Lecture Series

Heterogeneous Catalysis

Modern Methods in Heterogeneous Catalysis Research

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Diffuse Reflectance
IR and UV-vis Spectroscopy

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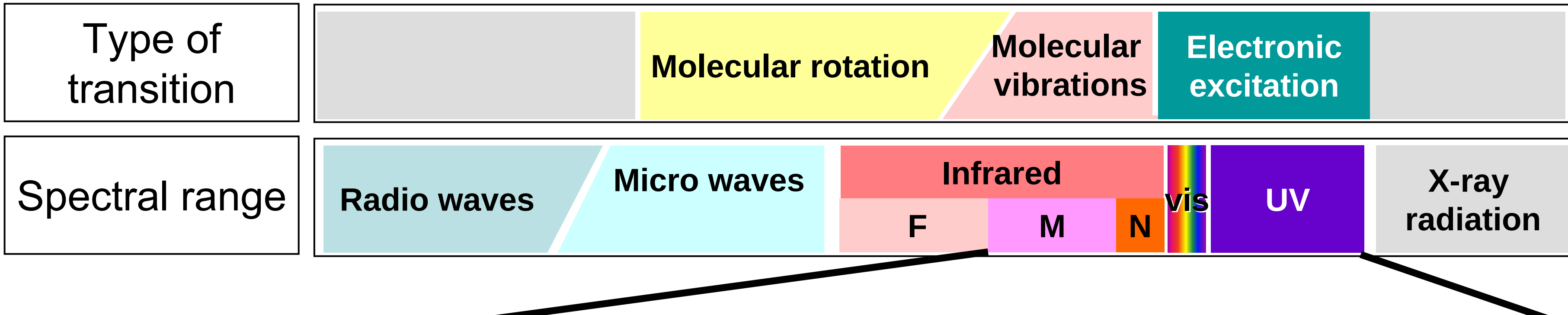
Outline

1. **Introduction & Challenges**
2. **Fundamentals of Transmission and Reflection Spectroscopy**
   - Lambert-Beer law
   - Scattering and reflection phenomena
   - Schuster-Kubelka-Munk theory
3. **Experimental**
   - Integrating spheres
   - Mirror optics
   - Fiber optics
4. **Applications**
   - Bulk structure
   - Surface species / functional groups
   - Probing surface sites
   - Reaction intermediates and products
   - Gas phase analysis

MIR - NIR – vis – UV



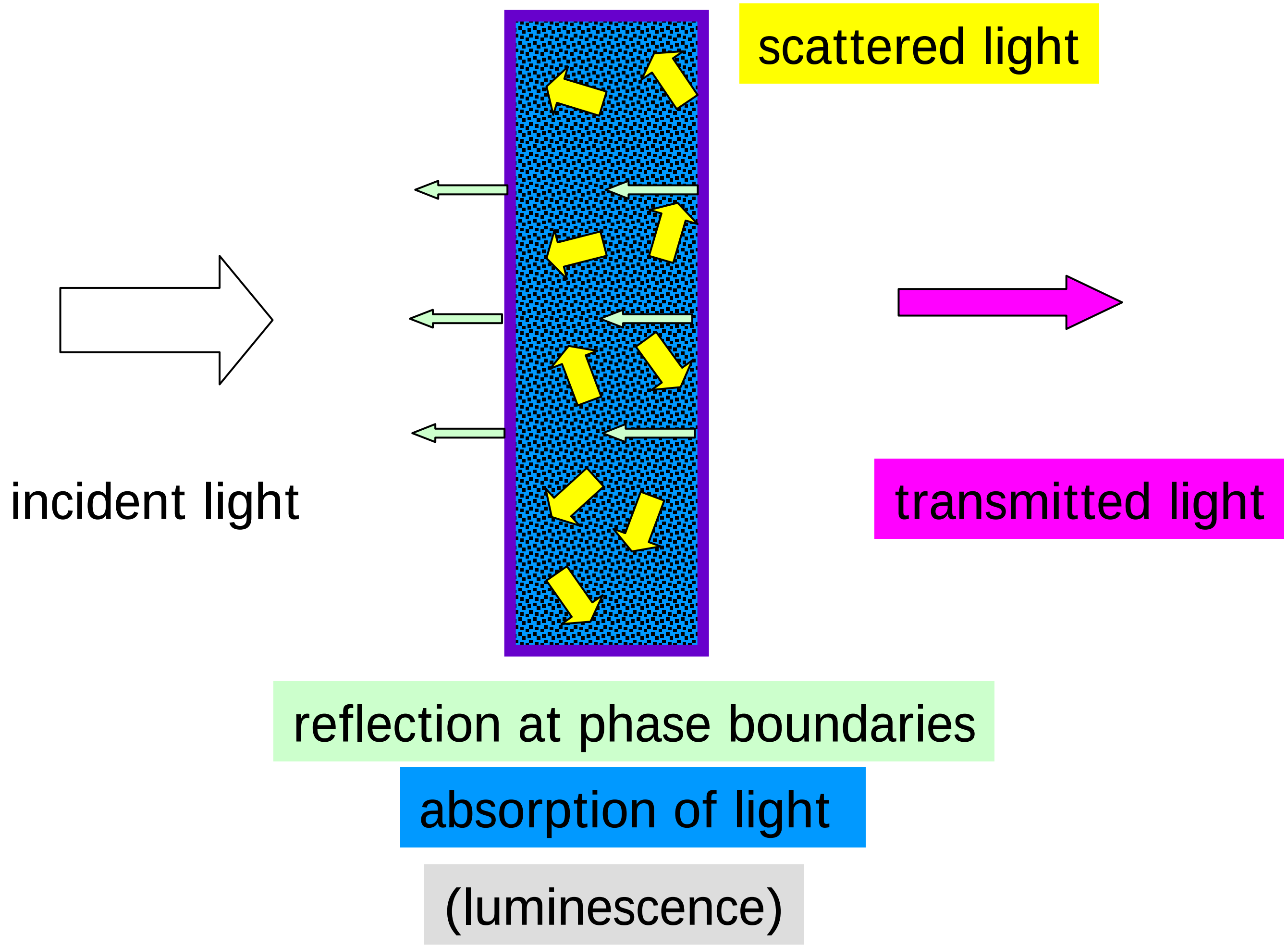
	Mid IR (MIR)	Near IR (NIR)	UV-vis
Wavenumber / cm^{-1}	3300 to 250	12500 to 3300	50000 to 12500
Wavelength / nm	3000 to (25000-40000)	(700-1000) to 3000	200 to 800
Energy / eV			6.2 to 1.5

- electronic transitions, vibrations (rotations)

Spectroscopy with Powder Samples

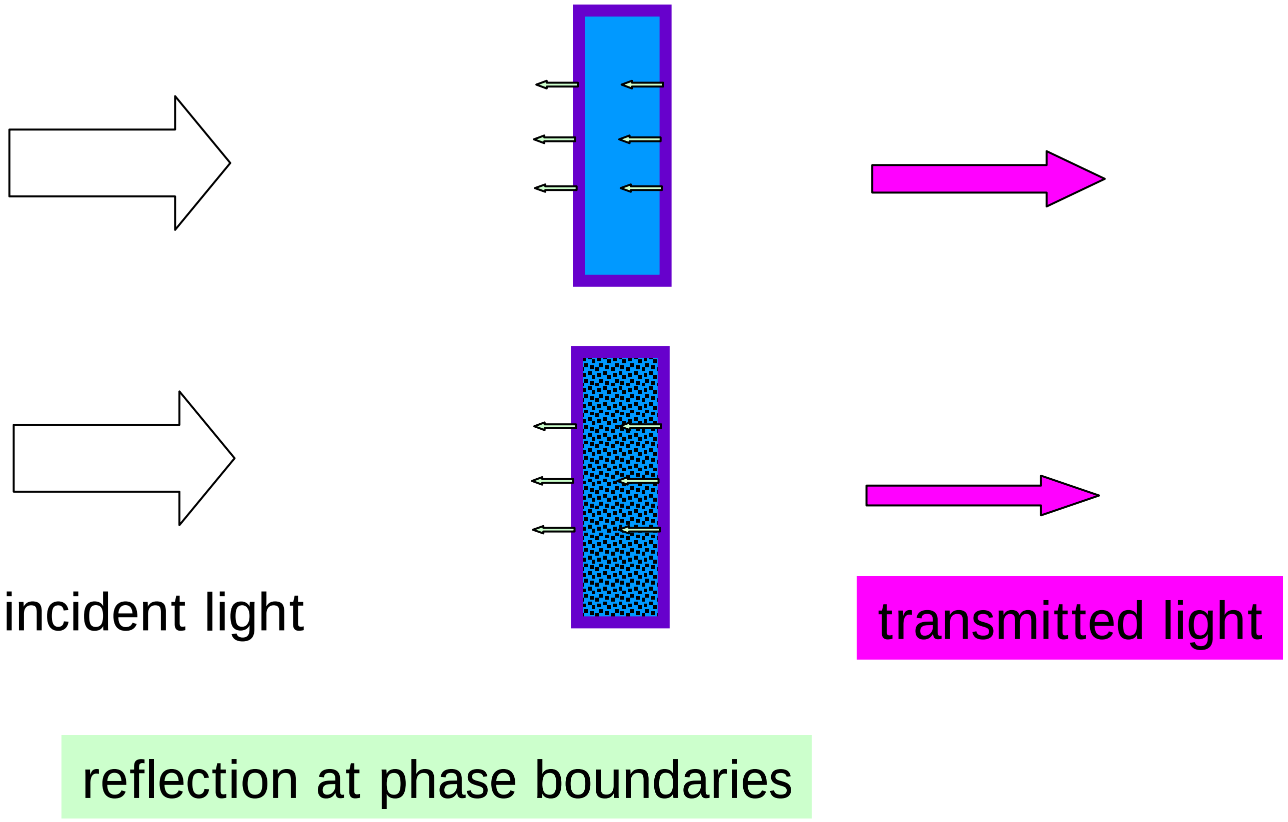
- How to measure spectra of a powderous solid?
- Absorption as a function of wavelength, qualitatively and quantitatively

Interaction of Light with Sample



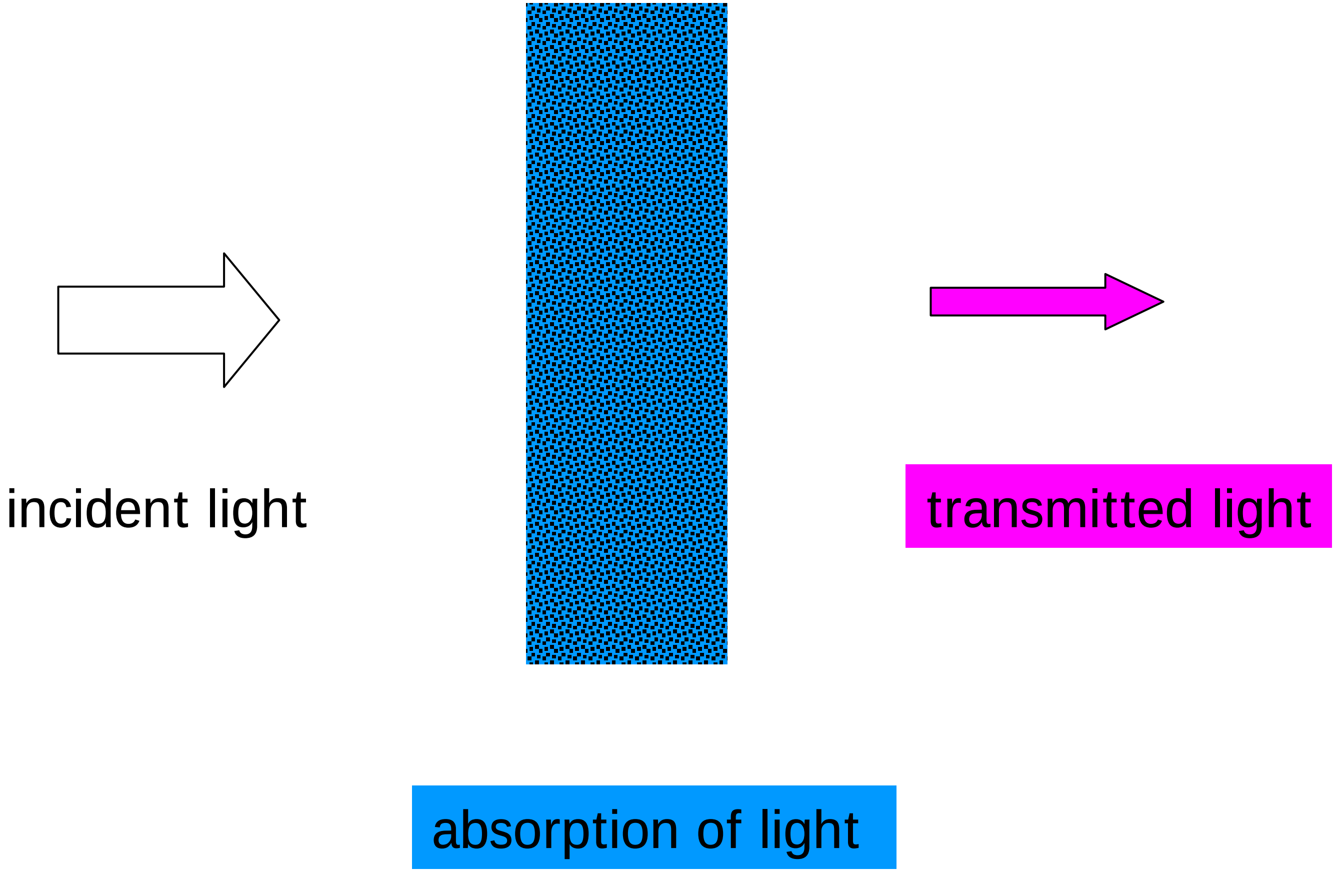
- how to extract absorption properties from transmitted light?
- how to deal with reflection and scattering?

How to Deal with Phase Boundary Reflection



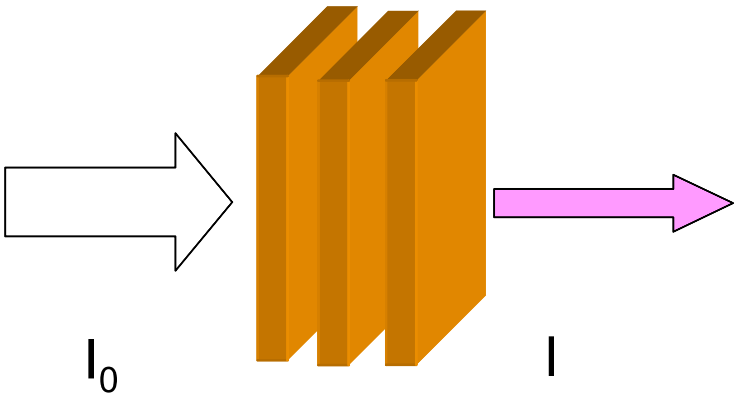
- fraction of reflected light can be eliminated through reference measurement with same materials (cuvette+ solvent)

Interaction of Light with Sample



➢ Absorption properties from transmitted light?

