NITheCS Mini-School on "Modelling Optical Spectra"

Lecture 1: Basic principles of electronic spectroscopy

7 August 2024

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Outline of the 4 lectures

1. Basic principles of electronic spectroscopy
2. Coupled molecular dipoles: Förster interactions & molecular excitons
3. Linear & nonlinear spectroscopy → Dr. Towan Nöthling
4. Linear & nonlinear spectroscopy → Dr. Towan Nöthling

Outline of this lecture

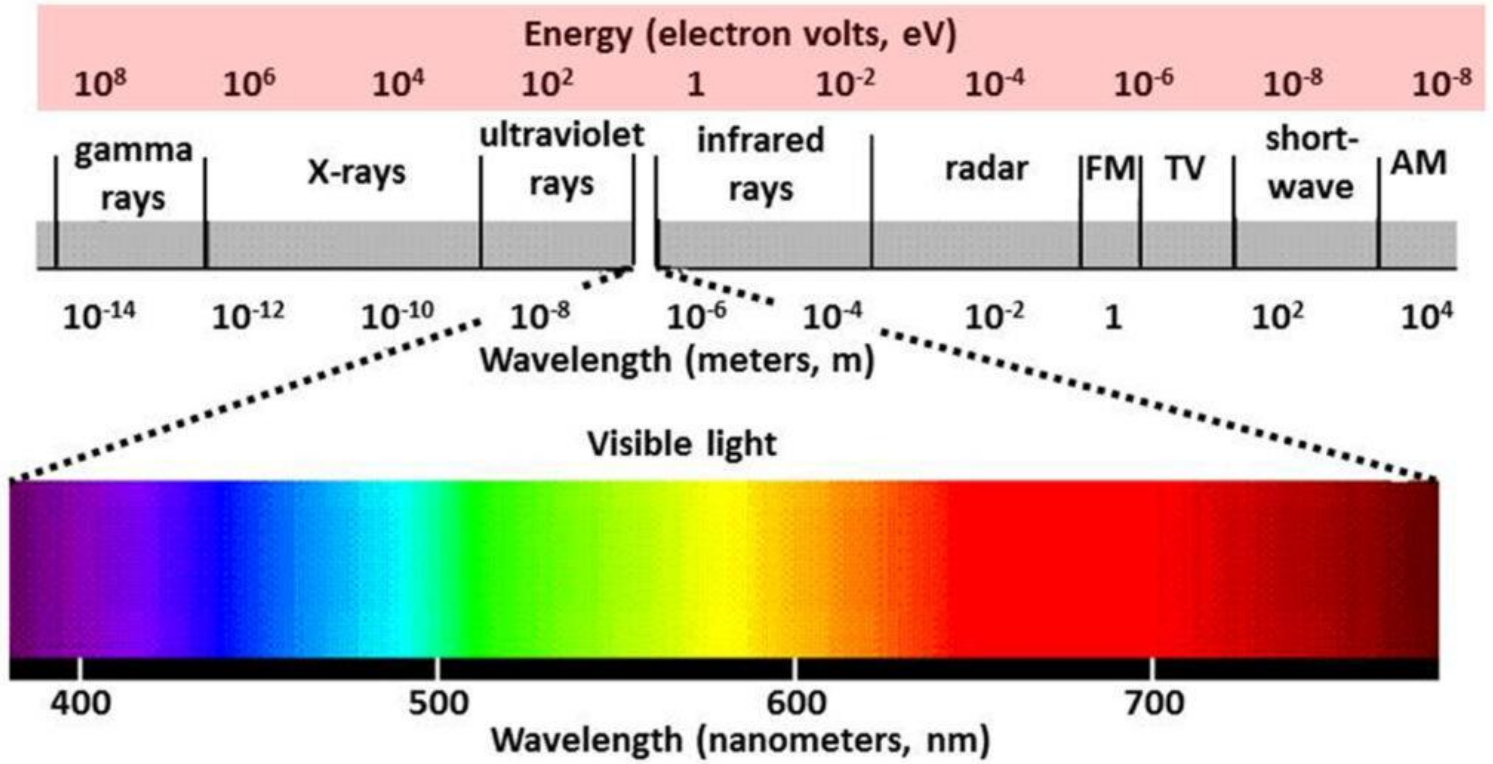
1. Einstein coefficients
2. Law of Lambert-Beer
3. Time-dependent perturbation theory
4. Franck-Condon principle
5. Jablonski diagram
6. Spectral lineshapes/line-broadening

Pre-knowledge

Basic introduction to…

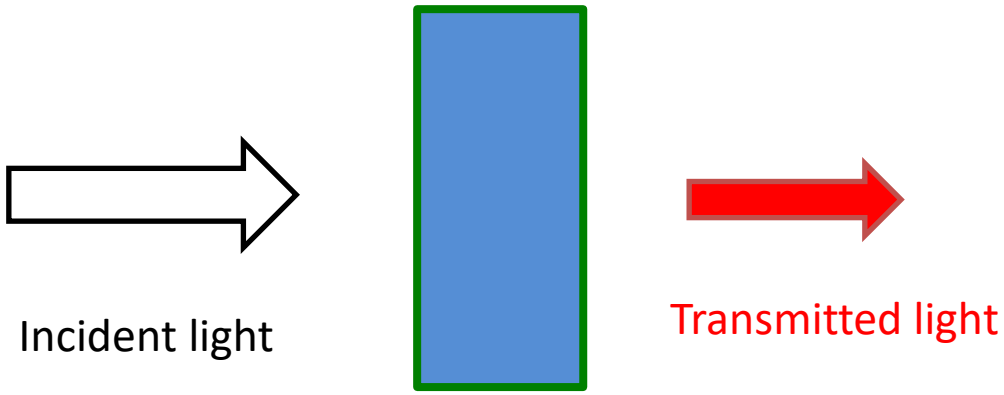
- ✓ Quantum Mechanics
- ✓ Classical Electromagnetism
  - Electrostatics
  - Electromagnetic waves

Spectroscopy = study of light-matter interaction = quantum mechanics



https://ozonedepletiontheory.info/what-is-radiation

Interaction of light with a sample



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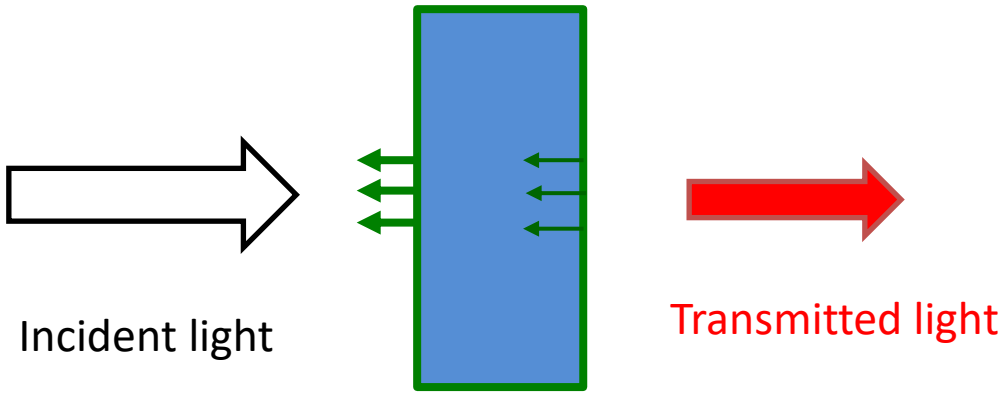
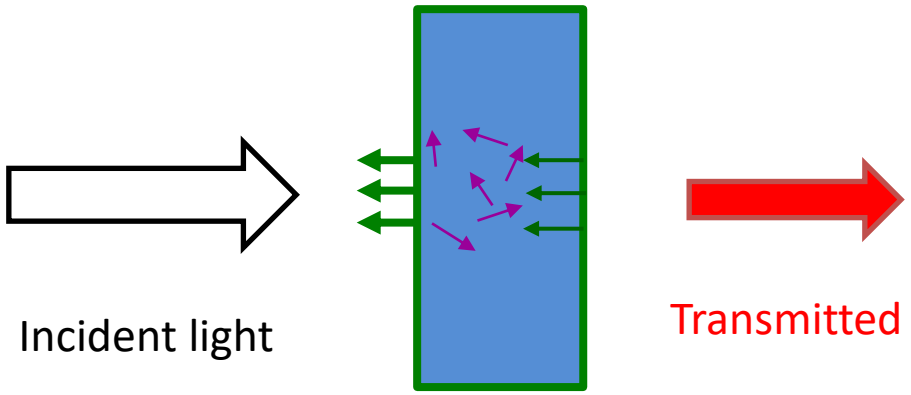


Absorption

Reflection at interfaces

Interaction of light with a sample



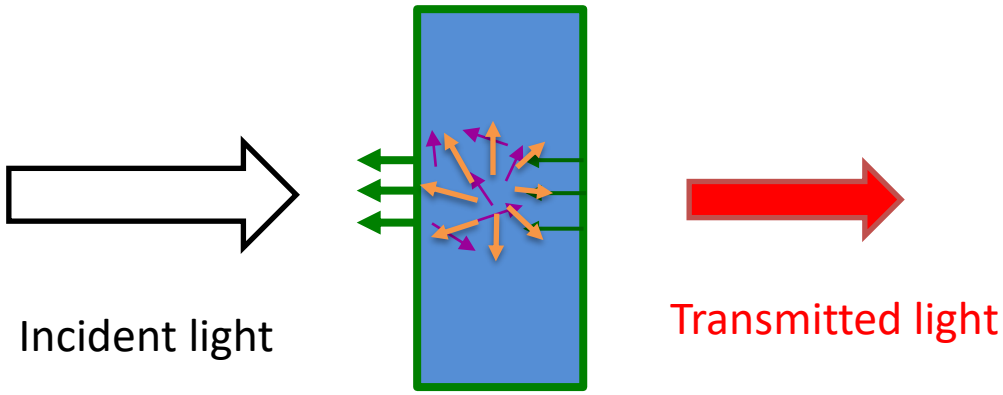
Absorption

Reflection at interfaces

Scattering (Rayleigh, Mie & Raman)

(1871, 1904, 1928)

Interaction of light with a sample



Absorption

Reflection at interfaces

Scattering (Rayleigh, Mie & Raman)

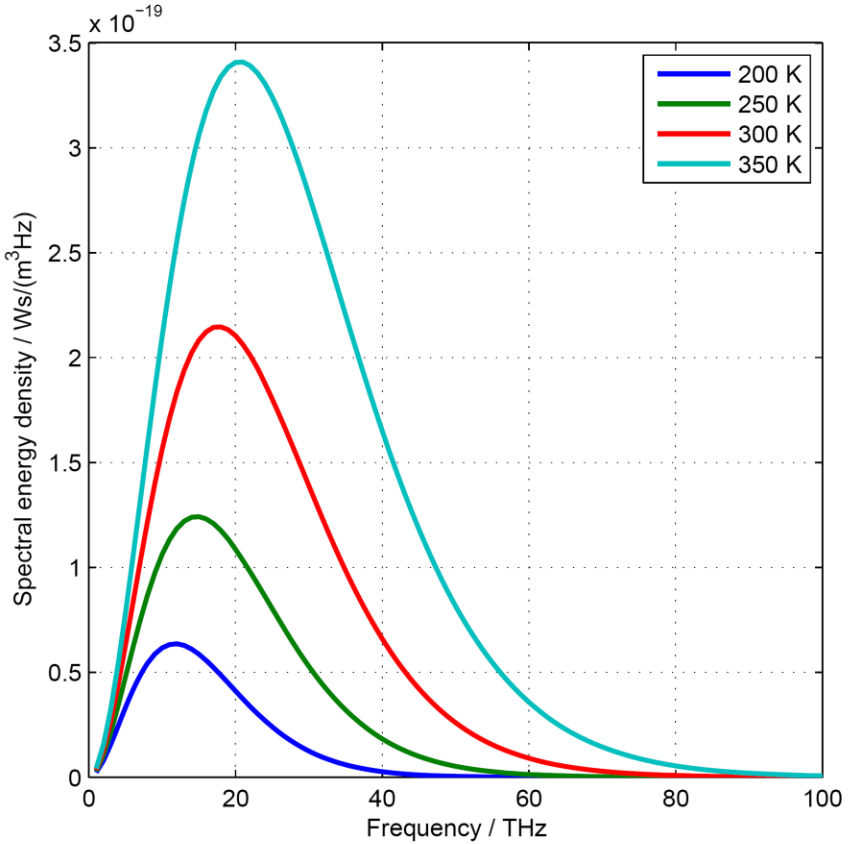
(1871, 1904, 1928)

