Modern Methods in Heterogeneous Catalysis Research

Diffuse Reflectance Spectroscopy in Heterogeneous Catalysis

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Lecture Series
Heterogeneous Catalysis

Outline

1. Some theory
2. Technical solutions
3. Applications

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2. Technical solutions
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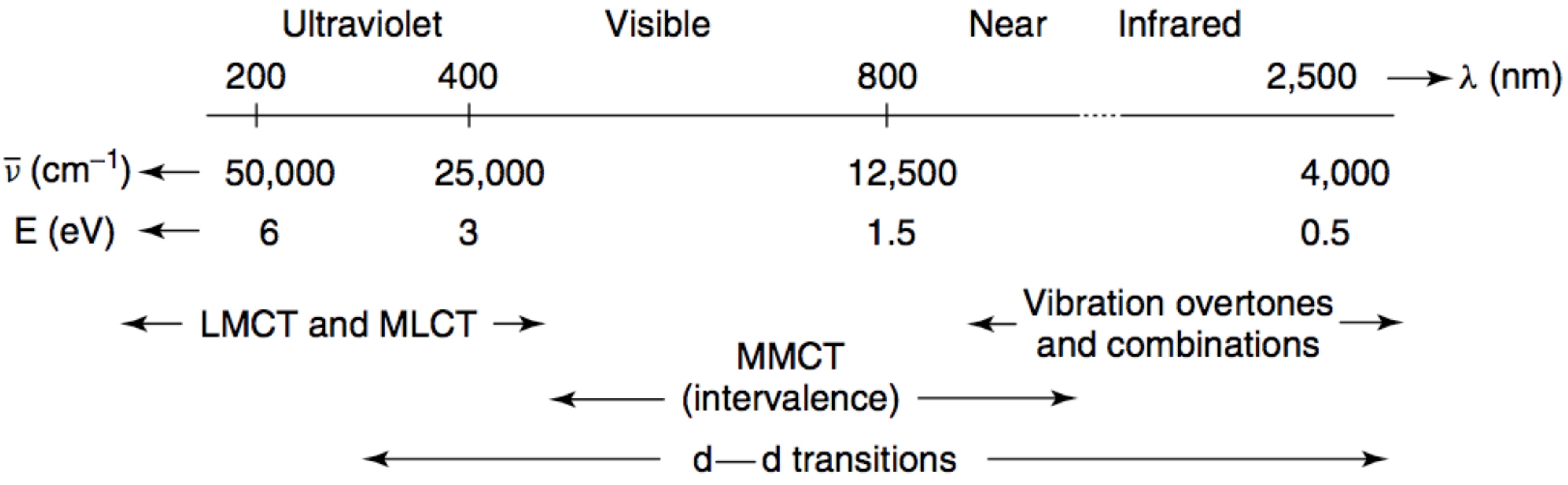
Electromagnetic spectrum and transitions in molecules



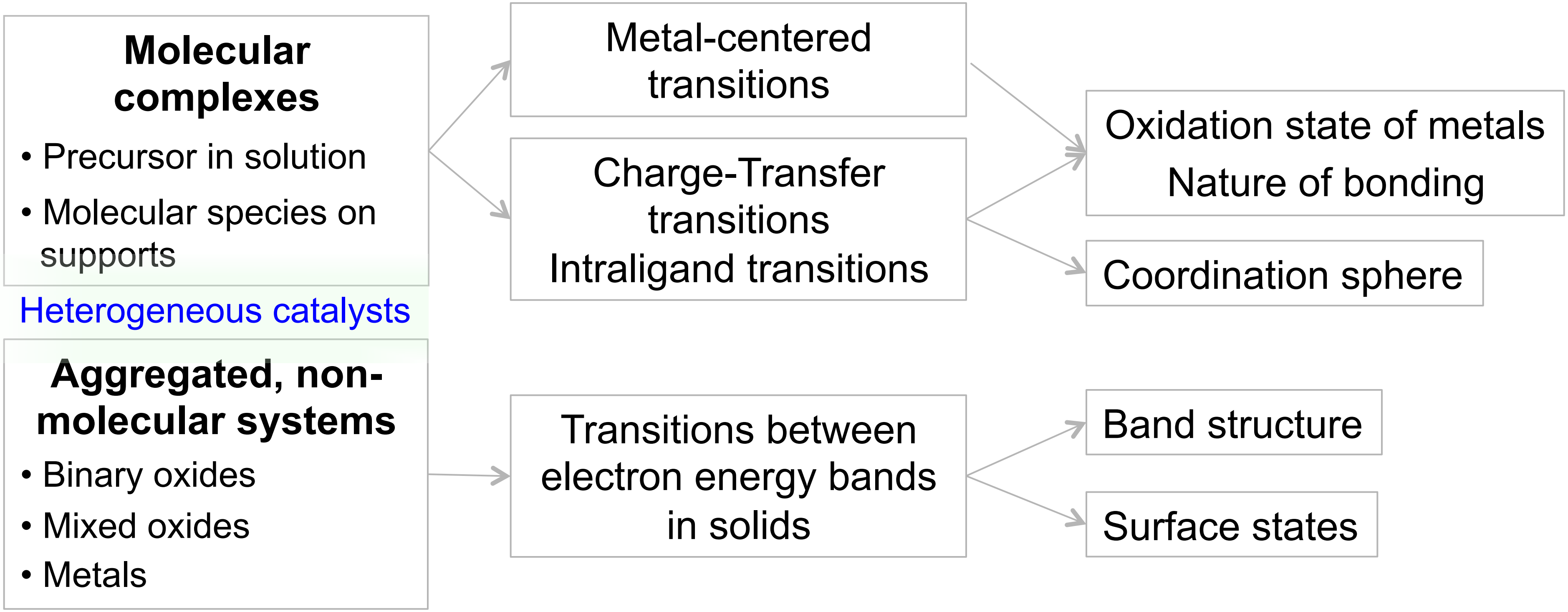
Z. Sojka et al. Handbook of Heterogeneous Catalyis ,Chapter 3.2.3.2

LMCT	ligand-to-metal-charge-transfer
MLCT	metal-to-ligand-charge-transfer
MMCT	metal-to-metal-charge-transfer

Spectroscopy using UV-visible-NIR light

What can we learn from UV-vis-NIR spectroscopy in heterogeneous catalysis?

The spectrum is a function of the physical-chemical properties of the absorbing / emitting system



Molecular complexes

- Precursor in solution
- Molecular species on supports

Heterogeneous catalysts

Aggregated, non-molecular systems

- Binary oxides
- Mixed oxides
- Metals

Metal-centered transitions

Charge-Transfer transitions
Intraligand transitions

Transitions between electron energy bands in solids

Oxidation state of metals
Nature of bonding

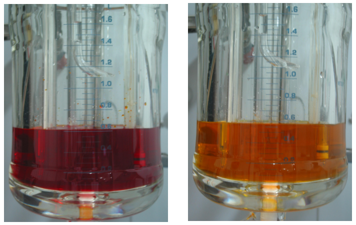
Coordination sphere

Band structure

Surface states

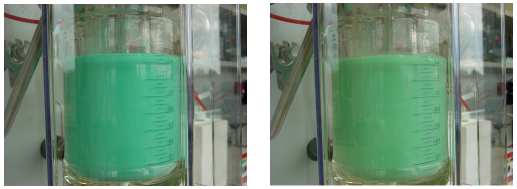
Investigations in heterogeneous catalysis using UV-visible-NIR light

- Analysis of precursor solutions



→ **Transmisssion spectroscopy (TS)**

- Interactions of precursor solutions with supports
- Precipitation and aging



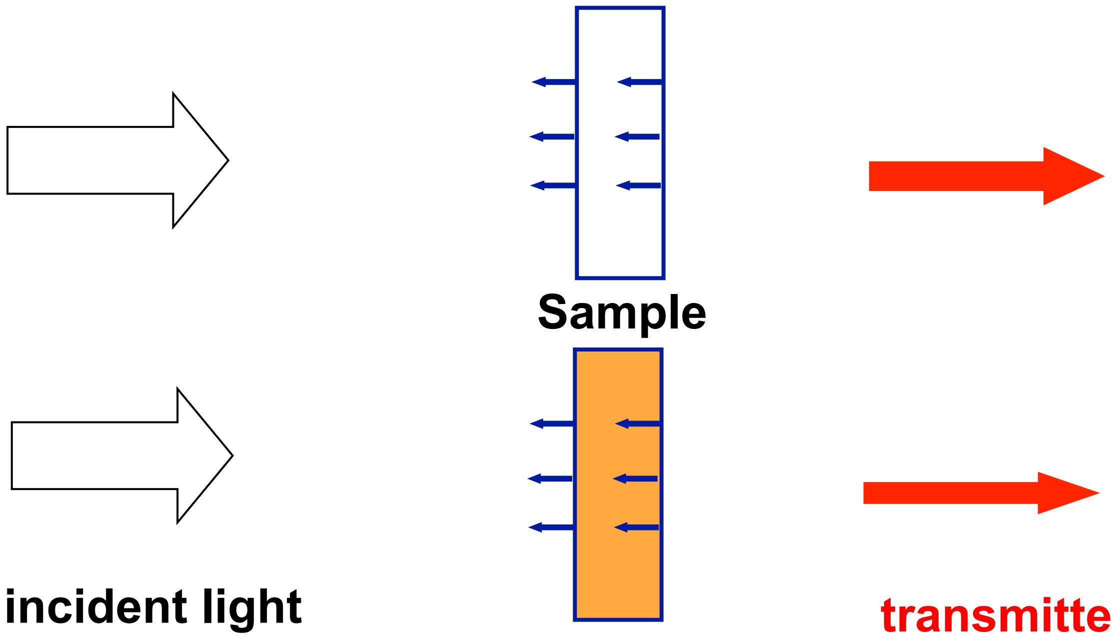
→ **Fiber optics**

- Structure and dispersion of supported species
- Chemical changes during thermal treatment and reaction
- Particle size
- Band gap of semiconductors

→ **Diffuse refectance spectroscopy (DRS)**

- Nature of adsorbed species (intermediates, spectators or poison)

Interaction of light with a solution in transmission



Reference: empty or solvent

Sample

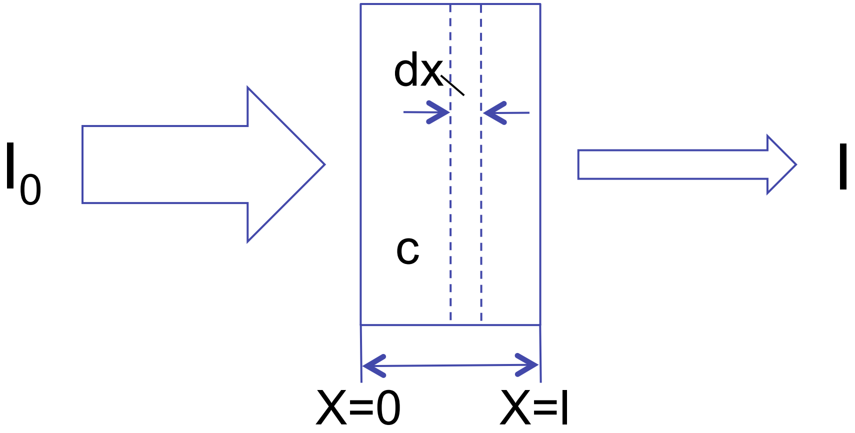
incident light

transmitted light

reflection at phase boundaries

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

Transmitted light and absorption properties



τ: transmittance

α: absorptance

$$\boxed{\tau_\lambda = \frac{I}{I_0} \qquad \alpha_\lambda = \frac{I_0 - I}{I_0} \qquad \tau_\lambda = 1 - \alpha_\lambda}$$

$$dI = -I\,\kappa\,c\,dx$$

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]

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

separation of variables and integration over sample thickness l

Transmitted light and absorption properties

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

Lambert-Beer Law

$$\ln\left(\frac{I}{I_0}\right)_\lambda = A_e = \kappa\, c\, l = -\ln(\tau)$$

napierian absorbance
Napier-Absorbanz

$$\log e = 0.434$$

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

$$\varepsilon = 0.434\kappa$$

(decadic) absorbance
dekadische Absorbanz

standard spectroscopy software uses A_{10}!

extinction	E (means absorbed + scattered light (negligible in solutions))
absorbance	A (A_{10} or A_e)

These quantities are DIMENSIONLESS !!!!

Valid only in diluted solutions c< 0.01 mol/l

Study of precursor solutions in catalyst synthesis

Investigation of precursor solutions and mother liquor during synthesis of a complex MoVTeNb oxide by hydrothermal synthesis

Filtrate

(mother liquor)

$Mo^{VI}Mo^{V}$

Molybdenum blue

and

$[Te(Mo,V)_6O_{24}]^{n-}$

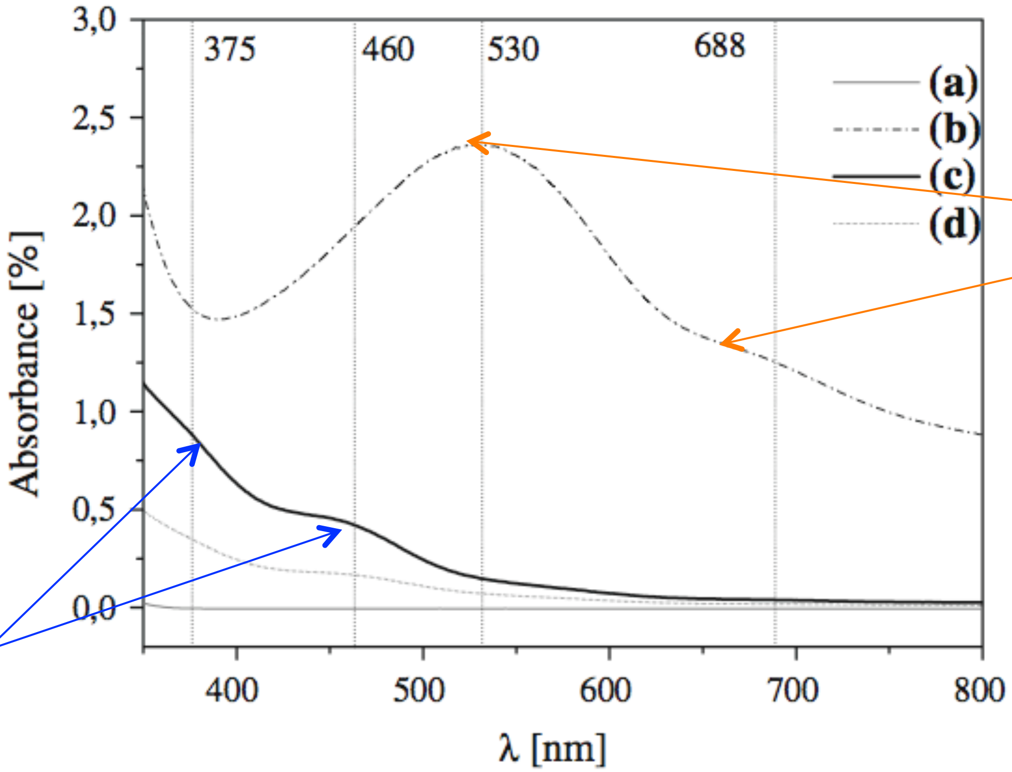
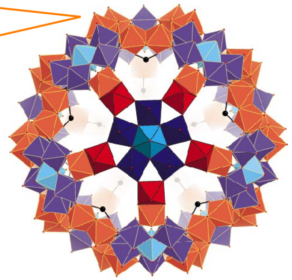