Transmitted Light and Sample Absorption Properties



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

τ: transmittance

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

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

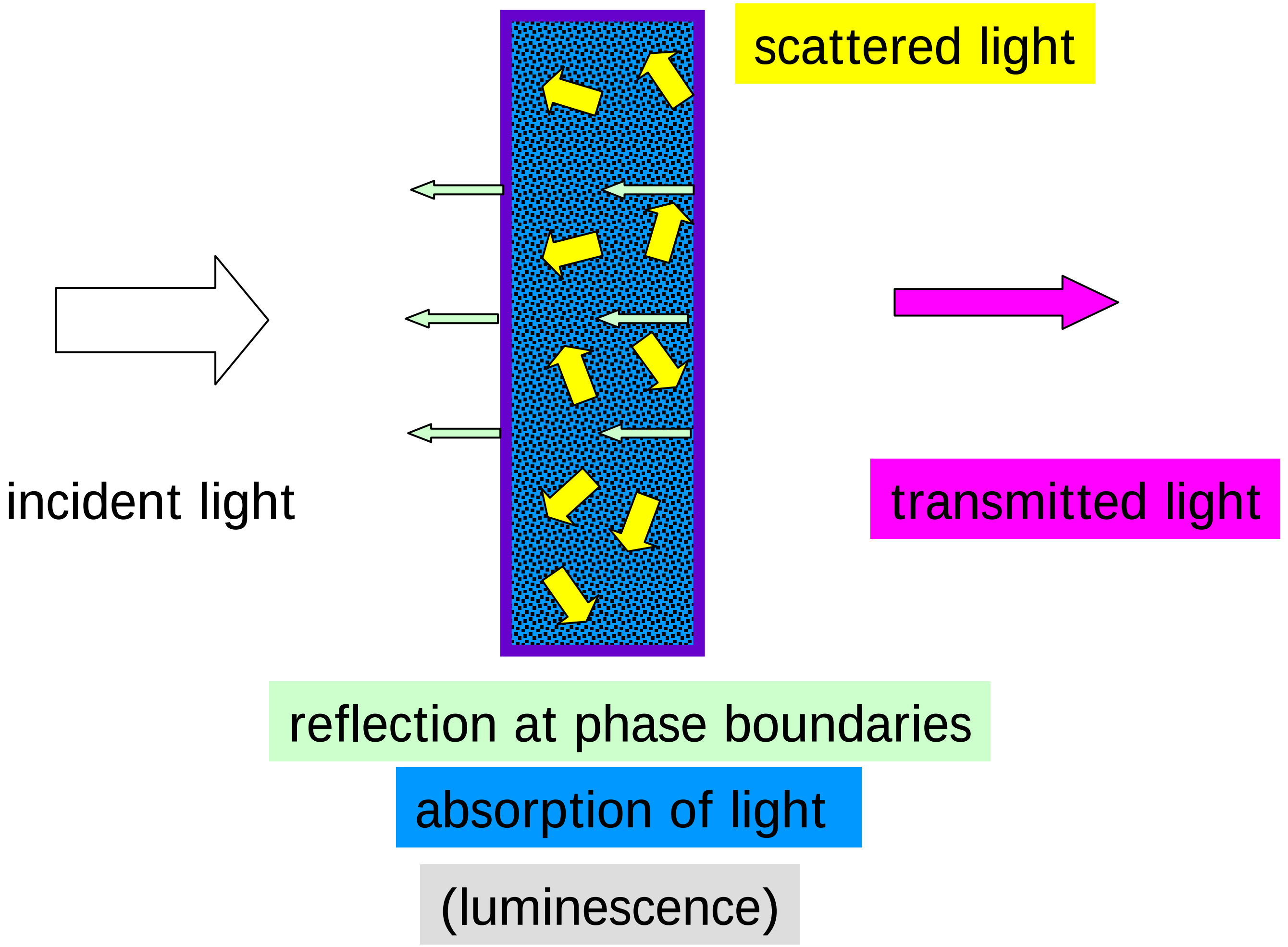
$$A_{10} = \varepsilon c l = -\log(\tau)$$

(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 !!!!

Interaction of Light with Sample



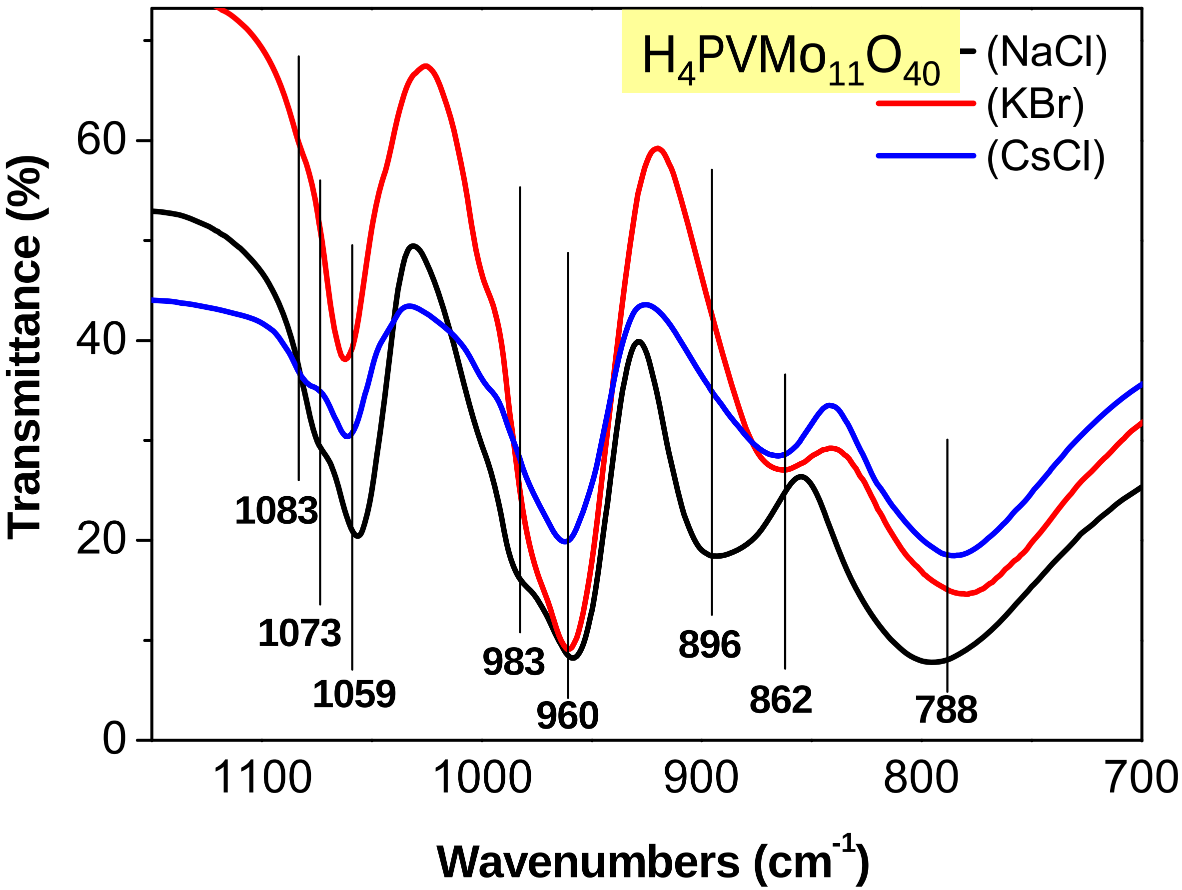
Scattering

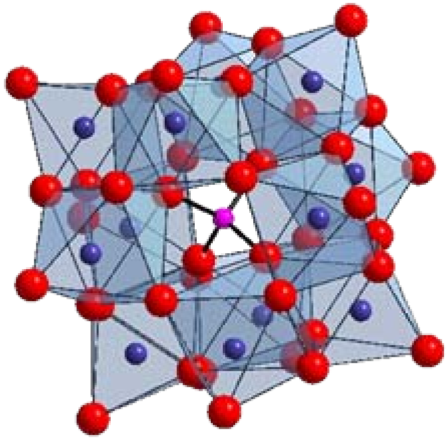
- Scattering is negligible in molecular disperse media (solutions)
- Scattering is considerable for colloids and solids when the wavelength is in the order of magnitude of the particle size

	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

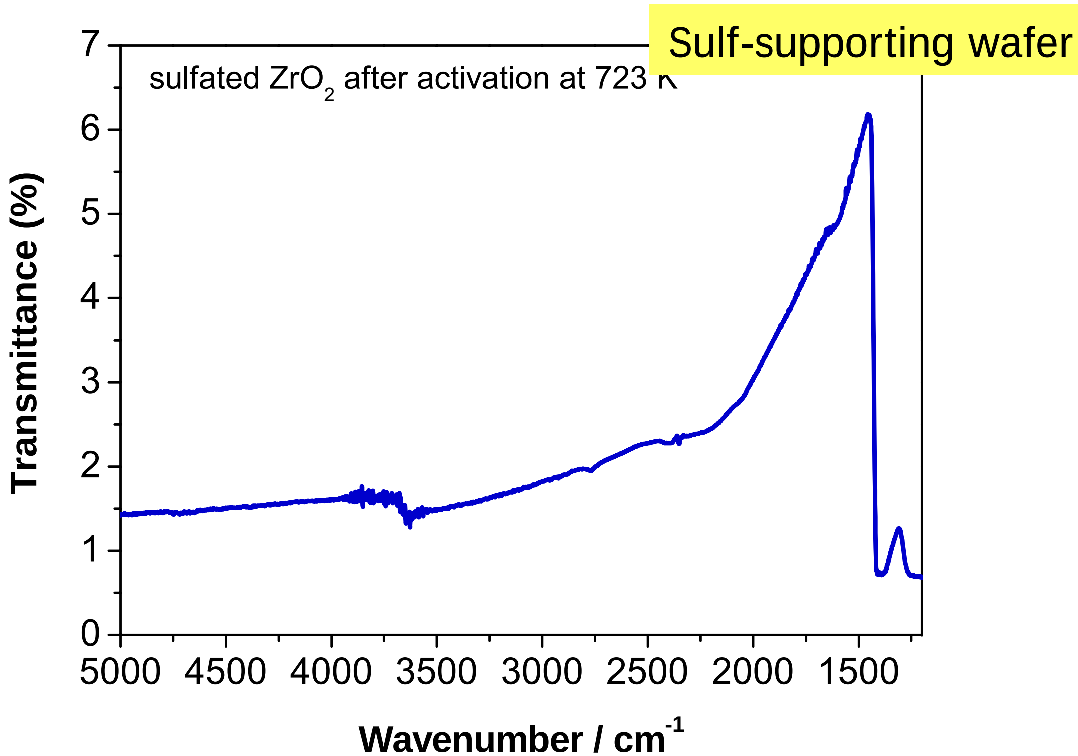
But.......Reaction with Material Used for Embedding





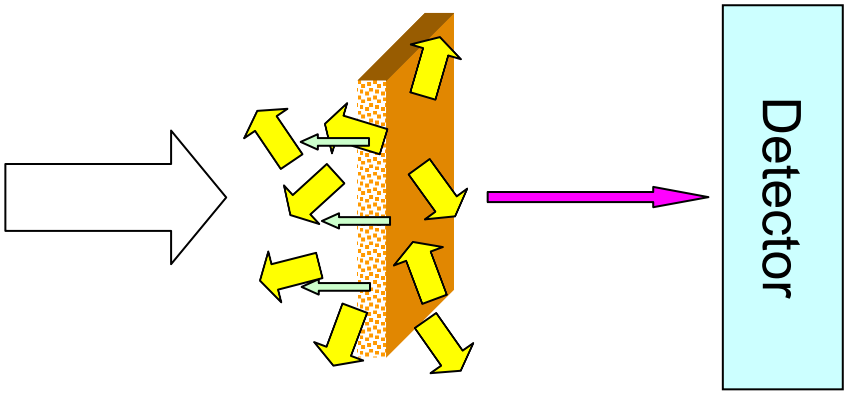
- Reaction with diluent possible
- Dilution usually not suitable for experiments at high T/ with reactive gases

Limitations of Transmission Spectroscopy

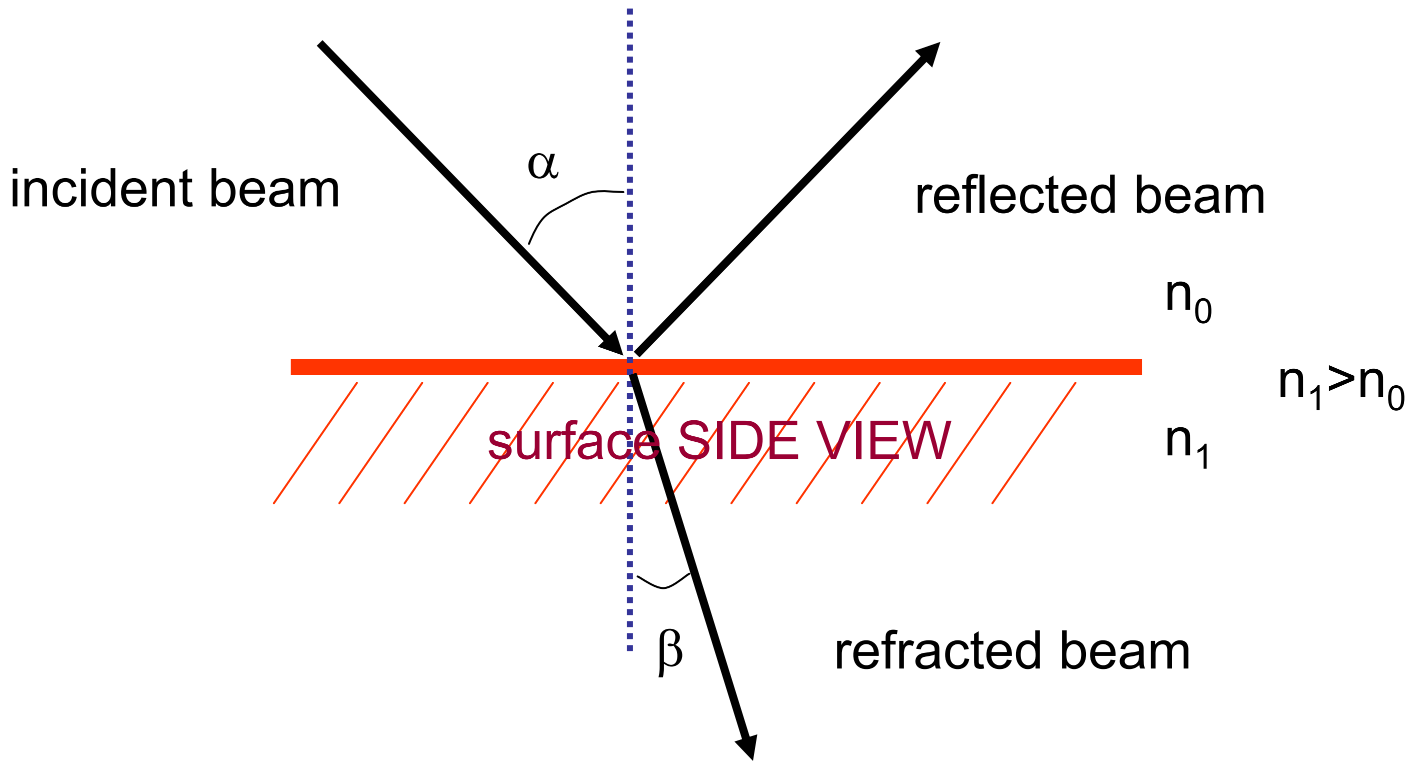


Can We Use the Reflected Light?

- 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?

