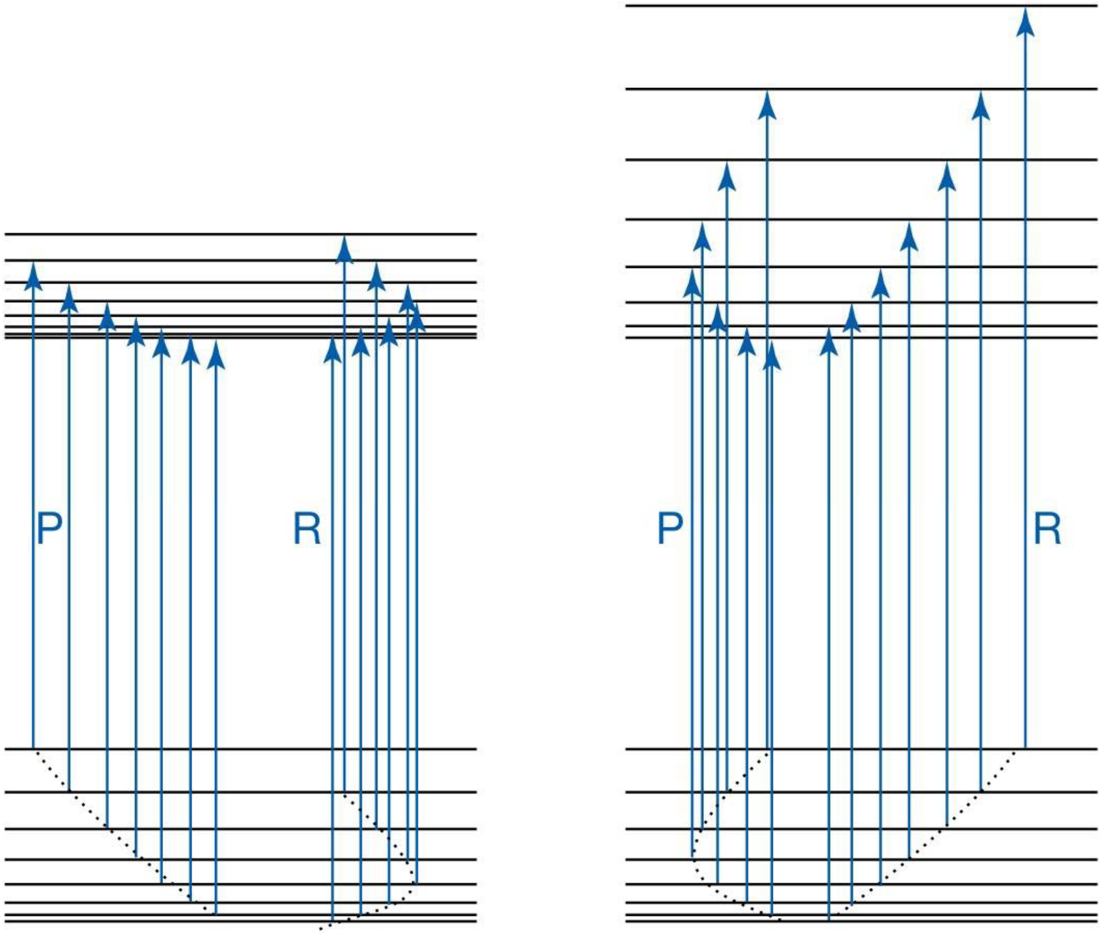
$$\Psi = \Psi_e \Psi_v \Psi_{rot}$$

$$W \sim |\langle\Psi_f|\mu_Z|\Psi_i\rangle|^2 \approx$$

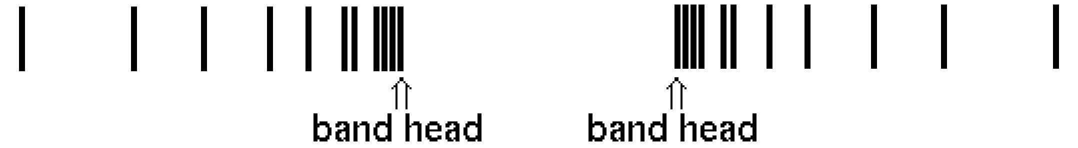
$$\approx |\langle\Psi_{v'}|\Psi_v\rangle|^2 \, |\langle\Psi_{e'}\Psi_{J'}|\mu_Z|\Psi_{e'}\Psi_J\rangle|^2$$

