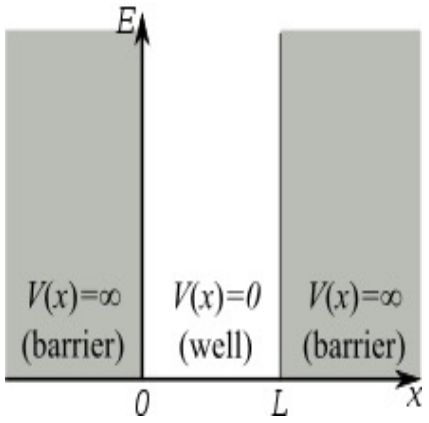
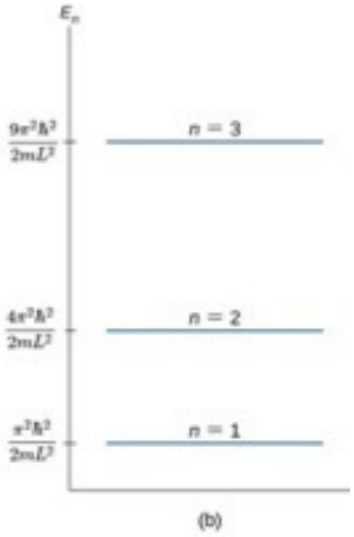
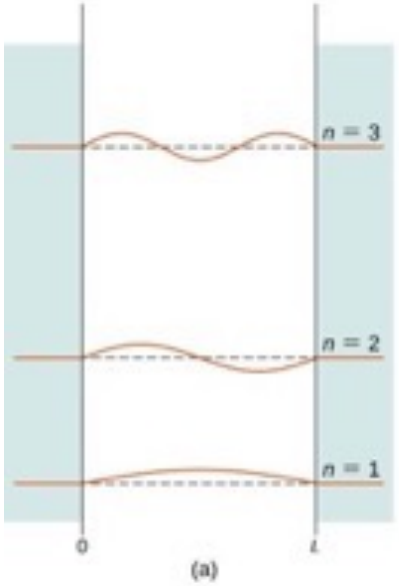
Some facts from quantum mechanics

- Molecule is a confined system, => molecular energy is quantized;
- Solving Schrödinger equation outputs discreet energy levels and molecular wave functions;







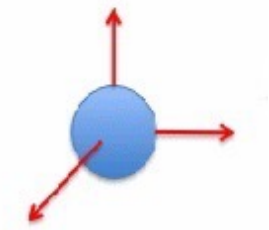
A free molecule, as a system of bound nuclei has 3 types of confined motions: **translational** as a whole**,** **rotational** and **vibrational** for nuclei.
In addition, electrons that bind the nuclei also confined: **electronic** motion.

- In the adiabatic approximation different motions can be considered separately.

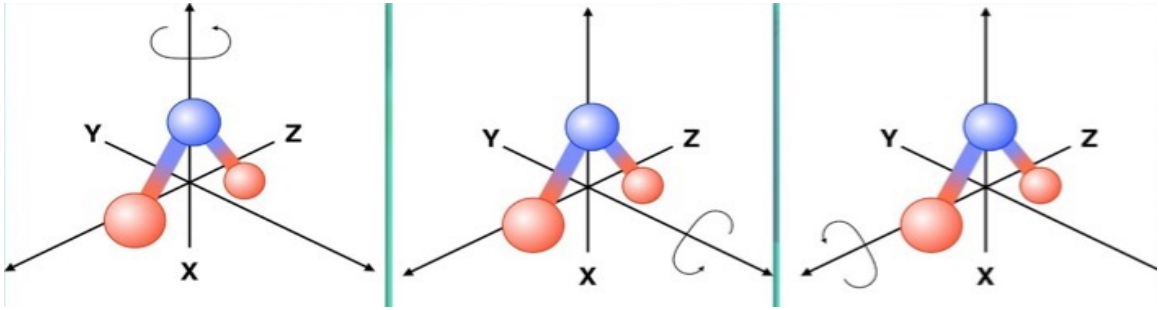
$$\mathbf{V_{el} >> V_{vib} >> V_{rot}}$$

Molecular degrees of freedom

- A system of ***N*** particles owns 3***N*** degrees of freedom, =>
- A nonlinear molecule has 3 translations and 3 rotations around 3 space axis;
- There are however only 2 rotations for a linear molecule (no rotation around axis of molecule), they are equal (degenerate);
- This leaves 3N-**6** vibrations for non-linear and 3N-**5** vibrations for linear molecules.

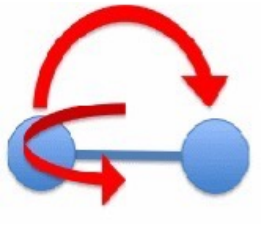


3 translations



3 rotations in nonlinear molecule

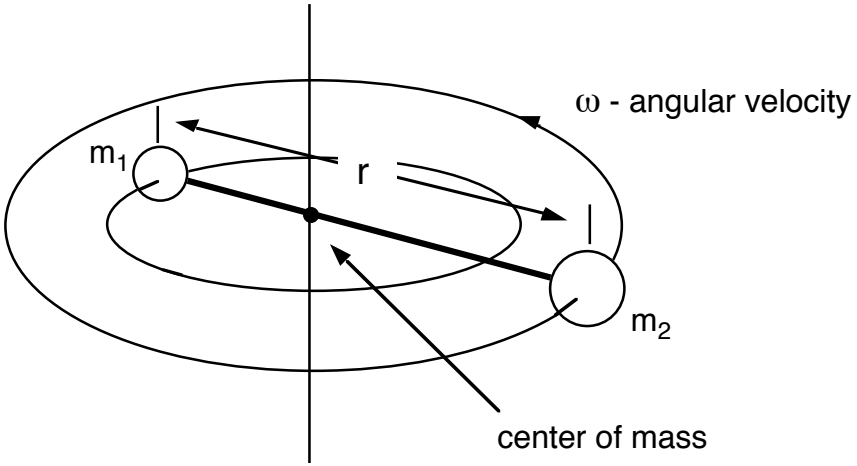
3N-6 vibrations



2 rotations in linear molecule

3N-5 vibrations

Rotational motion in a rigid rotor



Energy levels: $$E_{rot} = \frac{\hbar^2 J(J+1)}{2\mu r^2} = \frac{\hbar^2 J(J+1)}{2I};$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}, \qquad J=0, 1, 2,\ldots$$

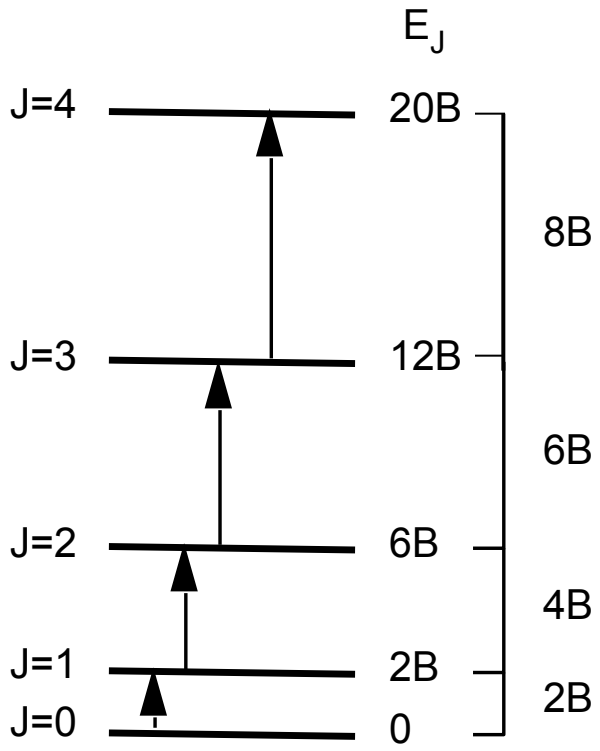
Rotational energy levels:

$$E_{rot} = B\,J(J+1);$$

$$B = \frac{\hbar^2}{2I}, \quad J=0, 1, 2,\ldots$$

H_2 ⇨ B=60.8 cm^{-1}

CO ⇨ B=1.93 cm^{-1}



Spacing increases by 2B!

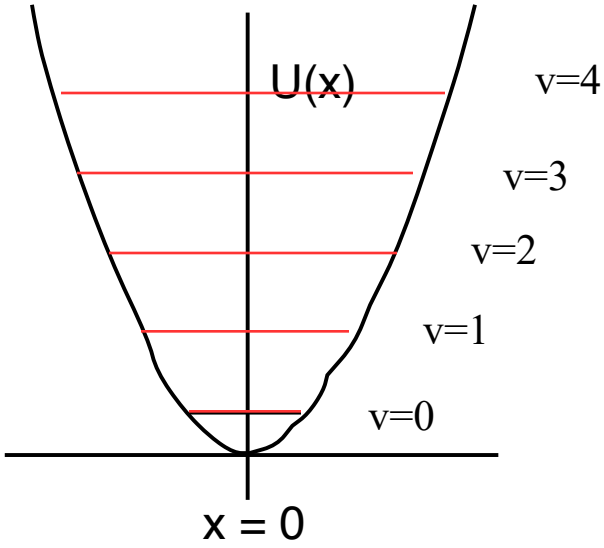
Vibrational motion: harmonic oscillator

$F = -kx$; $U = -1/2kx^2$;

Energy levels:

$$E_{vib} = \hbar\omega\left(v + \tfrac{1}{2}\right), \qquad v = 0,1,2\ldots$$

$$\omega = \sqrt{k/\mu}$$



H_2 4395.2 cm^{-1}; CO 2170.21 cm^{-1};

N_2 1460.37 cm^{-1}; O_2 1580.36 cm^{-1}.

