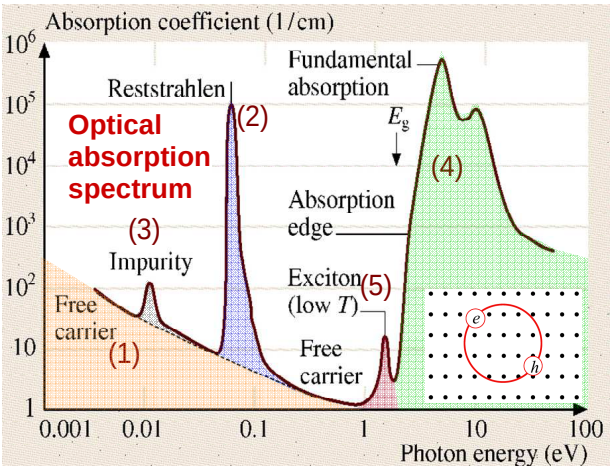
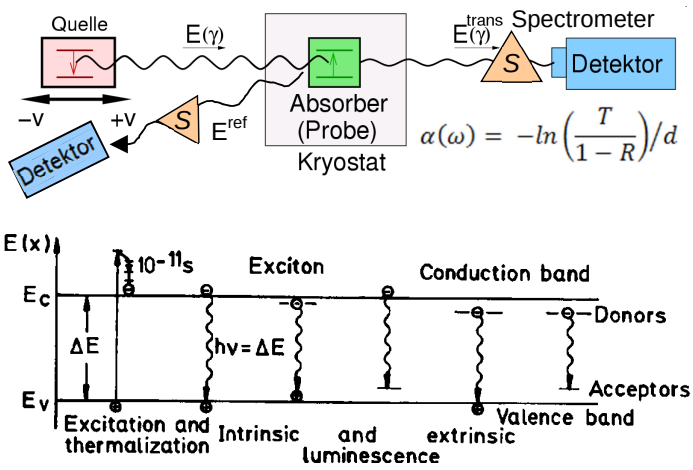
Chapter 3

Spectroscopy using VIS/IR Photons





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Spectroscopy using VIS & IR Photons

3.1 Introduction

Optical methods are most well-developed characterization techniques because ***highly advanced instrumentation*** is available, developed over more than 100 years. Moreover:

- Visible and IR **photon energies** (0.2 – 6 eV) are in the range of the most important electronic transitions (intra- and interband transitions, phonons, plasmons, etc.) relevant for many applications.
- photons are highly sensitive to ***quantum size effects*** **in nanostructures** with very high resolution.
- can be applied in **many different environmental conditions** such as in air, vacuum, liquids even solids, at very high/low temperatures, high pressures, high magnetic fields, etc. .

Probe - in	Interaction	Probe - out	⇨ Measurement Method
Photons (optical) ~ meV.. eV	**reflection**	**photons**	Energy spectrum: Optical spectroscopy, ellipsometry, FTIR
	transmission	**photons**	Spatial distribution: Microscopy, SNOM
	absorption	**photons**	Excitation spectrum = Photoluminescence, Raman spec.
	inelastic excitation	**electrons atoms & ions**	Energy spectrum = photoelectron spectroscopy Mass spectroscopy = laser ablation

- ***Absorption spectroscopy*** » information on electronic and vibrational properties and their excitations
- ***Photoluminescence*** or ***fluorescence*** = secondary emission resulting from excitation/absorption.
- ***Photoconductivity*** = change of carrier concentration due to electron-hole pairs created by absorption
- ***Photoelectron spectroscopy*** = detection of electrons knocked out by photons with $h\nu > E_{binding}$
- Mass spectroscopy of ions knocked out by high power laser ablation.

Limitations: (a) Since for visible/IR photons $h\nu < 5$ eV, only **low energy excitations** can be probed.
(b) the relatively long wavelength $\lambda > 400$nm limits the spatial resolution to > 200nm.

3.2 Instrumentation

Optical methods rely on a **wide selection of advanced instrumentation** such as:

- **High quality elements for beam steering/shaping and control of light properties:** high reflectivity lenses, mirrors, polarizers, interference filters, phase shifters, optical fibers, nonlinear elements, integrated optics, …

- **Versatile and powerful light sources** that cover the whole IR&VIS spectrum: Broad band / narrow band sources, high power, tunable and single mode lasers, pulsed lasers down to femtoseconds ,…

- **Highly sensitive photodetectors** for different wavelengths: » Detection down to the single photon counting level.

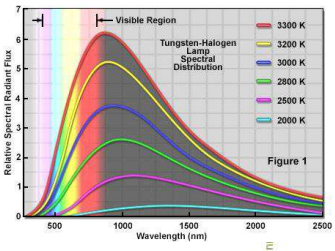
- **High resolution spectrometers** using gratings, prisms, interferometers, Fourier spectrometer, Fabry Perot filters: » µeV resolution possible.

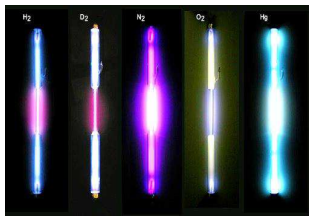
- **Aberration corrected optical imaging systems** with spatial resolution at the Abbe diffraction limit (λ/2). (see Chapter: Optical Microscopy).

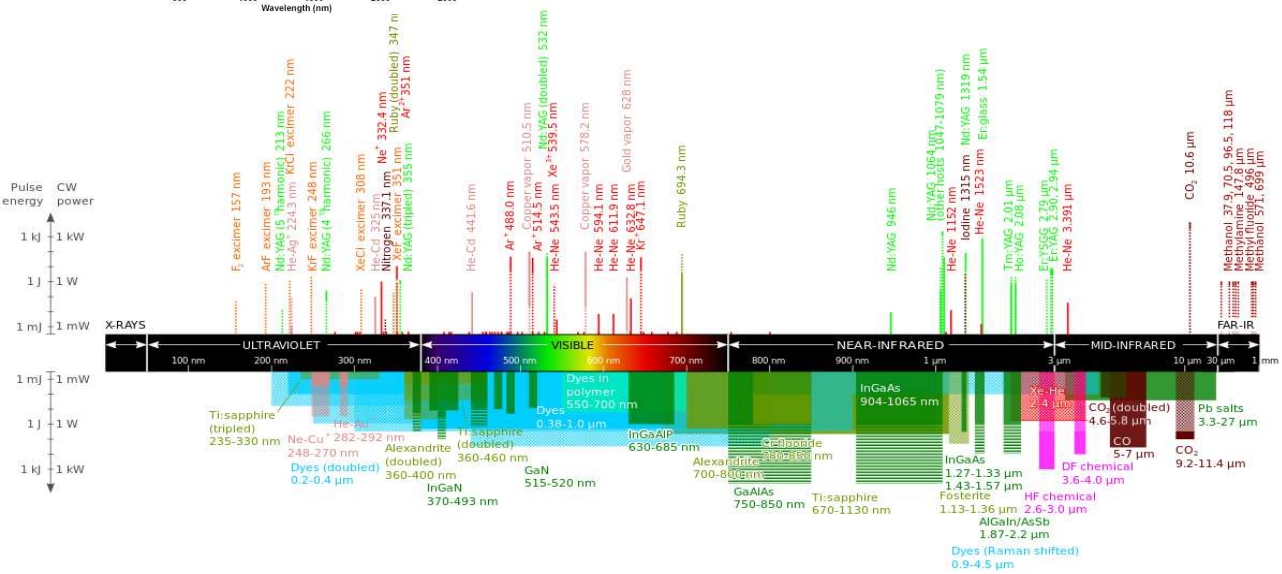
(A) Light sources: Wide range of light sources are available for different applications

» **Broad band emitters** as required for absorption and transmission spectroscopy:
(i) Black body thermal emitters such as glow bar, light bulb, (ii) gas discharge lamps, (iii) LEDs

» **Monochromatic sources** used for luminescence and excitation spectroscopy: Lasers, including semiconductor diode lasers, gas lasers, solid state lasers, fiber lasers,.. High power, cw/pulsed

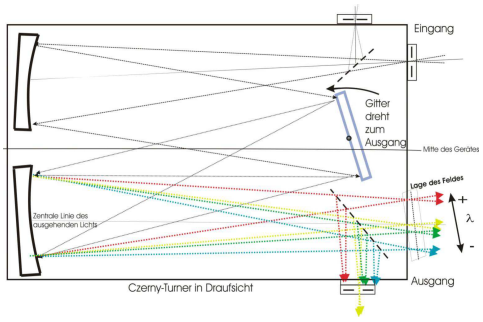


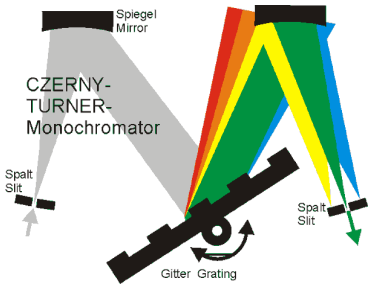




(B) Spectrometers: Grating/prism spectrometers, Fabry-Perot Interferometers, Fourier spectrometers

(i) Grating spectrometer

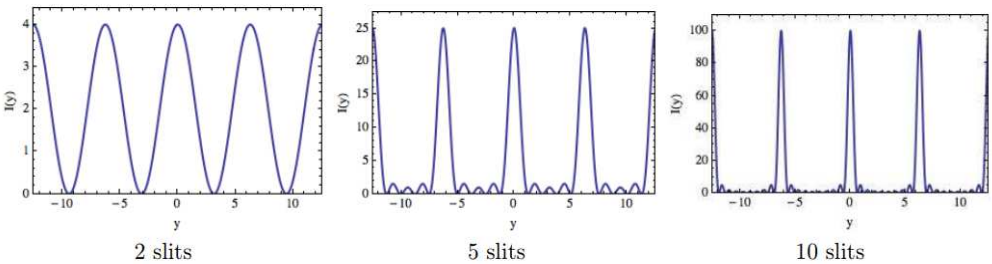




Resolution:

Sharpness of the diffraction pattern depends on how many lines *N* of the grating are illuminated.