Frank-Condon integral

Rotational Structure of Electronic Transitions

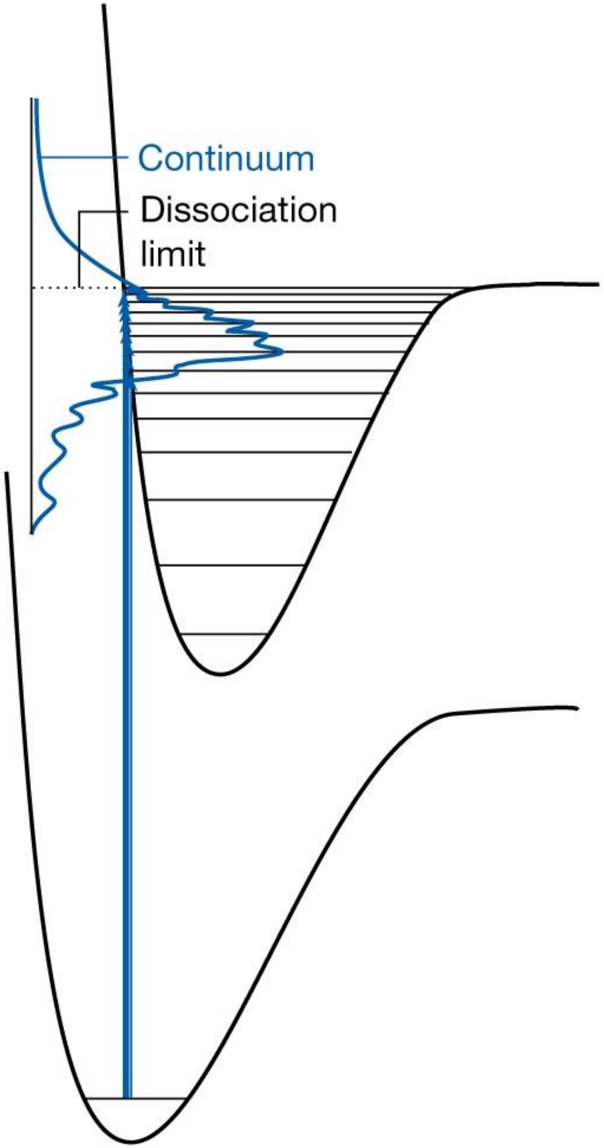


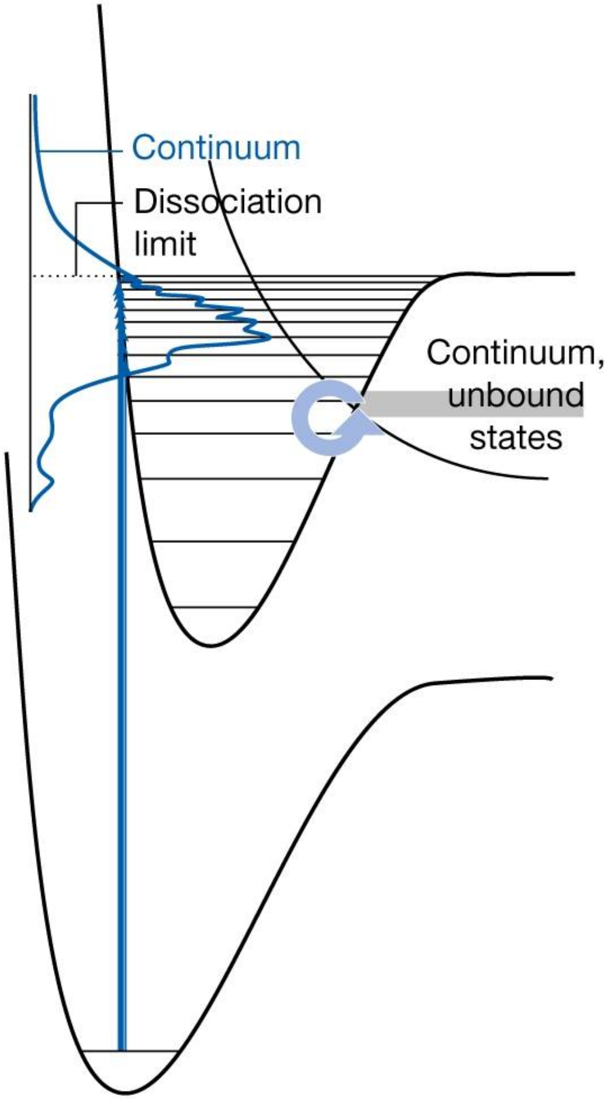
(a) $B' < B$ (b) $B' > B$



Red shadowed **Blue shadowed**

Dissociation and Predissociation

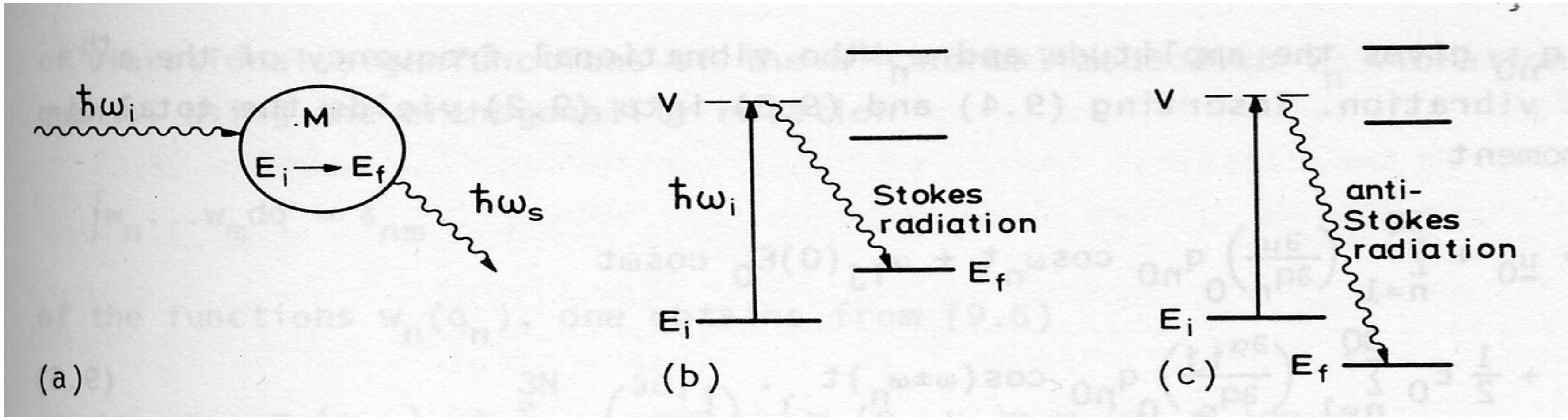




Multiphoton Transitions

Photon scattering on a molecule:

$$h\nu_i + M(E_i) \rightarrow h\nu_s + M(E_s)$$



If $\nu_i = \nu_s$, it's called Rayleigh Scattering
If $\nu_i > \nu_s$, it's called Stokes Scattering
If $\nu_i < \nu_s$, it's called anti-Stokes Scattering

In general, the transition for each of the two photons is not resonance: $E_v - E_i \neq h\nu_i$, $E_v - E_f \neq h\nu_s$ and the corresponding upper energy state is said to be virtual.