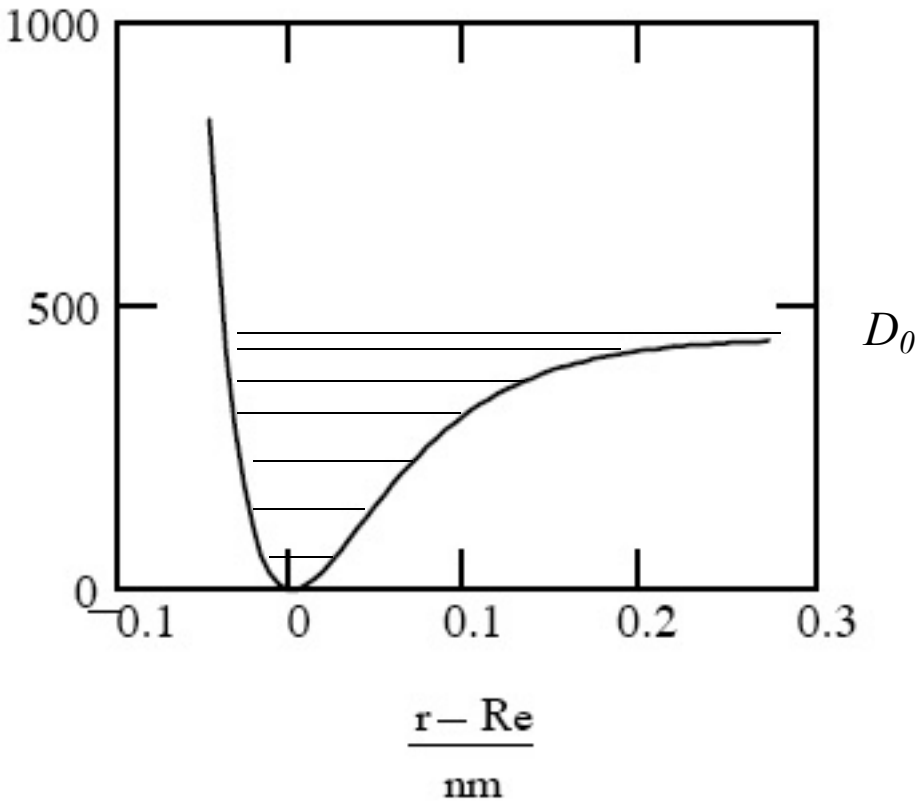
Vibrational motion: anharmonic oscillator

Morse potential

$R \to 0 \quad U \to 0;$

$R \to \infty \quad U \to D_0$

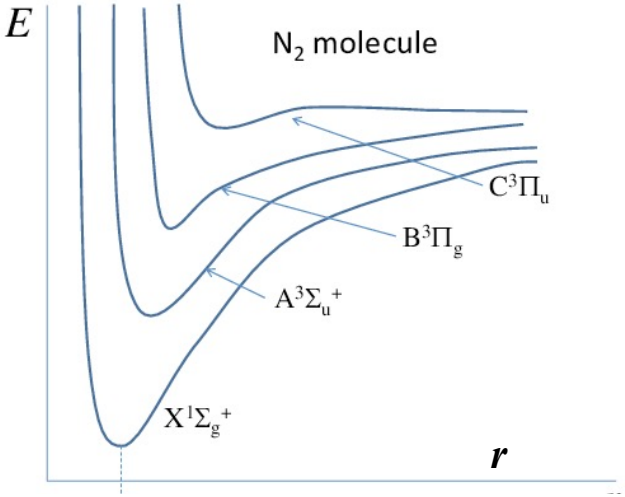
$$E(r) := D_e \cdot (1 - \exp(-\beta \cdot (r - Re)))^2$$



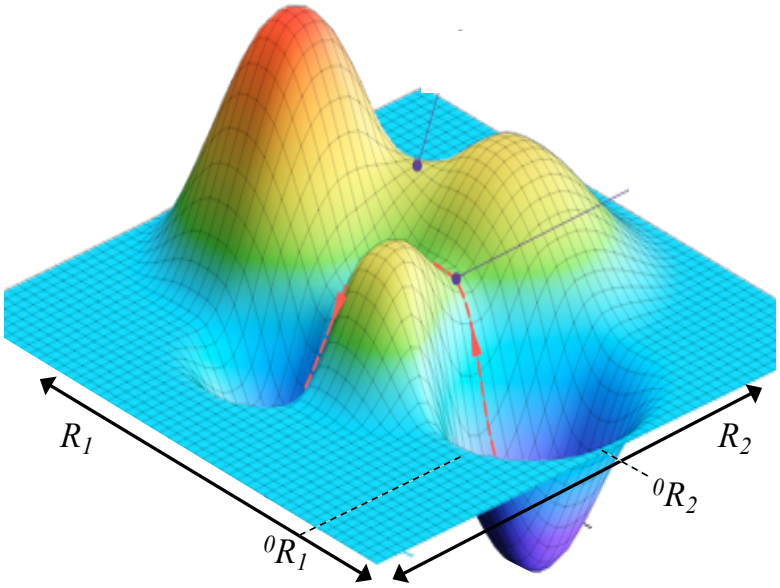
$$E_{vib}(n) = hc \cdot [(n+1/2) \cdot \omega_e - (n+1/2)^2 \cdot \omega_e \cdot \chi_e]$$

Electronic energy levels

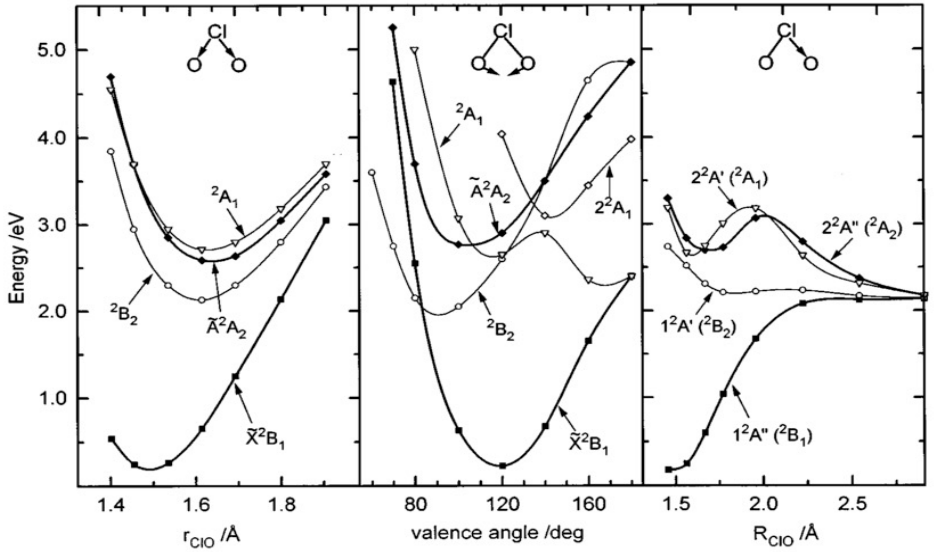
- Electronic energy depends on position of nuclei =>
- *EE* is a function of 3N-6 or 3N-5 vibrational coordinates (lengths of bonds, angles between bonds).
- Electronic energy is a multi-dimensional surface. Electronic states are difficult to calculate; they have complex notations due to many quantum numbers assigned to each state.



Diatomic

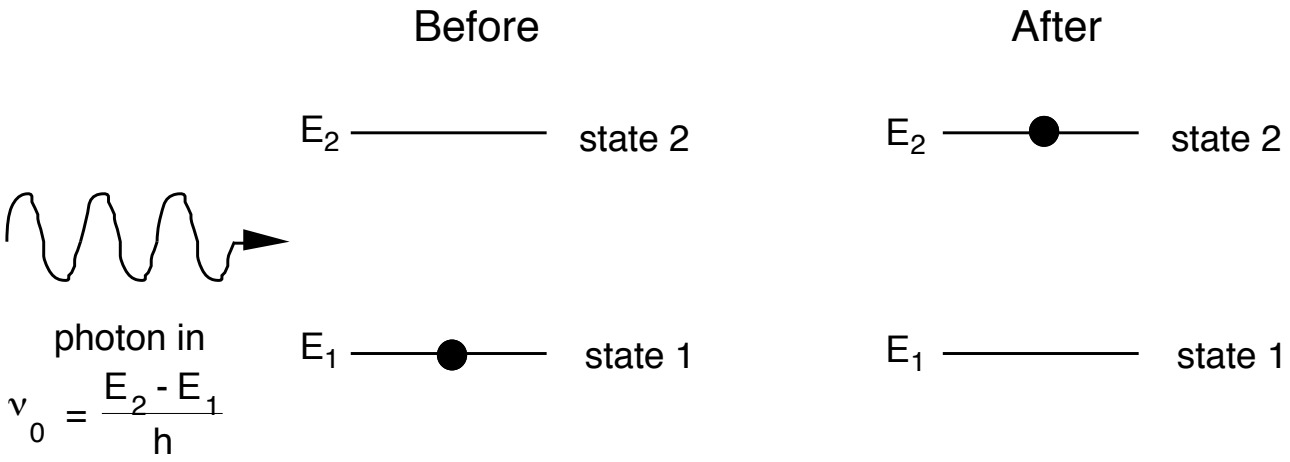


2D PES for triatomic molecule



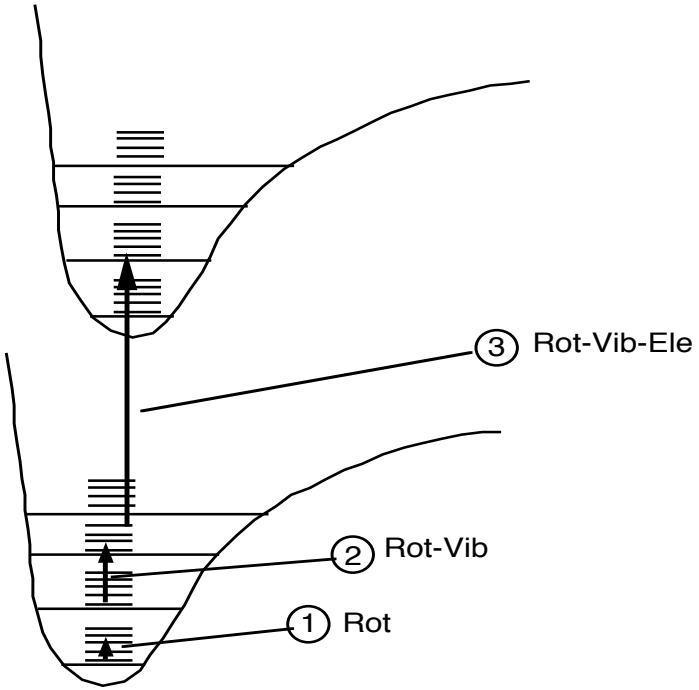
Cuts of PES for a triatomic molecule

Spectroscopic transitions



Rotational:
10^{-3}-10^{-1} m,
Rotational-vibrational (rovibrational):
3-30 micron,
Rovibrational-electronic (rovibronic):
500-100 nm.

