



Modern Methods in Heterogeneous Catalysis Research



# UV-vis-NIR Diffuse Reflectance and Photoluminescence Spectroscopy in Heterogeneous Catalysis

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# Spectroscopy using UV-visible-NIR light



## Electronic transitions

### UV-vis-NIR Spectroscopy (energy of radiation 600-60 kJ/mol)

**Absorption** of electromagnetic radiation as a consequence of transitions among the energy states of **outer shell electrons in atoms/ions or molecules** and transitions between **electron energy bands in solids**

$\Delta S = 0$  spin multiplicity of terms involved is the same

**Energy of absorption:**  $\Delta E_{j \rightarrow j+1} = E_{j+1} - E_j = h\nu$

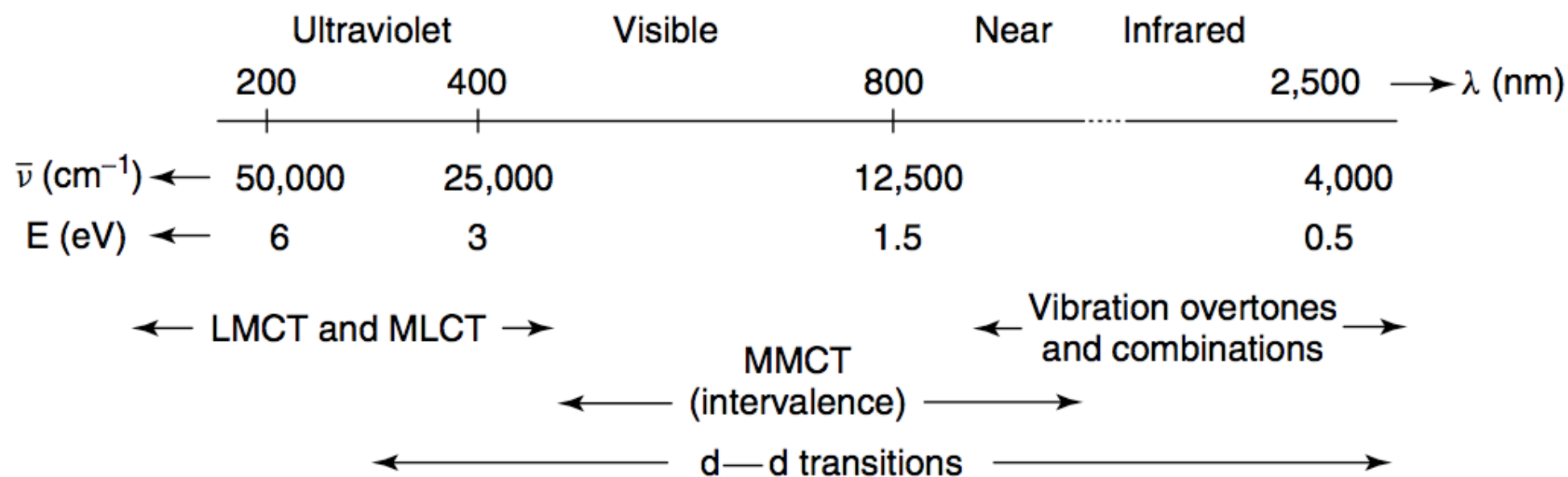
**Intensity:** change of charge distribution (absorption coefficient  $\alpha$ )

**Fine structure of absorption band:**  $\nu = \nu_{el} \pm \nu_{vib} \pm \nu_{rot}$

### UV-vis-NIR Photoluminescence Spectroscopy

**Emission** of electromagnetic radiation by a system that returns to the electronic ground state from an excited state populated by preceding absorption of UV-vis-NIR light

# Electromagnetic spectrum and transitions in molecules



LMCT ligand-to-metal-charge-transfer

MLCT metal-to-ligand-charge-transfer

MMCT metal-to-metal-charge-transfer

## Energy conversion

$$\Delta E = h\nu \qquad \nu = \frac{c}{\lambda} \qquad \tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{hc}$$

$$\begin{aligned} h &= 6.62606896(33) \cdot 10^{-34} \text{ Js} \\ &= 4.13566733(10) \cdot 10^{-15} \text{ eVs} \\ c &= 29\,979\,245\,800 \text{ cm} \cdot \text{s}^{-1} \end{aligned}$$

$$1 \text{ cm}^{-1} = 1.24 \cdot 10^{-4} \text{ eV}$$

number of waves per cm

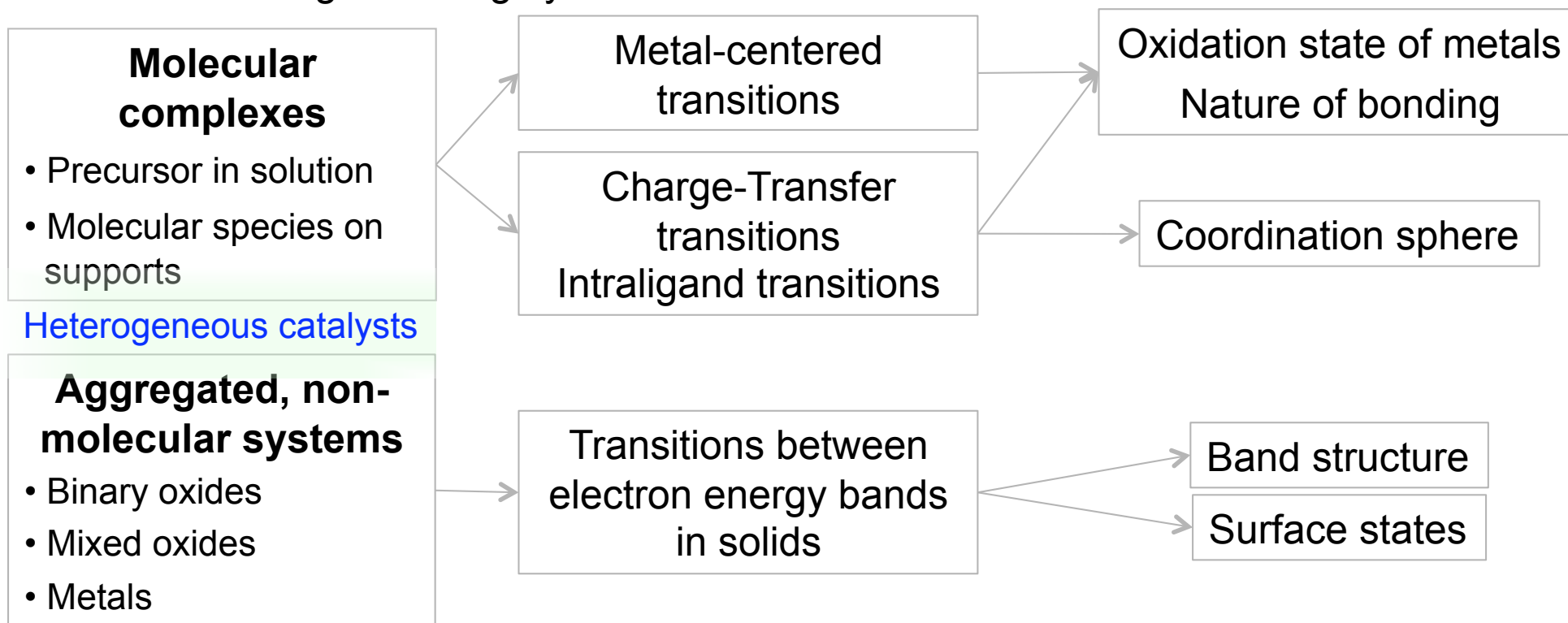
	$\lambda$ (nm)	$\tilde{\nu}$ (cm <sup>-1</sup> )	E (eV)
$\lambda$ (nm)	1	$(1/\lambda) \cdot 10^{-7}$	1240/ $\lambda$
$\tilde{\nu}$ (cm <sup>-1</sup> )	$(1/\tilde{\nu}) \cdot 10^7$	1	$\tilde{\nu}/8065.5$
E (eV)	1240/E	$E \cdot 8065.5$	1

# Spectroscopy using UV-visible-NIR light



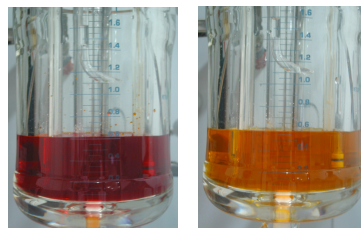
## What can we learn from UV-vis-NIR spectroscopy in heterogeneous catalysis?

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



# Investigations in heterogeneous catalysis using UV-visible-NIR light

- Analysis of precursor solutions



→ **Transmission 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

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



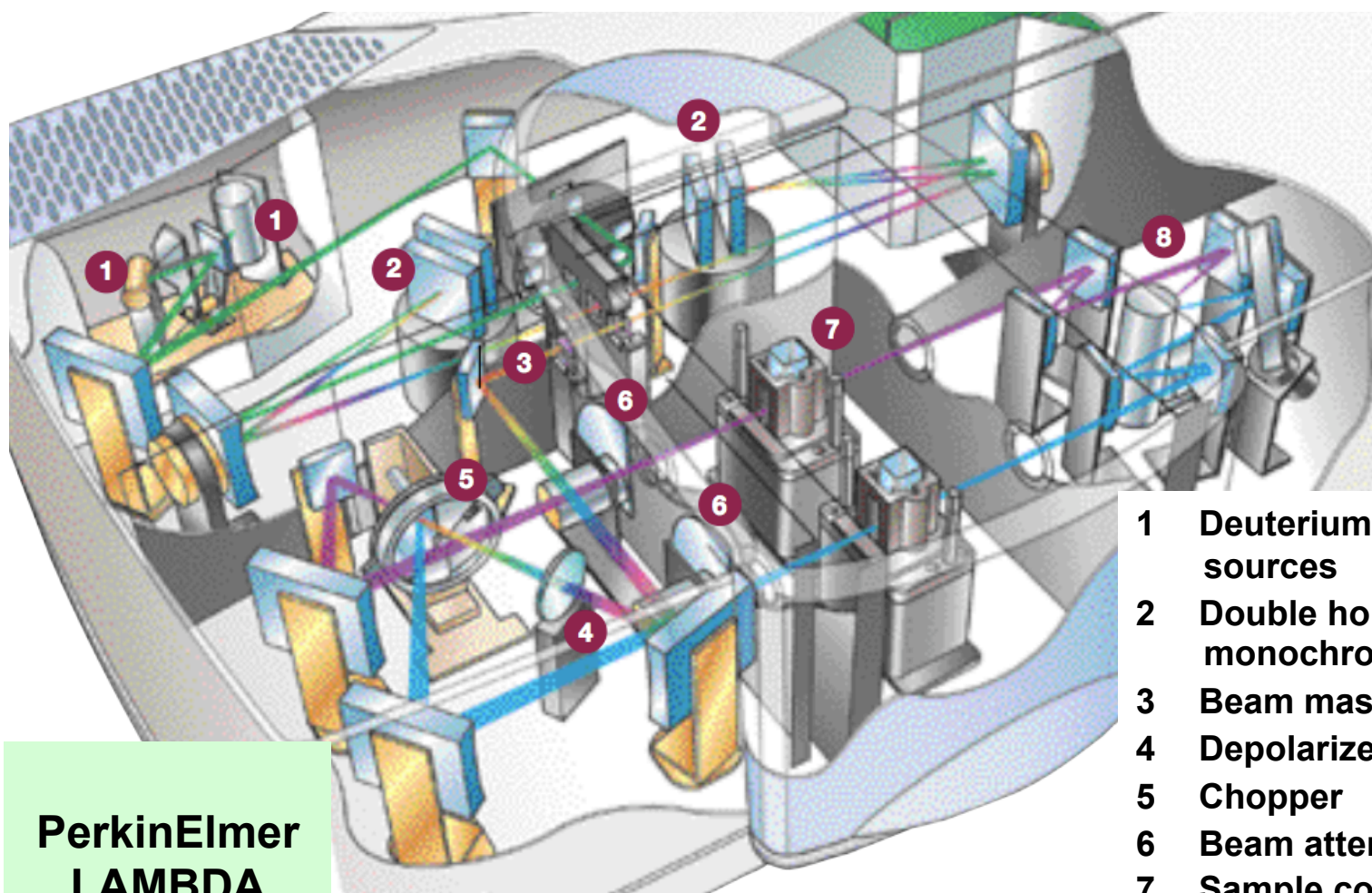
→ **Diffuse reflectance spectroscopy (DRS)**

# Outline



1. Spectroscopic techniques and data analysis
2. Types of electron transitions and relevance for catalyst/precursor characterization
3. Conclusions