Example: Diffraction pattern for gratings for increasing number of slits for ideal monochromatic light

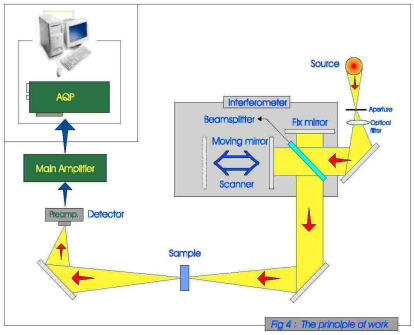


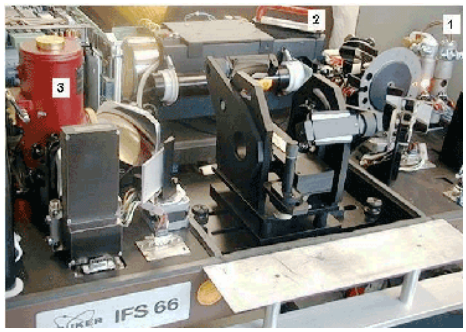
$$I(y) = I_0 \frac{\sin^2\left(\pi N \frac{dy}{\lambda L}\right)}{\sin^2\left(\pi \frac{dy}{\lambda L}\right)}$$

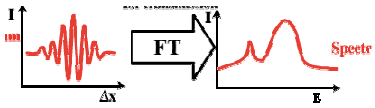
» **ultimate resolution** ≈ width of the diffraction peaks = $\frac{\Delta\lambda}{\lambda} = \frac{\Delta E}{E} = \frac{1}{N}$ (for infinitesimal small exit slit).

Example: N = 5000, hν = 1 eV, ΔE = 0.2 meV

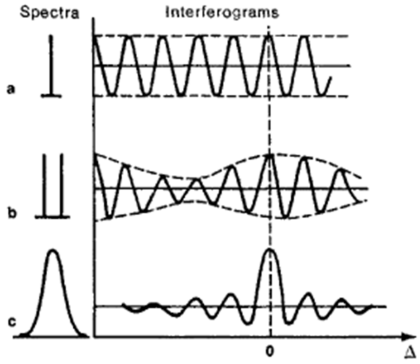
(ii) Fourier spectrometer (= Michelson Interferometer)

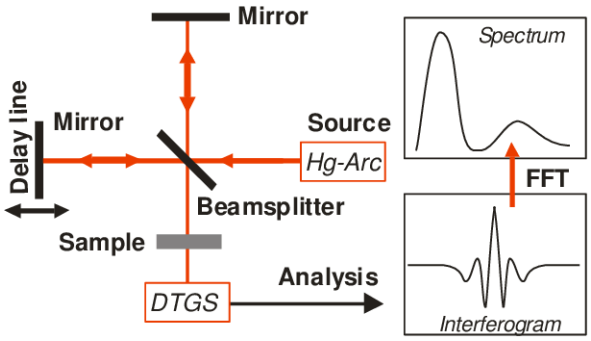






From the interferogram, the energy or wavelength spectrum is obtained by Fourier transformation





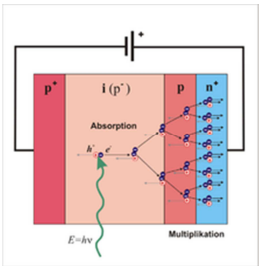
Resolution: Two spectral lines can be resolved when the mirror travel length is $\boldsymbol{L = (\Delta k)^{-1}}$
(= travel length required to observe one beating period), where $\boldsymbol{\Delta k = \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)}$

Example: L = 10cm » Δk = 0.1cm^{-1} » $\Delta E = \Delta k \cdot h \cdot c$ = 0.0124 meV

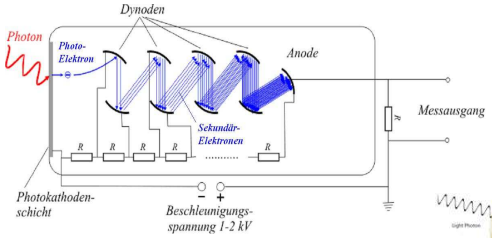
(C) Photodetectors:

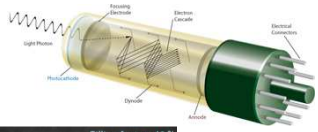
Many different types exist, optimized for different wavelength ranges and low background noise.

Semiconductor detectors:
Photoconductors or photovoltaic photodiodes, avalanche diodes,



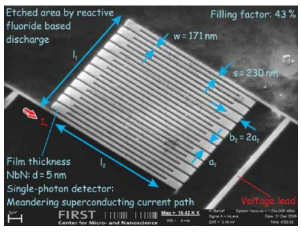
Photomultipliers:



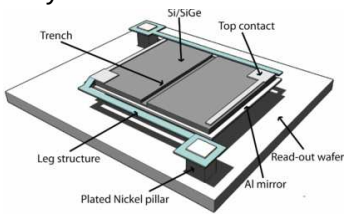


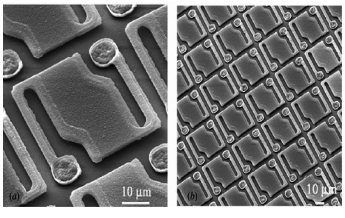
Bolometers (pyroelectric, thermistors):
measuring of heating by thermal irradiation

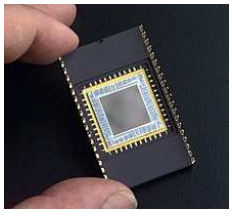
Superconducting photodetectors:
Josephson junctions that become normal when a photon is absorbed.



Focal plane arrays & CCD Cameras



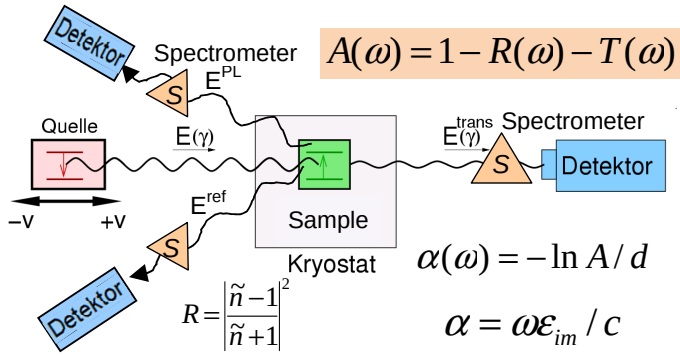




3.3 Measurement Techniques

- **Absorption A(ω), transmission T(ω) and reflectivity R(ω) spectroscopy** as a function of wavelength and photon energy using tunable or broad band light sources. » Yields direct information on the electronic and vibrational properties (phonons, band gaps, transition energies)
- **Photoluminescence and fluorescence spectroscopy:** Measurement *of secondary emission* induced by optical excitation with high power, higher photon energy pump lasers.
  The luminescence emission is separated from the pump using a low pass filter.
- **Optical microscopy**: Measurement of the spatial distribution of the optical response of the sample using scanning or imaging methods, optical tomography, single molecule imaging, ..
- **Other techniques**: Ellipsometry, Raman spectroscopy, photocurrent spectroscopy, time resolved pump-probe experiments, non-linear spectroscopies, magneto-optics,….

Experimental: Transmission, Reflection, Luminescence



$$A(\omega) = 1 - R(\omega) - T(\omega)$$

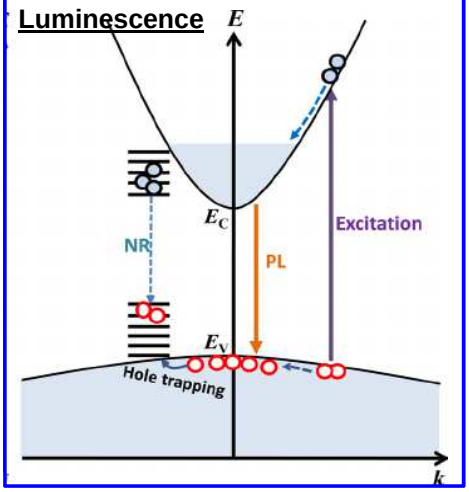
$$\alpha(\omega) = -\ln A / d$$

$$R = \left|\frac{\tilde{n}-1}{\tilde{n}+1}\right|^2$$

$$\alpha = \omega\varepsilon_{im} / c$$

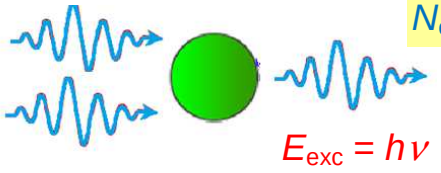
Dispersion of $A(\omega)$, $n(\omega)$, $\alpha(\omega)$, $I^{PL}(\omega)$
= ***Absorption or emission spectrum***

Luminescence



3.4 Absorption Coefficient

Photons are generally absorbed in a ***one-step process***, where the *whole* photon energy is transferred *at once* to a fundamental excitation of the sample:



$N_{out} = N_{in} - 1$

$E_{exc} = h\nu$

As a result, when passing through the sample, the ***number of photons N_{ph}***, i.e., the ***intensity I_{ph} decreases*** due to photon absorption - but the **photon energy *h*ν is unchanged !**

[**Side note**: Exceptions exist, such as Raman scattering, where a small amount of the photon energy is transferred to/from low energy phonons, i.e., the photon energy is slightly changed in the Raman scattering process. However, the probability for this process is usually very small, for which reason high power pump lasers must be used.]

The ***absorption probability*** per unit travel length dl is quantified by the ***absorption coefficient*** α that corresponds to the change in the number of photons per path length:

$$\alpha(h\nu) = -\frac{1}{N_{ph}}\frac{dN_{ph}}{dl}$$

α is measured in units of [cm^{-1}] and is a direct measure of the *strength* of the photon-sample interaction.

⇨ The absorption coefficient can *vary over a very wide range* by several orders of magnitude as a function of wavelength and material properties.

⇨ Thus, it ranges from α = 0 for transparent media such as gases, glass, semiconductors or insulators to α =10^7 cm^{-1} for opaque (nontransparent) materials such as metals and conductors.

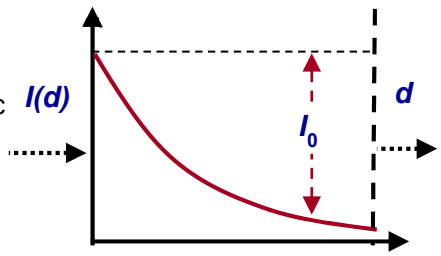
3.4.1 Beer Lambert Law and Measurement of the Absorption

When the sample is homogenous, the ***absorption probability α is constant*** in time and travelled path length *l*.

Thus, the relative change of the intensity I (=number of photons/sec cm^2) per path length *dl* is given by:

$$dN_{ph}/dl = -\alpha N_{ph} \;\rightarrow\; \int \frac{1}{NI_{ph}} dI_{ph} = -\int \alpha dl$$

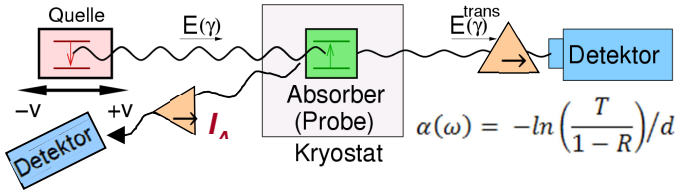
This is the ***Beer Lamberts law*** that describes the intensity decrease as a function of path length.



$$I_{ph}(l) = I_0 e^{-\alpha l}$$

Measurement of Absorption

» Illumination of the sample with a **broad band light source** and measuring *both* the ***reflectivity R(ω)*** *and* ***transmission T(ω) spectra*** as a function of wavelength, selected by a monochromator.