Absorption (emission) changes
translational energy only very tiny



Probability of spectroscopic transitions

In Born Oppenheimer approximation the state of a molecule:

$$\Psi = \psi_{el}(r, R_e) \cdot \psi_{vib}(R) \cdot, \psi_{rot}(\varphi),$$

- Absorption, spontaneous and stimulated emissions occur due to a change of transition electric dipole moment (DM) of a molecule.

$$\mu(\vec{r}) = \sum_k q_k \cdot \vec{r}_k, \quad \text{Sum over all nuclei and electrons;} \qquad \vec{r} \in (r, R, \varphi).$$

- The probability for optical transition 2 ← 1 is determined by the square of transition DM integral M_{21}:

$$\vec{M}_{21} \left\langle \Psi' \middle| \vec{\mu} \middle| \Psi'' \right\rangle = \int \Psi'(\vec{r}) \hat{\mu}(\vec{r}) \Psi''(\vec{r}) d\vec{r},$$

$$M_{21} = \iiint \psi'_{el}(r, R_e) \psi'_{vib}(R) \psi'_{rot}(\varphi) \cdot (\hat{\mu}_{el} + \hat{\mu}_{vib} + \hat{\mu}_{rot}) \psi''_{el}(r, R_e) \psi''_{vib}(R) \psi''_{rot} \, d\vec{r},$$

$$d\vec{r} \equiv dr \cdot dR \cdot d\varphi.$$

Because ***r***, ***R*** and **φ** are independent this expression can be simplified.

Probability of spectroscopic transitions

$$M_{21} = \iiint \psi'_{el}(r,R_e)\psi'_{vib}(R)\psi'_{rot}\cdot(\mu_{el}+\mu_{vib}+\mu_{rot})\psi''_{el}(r,R_e)\psi''_{vib}(R)\psi''_{rot}\,d\vec{r},$$

The three parts of the triple integral can be rearranged:

$$M'_{21} = \int(\psi'_{el}\mu_{el}\psi''_{el})dr\cdot\int(\psi'_{vib}\psi''_{vib})dR\cdot\int(\psi'_{rot}\psi''_{rot})d\varphi;$$

$$M''_{21} = \int(\psi'_{el}\psi''_{el})dr\cdot\int(\psi'_{vib}\mu_{vib}\psi''_{vib})dR\cdot\int(\psi'_{rot}\psi''_{rot})d\varphi;$$

$$M'''_{21} = \int(\psi'_{el}\psi''_{el})dr\cdot\int(\psi'_{vib}\psi''_{vib})dR\cdot\int(\psi'_{rot}\mu_{rot}\psi''_{rot})d\varphi.$$

For a rovibronic transition: $\psi'_{el}\perp\psi''_{el}$; while ψ'_{vib},ψ''_{vib} and ψ'_{rot},ψ''_{rot} are not.

=> M''=M'''=0: $M_{21}^{rve} = \int(\psi'_{el}\mu_{el}\psi''_{el})dr\int(\psi'_{vib}\psi''_{vib})dR\int(\psi'_{rot}\psi''_{rot})d\varphi;$

For a rovibrational transition: $\psi'_{el}=\psi''_{el};\ \psi'_{vib}\perp\psi''_{vib}$.

=> M'=M'''=0: $M_{21}^{rv} = 1\cdot\int(\psi'_{vib}\mu_{vib}\psi''_{vib})dR\cdot\int(\psi'_{rot}\psi''_{rot})d\varphi.$

For a purely rotational transition: $\psi'_{el}=\psi''_{el};\ \psi'_{vib}=\psi''_{vib};\ \psi'_{rot}\perp\psi''_{rot}$.

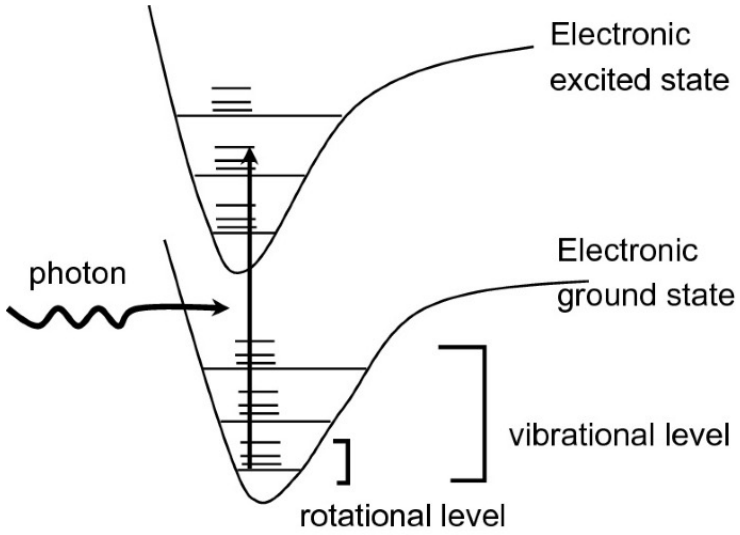
=> M'=M''=0: $M_{21}^{r} = \int(\psi'_{rot}\mu_{rot}\psi''_{rot})d\varphi;$

Probability of rovibronic transitions

$$M_{21}^{rve} = \int (\psi'_{el} \mu_{el} \psi''_{el}) dr \int (\psi'_{vib} \psi''_{vib}) dR \int (\psi'_{rot} \psi''_{rot}) d\varphi;$$

The probability for a molecule to change its quantum state due to absorption (emission) of a photon is proportional to M_{21}^2 .

The **1st** factor is called **electronic** TDM;
the square of the **2nd** factor is Franck-Condon.



The coordinates are complex:

electron spin

$$r = (r_1, \ldots r_m;\ s_1, \ldots s_m);$$

$$R = (R_1, \ldots R_n;\ I_1, \ldots I_n);$$

nuclear spin

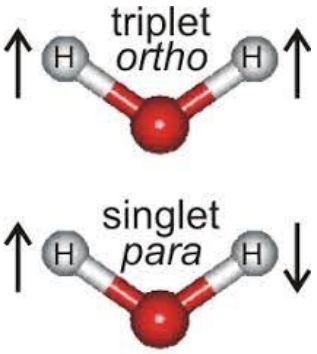
$$\varphi = (\varphi, \theta)$$

Often, only valent electrons can change their orbitals upon excitation, =>
The number of electrons (and of their ***r***) to consider is often a few in a given spectral range.

Probability of rovibronic transitions

$$M_{21}^{rve} = \int (\psi'_{el} \mu_{el} \psi''_{el}) dr \int (\psi'_{vib} \psi''_{vib}) dR \int (\psi'_{rot} \psi''_{rot}) d\varphi;$$

There are some strict physical rules:



- Nuclear **spins** do not flip upon optical excitation.
  Example: ortho- and para- water.
- Electronic **spins** do not flip: only singlet-singlet and triplet-triplet transitions are allowed.
- Total **angular momentum** of (molecular + spin of photon, S=±1, 0) must be conserved.=> $\boldsymbol{J}_{rot}$=±1 (always), =0 (for molecules of certain symmetries)

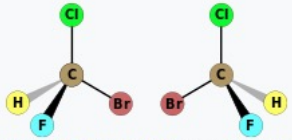
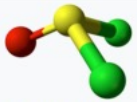
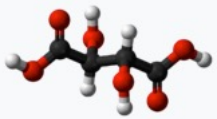
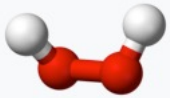
Electronic TDM is non-zero, if the sub-integral function is **even** for the components of its multi-dimensional variable that change upon excitation (unchanged are equal). =>

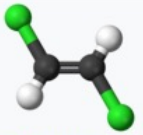
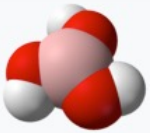
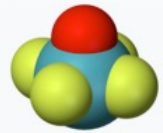
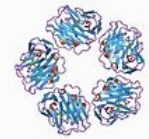
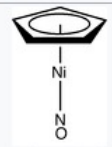
$$\int_{-\infty}^{+\infty} even(r) \cdot odd(r) \cdot even(r) dr = even \Big|_{-\infty}^{+\infty} = 0$$

Whether TDM ≠ 0 is determined by mutual symmetry of Ψ', Ψ'', and μ_{el} . This can be determined from the symmetry of a molecule with respect to 5 symmetry operations using point **group symmetry** classification.

The lowest state is always symmetrical => Ψ' and $\boldsymbol{\mu}_{el}$(x, y, z) must have, at least, one component of the same group.