# UV-vis-NIR Spectroscopy in transmission

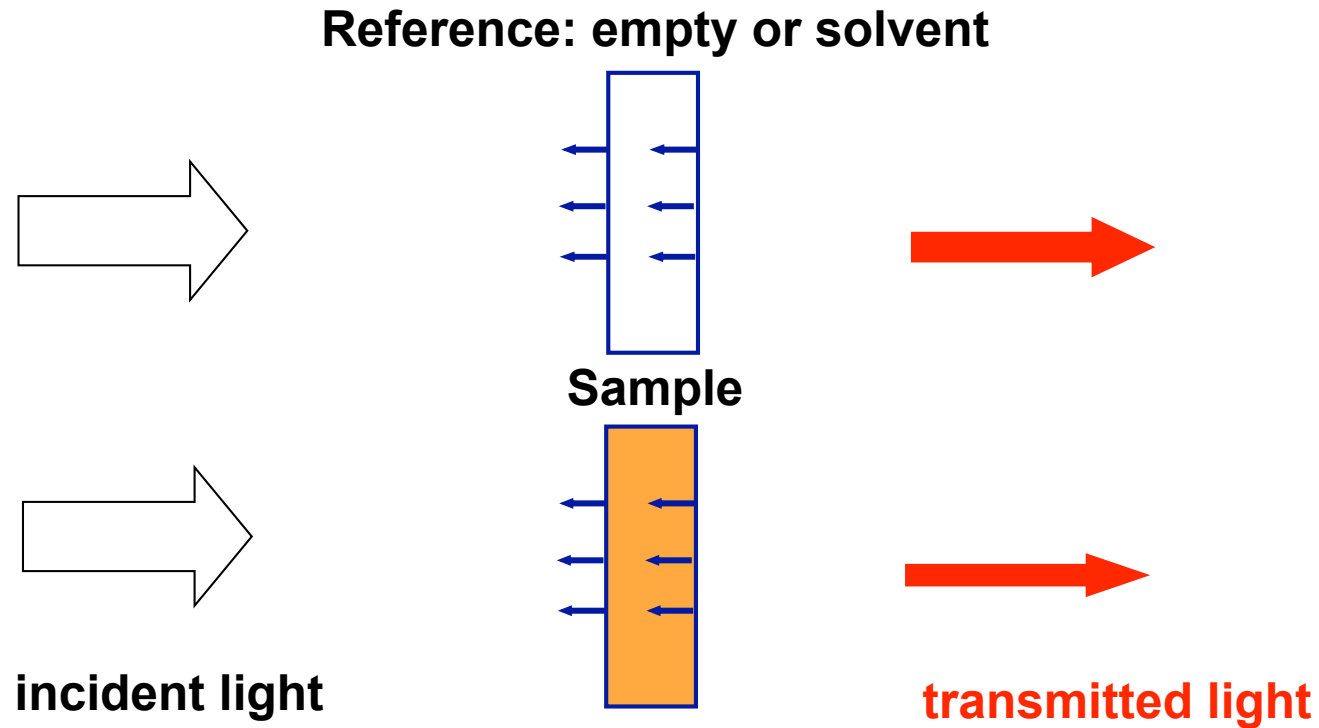


- 1 Deuterium and Tungsten light sources
- 2 Double holographic grating monochromator
- 3 Beam mask
- 4 Depolarizer
- 5 Chopper
- 6 Beam attenuators
- 7 Sample compartment
- 8 Photomultiplier (UV-vis) and Peltier-controlled PbS (NIR)

**PerkinElmer  
LAMBDA**



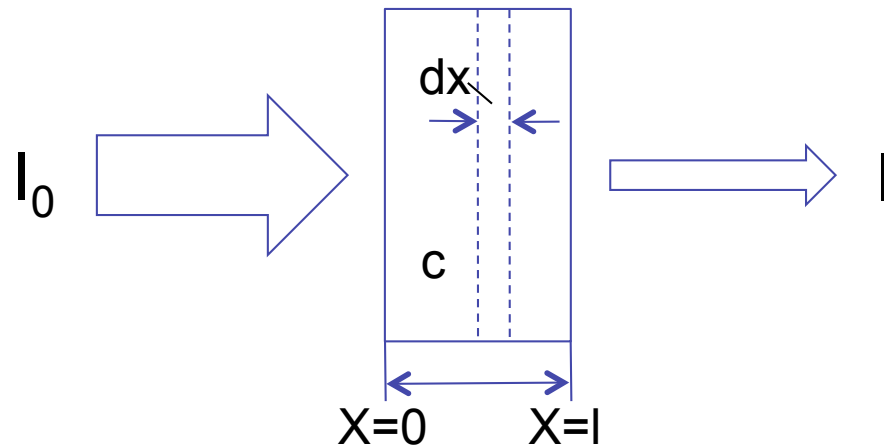
# Interaction of light with a solution in transmission



## reflection at phase boundaries

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

# Transmitted light and absorption properties



$\tau$ : transmittance

$\alpha$ : absorptance

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

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

decrease of I in an infinitesimally thin layer

c: molar concentration of absorbing species [mol/m<sup>3</sup>]

$\kappa$ : the molar napierian extinction coefficient [m<sup>2</sup>/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))

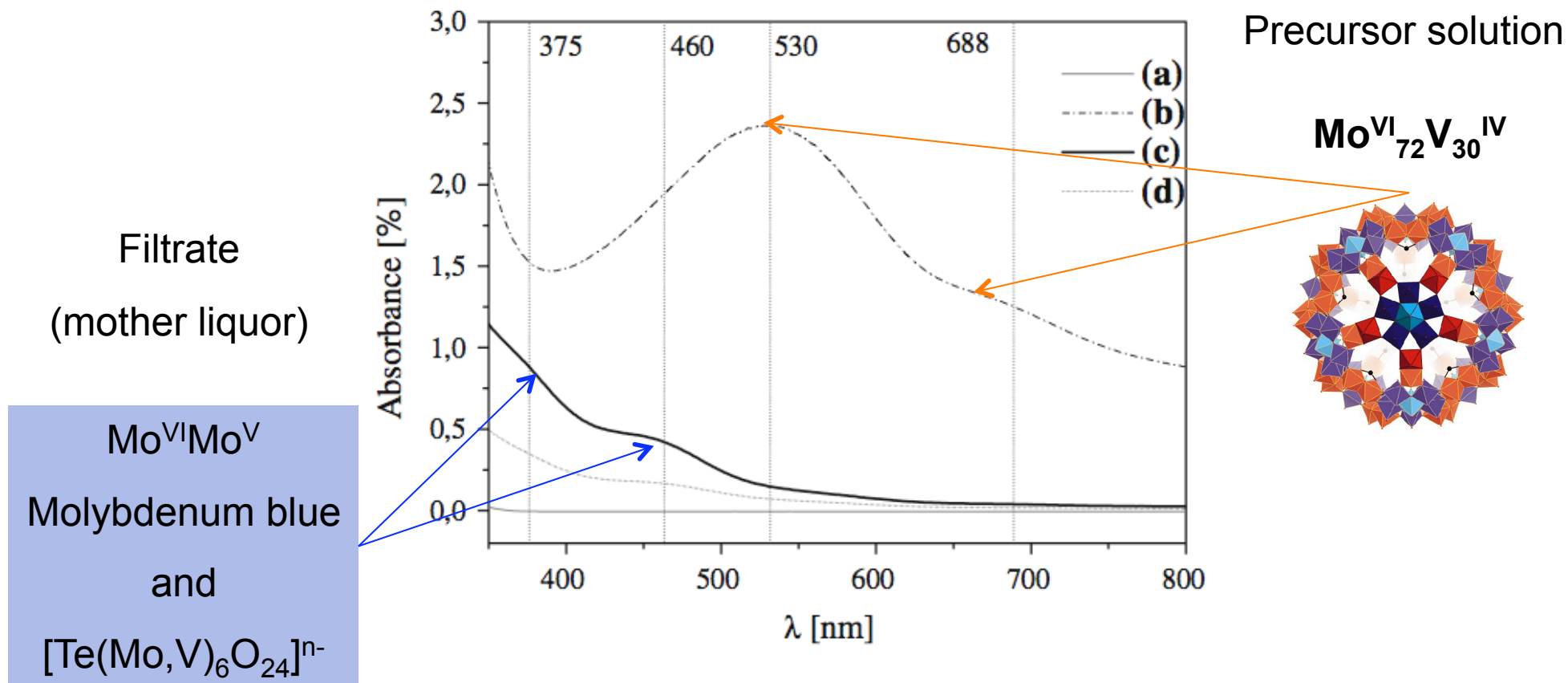
absorbance            A ( $A_{10}$  or  $A_e$ )

These quantities are DIMENSIONLESS !!!!

# Study of precursor solutions



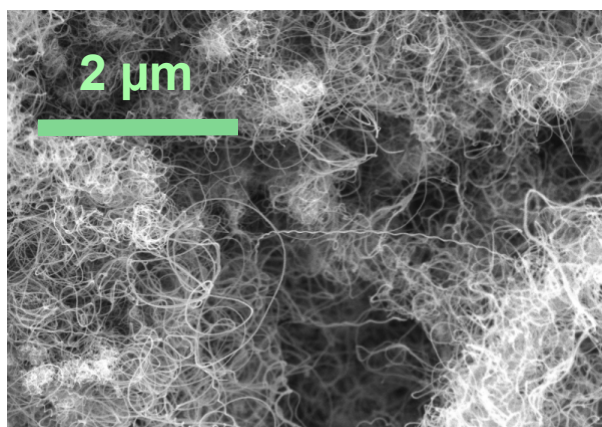
Investigation of precursor solutions and mother liquor during synthesis of a complex MoVTeNb oxide by hydrothermal synthesis



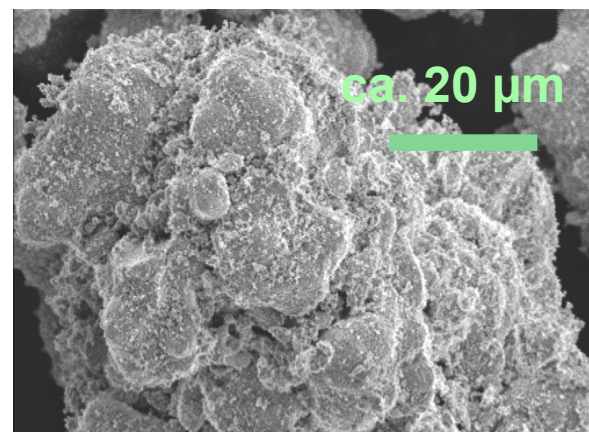
# Solid catalysts are mainly powders - typical catalyst particles



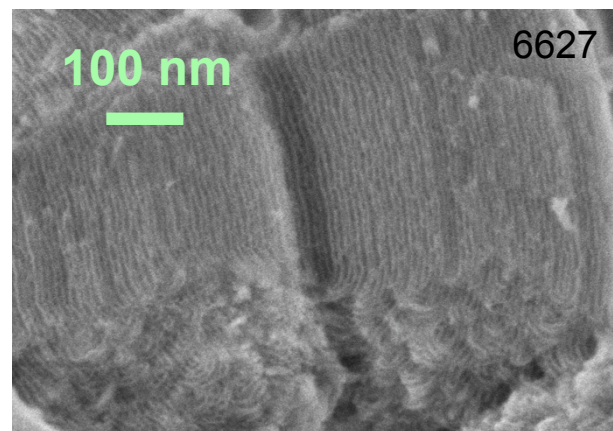
MWCNT



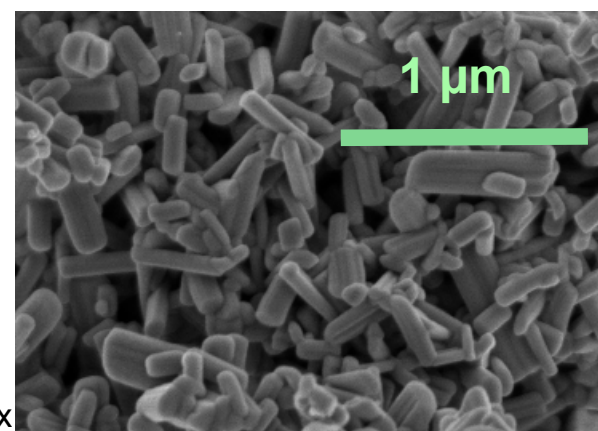
ZrO<sub>2</sub>



SiO<sub>2</sub>



MoVTenbO<sub>x</sub>



# Interaction of light with solid matter in transmission

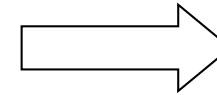
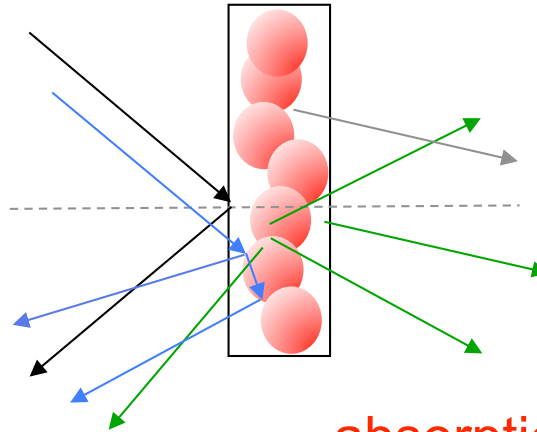
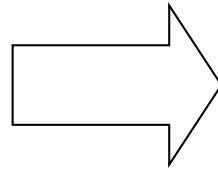


light source

powdered sample

detector

$I_0(\nu)$



$I(\nu)$

specular reflection

diffuse reflection:  
multiple reflection at  
phase boundaries

refraction

absorption

scattering

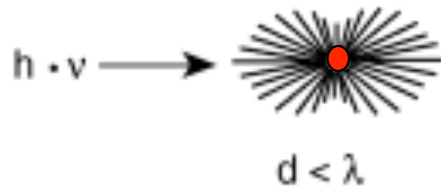
- elastic (Rayleigh, Mie)  $\nu$
- inelastic (Raman)  $\nu \pm \nu_i$

emission  $\nu_e$

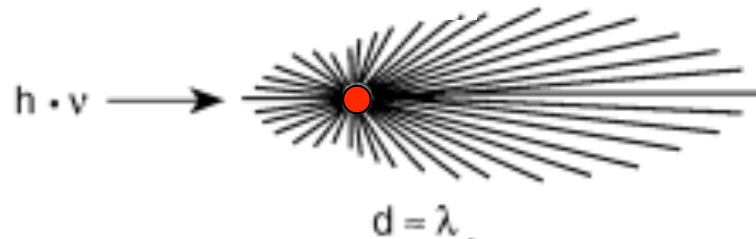
$$I_0 = I_r + I_s + I_a + I_e$$

# Single scattering and particle size

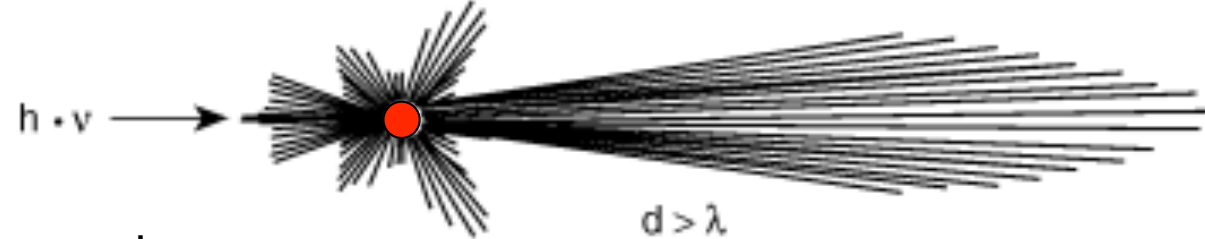
deflection of electromagnetic or corpuscular radiation from its original direction