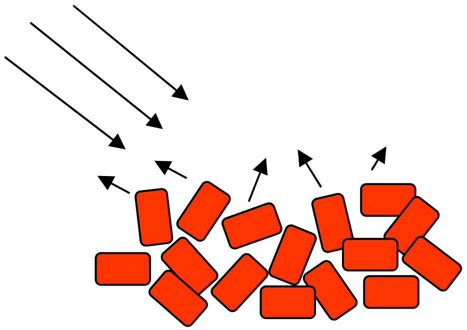


Specular Reflection (Non-Absorbing Media)



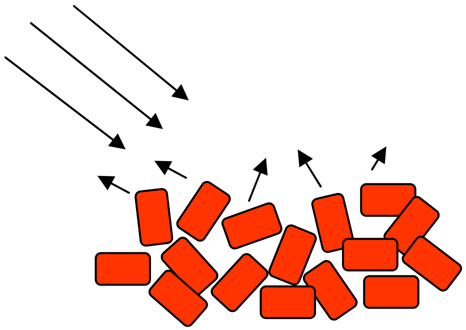
- fraction of reflected light increases with α
- β depends on α and ratio of the refractive indices (Snell law)
- insignificant for non-absorbing media, for air/glass about 4%

Diffuse Reflection

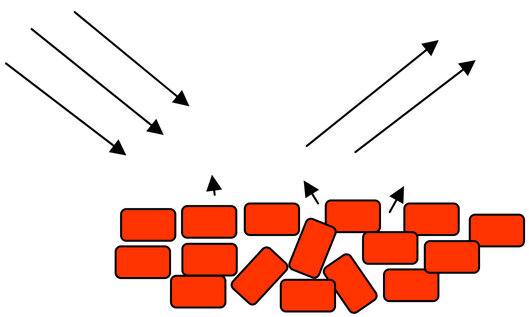


- Intensity of diffusely reflected light independent of angle of incidence
- Result of multiple reflection, refraction, and diffraction (scattering) inside the sample

Diffuse Reflection



- 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 & Diffuse Reflection

Reflection of radiant energy at boundary surfaces

mirror-type (polished) surfaces

mat (dull, scattering) surfaces

Specular

mirror-type reflection
mirror reflection
surface reflection
specular reflection
reguläre Reflexion
gerichtete Reflexion

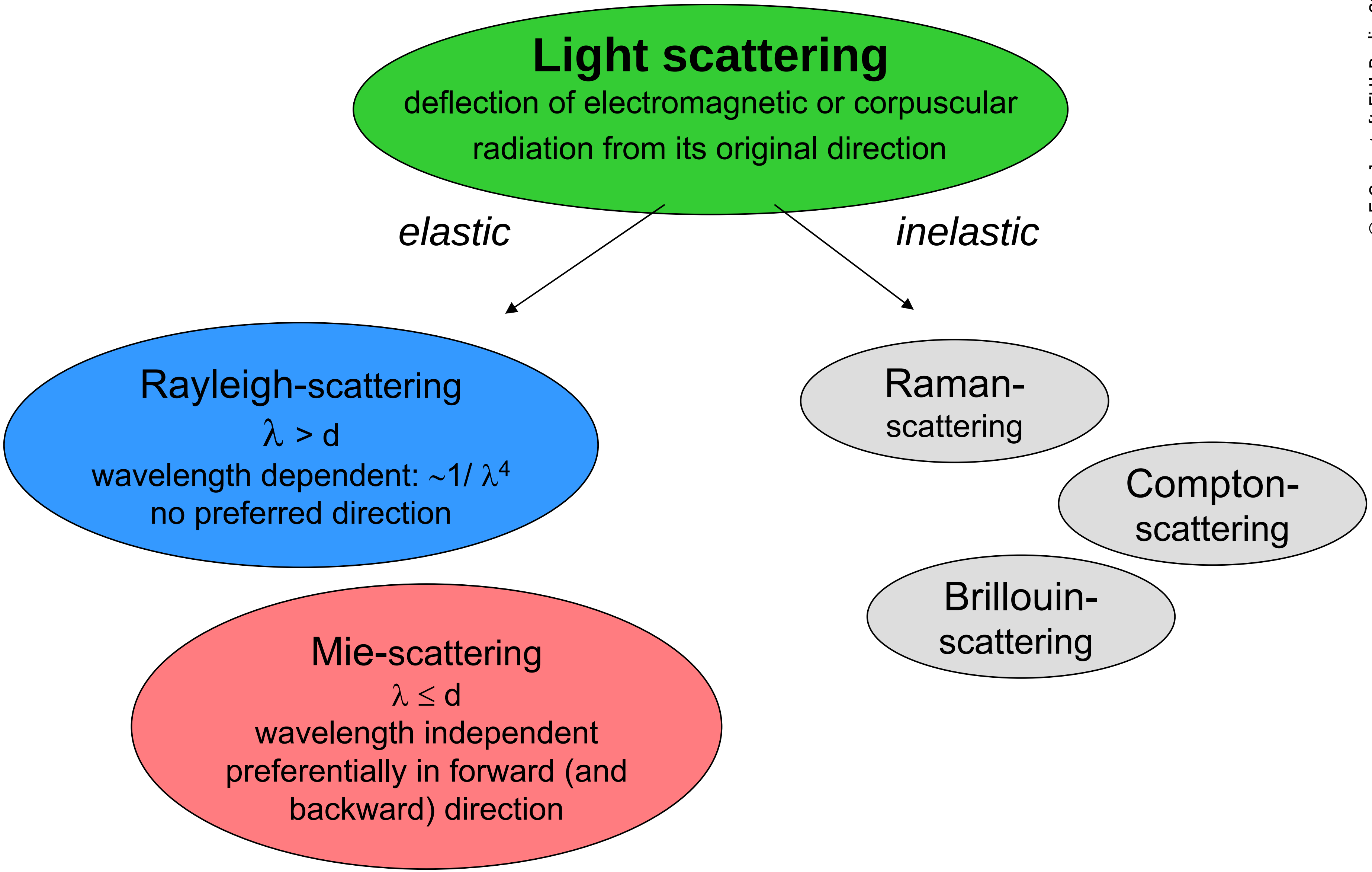
reflecting power called "reflectivity"

Diffuse

multiple reflections at surfaces of small particles

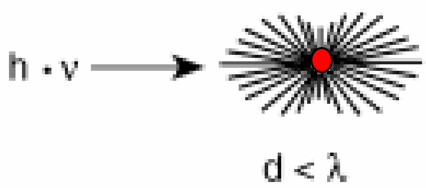
reflecting power called "reflectance"

Scattering

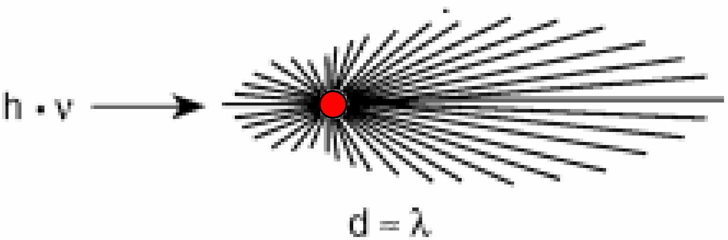


Light scattering
deflection of electromagnetic or corpuscular radiation from its original direction
elastic
inelastic
Rayleigh-scattering
$\lambda > d$
wavelength dependent: $\sim 1/\lambda^4$
no preferred direction
Mie-scattering
$\lambda \leq d$
wavelength independent
preferentially in forward (and backward) direction
Raman-scattering
Compton-scattering
Brillouin-scattering

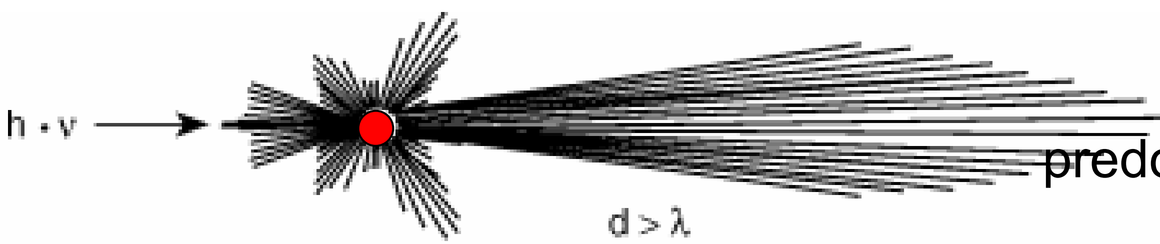
Rayleigh- and Mie-Scattering



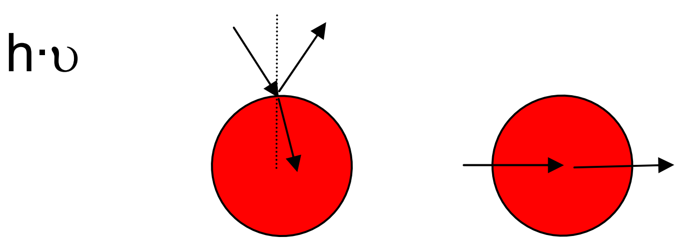
d < λ: Rayleigh-Scattering
isotropic distribution



d = λ: Mie-Scattering
in forward and backward directions



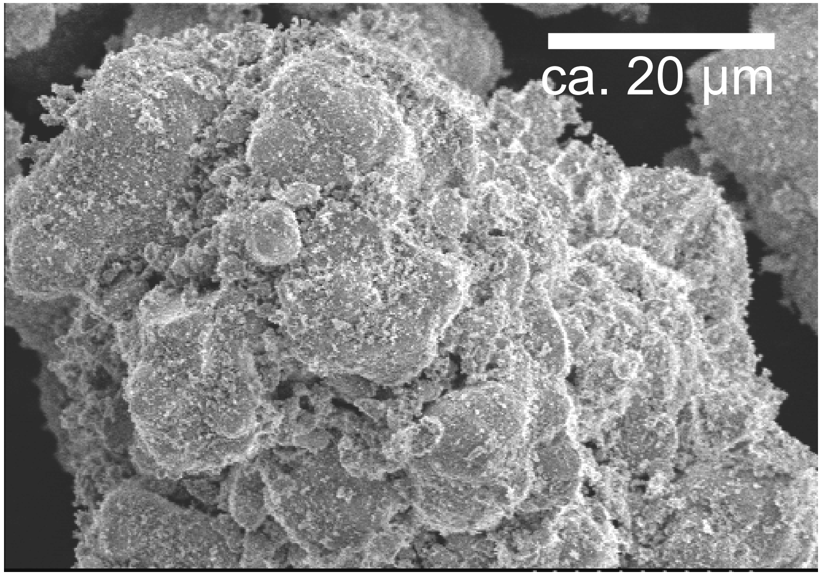
d > λ: Mie-Scattering
predominantly in forward direction



d >> λ: Mie-Theory approaches laws of geometric optics

Quelle: RÖMPP on line

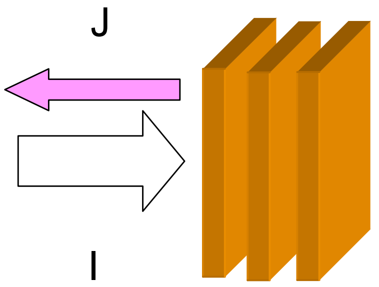
Typical Catalyst Particles



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

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

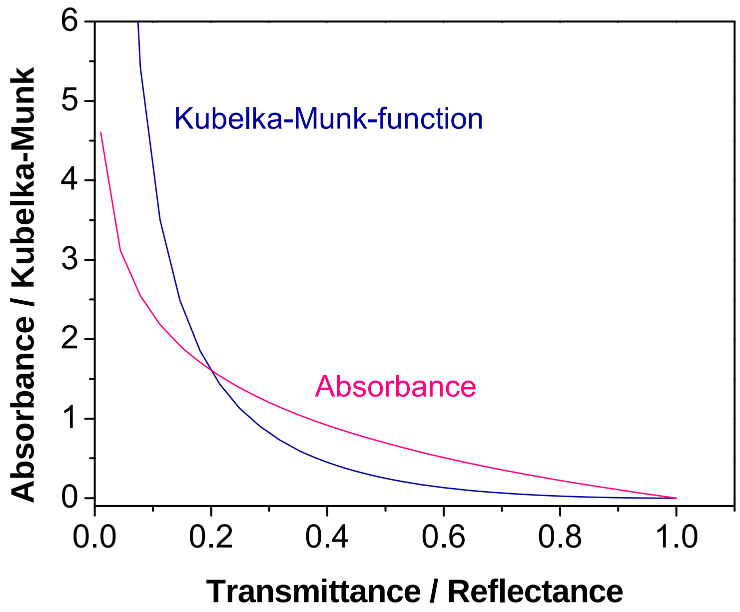
Kubelka-Munk function
remission function

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

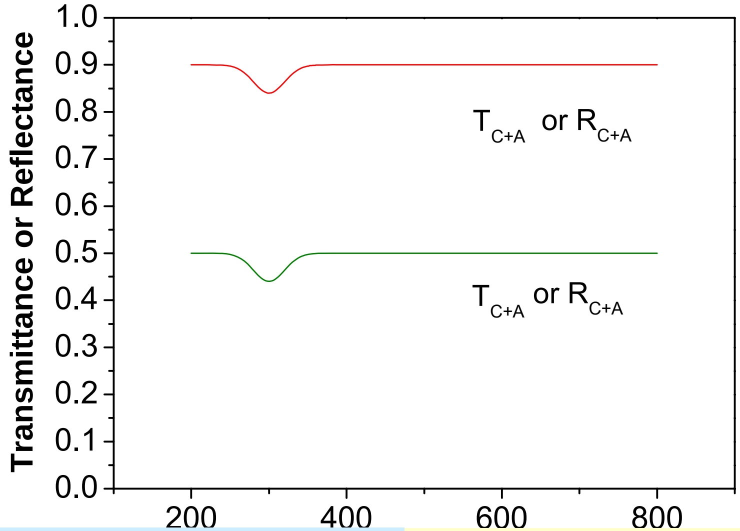
Transmission vs. Reflection Spectroscopy

- For quantification and to be able to calculate difference spectra: calculate absorbance / Kubelka-Munk function