Examples of symmetry point groups

Point group	Symmetry operations[14]	Simple description of typical geometry	Example 1
C_1	E	no symmetry, chiral	 bromochlorofluoromethane (both enantiomers shown)
C_s	$E\ \sigma_h$	mirror plane	 thionyl chloride
C_i	$E\ i$	inversion center	 *meso*-tartaric acid
$C_{\infty v}$	$E\ 2C_\infty^\Phi\ \infty\sigma_v$	linear	 hydrogen fluoride (and all other heteronuclear diatomic molecules)
$D_{\infty h}$	$E\ 2C_\infty^\Phi\ \infty\sigma_i\ i\ 2S_\infty^\Phi\ \infty C_2$	linear with inversion center	 oxygen (and all other homonuclear diatomic molecules)
C_2	$E\ C_2$	"open book geometry", chiral	 hydrogen peroxide
C_3	$E\ C_3\ C_3^2$	propeller, chiral	 triphenylphosphine

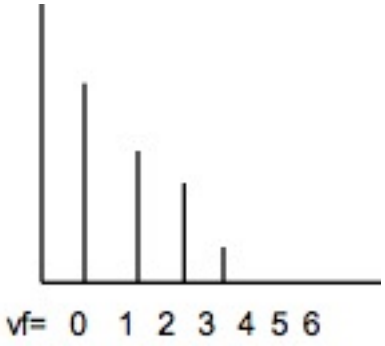
Point group	Symmetry operations[14]	Simple description of typical geometry	Example 1
C_{2h}	$E\ C_2\ i\ \sigma_h$	planar with inversion center, no vertical plane	 *trans*-1,2-dichloroethylene
C_{2v}	$E\ C_2\ \sigma_v(xz)\ \sigma_v'(yz)$	angular (H_2O) or see-saw (SF_4)	 water
C_{3h}	$E\ C_3\ C_3^2\ \sigma_h\ S_3\ S_3^5$	propeller	 boric acid
C_{3v}	$E\ 2C_3\ 3\sigma_v$	trigonal pyramidal	 ammonia (if pyramidal inversion is neglected)
C_{4v}	$E\ 2C_4\ C_2\ 2\sigma_v\ 2\sigma_d$	square pyramidal	 xenon oxytetrafluoride
C_5	$E\ 2C_5\ 2C_5^2$	five-fold rotational symmetry	 C-reactive protein
C_{5v}	$E\ 2C_5\ 2C_5^2\ 5\sigma_v$	'milking stool' complex	 $Ni(C_5H_5)(NO)$

Franck-Condon factor

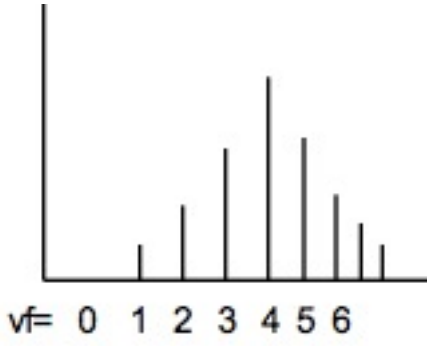
$$M_{21}^{rve} = \int (\psi'_{el} \mu_{el} \psi''_{el}) dr \int (\psi'_{vib} \psi''_{vib}) dR \int (\psi'_{rot} \psi''_{rot}) d\varphi;$$

$$FCF = \left| \int (\psi'_{vib} \psi''_{vib}) dR \right|^2$$

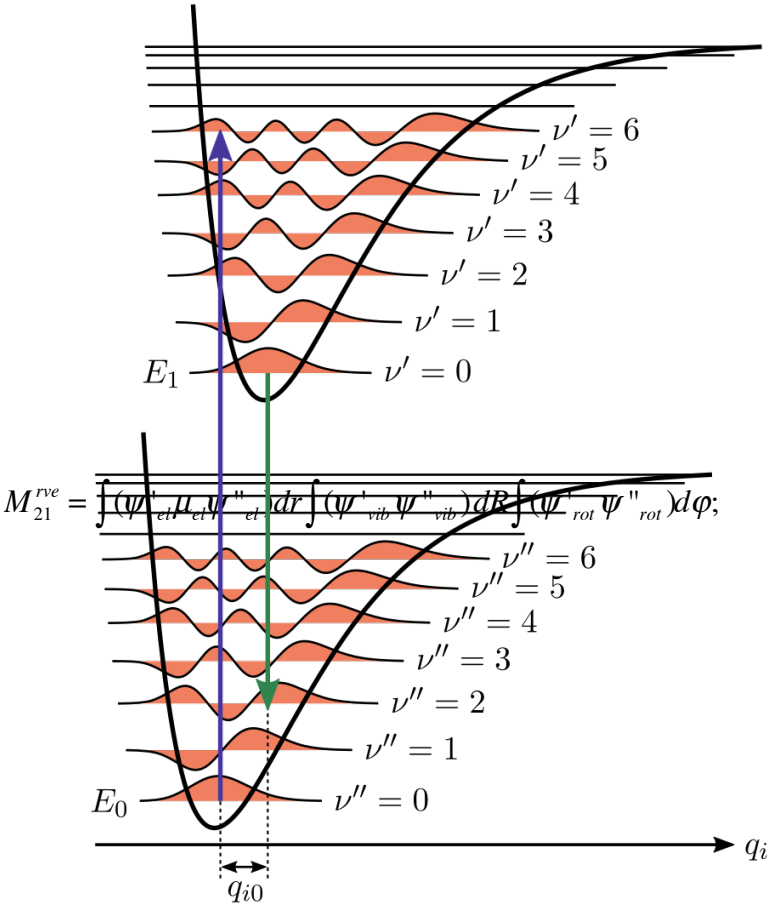
F-C factor controls intensity of vibronic transitions. Because Ψ'_{vib} and Ψ'_{vib} belong to different electronic states, FCF, in general, is non-zero. It is determined by the overlap of the wavefunctions and reflects alignment of electronic PES:



aligned



shifted



Transitions are shown vertical because nuclei do not move during electronic transition

Probability for rovibrational transitions

$$M_{21}^{rv} = 1 \cdot \int (\psi'_{vib}\, \mu_{vib} \psi''_{vib})\, dR \cdot \int (\psi'_{rot}\, \psi''_{rot})\, d\varphi.$$

Rotational selection rules remain the same;

Vibrational selection rules for harmonic oscillator: $\Delta v = \pm 1$; (fundamental)

Anharmonicity adds much weaker transitions with $\Delta v = \pm 2, \pm 3 \ldots$ (1^{st}, 2^{nd},…overtones)

Typically, intensity of vibrational overtones scales as: $I(\Delta v)/I(1 \leftarrow 0) \sim 10^{\Delta v - 1}$

Pure rotational transitions

$$M_{21}^{r} = \int (\psi'_{rot}\, \mu_{rot} \psi''_{rot})\, d\varphi;$$

Because rotation of a molecule does not change separation of electrons and nuclei, pure rotational transitions (microwave) are only possible for molecules with a permanent dipole moment. Selection rules are $\Delta J = \pm 1$ (fundamental)

Probability for rovibrational transitions

$$M_{21}^{rv} = 1 \cdot \int (\psi'_{vib}\, \mu_{vib} \psi''_{vib})\, dR \cdot \int (\psi'_{rot}\, \psi''_{rot})\, d\varphi.$$

Rotational selection rules remain the same;
Vibrational selection rules for harmonic oscillator: $\Delta v = \pm 1$; (fundamental)
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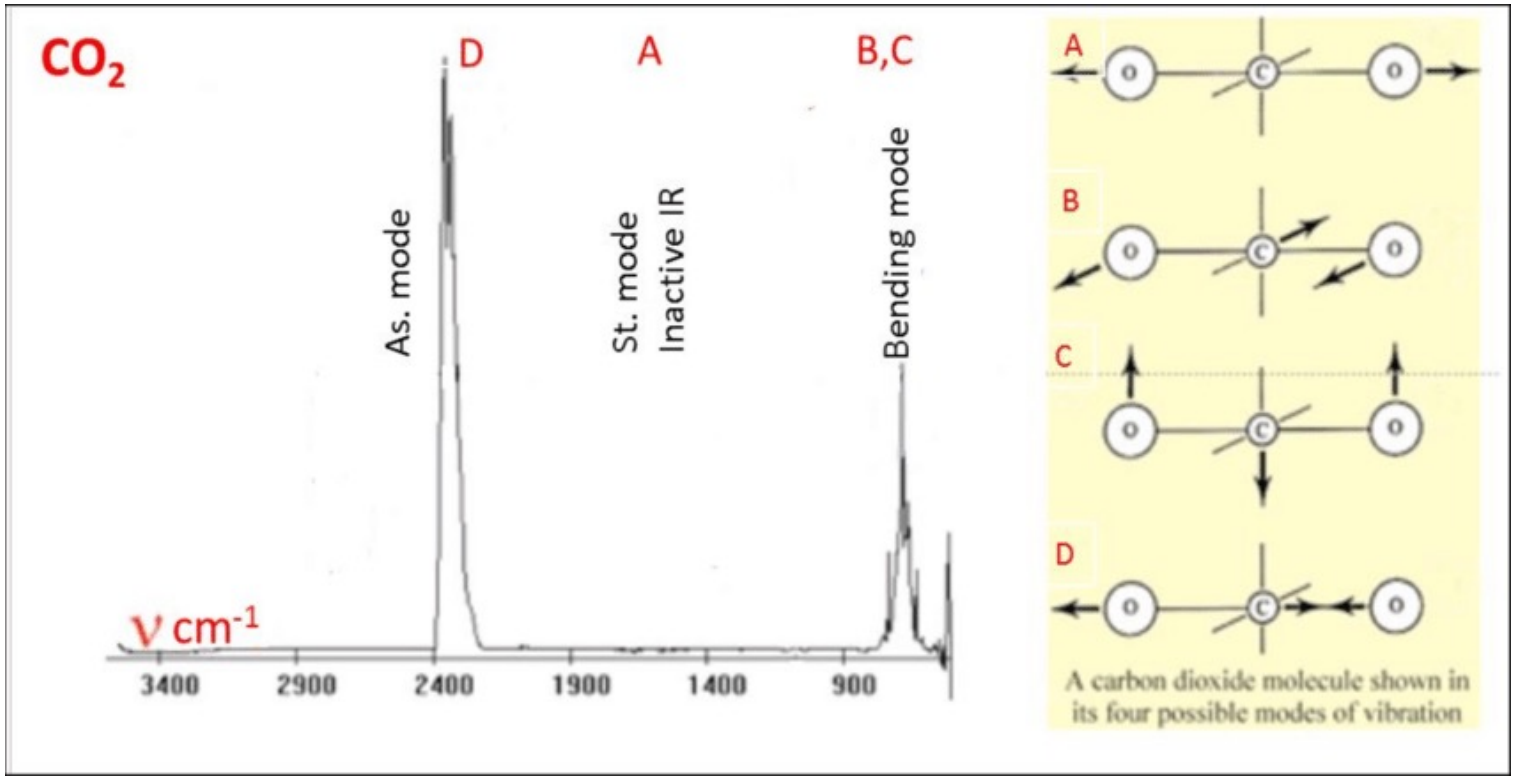