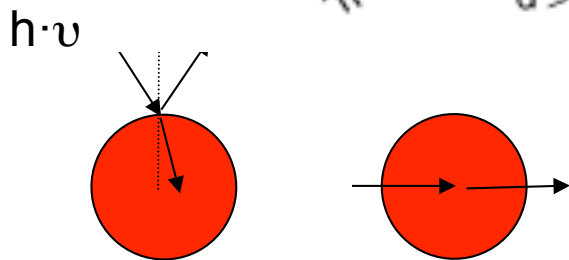
$d < \lambda$ : Rayleigh scattering  
isotropic distribution  
wavelength dependent:  $I_s \sim 1/\lambda^4$



$d = \lambda$ : Mie scattering  
in forward and backward directions  
wavelength independent



$d > \lambda$ : Mie scattering  
predominantly in forward direction  
wavelength independent



$d \gg \lambda$ : Mie Theory approaches laws of  
geometric optics

Mie Theory:

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

Quelle: RÖMPP on line

	Wavenumber	Wavelength
Mid-IR (MIR)	3300 to 250 $\text{cm}^{-1}$	3 to (25-40) $\mu\text{m}$
Near-IR (NIR)	12500 to 3300 $\text{cm}^{-1}$	(700-1000) to 3000 nm
UV-vis	50000 to 12500 $\text{cm}^{-1}$	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

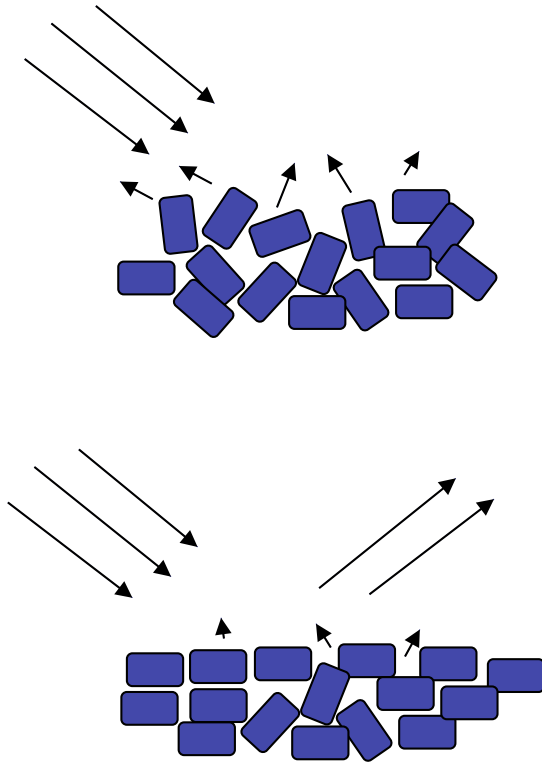
Result of multiple reflection, refraction, and scattering inside the sample

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

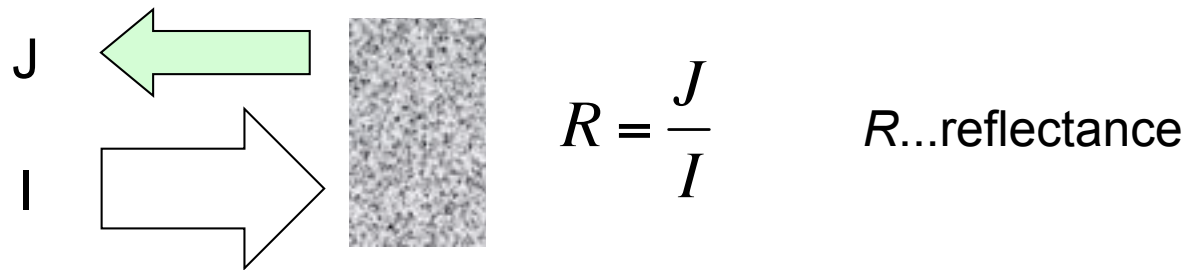
Can be prevented by dilution



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  $R(\nu)$ , which is **not** proportional to the concentration of the absorbing entity



2 constants are needed to describe the reflectance:

absorption coefficient      **K**      (function of the frequency)  
scattering coefficient      **S**

Experimental condition: diffuse reflectance of a layer with infinite thickness  $R_\infty$

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

## 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  $R_\infty$  is linked with the absorption coefficient  $K$  and the scattering coefficient  $S$  by the Schuster-Kubelka-Munk or remission function:

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

Kubelka-Munk function

- The Kubelka-Munk function transforms the measured spectrum  $R(\nu)$  into the absorption spectrum  $K(\nu)$

## Quantification of DR spectra: Remission function

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

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

- The spectrometer measures  $R_\infty'$

$$R_\infty' = R_\infty(\text{sample}) / R_\infty(\text{reference})$$

$$R_\infty' = R_\infty \text{ if } R_\infty(\text{reference}) = 1 \text{ (} K \rightarrow 0 \text{)}$$

No absorption of the reference, all light reflected !

Ideal property of white standard!

- The “**infinite thickness**” is generally obtained with a layer depth of 1-2 mm
- Strongly scattering powders (silica) require up to 5 mm

The remission function is proportional to  $K$  **only if  $S$  is independent of  $\lambda$**   
→ **particle size!** ( $S$  increases with energy in case of fine powders  $d < \lambda$ )

- The relative intensities of the bands are not true
- Error due to red-shift of bands
- Reduced scattering due to very small particles favors deep penetration of the radiation into the sample
- Packing density matters

# Scattering coefficients

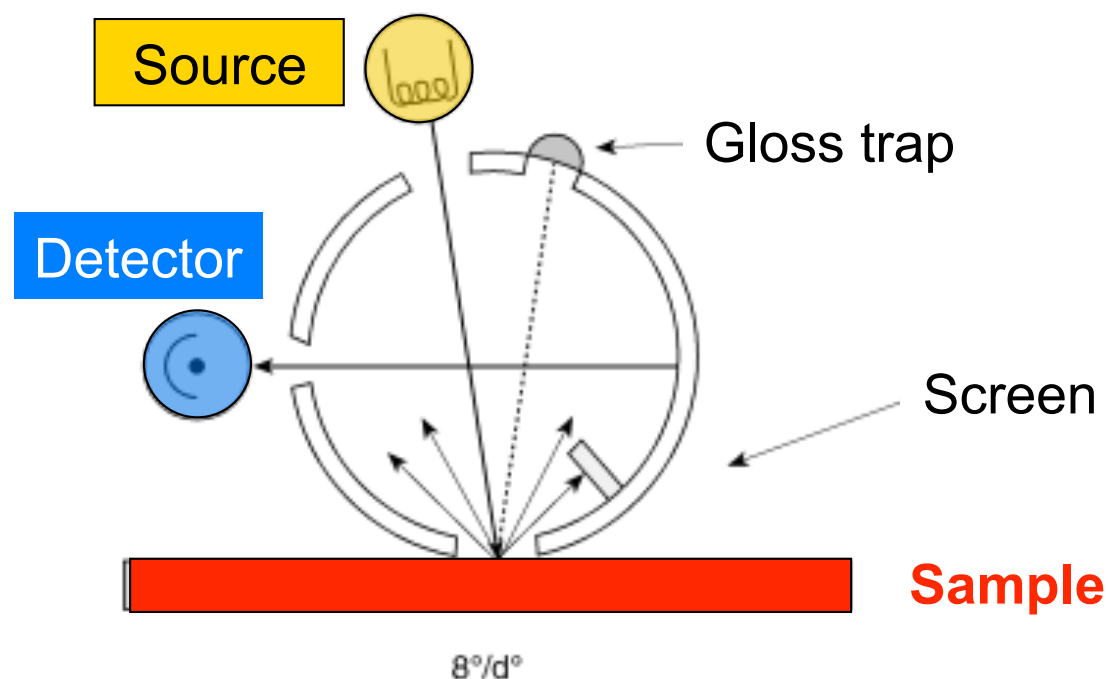
Table 12. Scattering coefficients of the Kubelka-Munk theory

Substance tested	Specific surface according to BET [m <sup>2</sup> /g]	Average grain size $d$ [μ]	Making and preparing	Quantities measured	Power $\alpha$ of the wave-number dependence of $S(S = \text{const. } \nu^\alpha)$	
Aerosils	376 294 196 106 38	0.01 0.015 0.02 0.04 0.08	heated at 600° C for 1 hr.	$T_{1,2,3}, R_\infty$	3.6 3.5 3.2 3.0 2.6	Grain size $< \lambda$
Calciumfluoride SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> cracking catalyst	520 (inner surface)	$\cong 0.2$ 0.2-0.4	precipitated heated at 600° C for 2 hrs. ground for 20 hrs.	$T_{1,2}, R_\infty$ $T_{1,2}, R_\infty$	$\cong 1$ $\cong 1$	Grain size $\cong \lambda$
Sodium chloride	8	$\cong 0.4$	heated at 600° C for 2 hrs.	$R_0, R_\infty$	$\cong 1$	
Magnesiumoxide		0.1-0.2	freshly prepared on black background	$R_0$	$\cong 1$	

## True absorption spectrum from DRS: Suitable measurement conditions

- Regular reflection parts are eliminated through sufficiently high dilution of the sample with a white standard
- The scattering coefficients of the standard are independent of the wavenumber in the spectral range used (or the scattering coefficients have to be measured)
- Reflectance values  $R_{\infty}' < 0.6$  should not be measured due to deviations from the Kubelka-Munk theory in case of higher absorption (dilution is also here recommended)
- When molecular species on the surface of a support are investigated, dilution with the support eliminates the size dependence of the absorption coefficient of the support
- Dilution can be a problem in in-situ experiments!

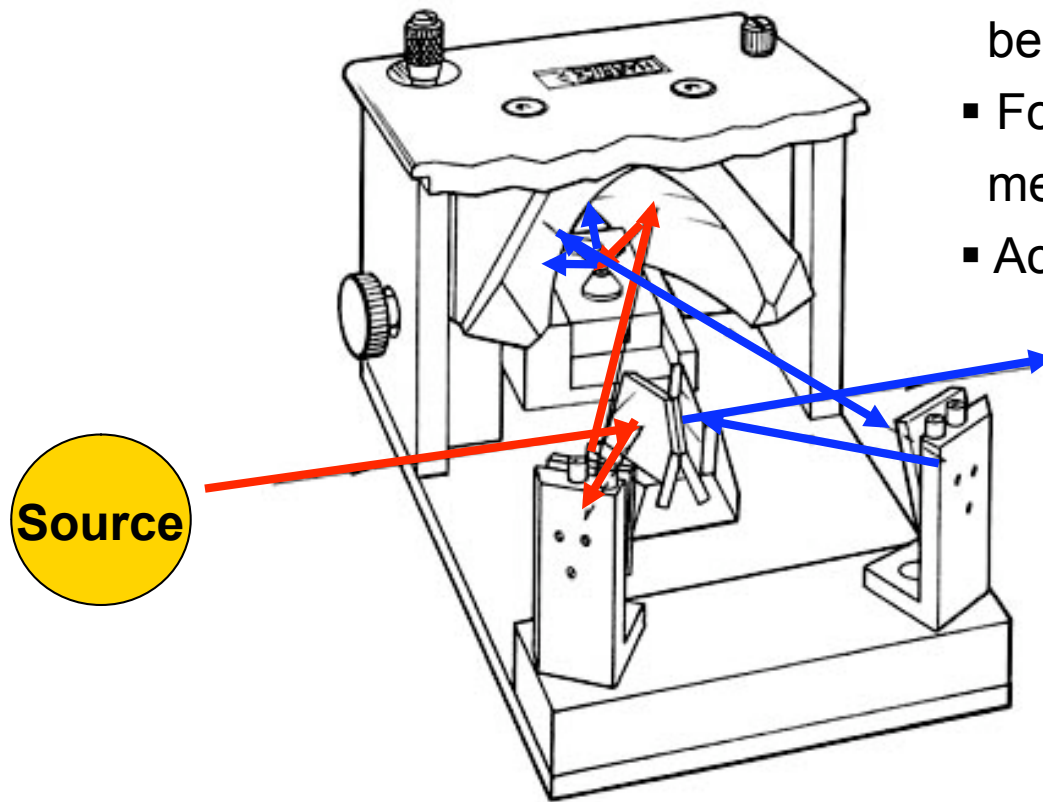
## Integrating sphere



- 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:  $\text{BaSO}_4$ , Spectralon (for UV-vis), Au
- The flux onto the detector corresponds to 1% of the incident flux or less