Emission (1852 by Sir George Stokes)

Light emission

Planck's blackbody radiation law (1900)

$E = \hbar\omega$ ⇒ Spectral energy density $\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{(\hbar\omega/kT)}-1}$



Einstein's theory of the photoelectric effect (1905)

$E_{photon} = \hbar\omega$

http://www.seos-project.eu/modules/earthspectra/earthspectra-c02-p06.ar.html

Light emission

Planck's blackbody radiation law (1900)

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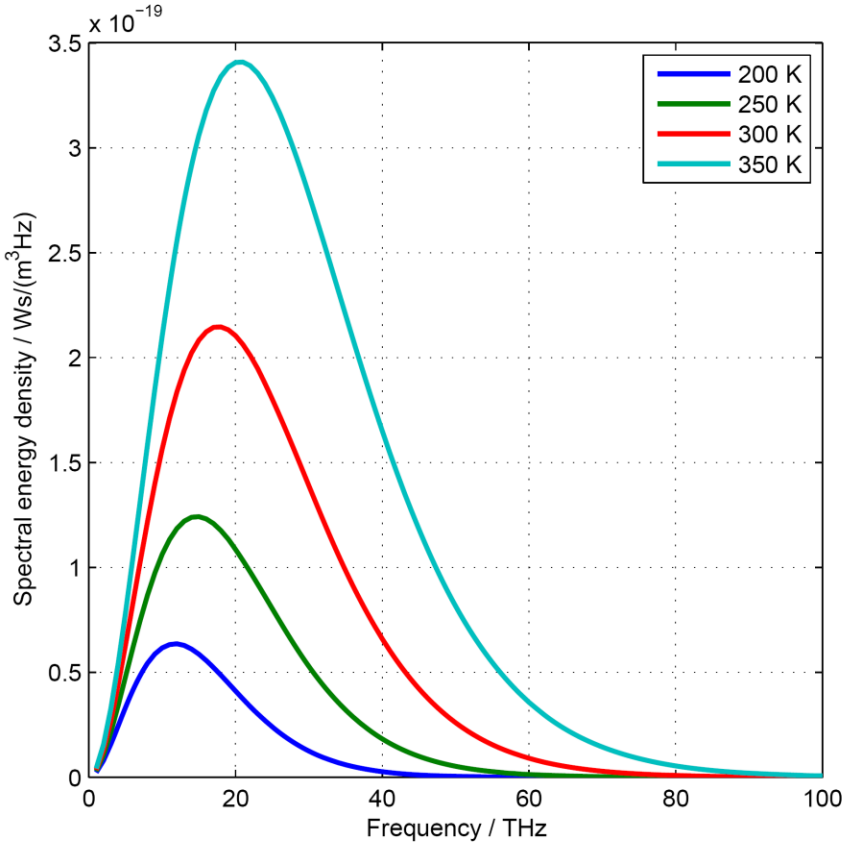
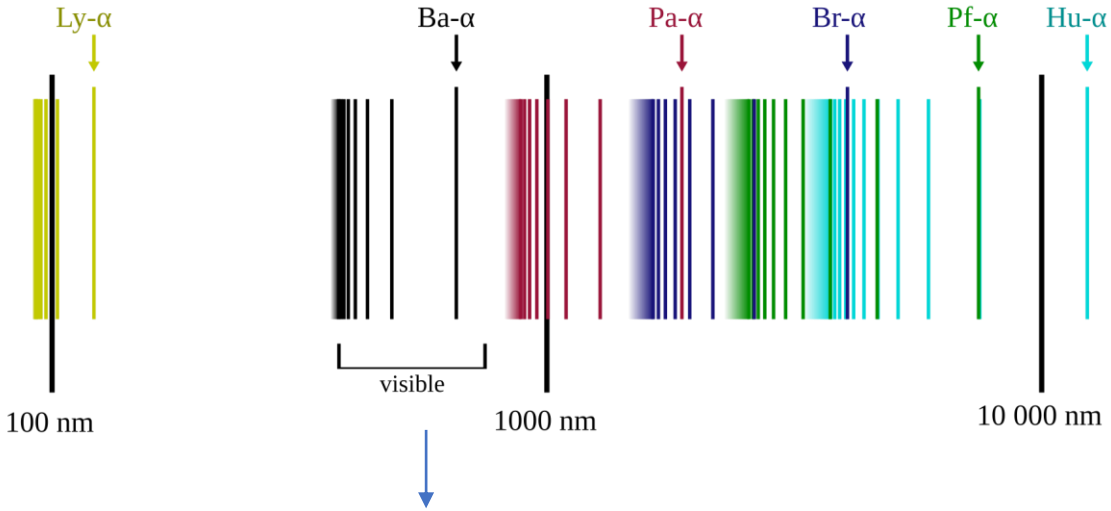


H-atom's emission lines



Balmer (1885)

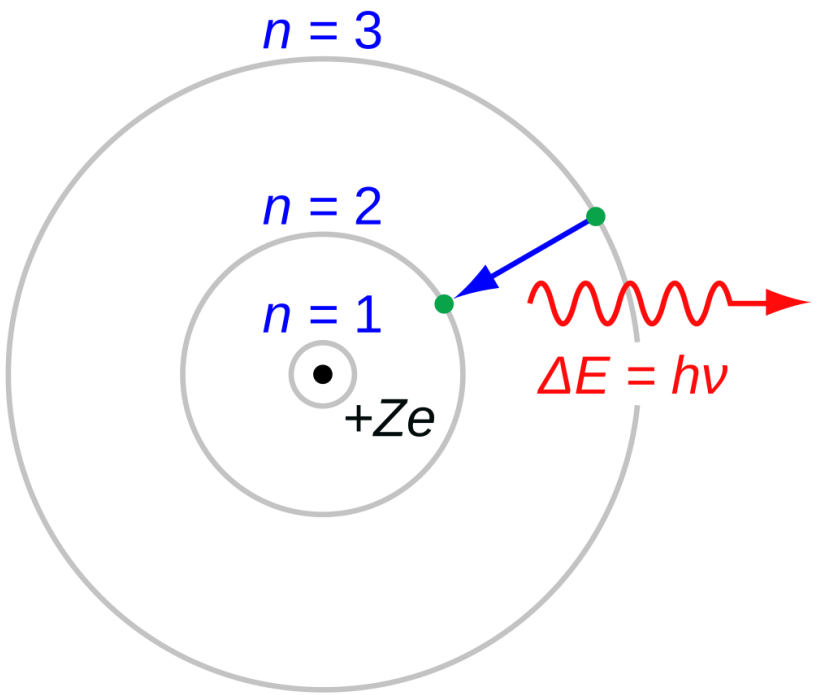
Rydberg (1888): $\frac{1}{\lambda_{\text{vac}}} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

http://www.seos-project.eu/modules/earthspectra/earthspectra-c02-p06.ar.html

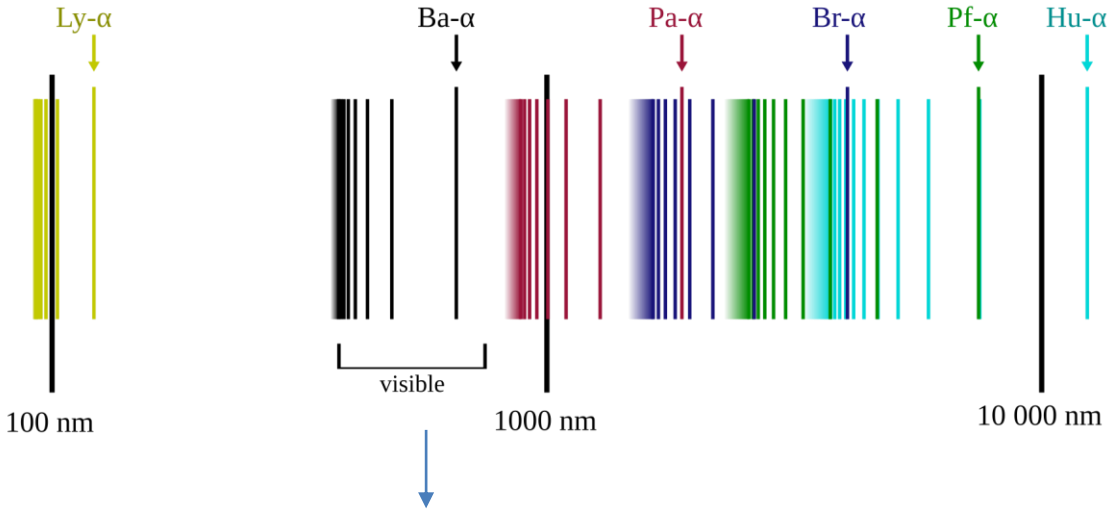
https://commons.wikimedia.org/wiki/File:Hydrogen_spectrum.svg

Light emission

Bohr model of the H-atom (1913)



H-atom's emission lines



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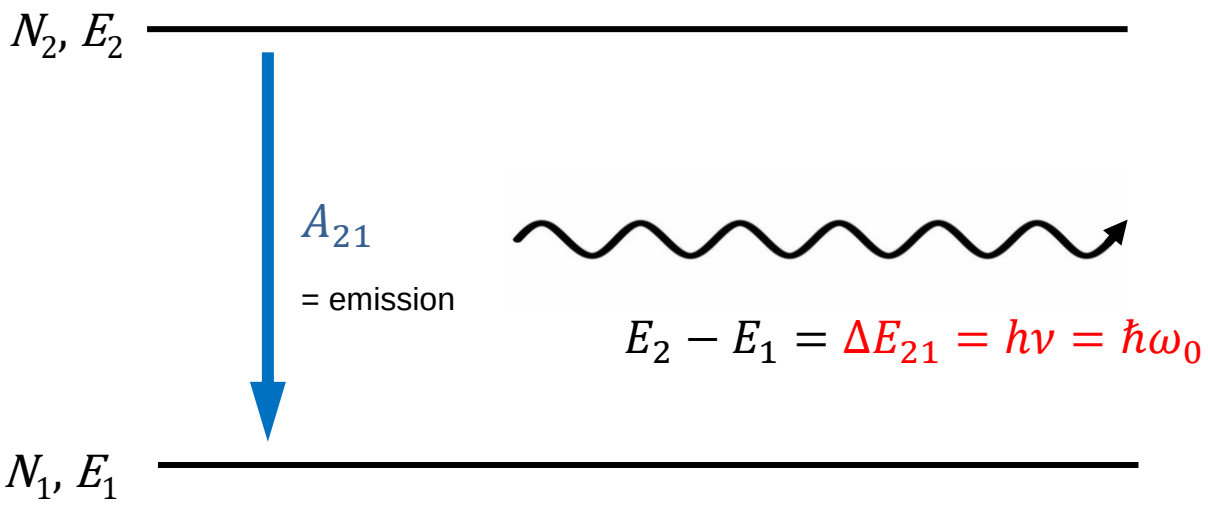
https://commons.wikimedia.org/wiki/File:Hydrogen_spectrum.svg