The **transmission *T*(ω)** = I_{trans} / I_0 is given by: $T(\omega) = 1 - R(\omega) - A(\omega)$ $\quad T(\omega) = (1-R)\cdot e^{-ad}$

and the **reflectivity *R*(ω)** = I_{ref} / I_0 by: $R = |(\tilde{n}-1)/(\tilde{n}+1)|^2$ where *n* is the refractive index

Using the Beer-Lambert law $T(\omega) = (1-R)\cdot e^{-ad}$ yields: $\alpha(\omega) = -\ln\left(\frac{T}{1-R}\right)/d$

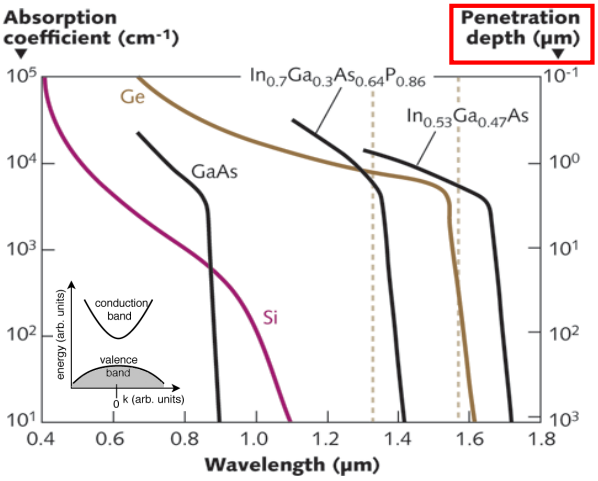
Decay length / penetration depth λ_{dec}

= Depth where the intensity is reduced by a factor of 1/*e*, i.e., $I_{ph}(\lambda) = I_0 e^{-1}$ » $\alpha\,\lambda_{decay} = 1$.

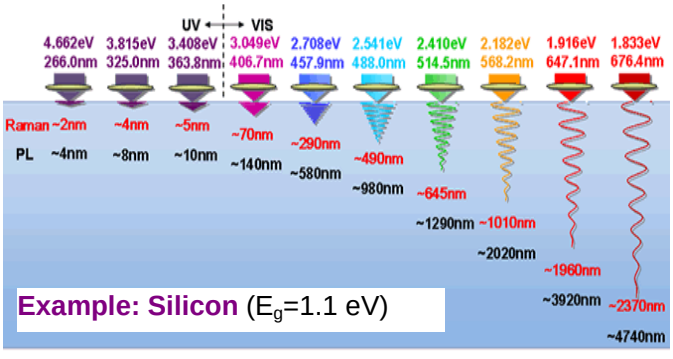
$$\lambda_{decay}(E_{hv}) = 1/\alpha_{abs}$$

Infrared & visible range:

The absorption coefficient strongly changes as a function of energy due to the fundamental band gap, where α changes by up to 6 orders of magnitude.



Penetration depth for Silicon



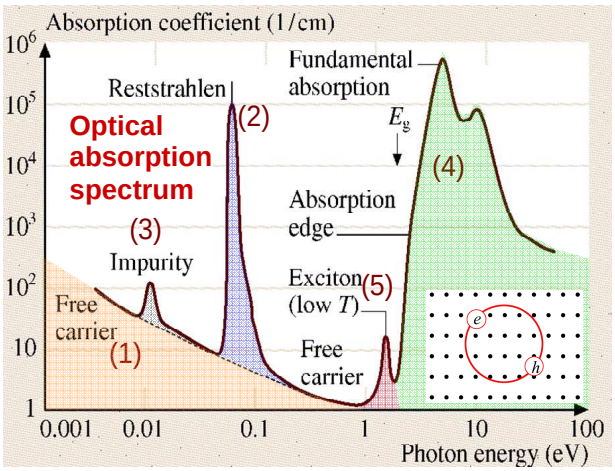
3.4.2 Absorption Spectrum α(E) = Sum of all Possible Excitations

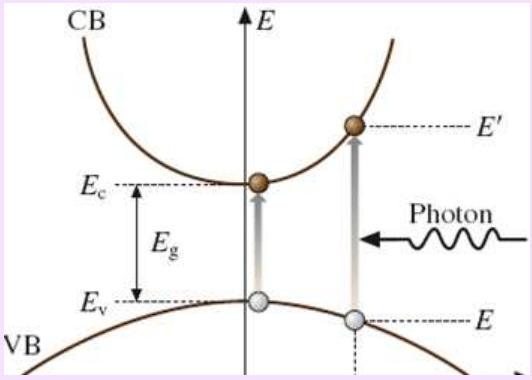
Different ***processes*** lead to photon absorption such as:

$$\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e}}$$

$$\alpha_{abs}(\omega) = \frac{\sqrt{\varepsilon_0}\omega_p^2}{c\omega^2\tau}$$

1. **Free carrier absorption ,** i.e., excitation of collective **plasma oscillations of free carriers.** Characterized by the plasma frequency ω_p that is determined by the free carrier concentration n_e
2. Absorption through ***optical phonons*** (lattice vibrations): *Reststrahlenbande"* (hν ~10 – 100 meV) = damped harmonic oscillator driven by the AC electromagnetic field
3. Excitations of electrons from localized **defect/trap states** (~0.01 – 1 eV)
4. **Fundamental absorption** by excitation of electrons from the VB to the CB band (~ eV)
5. **Exciton absorption** = Excitation of bound electron-hole pairs (~ eV)





3.4.3 Free Carrier Absorption

Mobile, i.e, ***free carriers*** in the solid are accelerated by an electric field until they scatter within the crystal after a certain average scattering time τ.

This leads to the ***DC conductivity*** of the material given by:

$$\sigma_{0,DC} = \frac{ne^2\tau}{m^*} = n\,e\mu$$

where *n* is the carrier concentration, *μ* the mobility and *m** the effective mass of the carriers.

In an *AC field*, the electrons are driven by the varying electromagnetic field in an oscillatory motion according to:

$$m^*\ddot{u} + \frac{m^*\dot{u}}{\tau} = -e\mathcal{E}(t) = \mathcal{E}_0\exp[-i(\omega t - kx)]$$

In the Drude model, this results in an ***AC conductivity*** given by:

$$\sigma(\omega) = \frac{\sigma_0}{(1-\omega\tau)} = \frac{ne^2\tau}{m^*}\frac{1}{(1-\omega\tau)} = \frac{ne^2\tau}{m^*}\frac{1}{(1-\omega\tau)}$$

The AC conductivity is proportional to the damping that leads to the energy dissipation and absorption.

The free carrier ***absorption coefficient*** is thus given by:

$$\alpha(\omega) = \frac{2\sigma(\omega)}{\varepsilon_0 c} = \frac{2ne^2\tau}{\varepsilon_0 c\cdot m^*}\frac{1}{(1-\omega\tau)}$$

The free carrier absorption is proportional to the free carrier density *n* and decreases rapidly with increasing frequency ω because the electrons can no longer follow the varying AC field.

3.4.4 Absorption via Phonons and Plasmons

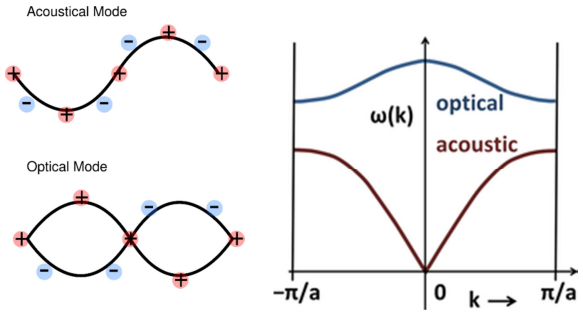
Vibration of positive and negative charges in the solid with respect to each other creates an oscillating dipole moment that couples to the electromagnetic waves and thus results in absorption.

The vibrations can be described as damped harmonic oscillators with a resonance frequency ω_0 and a damping factor γ driven by the electromagnetic wave.

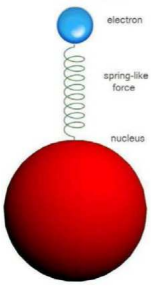
Optical phonons = phonons in which the positive and negative charged atoms vibrate counter phase to each other and thus, couple to the electromagnetic field (does not apply for acoustic phonons.) The resonance curve corresponds to that of a *damped harmonic oscillator* .

Thus, the absorption coefficient is given by:

$$\alpha_{phonon}(\omega) = \frac{f}{n}\frac{\omega^2\omega_{phonon}^2}{\left(\omega_{phonon}^2-\omega^2\right)^2+\gamma^2\omega^2}$$



Plasmons: For free electrons in metals/semiconductors, the electrons can oscillate against the fixed positive charges of the atom cores. This yields an absorption coefficient of: $\alpha_{plasmon}(\omega) = \frac{\omega_p^2}{n}\frac{\omega^2}{\omega^4+\gamma^2\omega^2}$ with the ***plasma frequency*** $\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 \varepsilon_s m_e}}$



The plasma frequency depends only on the electron concentration n_e, electron mass m_e and the dielectric constant ε_s of the material.

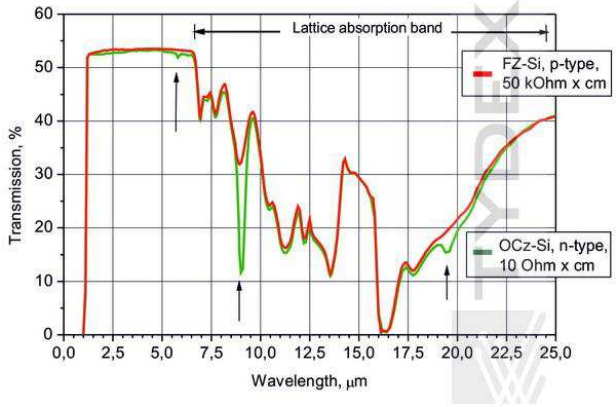
Note: Free carrier absorption is due to the *transversal* motion of the electrons accelerated by the oscillating electromagnetic field. This motion is damped due to the electrical resistance of the material. In contrary, plasmons correspond to (quantized) longitudinal electron oscillations. Due to the selection rules these do not directly couple to light, but can only be observed by electron spectroscopy.