Fig. 2 UV/Vis spectra of aqueous solutions of (**a**) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (298 K, pH = 5.2, [Mo] = 0.3 M), (**b**) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ + $VOSO_4 \cdot 5H_2O$ (T = 298 K, pH = 3.05, [Mo] = 0.3 M, molar ratio Mo/V = 1/0.25), (**c**) MoVTe filtrate, and (**d**) MoVTeNb filtrate

Precursor solution

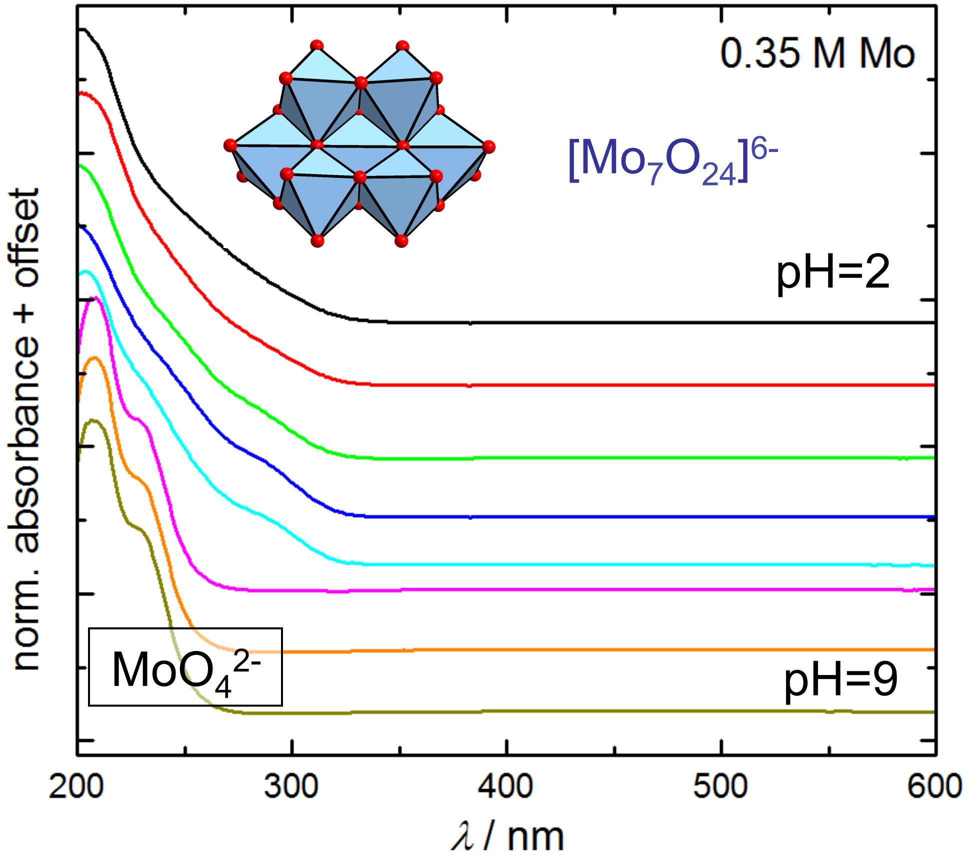
$Mo^{VI}_{72}V^{IV}_{30}$



A. Celaya Sanfiz et al., Topics in Catalysis, 50 (2008) 19.

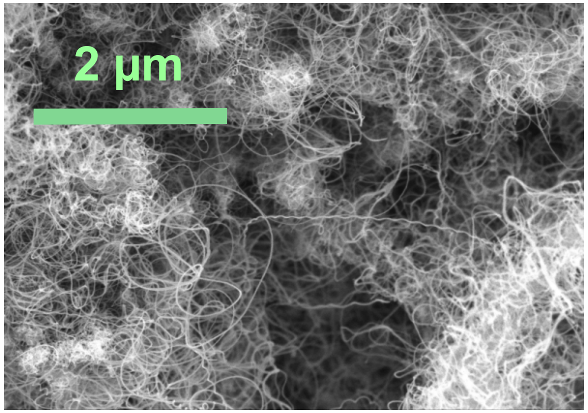
Study of precursor solutions in catalyst synthesis

Condensation of Mo oxo ions in aqueous solutions
Measurements Sabrina Jung, data analysis required

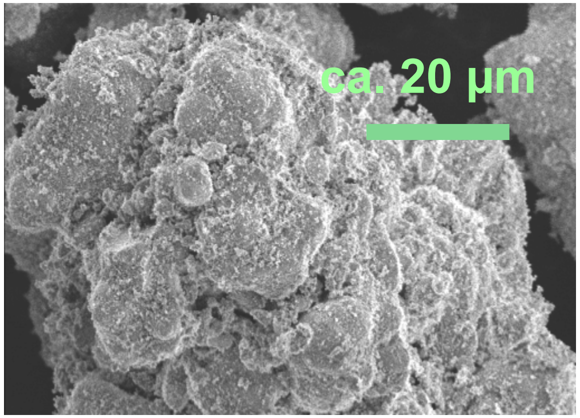


Anal. Chem. 1988, *60,*2055-2059.

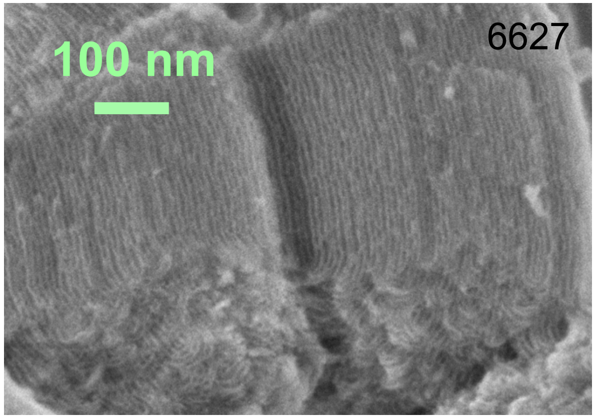
Solid catalysts are mainly powders - typical catalyst particles