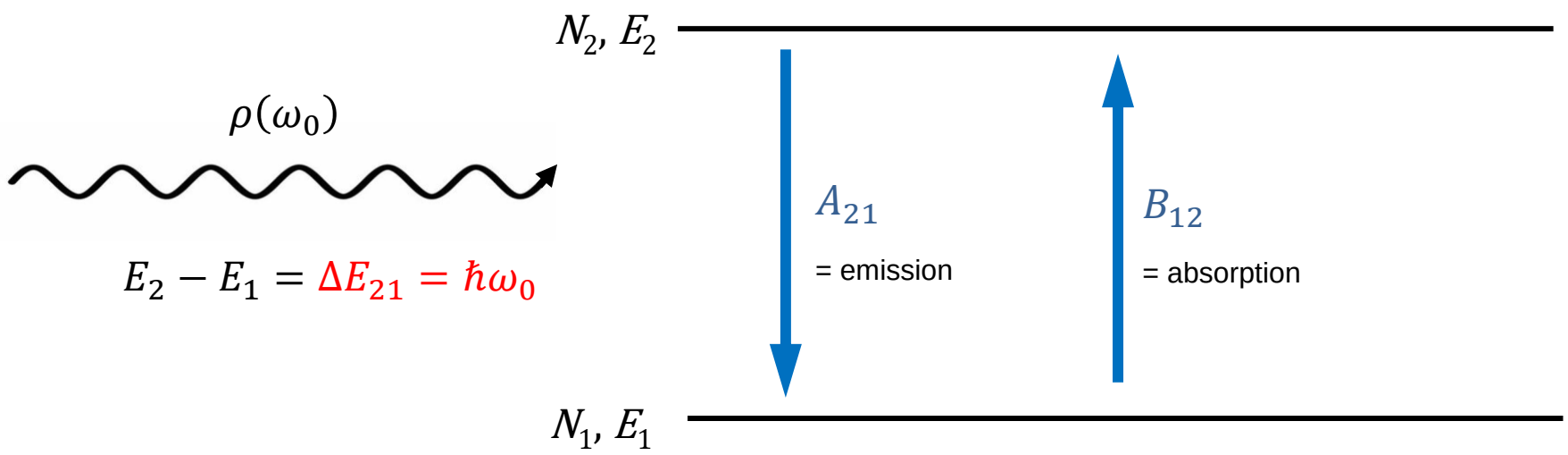
Einstein Coefficients (1917)



$$E_2 - E_1 = \Delta E_{21} = h\nu = \hbar\omega_0$$

$$\frac{\partial N_2}{\partial t} = -A_{21}N_2$$

Einstein Coefficients (1917)



$$E_2 - E_1 = \Delta E_{21} = \hbar\omega_0$$

$$\frac{\partial N_2}{\partial t} = -A_{21}N_2 \qquad \frac{\partial N_1}{\partial t} = -B_{12}\rho(\omega_0)N_1$$

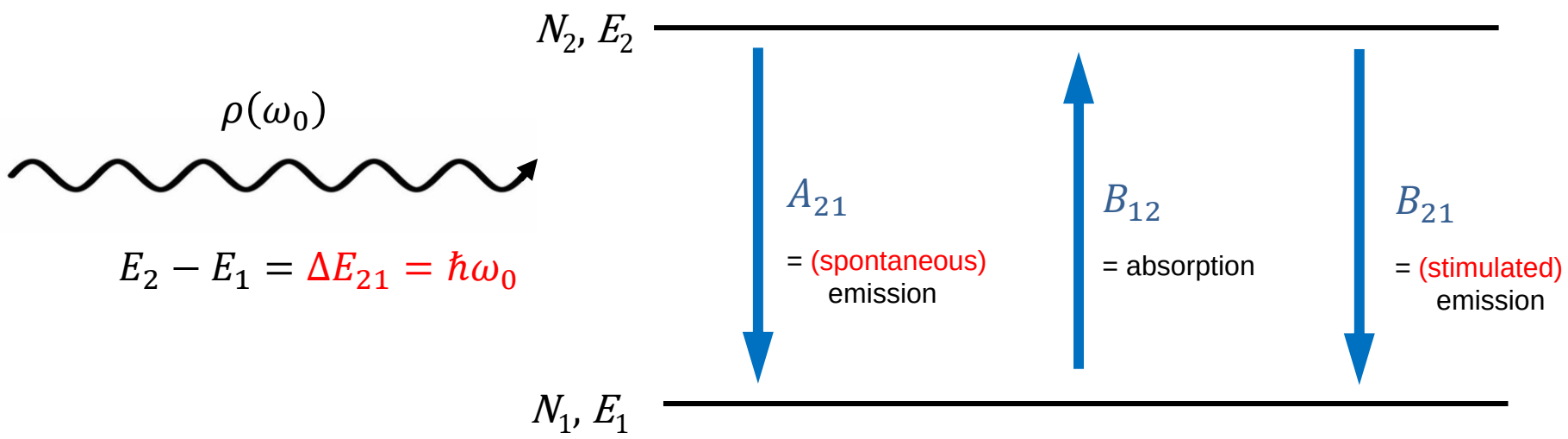
Steady state: (1) $\frac{\partial N_1}{\partial t} = \frac{\partial N_2}{\partial t} \Rightarrow A_{21}N_2 = B_{12}\rho(\omega_0)N_1 \quad \Rightarrow \quad \rho(\omega_0) = \frac{A_{21}N_2}{B_{12}N_1}$

(2) $\frac{N_2}{N_1} = \underbrace{e^{\frac{-\Delta E_{21}}{kT}}}_{\text{Boltzmann factor}} = e^{\frac{-\hbar\omega_0}{kT}} \quad \Rightarrow \quad \rho(\omega_0) = \frac{A_{21}}{B_{12}}\frac{1}{e^{\hbar\omega_0/kT}}$

But $\rho(\omega_0) = \frac{\hbar\omega_0^3}{\pi^2c^3}\frac{1}{e^{\hbar\omega_0/kT}-1}$

There must be an additional, stimulated emission process with $\boldsymbol{B_{21} = B_{12}}$!

Einstein Coefficients (1917)



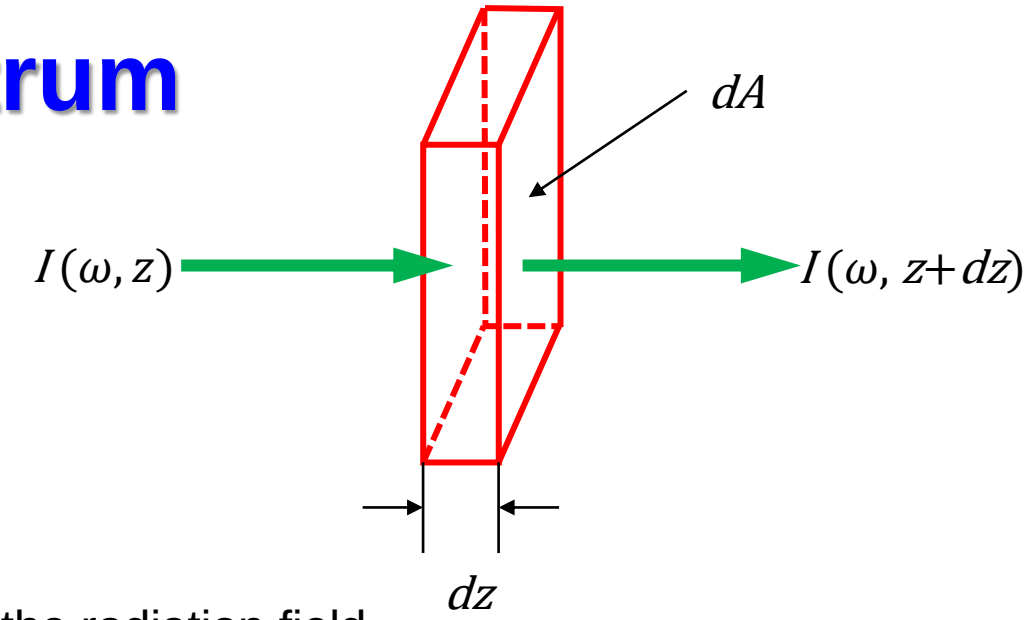
$$E_2 - E_1 = \Delta E_{21} = \hbar\omega_0$$

$$\frac{\partial N_2}{\partial t} = -A_{21}N_2 \qquad \frac{\partial N_1}{\partial t} = -B_{12}\rho(\omega_0)N_1 \qquad \frac{\partial N_2}{\partial t} = -B_{21}\rho(\omega_0)N_2$$

Now $\rho(\omega_0) = \frac{A_{21}}{B_{12}e^{(\hbar\omega_0/kT)} - B_{21}}$ agrees with $\rho(\omega_0) = \frac{\hbar\omega_0^3}{\pi^2c^3}\frac{1}{e^{(\hbar\omega_0/kT)}-1}$,

giving $\frac{A_{21}}{B_{21}} = \frac{\hbar\omega_0^3}{\pi^2c^3}$ and $B_{21} = B_{12}$

Absorption spectrum



Let's consider a beam of light moving through a small distance *dz* of a medium with cross-sectional area *dA*.

Steady state: $-B_{21}N_2\rho(\omega_0) + B_{12}N_1\rho(\omega_0) - A_{21}N_2 = 0$

Since $B_{21} = B_{12}$, only spontaneous emission removes energy from the radiation field.

The corresponding power removed is $P = A_{21}N_2\hbar\omega_0 \quad = \rho(\omega_0)B_{12}(N_1 - N_2)\hbar\omega_0$ ---(1)

The power absorbed from the radiation field $\rho(\omega_0)$ is $P = (N_1 - N_2)\int \sigma(\omega)I(\omega)d\omega$ ---(2)

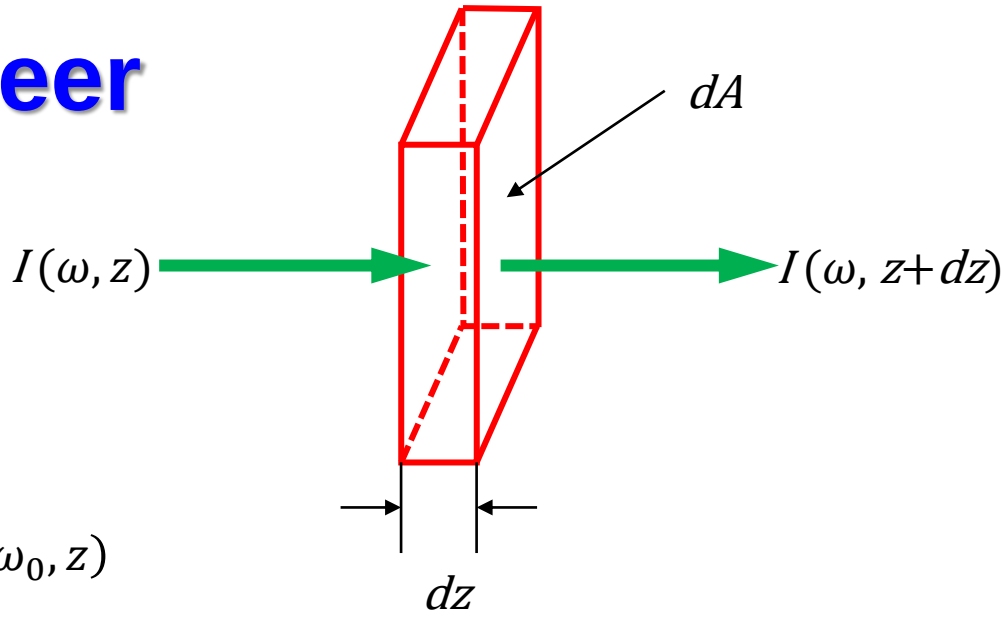
Optical cross-section (for abs. & st. em.)

But irradiance (intensity) ≡ (time-averaged) surface power density, hence $I(\omega) = \rho(\omega)c$, so $\rho(\omega_0) = I(\omega_0)/c$

Hence, comparing (1) and (2) leads to $B_{12} = \frac{c}{\hbar\omega_0}\int \sigma(\omega)d\omega$

(measurable) absorption spectrum!!

Law of Lambert-Beer



Assuming a spectrally narrow excitation beam, let's consider the resonance condition: $I(\omega) \rightarrow I(\omega)\delta(\omega - \omega_0) = I(\omega_0)$ and, similarly, $\rho(\omega) \rightarrow \rho(\omega_0)$.