# 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



**Detector**

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

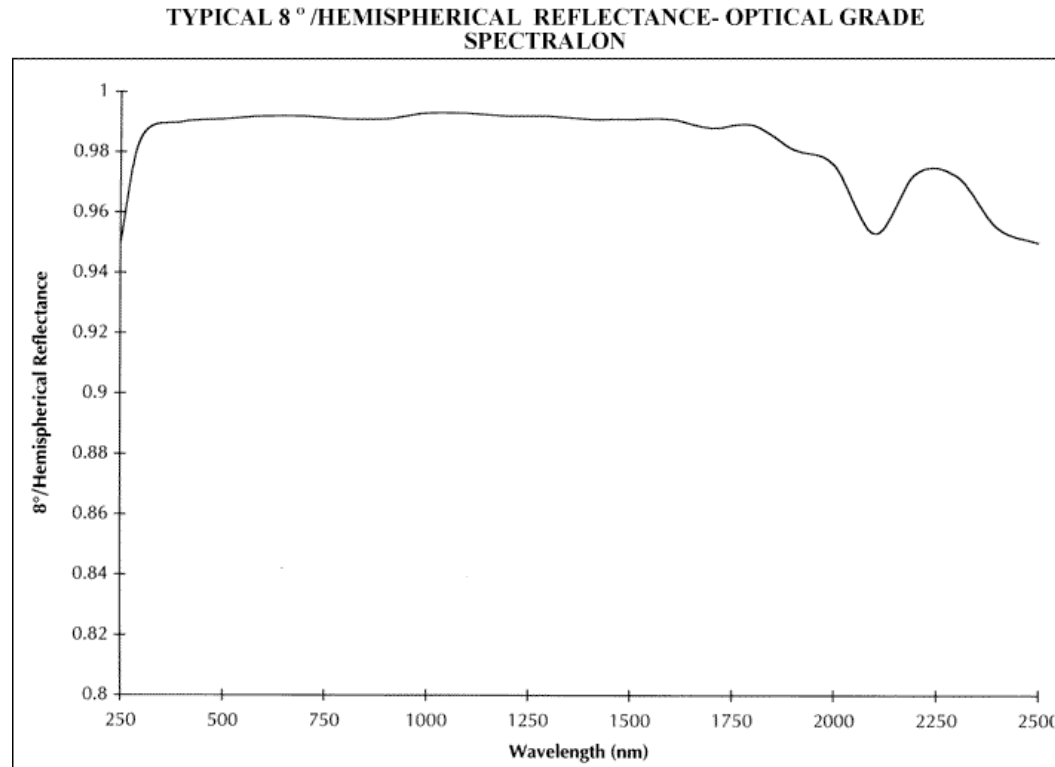
Specular reflection is strongest in forward direction  
Collect light in off-axis configuration

- 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



## White standards

- BaSO<sub>4</sub>: UV-vis
- MgO (not stable!): UV-vis
- Spectralon: UV-vis-NIR

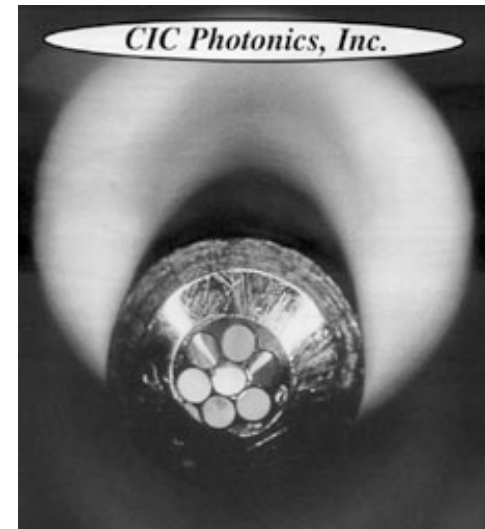
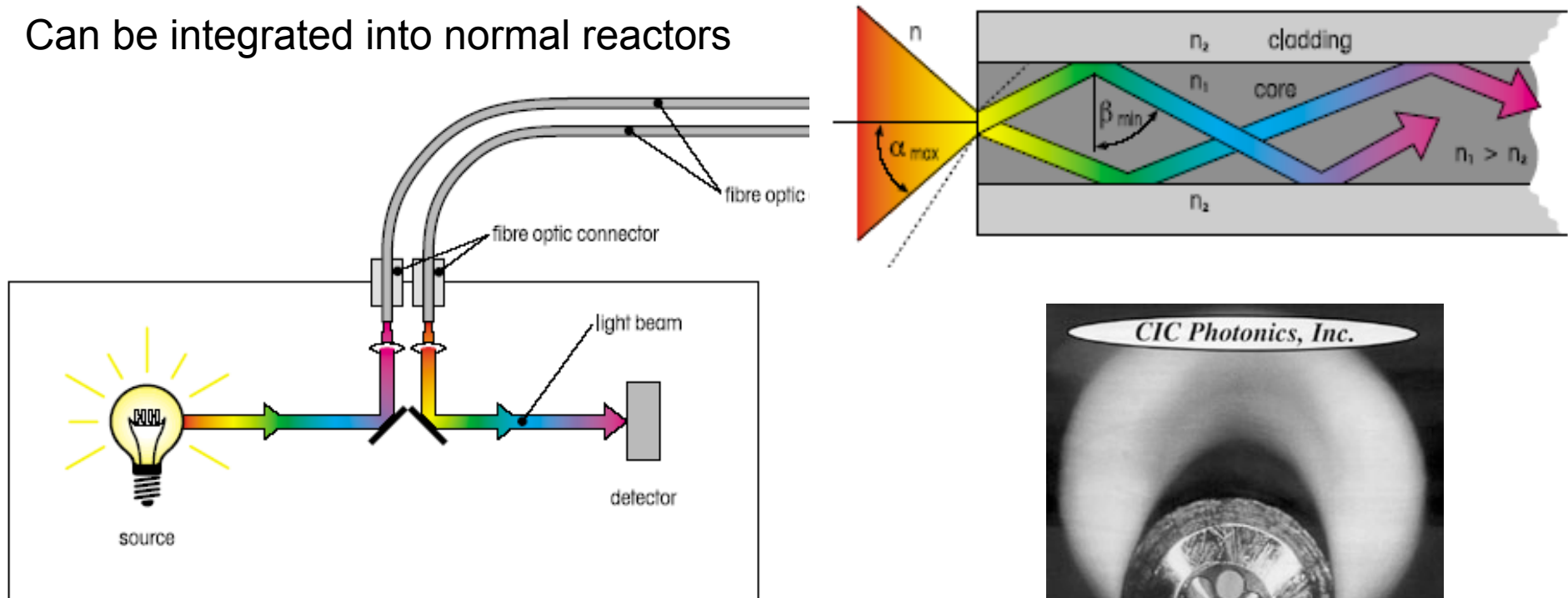


Spectralon® thermoplastic resin, excellent reflectance in UV-vis region

<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



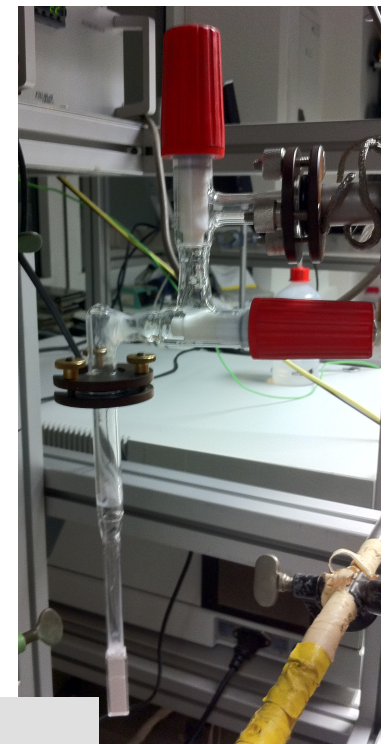
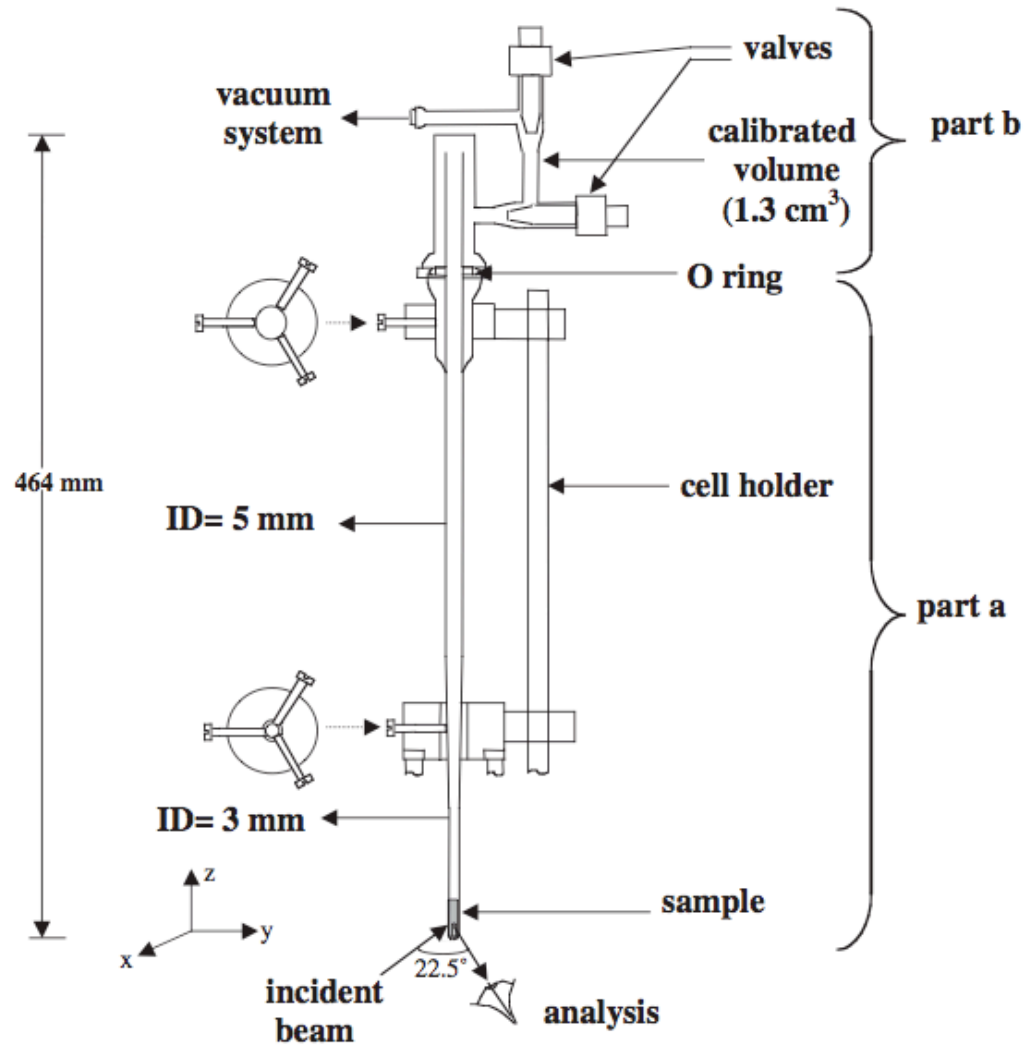
- Fibers made of silica
- Light conducted through total reflectance
- Fiber bundle with 6 illumination fibers around 1 read fiber
- Arrangement avoids collection of specularly reflected light

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

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

# Photoluminescence spectroscopy

Relaxation of electronically excited states (radiative decay)



- Vacuum pretreatment at high T
- Dosing of probe molecules
- Liquid N<sub>2</sub> cooling