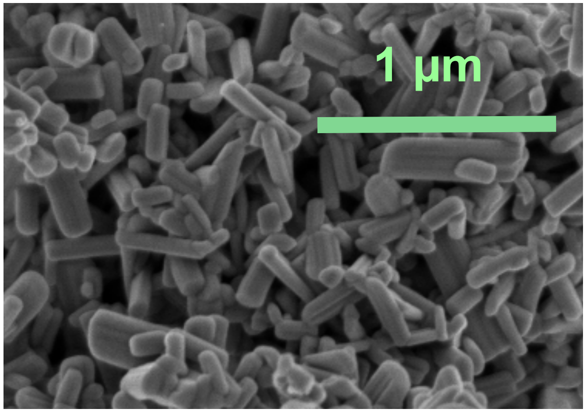
MWCNT



ZrO_2



SiO_2



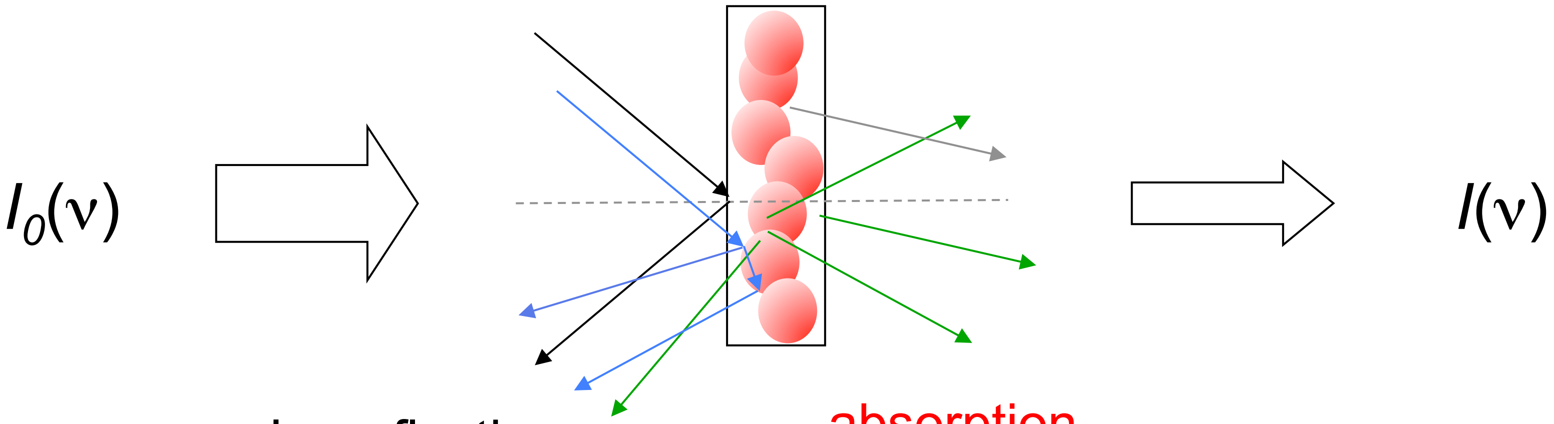
$MoVTeNbO_x$

Interaction of light with solid matter in transmission

light source

Pressed disk of powdered sample

detector



$I_0(\nu)$

$I(\nu)$

specular reflection

diffuse reflection: multiple reflection at phase boundaries

refraction

absorption

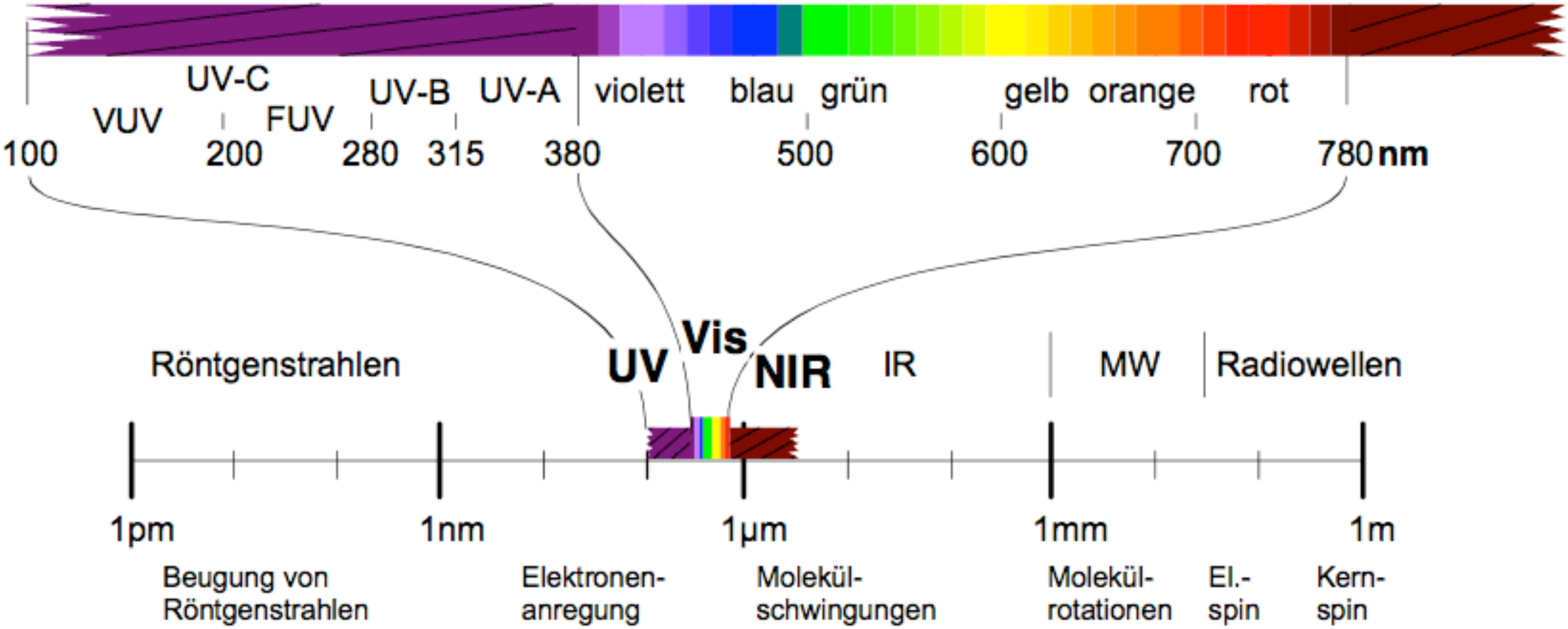
scattering

- elastic (Rayleigh, Mie) ν
  inelastic (Raman) $\nu \pm \nu_i$

emission ν_e

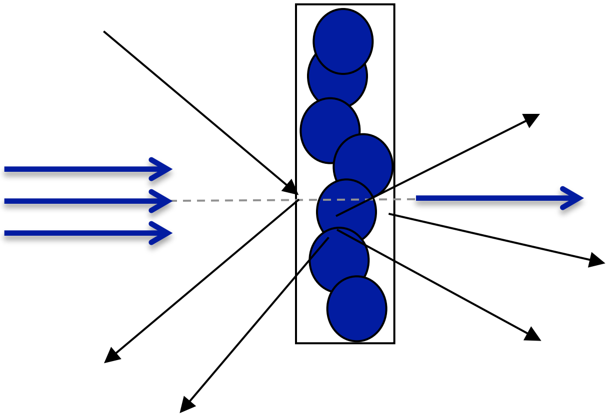
$$\boxed{I_0 = I_r + I_s + I_a + I}$$

Electromagnetic spectrum: wavelength

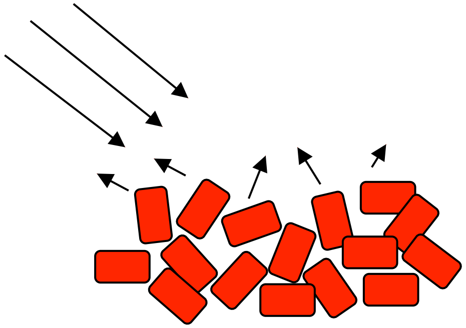


IR spectroscopy of powders

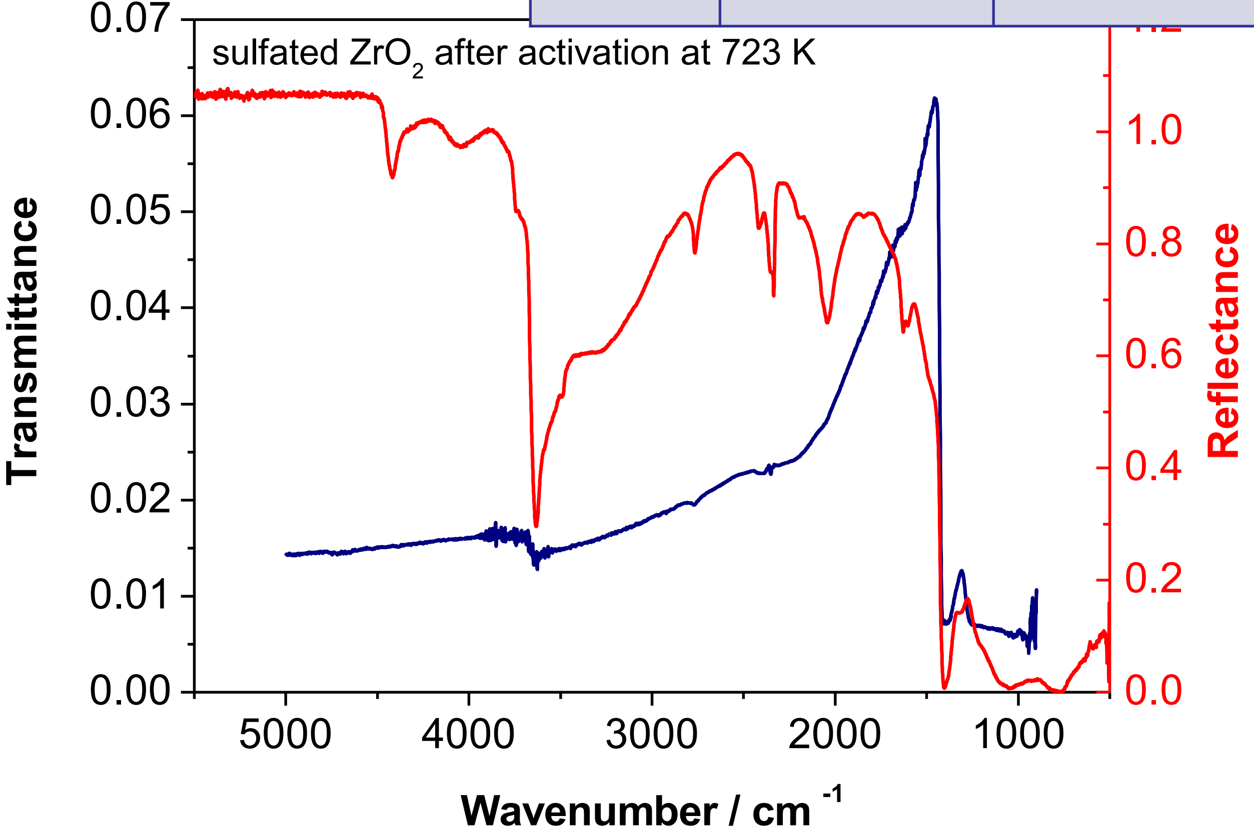
Infrared region	Wavelength (nm)	Wavenumber (cm^{-1})
far	1×10^6 - 5×10^4	10-200
mid	5×10^4 - 2500	200-4000
near	2500 - 1000	4000-10000



Transmission



Reflectance

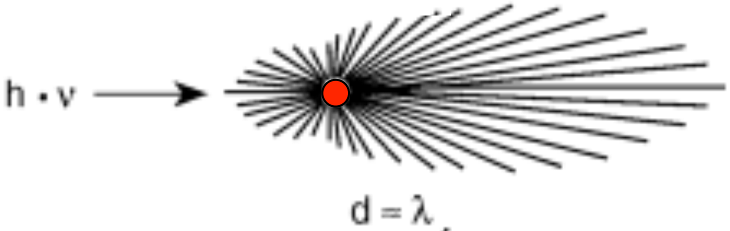


- Scattering is considerable for colloids and solids when the wavelength is in the order of magnitude of the particle size – DRIFTS beneficial
- Transmission provides advantage in terms of quantification

Single scattering and particle size

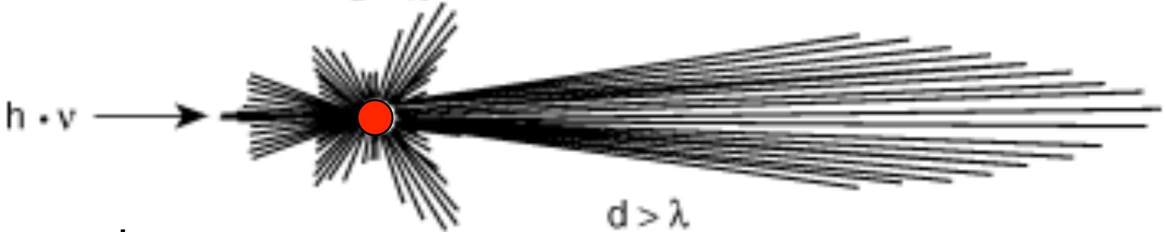
deflection of electromagnetic or corpuscular radiation from its original direction

d < λ: Rayleigh scattering
isotropic distribution
wavelength dependent: $I_s \sim 1/\lambda^4$

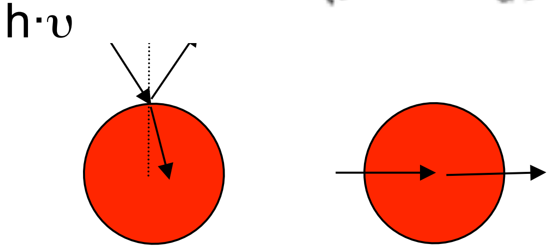


d = λ: Mie scattering
in forward and backward directions
wavelength independent

Mie Theory:
- Isotropic particles
- Not in contact with each other
- Important in colloidal media



d > λ: Mie scattering
predominantly in forward direction
wavelength independent



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

Quelle: RÖMPP on line

	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

Specular and 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

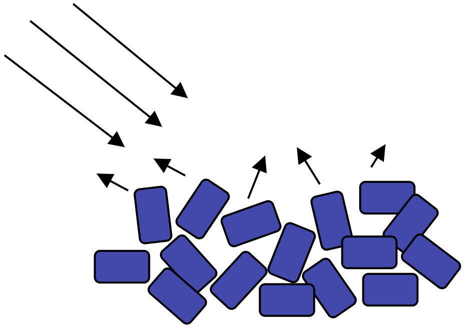
reflecting power called
"reflectivity"

Diffuse

multiple reflections at
surfaces of small
particles

reflecting power called
"reflectance"

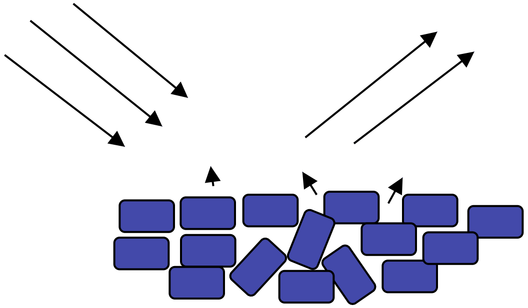
Diffuse reflection (DR)



Intensity of diffusely reflected light independent of angle of incidence

Result of multiple reflection, refraction, and scattering inside the sample

Randomly oriented crystals in a powder:
light diffusely reflected

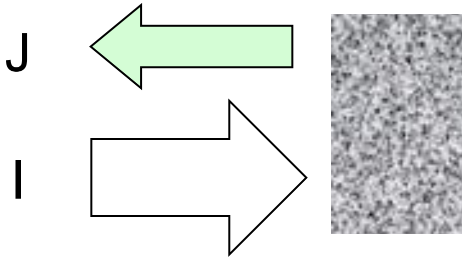


Flattening of the surface or pressing of a pellet can cause orientation of the crystals, which are “elementary mirrors”
Causes “glossy peaks” if angle of observation corresponds to angle of incidence
Can be prevented by dilution

Can we extract the absorption properties of our sample from the diffuse reflected light?

Theory of Diffuse Reflectance Spectroscopy (DRS)

- For analysis of the multiple scattered light, a phenomenological theory is used that allows separation of absorbance and scattering constants
- The spectrometer measures the Reflectance R(v), which is **not** proportional to the concentration of the absorbing entity



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

R...reflectance

2 constants are needed to describe the reflectance:

absorption coefficient	***K***	(function of the frequency)
scattering coefficient	***S***	(independent of frequency, but S increases with energy in case of fine powders d<λ, $I_s \sim 1/\lambda^4$)

Experimental condition: diffuse reflectance of a layer with infinite thickness R_∞

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

G. Kortüm, "Reflectance Spectroscopy" / "Reflexionsspektroskopie" Springer, Berlin 1969.

Quantification of DR spectra: Remission function

- The Schuster-Kubelka-Munk (SKM) model allows to obtain **quantitatively** the absorption spectrum of a solid from a diffuse reflectance measurement, provided a number of **experimental conditions** are fulfilled
- The diffuse reflectance of a layer with infinite thickness R_∞ is linked with the absorption coefficient *K* and the scattering coefficient *S* by the Schuster-Kubelka-Munk or remission function:

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

Kubelka-Munk function

- The Kubelka-Munk function transforms the measured spectrum *R(v)* into the absorption spectrum *K(v)*
- In the derivation of the Kubelka-Munk function, monochromatic radiation is assumed !
- The **"infinite thickness"** is generally obtained with a layer depth of 1-2 mm
- Strongly scattering powders (silica) require up to 5 mm

G. Kortüm, "Reflectance Spectroscopy" / "Reflexionsspektroskopie" Springer, Berlin 1969.

Quantification of DR spectra: Remission function

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

$$\log F(R_\infty) = \log K(\lambda) - \log S$$

- A plot of $F(R_\infty)$ as a function of the extinction coefficient K, which is known from transmission measurements, should yield a straight line (confirmed only for weakly absorbing materials)

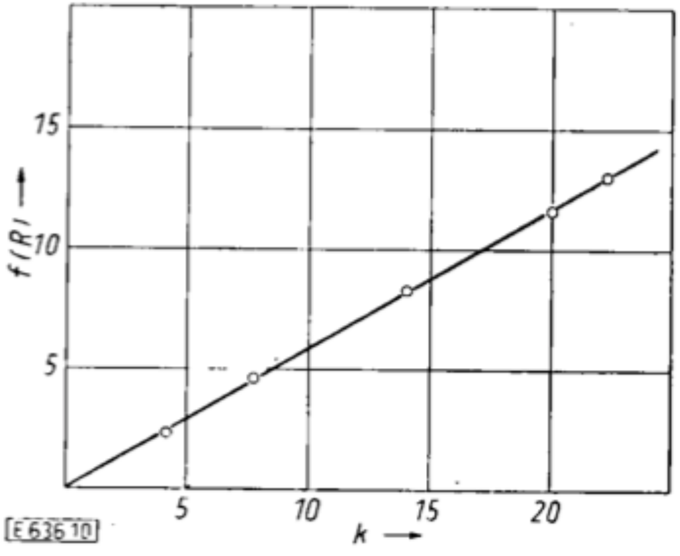


Abb. 10

$$K = \varepsilon c \quad \text{-->} \quad \log F(R_\infty) = (\log \varepsilon + \log c) - \log S$$

- The spectrometer measures R_∞'

$$R_\infty' = R_\infty(sample) / R_\infty(reference)$$

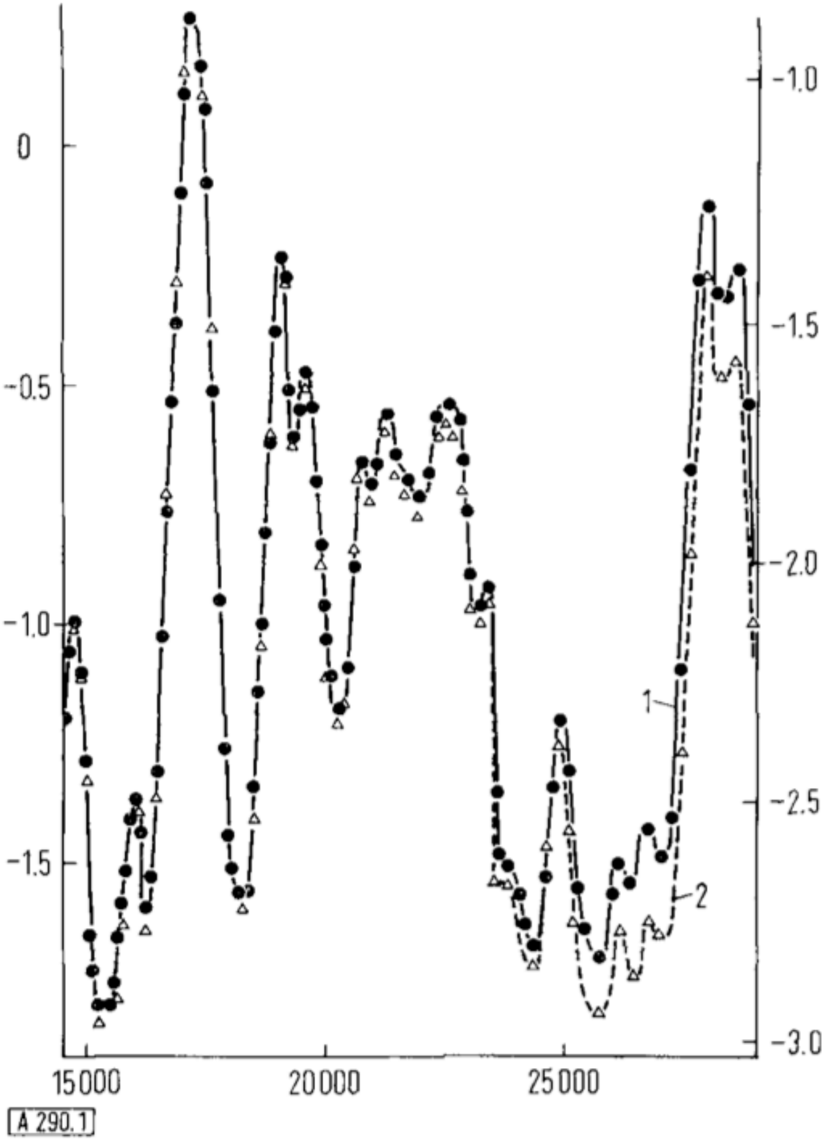
$$R_\infty' = R_\infty \quad if \quad R_\infty(reference) = 1 \;\; (K \rightarrow 0)$$

No absorption of the reference, all light reflected !