Hence, $P(\omega_0) = (N_1 - N_2)\,\sigma(\omega_0) I(\omega_0)$

But $P(\omega_0) = -\frac{d\rho(\omega_0)}{dt}\Delta V = -c\frac{d\rho(\omega_0)}{dz}\Delta V = -\frac{dI(\omega_0)}{dz}\Delta V,$

with $dI(\omega_0) \equiv I(\omega_0, z + dz) - I(\omega_0, z)$

Hence, $\frac{dI(\omega_0)}{dz} = -\sigma(\omega_0) I(\omega_0) \frac{N_1 - N_2}{\Delta V}$

Rearranging, we get $\frac{dI(\omega_0)}{I(\omega_0)} = -\sigma(\omega_0)\frac{N_1 - N_2}{\Delta V} dz$

$$\therefore I(\omega_0, z) = I(\omega_0, 0) e^{-\sigma(\omega_0)\frac{N_1 - N_2}{\Delta V} z}$$

$$\cong I(\omega_0, 0) e^{-\sigma(\omega_0) n z}$$ ($N_2 << N_1$, i.e., absorption dominates)

Convert $\sigma(\omega_0)$ → $\boldsymbol{\varepsilon}(\omega_0)$ (extinction coefficient) and n → C (concentration): $\varepsilon(\omega_0) = \frac{N_A}{\ln 10}\sigma(\omega_0)$ and $C = \frac{n}{V}$

Integrating over a pathlength l gives $\boxed{I(l) = I(0) \times 10^{-OD}}$, the famous **Law of Lambert-Beer**

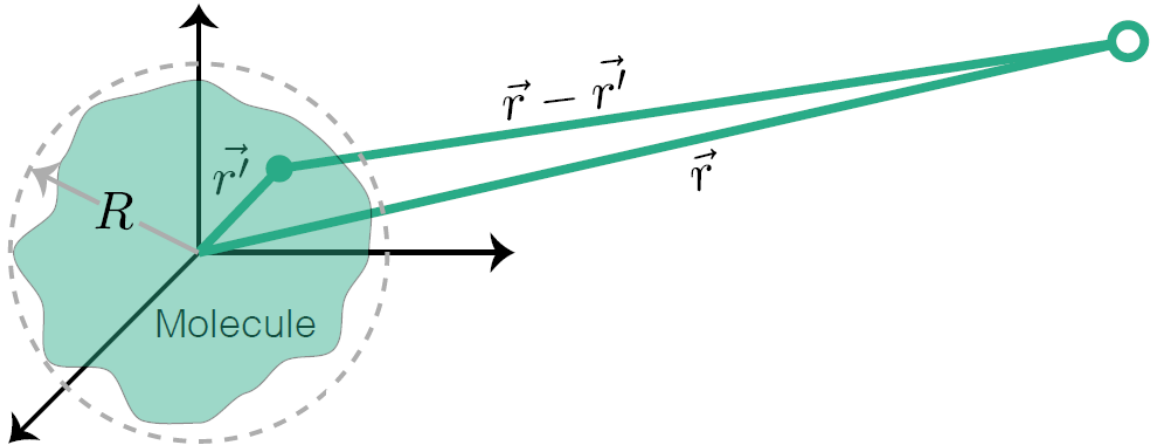
in terms of the **optical density** $OD(\omega_0) = \varepsilon(\omega_0) l C$

Physical basis for light absorption

Interaction between the atom/molecule's electronic charge distribution and the electric field of the light.

We can understand this interaction by using the theory of electrostatics. Let's consider a molecule's electron cloud with a continuous volume charge density $\rho(\vec{r}')$, generating an electric potential at $\vec{r}$:

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0}\int_V \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\tau'$$



If $|\vec{r}| \gg R$ we can do Taylor series expansion about $\vec{r}' = 0$

$$\frac{1}{|\vec{r}-\vec{r}'|} = \frac{1}{r} - (\vec{r}'\cdot\nabla)\frac{1}{r} + \frac{1}{2}(\vec{r}'\cdot\nabla)^2\frac{1}{r} - \cdots$$

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0}\left[\frac{q}{r} + \frac{\vec{\mu}\cdot\vec{r}}{r^3} + \frac{1}{2}\frac{\vec{r}\cdot\mathbf{Q}\cdot\vec{r}}{r^5} + \cdots\right]$$

Multipole moments of a charge distribution

Electric monopole: $q = \int_V \rho(\vec{r})\,d\tau$

Electric dipole: $\vec{\mu} = \int_V \vec{r}\rho(\vec{r})\,d\tau,$

Electric quadrupole: $Q_{i,j} = \int_V (3r_i r_j - r^2\delta_{i,j})\rho(\vec{r})\,d\tau,$

Physical basis for light absorption

A general electrostatic scalar potential $\varphi(\vec{r})$ with electric field $\vec{E}(\vec{r}) = -\nabla\varphi(\vec{r})$ (from Poisson's equation) interacts with a molecule's charge distribution with potential:

$$V = q\varphi(\vec{r}) - \vec{\mu}\cdot\vec{E}(\vec{r}) - \frac{1}{6}\mathbf{Q}\cdot\left(\frac{\partial\vec{E}(\vec{r})}{\partial\vec{r}}\right) + \cdots$$

For light, the first term is zero and the second term is by far the dominant term.

This causes a (small) perturbation: $H' = -\vec{\mu}\cdot\vec{E}$.

Electric dipole: $\vec{\mu} = \int_V \vec{r}\rho(\vec{r})\,d\tau,$

So we can use perturbation theory.

We must account for transitions between energy levels, i.e., time-dependent potentials.

Time-dependent PT for light-matter interactions

Consider a molecule with discrete energy levels E_k^0 and a complete set of orthonormal wavefunctions ψ_k^0 interacting with a beam of light.

Light off: $\hat{H}_0\psi_k^0 = E_k^0\psi_k^0$

Light on: $i\hbar\frac{\partial\psi}{\partial t} = \left(\hat{H}_0 + \hat{H}'(t)\right)\psi(t)$

where $\psi(t) = \sum_k c_k(t)\psi_k^0 e^{-iE_k t/\hbar}$

giving $\frac{dc_k(t)}{dt} = -\frac{i}{\hbar}\sum_n c_n(t)e^{i\omega_0 t}\langle k|H'|n\rangle$ for transition $|n\rangle \rightarrow |k\rangle$

(We have assumed $\langle n|H'|n\rangle = 0$)

Let's assume an instantaneous transition. Then $c_k(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_0 t'}\langle k|H'|n\rangle dt'$

But $H' = -\vec{\mu}\cdot\vec{E}$, so $\langle k|H'|n\rangle = -\langle k|\vec{\mu}|n\rangle\cdot\vec{E}$

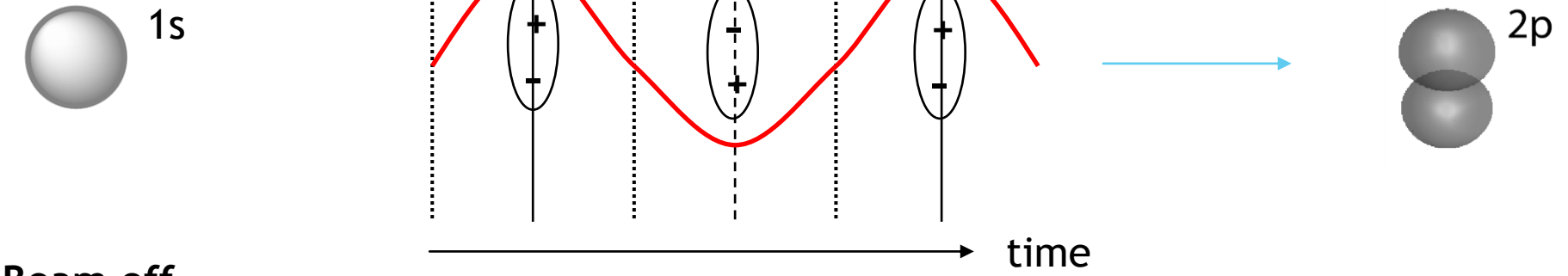
$\vec{\mu}_{nk}$

The transition dipole moment

$\vec{\mu}_{nk} \equiv \langle k|\vec{\mu}|n\rangle$

The transition dipole moment $\vec{\mu}_{nk}$ is the electric dipole moment $\vec{\mu}$ associated with an electronic transition from state $|n\rangle$ to state $|k\rangle$.

It's a transient dipole moment due to a fluctuating electron density.



Beam off

Beam on:
perturbation of electron density

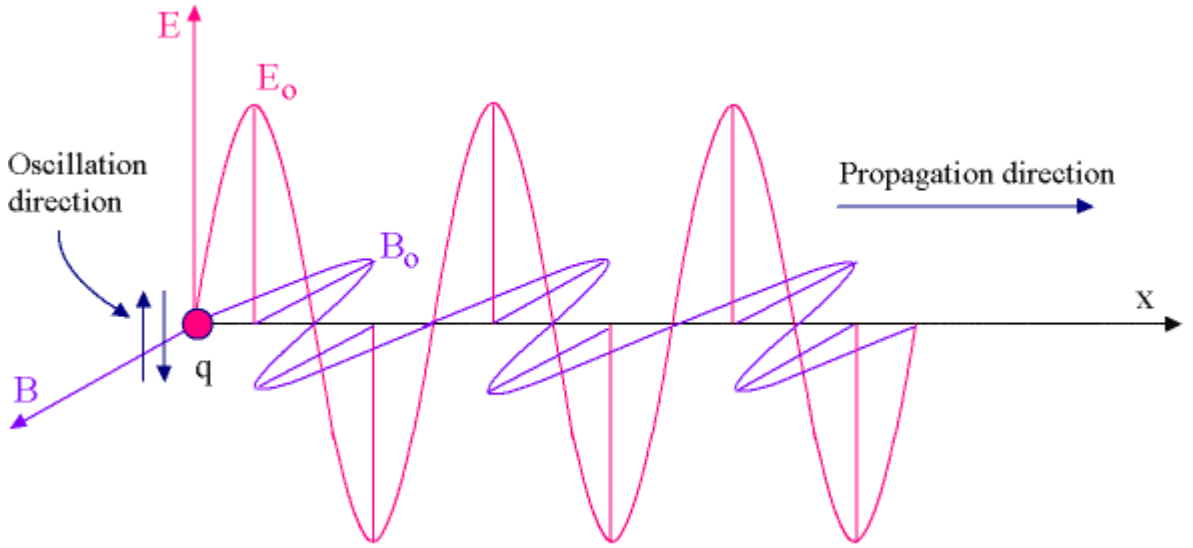
Time-dependent PT for light-matter interactions

Let's consider plane polarised light: $\vec{E}(t) = \vec{E}_{0y}\cos\omega t$

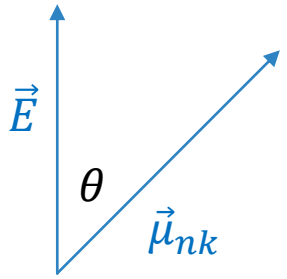
Then $c_k(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_0 t'}\langle k|H'|n\rangle dt'$

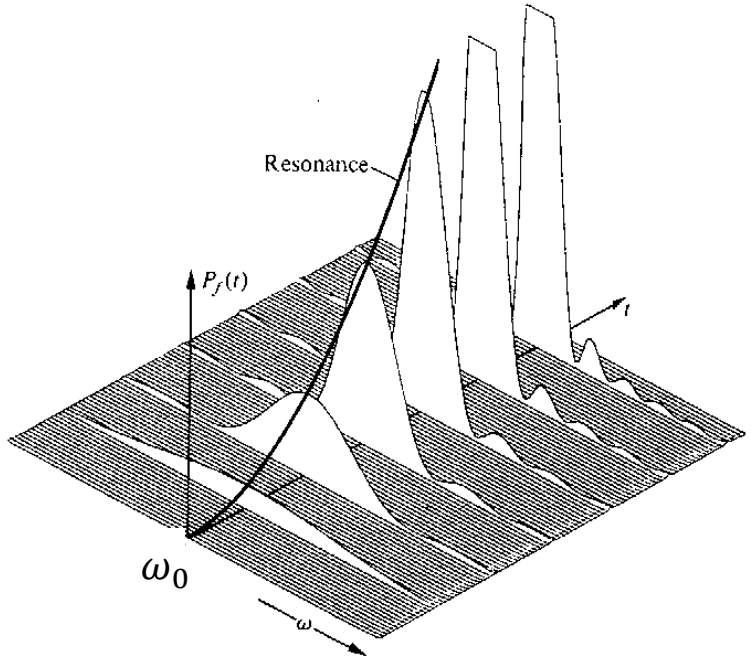
$$= \frac{i}{\hbar}\int_0^t e^{i\omega_0 t'}|\vec{\mu}_{nk}|E_0\cos\theta\ \cos\omega t\, dt'$$

When we are close to resonance, we may invoke the rotating-wave approximation: $\omega_0 + \omega \gg |\omega_0 - \omega|$



Then $P_{n\to k}(t) = |c_k(t)|^2 \approx \frac{1}{\hbar^2}|\vec{\mu}_{nk}|^2|E_0|^2\cos^2\theta\,\frac{\sin^2\frac{1}{2}(\omega_0-\omega)t}{(\omega_0-\omega)^2}$





This is for monochromatic light.