$$A = -\ln T \qquad\qquad F(R) = \frac{(1-R)^2}{2R}$$



Transmission vs. Reflection Spectroscopy



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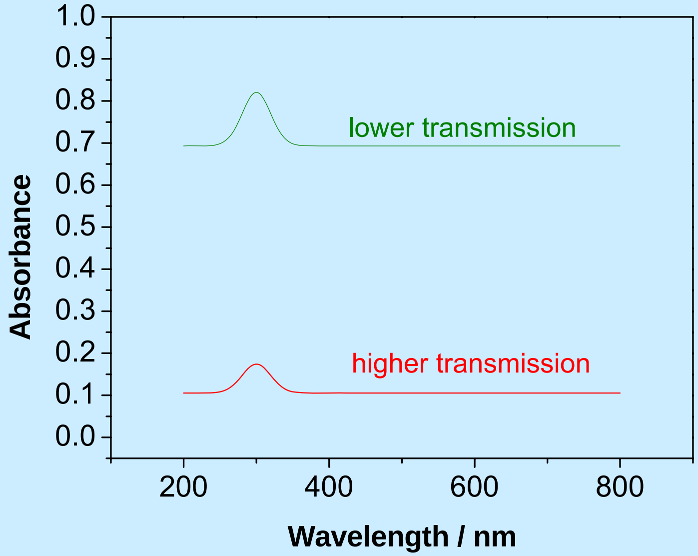
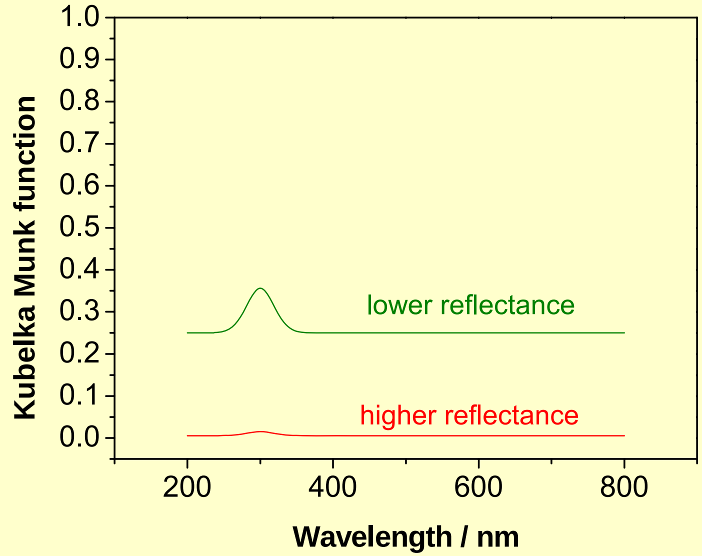
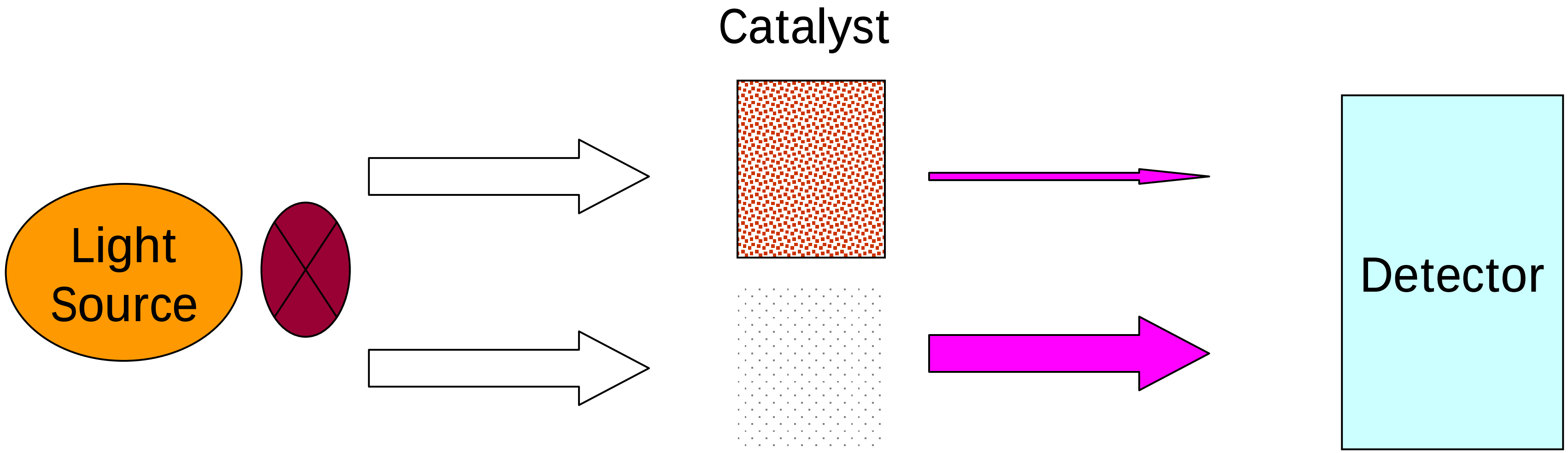




Spectroscopy in Transmission

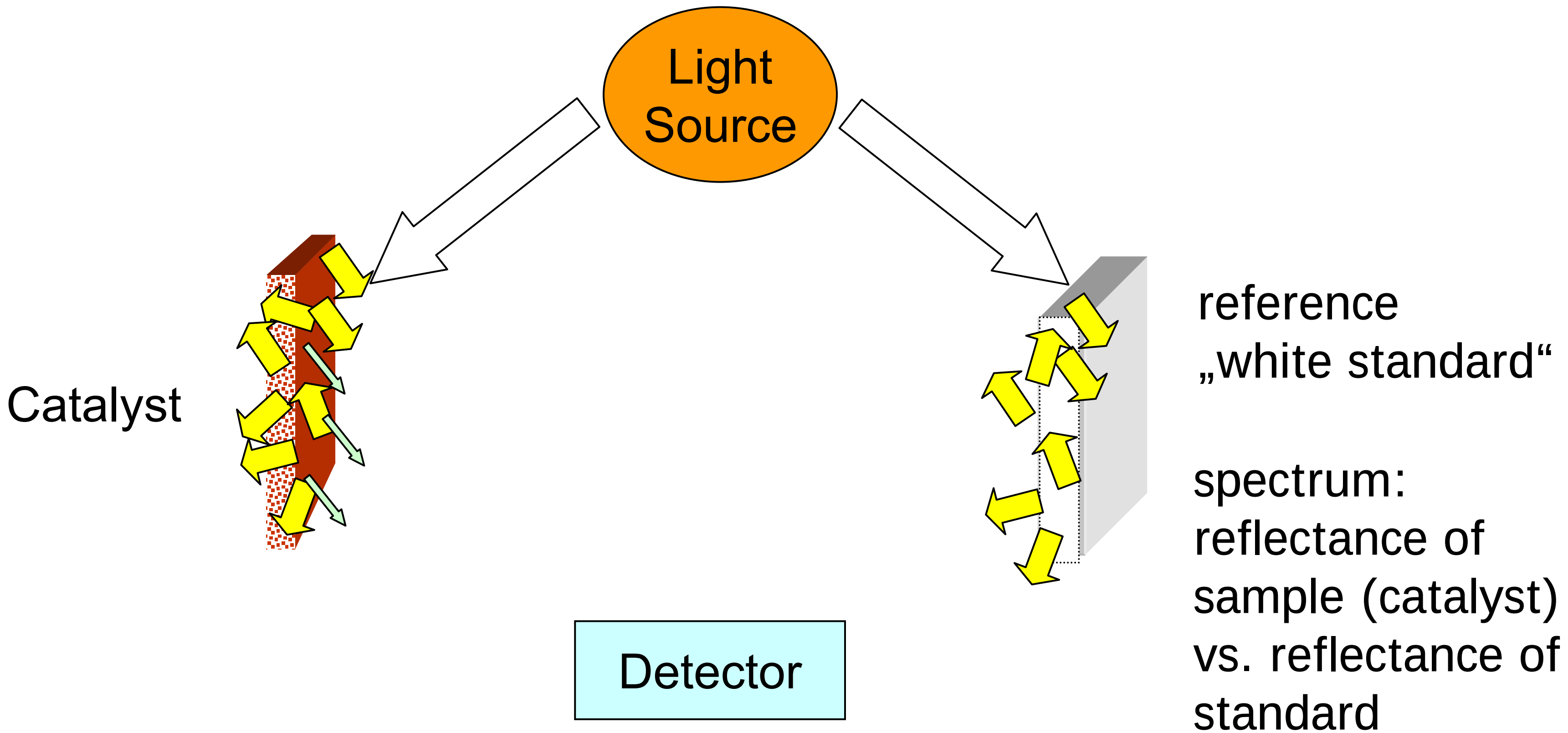


reference „nothing“
= void, empty cell, cuvette with solvent

spectrum: transmission of catalyst vs. transmission of reference

- Double beam spectrometer: direct comparison sample - reference
- Single beam spectrometer: consecutive measurement

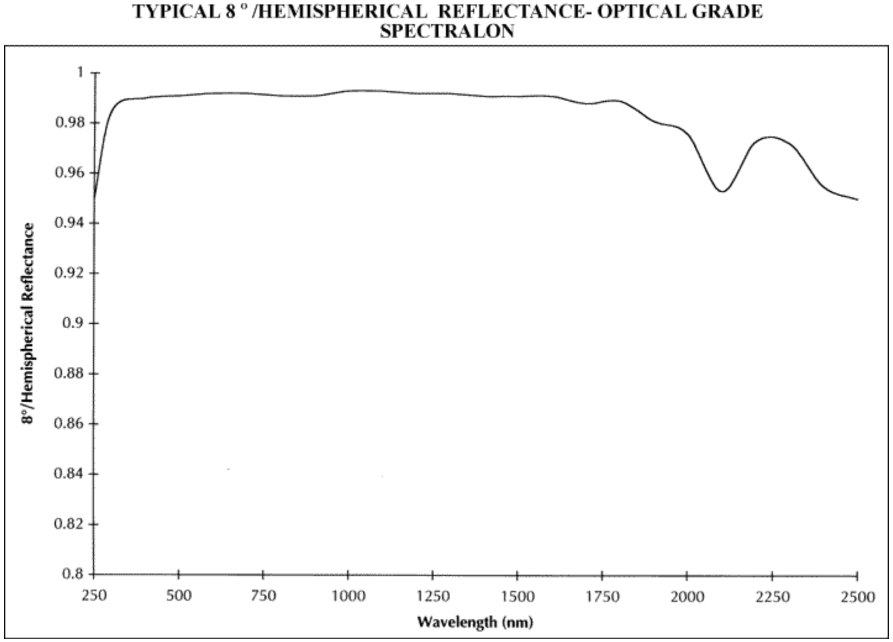
Diffuse Reflectance Spectroscopy



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

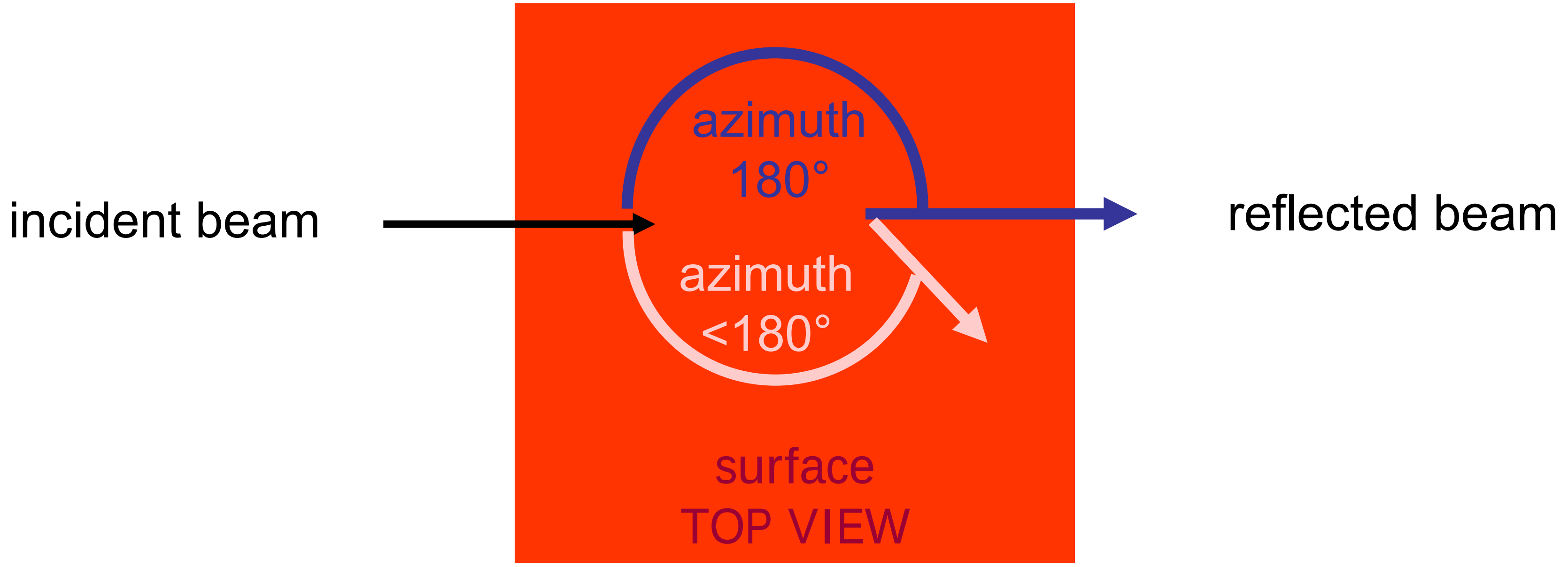
White Standards

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



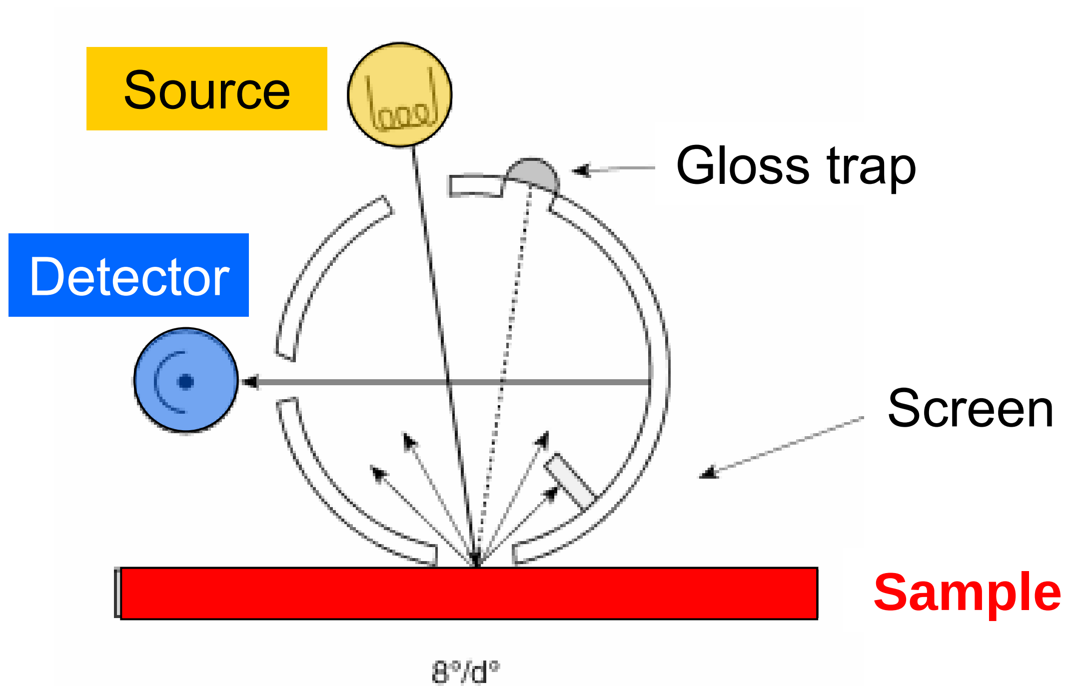
Spectralon® thermoplastic resin, excellent reflectance in UV-vis region