Probability for rovibrational transitions

$$M_{21}^{rv} = 1 \cdot \int (\psi'_{vib}\, \mu_{vib} \psi''_{vib})\, dR \cdot \int (\psi'_{rot}\, \psi''_{rot})\, d\varphi.$$

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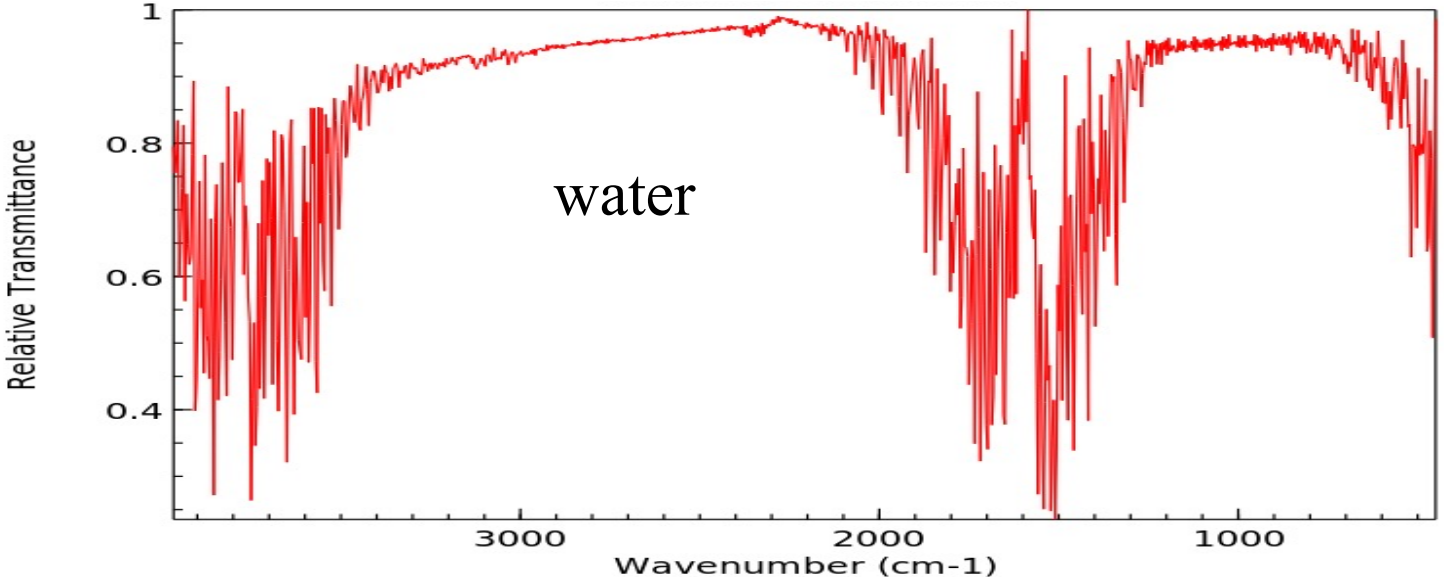
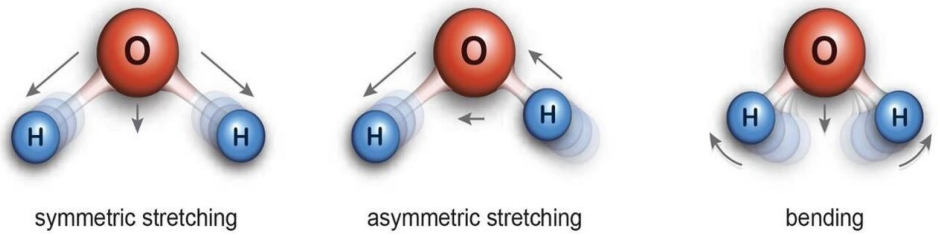
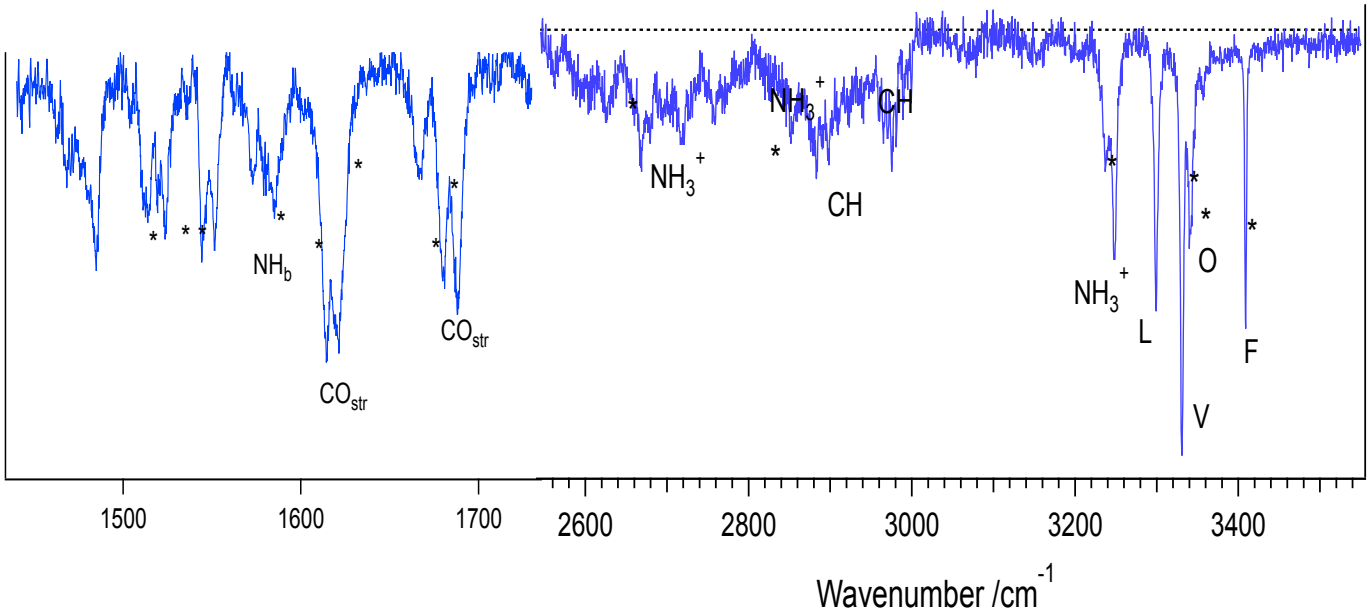


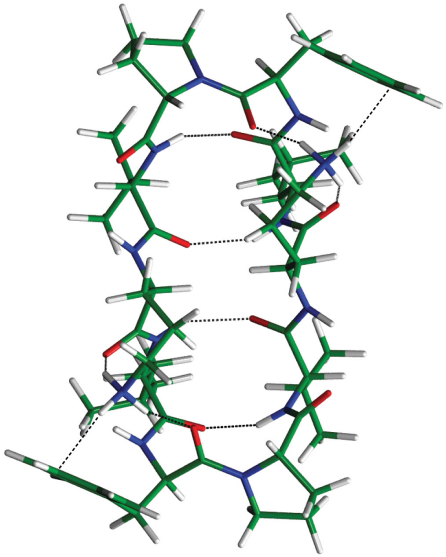


Probability for rovibrational transitions

$$M_{21}^{rv} = 1 \cdot \int (\psi'_{vib}\, \mu_{vib} \psi''_{vib})\, dR \cdot \int (\psi'_{rot}\, \psi''_{rot})\, d\varphi.$$

Rotational selection rules remain the same;
Vibrational selection rules for harmonic oscillator: $\Delta v = \pm 1$; (fundamental)
Anharmonicity adds much weaker transitions with $\Delta v = \pm 2, \pm 3 \ldots$ (1^{st}, 2^{nd},…overtones)
Typically, intensity of vibrational overtones scales as: $I(\Delta v)/I(1 \leftarrow 0) \sim 10^{\Delta v - 1}$





Decapeptide (146 atoms)