Time-dependent PT for light-matter interactions

If we consider the energy density $\rho(\omega)$ and integrate $P_{n\to k}(t)$ over a band around ω_0 for isotropic incident light, we get a transition rate:

$$\frac{dP_{n\to k}}{dt} \approx \frac{\pi}{3\varepsilon_0\hbar^2}|\vec{\mu}_{nk}|^2\rho(\omega_0)$$

If we start in the ground state and absorb a photon with frequency ω_0, then

$$\frac{dP_{1\to k}}{dt} \approx \frac{\pi}{3\varepsilon_0\hbar^2}|\vec{\mu}_{1k}|^2\rho(\omega_0)$$

But this transition rate is exactly $B_{1k}\rho(\omega_0)$

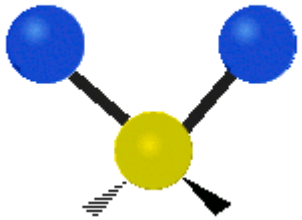
Therefore, $$B_{1k} = \frac{\pi}{3\varepsilon_0\hbar^2}|\vec{\mu}_{1k}|^2$$

$|\vec{\mu}_{1k}|^2$ is directly proportional to all three Einstein coefficients!

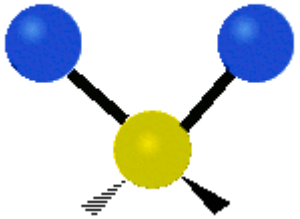
But $B_{1k} = \frac{c}{\hbar\omega_0}\int\sigma(\omega)d\omega \implies |\vec{\mu}_{1k}|^2 = \frac{3\varepsilon_0\hbar c}{\pi\omega_0}\int\sigma(\omega)d\omega$ (measurable) absorption spectrum!!

Molecular vibrations

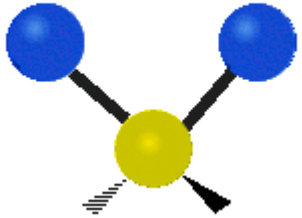
Asymmetrical Stretch



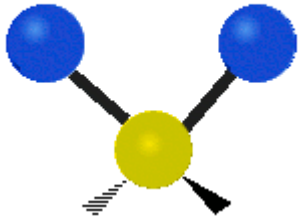
Symmetrical Stretch



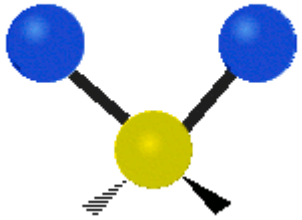
Bending or Scissoring



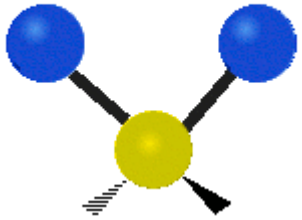
Rocking



Twisting

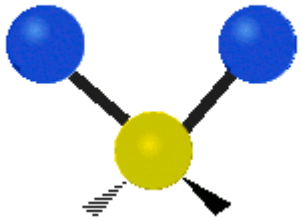


Wagging



Molecular vibrations

Asymmetrical Stretch



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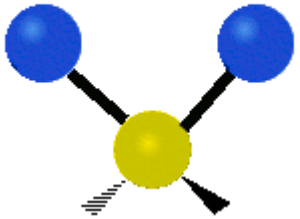

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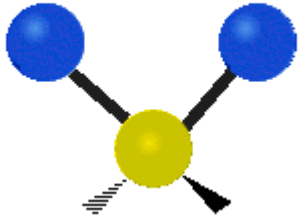

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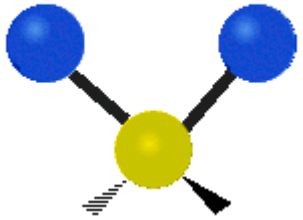
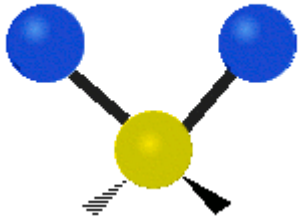
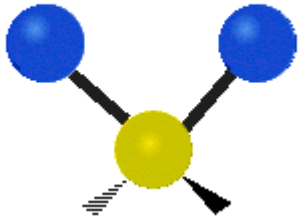


Twisting



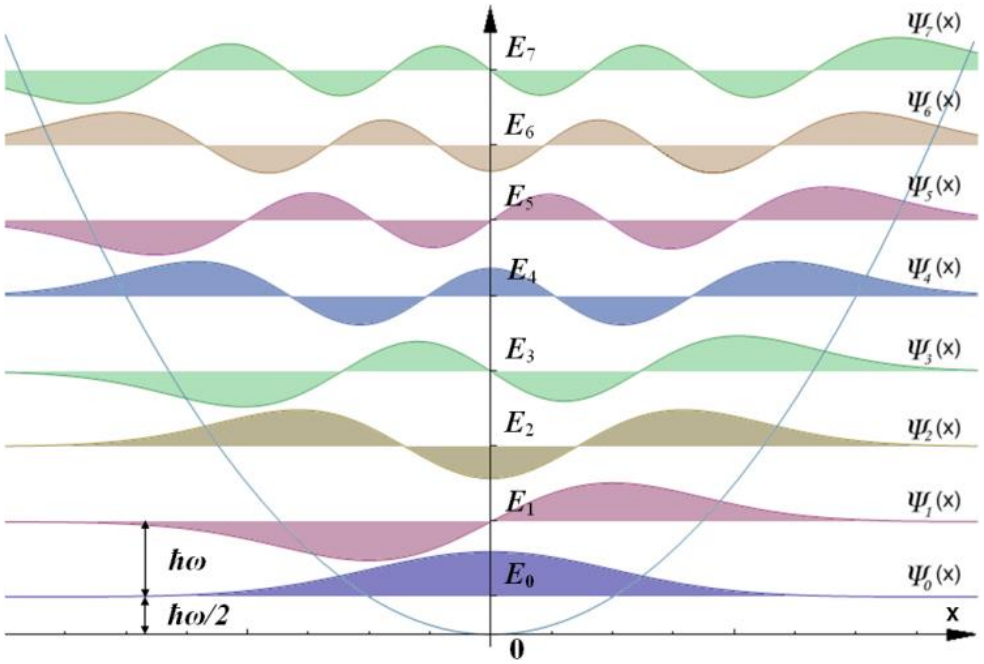
Wagging



Quantum Harmonic Oscillator

$$V(x) = \frac{1}{2}kx^2$$

Solutions: $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

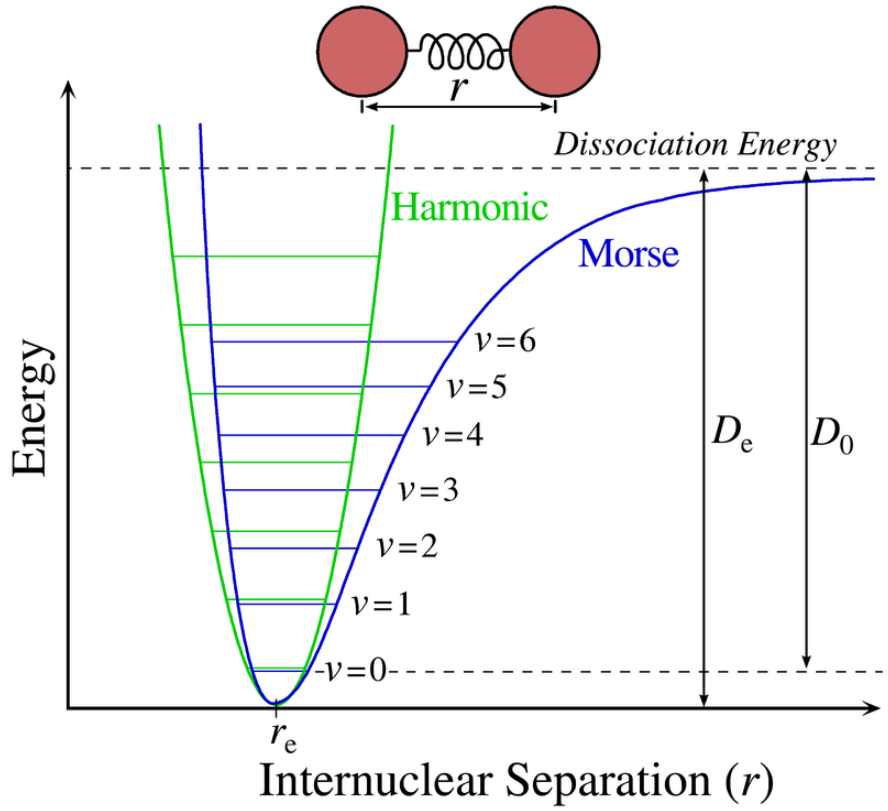


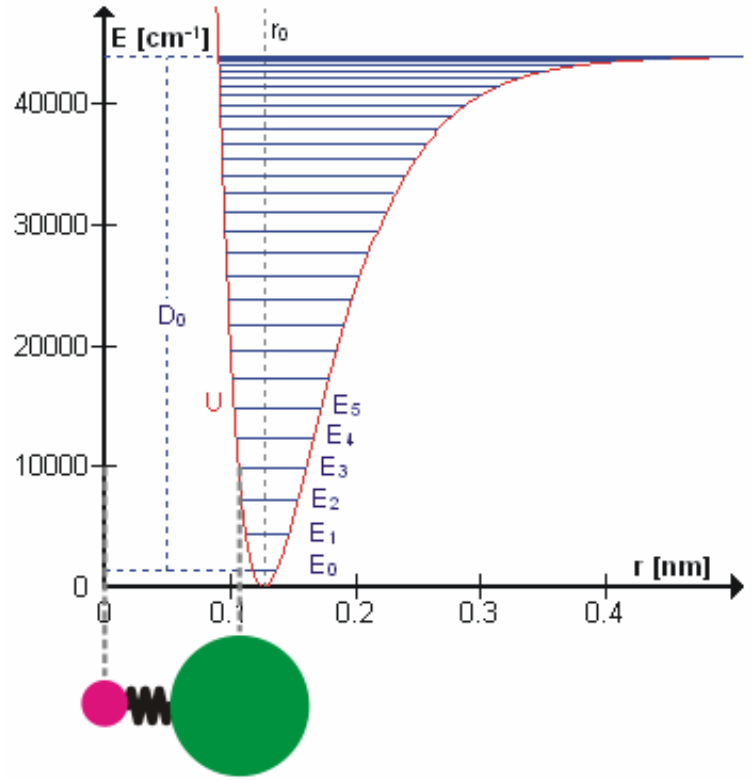
https://commons.wikimedia.org/wiki/File:HarmOsziFunktionen.png