Specular Reflection: Angular Distribution



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

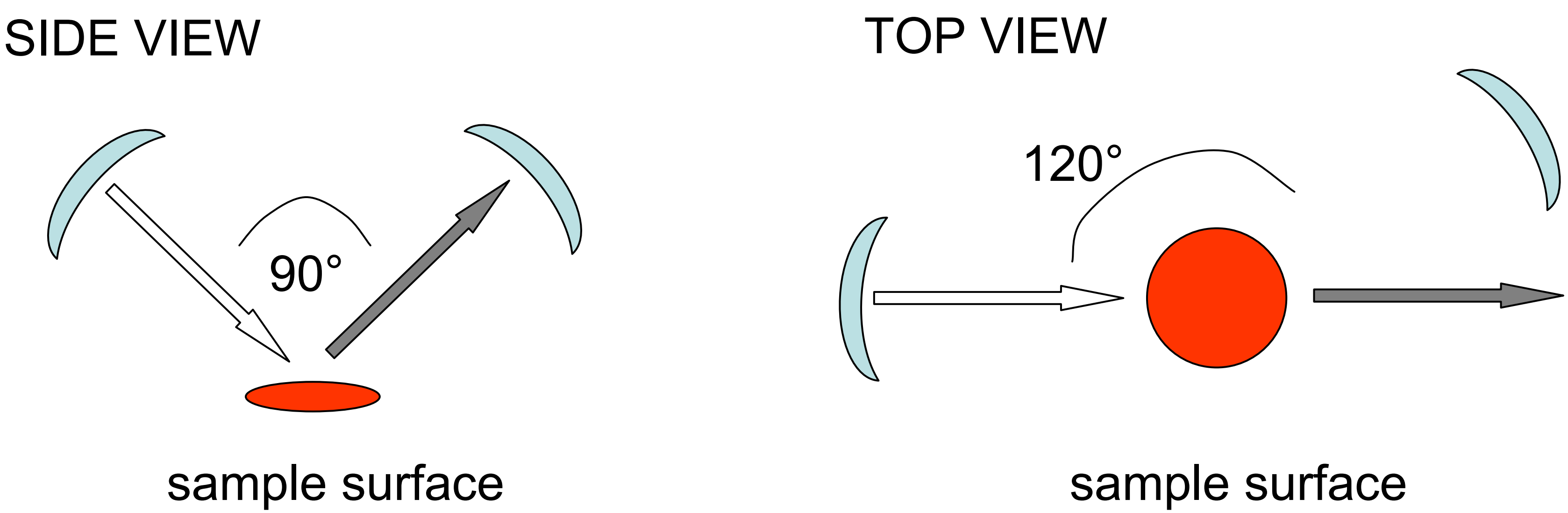
Integrating Sphere



- 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), Au

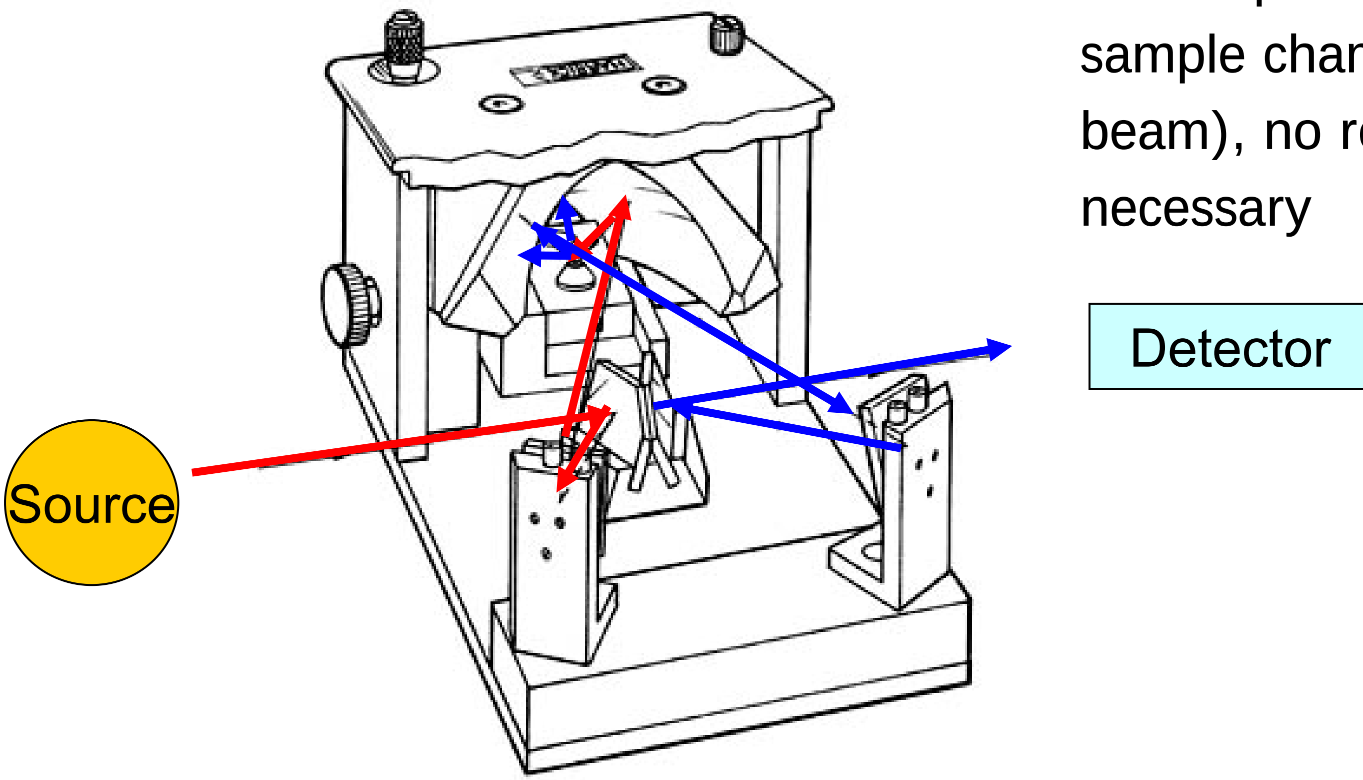
Image: Römpp on-line

How to Avoid Specular Reflection



- Specular reflection is strongest in forward direction
- Collect light in off-axis configuration

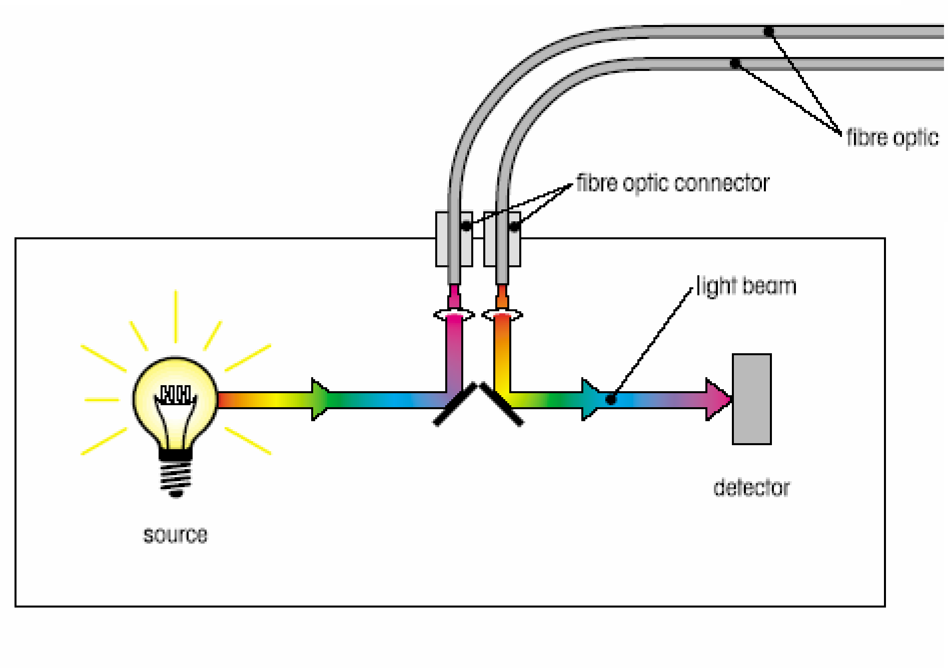
Mirror Optical Accessory

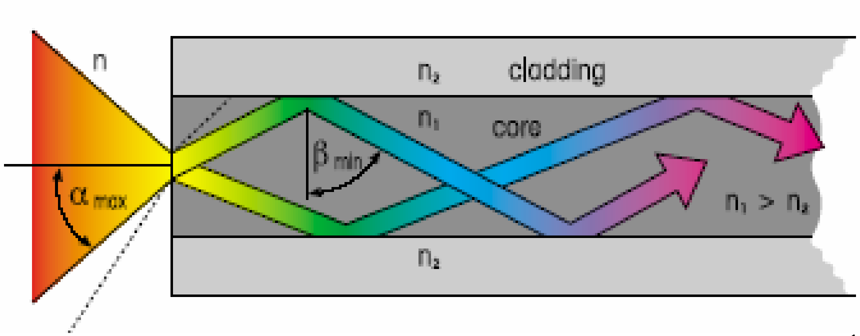


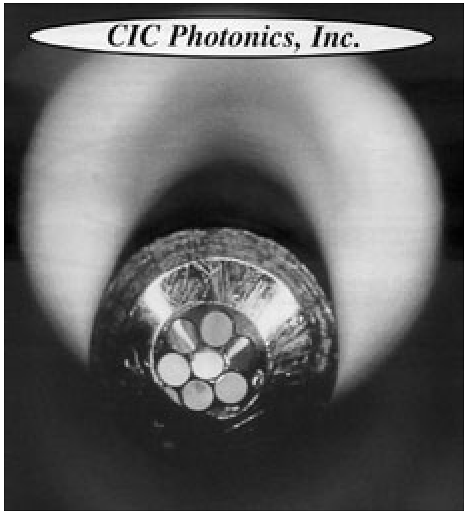
- can be placed into the normal sample chamber (in line with beam), no rearrangement necessary

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

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)

Methods in Catalysis Research

IR spectroscopy

Transmission

- Fourier-transform infrared spectroscopy (FTIR spectroscopy)

Diffuse Reflectance

- Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS)
- Collecting elements:
  - Mirror optics
  - Integrating spheres

UV-vis spectroscopy

[Transmission]

- UV-vis spectroscopy

Diffuse Reflectance

- Diffuse reflectance UV-vis spectroscopy (DR-UV-vis spectroscopy or DRS)
- Collecting Elements:
  - Mirror optics
  - Integrating spheres
  - Fiber optics

Possible Transitions

Transitions / Contribution from	Vibrations	Electronic transitions
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
Catalyst surface	Stretching and deformation modes of functional groups, vibrations of supported species: metal complexes	Charge transfer and d-d transitions of metal complexes, metal particles
Adsorbates	Probing of surface properties (functional groups), adsorbed reactants	Probing of surface properties, adsorbed reactants
	In situ: adsorbed reaction intermediates / products	In situ: reaction intermediates
Gas phase	Can be unwanted Product analysis	

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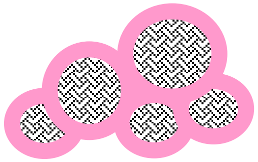
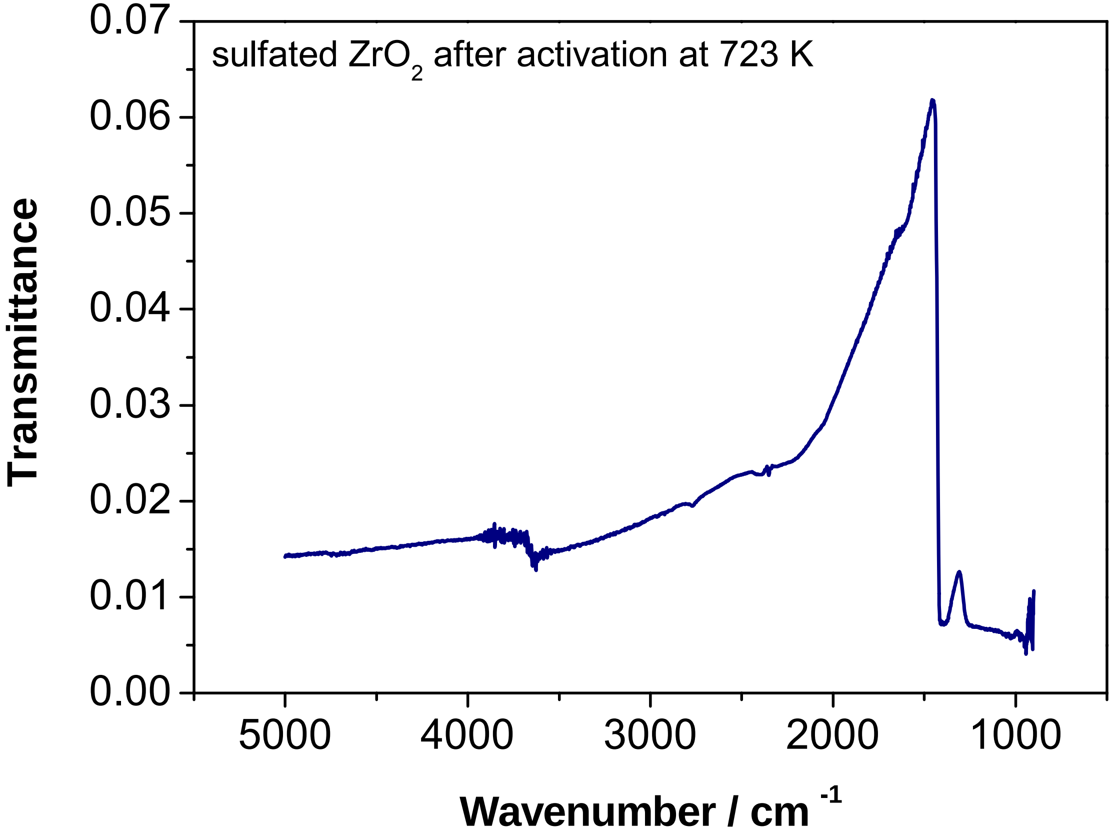
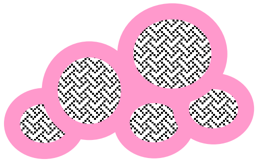
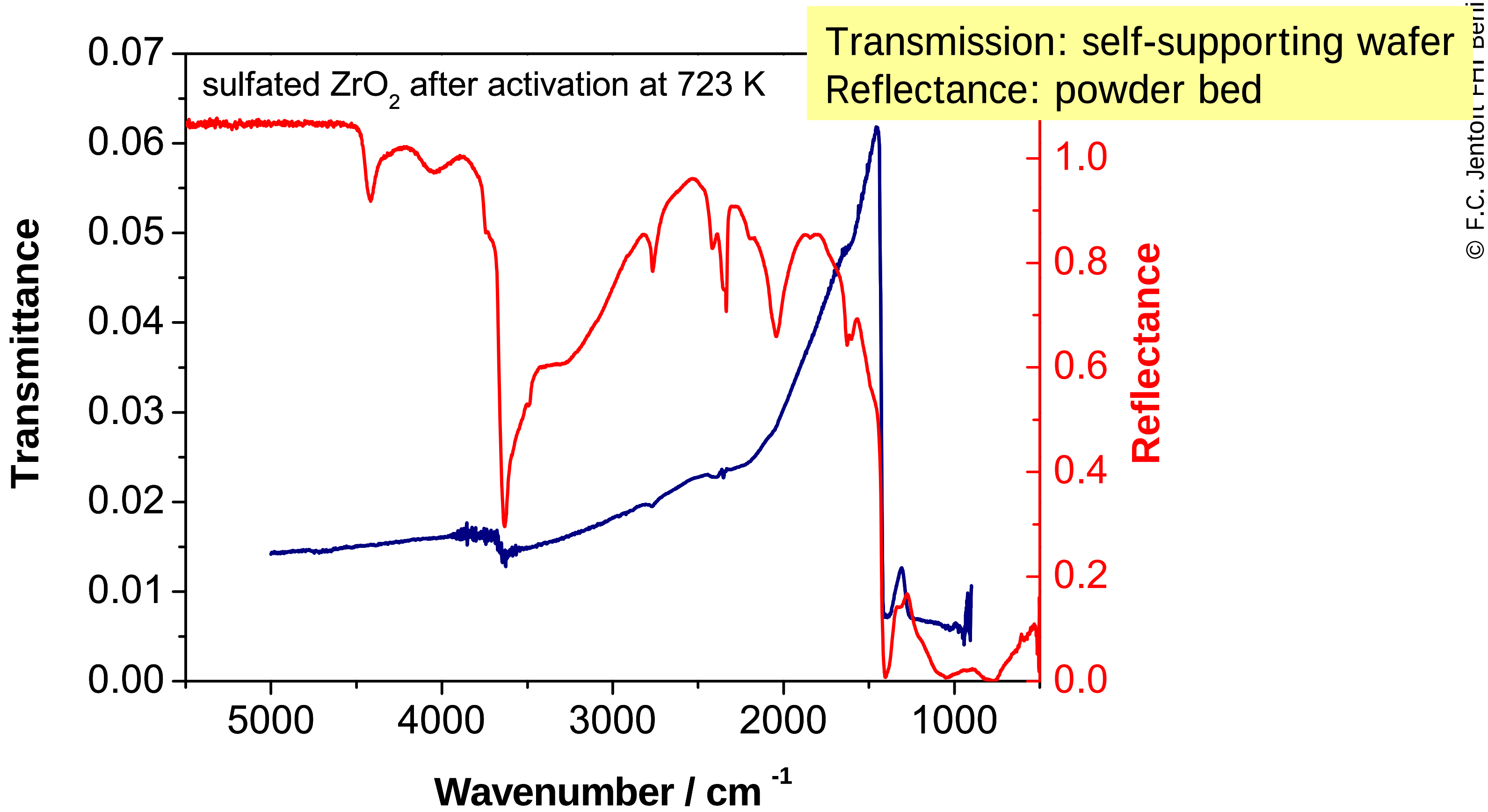
Limitations of Transmission IR Spectroscopy