- All vibrations are active
- No rotational resolution is possible

Non-radiative transitions

1. **Intramolecular**
2. **Collisional**

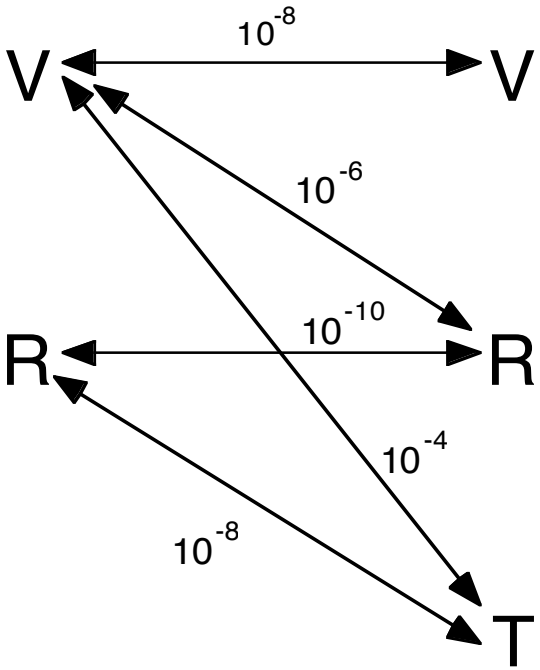
Resonant conditions

$$K \propto \frac{V_{ab}^2}{E_a - E_b};$$

Energy is still conserved!

$$\Delta(\sum E^d) = \Delta(\sum E^a);$$

Electronic ground state:

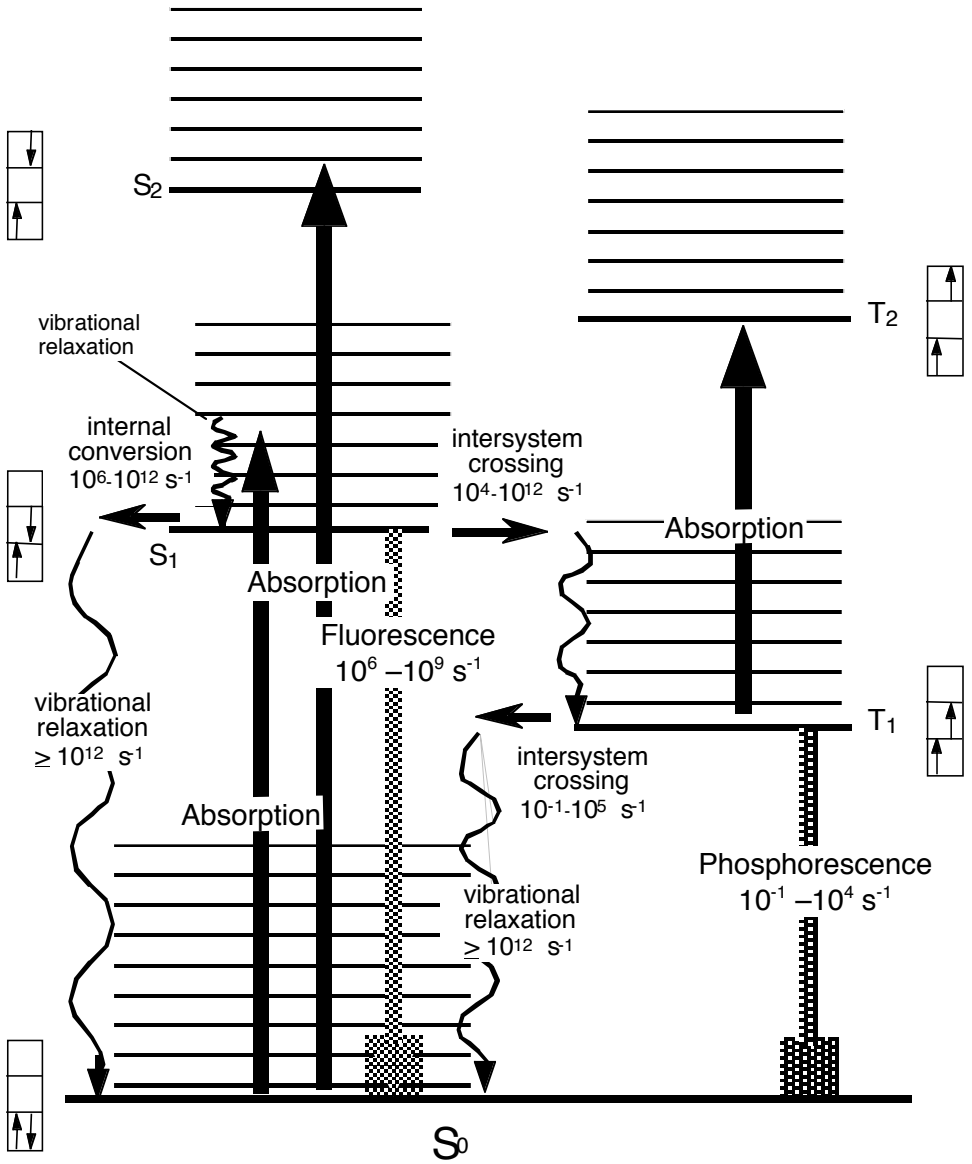


Schematic diagram showing the energy transfer processes occurring in thermal molecular collisions. V, R, and T refer to vibrational, rotational, and translational energy respectively. The numbers are typical values of $P\tau$ (atm s), the bulk "relaxation time" characterizing the particular mode of energy transfer (Adapted from W. H. Flygare, Accounts chem. Res **1**, 121 (1968)).

Non-radiative transitions

The lowest triplet state is labeled as T_1

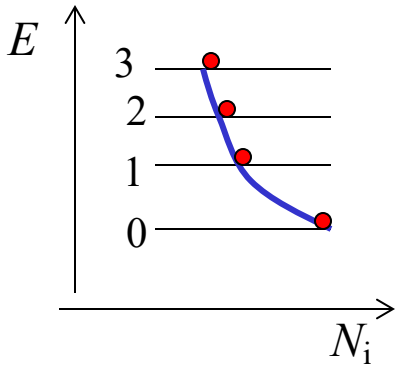
Electronic ground state, S_0, is always singlet



State populations

Apart from M_{21}^2 , intensity of a transition depends on number of molecules in the state Ψ_1

Temperature: T; T_{tr}, T_{rot}, T_{vib}, T_{el};



Boltzmann distribution:

$$N_i = c\, g_i\, e^{-E_i/k_b T}$$

Proportionality constant:

$$\sum_i N_i = N = c \sum_i g_i\, e^{-E_i/k_b T} \quad \Rightarrow \quad c = \frac{N}{\sum_i g_i\, e^{-E_i/k_b T}}$$

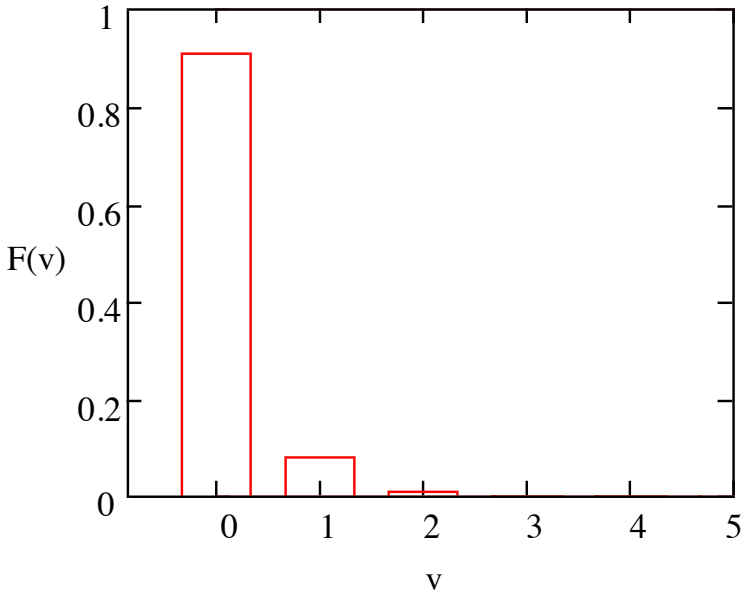
$$N_i = \frac{N g_i\, e^{-E_i/k_b T}}{\sum_i g_i\, e^{-E_i/k_b T}}$$

Thermal equilibrium:

$$n_i \equiv \frac{N_i}{g_i} = c\, e^{-E_i / k_b T}$$

$$\frac{n_2}{n_1} = e^{-(E_2 - E_1)_i / k_b T}$$

$$\left(\frac{N_2}{g_2} - \frac{N_1}{g_1}\right) \equiv (n_2 - n_1) = n_1 \left(e^{-(E_2 - E_1)_i / k_b T} - 1\right)$$



$E_2 > E_1 \Longrightarrow n_2 < n_1$

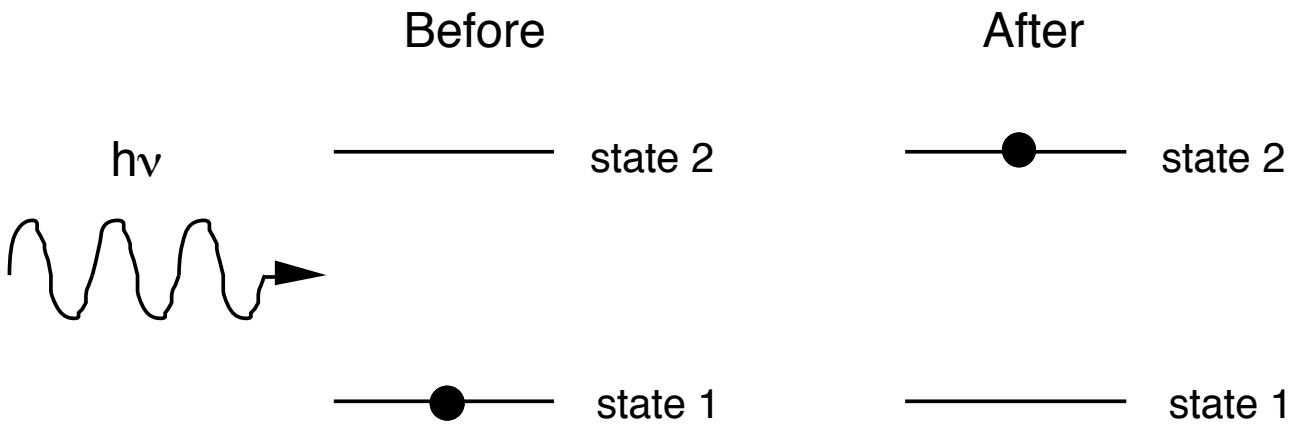
At thermal equilibrium the lower is a level the high is its population.