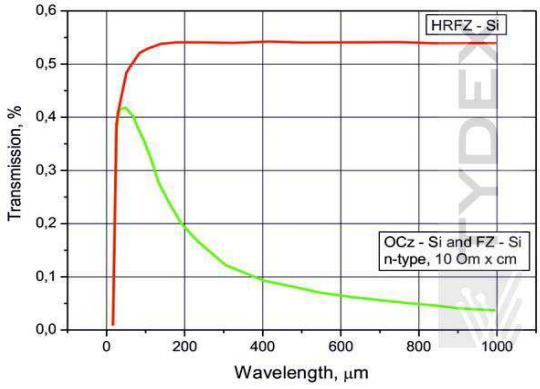
Example: Infrared Absorption Spectrum of Silicon

Phonon and free carrier absorption occurs in the infrared spectral range.

To optimize transmission for optical applications different grades of silicon are produced:
Optical Czochralski (OCz-Si), low oxygen float zone (FZ-Si), and high resistivity float zone Silicon (HRFZ-Si).

Transmission Spectra:





All grades have phonon absorption peaks by lattice absorption in the 6.5 to 25 µm range.
However, oxygen containing OCz-Si has additional peaks at 5.8 / 9.1 / 19.4 µm due to Si-O_2 vibrations.
Due to much less oxygen in FZ-Si (10^{16} cm^{-3} vs. ~10^{18} cm^{-3} in OCz-Si), FZ-Sí is free of these peaks.

The right hand figure shows the *effect of free carrier absorption* in the far-infrared region λ >20 µm for n-type Silicon *compared* to that of high resistive, high purity (undoped) Silicon that is fully transparent.

3.4.5 Absorption due to Fundamental (Interband) Optical Transitions

The absorption spectrum of any material contains different features (see previous slides) attributed to different optical excitations such as free electron absorption, phonon generation, intra- and interband transitions, as well as excitonic transitions.

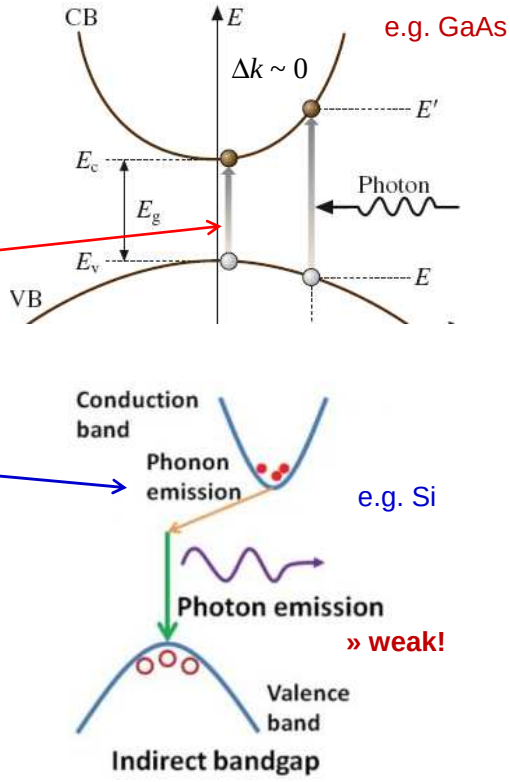
For such **optical transitions,** the following **rules** must be fulfilled in order to obtain absorption:

1. **Energy conservation** : $E_{excitation} = E_{photon}$
   The energy difference between initial and final excited state must be ***exactly* equal** to the photon energy.

2. **Momentum conservation** : $\Delta k = k_{photon,absorbed}$
   In the absorption process, the momentum of the photons must be transferred to the excitation. Because the momentum $k = 2\pi/\lambda$ of photons is small (<0.01nm^{-1}), this means that only ***optically direct*** transitions with $\Delta k \sim 0$ are allowed (if no other excitation is involved).

3. **Optical selection rules: Optical matrix element**
   For an optical transition to be allowed, in addition, the quantum mechanical transition matrix element H_{fi} between the initial v and final state c with the **dipole operator** $|\hat{e} \cdot \mathbf{p}|$ of the photons must be *nonzero*. $\hat{\mathbf{p}} = -i\hbar\nabla$

$$|H'_{fi}|^2 = |\langle c|\mathbf{H}_{em}|v\rangle|^2 = \frac{e^2|A|^2}{m^2}|\langle c|\hat{e}\cdot\mathbf{p}|v\rangle|^2 = \frac{e^2|A|^2}{m^2}|\mathbf{p}_{cv}|^2$$



3.4.6 Interband Transitions in Quantum Wells

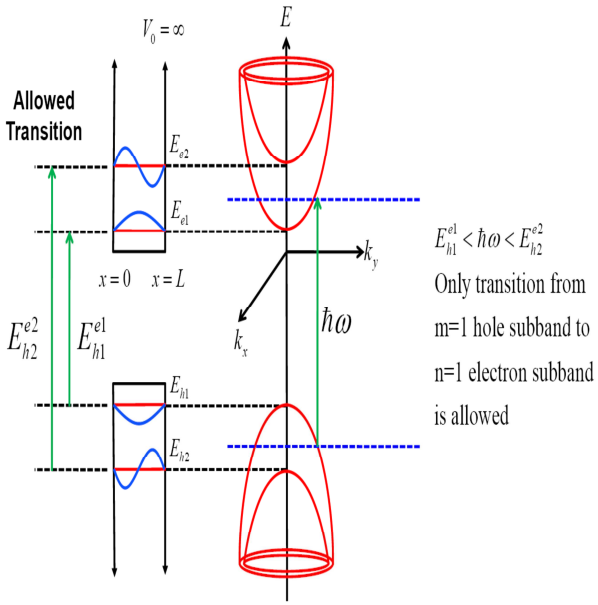
For quantum well structures, several quantum confined states (2D subbands) are formed due to size quantization, both in the conduction as well as the valence band.

To determine which optical transitions are allowed and which are forbidden, we need to look at the optical transition matrix elements between the initial and final state:

$$|H'_{fi}|^2 = |\langle c|\mathbf{H}_{em}|v\rangle|^2 = \frac{e^2|A|^2}{m^2}|\langle c|\hat{e}\cdot\mathbf{p}|v\rangle|^2$$

for the different combinations of initial and final states.

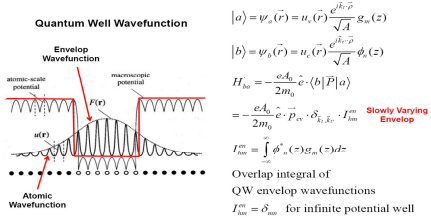
» This yields the ***selection rules*** for the corresponding optical transitions.



Envelope Function Approach:

To calculate the matrix elements, we employ the *evelope function approach* to describe the wave functions of the quantized QW states.

In this approach, the wave functions are *separated* into the lattice periodic Bloch function of the bulk and an evelope function that describes how the state is confined within the quantum well.



Envelope Function Approach to Derive the Matrix Elements

= <envelopes>×<bulk matrix element> + <matrix element of envelopes>×<bulk>

Selection Rules for Interband Transitions

The transition probability is zero for some combinations of initial and final states. This gives rise to selection rules: only certain transitions are allowed. The selection rules in band-to-band transitions are determined by the overlap between the envelope functions, $\langle cn|vm\rangle$. Investigating this overlap, we can list the following selection rules:

- The electron and hole state have to be of the same parity, provided that the potential is symmetric.
- If the well for electrons and holes are identical (i. e. $\Delta E_c = \Delta E_v$ and same m^*) then only transitions with the same quantum number for the electron and hole states are allowed ($\langle cn|vm\rangle = \delta_{n,m}$, "The $\Delta n = 0$ rule").
- Also when the electron and hole wells are not strictly identical, $\Delta n = 0$ usually gives the strongest transitions.

u_{j0} and u_{i0} are orthogonal (remember: Eigenstates of the same Hamiltonian)

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \langle\chi_j|\chi_i\rangle\langle u_{j0}|\mathbf{e}\cdot\hat{\mathbf{p}}|u_{i0}\rangle + \langle\chi_j|\mathbf{e}\cdot\hat{\mathbf{p}}|\chi_i\rangle\langle u_{j0}|u_{i0}\rangle \qquad (20)$$

$= 0$

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \langle\chi_j|\chi_i\rangle \underbrace{\langle u_{j0}|\mathbf{e}\cdot\hat{\mathbf{p}}|u_{i0}\rangle}_{\equiv \mathbf{e}\cdot\mathbf{p}_{ji}}$$

Thus, the interband matrix element is determined by the overlap of the envelope function: $\langle cn|vm\rangle$

$$\hat{\mathbf{p}} = -i\hbar\nabla = -i\hbar\frac{\partial}{\partial x}$$

Selection rules for interband transtions:

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The transition probability is zero for some combinations of initial and final states. This gives rise to selection rules: only certain transitions are allowed. The selection rules in band-to-band transitions are determined by the overlap between the envelope functions, $\langle cn|vm\rangle$. Investigating this overlap, we can list the following selection rules:

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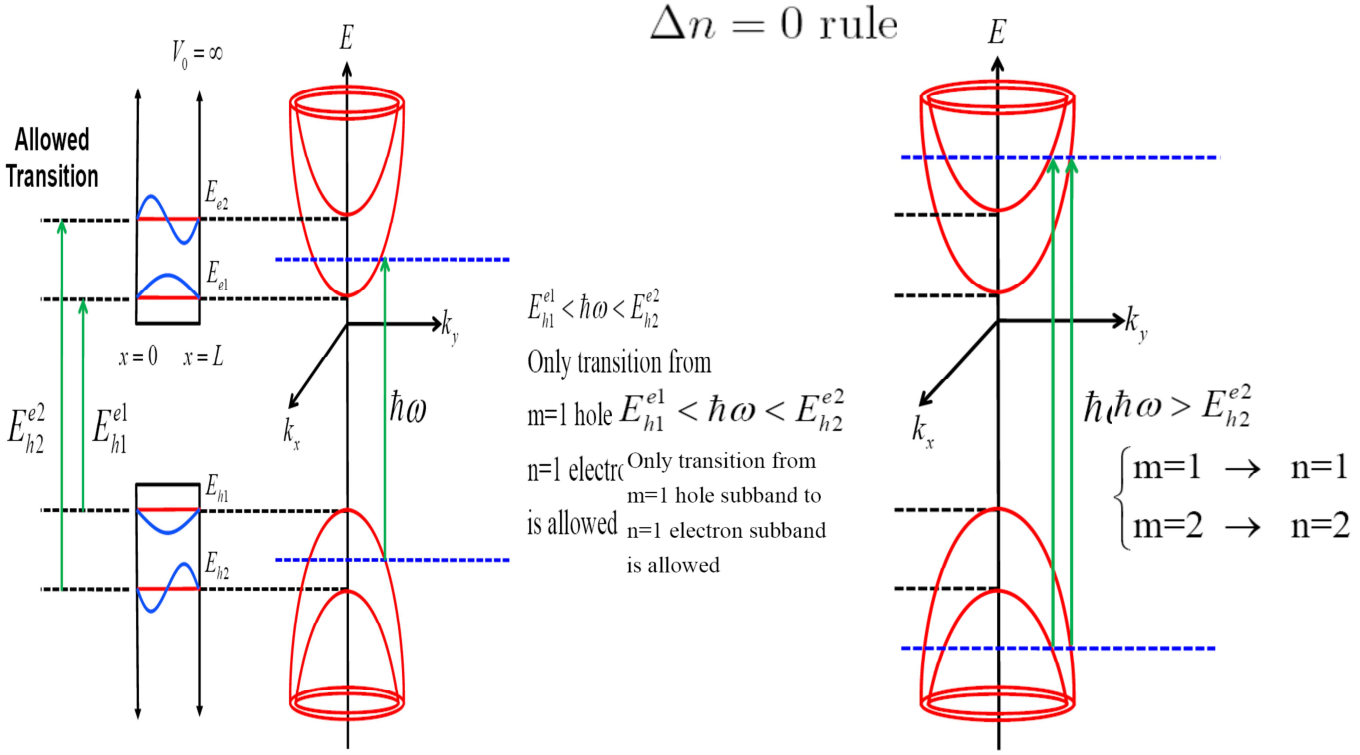
- Also when the electron and hole wells are not strictly identical, $\Delta n = 0$ usually gives the strongest transitions.