Vibrational states

Morse Oscillator

A more realistic potential for a diatomic molecule: $V(r) = D_e\left(1 - e^{-a(r-r_e)}\right)^2$





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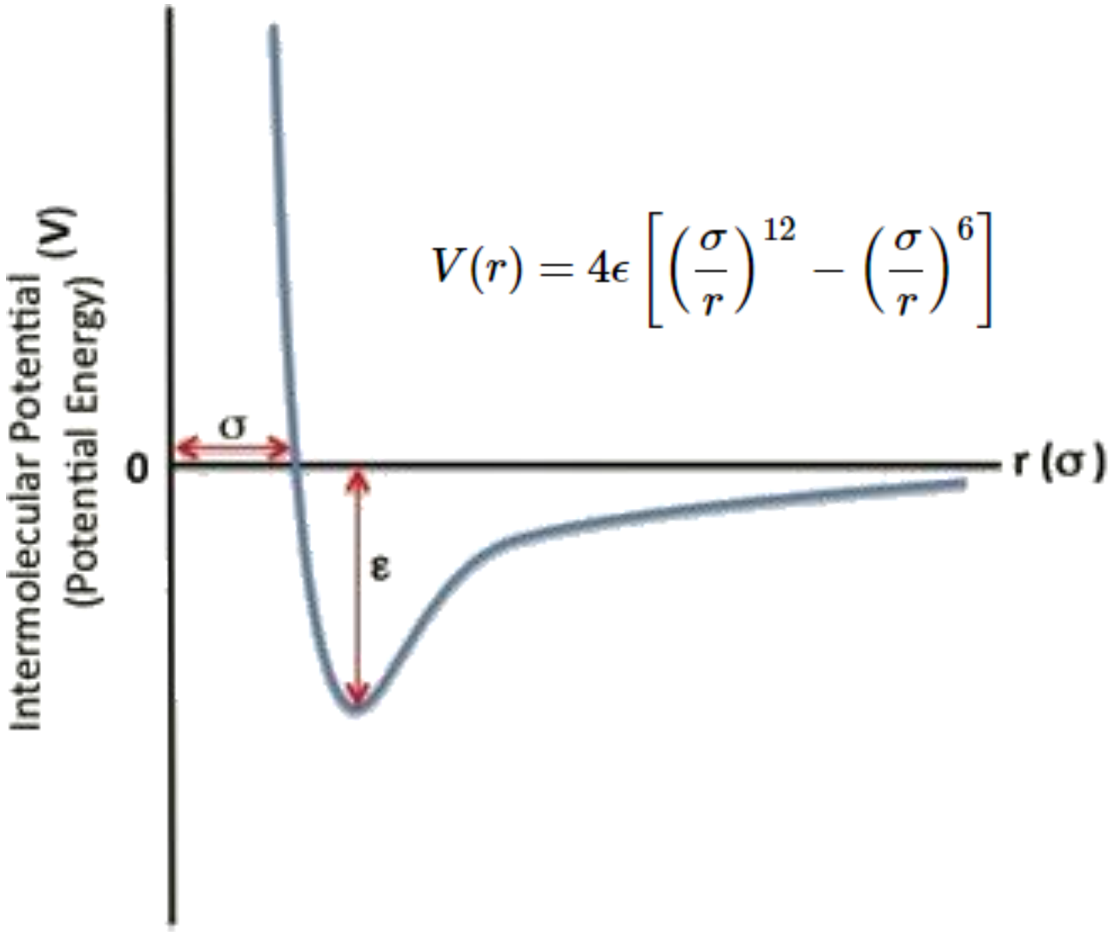
Mark M Somoza, https://commons.wikimedia.org/wiki/File:Morse-potential.png

https://commons.wikimedia.org/wiki/File:Anharmonic_oscillator.gif

Vibrational states

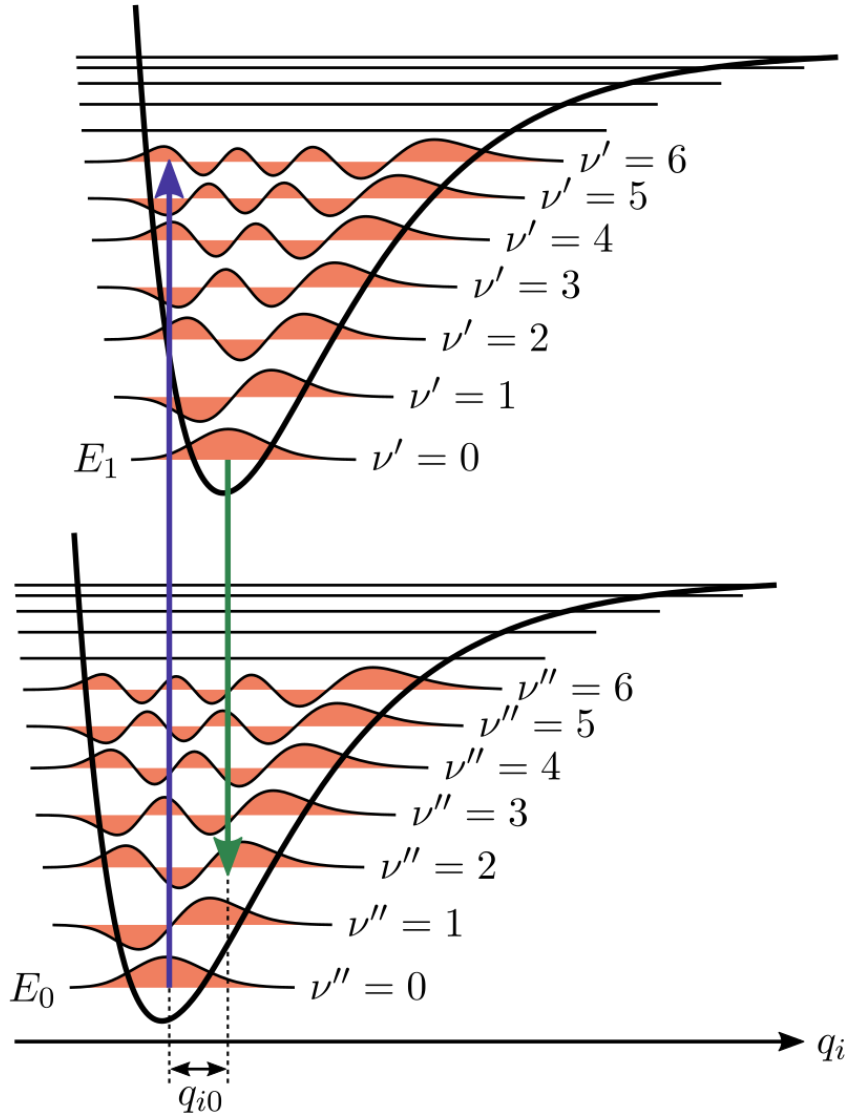
Lennard-Jones potential:

$$V_{\mathrm{LJ}}(r) = \frac{A_n}{r^n} - \frac{B_m}{r^m}$$



Source: Libretexts

Franck-Condon principle



$$\vec{\mu} = \vec{\mu}_e + \vec{\mu}_N = -e\sum_i \vec{r}_i + e\sum_k Z_k \vec{R}_k$$

$$\begin{aligned}\vec{\mu}_{if} &= \langle e_f \upsilon_f \sigma_f | \vec{\mu} | e_i \upsilon_i \sigma_i \rangle \\ &= -e\sum_i \langle e_f | \vec{r}_i | e_i \rangle \langle \upsilon_f | \upsilon_i \rangle \langle \sigma_f | \sigma_i \rangle + e\sum_k Z_k \langle e_f | e_i \rangle \langle \upsilon_f | \upsilon_i \rangle \langle \sigma_f | \sigma_i \rangle\end{aligned}$$

0

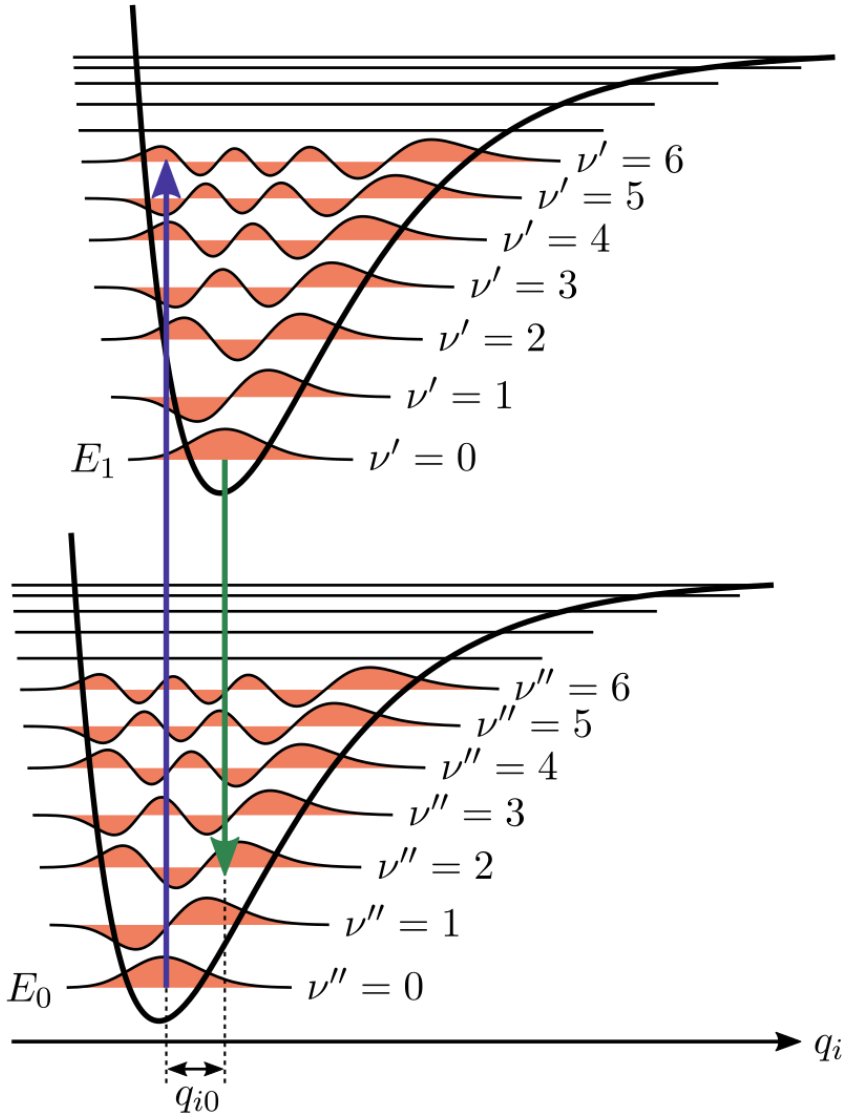
Laporte's orbital selection rules

FC factor

Spin selection rules

Mark M. Somoza, https://commons.wikimedia.org/wiki/File:Franck_Condon_Diagram.svg