Ideal property of white standard!

Kortüm, G.; Schottler, H., ABSORPTION DES MNO4(-)-IONS IN MISCHKRISTALLEN VERSCHIEDENER ZUSAMMENSETZUNG NACH DER REFLEXIONSMETHODE *Zeitschrift fürElektrochemie* 1953, *57* (5), 353-361.

Characteristic color curves



Obtained by displacement in the ordinate direction by – log *S*

$$\log F(R_\infty) = \log K(\lambda) - \log S$$

Fig. 1. Transmittance spectrum (Curve 1) and reflectance spectrum (Curve ***2)*** of a didymium-glass filter. The transmittance spectrum was measured relative to quartz glass ***0.5*** mm thick, the reflectance spectrum relative to powdered colorless glass.

Ordinates: left (Curve 1): log *E*.

right (Curve 2): log $F(R_\infty)$

Abscissa: Wavenumber [cm^{-1}].

Kortüm, G.; Braun, W.; Herzog, G., Principles and Techniques of Diffuse-Reflectance Spectroscopy. *Angewandte Chemie International Edition in English* 1963, *2* (7), 333-341.

Scattering coefficients

- The wavelength dependence of *S* can be estimated experimentally from the Kubelka-Munk function, if the related values of *K* are available from transmission measurements
- Here it is essential that the spectra be not altered by interactions due to solvation or adsorption

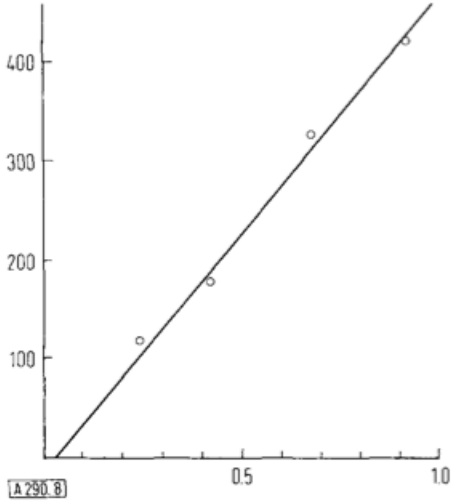


Fig. 8. Dependence of the scattering coefficient on grain-size, measured on the four samples described in Figure 7.

Ordinate: Scattering coefficient, s $[\mathrm{cm}^{-1}]$.

Abscissa: $1/\sqrt{\bar{d}^2}$ [d in μ].

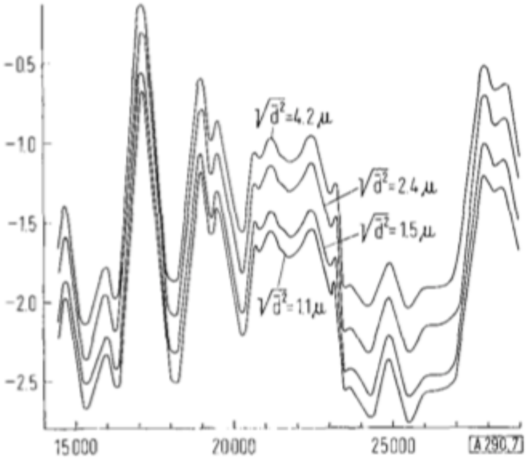


Fig. 7. Effect of grain-size (root-mean-square grain-diameter) on the reflectance spectrum of a pulverized didymium-glass filter, measured against MgO.

Ordinate: log $F(R_{\infty})$.

Abscissa: Wave number $[\mathrm{cm}^{-1}]$.

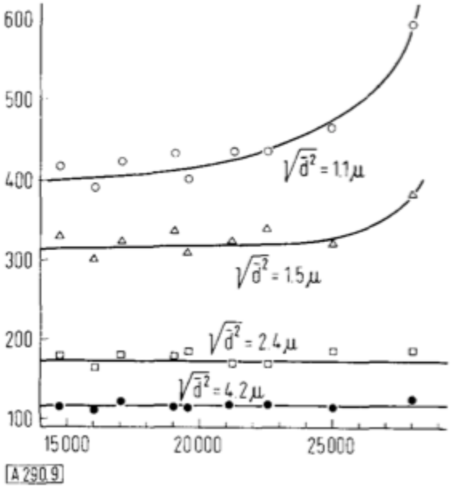


Fig. 9. Dependence of the scattering coefficient on wavelength, for various grain-sizes. Measured on the four samples described in Figure 7.

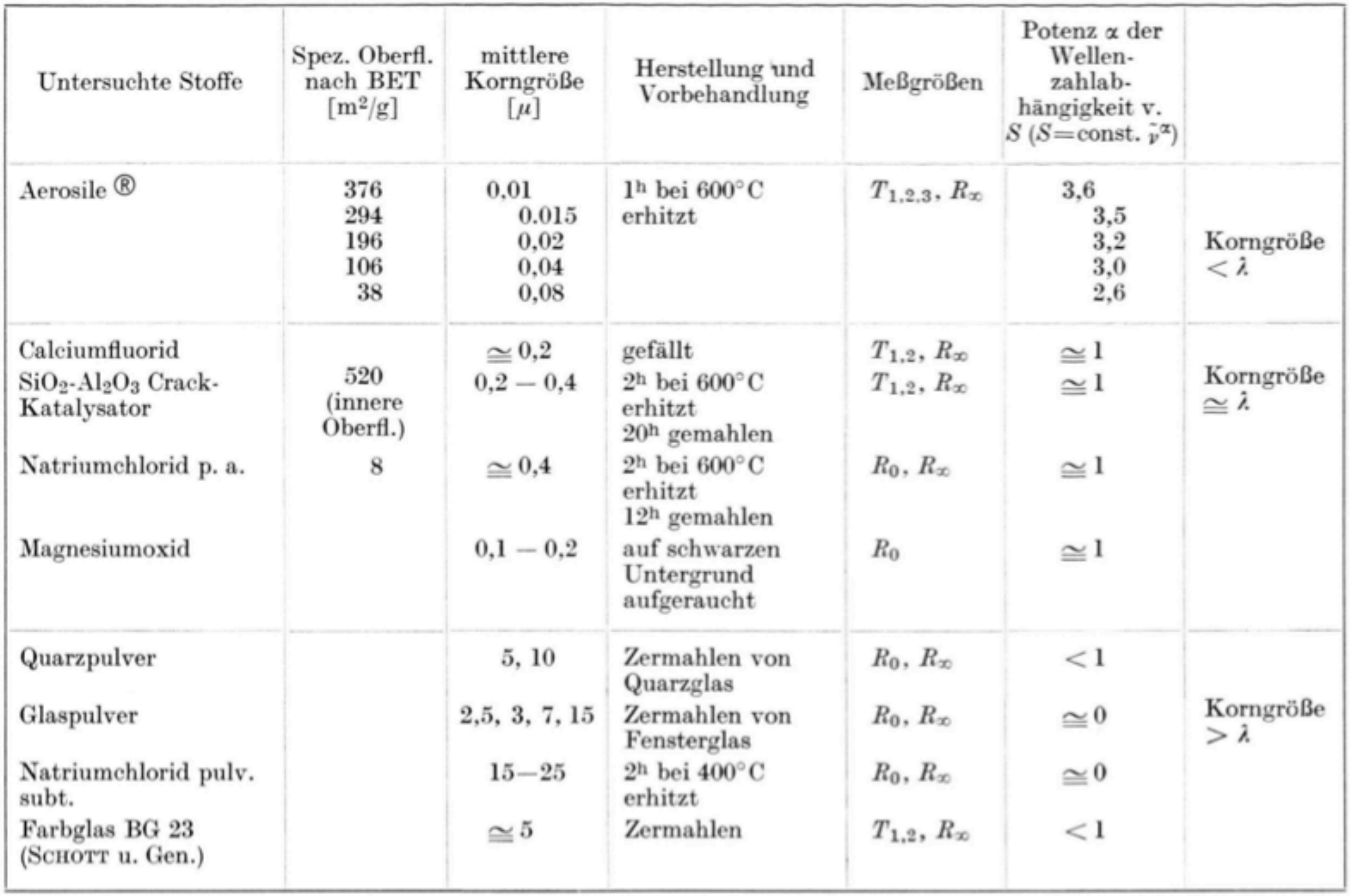
Ordinate: Scattering coefficient, s $[\mathrm{cm}^{-1}]$.

Abscissa: Wave number $[\mathrm{cm}^{-1}]$.

Kortum, G.; Oelkrug, D.
UBER DEN STREUKOEFFIZIENTEN DER KUBELKA-MUNK-THEORIE
*Zeitschrift für Naturforschung,*1964, *A 19* (1), 28-37.

Scattering coefficients $S \propto \bar{\nu}^{\alpha}$

Kortum, G.; Oelkrug, D.
UBER DEN STREUKOEFFIZIENTEN DER KUBELKA-MUNK-THEORIE
*Zeitschrift für Naturforschung,*1964, *A 19* (1), 28-37.



Untersuchte Stoffe	Spez. Oberfl. nach BET $[m^2/g]$	mittlere Korngröße $[\mu]$	Herstellung und Vorbehandlung	Meßgrößen	Potenz α der Wellenzahlabhängigkeit v. S (S=const. $\tilde{\nu}^{\alpha}$)	
Aerosile ®	376	0,01	1^h bei 600°C erhitzt	$T_{1,2,3}$, R_∞	3,6	Korngröße $< \lambda$
	294	0.015			3,5	
	196	0,02			3,2	
	106	0,04			3,0	
	38	0,08			2,6	
Calciumfluorid		$\simeq 0{,}2$	gefällt	$T_{1,2}$, R_∞	$\simeq 1$	Korngröße $\simeq \lambda$
SiO_2-Al_2O_3 Crack-Katalysator	520 (innere Oberfl.)	0,2 – 0,4	2^h bei 600°C erhitzt 20^h gemahlen	$T_{1,2}$, R_∞	$\simeq 1$	
Natriumchlorid p. a.	8	$\simeq 0{,}4$	2^h bei 600°C erhitzt 12^h gemahlen	R_0, R_∞	$\simeq 1$	
Magnesiumoxid		0,1 – 0,2	auf schwarzen Untergrund aufgeraucht	R_0	$\simeq 1$	
Quarzpulver		5, 10	Zermahlen von Quarzglas	R_0, R_∞	< 1	Korngröße $> \lambda$
Glaspulver		2,5, 3, 7, 15	Zermahlen von Fensterglas	R_0, R_∞	$\simeq 0$	
Natriumchlorid pulv. subt.		15–25	2^h bei 400°C erhitzt	R_0, R_∞	$\simeq 0$	
Farbglas BG 23 (Schott u. Gen.)		$\simeq 5$	Zermahlen	$T_{1,2}$, R_∞	< 1	

Tab. 2. Meßgrößen und Eigenschaften der untersuchten Stoffe.

Quantification of DR spectra of powders: Summary

- The wavelength dependence of *S* can be estimated experimentally from the Kubelka-Munk function, if the related values of *K* are available from transmission measurements (here it is essential that the spectra be not altered by interactions due to solvation or adsorption)
- The scattering coefficient of the standard has to be independent of the wavenumber in the spectral range used (or the wavelength dependence of the scattering coefficient has to be measured)
- The remission function is proportional to *K* **only if *S* is independent of λ ➔particle size!** (S increases with energy in case of fine powders d<λ); if *S=f(λ)*:
    - The relative intensities of the bands are not true
    - Error due to apparent red-shift of bands
    - Reduced scattering due to very small particles favors deep penetration of the radiation into the sample (transmission)
    - Packing density matters
- Regular reflection parts needs to be eliminated through sufficiently high dilution of the sample with a white standard
- Reflectance values R_∞ '< 0.6 should not be measured due to deviations from the Kubelka-Munk theory in case of higher absorption

DRS of adsorbed molecules

- The interaction between adsorbent and adsorptive can be studied as well using the same theory*
- When molecular species on the surface of a support are investigated, dilution with the support eliminates the particle size dependence of the absorption coefficient of the support
- Uncertainties regarding regular reflection are also eliminated
- Dilution can be a problem in in-situ experiments!

*Kortüm, G.; Braun, W.; Herzog, G., Principles and Techniques of Diffuse-Reflectance Spectroscopy. *Angewandte Chemie International Edition in English* 1963, *2* (7), 333-341.