Resulting Interband Transitions in Quantum Wells



⇨The matrix element is practically the same for these transitions

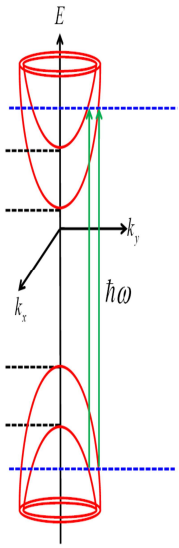
3.4.7 Absorption Coefficient and Density of States

The optical matrix element only defines the transition between *two individual initial and final states* with their given wave functions. In a medium, however, ***many* initial and final states with the same ΔE_{nm} exist** that can be excited simultaneously.

As a result, the **absorption coefficient** α(*E*) for a given photon energy must be calculated by ***summing up*** over all possible transitions with the same energy $\Delta E = h\nu$ weighed by their matrix element:,

$$\alpha = \frac{\pi e^2}{m_0^2 \omega \epsilon_0 c n \Omega} \sum_{n,m} \left|\mathbf{e}\cdot\mathbf{p}_{cn,vm}\right|^2 \left|\langle cn|vm\rangle\right|^2 2\sum_{\mathbf{k}',\mathbf{k}} \delta(\mathbf{k}'-\mathbf{k})\delta[E_{cn}(\mathbf{k}') - E_{vm}(\mathbf{k}) - \hbar\omega]$$

$$= \frac{\pi e^2}{m_0^2 \omega \epsilon_0 c n L} \sum_{n,m} \left|\mathbf{e}\cdot\mathbf{p}_{cn,vm}\right|^2 \left|\langle cn|vm\rangle\right|^2 \underbrace{\frac{2}{A}\sum_{\mathbf{k}} \delta[E_{cn}(\mathbf{k}) - E_{vm}(\mathbf{k}) - \hbar\omega]}_{joint\ density\ of\ states} \quad (25)$$



For a **2D quantum well** with confinement energies ε_{cn} and ε_{vm} and free-electron like parabolic in-plane dispersion in the k_x and k_y directions, this yields:

$$= \frac{2}{A}\sum \delta[E_g + \varepsilon_{cn} + \varepsilon_{vm} + \frac{\hbar^2(k_x^2 + k_y^2)}{2m_{nm}^*} - \hbar\omega]$$

$= \delta[(E_{cn} - E_{vm}) - h\nu]$

where ε_{cn} and ε_{vm} are the confinement in z-direction for electrons and holes and m_{nm}^* is the reduced effective mass defined by $1/m_{nm}^* = 1/m_{cn}^* + 1/m_{vm}^*$.

Interband Absorption and Density of States of Low Dimensional Structures

The summation over all possible transitions with the same transition energy $h\nu = \Delta E_{cn,vm}$ yields:

$$\alpha(\omega) = \frac{\omega}{hc}\left(\frac{2\pi e}{m\omega}\right)^2 |p_{cv}|^2 \, D_j(E_{cv})$$

In 3D :

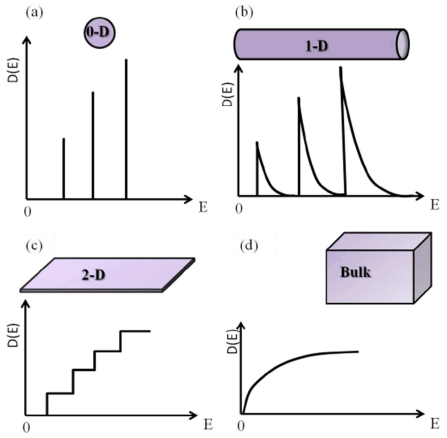
$$\alpha(\omega) = \frac{(2\pi e)^2}{cnm\omega} \cdot |p_{cv}|^2 \cdot D_0 \cdot (\hbar\omega - E_g)^{1/2}$$

where $D_j(E)$ or $\rho(E)$ is ***combined electronic density of states***, which is often approximated by the density of states (DOS) of the conduction and valence band with reduced mass.

⇨ Thus, the absorption spectrum directly shows the quantization and reduced dimensionality of electronic density of states in nanostructures !

For free-electron-like systems with parabolic E(k) dispersions and different dimensionality, these are:

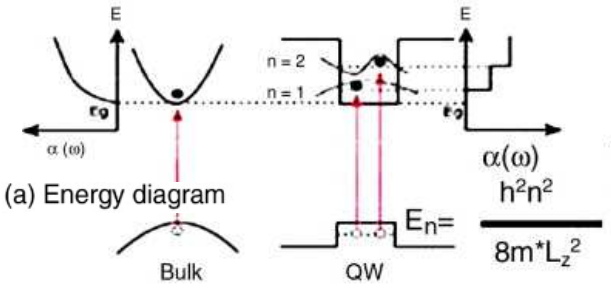
Degrees of freedom	Dispersion (kinetic energy)	Density of states
3 (bulk)	$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2)$	$\rho_{DOS}^{3D} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E - E_C}$
2 (slab)	$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2)$	$\rho_{DOS}^{2D} = \frac{m^*}{\pi\hbar^2}\sigma(E - E_C)$
1 (wire)	$E = \frac{\hbar^2}{2m^*}(k_x^2)$	$\rho_{DOS}^{1D} = \frac{m^*}{\pi\hbar}\sqrt{\frac{m^*}{2(E - E_C)}}$
0 (box)	–	$\rho_{DOS}^{0D} = 2\delta(E - E_C)$

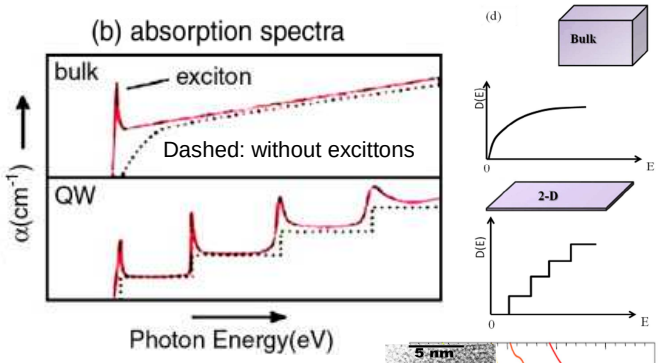


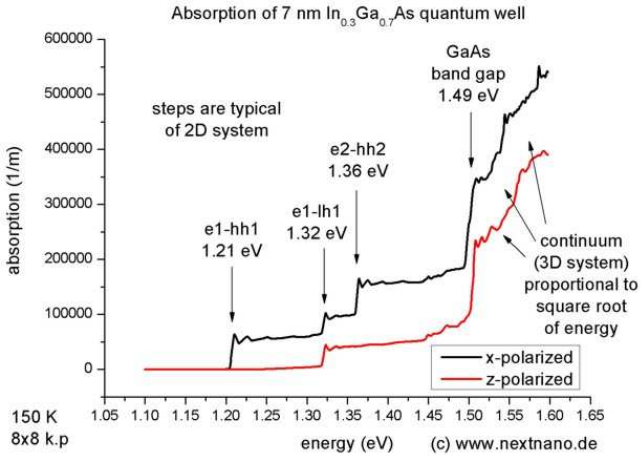
Application: Interband Absorption of 2D Quantum Wells

Examples: Absorption Spectrum of GaAs QWs and CdSe Quantum Dots

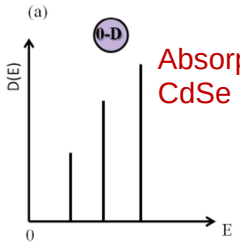
Example: GaAs Quantum Wells



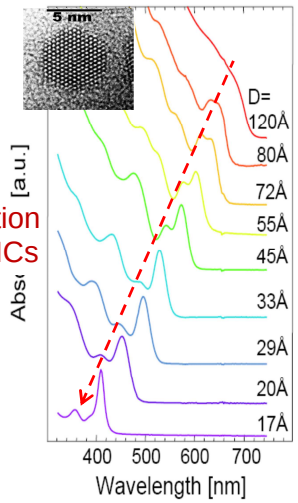




Example: CdSe Nanocrystals



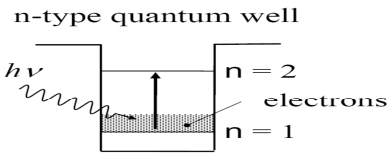
Absorption CdSe NCs



3.4.8 Intersubband Transitions

Intersubband transitions are *intraband* transitions *within* the conduction, or within the valence band only.

Example:



- Need z polarized light
- Parity selection rule: Δn – odd number

- Transition energy ~ 0.1 eV (~ 10 µm, infrared)
- Absorption used for infrared detectors
- Emission used for infrared lasers (Quantum cascade lasers)

In this case, the *intraband*

Assuming that there is a charge carrier (electron or hole) in the quantun ~~incoming photon can promote the charge carrier to~~ an excited state. In this case, both initial and final states are in the conduction band. This is an example of an *interband* transition, also called *intersubband* transition. Repeating Eq 20 with the two states originating from the same Bloch function, i. e. $u_{j0} = u_{i0}$:

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \langle\chi_j|\chi_i\rangle \underbrace{\langle u_{i0}|\mathbf{e}\cdot\hat{\mathbf{p}}|u_{i0}\rangle}_{=0} + \langle\chi_j|\mathbf{e}\cdot\hat{\mathbf{p}}|\chi_i\rangle \underbrace{\langle u_{i0}|u_{i0}\rangle}_{=1} \qquad (27)$$

The second term will no longer vanish but instead the first term will be zero. This is because u_{i0} is the wavefunction of a bulk electron at $k = 0$ and the matrix element with $\hat{\mathbf{p}}$ is therefore the expectation value of the momentum of an electron at the concuction band minimum. As with all band minima (and maxima) the momentum should be zero.

because the eigenstates (i.e., envelope functions in the z-direction) of the QW states χ are orthogonal to each other, and the integral over the $\boldsymbol{p}$ operator and Bloch states u_{i0} of the same band minimum is zero.