Apart from degeneracy, the ground state is always the most populated

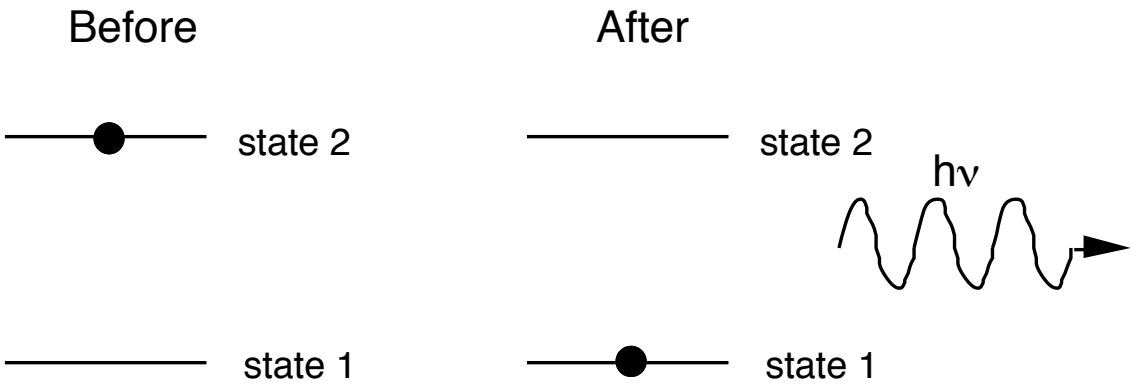
Rate Equation Approach

Interaction between radiation and matter

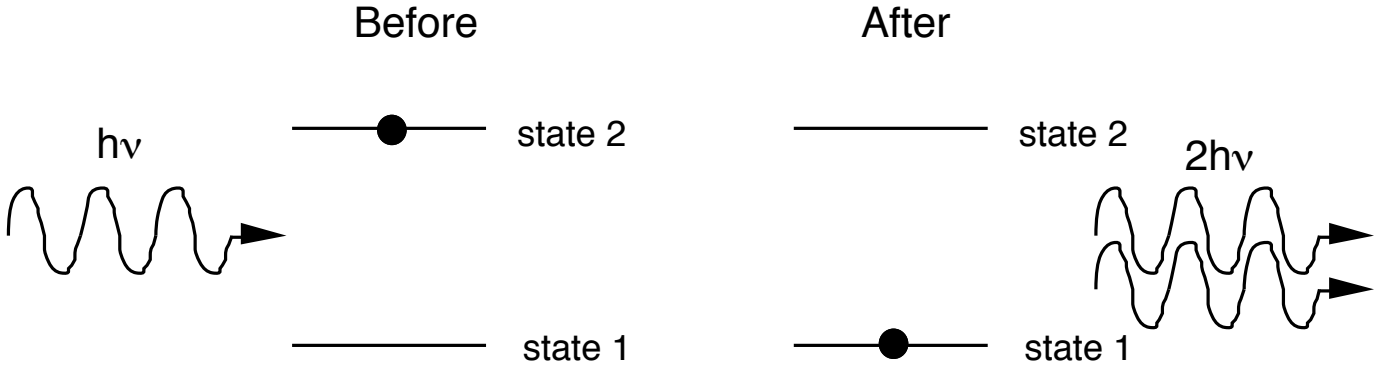
ABSORPTION



Spontaneous emission



Stimulated emission



Einstein Coefficients

$$N = N_1 + N_2$$

Spectral density of energy: $\rho(\nu): \quad \delta E = \rho(\nu)\cdot\delta V\cdot\delta\nu;$

$$[\rho(\nu)] = \frac{J\cdot s}{cm^3} = \frac{J}{cm^3\cdot Hz};$$

Absorption:

$$\frac{dN_2}{dt} = B_{12}\,\rho(\nu_{12})N_1$$

Spectral density of photons: $\delta n = \frac{\delta E}{h\nu} = \frac{\rho(\nu)\cdot\delta V\cdot\delta\nu}{h\nu};$

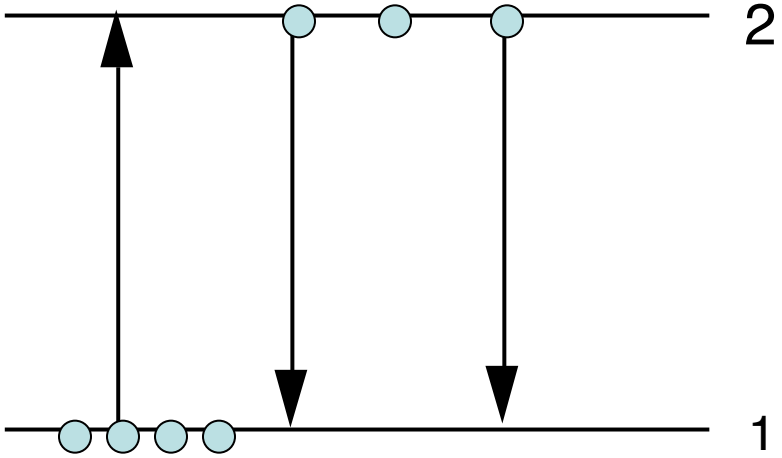
Spontaneous emission:

$$\frac{dN_2}{dt} = -A_{21}\,N_2$$

$$N_2 = c\cdot\exp(-A_{21}t), \qquad \tau = \frac{1}{A_{21}}$$

Stimulated emission:

$$\frac{dN_2}{dt} = -B_{21}\,\rho(\nu_{12})N_2$$



The systems are at equilibrium (T) !

System in equilibrium:

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0$$

$$B_{12}\,\rho(\nu_{12})N_1 - A_{21}\,N_2 - B_{21}\,\rho(\nu_{12})N_2 = 0$$

$$B_{12}\,\rho(\nu_{12})N_1 = A_{21}\,N_2 + B_{21}\,\rho(\nu_{12})N_2 = (A_{21} + B_{21}\,\rho(\nu_{12}))N_2$$

$$\frac{N_2}{N_1} = \frac{B_{12}\,\rho(\nu_{12})}{A_{21} + B_{21}\,\rho(\nu_{12})}$$

Taking into account:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{(E_2 - E_1)}{k_b T}} = \frac{g_2}{g_1} e^{-\frac{h\nu_{12}}{k_b T}}$$

$$\frac{B_{12}\,\rho(\nu_{12})}{A_{21} + B_{21}\,\rho(\nu_{12})} = \frac{g_2}{g_1} e^{-\frac{h\nu_{12}}{k_b T}}$$

$$\rho(\nu_{12}) = \frac{A_{21}\dfrac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}}{B_{12} - B_{21}\dfrac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}} = \frac{A_{21}}{B_{12}\dfrac{g_1}{g_2}e^{\frac{h\nu_{12}}{k_bT}} - B_{21}}$$

From Planck's law of black body radiation: $\rho(\nu_{12}) = \dfrac{8\pi h\nu^3}{c^3}\dfrac{1}{e^{\frac{h\nu}{k_bT}} - 1}$

$$\frac{8\pi h\nu_{12}^3}{c^3}\frac{1}{e^{\frac{h\nu_{12}}{k_bT}} - 1} = \frac{A_{21}}{B_{12}\dfrac{g_1}{g_2}e^{\frac{h\nu_{12}}{k_bT}} - B_{21}}$$

1) $B_{12}\dfrac{g_1}{g_2} = B_{21}$,

$\tau_{sp} \propto \dfrac{1}{\nu^3}$

2) $A_{21} = \dfrac{8\pi h}{c^3}\cdot\nu_{12}^3 B_{21}$

Einstein Coefficients

$$B_{12}\frac{g_1}{g_2} = B_{21},$$

Apart from degeneracy, the probability for a molecule to absorb and to emit a photon is the same.

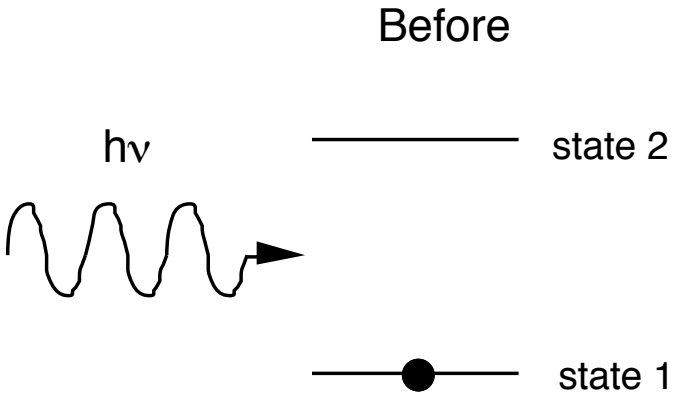
$$A_{21} = \frac{8\pi h}{c^3}\cdot\nu_{12}^3 B_{21}$$