Comparison
Transmission - Diffuse Reflectance (IR)

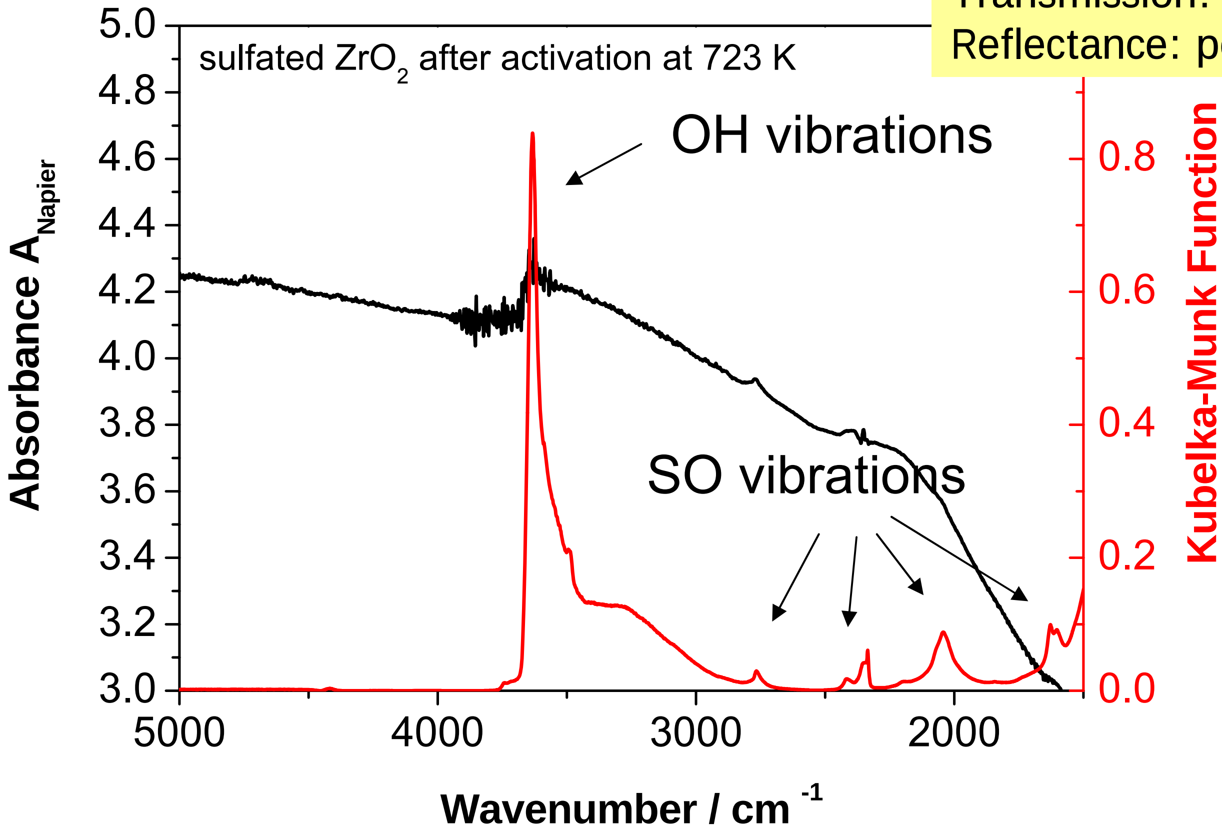




- Spectra can have very different appearance
- Transmittance decreases, reflectance increases with increasing wavenumber

Comparison
Transmission - Diffuse Reflectance (IR)

Transmission: self-supporting wafer
Reflectance: powder bed

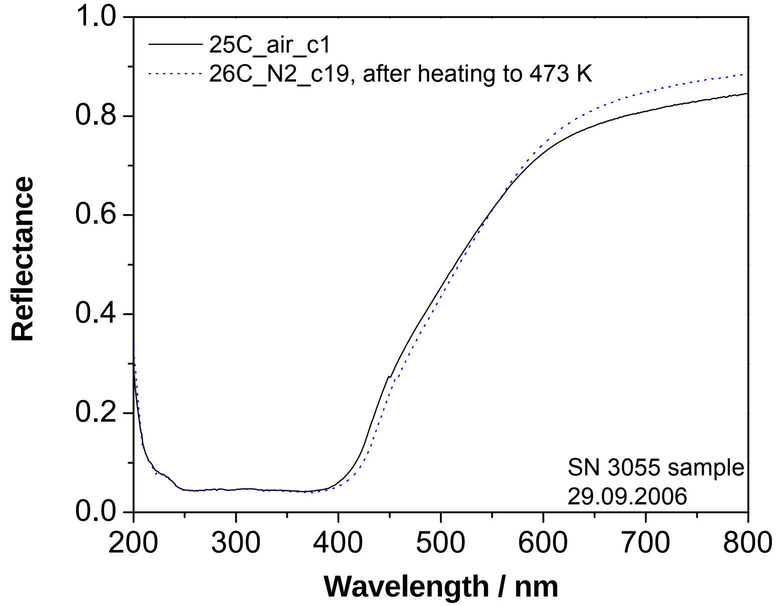


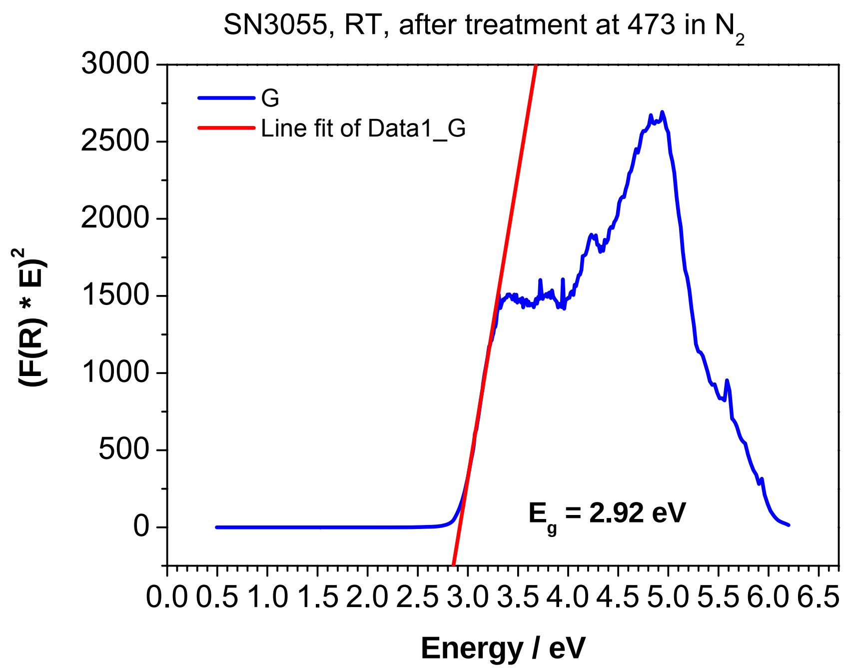
➢ Vibrations of surface species may be more evident in DR spectra

Possible Transitions

Transitions / Contribution from	Vibrations	Electronic transitions
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
Catalyst surface	Stretching and deformation modes of functional groups, vibrations of supported species: metal complexes	Charge transfer and d-d transitions of metal complexes, metal particles
Adsorbates	Probing of surface properties (functional groups), adsorbed reactants In situ: adsorbed reaction intermediates / products	Probing of surface properties, adsorbed reactants In situ: reaction intermediates
Gas phase	Can be unwanted Product analysis	

Band Gap Determination (DR-UV-vis)

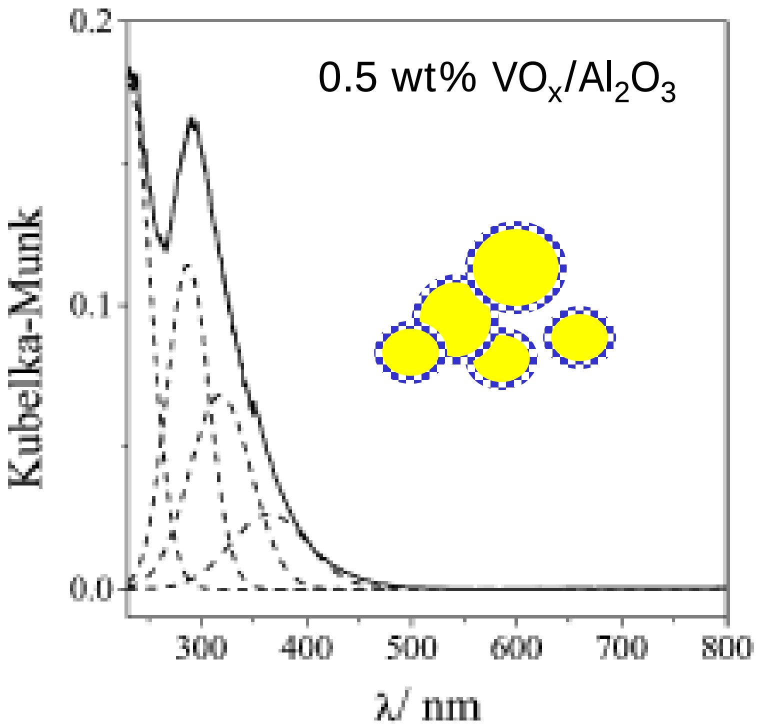


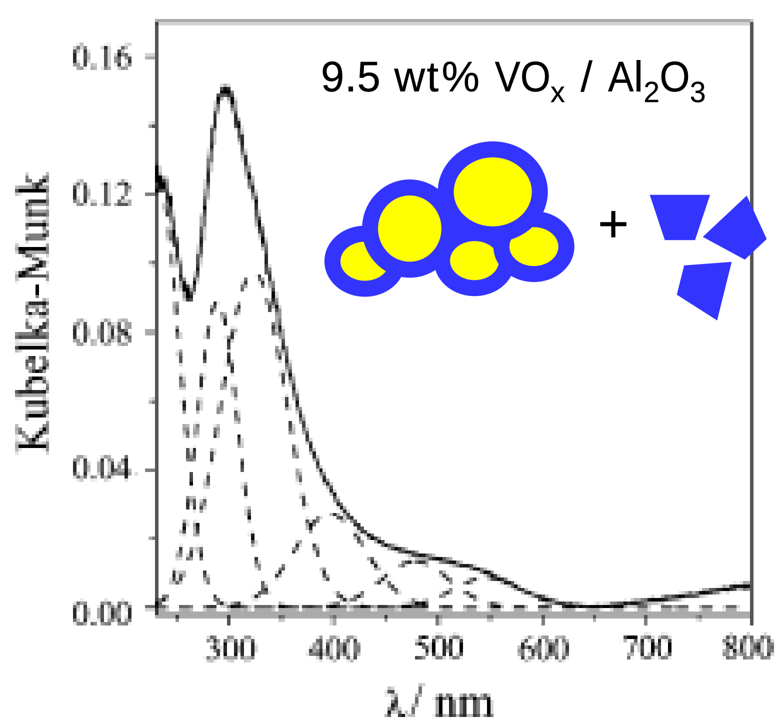


- Approximate composition "$C_6N_8H_z$"
- Friedel-Crafts Acylation

Catalyst: F. Goettmann, MPI KG Golm
Band gap determination: Weber, J. Catal. 1996

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

Possible Transitions

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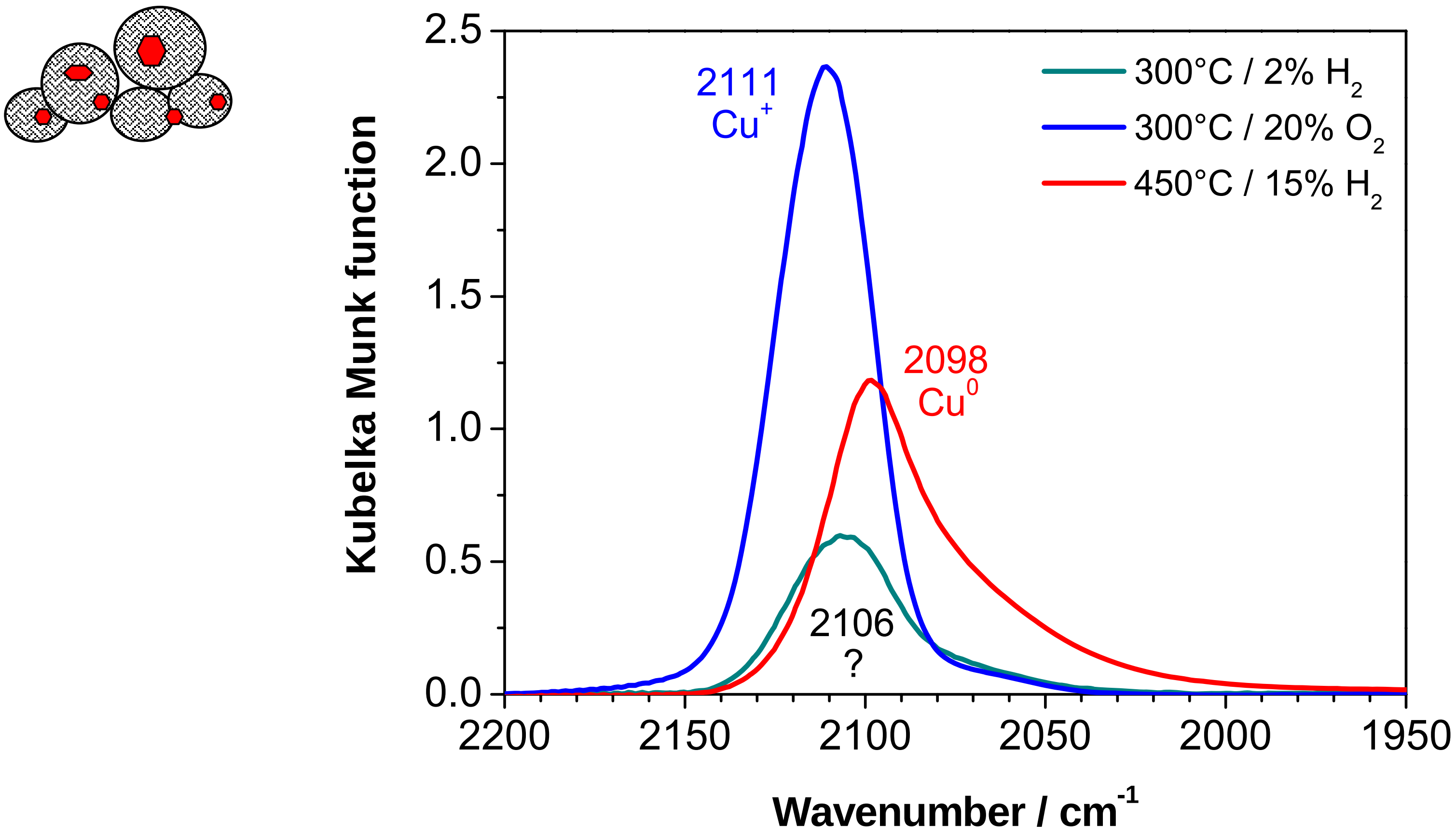
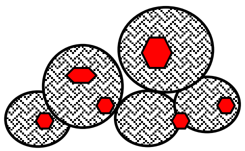
Gas phase	Can be unwanted Product analysis	