⇨ The ***intraband*** selection rules are given by the transition matrix between the χ envelope functions.

Selection Rules of Intersubband Transitions by Symmetry Considerations

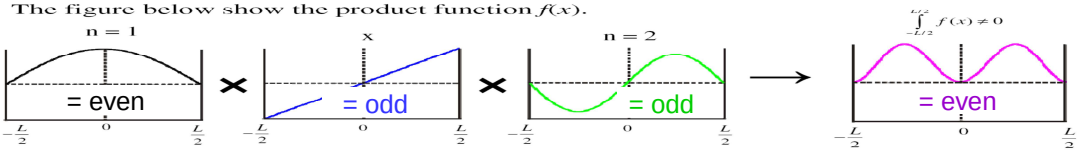
Consider the transition $n = 1 \rightarrow n = 2$ for which the transition dipole moment integral is:

$$\mu_{21} = -\frac{e}{L}\int_{-L/2}^{L/2} \sin\left(\frac{\pi x}{L}\right) x \cos\left(\frac{\pi x}{2L}\right) dx = -\frac{e}{L}\int_{-L/2}^{L/2} f(x)\,dx$$

Consider the transition $n = 1 \rightarrow n = 2$ for which the t

$$\mu_{21} = -\frac{e}{L}\int_{-L/2}^{L/2} \sin\left(\frac{\pi x}{L}\right) x \cos\left(\frac{\pi x}{2L}\right) dx = -\frac{e}{L}\int_{-L/2}^{L/2} f(x)\,dx$$

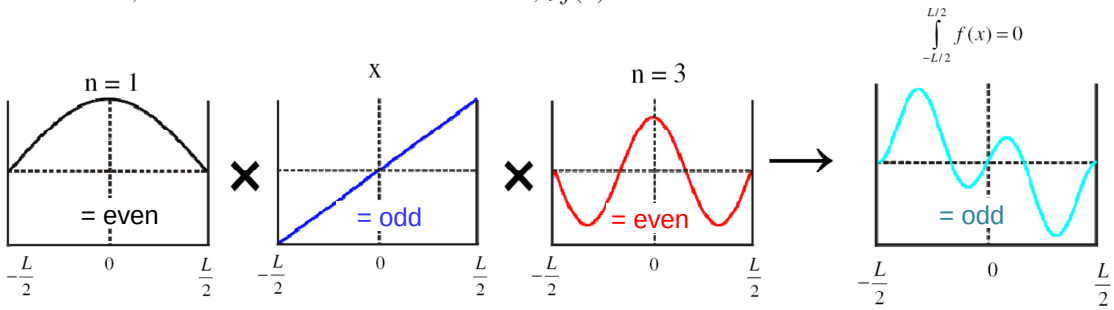
The figure below show the product function $f(x)$.



Clearly $\int f(x)dx \neq 0$ and the transition is allowed.

Clearly $\int f(x)dx \neq 0$ and the transition is allowed.

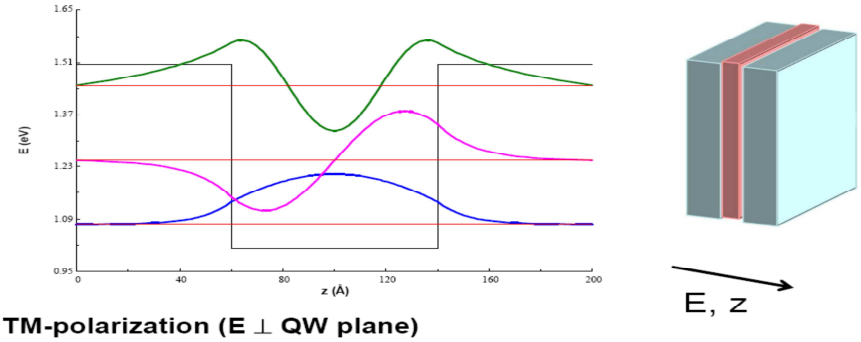
In contrast, for the transition $n = 1 \rightarrow n = 3$, $\int f(x)\,dx = 0$ and transition is forbidden.



Conclusion: if the integrand is odd / antisymmetric / *ungerade* then $\int f(x)\,dx = 0$ and transition is forbidden.

Intersubband Transitions: Polarization Dependence

Intersubband transitions: selection rules



- **Only TM-polarization (E ⊥ QW plane)**
- **Dipole matrix element:** $z_{mn} \propto \int f_m^*(z)\frac{\partial}{\partial z} f_n(z)\,dz$

f_1 and f_3 are even -> $z_{13} = 0$

For *normal incidence* the momentum operator ∂/∂x does not act on f(z) , which means that the integral of the dipole matrix element is zero.

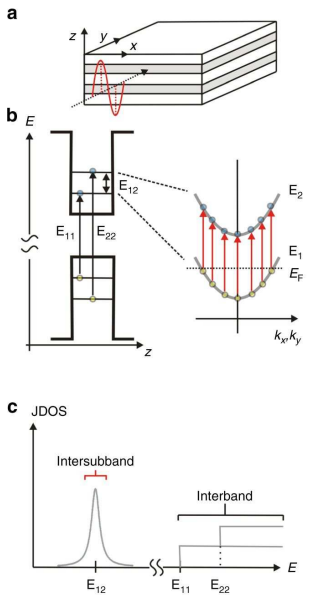
Thus, interband transitions are forbidden, i.e., intersubband absorption does not occur under normal but only under oblique incidence !

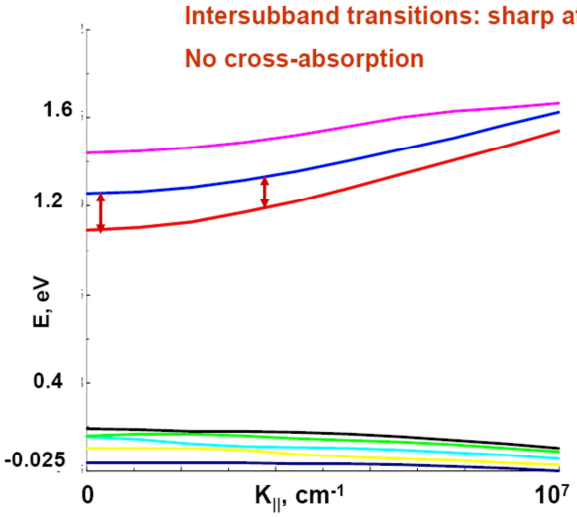
Intersubband Absorption Spectrum

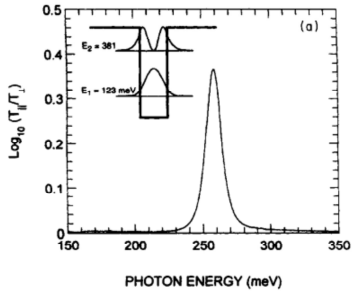
For interband transitions between QW subbands, the transition energy ΔE_{12} is nearly the same for all k-vectors because the subbands are nearly parallel to each other.

As a result, photon absorption occurs only at discreet energies $h\nu = E_{1,2}, E_{1,4}, \ldots$.

and thus, the absorption spectrum consists only of delta functions in this spectral range (infrared).





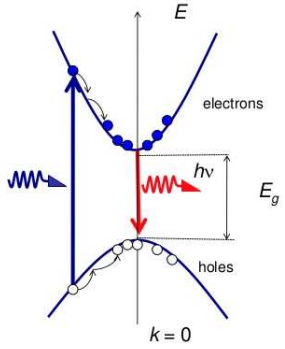


Line broadening ~ 10 meV due to interface roughness and non-parabolicity (in narrow-gap semiconductors)

Note: Absorption occurs only if the *ground state is populated* by electrons (or holes). Without population, no absorption occurs, i.e., the *absorption strength* depends on the QW doping level !

3.5 Luminescence: Secondary Photon Emission

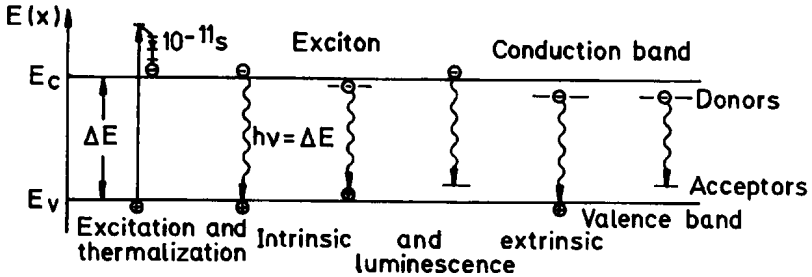
Optical excitation often leads to secondary photon emission from the sample. This secondary emission is called ***photoluminescence*** or ***fluorescence***.

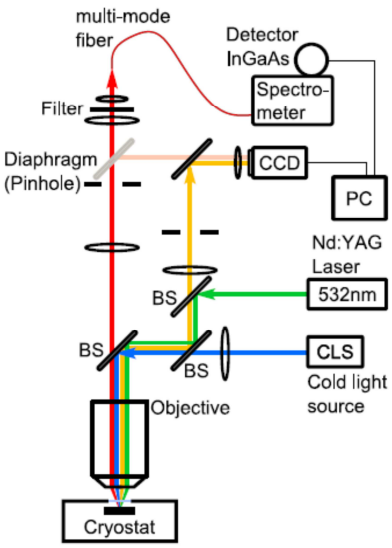


After excitation, the carriers relax to the bottom of the conduction band and top of the valence band, from where they recombine by emission of a photon. As a result, luminescence always occurs at a ***smaller energy*** than the excitation energy, i.e., $E_{lum} < E_{abs}(h\nu)$.

Note that to protect the detector against the strong pump laser, a cut-off filter must be inserted to block the excitation laser.

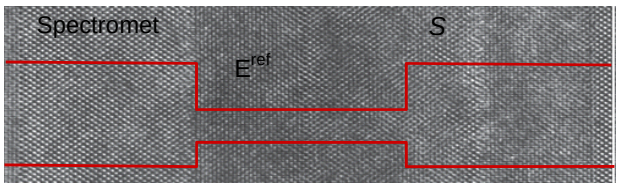
Photoluminescence is very sensitive to **excitons** and **defects** in the sample, which leads to luminescence below the band gap of the material.