Raman Scattering in Molecules

The molecule where the two-photon Raman transitions can occur must possess the anisotropic polarizability. This means that under influence of a strong laser radiation E the molecule acquires an induced electric dipole moment:

$$\mu_{\text{ind}} = \alpha E$$

Most of the homogeneous and heterogeneous diatomic molecules possess the anisotropic polarizability, they are is said to be the Raman active. However all atoms are spherically symmetric and therefore they are not Raman active. The selection rules for pure rotational Raman transitions in molecules are as follows:

Linear rotors: $\Delta J = 0, \pm 2$.
Symmetric rotors: $\Delta J = 0, \pm 1, \pm 2$; $\Delta K = 0$.
Spherical rotors: are not Rahman active

The $\Delta J = 0$ pure rotational transitions does not change the frequency of the scattering radiation and therefore they contribute only to the Rayleigh Scattering.

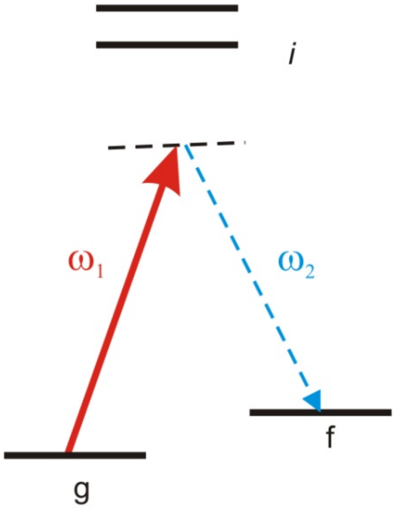
For ro-vibrational Raman transitions the selection rules for the quantum number J are the same as above. The Raman transitions between the states with $\Delta\upsilon = 1$ contribute to the Stokes Scattering, the Raman transitions between the states with $\Delta\upsilon = -1$ contribute to the anti-Stokes Scattering. The $\Delta J = 0$ transitions are named $Q-$ branch, the $\Delta J = -2$ transitions are named $O-$branch, and the $\Delta J = 2$ transitions are named $S-$branch.

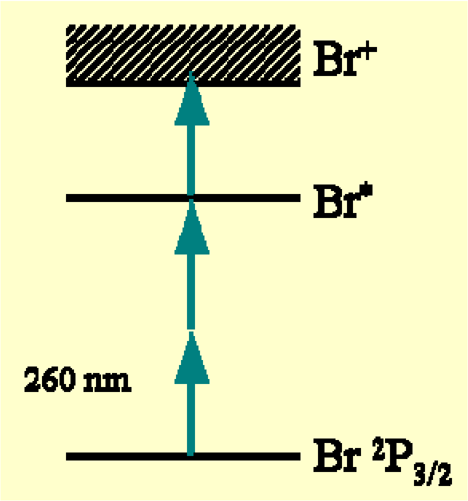
Quantum-Mechanical treatment of the Raman Scattering and Two-Photon Absorption

The probability of Raman scattering:

$$W_R = C_2 \sum_i \frac{\left| \langle f | \mu_2 | i \rangle \langle i | \mu_1 | g \rangle \right|^2}{\left(\omega_{ig} - \omega_1 + i\Gamma_i / 2 \right)\left(\omega_{ig} + \omega_2 - i\Gamma_i / 2 \right)}$$

where the constant C_2 is proportional to the squire of the light intensity.





REMPI 2+1

A similar effect is the two-photon absorption in atoms, molecules, and condensed phase

The probability of the tow-photon absorption is usually several orders of magnitude smaller than the probability of the one-photon absorption. Therefore, for observation of the two-photon absorption the laser beam is usually focused on the sample, thus achieving the necessary high density of the electromagnetic radiation.

Raman Spectroscopy of Rotational Molecular States