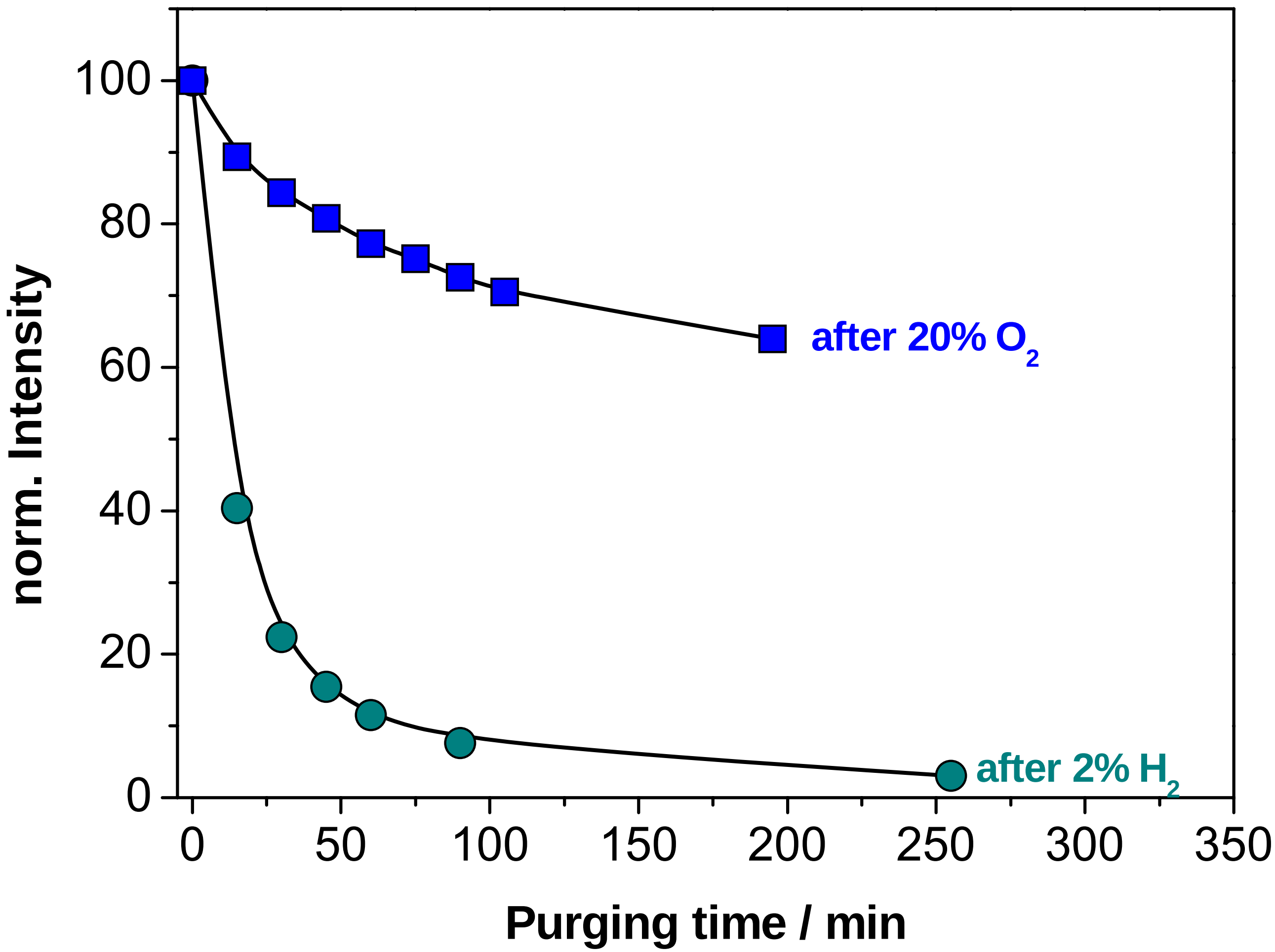
CO Adsorption at RT on Cu/ZrO_2



- Identification of copper oxidation states based on CO frequency can be ambiguous

CO Desorption at RT on Cu/ZrO_2





- Identification via stability of Cu-CO complex

Possible Transitions

Transitions / Contribution from	Vibrations	Electronic transitions
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
Catalyst surface	Stretching and deformation modes of functional groups, vibrations of supported species: metal complexes	Charge transfer and d-d transitions of metal complexes, metal particles
Adsorbates	Probing of surface properties (functional groups), adsorbed reactants	Probing of surface properties, adsorbed reactants
	In situ: adsorbed reaction intermediates / products	In situ: reaction intermediates
Gas phase	Can be unwanted Product analysis	

Hammett Indicators Adsorbed on Solids

TABLE 2–3 Basic indicators used for spectrophotometric determination of acid strength

Indicators	pK_a
Phenylazonaphthylamine	+4.0
p-Dimethylaminoazobenzene	+3.3
Aminoazobenzene	+2.8
Benzeneazodiphenylamine	+1.5
p-Nitroaniline	+1.1
o-Nitroaniline	−0.2
p-Nitrodiphenylamine	−2.4
2,4-Dichloro-6-nitroaniline	−3.2
p-Nitroazobenzene	−3.3
2,4-Dinitroaniline	−4.4
Benzalacetophenone	−5.6
p-Benzoyldiphenyl	−6.2
Anthraquinone	−8.1
2,4,6-Trinitroaniline	−9.3
3-Chloro-2,4,6-trinitroaniline	−9.7
p-Nitrotoluene	−10.5
Nitrobenzene	−11.4
2,4-Dinitrotoluene	−12.8

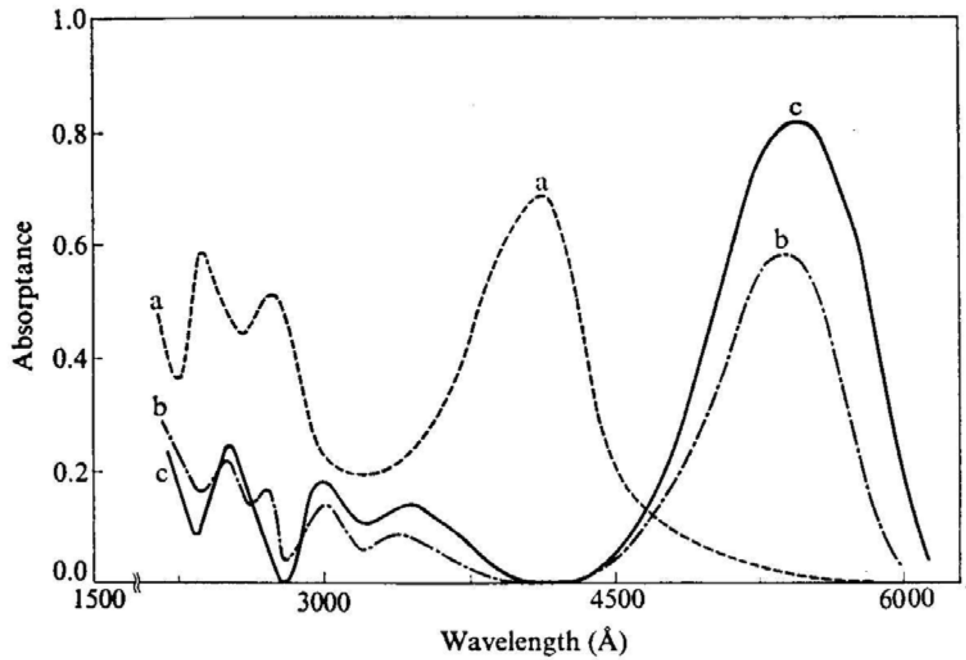
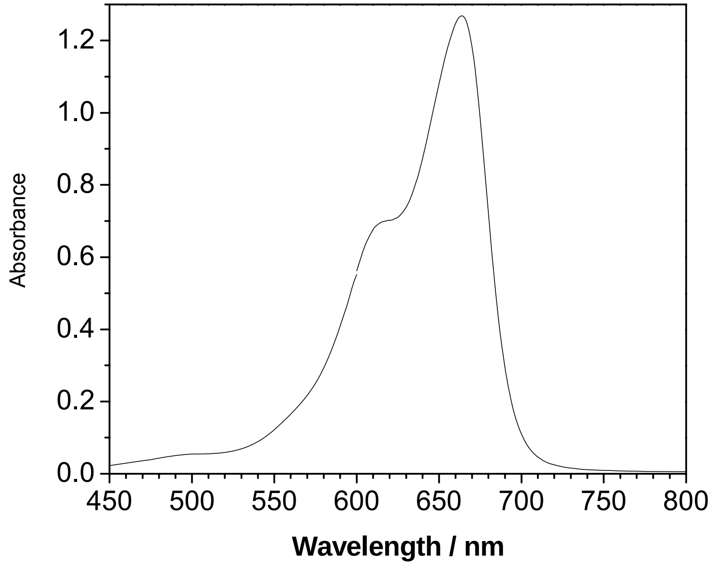
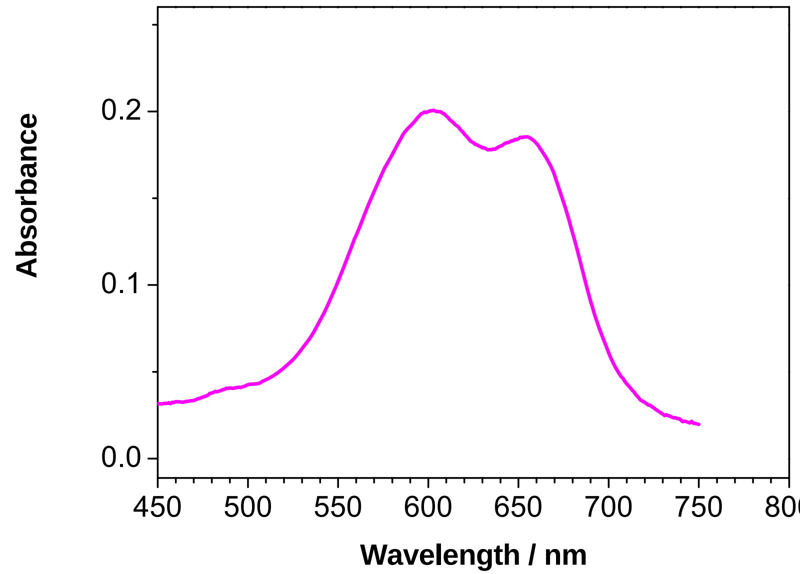


Fig. 2–1 Absorption spectra for phenylazonaphthylamine
a: in isooctane solution, b: in ethanolic HCl, c: adsorbed on silica-alumina

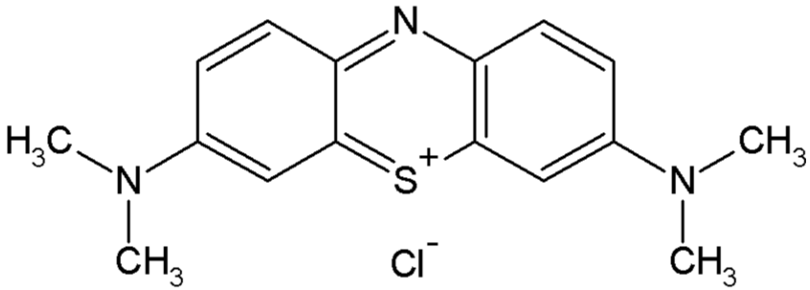
Example





Methylene blue in aqueous solution

Methylene blue adsorbed on TiO_2



Possible Transitions

Transitions / Contribution from	Vibrations	Electronic transitions
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
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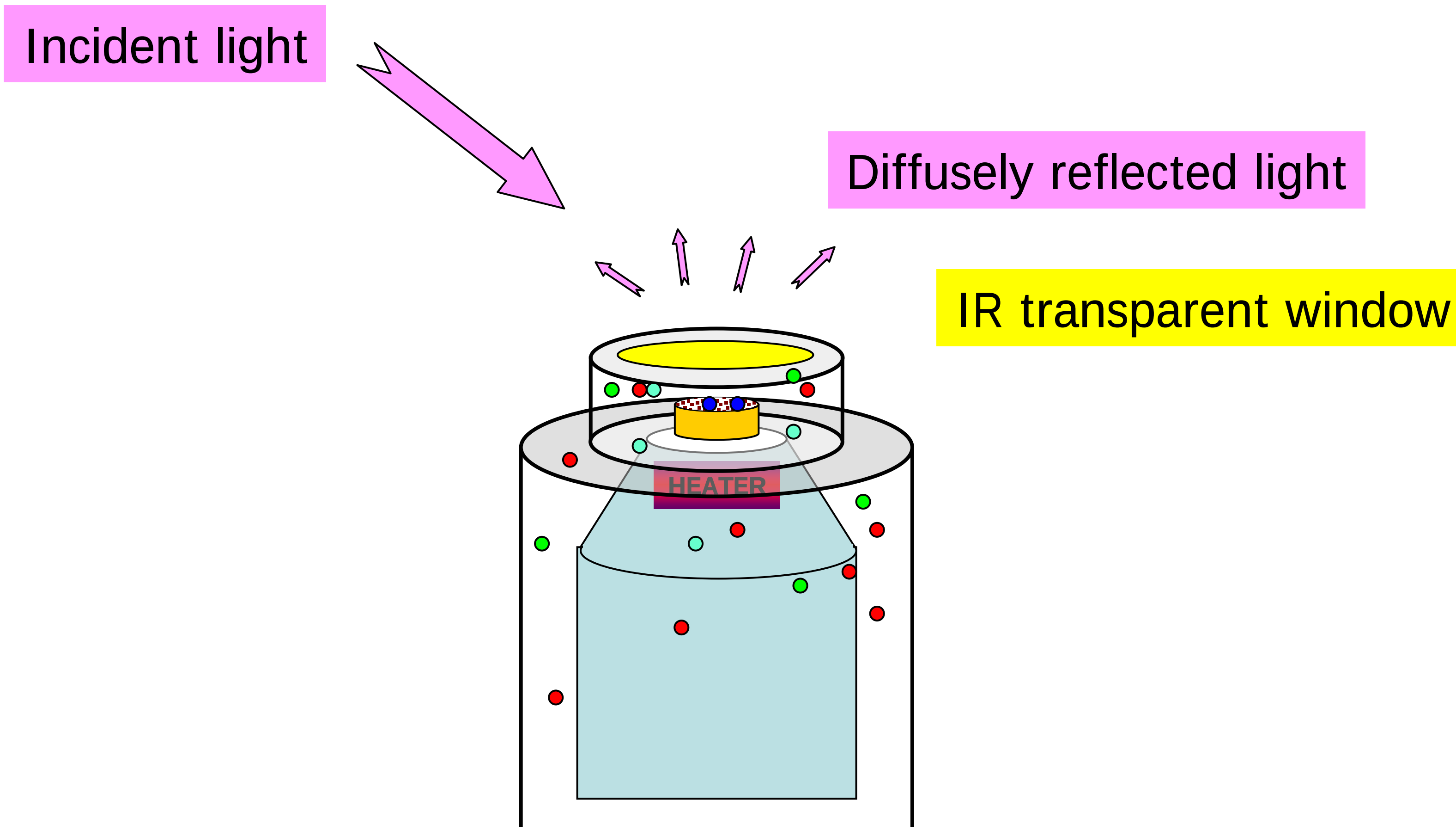
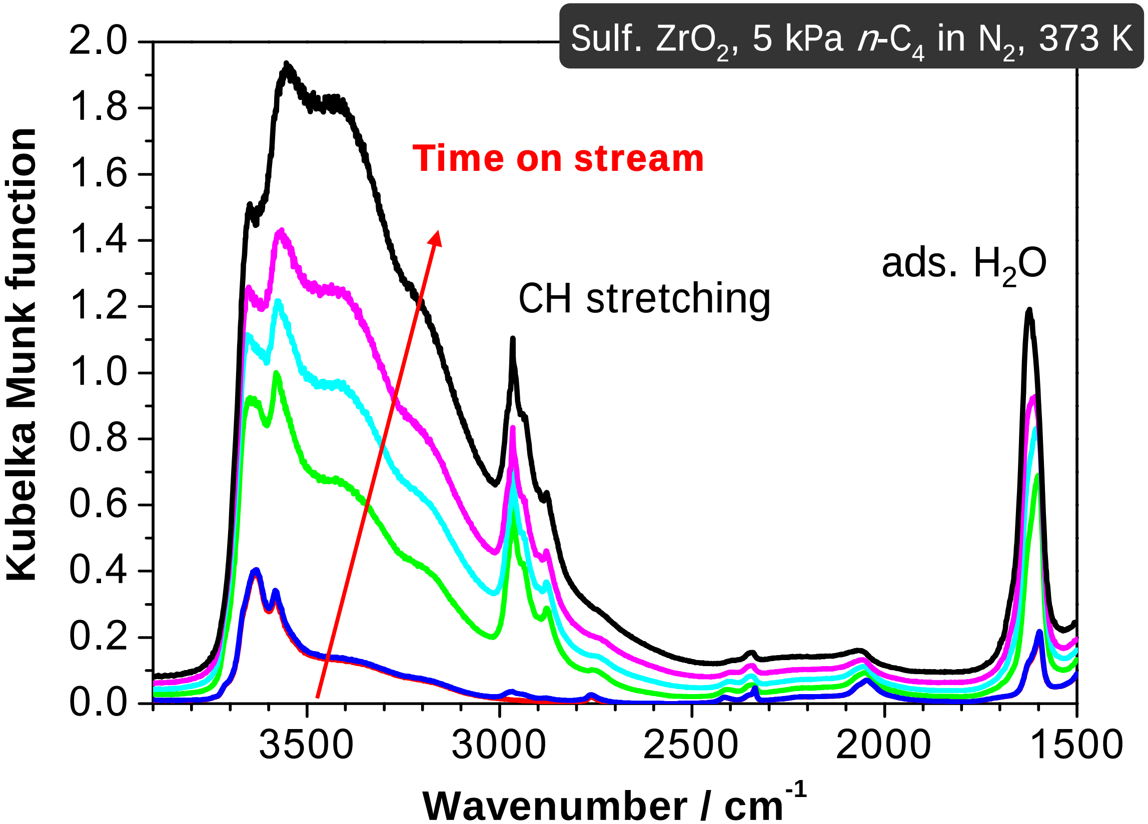
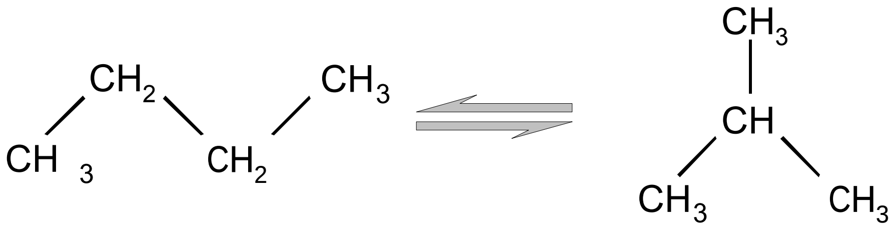
Adsorbates	Probing of surface properties (functional groups), adsorbed reactants	Probing of surface properties
	In situ: adsorbed reaction intermediates / products	In situ: reaction intermediates
Gas phase	Can be unwanted Product analysis	