**Thermal pretreatment in vacuum necessary!**

# Fluorescence

Electronic transitions:  $10^{-16}$  s

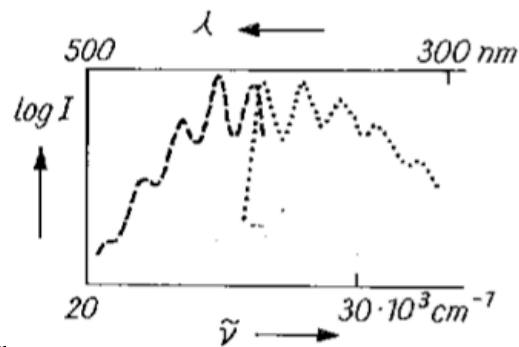
Vibrations:  $10^{-14}$  s

Fluorescence lifetime:  $10^{-9}$  s

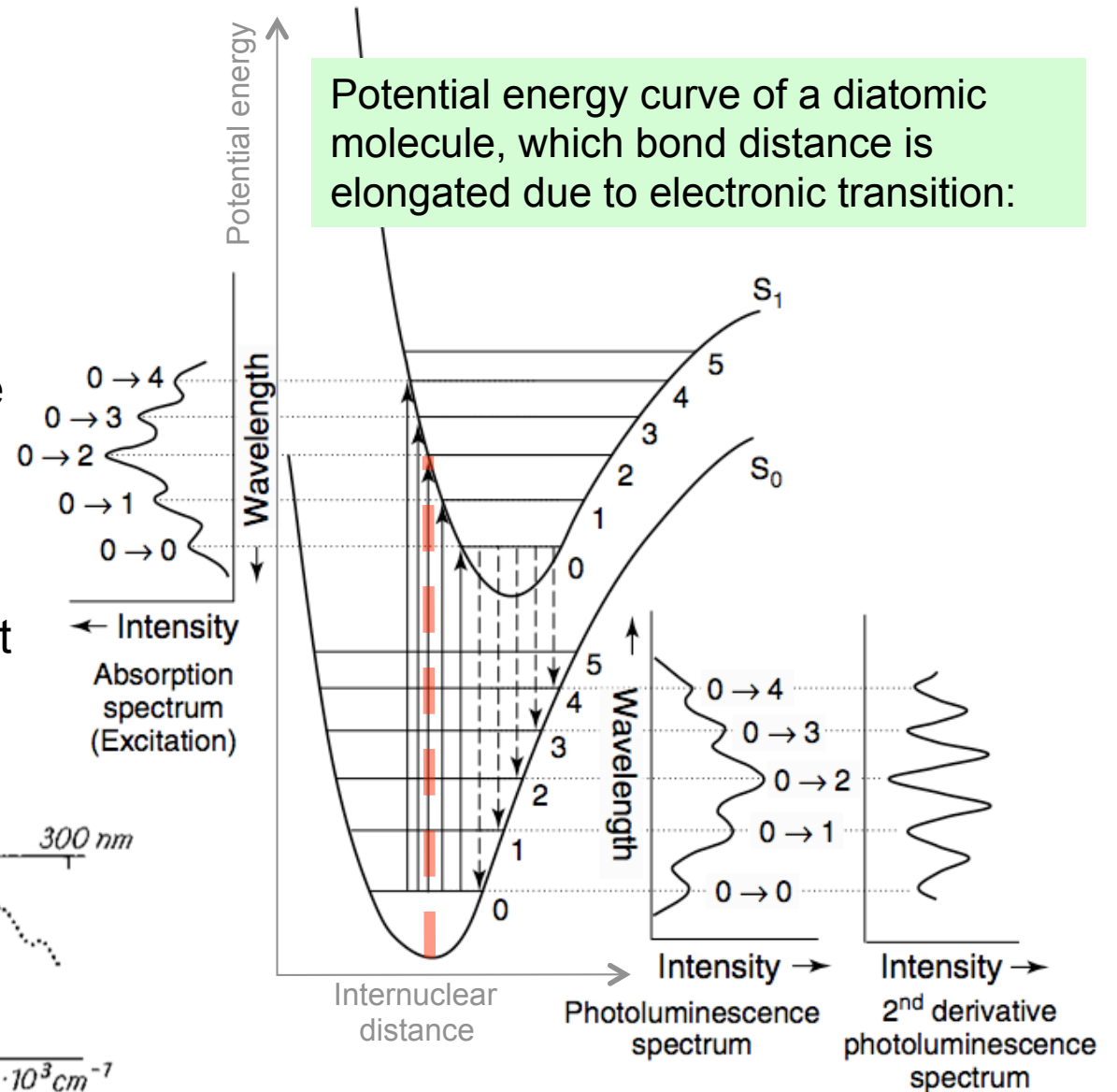
In electronic transitions, such vibrational states are most likely, which occur without changing the distance of the nuclei

Emission of light occurs from the lowest vibrational state of  $S_1$

Therefore, fluorescence occurs at a frequency lower than the absorption process (Stokes shift)

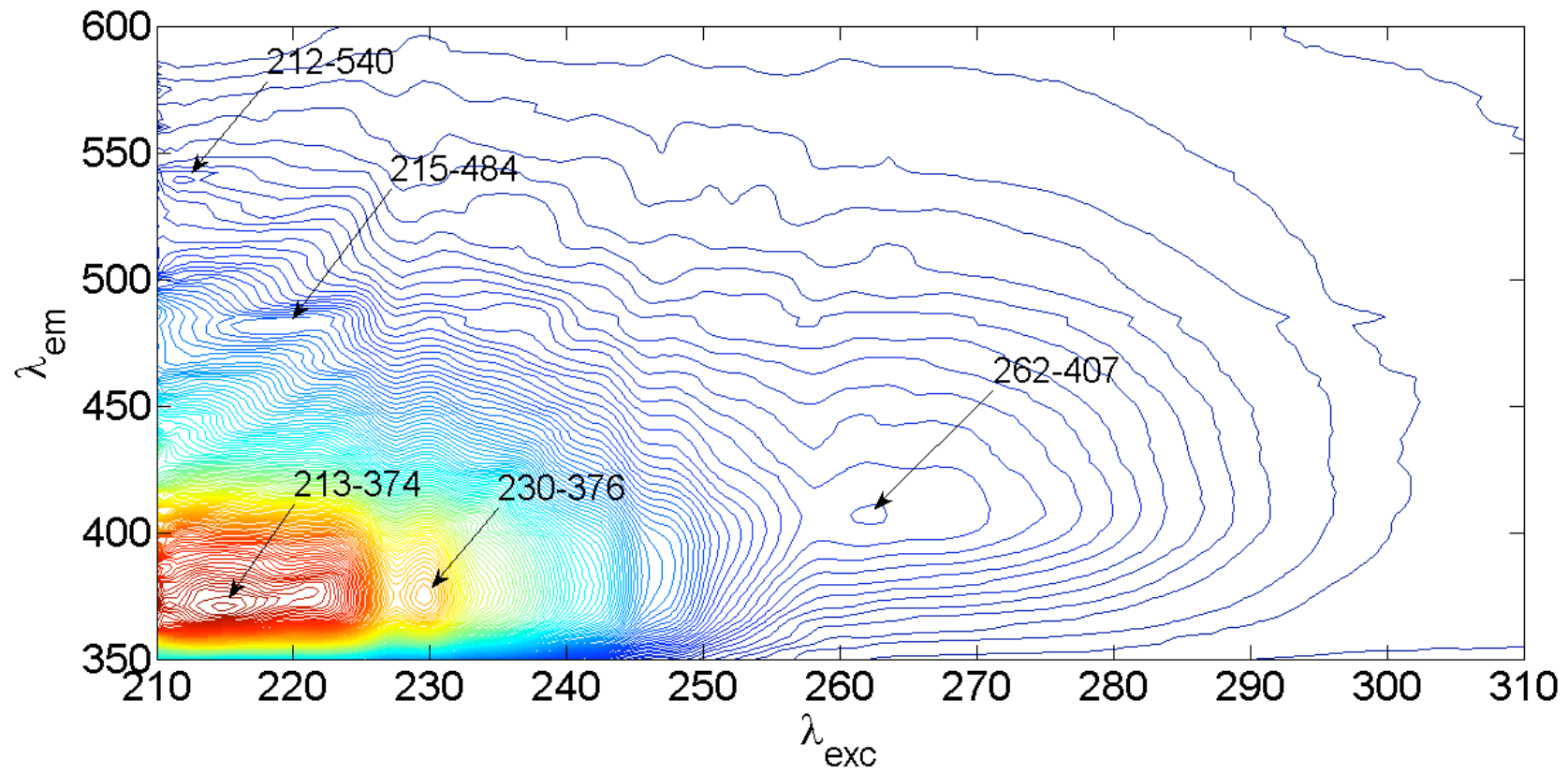


----- Fluoreszenzspektrum  
 ..... Absorptionsspektrum



Potential energy curve of a diatomic molecule, which bond distance is elongated due to electronic transition:

# Photoluminescence measurement



*MgO 14565, Measurement P. Schwach*

# Photoluminescence Spectroscopy

## Application of Photoluminescence spectroscopy

- High sensitivity to surface phenomena of oxides with large surface to volume ratio
- Structure, coordination and reactivity of metals for low metal loadings (1-2 wt%)
- Molecular structure of supported oxide species
- Adsorption of probe molecules

**Fluorescence:** Emission process between states with same spin multiplicity ( $10^{-9}$  s)

The intensity depends on the ability of the environment to accept the electronic or vibrational quanta (working at liquid nitrogen temperature)

**Phosphorescence:** Emission process between states with different spin multiplicity (e.g., triplet-singlet transitions) ( $10^{-3}$  s - minutes)

# Phosphorescence

Intersystem crossing

Populating a triplet state by spin flip occurs when the  $S_1$  potential energy curve intersects the  $T_1$  curve

Intensity usually lower than that of fluorescence, because transition is forbidden

Phosphorescence is enhanced for highly dispersed species in the matrix of a catalyst support (less efficient energy transfer)

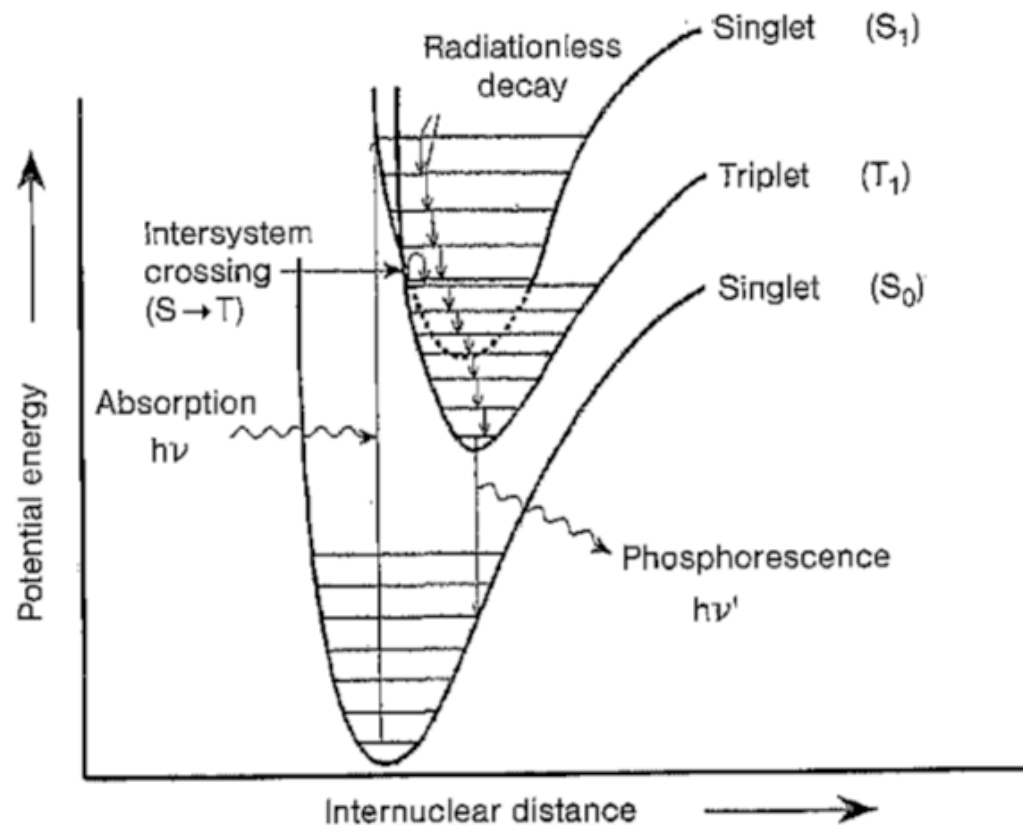
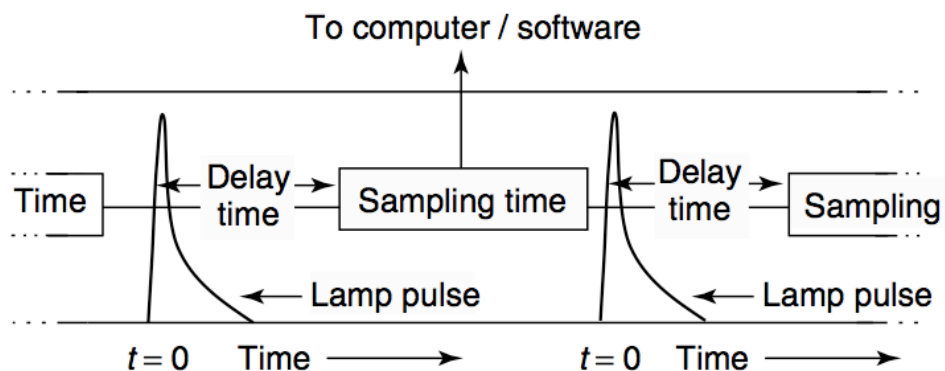


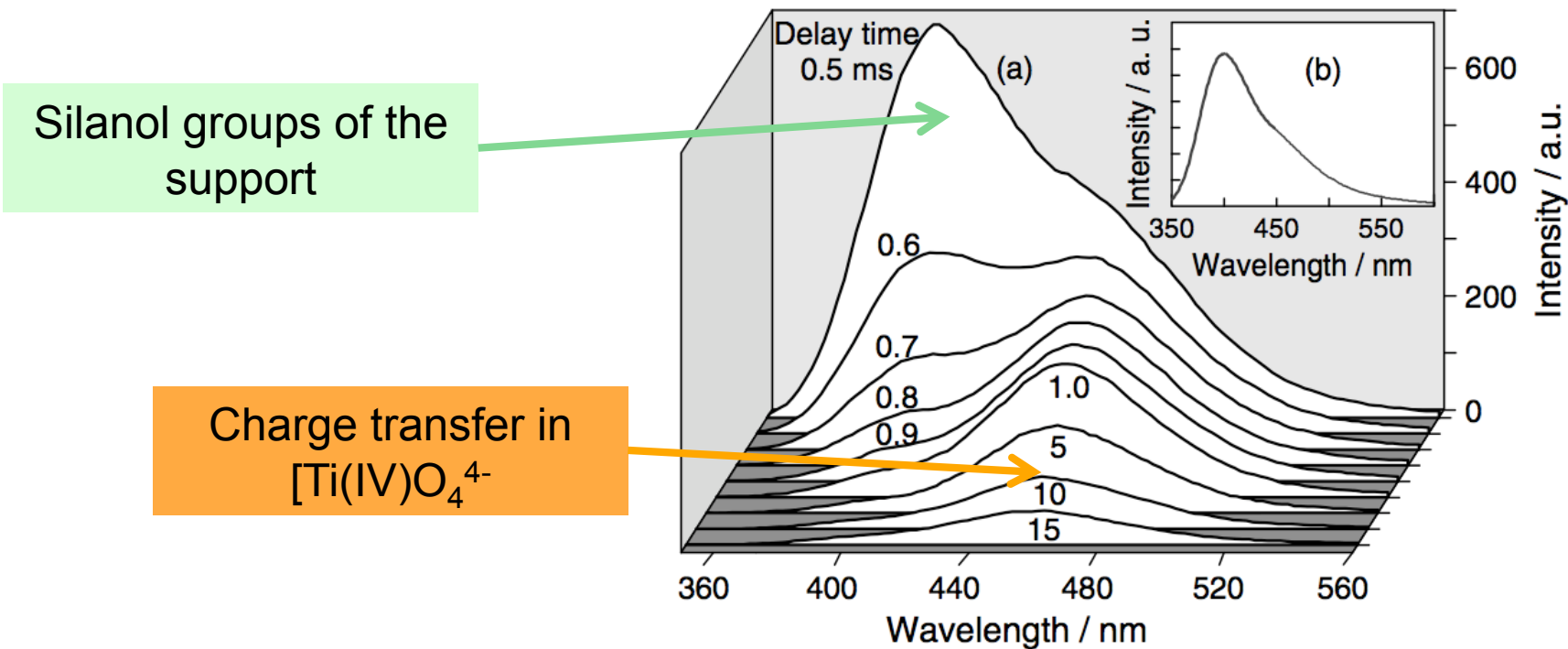
Figure 2.18 Potential energy curves for ground ( $S_0$ ) and excited singlet ( $S_1$ ) and triplet ( $T_1$ ) states. Reprinted from ref. [11], with permission from Elsevier.