Luminescence is highly sensitive to **quantum size effects** which ***blue shift*** the optical transitions. Contrary to absorption, however, usually only the ground state transition from the lowest energy levels can be observed, not the transitions between higher levels.

Example: Size dependent photoluminescence of GaAs/GaAlAs Quantum Wells



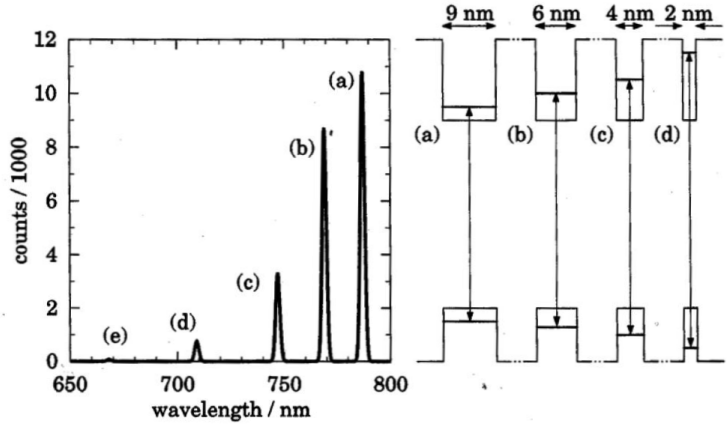


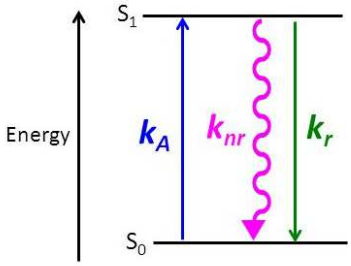
FIGURE 1.4. Photoluminescence as a function of wavelength for a sample with four quantum wells of different widths, whose conduction and valence bands are shown on the right. The barriers between the wells are much thicker than drawn. [Data kindly supplied by Prof. E. L. Hu, University of California at Santa Barbara.]

Luminescence efficiency:

(Quantum Yield)

$$\Phi = \frac{k_r}{k_{nr} + k_r}$$

= determined by the ***competition*** between *radiative* and *non-radiative* recombination processes.

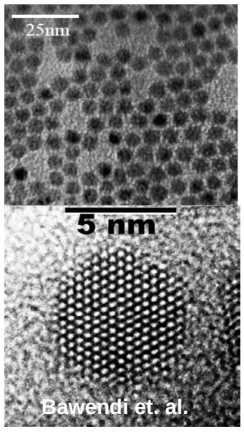


k_A = excitation rate
k_r = radiative rate
k_{nr} = non-radiative rate

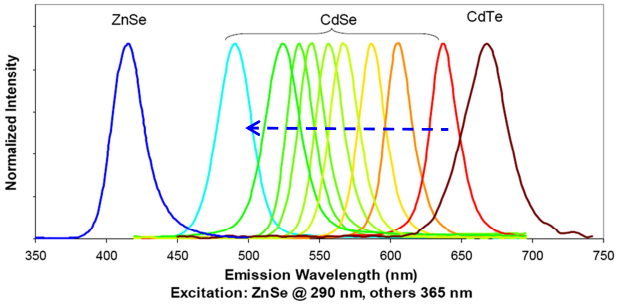
⇨ Radiative recombination rates k_r are determined by the optical matrix elements, non-radiative recombination rates by the probability of alternative processes that strongly depend on material quality. Thus, high PL intensity can be observed only in high purity/high quality material.

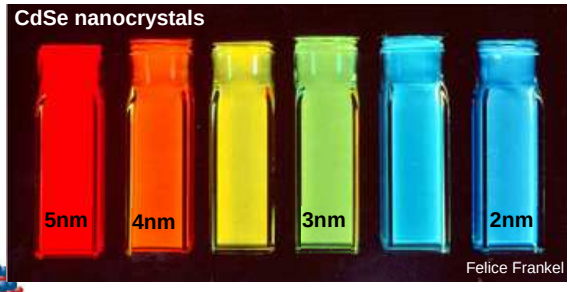
Example: Size dependendent luminescence and absorption of CdSe nanocrystals

Sizes from 2 - 6 nm

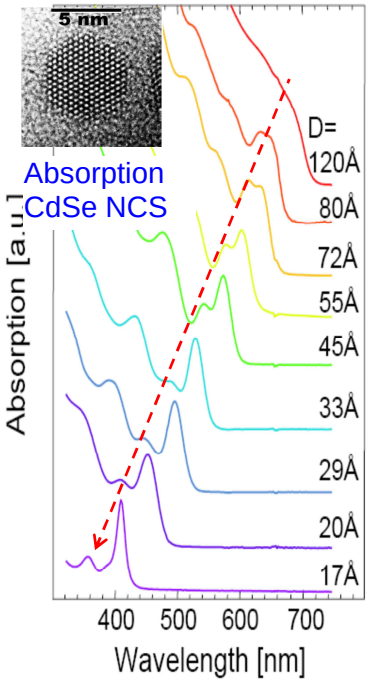


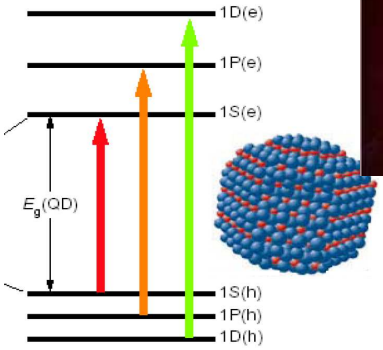
Luminescence emission by optical excitation





Absorption spectra





⇨ Blue shift of the emission and absorption due to quantum size effect

3.6 Fluorescence of Molecules

Luminescence of molecules and atoms after photo-excitation is called ***fluorescence***.

Whereas in semiconductors, this excitation creates electrons and holes that can move freely around before recombination and do not disturb the local lattice and band structure, in molecules excitation of electrons from the ***homo*** to the ***lumo state*** is often ***accompanied by conformal structural changes*** (metastable states) because the electrons usually participate in the local bonding between the atoms.

Molecular transitions also split up in ***vibrational and/or rotational bands*** because molecules are always in motion in quantized rotational/vibrational states. The transition between the vibrational/rotational levels obey certain selection rules for the changes in rotational and vibrational quantum numbers.

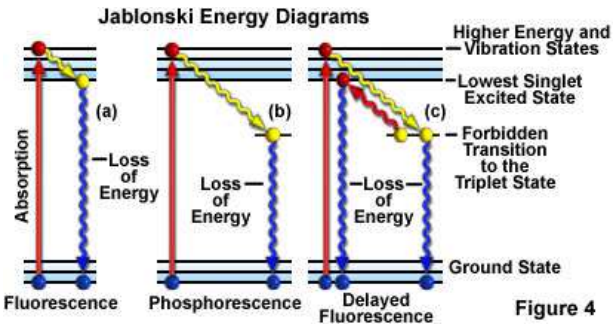
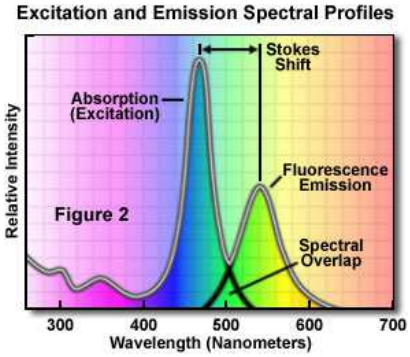


Figure 4



Thus, the fluorescence always has a ***longer wavelength*** than the excitation light (= ***Stokes shift***), as is illustrated in the fluorescence and absorption spectrum below and described by ***Jablonski diagrams.***

After excitation, the electrons loose some vibrational energy within picoseconds and relax to the lowest excited singlet state from where they relax to the ground state through fluorescent emission.

Phosphorescence: Occasionally, excited electrons make a forbidden transition to a metastable long lived triplet state, from where relaxation to the ground by fluorescence is delayed up to several seconds.

3.7 Rotational-Vibrational Absorption of Molecules

Molecules exhibit a quantized rotation and vibrational motion with a discreet energy spectrum.

The vibrational energies are given by: $E_{vib} = \hbar\omega(v + \frac{1}{2})$, rotational energies by: $E_{rot} = \frac{\hbar^2}{2\mu r^2} J(J+1)$

with typically $E_{rot} << E_{vib}$. Optical transitions are allowed only according to the following

Selection rules: (diatomic) $\Delta v = \pm 1$ (anharmonic, i.e., weak ±2, ±3, …) and $\Delta J = \pm 1$

The selection rules have several consequences:

1. The transition with Δv=±1 is the fundamental transition with $\Delta E_{vib} = \pm h\omega_0$.
2. Both vibrational and rotational quantum numbers must change during the transition.
3. The energy change of rotation $\Delta E_{rot} = 2(J+1)E_{J=0}$ can be either subtracted or added to $\Delta E_{vib} = h\omega_0$ giving the P- and R- branches of absorption, respectively. The Δv=0 transition (Q-branch) is forbidden

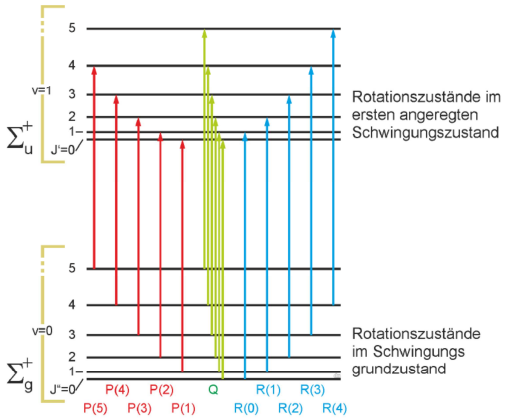
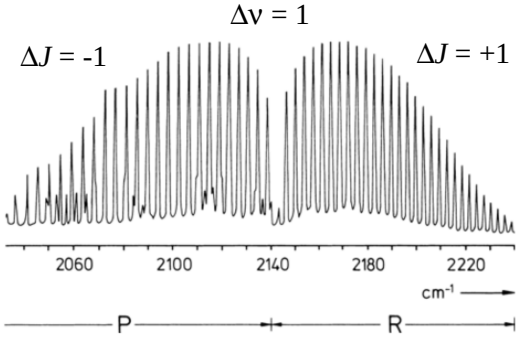


Abbildung 4: Termschema eines linearen Moleküls

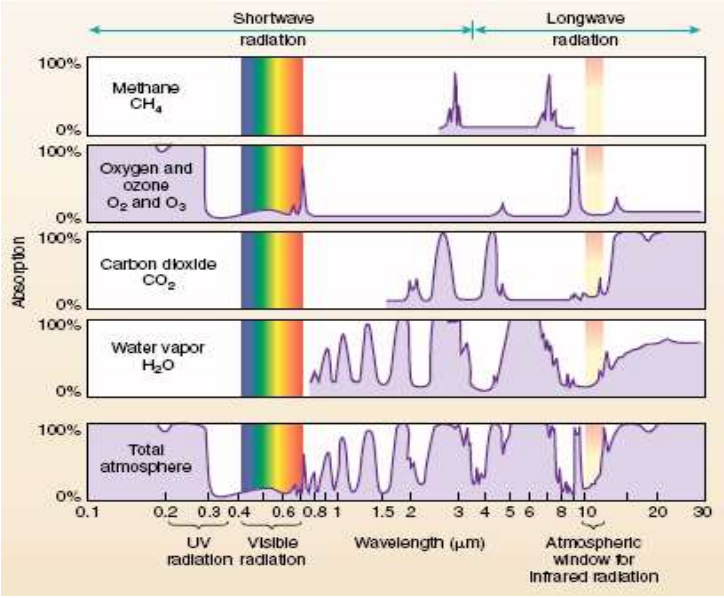
Example: Absorption spectrum of CO_2 molecule

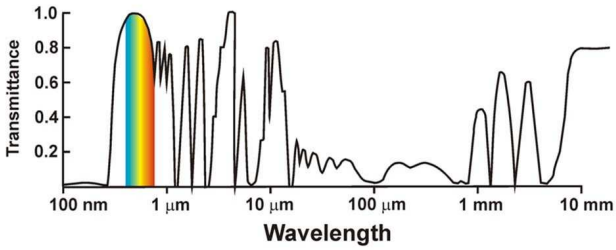


Absorption of Air

Atmospheric molecules lead to absorption of light passing through air as shown below.