Origin of Surface and Gas Phase Contributions

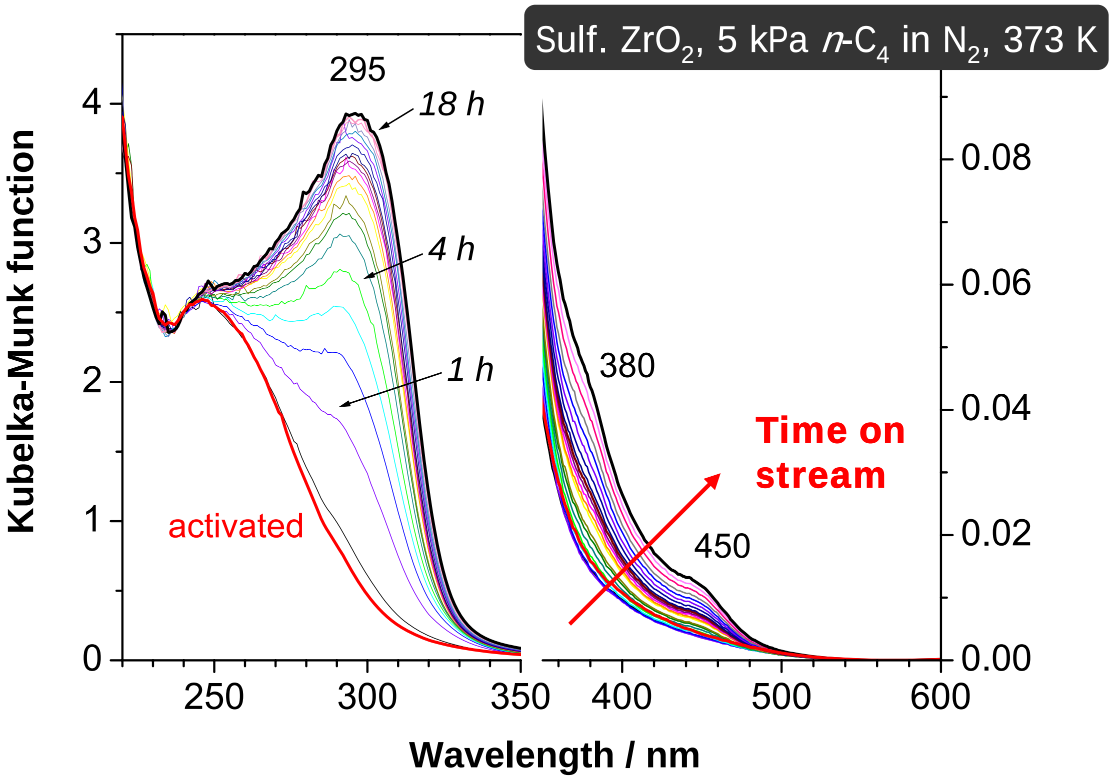


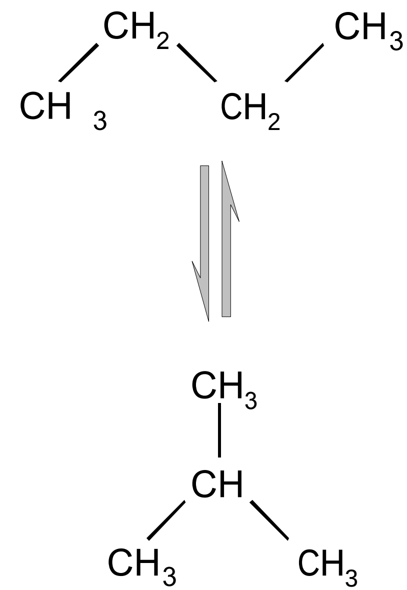
DRIFTS: *n*-Butane Isomerization

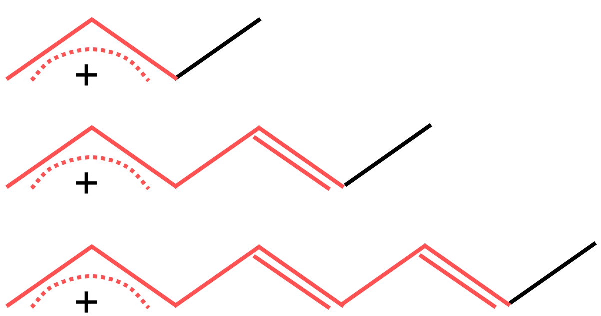




DR-UV-vis: *n*-Butane Isomerization







300 nm

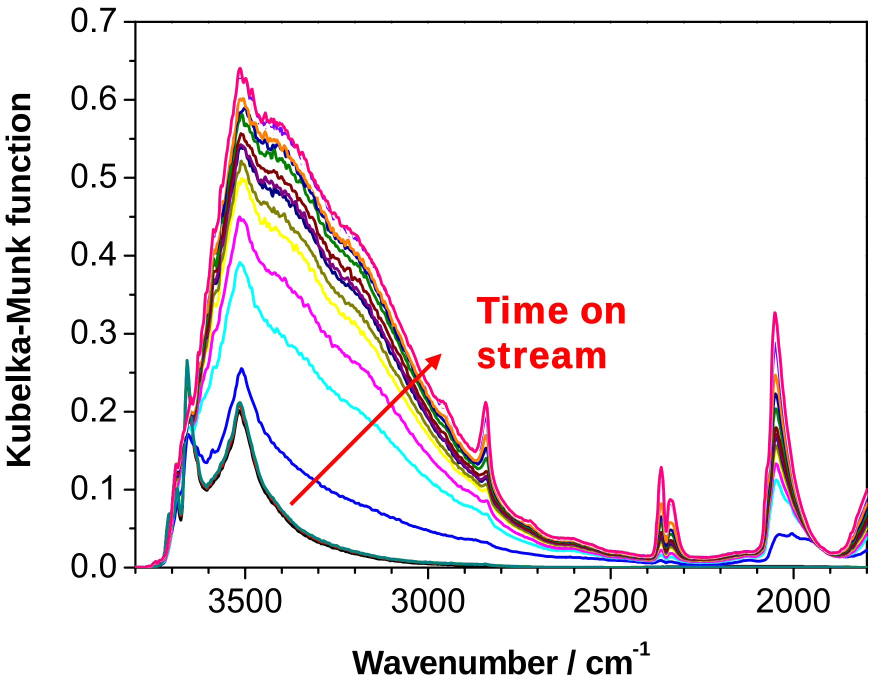
350-370 nm

430-440nm

Possible Transitions

Transitions / Contribution from	Vibrations	Electronic transitions
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
Catalyst surface	Stretching and deformation modes of functional groups, vibrations of supported species: metal complexes	Charge transfer and d-d transitions of metal complexes, metal particles
Adsorbates	Probing of surface properties (functional groups), adsorbed reactants	Probing of surface properties, adsorbed reactants
	In situ: adsorbed reaction intermediates / products	In situ: reaction intermediates
Gas phase	Can be unwanted Product analysis	

DRIFTS: Preferential Oxidation of CO (PROX)

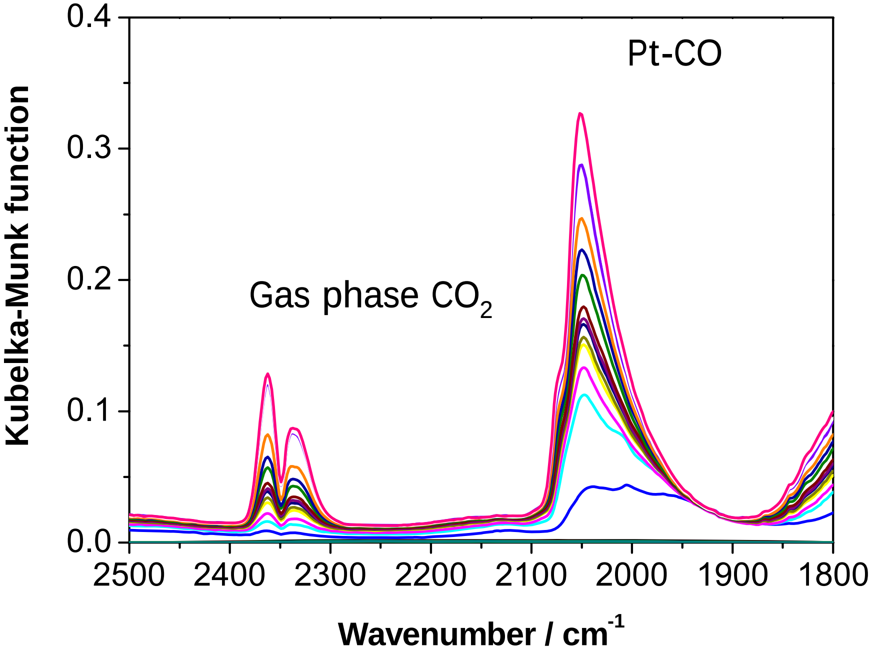


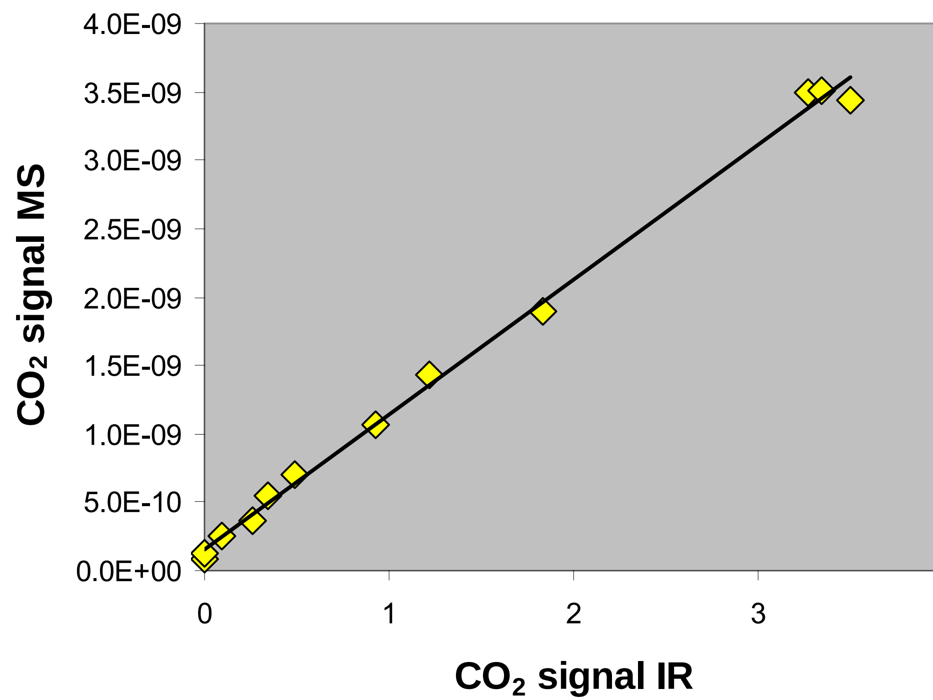
$CO + ½\ O_2 \rightarrow CO_2$

in excess H_2

1% Pt/CeO_2 at T = 383 K, 1% CO/1% O_2 in H_2

IR Gas Phase Analysis: PROX





- IR band area of CO_2 vibration corresponds to CO_2 MS signal in effluent gas
- Quantification of gas phase composition possible

Analysis by Detre Teschner

Possible Transitions

Transitions / Contribution from	**Vibrations**	**Electronic transitions**
Catalyst bulk	Lattice, structural units	Band gap energy of semiconductors
Catalyst surface	Stretching and deformation modes of functional groups, vibrations of supported species: metal complexes	Charge transfer and d-d transitions of metal complexes, metal particles
Adsorbates	Probing of surface properties (functional groups), adsorbed reactants	Probing of surface properties
	In situ: adsorbed reaction intermediates / products	In situ: reaction intermediates
Gas phase	Can be unwanted Product analysis	

Literature

- W. WM. Wendlandt, H.G. Hecht, “Reflectance Spectroscopy”, Interscience Publishers/John Wiley 1966
- G. Kortüm, “Reflectance Spectroscopy” / “Reflexionsspektroskopie” Springer 1969