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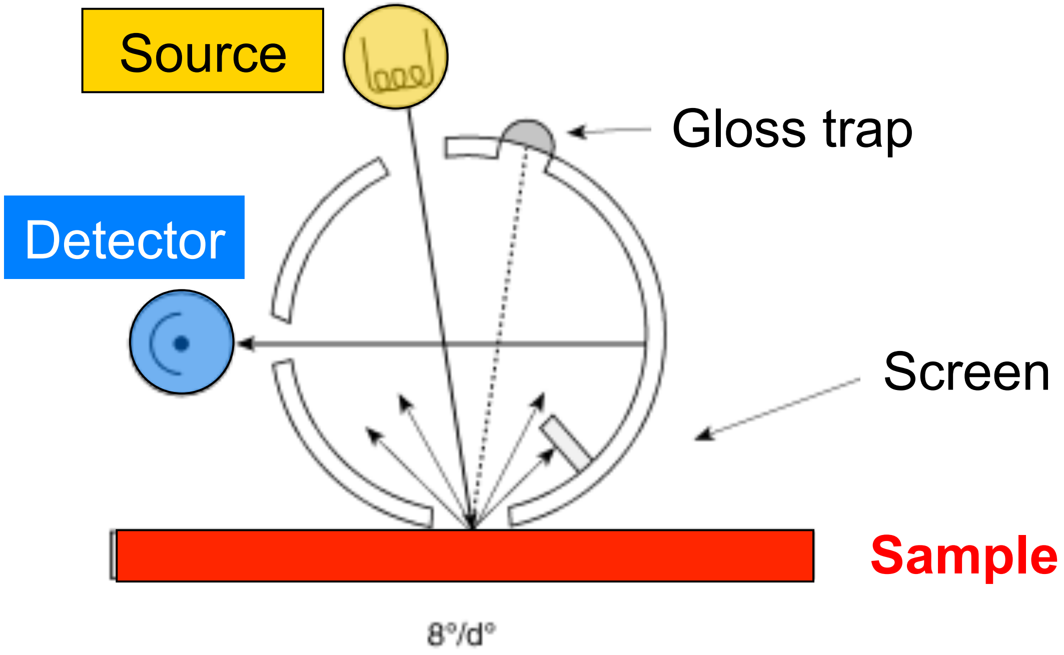
Integrating sphere

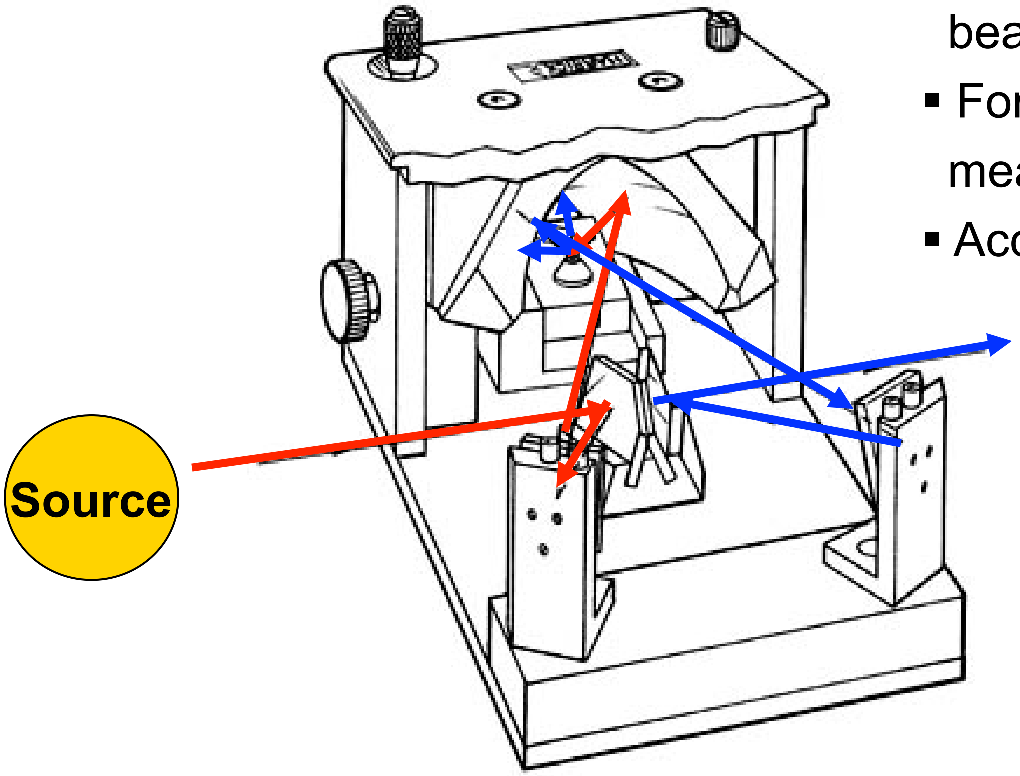


- the larger the sphere the smaller errors from the ports
- the larger the sphere the lower the intensity onto the detector
- typically 60-150 mm diameter
- coatings: $BaSO_4$, Spectralon (for UV-vis), Au
- The flux onto the detector corresponds to 1% of the incident flux or less

F.C. Jentoft, Advances in Catalysis, 52 (2009) 129.
Image: Römpp on-line

Mirror optical accessory for reflection spectroscopy

- Can be placed into the normal sample chamber (in line with beam), no rearrangement necessary
- For reference, consecutive measurement of white standard
- Accessory needs to be aligned



Source

Detector

http://www.harricksci.com/ftir/accessories/group/Praying-Mantis%E2%84%A2-Diffuse-Reflection-Accessory

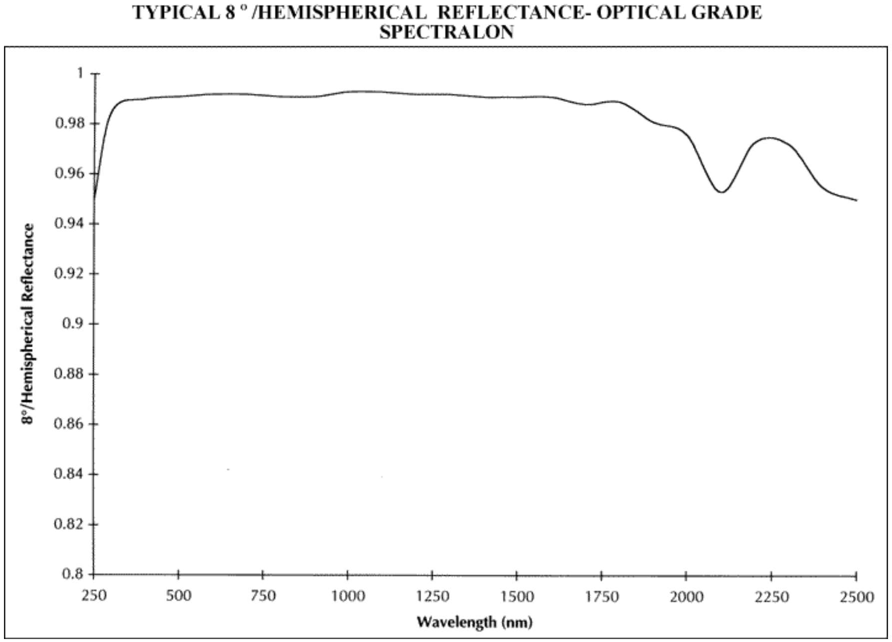
Specular reflection is strongest in forward direction
Collect light in off-axis configuration

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

B. M. Weckhuysen et al., Catalysis Today 49 (1999) 441

White standards

- $BaSO_4$: UV-vis
- MgO (not stable!): UV-vis
- Spectralon: UV-vis-NIR

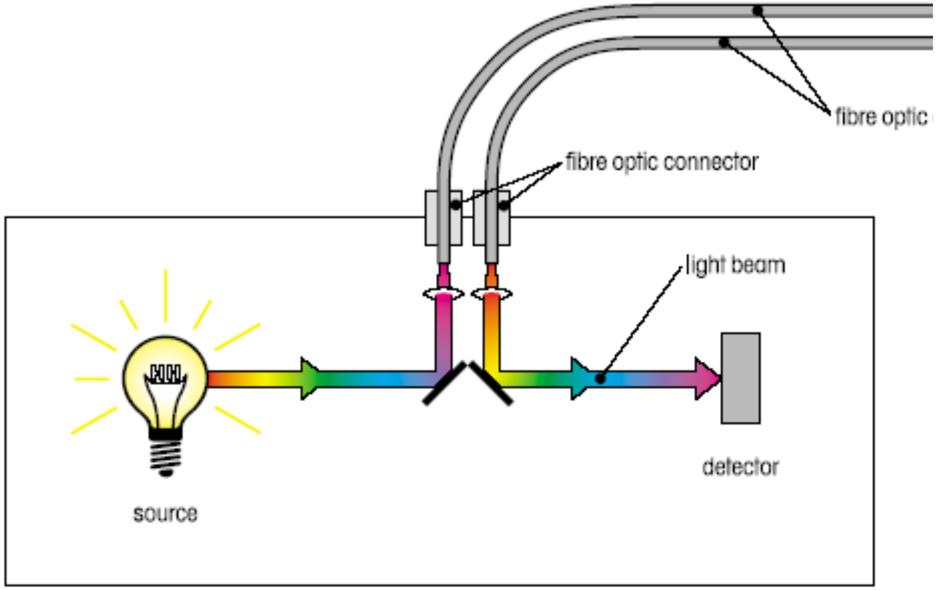


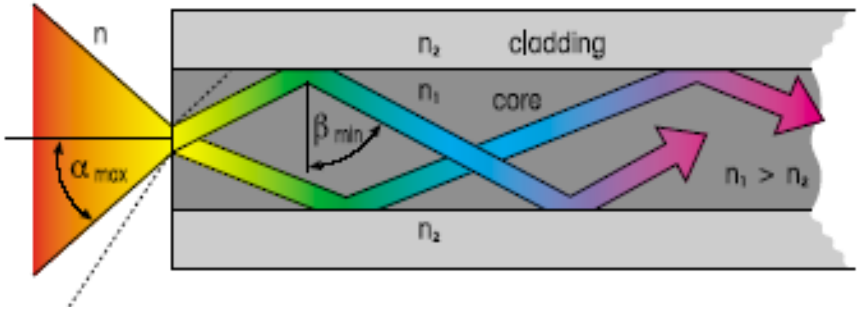
Spectralon® thermoplastic resin, excellent reflectance in UV-vis region

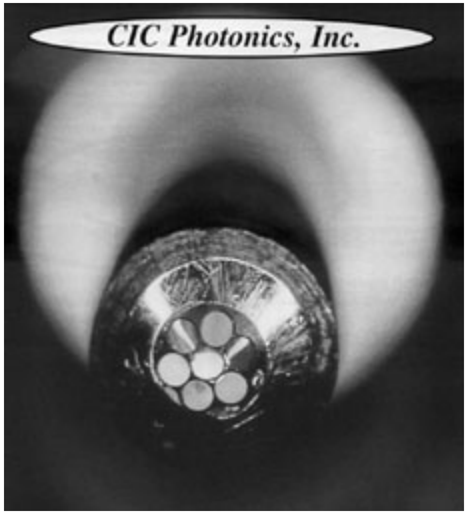
http://www.labsphere.com/products/reflectance-standards-and-targets/reflectance-targets/spectralon-targets.aspx

Fiber optics for UV-vis

Can be integrated into normal reactors







- Fibers made of silica
- Light conducted through total reflectance
- Fiber bundle with 6 illumination fibers around 1 read fiber
- Arrangement avoids collection of specularly reflected light

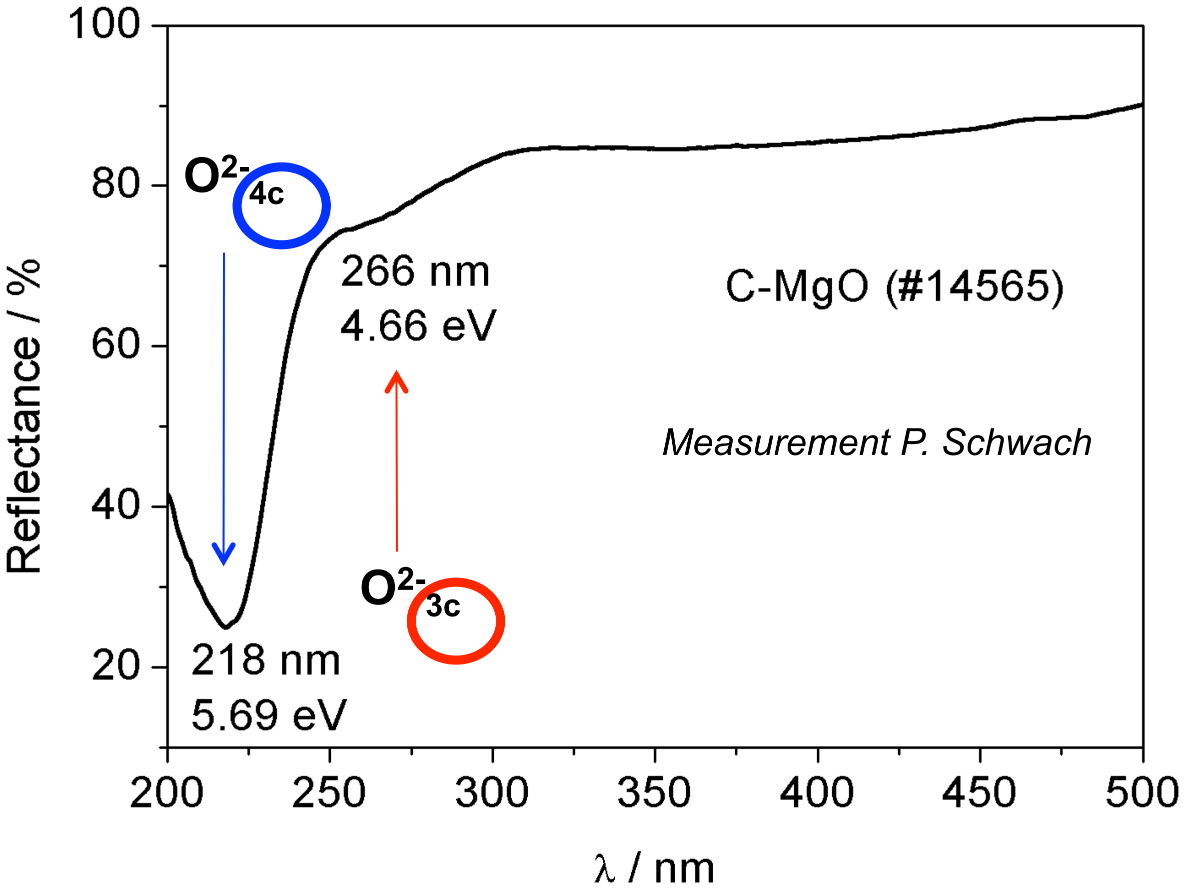
http://www.oceanoptics.com/Products/spectrometers.asp

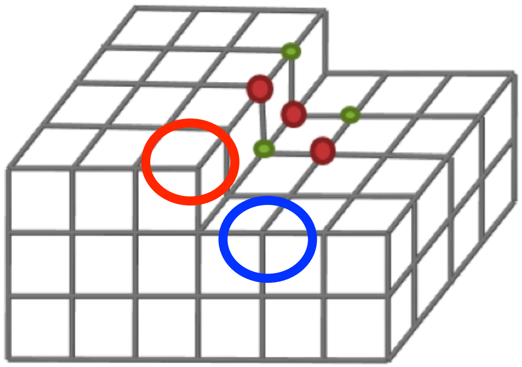
Images: Hellma (http://www.hellma-worldwide.de) and CICP (http://www.cicp.com/home.html)

Outline

1. Some theory
2. Technical solutions
3. Applications

Insulating oxides – typical catalyst supports





P. Schwach *et al.*, Journal of Catalysis 329 (2015) 574–587.

E. Garrone *et al., PHILOSPHICAL MAGAZINE B 42 (1980) 683.*

Semiconductor oxides – supports and bulk catalysts

TiO_2, ZrO_2, CeO_2, ZnO, SnO.