# Time-resolved photoluminescence spectra



Time-resolved (a) and steady-state (b) spectra of Ti/MCM-41

Excitation: 260 nm





# Outline



1. Spectroscopic techniques and data analysis
2. Types of electron transitions and relevance for catalyst/precursor characterization
3. Conclusions

# Types of electron transitions

- Molecules or atoms/ions
  - Metal-centered transitions
  - Charge-Transfer transitions
- Non-molecular solids
  - Transitions between electron energy bands

## Metal-centered transitions

Transitions among the energy levels in incompletely filled subshells

$d \rightarrow d$	transition elements (e.g., hexa-aquo complexes in solution)
$(n-1)d \rightarrow ns$	transition elements ( $\text{Cu}^+$ , $\text{Ag}^+$ )
$f \rightarrow f$	rare earth elements $L^{3+}$ ( $L = \text{Ce}, \text{Sm}, \text{Eu}, \text{Yb}$ ) weak narrow bands
$4f \rightarrow 5d$	$\text{Ce}^{3+}$ , $\text{U}^{4+}$
$ns \rightarrow np$	main group elements $\text{Sn}^{2+}$ , $\text{Sb}^{3+}$ , $\text{Bi}^{3+}$

- The electronic configuration and the symmetry of the complex are important in particular for d-d transitions
- f-f transitions are little sensitive to complex geometry (impact of ligand field ca. 100 times smaller)

### Ruby

Absorption of	
yellow-green light	18 000 $\text{cm}^{-1}$ (556 nm)
purple light	24 000 $\text{cm}^{-1}$ (417 nm)

## Metal-centered transitions

Selection rules:

$\Delta S = 0$  spin multiplicity of terms involved be the same

$\Delta l = \pm 1$  Laporte rule

d-d transitions are forbidden, but weak due to

- vibronic coupling with the ligands
- electron interactions (spin-orbit-coupling, exchange interactions)

Type of d-d transition	Approximate $\epsilon$
Spin-forbidden, Laporte forbidden	0.1
Spin-allowed, Laporte forbidden	10
Spin-allowed, Laporte forbidden, d-p mixing in td symmetry	100
Spin-allowed, Laporte forbidden (forbidden and allowed transitions involve excited states close in energy to allow mixing of wavefunctions via a vibrational mode)	1000

## Metal-centered transitions

d-d transitions in incompletely filled  $d^n$  subshells ( $1 \leq n \leq 9$ ) occur due to

- Splitting in the ligand field (crystal field parameter  $\Delta$ )
- Electron interactions
- Configuration interactions
- Jahn-Teller effect



The splitting is determined by

- Nature of metal ion
- Oxidation state
- Number and type of ligands
- Geometry of ligand arrangement



Information relevant for catalyst and precursor characterization:

- Electronic and geometric structure of the transition metal ion in its surrounding
- Character of chemical bond (ionic-covalent)

# Metal-centered transitions

## Ligand or crystal field splitting in octahedral ligand field

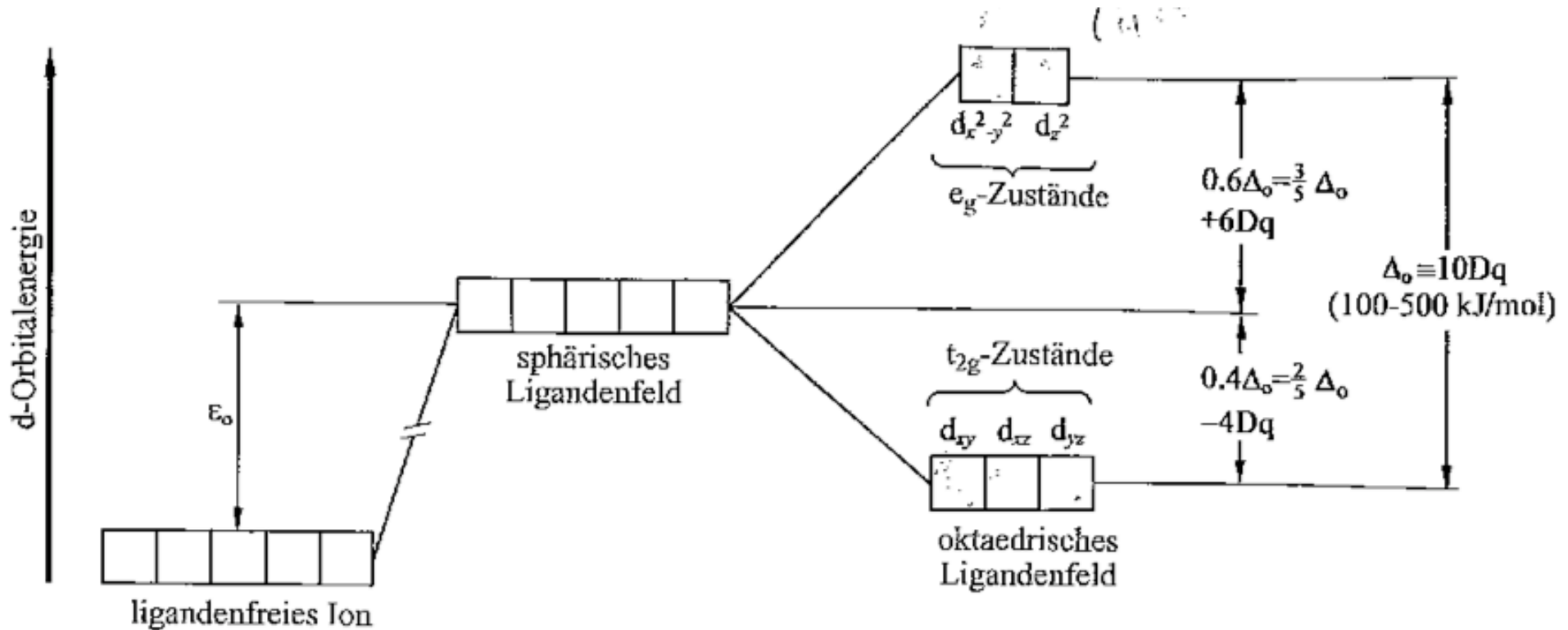
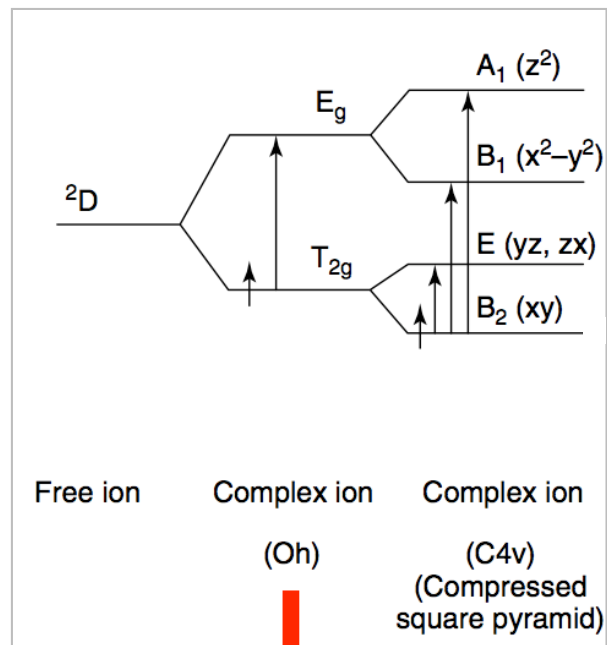


Fig. 285 Aufspaltung der fünf energiegleichen d-Zustände eines Zentralatoms oder -ions in zwei energievverschiedene d-Gruppen im oktaedrischen Ligandenfeld<sup>16</sup> (vgl. Fig. 284).

# Metal-centered transitions

The simplest case:  $d^1$

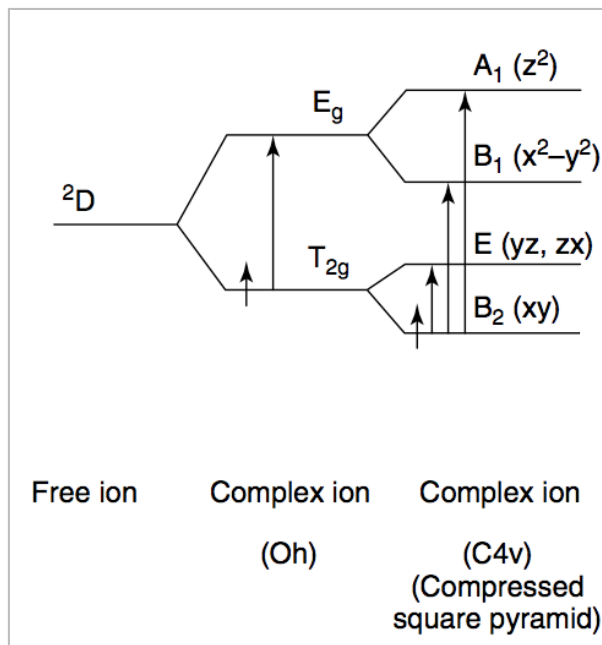


$$h\nu = \Delta E = E(E_g) - E(T_{2g}) = \Delta_o$$

# Metal-centered transitions

The simplest case:  $d^1$

$d^n$ : electron interactions - transitions between different ground and excited terms



	$d^1$	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$	$d^9$
$e_g$	$\overline{\overline{\uparrow}}$	$\overline{\overline{\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\uparrow\downarrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\uparrow\downarrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow}}$
<b>Number of transitions</b>	(1)	(3)	(3)	(1)	(0)	(1)	(3)	(3)	(1)
$t_{2g}$	$\overline{\overline{\uparrow}}$	$\overline{\overline{\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\downarrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\downarrow\downarrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\downarrow\downarrow}}$	$\overline{\overline{\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow}}$
<b>(a) High spin</b>									
<b>Excited terms</b>		$^3A_{2g}$	$^4T_{1g}$	$^4T_{1g}$	<b>Spin-forbidden</b>	$^4A_{2g}$	$^3T_{1g}$	$^3T_{1g}$	$^2T_{2g}$
<b>Ground term</b>	$^2E_g$	$^3T_{2g}$	$^4T_{2g}$	$^5T_{2g}$	$^6A_{1g}$	$^5E_g$	$^4T_{2g}$	$^3T_{2g}$	$^2T_{2g}$
	$^2T_{2g}$	$^3T_{1g}$	$^4A_{2g}$	$^5E_g$		$^5T_{2g}$	$^4T_{1g}$	$^3A_{2g}$	$^2E_g$
<b>(b) Low spin</b>									
<b>Number of transitions</b>						(*)	(*)	(2)	(*)
$e_g$						$\overline{\overline{\uparrow}}$	$\overline{\overline{\uparrow}}$	$\overline{\overline{\uparrow}}$	$\overline{\overline{\uparrow}}$
$t_{2g}$						$\overline{\overline{\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow}}$	$\overline{\overline{\uparrow\uparrow}}$
<b>Excited terms</b>						$^1T_{2g}$	$^1T_{1g}$		
<b>Ground term</b>						$^3T_{1g}$	$^2T_{2g}$	$^1A_{1g}$	$^2E_g$

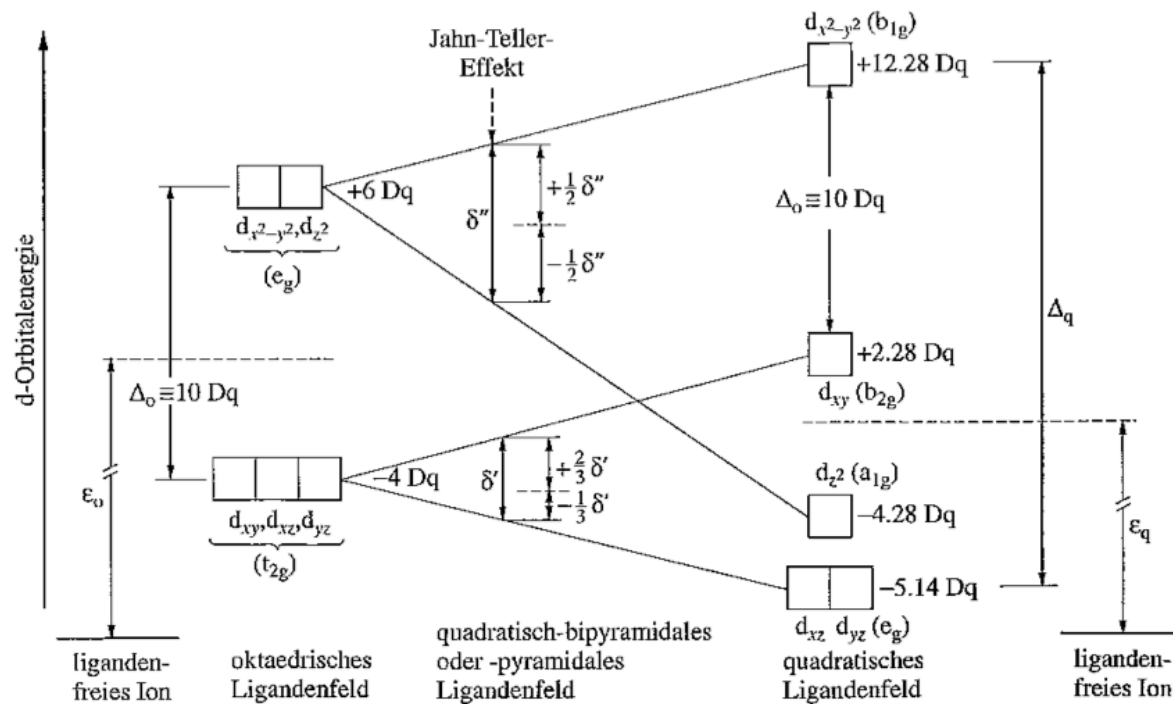
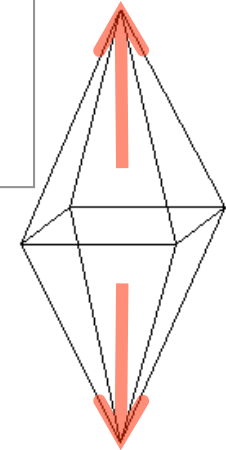
Spin-allowed d-d transitions in octahedral complexes



# Metal-centered transitions

## Electronically driven structural distortion: Jahn-Teller effect

Any non-linear molecule with an incompletely filled, degenerate HOMO should undergo a structural distortion that removes the degeneracy and lowers the energy



$d^9$  ( $\text{Cu}^{2+}$ ):

HOMO  $e_g$  has a strong  $\sigma$ -antibonding overlap with oxygen

Distortion leads to stabilization of  $d_{z^2}$  and destabilization of  $d_{x^2-y^2}$

This results in double occupation of the  $d_{z^2}$  orbital, whose energy is further stabilized by mixing with the empty Cu 4s orbital

N. Wieberg, *Lehrbuch der Anorganischen Chemie*, 102. Auflage, De Gruyter, Berlin, 2007, S. 1361.

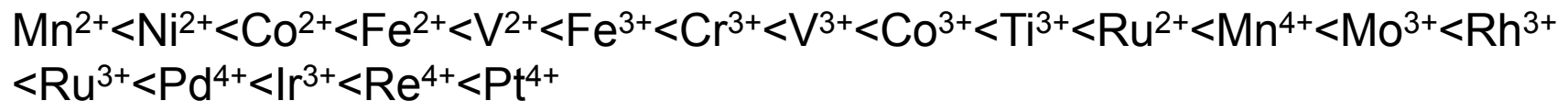
P.M. Woodward et al., *The Electronic Structure of Metal Oxides in Metal Oxides-Chemistry and Application*, ed. by J.L.G. Fierro, CRC Press, Boca Raton, 2006, p. 133.

# Metal-centered transitions

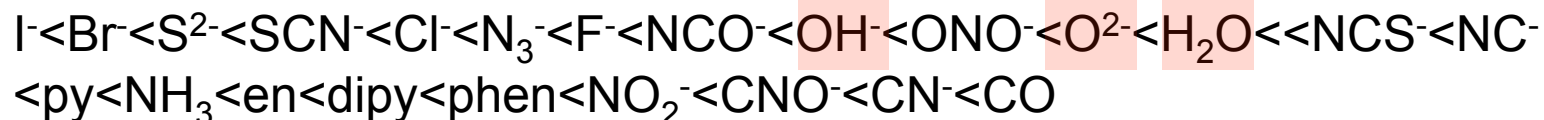
## Crystal field parameter $\Delta$ and spectrochemical series

- $\Delta_t < \Delta_o$  (40-50%)
- With increasing oxidation state the metal-ligand distance decreases and the ligand field splitting increases
- The ligand field splitting increases upon moving down a group

- Increasing splitting:



- Increasing ligand field:



*K.F. Purcell, J.C.Kotz, Inorganic Chemistry, Saunders, Philadelphia 1977.*

*N.Wieberg, Lehrbuch der Anorganischen Chemie, 102. Auflage, De Gruyter, Berlin, 2007, S. 1361.*

*P.M. Woodward et al., The Electronic Structure of Metal Oxides in Metal Oxides-Chemistry and Application, ed. by J.L.G. Fierro, CRC Press, Boca Raton, 2006, p. 133.*

## Metal-centered transitions

Spectrochemical series of supports\*  $\Delta(\text{Cl}) < \Delta(\text{AlO}) < \Delta(\text{ZO}) < \Delta(\text{SiO}) = \Delta(\text{H}_2\text{O})$

**TABLE 4: Values of  $\Delta_0$  and  $B$  for Unsupported and Supported Ni Complexes**

compound	$\Delta_0$ (cm <sup>-1</sup> )	$B$ (cm <sup>-1</sup> )
[Ni(en) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> , 0.5 M solution	11350	908
[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> , 0.5 M solution	10835	913
[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]/SiO <sub>2</sub>	10800	n.d.
[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]/ $\delta$ -Al <sub>2</sub> O <sub>3</sub>	10470	n.d.
[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	10440	774
[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]/NaY	10785	882

$B$  is a term that reflects the magnitude of electron-electron repulsion energy

$B$  gives information about covalent character of bonding and reactivity

See also the following concepts\*\*:

Optical electronegativity

Optical basicity

\*J.-F. Lambert, *J. Phys. Chem. B* 101 (1997) 10347.

\*\*E. Bordes-Richard et al., *Optical Basicity: A Scale of Acidity/Basicity of Solids and Its Application to Oxidation Catalysis in Metal Oxides-Chemistry and Application*, ed. by J.L.G. Fierro, CRC Press, Boca Raton, 2006, p. 319.

# Charge transfer (CT) transitions in molecules

- Electron movement from one group of atoms to another
- Intense bands
- Sensitive to nature of donor and acceptor and to local bonding geometry

Ligand-to-Metal charge transfer (LMCT)

Metal-to-Ligand charge transfer (MLCT)

Metal-to-Metal charge transfer (MMCT, intervalence transitions)

Intraligand or ligand-centered charge transfer (LC)

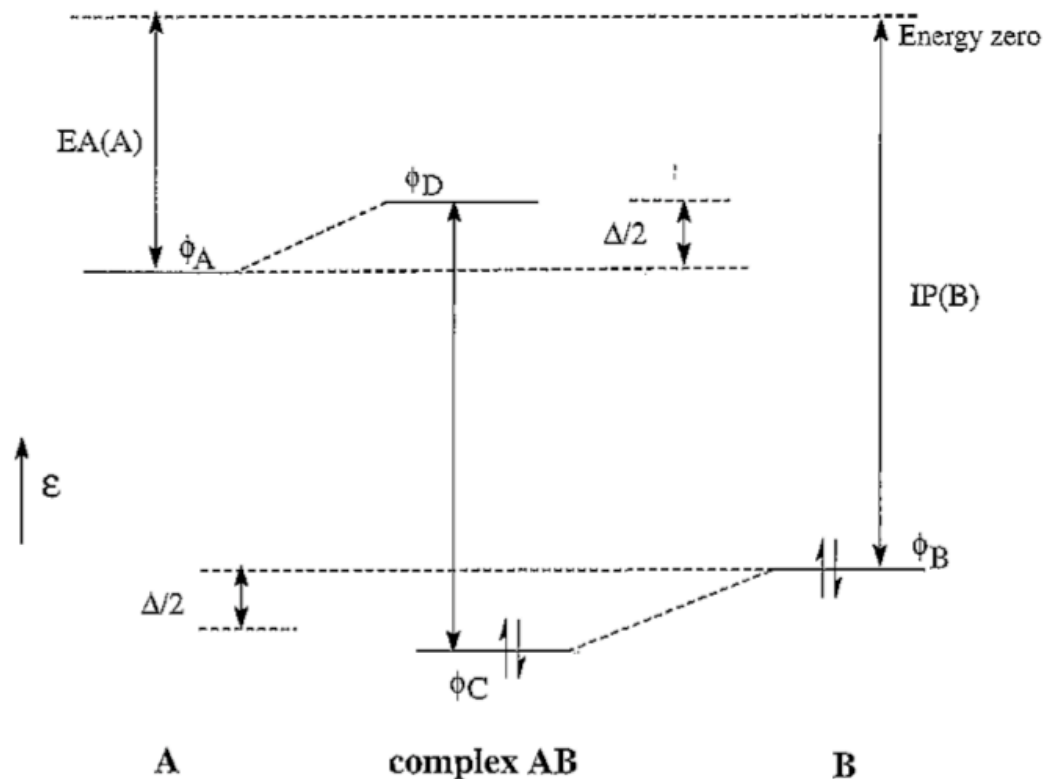
# Charge transfer (CT) transitions in molecules

## Ligand-to-Metal charge transfer (LMCT)

Metal oxidation state decreases formally by 1

$d^0$ , e.g.,  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$

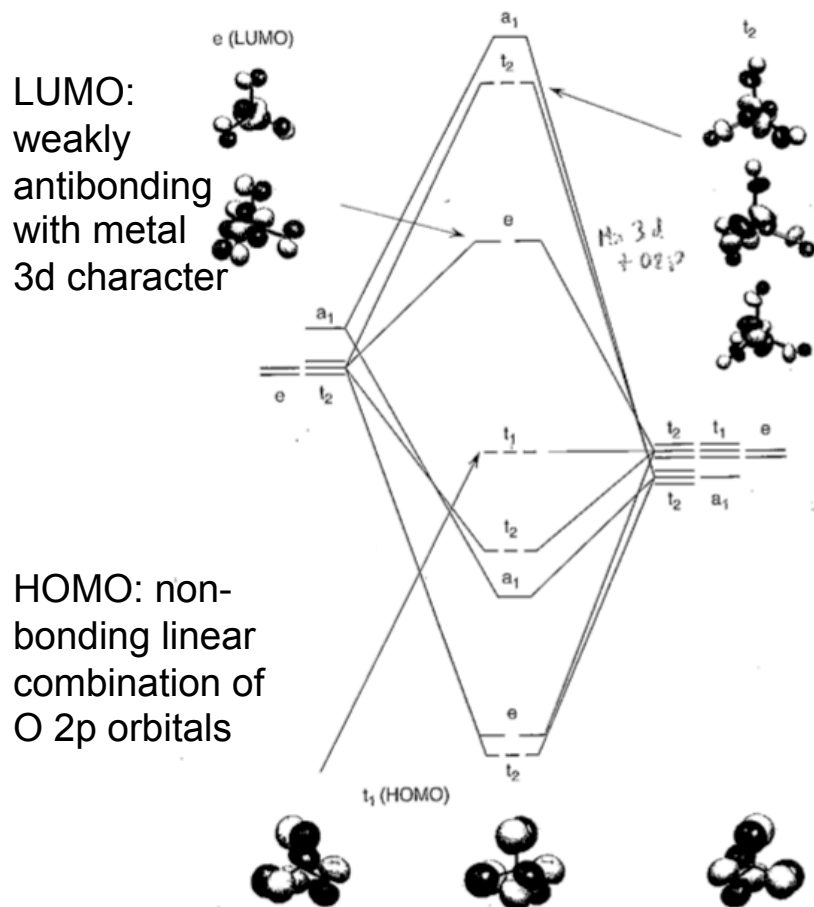
Small interaction between the orbitals of A and B:



**Figure 2.3** Schematic representation of CT transitions.  $EA(A)$  = electron affinity of species A;  $IP(B)$  = ionization potential of species B;  $\Delta$  = stabilization energy of AB. Adapted from ref. [19].

# Charge transfer (CT) transitions in molecules

## Tetrahedral $d^0$ complexes



Complex	M-O Distance (Å)	$t_1 \rightarrow e$ Calculated (eV)	$t_1 \rightarrow e$ Observed (eV) <sup>a</sup>	$t_1 \rightarrow e$ Calculated (eV) <sup>a</sup>
$\text{VO}_4^{3-}$	1.72	4.3	4.5	4.8
$\text{CrO}_4^{2-}$	1.64	3.4	3.3	3.5
$\text{MnO}_4^-$	1.63	2.2	2.2	2.6
$\text{MoO}_4^{2-}$	1.76	5.1	5.3	5.3
$\text{TcO}_4^-$	1.72	4.1	4.3	4.1
$\text{RuO}_4$	1.71	2.9	3.1	3.1
$\text{WO}_4^{2-}$	1.77	6.0	6.2	6.1
$\text{ReO}_4^-$	1.72	5.1	5.3	5.3
$\text{OsO}_4$	1.70	4.1	4.0	4.1

<sup>a</sup> The last two columns show the antibonding M d-O 2p LUMO with e symmetry for tetrahedral  $\text{MO}_4^{n-}$  complexes. Ideal M-O distances were calculated from bond valences [26], which tended to be in good agreement with experimental bond distances. For  $\text{MnO}_4^-$ ,  $\text{TcO}_4^-$ ,  $\text{RuO}_4$ , and  $\text{OsO}_4$  the discrepancy was largest considering the observed and calculated values given in Reference 14.