Franck-Condon principle



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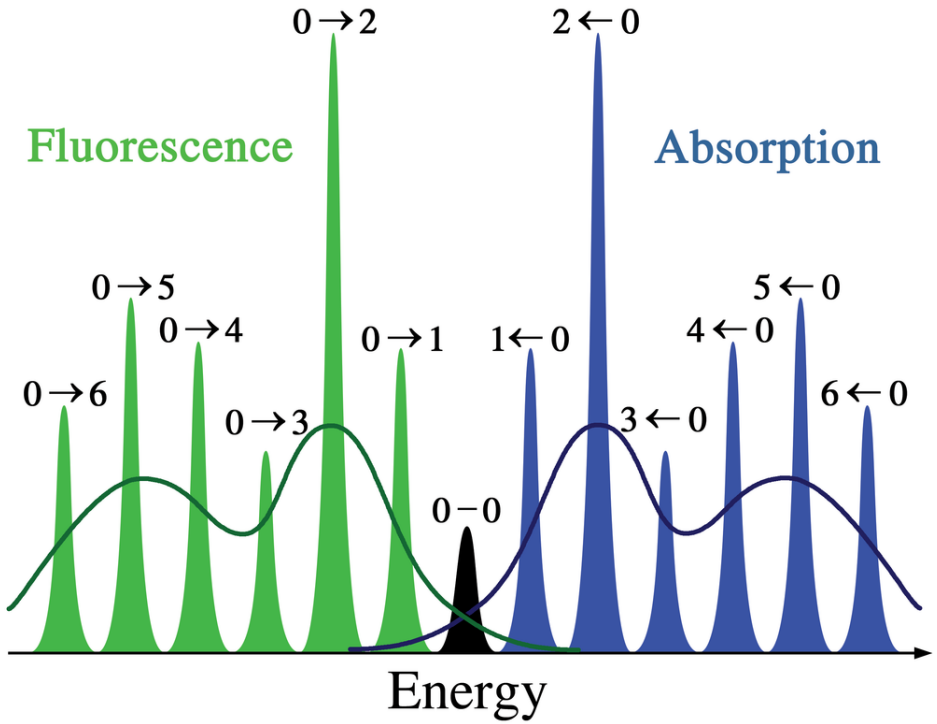
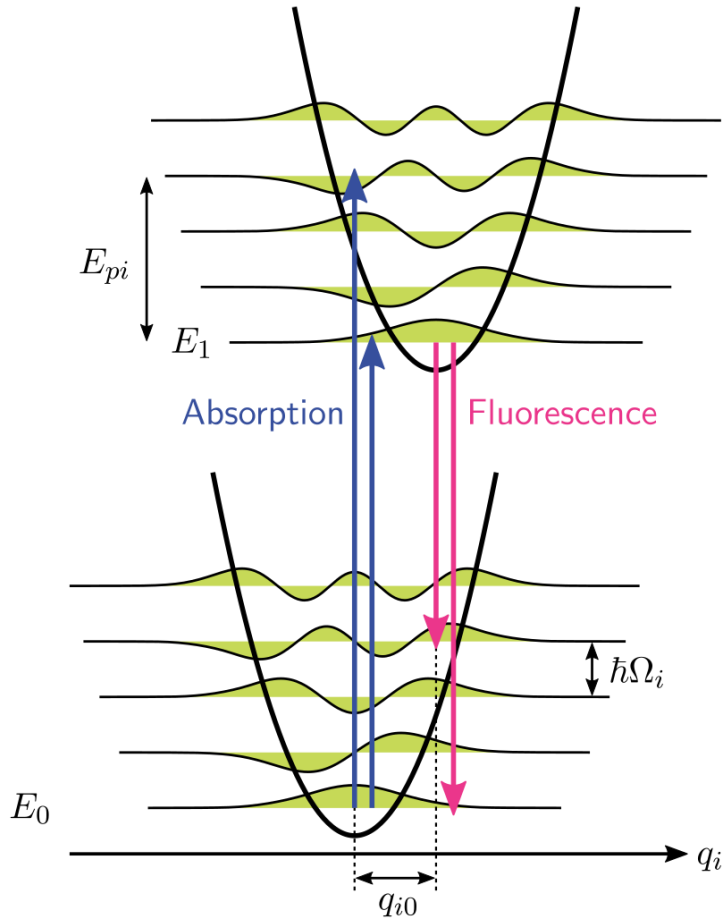
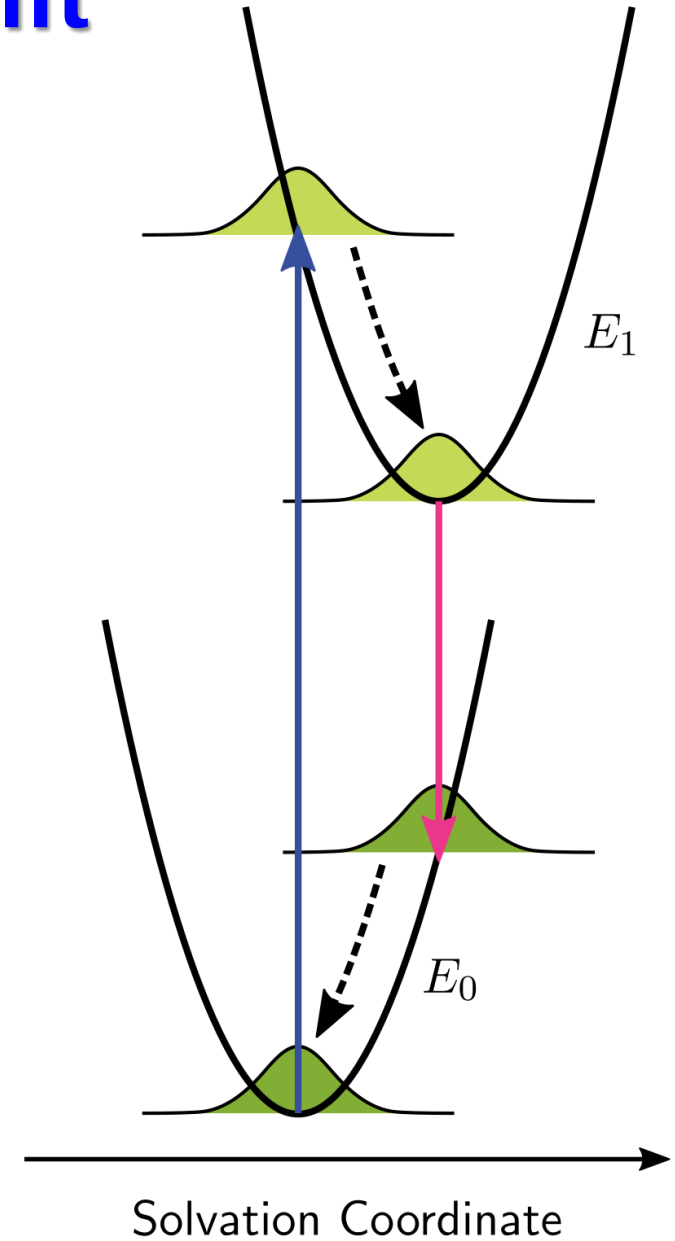


Exact mirror symmetry occurs when the ground and excited state potential wells have identical shapes.

Mark M. Somoza, https://commons.wikimedia.org/wiki/File:Vibration-fluor-abs.png

Stokes shift

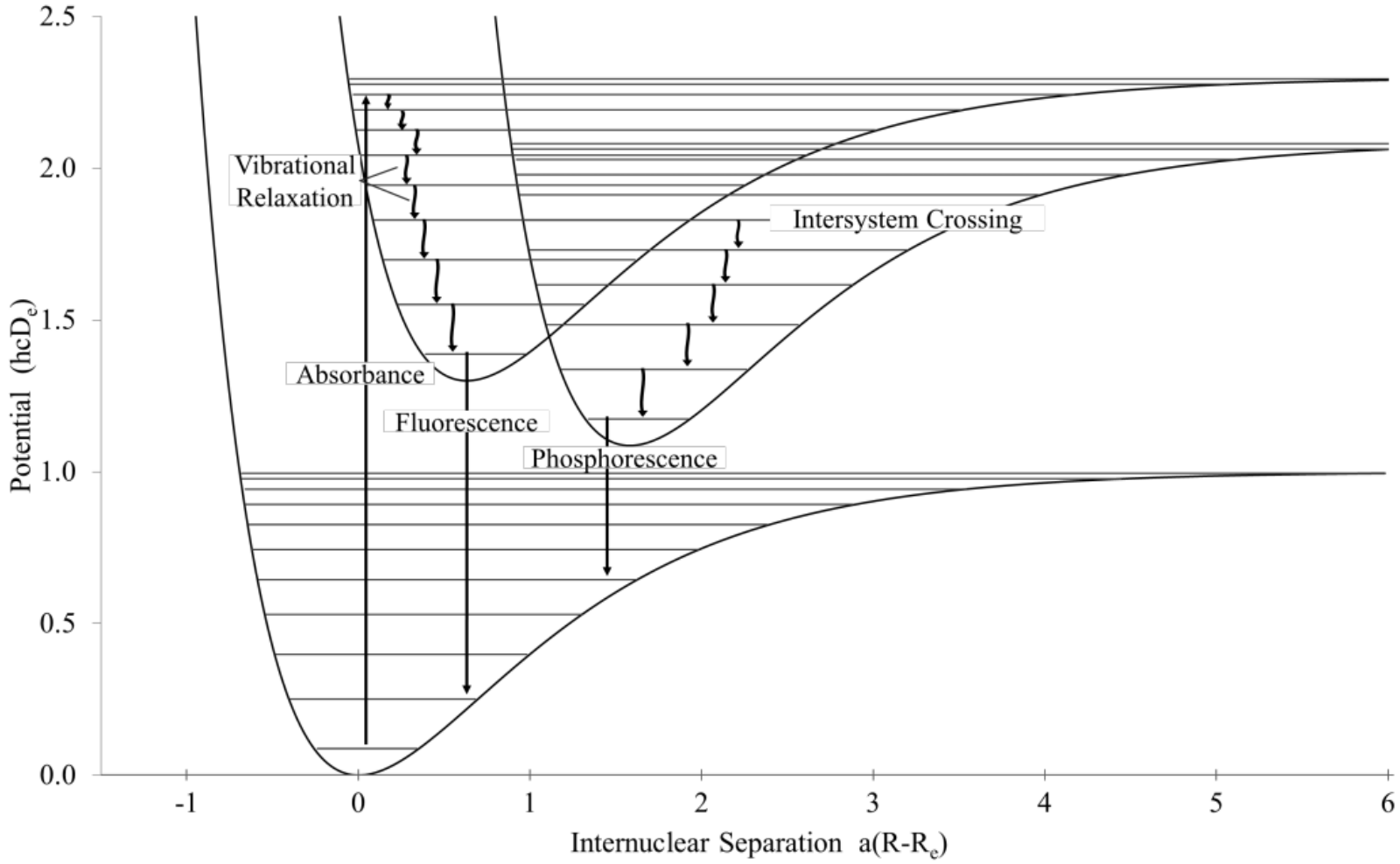




https://commons.wikimedia.org/wiki/File:Phonon_Energy_Diagram.svg

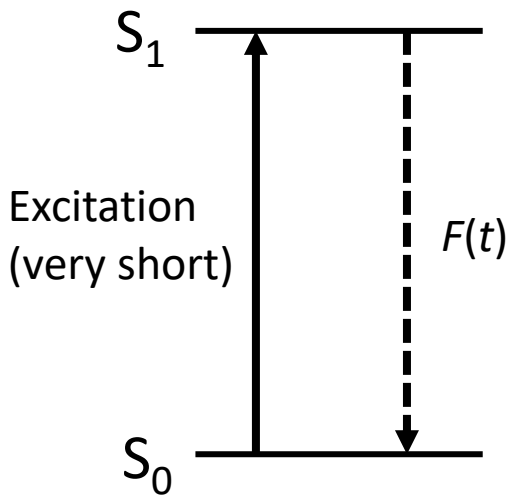
https://en.wikipedia.org/wiki/File:Solvation_Energy_Diagram.svg