Fe_2O_3, V_2O_5, MoO_3, WO_3, Nb_2O_5, …

(A) Direct transition:

Photons excite electrons

(B) Indirect transition:

Excitation of electrons by photons assisted by concerted vibrations of the crystal lattice (phonons)

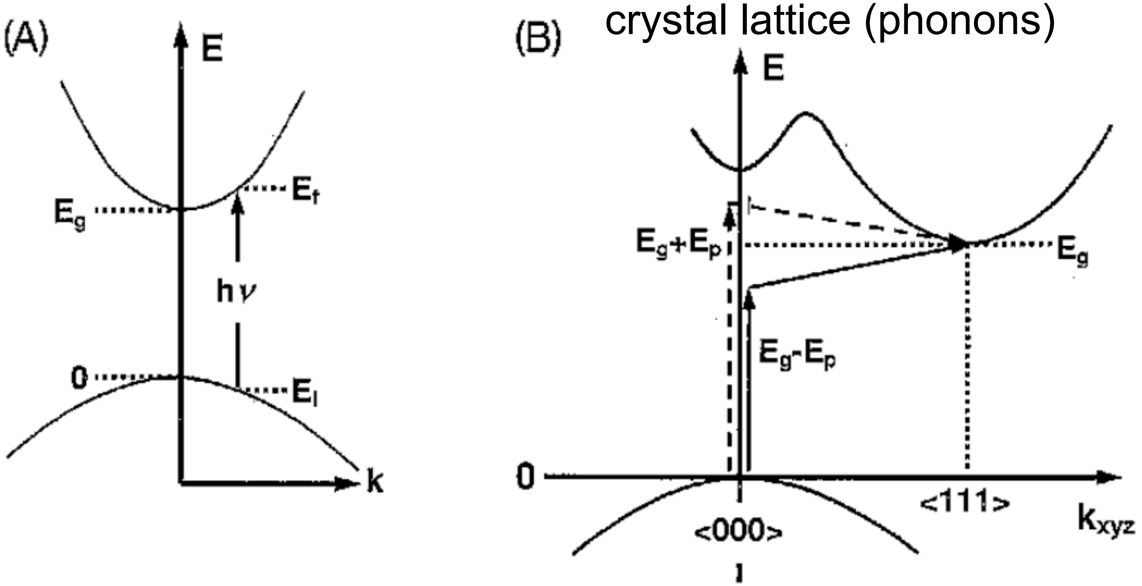


Figure 2.4 Energy versus momentum and possible interband transitions in: (A) a direct-gap two-band system and (B) a solid with conduction band valleys at *k* = <000> and *k* = <111>. Adapted from ref. [26].

Determination of the edge energy

The optical absorption edge energy is defined as the minimum photon energy required to excite an electron from the highest occupied molecular orbital (HOMO, at the top of the valence band in semiconductor domains) to the lowest unoccupied molecular orbital (LUMO, at the bottom of the conduction band)

G. Martra et al., Chapter 2 in Metal Oxide Catalysis, Ed. by S.D. Jackson et al., Wiley-VCH, Weinheim, 2009.

Estimation of E_g from DRS

$$\alpha \propto \frac{(h\nu - E_g)^\eta}{h\nu}$$

$$(\alpha h\nu)^{\frac{1}{\eta}} \propto h\nu - E_g$$

$$Plot \;\; in \;\; in \;\; linear \;\; range:$$

$$y = A(x - B)$$

$$y = (\alpha h\nu)^{\frac{1}{\eta}}$$

$$x = h\nu = photon \;\; energy \;\; (eV)$$

$$x @ y = 0 = B = E_g$$

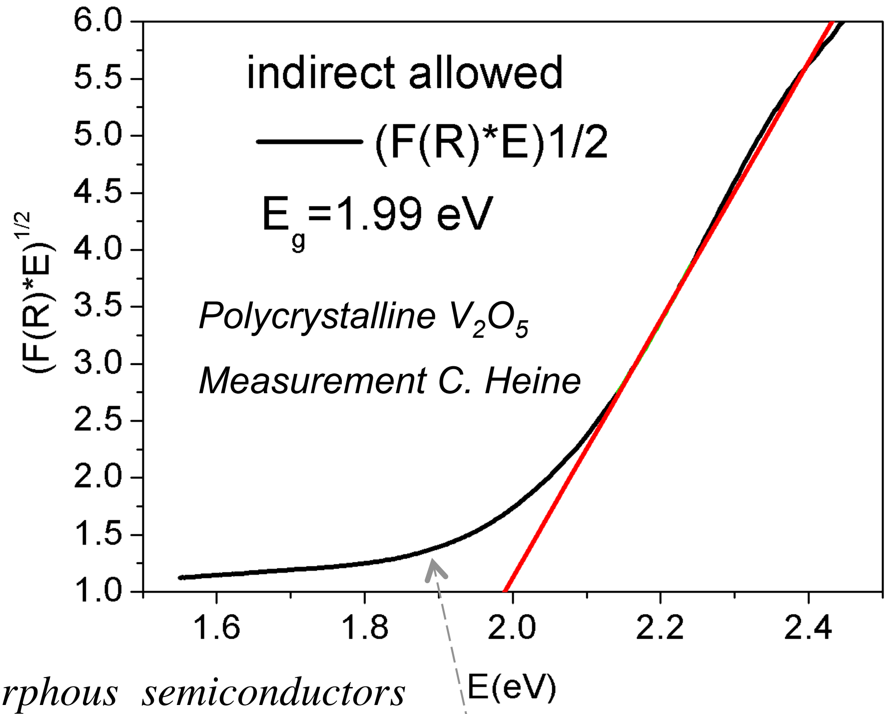
η in crystalline semiconductors:

$\eta = 1/2$ direct – allowed

$\eta = 3/2$ direct – forbidden

$\eta = 2$ indirect – allowed

$\eta = 3$ indirect – forbidden



$\eta = 2$ amorphous semiconductors

α...absorption coefficient in transmission – use F(R) in DRS

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

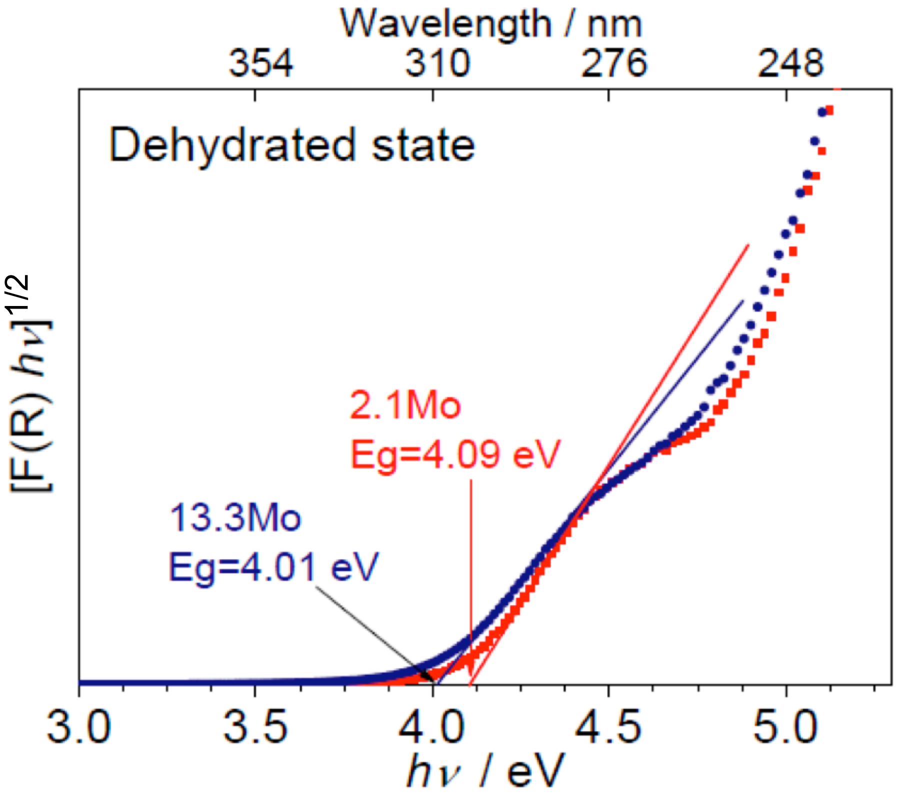
$$K \propto F(R_\infty) \;\; if \;\; S = const.$$

Urbach tail
"fluctuations in the
band gap"

D.G. Barton et al., *J. Phys. Chem. B, 103 (1999) 630.*

Heine, C.; Girgsdies, F.; Trunschke, A.; Schlögl, R.; Eichelbaum, M., The model oxidation catalyst α-V_2O_5: insights from contactless in situ microwave permittivity and conductivity measurements. *Appl. Phys. A* 2013, *112* (2), 289-296.

Supported oxides – small surface domains

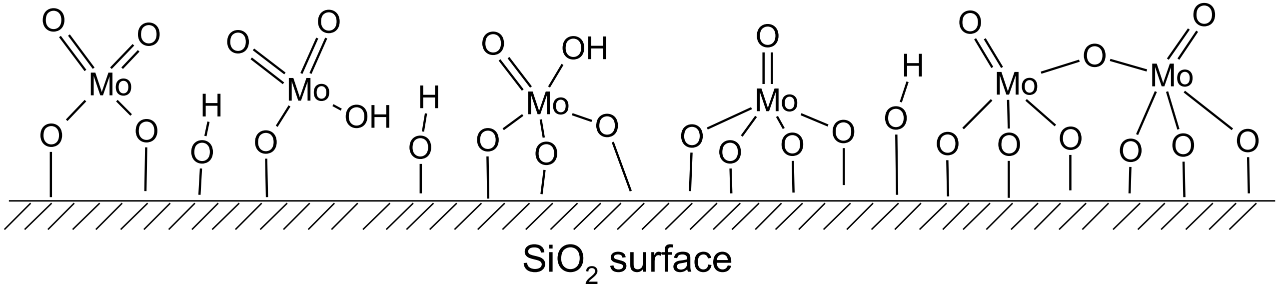


E_g of three-dimensional particles depends on

- Particle size (Q-size effect)
- Bonding geometry/structure

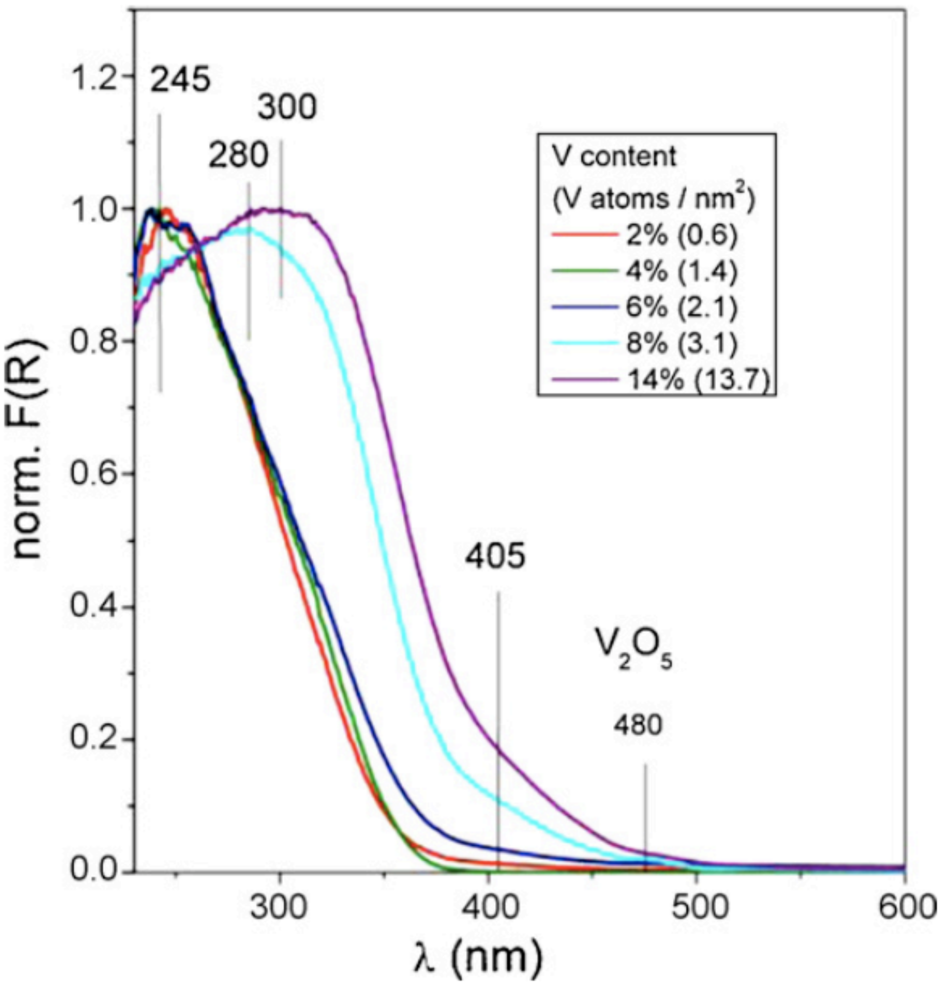
Supported metal oxides

- For small M_xO_y surface domains, the band theory does not apply, but analysis has shown that the broad distribution of energy levels in surface clusters can be treated like bands
- Spectrum requires deconvolution when different clusters are present



K. Amakawa *et al.*, *Angewandte Chemie International Edition* 2013, *52*, 13553.

Highly dispersed vanadium oxide species - LMCT



Isolated and polymerized V_xO_y ?