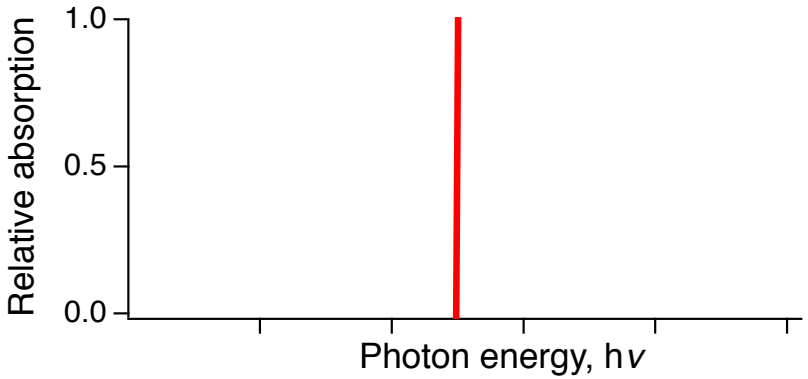
Intensity of spontaneous emission (fluorescence) scales up with photon energy:
Electronic: λ= 0.3-0.7 μm
Vibrational: λ= 3-10 μm; => 10^3 times weaker
Rotational: λ= 10^3-10^4 μm; => 10^6-10^7 times weaker

$$\tau_{sp} \propto \frac{1}{\nu^3}$$

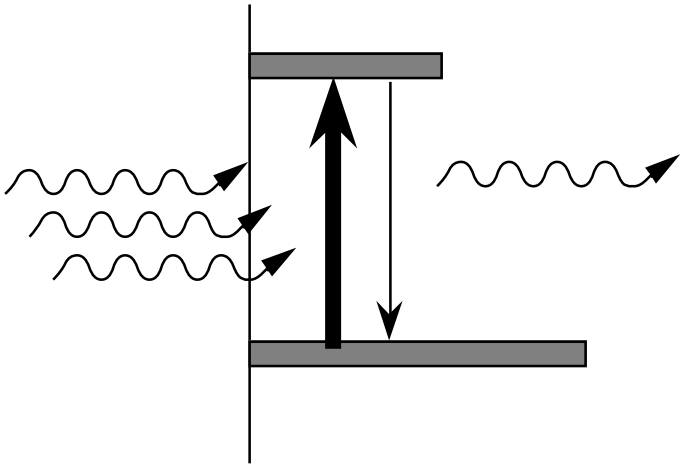
Consistently, lifetime of electronic states is 10^3 and 10^7 times shorter than of vibrational and rotational states, respectively.

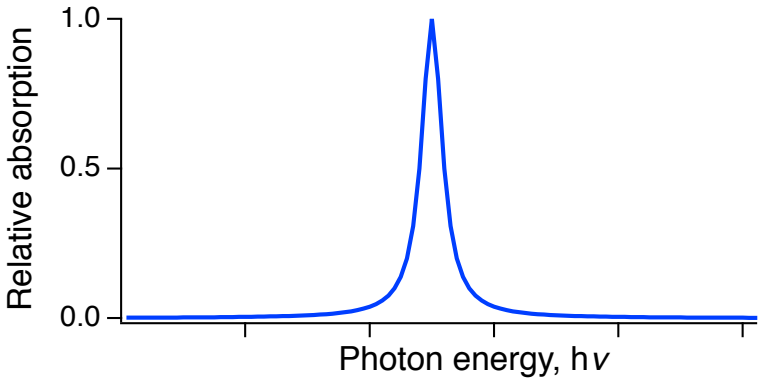
Spectral lineshape





Spectral lineshape





Life-time spectral broadening:

Uncertainty principle: $\Delta E\,\tau \geq \hbar$ or $(\Delta E = h\,\Delta\nu)$

$$\Delta\nu \geq \frac{1}{2\pi\tau}$$

1. *Natural linewidth:* $\tau = \frac{1}{A} \propto \frac{1}{\nu^3}$ $\quad \Delta\tilde{\nu} \geq \frac{1}{2\pi c\tau}$ (cm^{-1}); $\quad \Delta\tilde{\nu} \propto \tilde{\nu}^3$

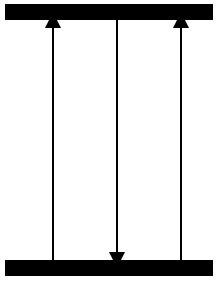
Lorentzian: $$g(\nu) = \frac{\Delta\nu / 2\pi}{(\nu - \nu_0)^2 + \Delta\nu^2 / 4}$$

Homogeneous broadening (Lorentzian)

2. Pressure broadening:

$$\Delta\nu \propto \frac{1}{\tau_{coll}} \quad (\tau_{coll} \propto \frac{1}{P}) \Rightarrow \Delta\nu = b\,P \quad \text{(b ~ 10 MHz per mBar)}$$

3. Power broadening



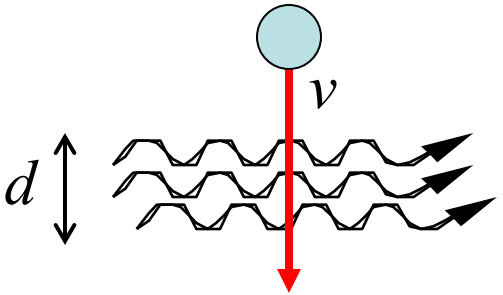
$$\langle n_1 \rangle \cong \langle n_2 \rangle$$

$$n_1 \propto \cos^2(2\pi ft)$$

$$n_2 \propto \sin^2(2\pi ft)$$

$$\Delta\nu = \frac{1}{\tau} \cong f$$

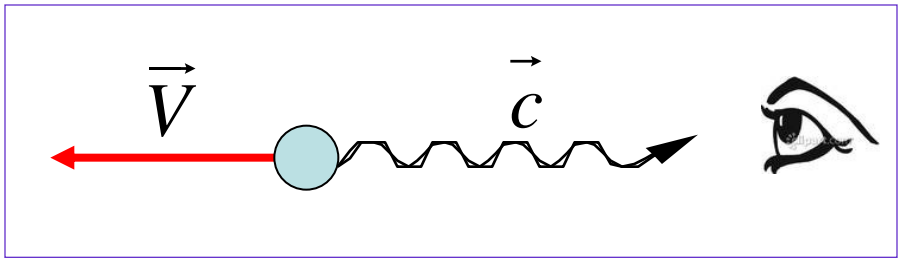
4 Transient time broadening



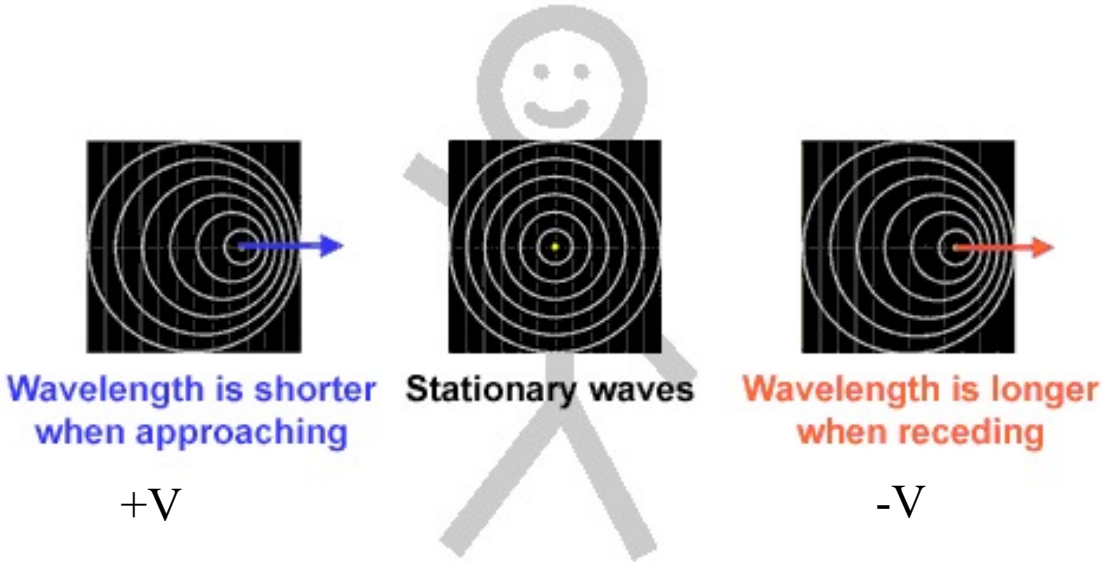
$\tau \cong$ d/v

Inhomogeneous Broadening

Doppler Broadening:



$$\nu_a = \nu_0 \left(1 - \frac{v_a}{c}\right)^{-1} \Rightarrow V_a = \frac{(\nu - \nu_0)c}{\nu}$$



Inhomogeneous Broadening

Doppler Broadening:

$$\nu_a = \nu_0\left(1-\frac{v_a}{c}\right)^{-1} \Rightarrow V_a = \frac{(\nu-\nu_0)c}{\nu}$$

$$dn(V) = p(V)dV;\ p(V) = \left(\frac{m}{2\pi k_b T}\right)^{1/2} e^{-\frac{mV^2}{2k_bT}}$$

$$dn(V) = p(V)\cdot\frac{dV}{d\nu}d\nu \equiv g(\nu)d\nu$$

$$\frac{dV}{d\nu} = \frac{\nu_0\cdot c}{\nu^2} \simeq \frac{c}{\nu_0} \Rightarrow$$

$$g_D(\nu) = \frac{1}{\nu_0}\left(\frac{mc^2}{2\pi k_b T}\right)^{1/2} e^{-\frac{mc^2(\nu-\nu_0)^2}{2k_bT\nu_0^2}}$$

$$g(\nu) = p(V)\cdot\frac{c}{\nu_0} = \frac{c}{\nu_0}\left(\frac{m}{2\pi k_b T}\right)^{1/2} e^{-\frac{mV^2}{2k_bT}}$$

Gaussian line shape

$$\Delta\nu = \frac{2\nu_0}{c}\left(\frac{2k_bT\ln 2}{m}\right)^{1/2} \Rightarrow \Delta\tilde{\nu} = 7.1\cdot 10^{-7}\tilde{\nu}_0\sqrt{\frac{T}{\bar{m}}}$$

(cm^{-1}, m is in a.m.u.)

Inhomogeneous Broadening

Thermal congestion: