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Physicochemical Characterization: IR and UV-vis Spectroscopy

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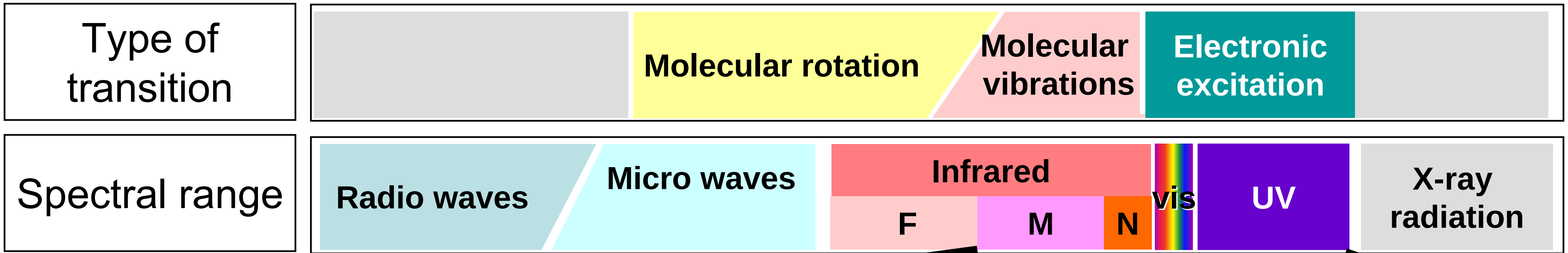
October 30, 2006

Outline

1. **Introduction**
   When to use (UV-vis and IR) spectroscopy in heterogeneous catalysis research?
2. **Measurement of solid materials**
   Transmission and Diffuse Reflection
3. **Examples**
   Catalyst and catalyst surfaces
   Characterization of sites through adsorption of probe molecules
   Spectroscopy during catalysis

MIR - NIR – vis – UV



	Mid IR (MIR)	Near IR (NIR)	UV-vis
Wavenumber / cm^{-1}	3300 to 250	12500 to 3300	50000 to 12500
Wavelength / nm	3000 to (25000-40000)	(700-1000) to 3000	200 to 800
Energy / eV			6.2 to 1.5

- electronic transitions, vibrations (rotations)

A Catalyst Life – When to Use Spectroscopy?

1. Preparation of a Solid (a Heterogeneous Catalyst)

   Formation of a solid from solution (e.g. precipitation, sol-gel method)

   Modification of solid (e.g. preparation of a supported catalyst)

2. Catalyst Characterization

   Catalyst structure, surface functionalities

   Surface sites: non-reactive interactions with probe molecules

3. During Catalytic Reaction

   Gas phase

   Liquid phase

4. Aged / Spent Catalyst

   Changes to structure & surface functionalities, deposits on surface

   Remaining surface sites

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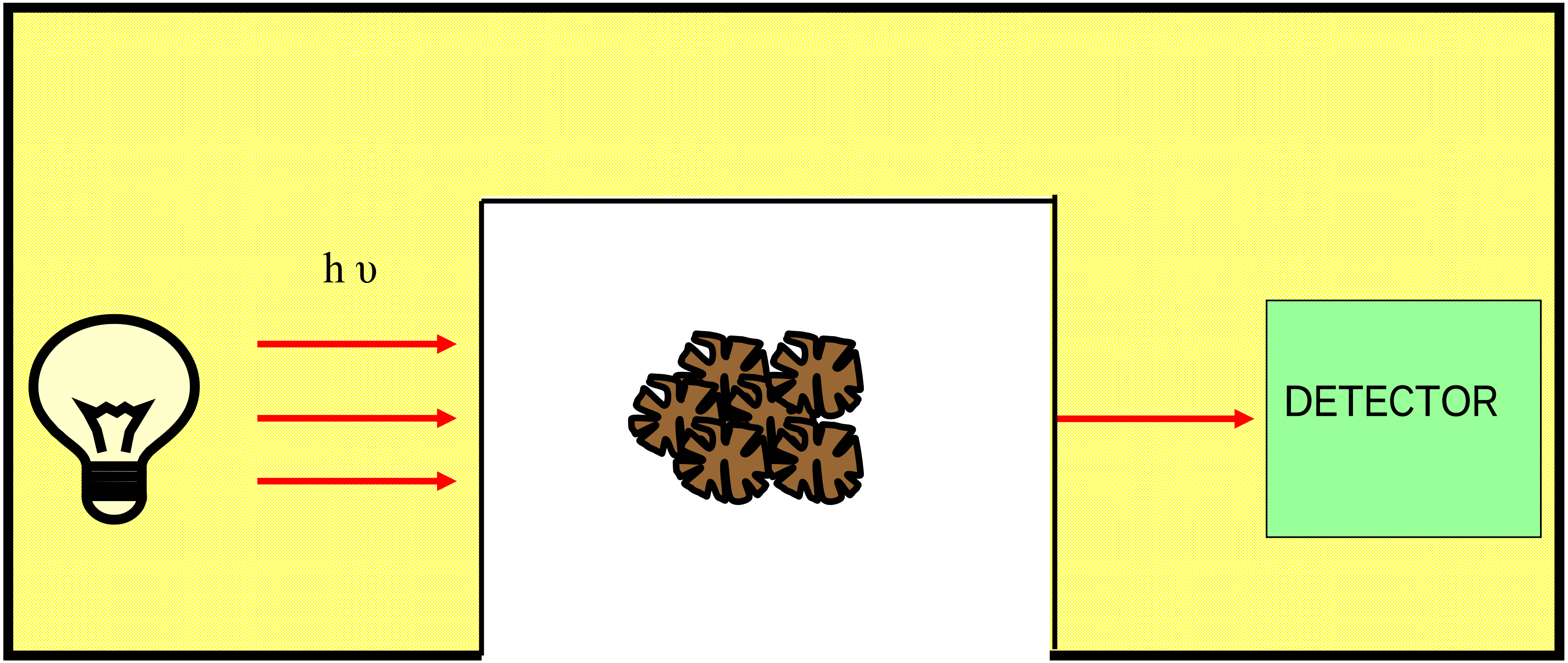
   Remaining sites

From An Experimental Point of View

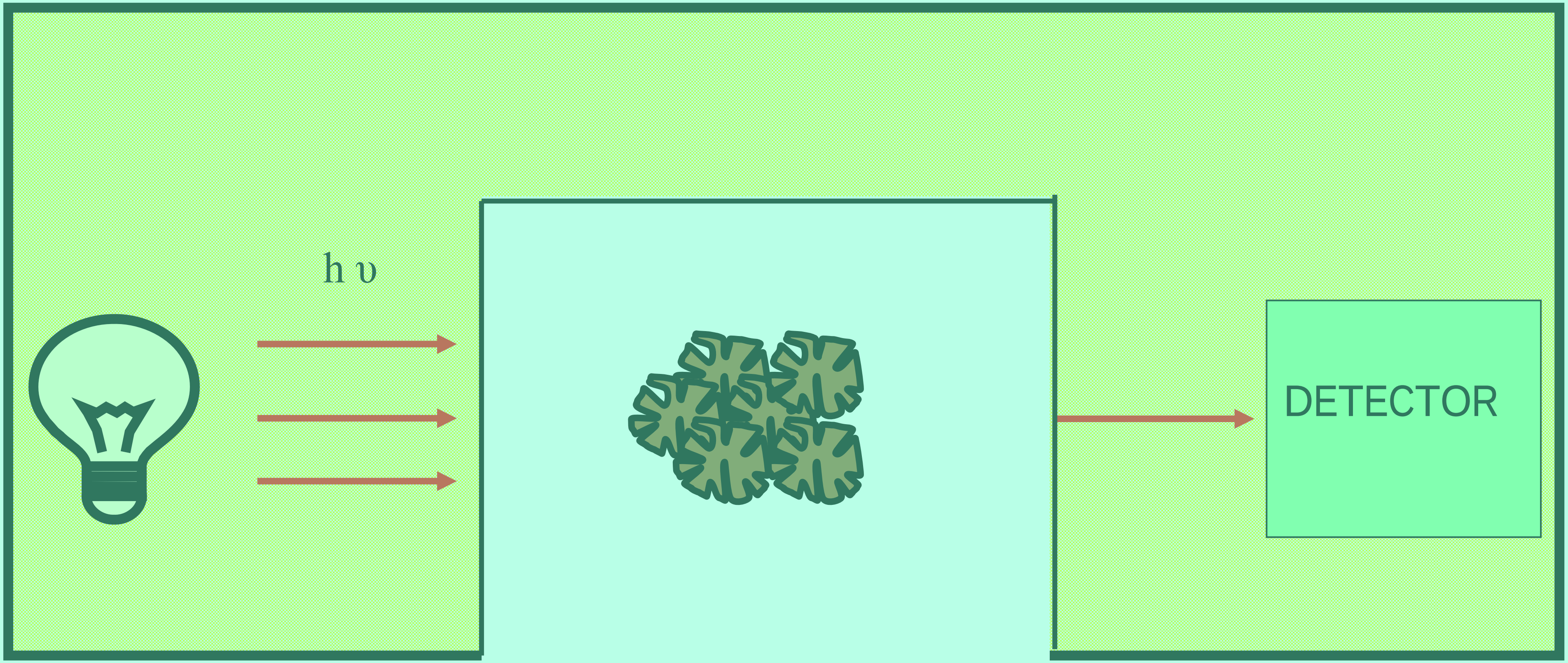
- Spectroscopy of a solid
  preparation steps, product, spent material
- Spectroscopy of solid and surrounding gas phase
  Probing sites on fresh/spent catalyst (RT or low T, p of probe small)
  During catalytic reaction: in situ (p usually atm or larger, T > RT)
- Spectroscopy of solid and surrounding liquid
  Preparation steps: formation / modification of solid
  During catalytic reaction: in situ (suspension or thin film phase boundary)

Spectroscopy of a Solid



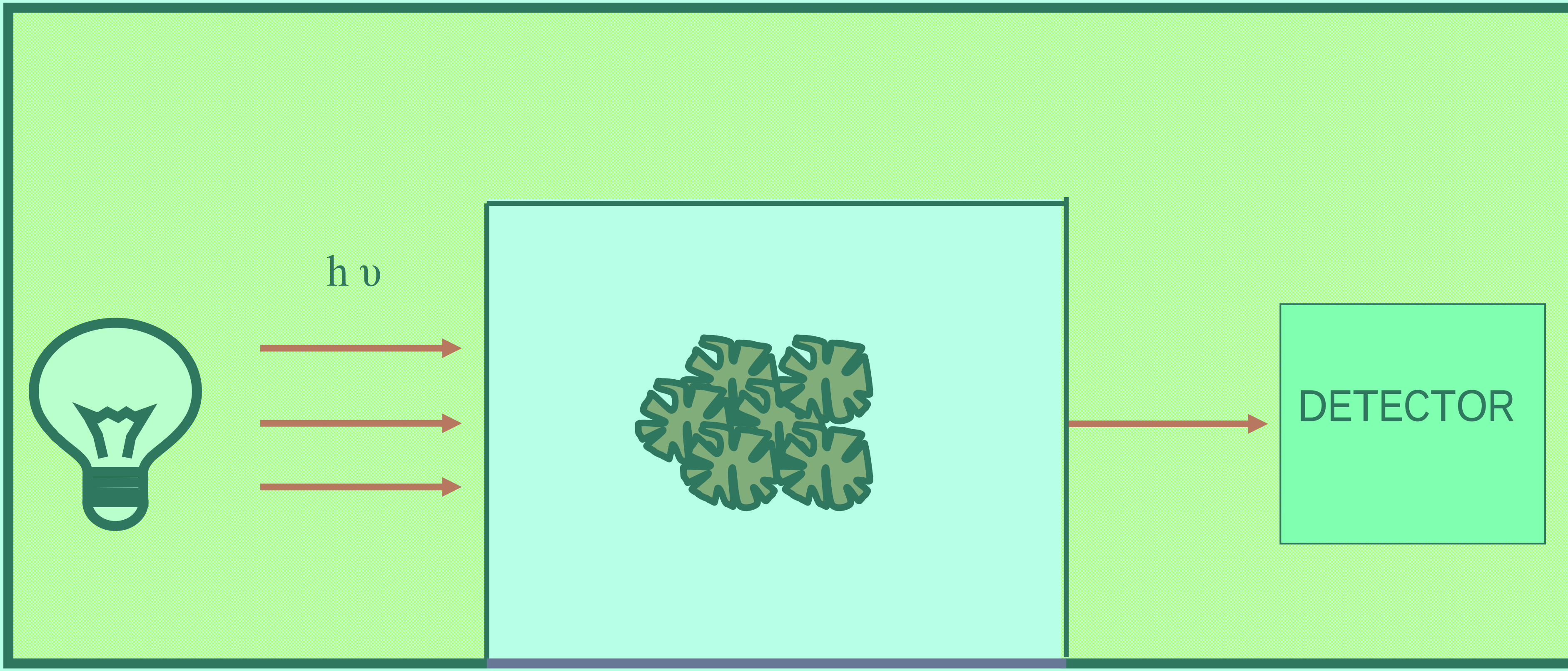
- place sample in sample holder/accessory in sample compartment of spectrometer

Spectroscopy of a Solid



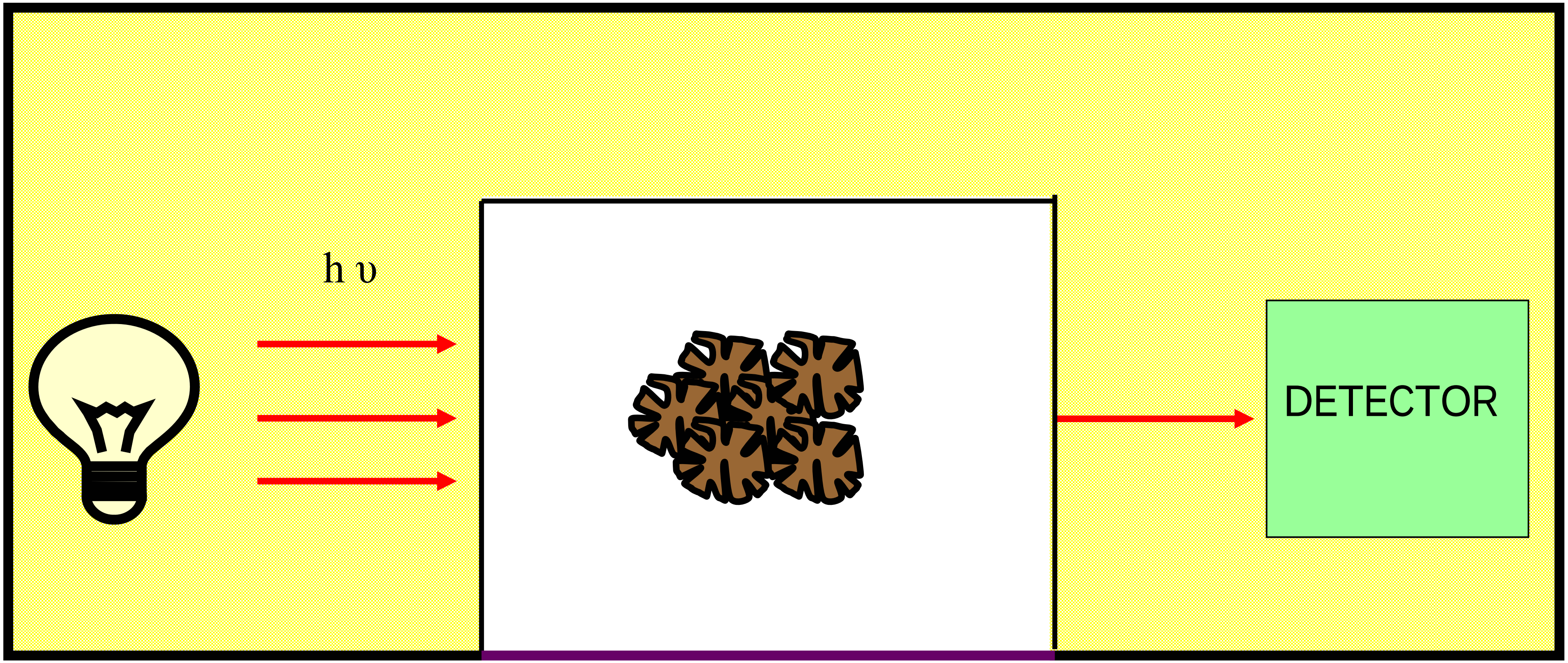
- if no special measures are taken, sample compartment + parts of the spectrometer are in air
- gas phase N_2, O_2: no absorption bands in (UV)-vis-NIR-MIR
- gas phase CO_2, H_2O: rotational vibrational bands in NIR and MIR

Spectroscopy of a Solid



- can correct for air absorption through reference measurement provided there is no change in composition with time
- modern spectroscopy software can make a calculated correction

Spectroscopy of a Solid



- can correct for air absorption through reference measurement provided there is no change in composition with time
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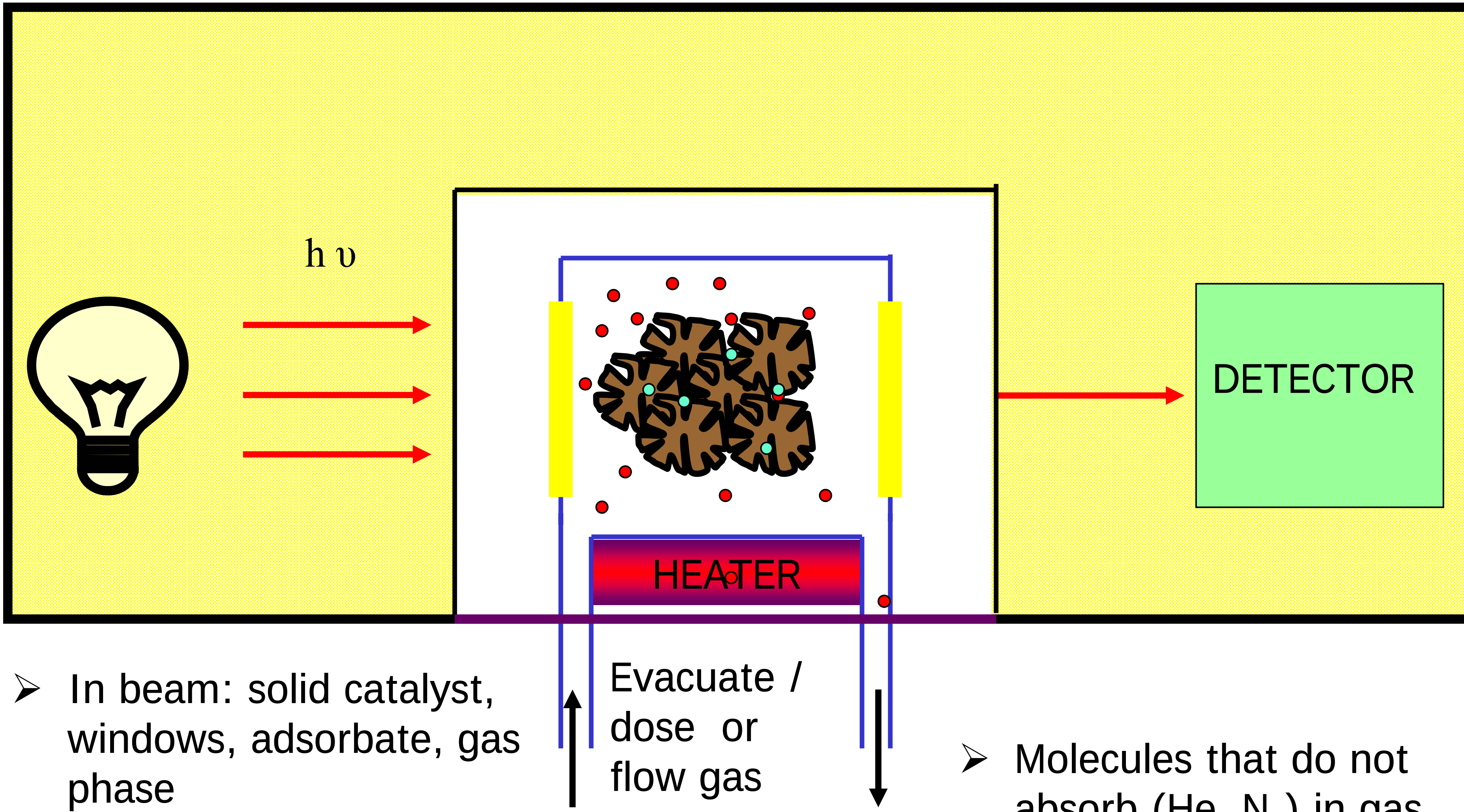
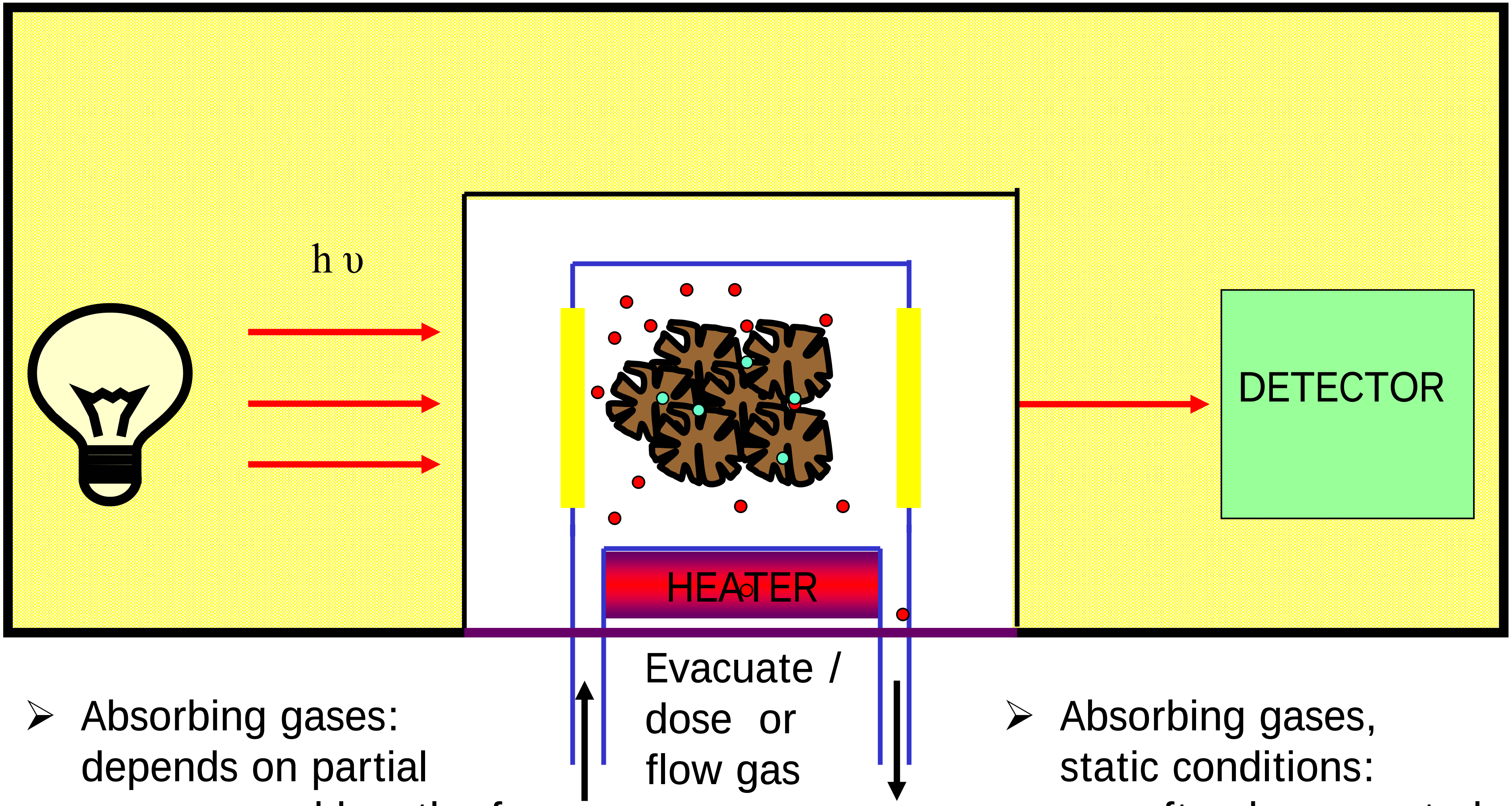
Spectroscopy of Solid in Controlled Gas Atmosphere



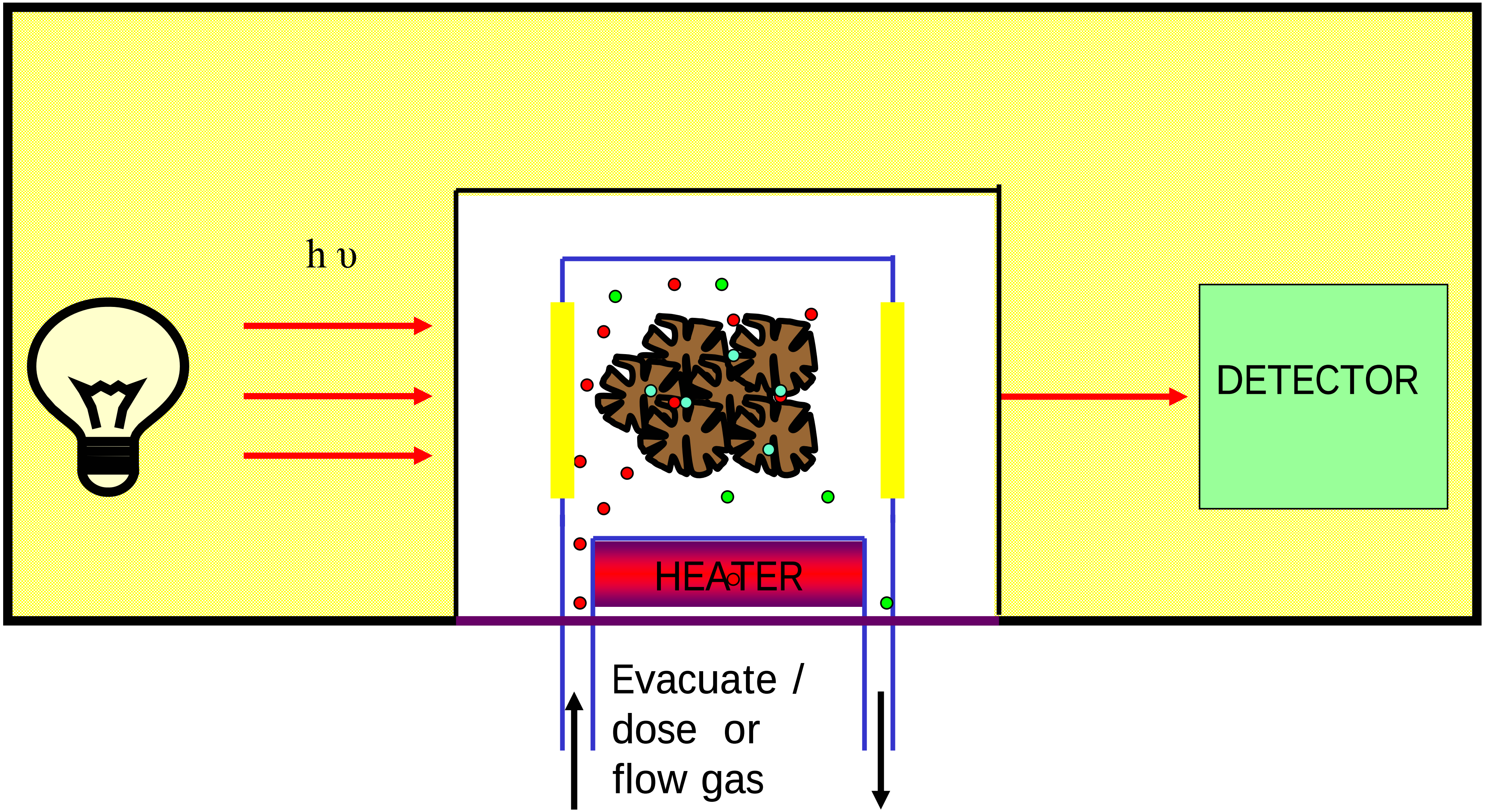
- In beam: solid catalyst, windows, adsorbate, gas phase
- Usually interested in solid and adsorbate
- Molecules that do not absorb (He, N_2) in gas phase: no problem

Spectroscopy of Solid in Controlled Gas Atmosphere



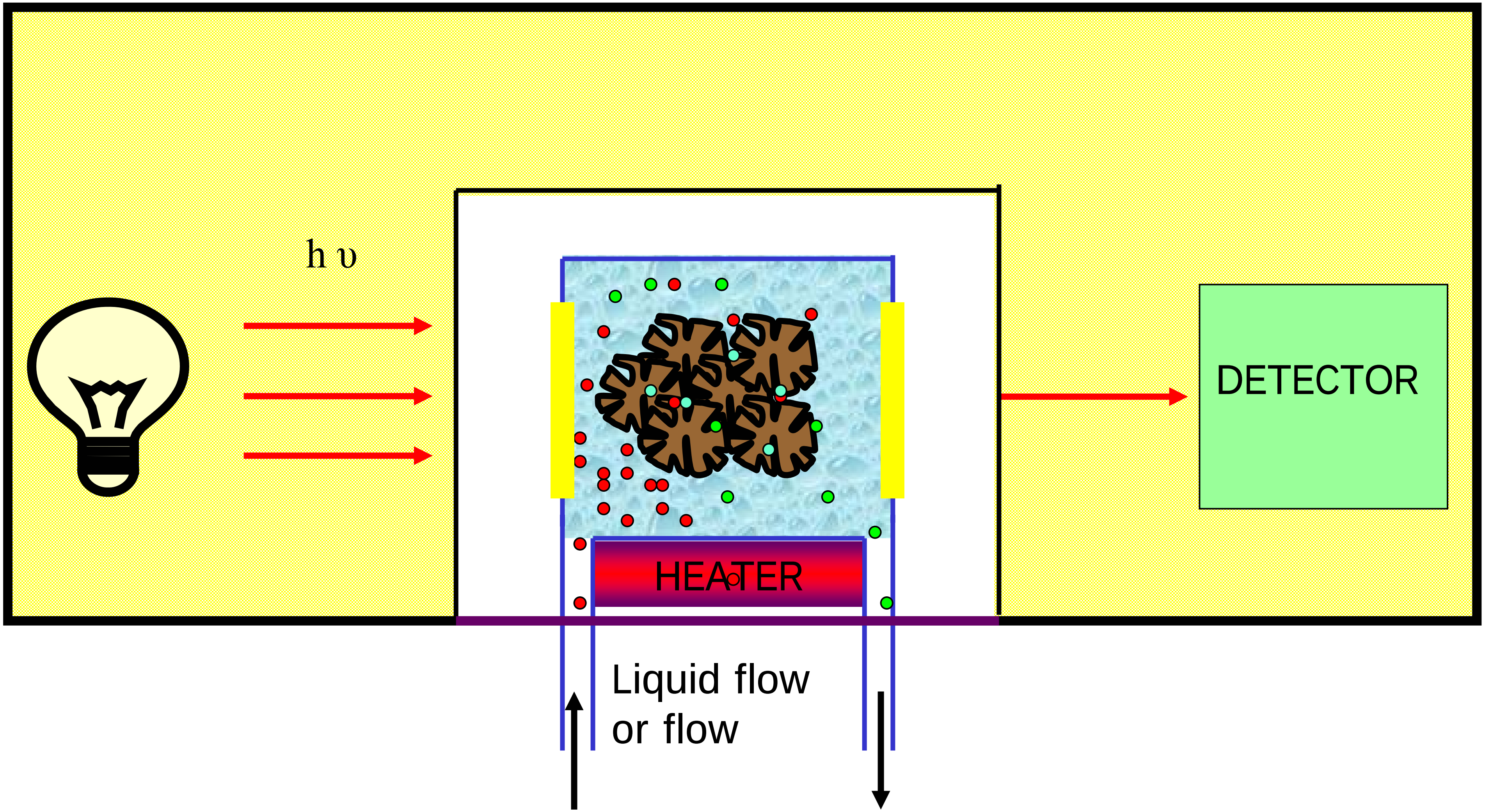
- Absorbing gases: depends on partial pressure and length of beam path in gas phase
- Absorbing gases, static conditions: can often be corrected

Spectroscopy of Solid in Controlled Gas Atmosphere



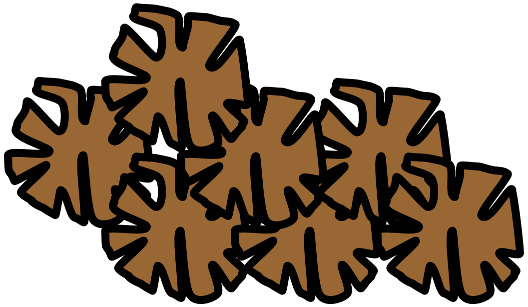
- Absorbing gases, dynamic conditions (catalysis): often problem

Spectroscopy of Solid and Liquid Surrounding



- Absorbing liquids, dynamic conditions: very difficult!

Possible Transitions



Heterogeneous Catalysts = Solids

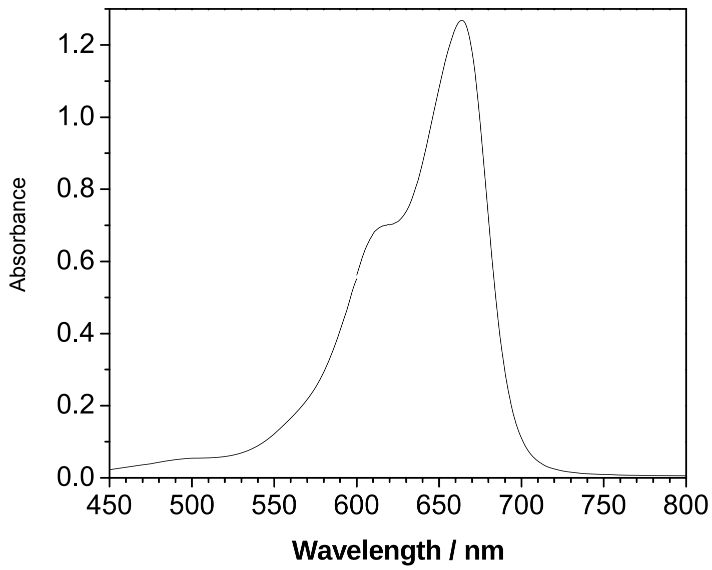
- Inorganic materials: salts, oxides, carbon, metals...
- Resins (functionalized polymers)

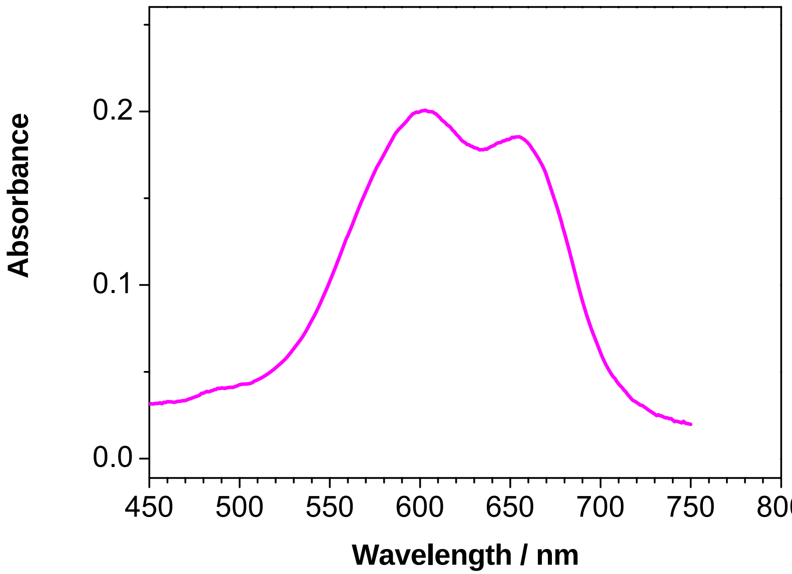
Characterization	Vibrations	Electronic transitions
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
Catalyst surface	Stretching and deformation vibrations of functional groups, vibrations of supported species: metal complexes	Charge transfer and d-d transitions of metal complexes, metal particles
Adsorbates	Functional groups	Must have chromophores

Spectral Interpretation - Analoga

Catalyst	Reference compounds in Organic and Inorganic Chemistry
Catalyst surface functional groups (-OH, -COOH, -SO_3H, -NH_2) Supported metal complexes	Functional group fingerprints Metal complexes in solution
Adsorbed inorganic or organic molecules	Gas or liquid phase spectra of free molecules

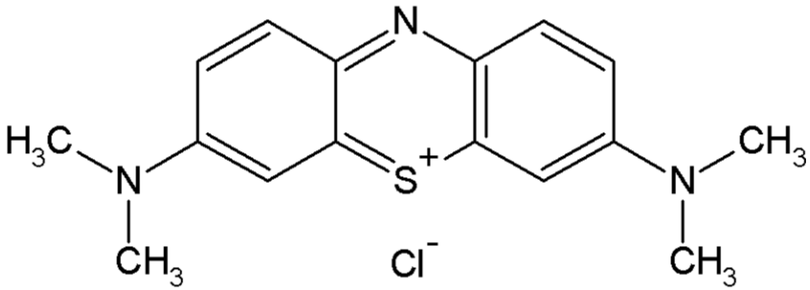
Example



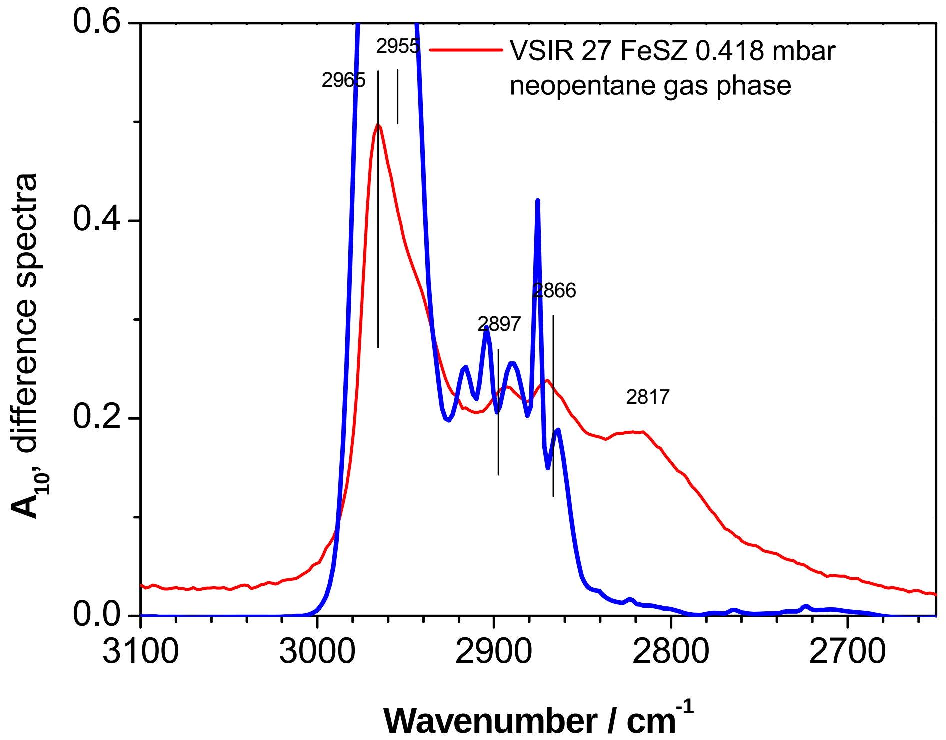


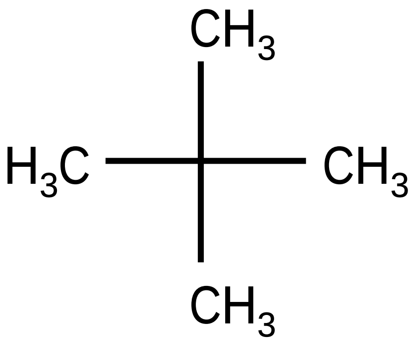
Methylene blue in aqueous solution

Methylene blue adsorbed on TiO_2



Example



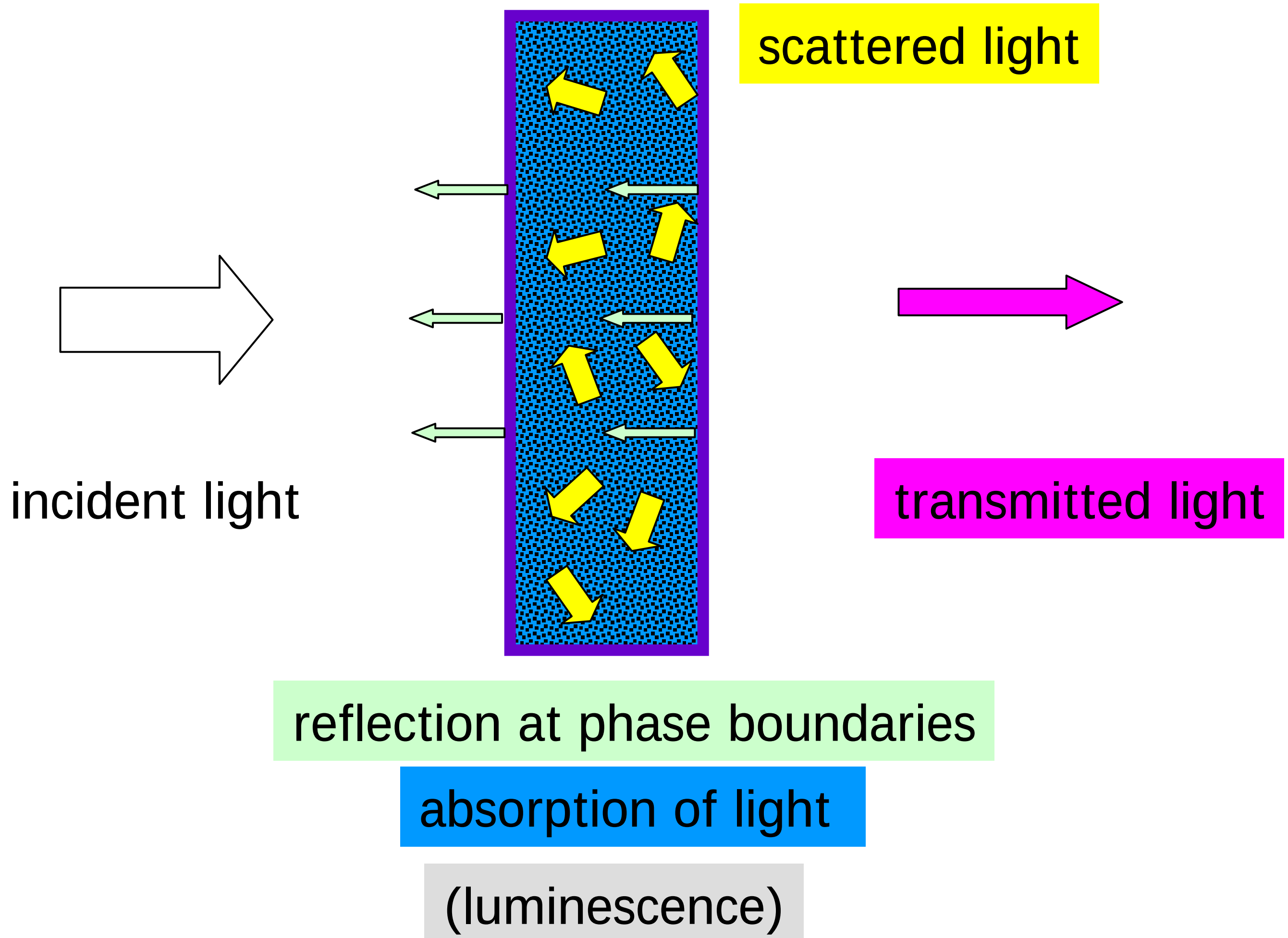


2,2-Dimethylpropan
(Neopentan)

Spectroscopy with Powder Samples

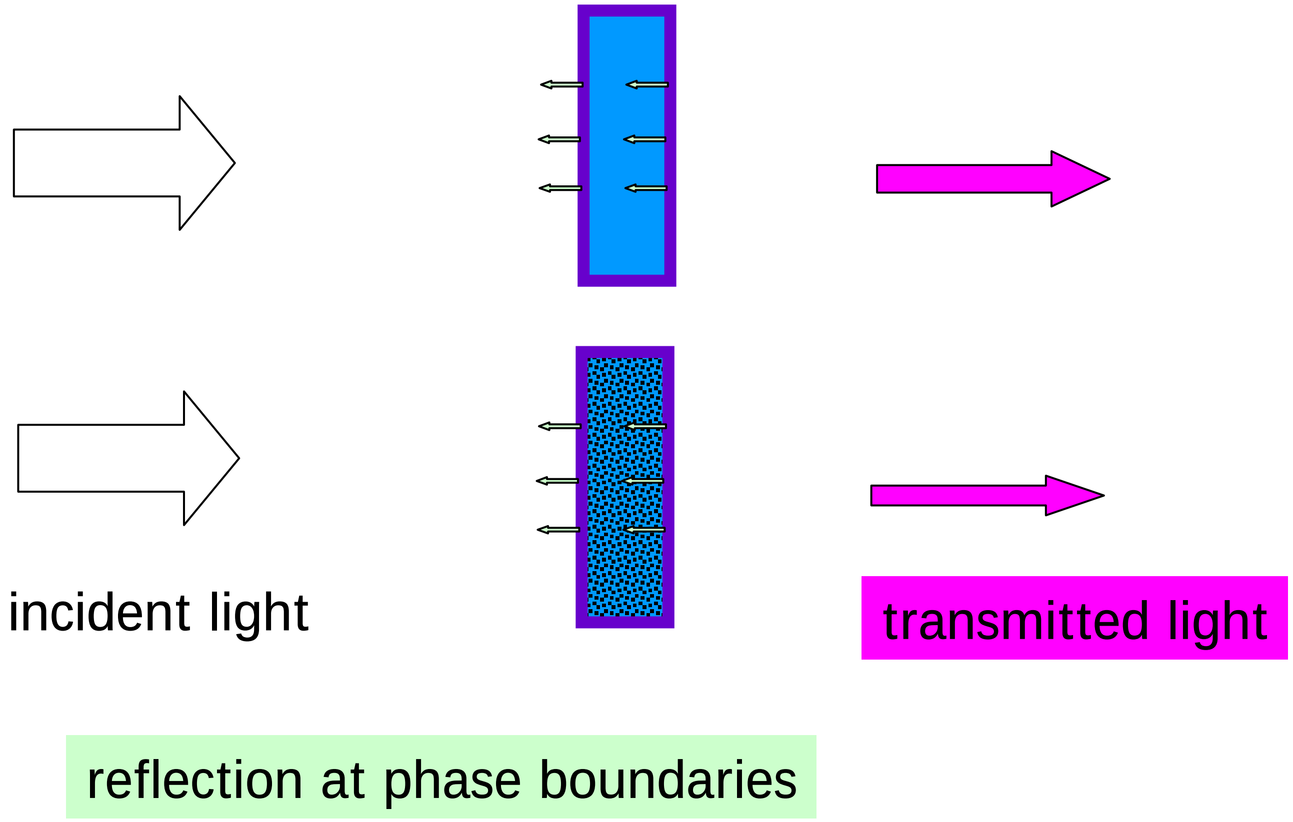
- how to measure spectra of a powderous solid?
- absorption as a function of wavelength, qualitatively and quantitatively

Interaction of Light with Sample



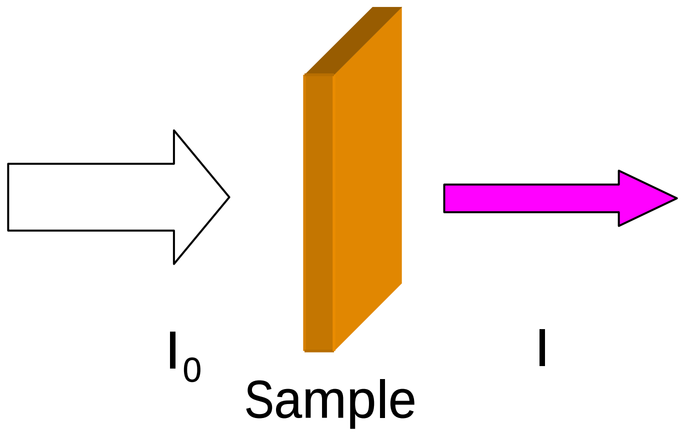
- how to extract absorption properties from transmitted light?
- how to deal with reflection and scattering?

How to Deal with Reflection (1)



- fraction of reflected light can be eliminated through reference measurement with same materials (cuvette+ solvent)

Transmittance



$$\tau = \frac{I}{I_0}$$

if luminescence and scattering are negligible:

$1 = \alpha + \tau + \rho$

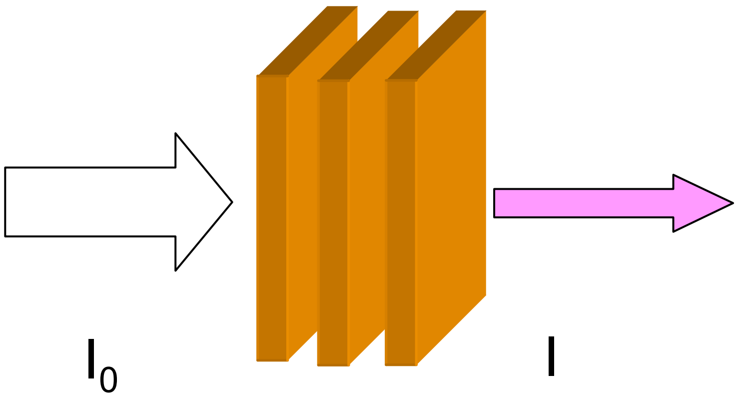
α	absorptance, absorption factor, *Absorptionsgrad*
τ(T)	transmittance, transmission factor, *Transmissionsgrad*
ρ	reflectance, reflection factor, *Reflexionsgrad*

if we manage to eliminate reflection:

$1 = \alpha + \tau$

in this case, the absorption properties of the sample can be calculated from the transmitted light

Transmitted Light and Sample Absorption Properties



$$\tau = \frac{I}{I_0}$$

$$dI = -I\,k\,dl = -I\,\kappa\,c\,dl$$

decrease of I in an infinitesimally thin layer

c: molar concentration of absorbing species [mol/m^{-3}]
κ: the molar napierian extinction coefficient [m^2/mol]

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{0}^{l} \kappa\,c\,dl$$

separation of variables and integration

sample thickness: l

$$\ln\frac{I}{I_0} = -\kappa\,c\,l$$

Transmitted Light and Sample Absorption Properties

$$\tau = \frac{I}{I_0} = e^{-\kappa c l} = 1 - \alpha$$

Lambert-Beer Law

$$A_e = B = \kappa c l = -\ln(\tau)$$

napierian absorbance
Napier-Absorbanz

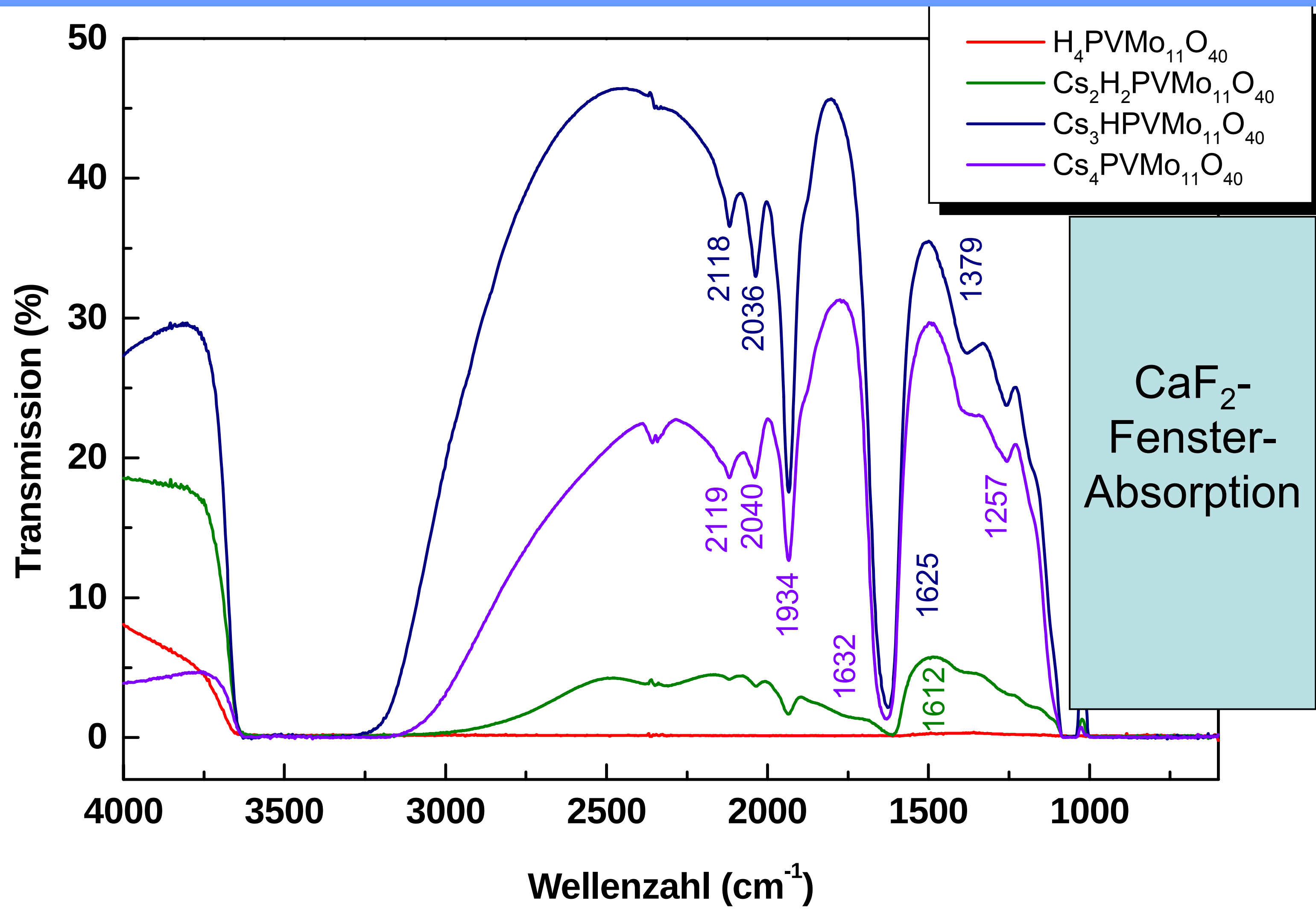
$$A_{10} = \varepsilon c l = -\log(\tau)$$

(decadic) absorbance
dekadische Absorbanz
standard spectroscopy software uses A_{10}!

extinction	E (means absorbed + scattered light)
absorbance	A (A_{10} or A_e)
optical density	O.D.

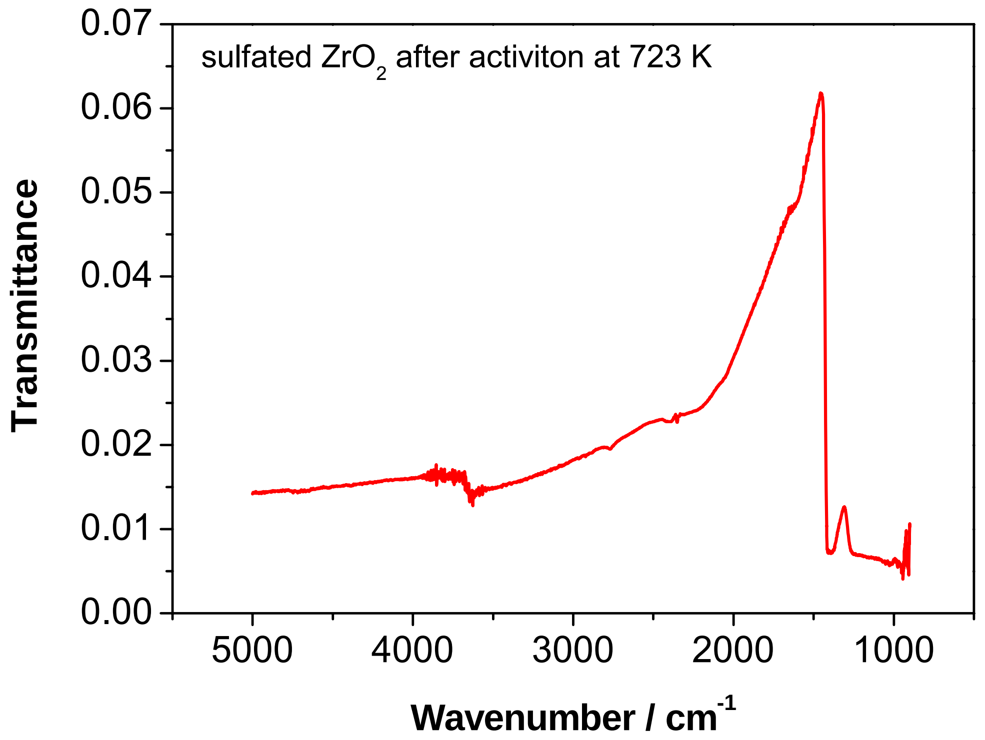
all these quantities are DIMENSIONLESS !!!!

Self-Supporting Wafers



- Catalysts may absorb strongly!

Limitations of Transmission Spectroscopy



- Catalysts are fine powders (high surface area) and may scatter strongly

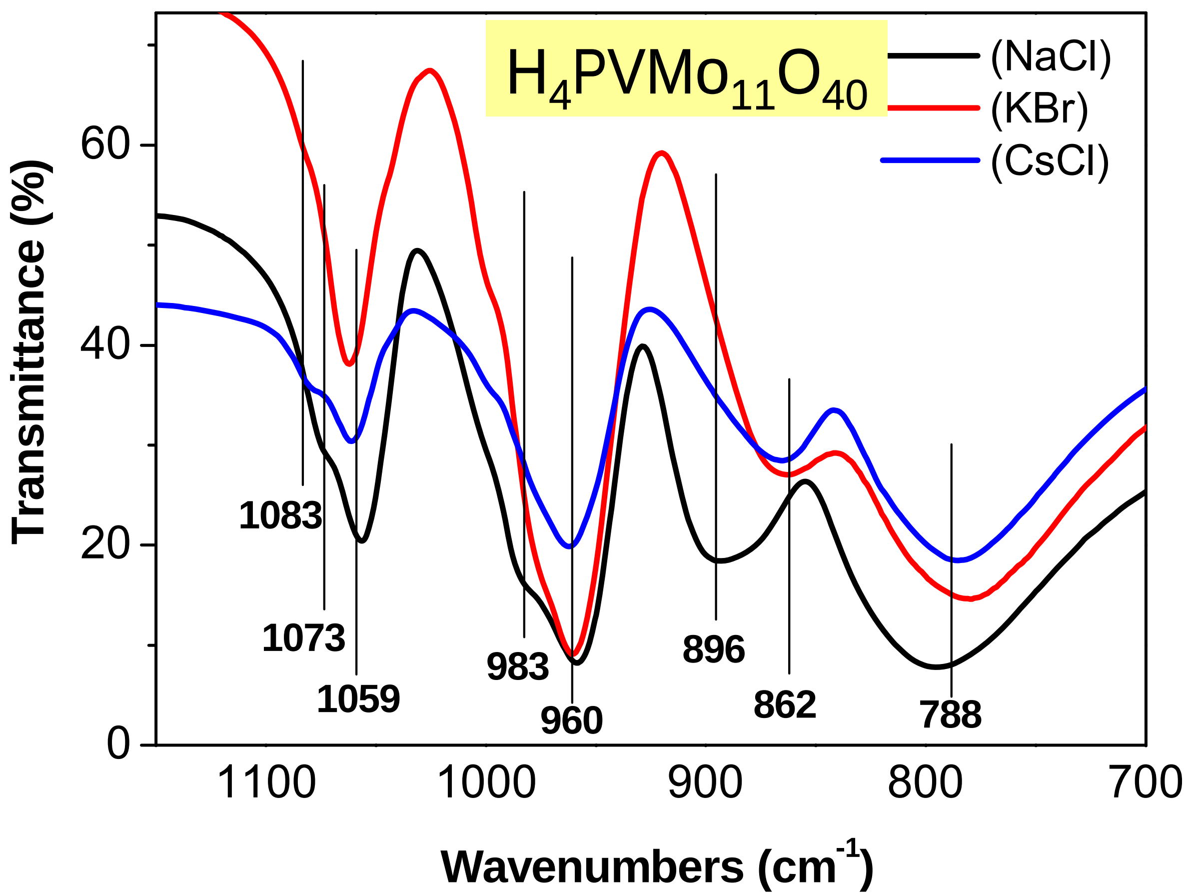
Scattering

- scattering is negligible in molecular disperse media (solutions)
- scattering is considerable for colloids and solids when the wavelength is in the order of magnitude of the particle size

	Wavenumber	Wavelength
Mid-IR (MIR)	3300 to 250 cm^{-1}	3 to (25-40) µm
Near-IR (NIR)	12500 to 3300 cm^{-1}	(700-1000) to 3000 nm
UV-vis	50000 to 12500 cm^{-1}	200 to 800 nm

- scattering is reduced through embedding of the particles in media with similar refractive index: KBr wafer (clear!) technique, immersion in Nujol

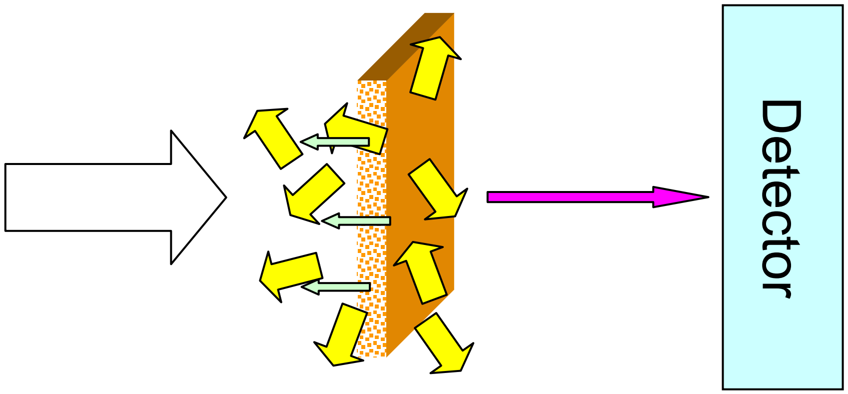
But…….Reaction with Material Used for Embedding



- reaction with diluent possible
- dilution usually not suitable for experiments at high T/ with reactive gases

Can We Use the Reflected Light?

- instead of measuring the transmitted light, we could measure the reflected light
- can we extract the absorption properties of our sample from the reflected light?



Reflection of Radiation

mirror-type (polished) surfaces

Specular

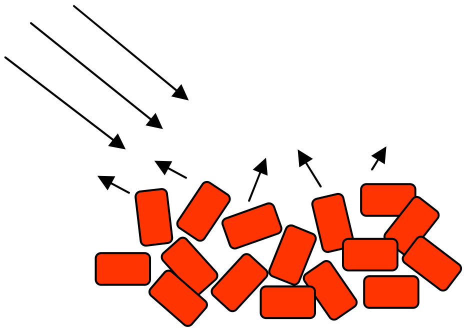
mirror-type reflection
mirror reflection
surface reflection

mat (dull, scattering) surfaces

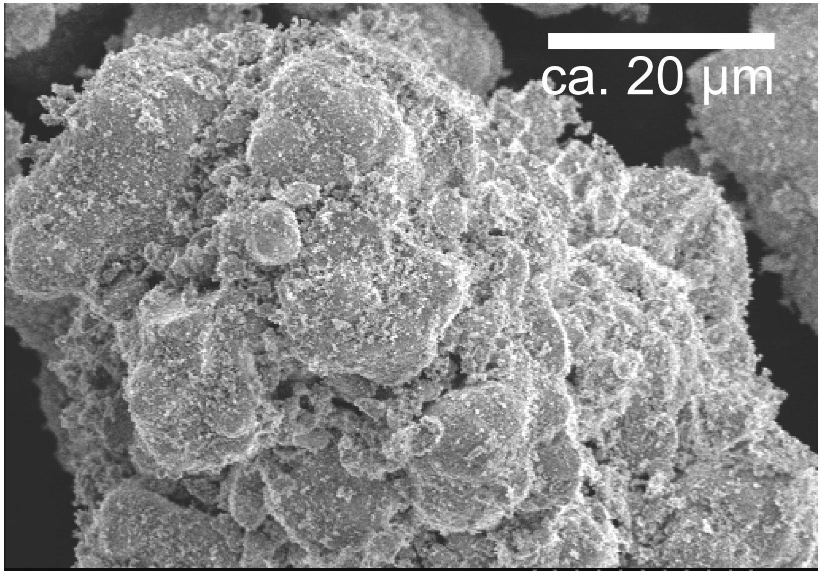
Diffuse

equally intense in all directions (isotropic)

Diffuse Reflection



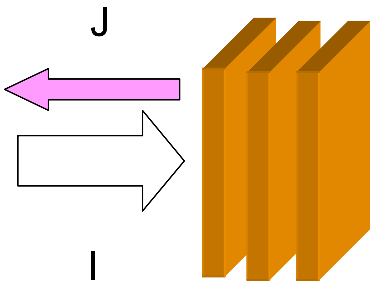
- intensity of diffusely reflected light independent of angle of incidence (isotropic)
- due to multiple reflection, refraction, and diffraction (scattering) inside the sample



scanning electron microscopy image

- need theory that treats light transfer in an absorbing and scattering medium
- want to extract absorption properties!

A Simplified Derivation of the Schuster-Kubelka-Munk (or Remission) Function



$$R = \frac{J}{I}$$

$$dI = -I\ K\ dl - I\ S\ dl + J\ S\ dl$$

$$dJ = -J\ K\ dl - J\ S\ dl + I\ S\ dl$$

with K, S: absorption and scattering coefficient [cm^{-1}]

Divide equations by I or J, respectively, separate variables, introduce R=J/I

$$\int_{R_0}^{R\infty} \frac{2dR}{R^2 - 2R(1+\frac{K}{S}) + 1} = S\int_0^l dl$$

Integrate via partial-fraction expansion

A Simplified Derivation of the SKM Function

assume black background, so that $R_0 = 0$
make sample infinitely thick, i.e. no transmitted light (typical sample thickness in experiment ca. 3 mm)

$$R_\infty = \frac{S}{K + S + \sqrt{K(K+2S)}}$$

2 constants are needed to describe the reflectance:
absorption coefficient K
scattering coefficient S

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S}$$

Kubelka-Munk function
remission function

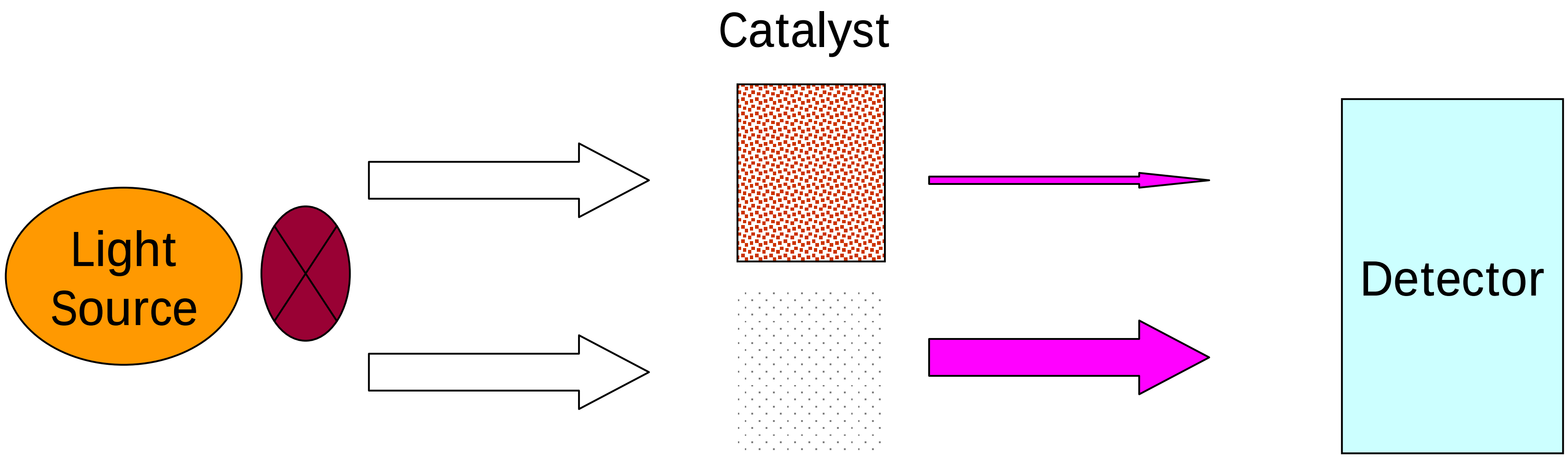
for $K \rightarrow 0$ (no absorption) $R_\infty \rightarrow 1$, i.e. all light reflected
for $S \rightarrow 0$ (no scattering) $R_\infty \rightarrow 0$, i.e. all light transmitted or absorbed

Kubelka-Munk Function

- mostly we measure R'_∞, i.e. not the absolute reflectance R_∞ but the reflectance relative to a standard
- depends on wavelength $F(R'_\infty)_\lambda$
- corresponds to extinction in transmission spectroscopy
- in case of a dilute species is proportional to the concentration of the species (similar to the Lambert-Beer law):

$$F(R'_\infty) \propto \frac{\varepsilon\, c}{s}$$

Spectroscopy in Transmission

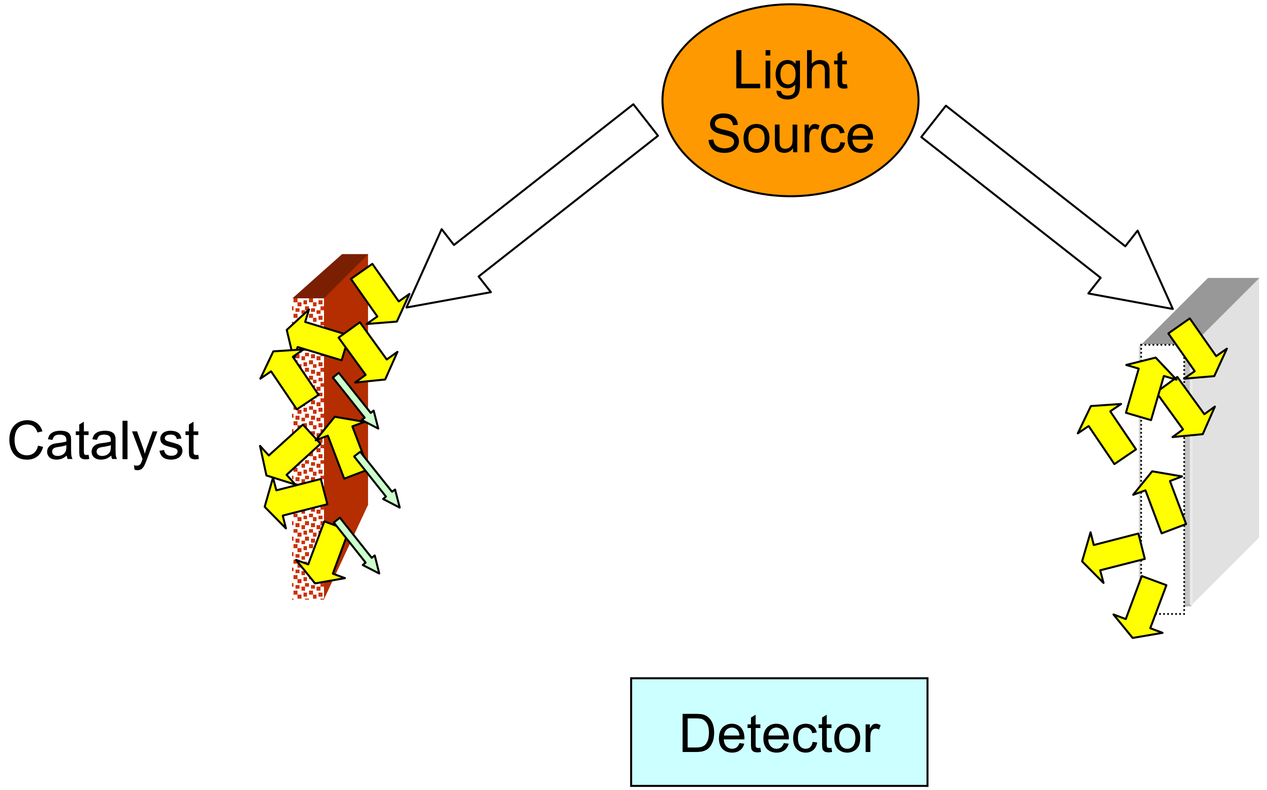


reference „nothing“
= void, empty cell, cuvette
with solvent

spectrum:
transmission of
catalyst vs.
transmission of
reference

- in IR transmission is widely applied for solids
- in UV-vis transmission is rarely used for solids (zeolites!)

Diffuse Reflectance Spectroscopy

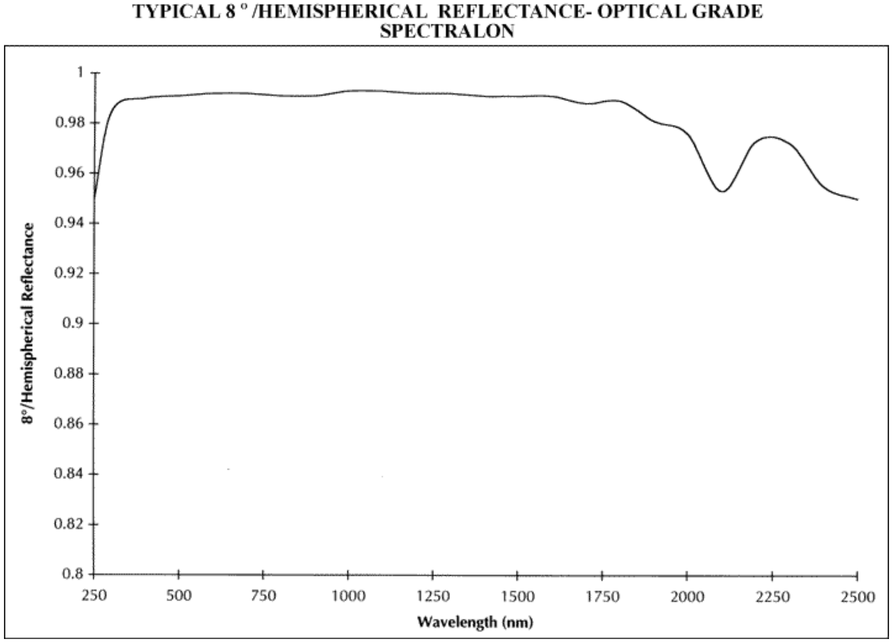


spectrum: reflectance of sample (catalyst) vs. reflectance of standard

- need element that collects diffusely reflected light
- need to avoid specularly reflected light
- need reference standard (white standard)

White Standards

- KBr: IR (43500-400 cm^{-1})
- $BaSO_4$: UV-vis
- MgO: UV-vis
- Spectralon: UV-vis-NIR



Spectralon® thermoplastic resin, excellent reflectance in UV-vis region

Methods and Collecting Elements

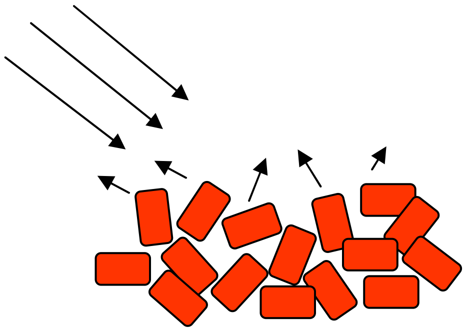
Methods

- diffuse reflectance UV-vis spectroscopy (DR-UV-vis spectroscopy or DRS)
- diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS)

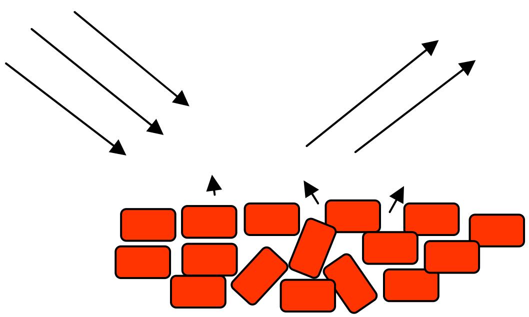
Collecting Elements

- integrating spheres (IR and UV-vis-NIR)
- fiber optics (UV-vis-NIR)
- mirror optics (IR and UV-vis-NIR)

Diffuse Reflection & Macroscopic Surface Properties

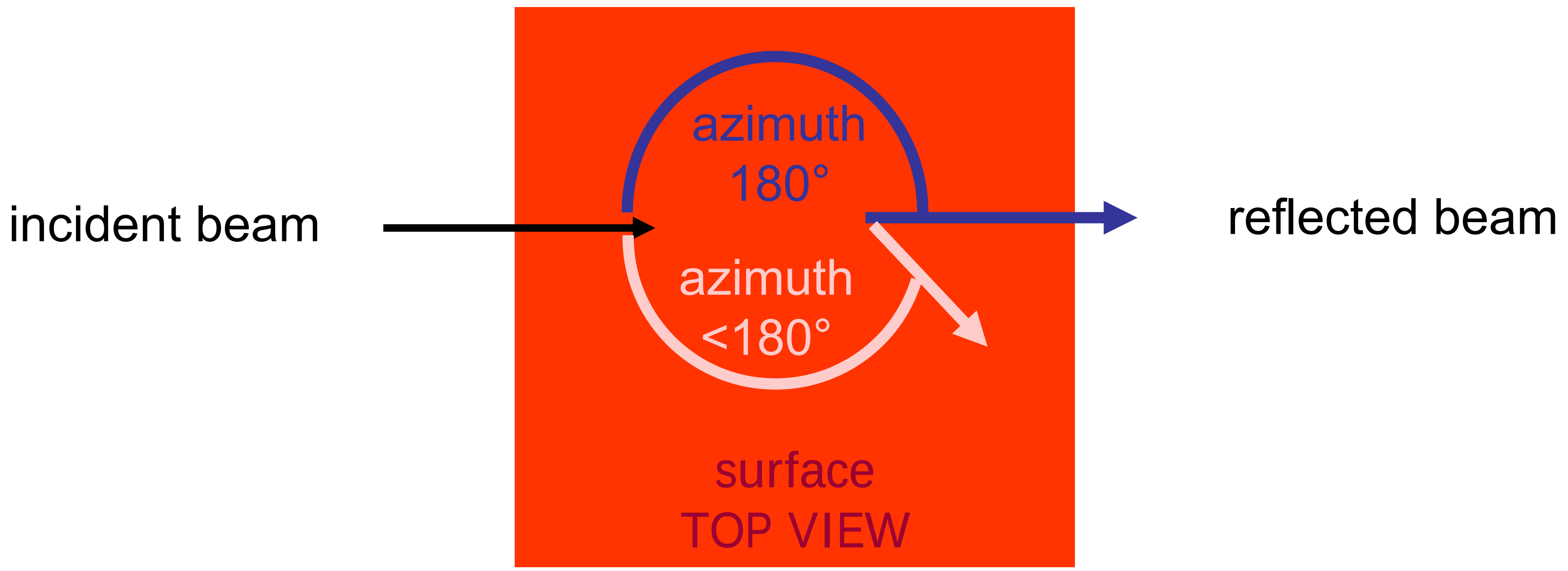


- randomly oriented crystals in a powder: light diffusely reflected



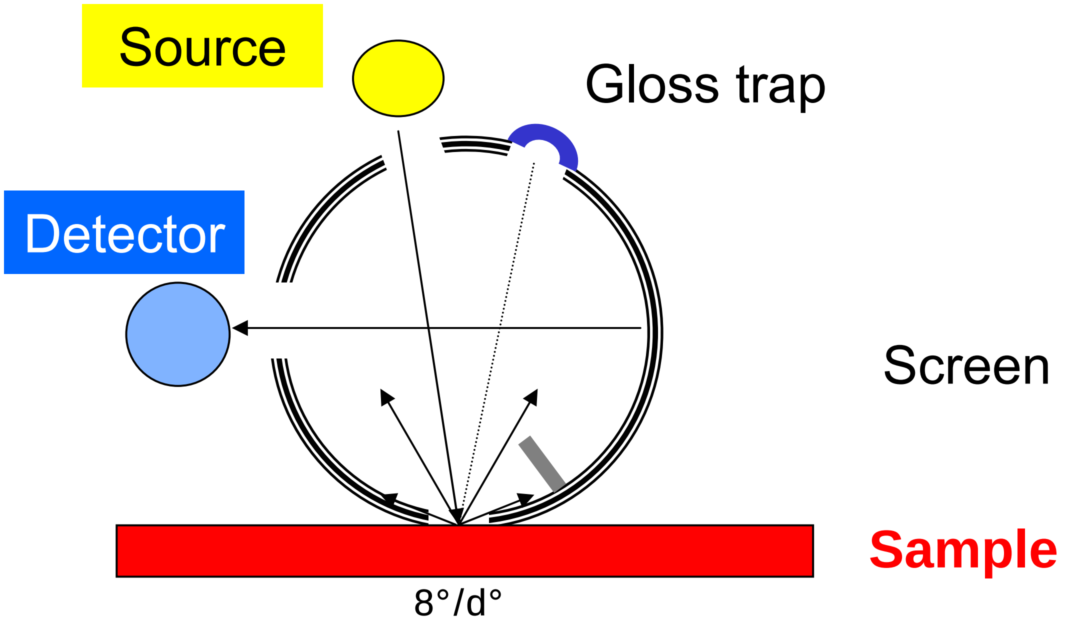
- flattening of the surface or pressing of a pellet can cause orientation of the crystals, which are “elementary mirrors”
- causes “glossy peaks” if angle of observation corresponds to angle of incidence
- solution: roughen surface with (sand)paper or press between rough paper, or use different observation angle!

Specular Reflection: Angular Distribution



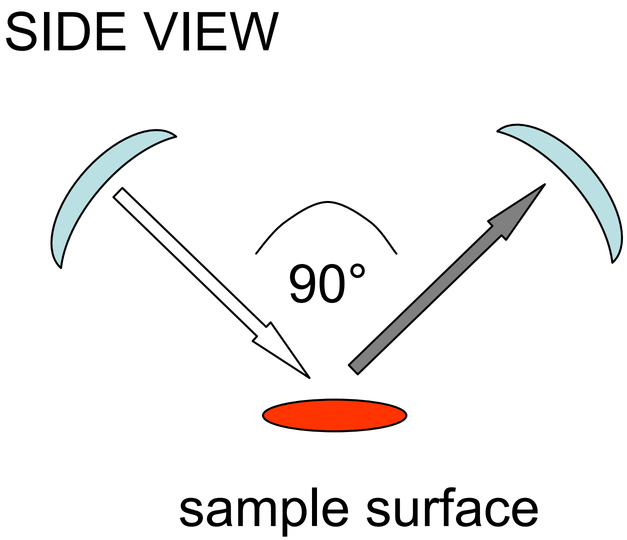
- the intensity of the specularly reflected light is largest at an azimuth of 180°

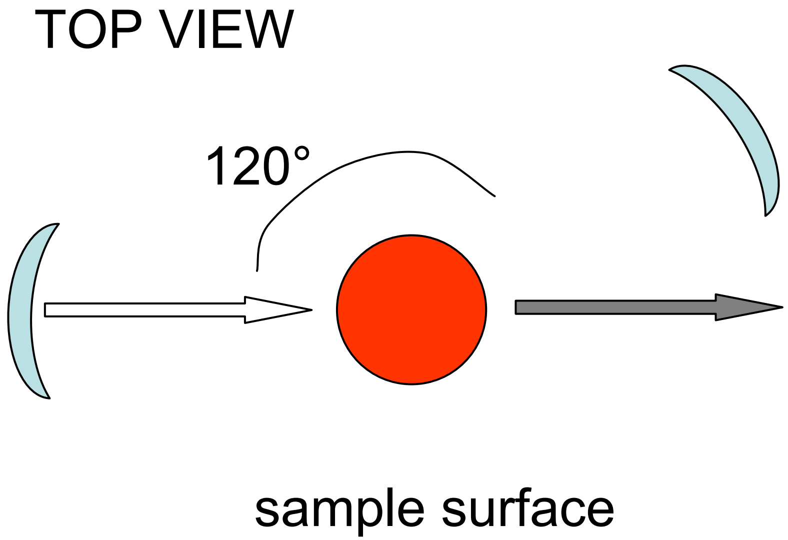
Integrating Sphere



- the larger the sphere the smaller errors from the ports
- the larger the sphere the lower the intensity onto the detector
- typically 60-150 mm diameter
- coatings: $BaSO_4$, Spectralon (for UV-vis)

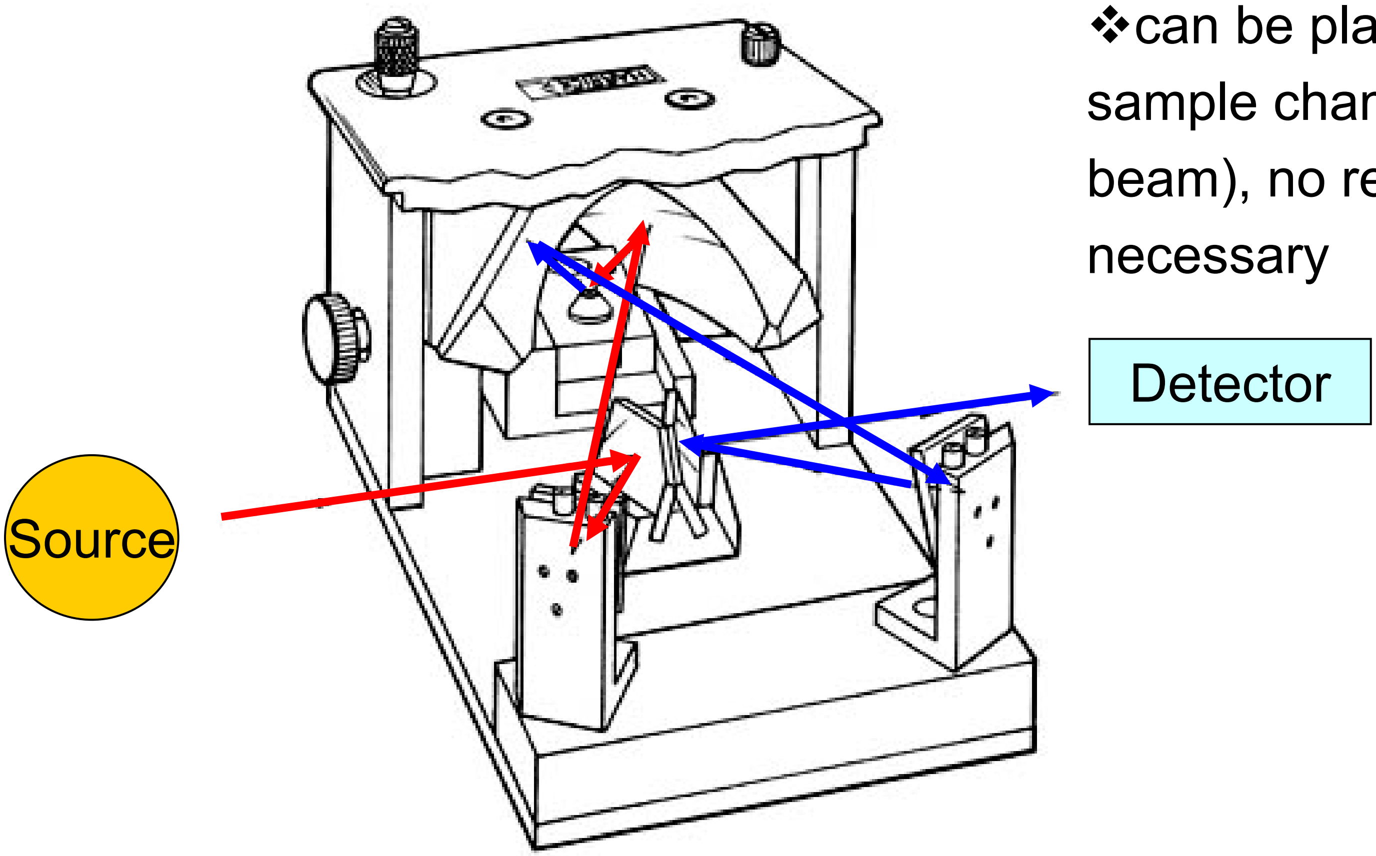
How to Avoid Specular Reflection





- specular reflection is strongest in forward direction
- collect light in off-axis configuration

Praying Mantis Optical Accessory (Harrick)

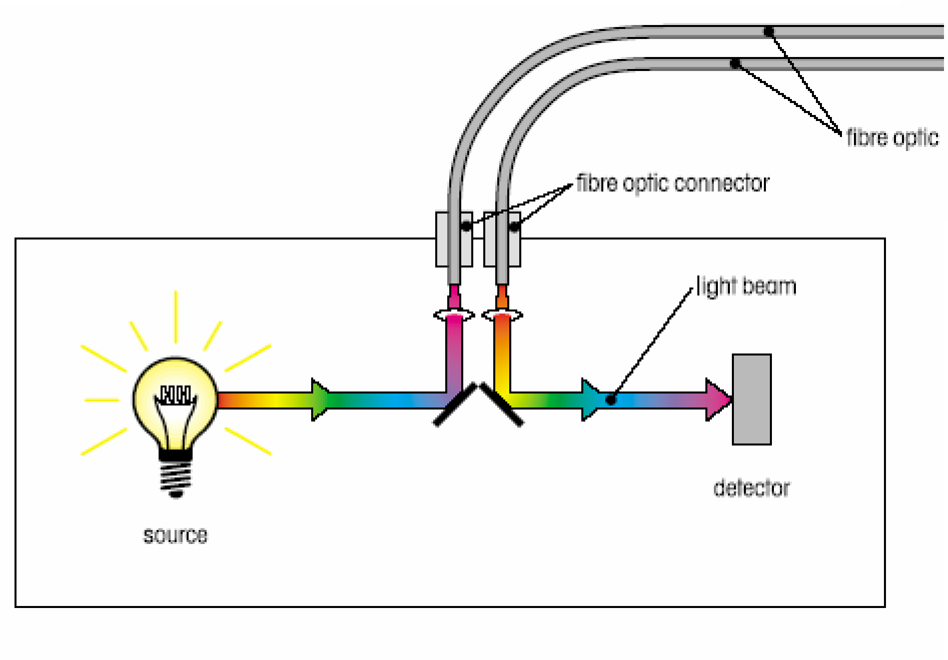


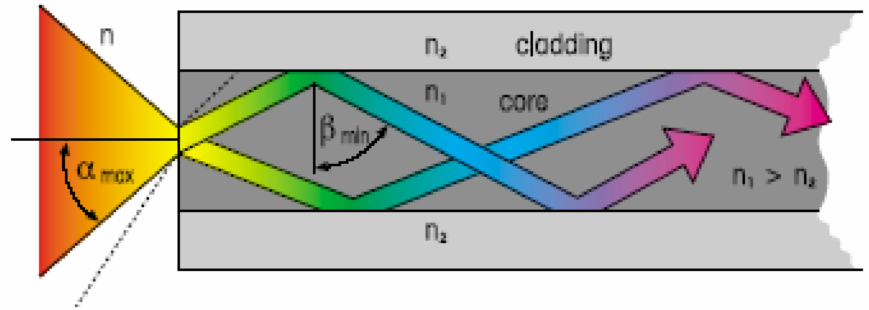
❖can be placed into the normal sample chamber (in line with beam), no rearrangement necessary

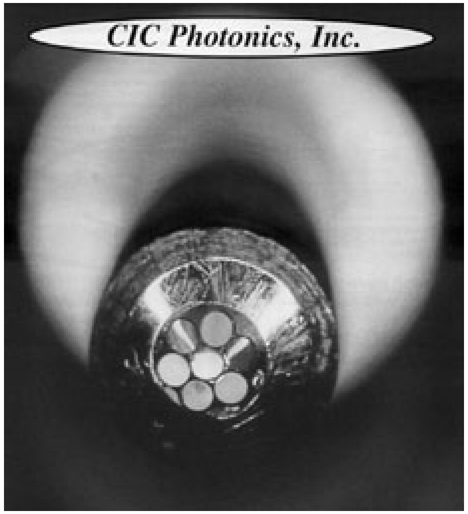
- first ellipsoidal mirror focuses beam on sample
- second ellipsoidal mirror collects reflected light
- 20% of the diffusely reflected light is collected

http://www.harricksci.com/

Fiber Optics for UV-vis



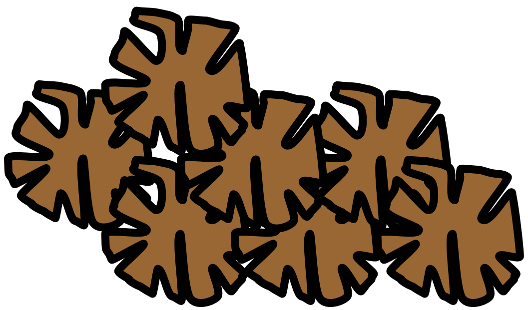




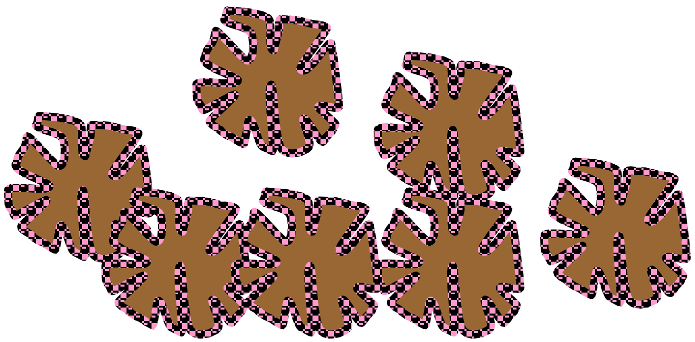
- light conducted through total reflectance
- fiber bundle with 6 around 1 configuration: illumination through 6 (45°), signal through 1
- avoids collection of specularly reflected light