P. Gruene et al., Catalysis Today 157 (2010) 137.

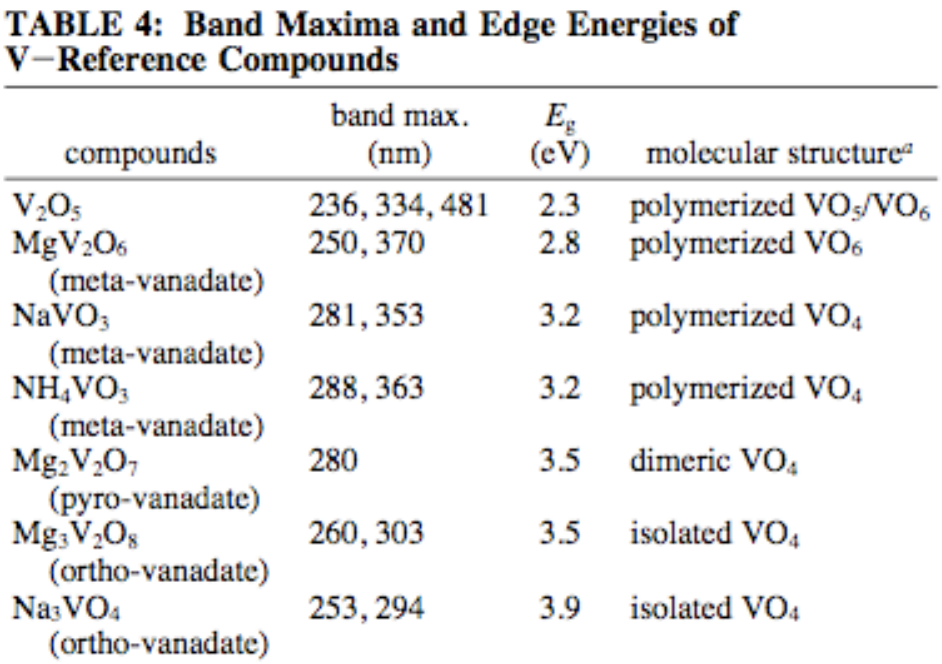
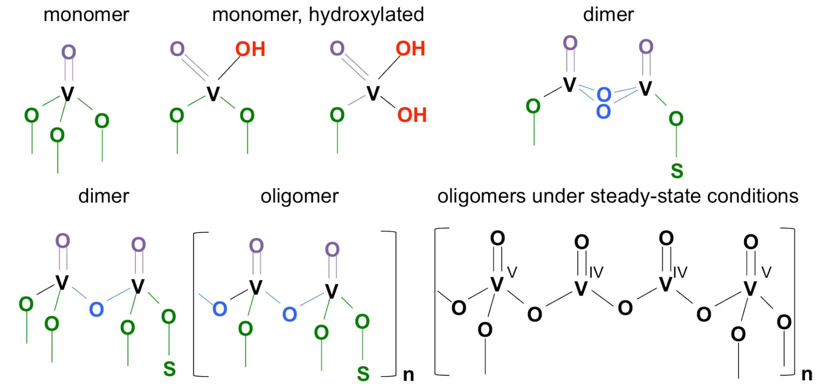


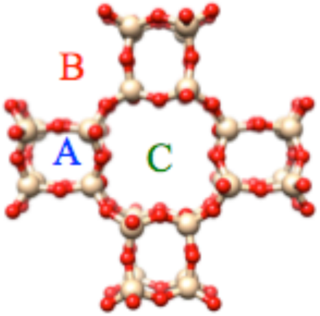
TABLE 4: Band Maxima and Edge Energies of V−Reference Compounds

compounds	band max. (nm)	E_g (eV)	molecular structure[a]
V_2O_5	236, 334, 481	2.3	polymerized VO_5/VO_6
MgV_2O_6 (meta-vanadate)	250, 370	2.8	polymerized VO_6
$NaVO_3$ (meta-vanadate)	281, 353	3.2	polymerized VO_4
NH_4VO_3 (meta-vanadate)	288, 363	3.2	polymerized VO_4
$Mg_2V_2O_7$ (pyro-vanadate)	280	3.5	dimeric VO_4
$Mg_3V_2O_8$ (ortho-vanadate)	260, 303	3.5	isolated VO_4
Na_3VO_4 (ortho-vanadate)	253, 294	3.9	isolated VO_4

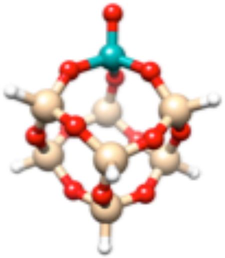
Gao et al., J. Phys. Chem. B 102 (1998) 10842.



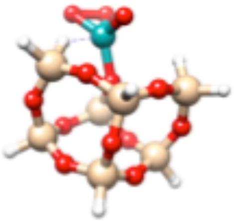
Models of supported vanadium oxide species



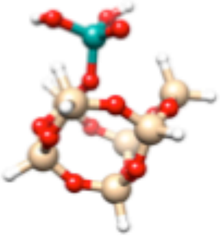
$Si_{32}O_{80}$



A:$VSi_7O_{13}H_7$



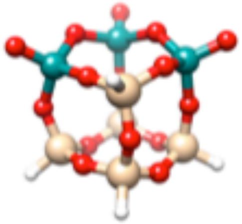
A:$VSi_7O_{13}H_9$



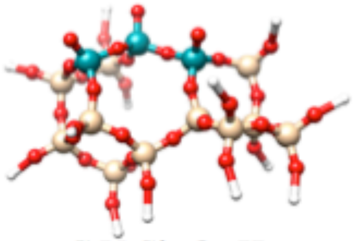
A:$VSi_7O_{13}H_{11}$

A:$V_2Si_6O_{14}H_6$

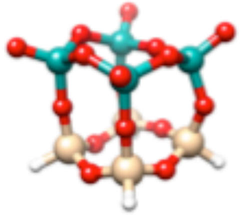
B:$V_2Si_{12}O_{23}H_{12}$



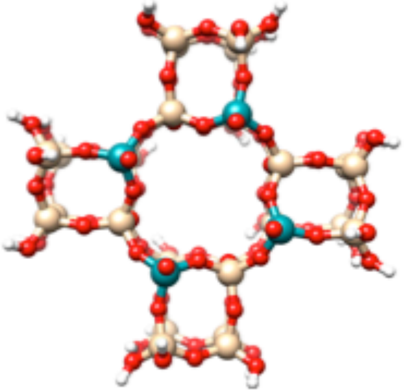
A:$V_3Si_5O_{15}H_5$



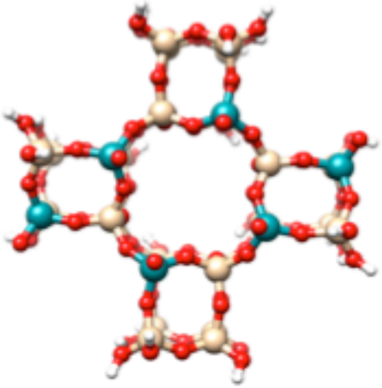
C:$V_3Si_{11}O_{37}H_{15}$



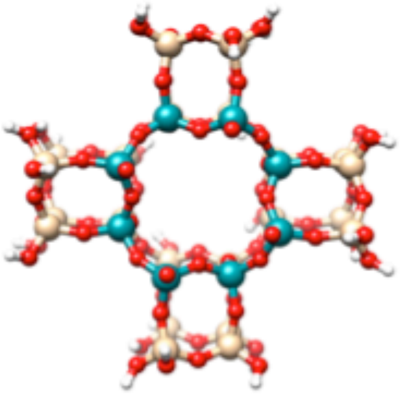
A:$V_4Si_4O_{16}H_4$



C:$V_4Si_{28}O_{80}H_{28}$



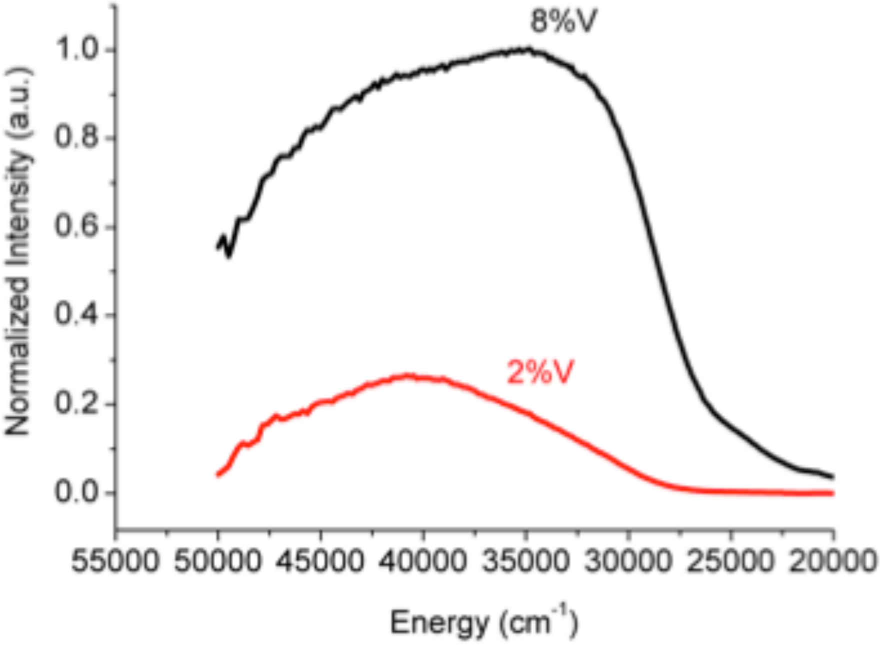
A,C:$V_6Si_{26}O_{80}H_{28}$

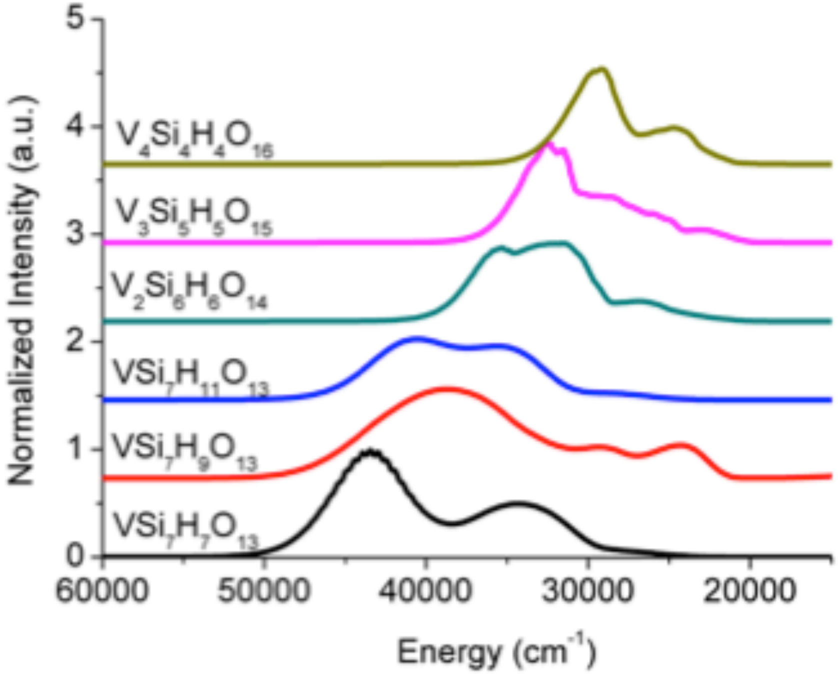


C:$V_8Si_{24}O_{80}H_{28}$

D. Maganas *et al.*, Faraday Discuss., 2016, 188, 181–197

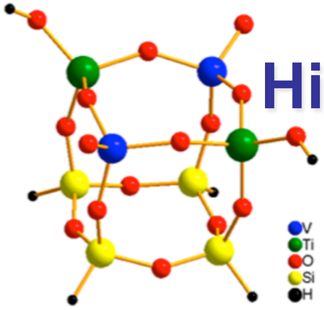
Highly dispersed vanadium oxide species





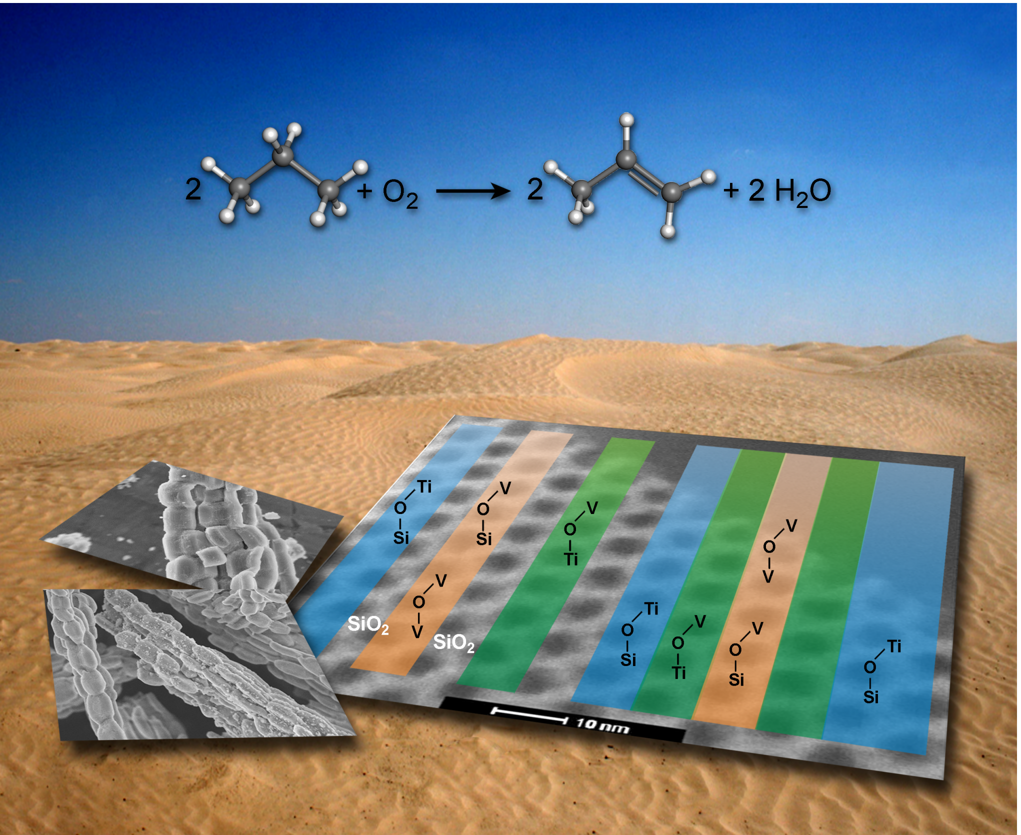
D. Maganas *et al.*, Faraday Discuss., 2016, 188, 181–197

Highly dispersed VO$_x$-TiO$_x$ species - LMCT



(f) $Ti_2V_2Si_4O_{16}H_6$

N. Hamilton, *et al.*, *Catalysis Science & Technology* 2012, *2*, 1346.
S. Klokishner, *et al.*, *Journal of Physical Chemistry C*, 2014, *118*, 14677.