The primary gases responsible for atmospheric absorption are water vapor, carbon dioxide, and ozone.



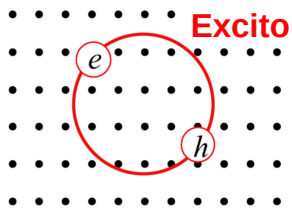


- **Water Vapor (H_2O)**: Very strong absorber in infrared 5.5 - 7.0 μm wavelength range and at > 27 μm. Water vapor in the atmosphere is highly variable in time and space.
- **Carbon Dioxide (CO_2)** : Primarily absorbs in the mid and far infrared spectrum
- **Ozone (O_3)** : Absorbs strongly in the UV portion of the spectrum (short wavelengths)

Consequence: Spectroscopy in the MIR vacuum is needed, for visible range air is sufficiently transparent.

3.8 Excitonic Emission and Absorption

Due to the attractive electron-hole interaction, in semiconductors ***bound electron-hole states*** are formed, called "***excitons" "X***". This slightly reduces the interband transition energy by the exciton binding energy E_{exc} .



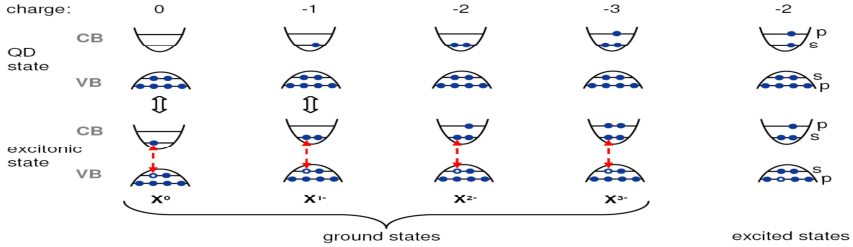
$E_{ex,0}$ (meV)	
Si	14.7
Ge	4.15
GaAs	4.2
GaP	3.5
CdS	29
CdSe	15

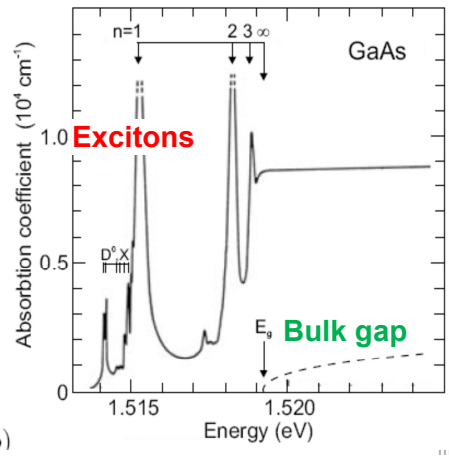
The **exciton binding energy** is given by the binding energy of the hydrogen atom $E_{B,H} = m_e e^4/8c\varepsilon_0 h^3 = R_H = 13.6$ eV (=Rydberg constant), *corrected* by the reduced mass μ of the electron and hole pair and the dielectric constant ε of the material according to:

$$E_{ex,1} = \frac{\mu}{m_e} \cdot \frac{1}{\epsilon^2} \cdot 13.6e\,\mathrm{V} \qquad \mu = \frac{m_e \cdot m_h}{m_e + m_h}$$

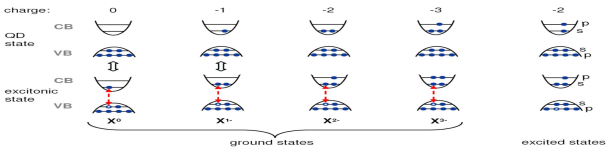
In ***nanostructures*** such as quantum wells, quantum wires or quantum dots, the exciton binding energies are increased because the spatial confinement *increases the Coulomb interaction* due to the reduced distance between the electrons and holes.

Under strong excitation, in addition ***multi-excitons*** such as bi-excitons, tri-excitons, etc. are formed, where several electrons and holes are confined and interact with each other.

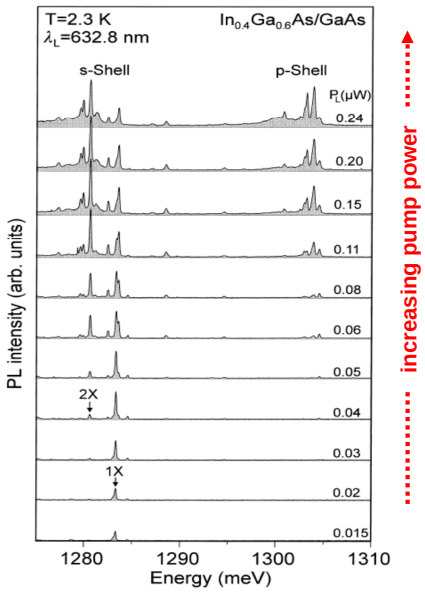


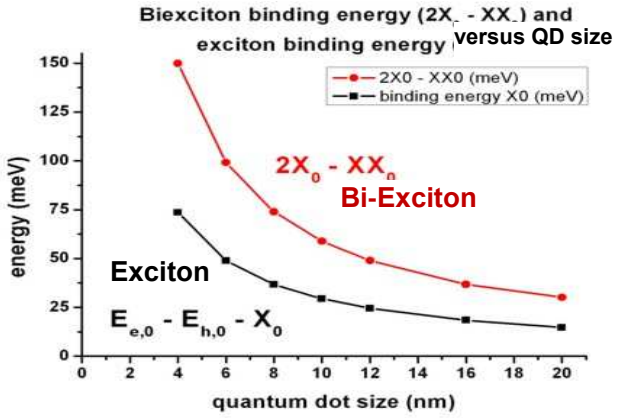


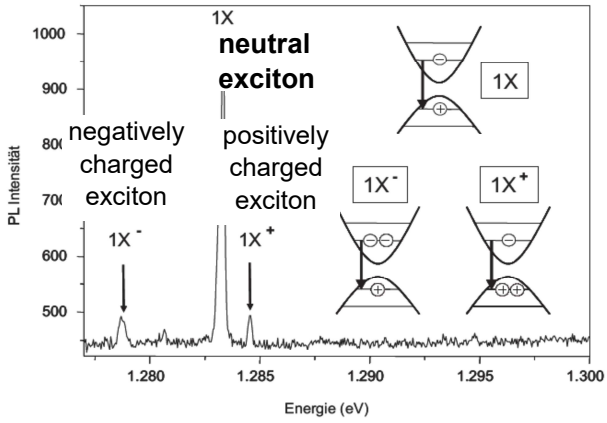
Example: Multi-Excitons in Quantum Dots



PL of InGaAs QDs for increasing pump power







⇨ Note: Single QDs can emit super sharp exciton lines with µeV line width. These can be used for realization of single photon and entangled photon sources for quantum communication !

3.9 Summary: Optical techniques provide ….

+ very ***high energy resolution*** down to ***µeV*** due to spectrometers with high resolving power,
  ⇨ highly sensitive to energy level structure and quantization effects in nanostructures.

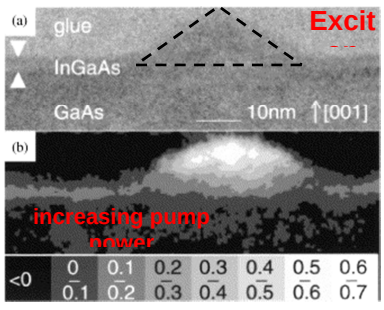
+ ***high sensitivity*** due to low noise detectors, single photon counting possible.

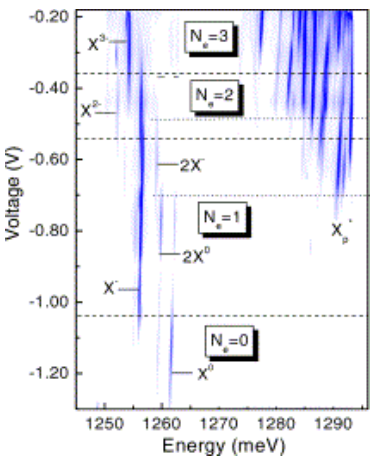
+ can be performed in air, vacuum, at cryogenic temperatures, in high magnetic fields, ….

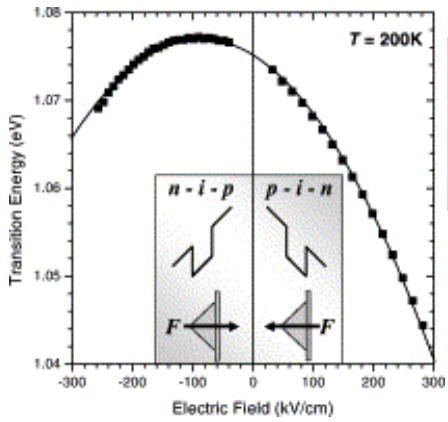
+ ***powerful light sources***: cw / pulsed lasers for excitation, femtosecond time resolution,

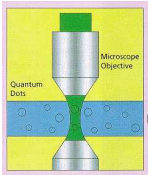
+ provides essential information for many optoelectronic and photonic device applications

Example: Single quantum dot spectroscopy: InAs/GaAs QD in a pin LED









Disadvantages:

- spatial resolution limited to about ½ of the wavelength λ, i.e. to > 200 nm.