Bilder: Hellma (http://www.hellma-worldwide.de) and CICP (http://www.cicp.com/home.html)

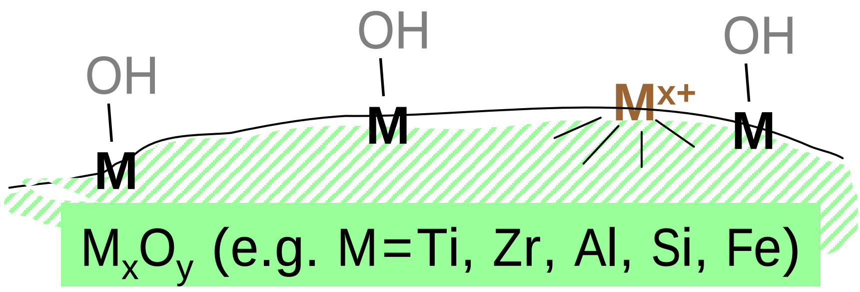
Catalyst Bulk & Catalyst Surface

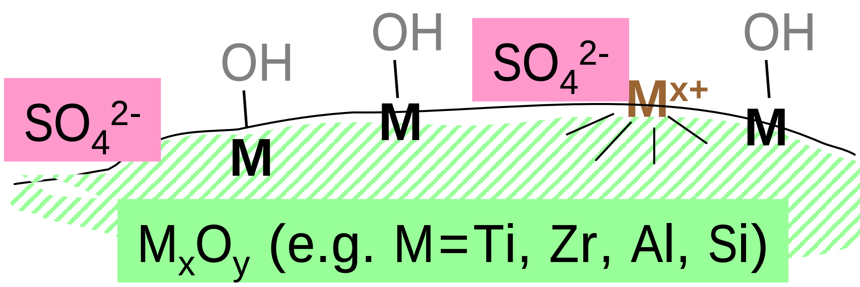


Support with functional groups

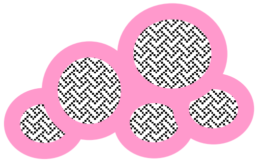


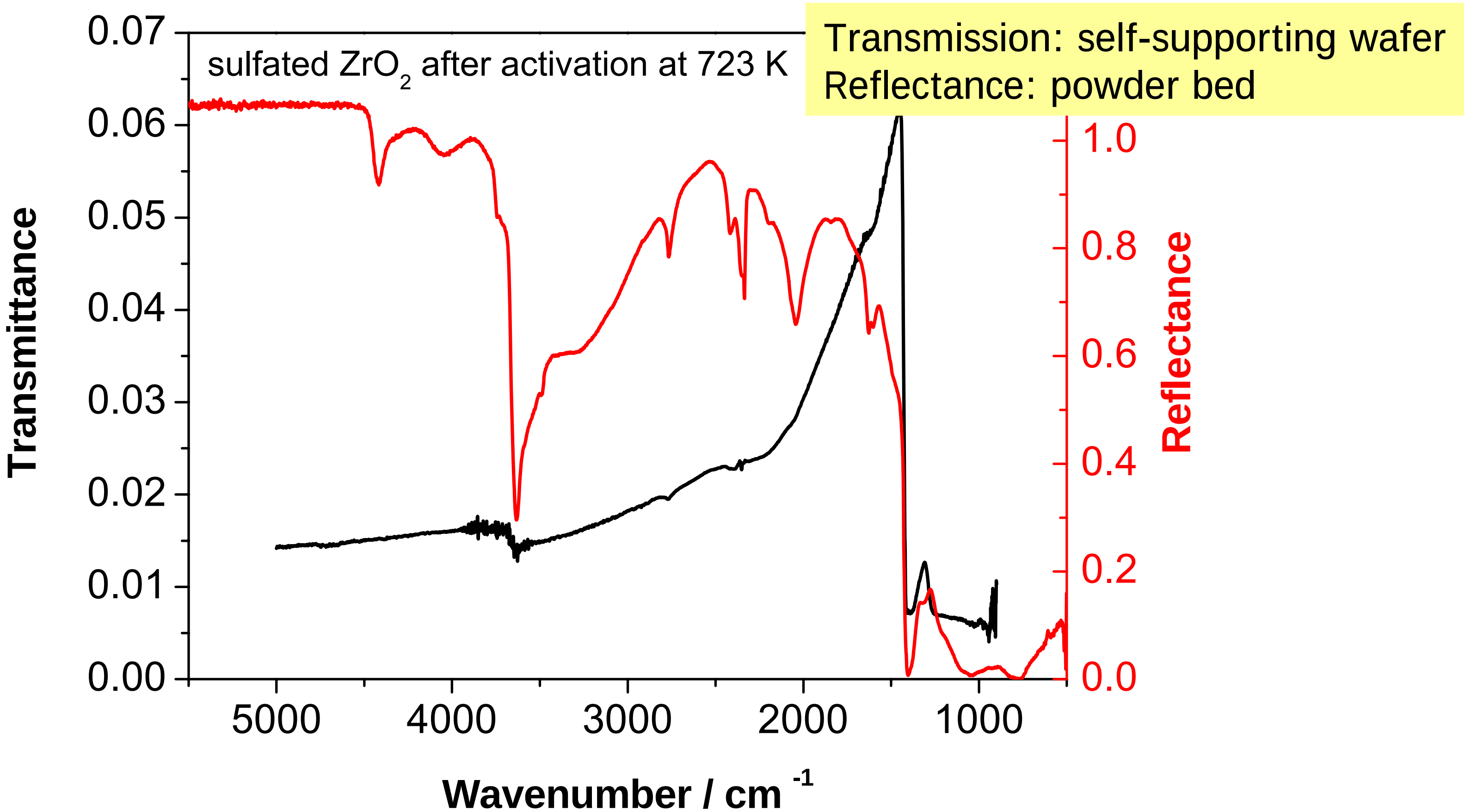
Support + dispersed species





Comparison
Transmission - Diffuse Reflectance (IR)

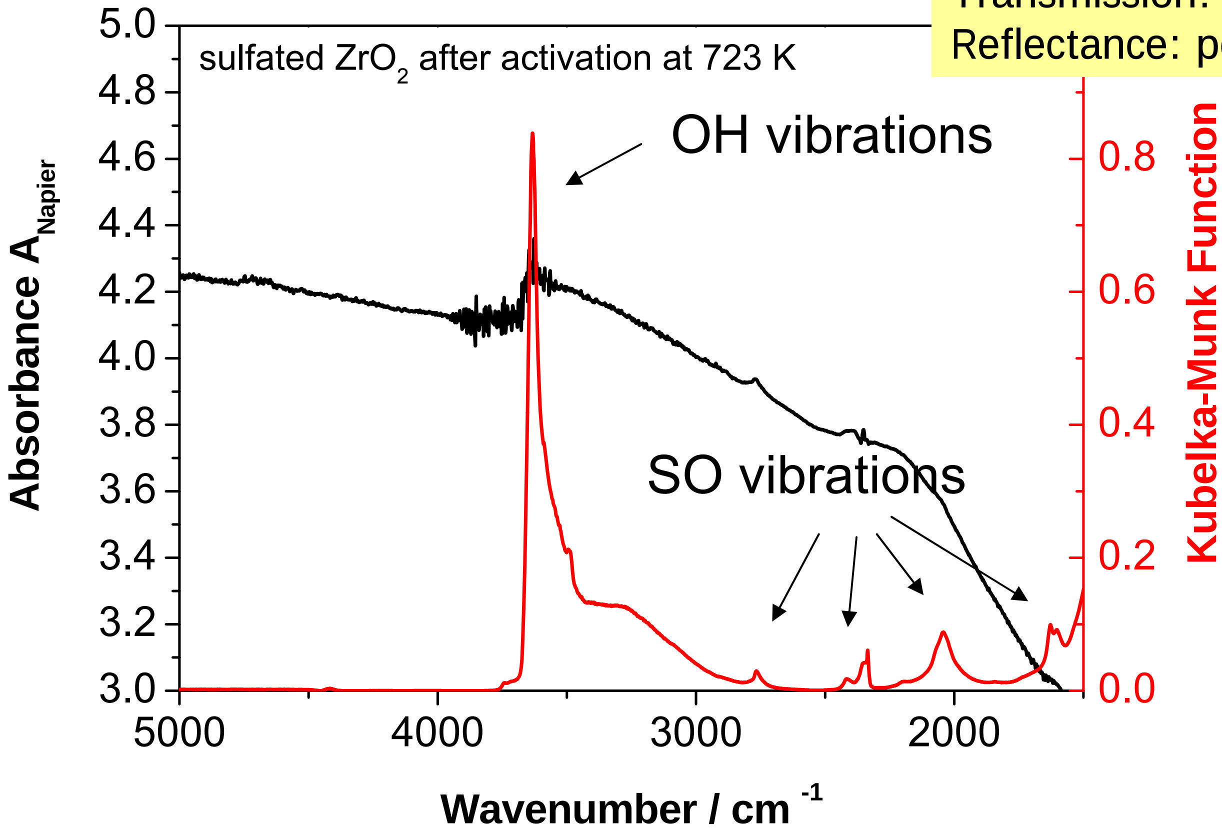




- spectra can have completely different appearance
- transmission decreases, reflectance increases with increasing wavenumber

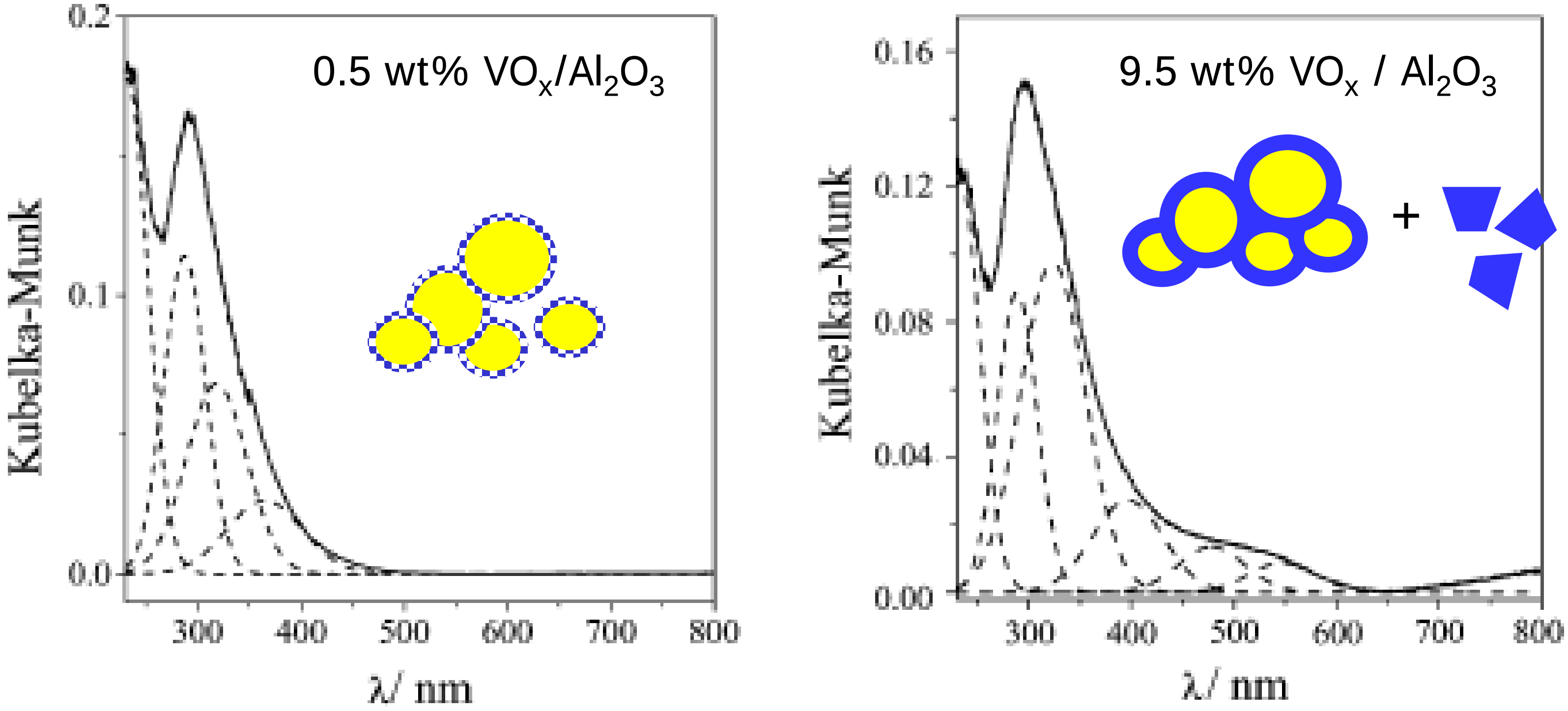
Comparison
Transmission - Diffuse Reflectance

Transmission: self-supporting wafer
Reflectance: powder bed



- vibrations of surface species may be more evident in DR spectra

Dispersed V_xO_y Species (DR-UV-vis)



- CT bands at 359 and 376 nm: isolated octahedrally co-ordinated V^{5+} species
- CT bands at 468 and 535 nm: octahedraly co-ordinated V^{5+} species in V_2O_5 clusters (XRD shows crystalline form of V_2O_5)

Kondratenko and Baerns, Appl. Catal. 2001