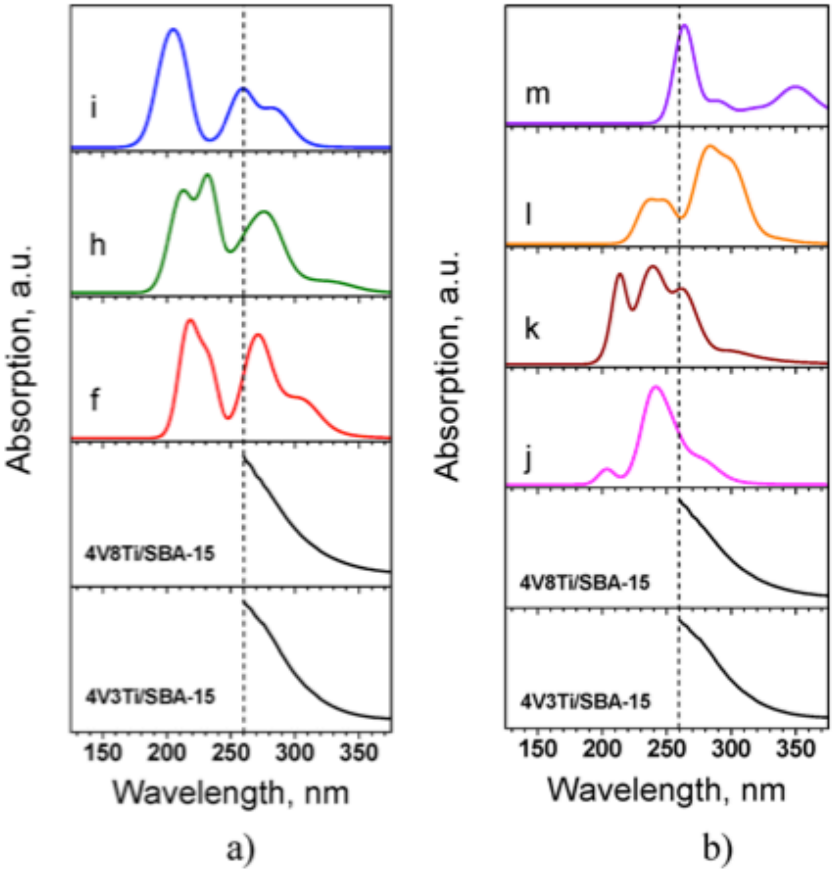
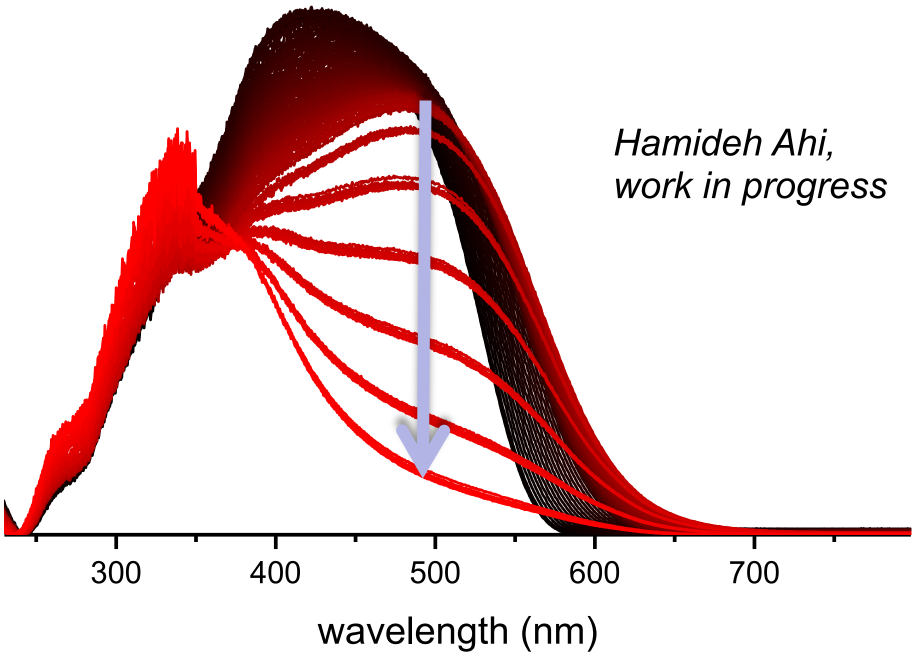


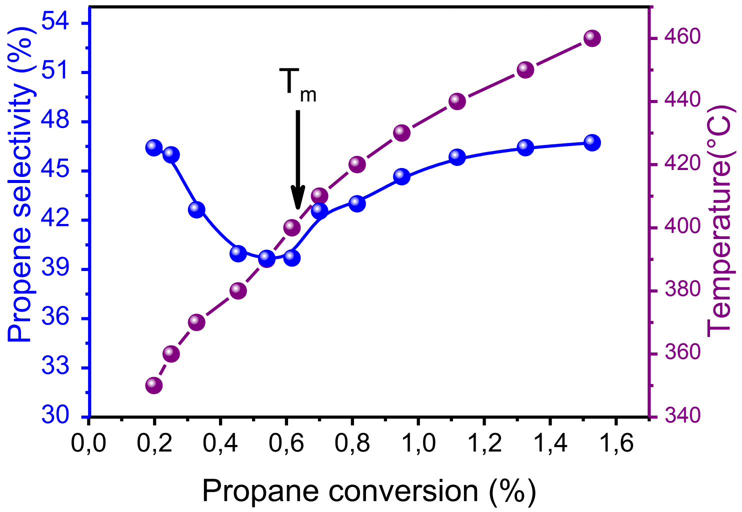
Figure 16. Calculated absorption spectra of species $Ti_2V_2Si_4O_{16}H_6$ (f), $Ti_2V_2Si_4O_{16}H_6$ (h), $Ti_3VSi_4O_{16}H_7$ (i), $Ti_4VSi_4O_{19}H_9$ (j), $Ti_4V_2Si_4O_{21}H_8$ (k), $Ti_4V_3Si_4O_{23}H_7$ (l), and $Ti_4V_4Si_4O_{24}H_4$ (m) and the observed apparent absorption spectra for 4V3Ti/SBA-15 and 4V8Ti/SBA-15. The numeration of species corresponds to that in Figure 4.

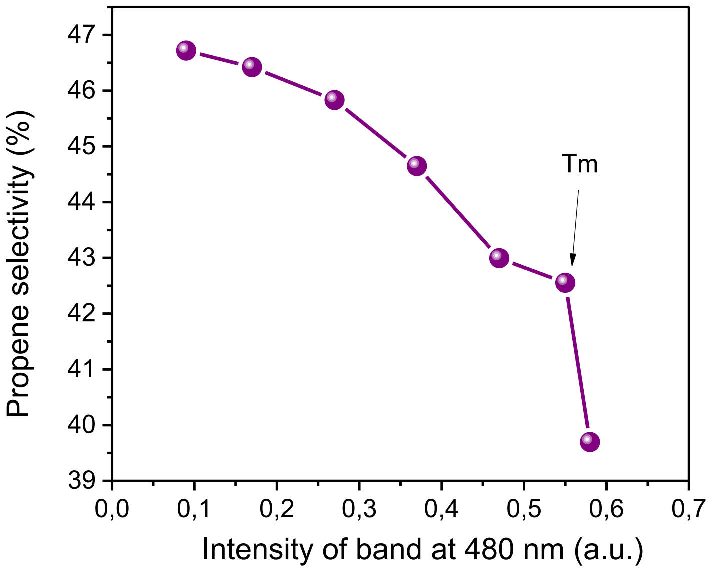
In-situ UV-vis: propane oxidation on K-V_xO_y/SiO_2

LMCT O-2sp → V-3d



Hamideh Ahi,
work in progress

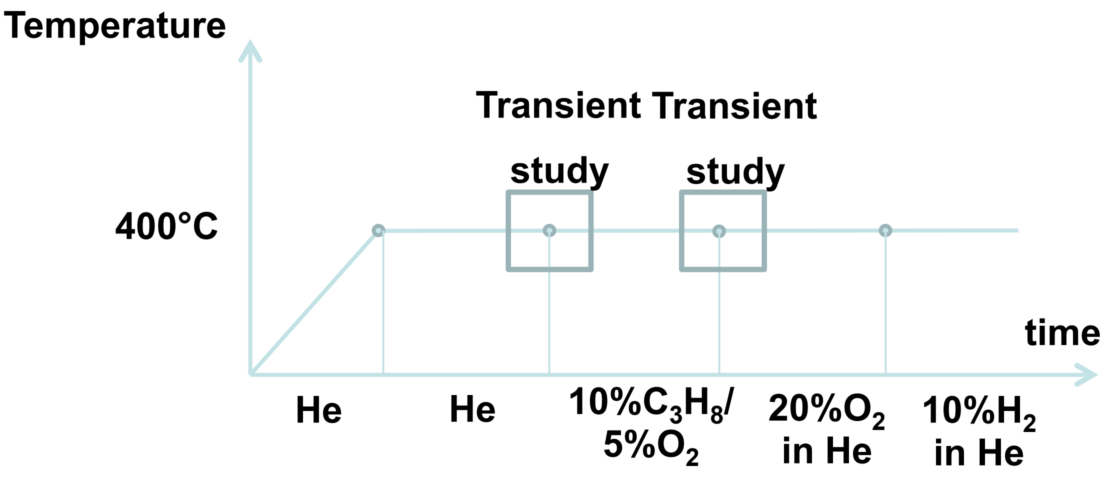




- UV-vis spectroscopy under operation clearly shows that the change in the local coordination of V from square pyramidal (VO_5) to tetrahedral* during melting is reflected in an increase in selectivity

  * to be confirmed by theory

In-situ UV-vis: redox properties / propane oxidation



Temperature

400°C

Transient study

Transient study

time

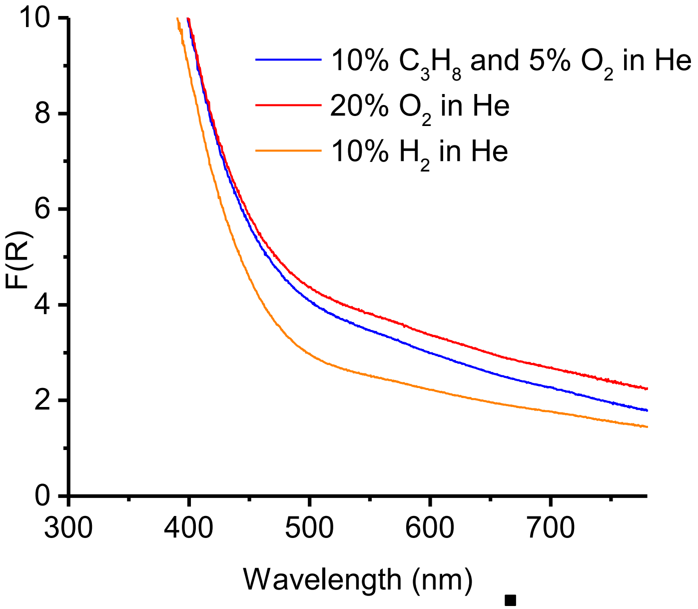
He

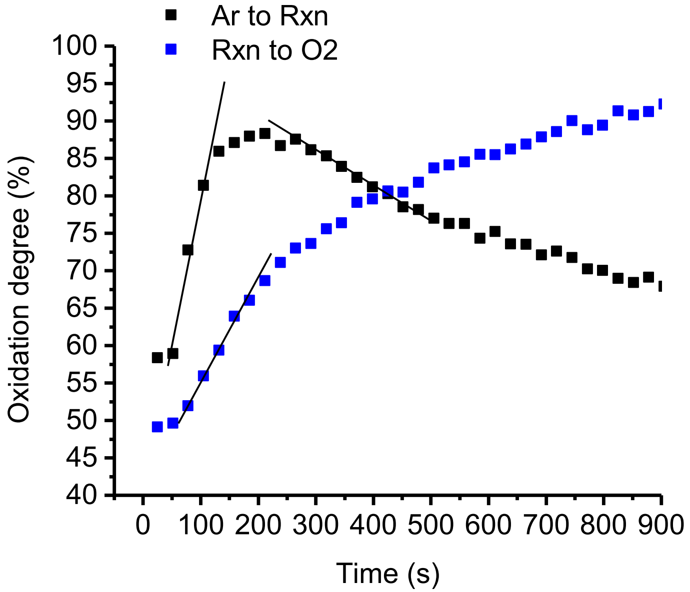
He

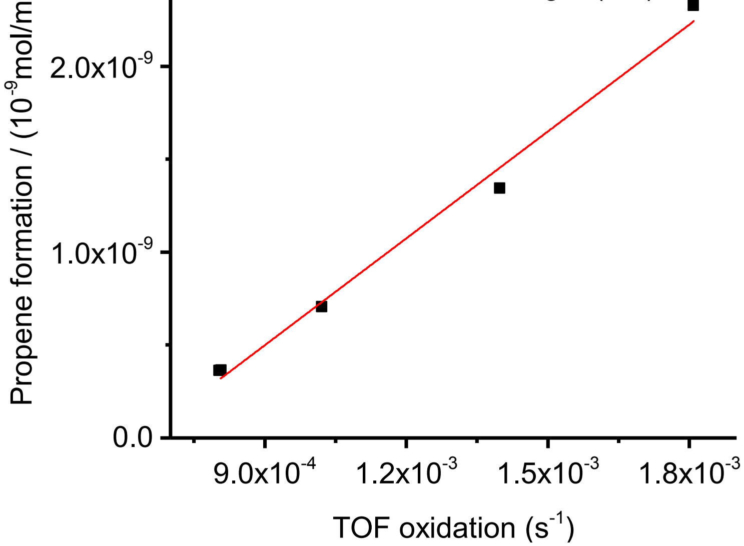
10%C_3H_8/ 5%O_2

20%O_2 in He

10%H_2 in He







Xuan Li, preliminary results

Conclusions

- Diffuse reflectance spectroscopy (in UV-vis and IR) is a useful techniques for characterization of heterogeneous catalysts and their precursors with respect to local and solid state structures
- The method provides information about, e.g., oxidation state, coordination number, coordination geometry, nature of chemical bonding, degree of condensation, particle size, band gap, nature and dynamics of surface and adsorbed species
- Theory is necessary for interpretation of the spectra
- The measurements are comparatively cheap and easy
- UV-vis-NIR spectroscopy can be performed in-situ or under operation
- Adsorption of probe molecules and characterization of bulk structure and surface functional groups can also be performed by Diffuse Reflectance Infrared Spectroscopy (DRIFTS) – not very much discussed in the present lecture

Further reading

1. G. Kortüm, “Reflectance Spectroscopy” / “Reflexionsspektroskopie” Springer, Berlin 1969.
2. S.D. Jackson, J.S.J. Hargreaves (Eds.), “Metal Oxide Catalysis”, Chapter 2, Wiley-VCH, Weinheim, 2009.
3. Advances in Catalysis, Volume 52, Chapter 1 and 3, Elsevier, Amsterdam 2009.
4. D. J. Dahm, K. D. Dahm, “Interpreting Diffuse Reflectance and Transmittance”, IM Publications, Chinchester 2007.
5. W. WM. Wendlandt, H.G. Hecht, “Reflectance Spectroscopy”, Interscience Publishers/John Wileyy, NY 1966.

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