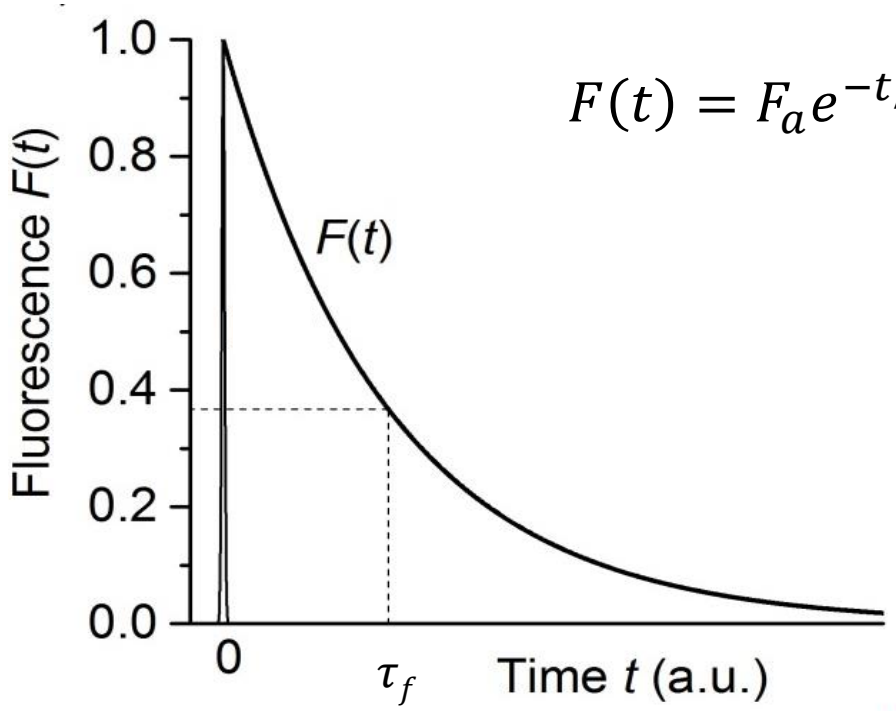
Jablonski diagram



Spectral lineshapes

1. Natural / lifetime / uncertainty broadening





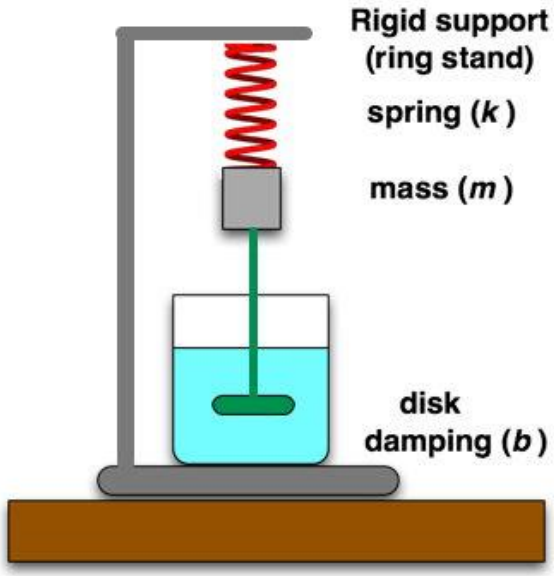
$$F(t) = F_a e^{-t/\tau_f}$$

$$\tau_f = \langle t_{exc} \rangle$$

Spectral lineshapes

1. Natural / lifetime / uncertainty broadening

Consider a damped harmonic oscillator

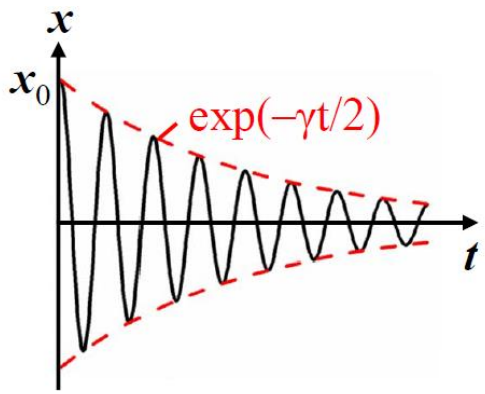


We can solve the amplitude of the oscillation $x(t)$ by solving $\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0$

If $\gamma \ll \omega_0$, then $x(t) = x_0\, e^{-(\gamma/2)t} \cos \omega_0 t$

Compare with $F(t) = F_a e^{-t/2\tau_f}$

resonance frequency of atomic transition



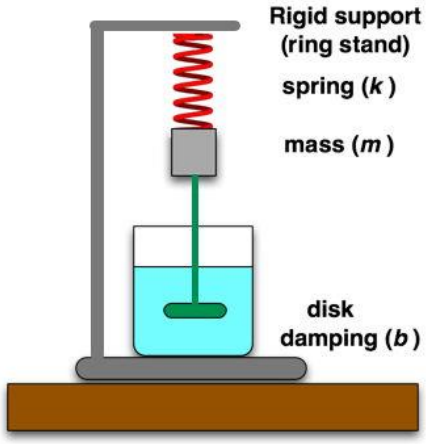
$x(t)$ decreases $\Longrightarrow$ ω changes

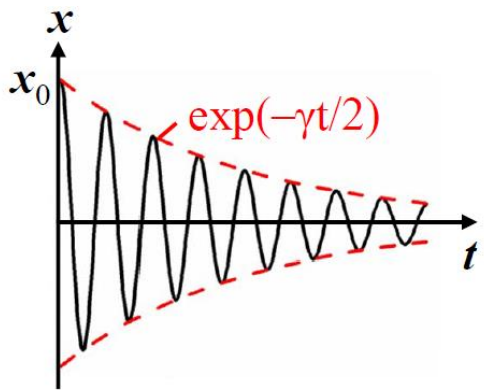
Spectral lineshapes

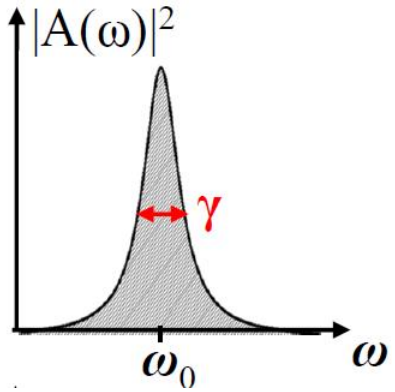
1. Natural / lifetime / uncertainty broadening

$$x(t) = \frac{1}{2\sqrt{2\pi}} \int_0^{\infty} A(\omega)\, e^{i\omega t}\, d\omega \quad \longrightarrow \quad A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x(t) \exp(-i\omega t) dt$$

Fourier transformation







Damped harmonic oscillator

Spectral lineshapes

1. Natural / lifetime / uncertainty broadening

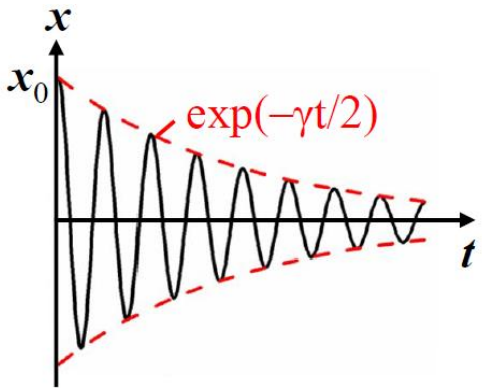
$$= \frac{1}{2\sqrt{2\pi}} \int_0^{\infty} A(\omega)\, e^{i\omega t}\, d\omega$$

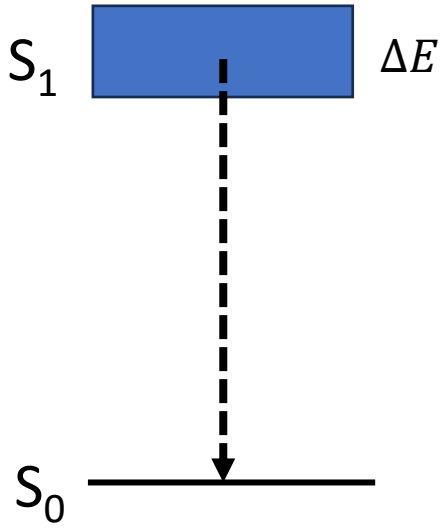
$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x(t) \exp(-i\omega t) dt$$

$$= \frac{x_0}{\sqrt{8\pi}} \left(\frac{1}{i(\omega - \omega_0) + \gamma/2} + \frac{1}{i(\omega + \omega_0) + \gamma/2} \right)$$

$$I(\omega) \propto A(\omega) A^*(\omega), L = I / I_0$$

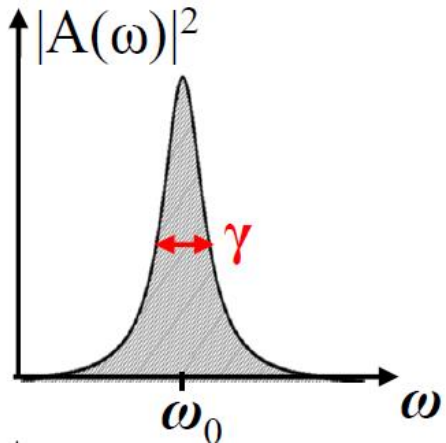
$$L(\omega - \omega_0) = \frac{1}{\pi} \frac{\gamma/2}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$





FWHM: $\Delta\omega = \gamma = 1/\tau_f$

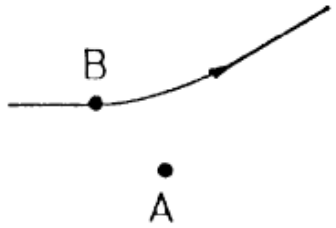
$\therefore \Delta E = \hbar/\tau_f$



Spectral lineshapes

2. Collisional/pressure broadening

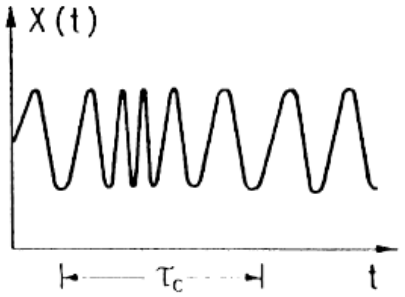
(May also result from exciton–phonon interactions)



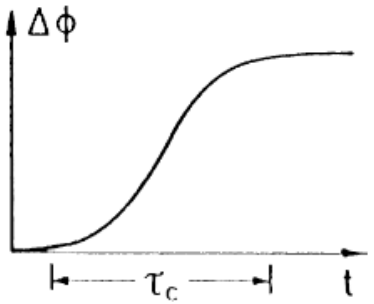
Classical path approximation of colliding particles

Dephasing due to shifted energy levels during a collision ⇒ $\Delta E(t)$ (exponential function)

Fourier transformation $\Delta E(\omega)$ (Lorentzian function)



Frequency change of oscillator *A*(*t*) during the collision

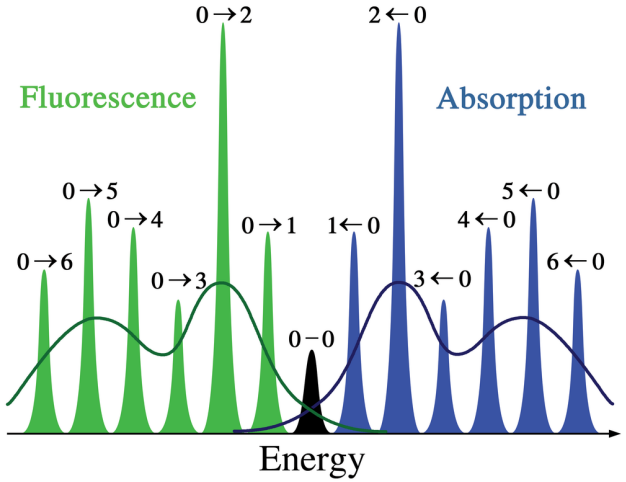


Resulting phase shift

Spectral lineshapes

Lineshape	Type of broadening
Lorentzian (homogenous process)	1. Natural / lifetime / uncertainty broadening
	2. Collisional/pressure broadening
Gaussian (inhomogenous process)	3. Doppler broadening
	4. Proximity broadening
	5. Rovibrational broadening

Lineshape of excitation source



What we have learned

1. Einstein coefficients
2. Law of Lambert-Beer
3. Time-dependent perturbation theory
4. Franck-Condon principle
5. Jablonski diagram
6. Spectral lineshapes/line-broadening

Next lectures

1. Basic principles of electronic spectroscopy
2. Coupled molecular dipoles: Förster interactions & molecular excitons
3. Linear & nonlinear spectroscopy → Dr. Towan Nöthling
4. Linear & nonlinear spectroscopy → Dr. Towan Nöthling

NITheCS Mini-School on "Modelling Optical Spectra"

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