Splitting decreases from left to right in the periodic table and increases moving down a group

# Charge transfer (CT) transitions in molecules

## Metal-to-ligand charge transfer (MLCT)

e.g., metal carbonyls ( $\pi$ -backbonding)

Metal oxidation state increases formally by 1

## Metal-to-metal charge transfer (MMCT)

Intervalence transitions, e.g.,  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$

Berliner Blau  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6]^-$ , molybdenum blue, “Menninge”  $[\text{Pb}^{\text{II}}_2\text{Pb}^{\text{IV}}\text{O}_2]$

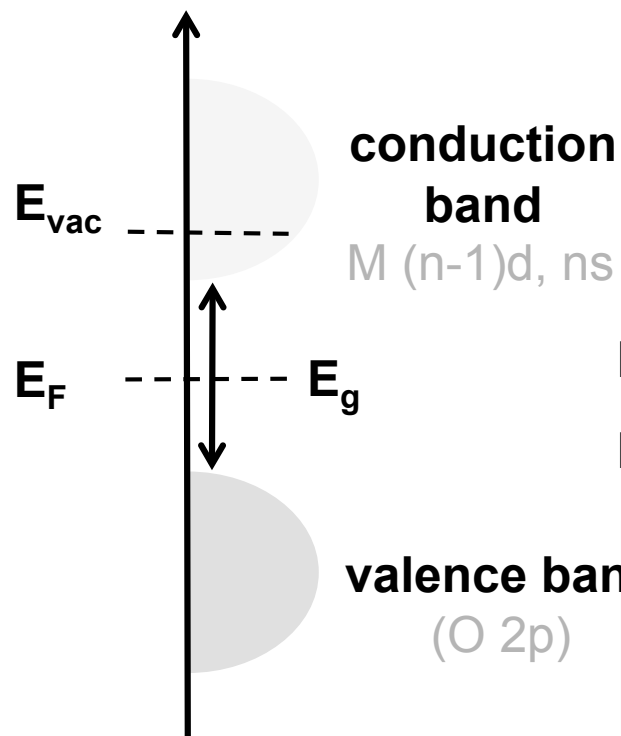


## Intraligand transitions

$n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions in organic or inorganic ligands

Frequently used counter ions in catalysis:  $\text{NO}_3^-$  (300 nm),  $\text{Cl}^-$  (198 nm)

# Transitions between electron energy bands in solids

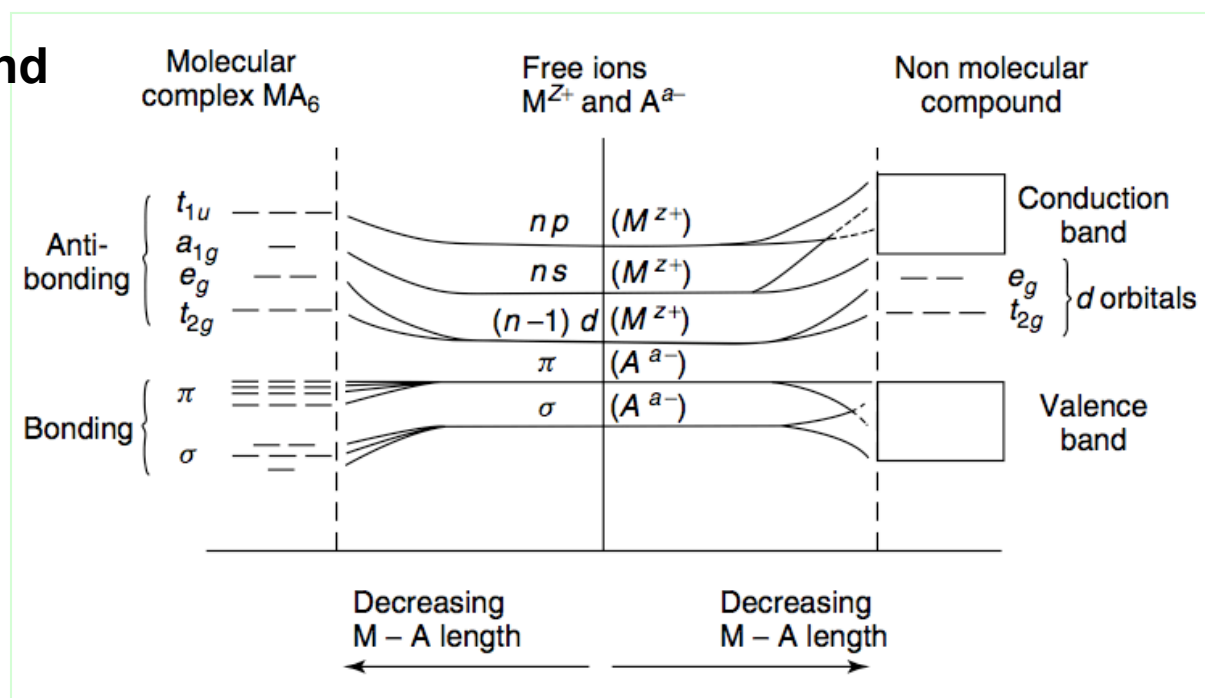


$E_g > 3 \text{ eV}$  insulator

$E_g < 3 \text{ eV}$  semiconductor

Catalyst supports	Approximate band gap (eV)
SiO <sub>2</sub>	9
MgO	8
Al <sub>2</sub> O <sub>3</sub>	7

Due to the electronic configuration, the interband transition can be considered analogous to LMCT

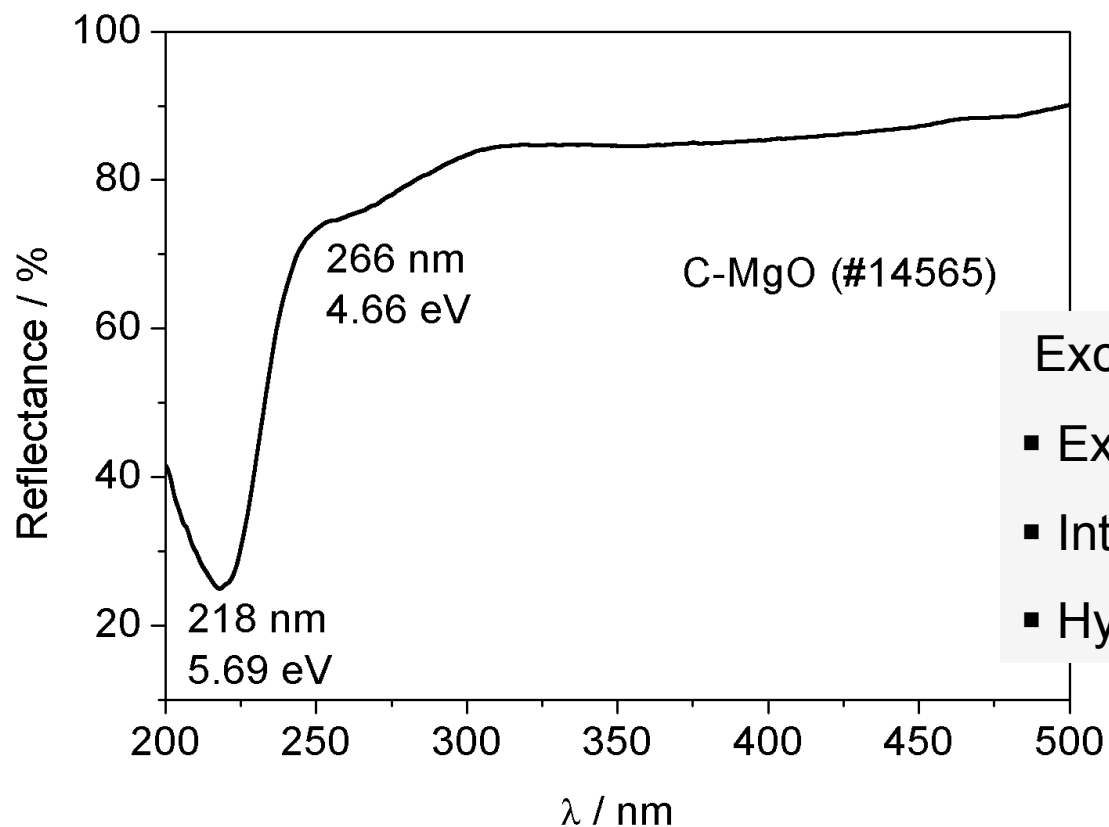




## Insulating oxides – typical catalyst supports

The bulk band gap for MgO is 8.7 eV.

Why do we observe absorption in the UV?



Excitons ( $e^-/h^+$  pairs) due to

- Extrinsic defects (impurities)
- Intrinsic defects, e.g. point defects
- Hydroxyl groups

## Insulating oxides – typical catalyst supports

Exciton gap for surface ions in of highly ionic crystal lattices

$$E_s = A - I + 2V_s$$

$$V_s = z\alpha_s e^2 / a$$

A...electron affinity of anion  
 I...ionization potential of cation  
 V<sub>s</sub>...surface Madelung potential  
 z...charge of the ion  
 α<sub>s</sub>...surface Madelung constant  
 a...lattice constant

*J.D. Levine and P. Mark. Phys. Rev. 144 (1966) 751.*

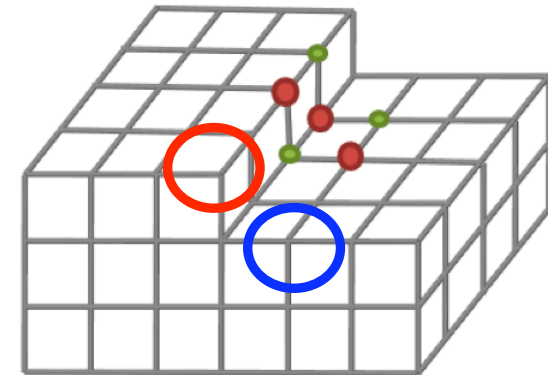
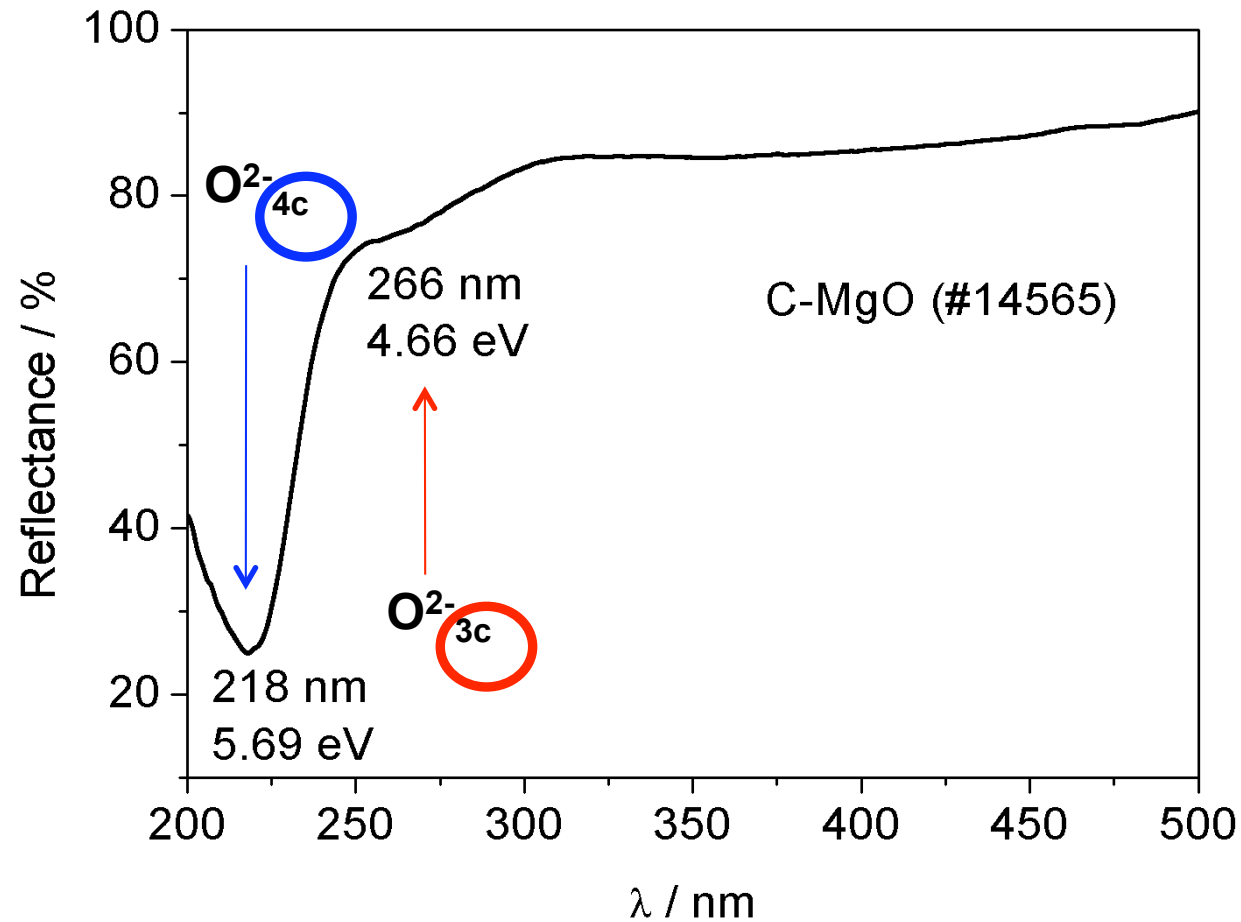
Calculated values for the surface band gap  $E_s$  for different surface planes of MgO

Surface plane	$\gamma$	$\mu$	$\epsilon$	$E_{sg}$ (eV)
100	0.96	0.23	0.95	8.25
110	0.86	0.23	0.82	7.1
210	0.77	0.23	0.70	6.1
211	0.60	0.23	0.48	4.2

Deviations indicate covalent character of involved bonds

*A.J. Tench et al., Chem. Phys. Lett. 26 (1974) 590.*

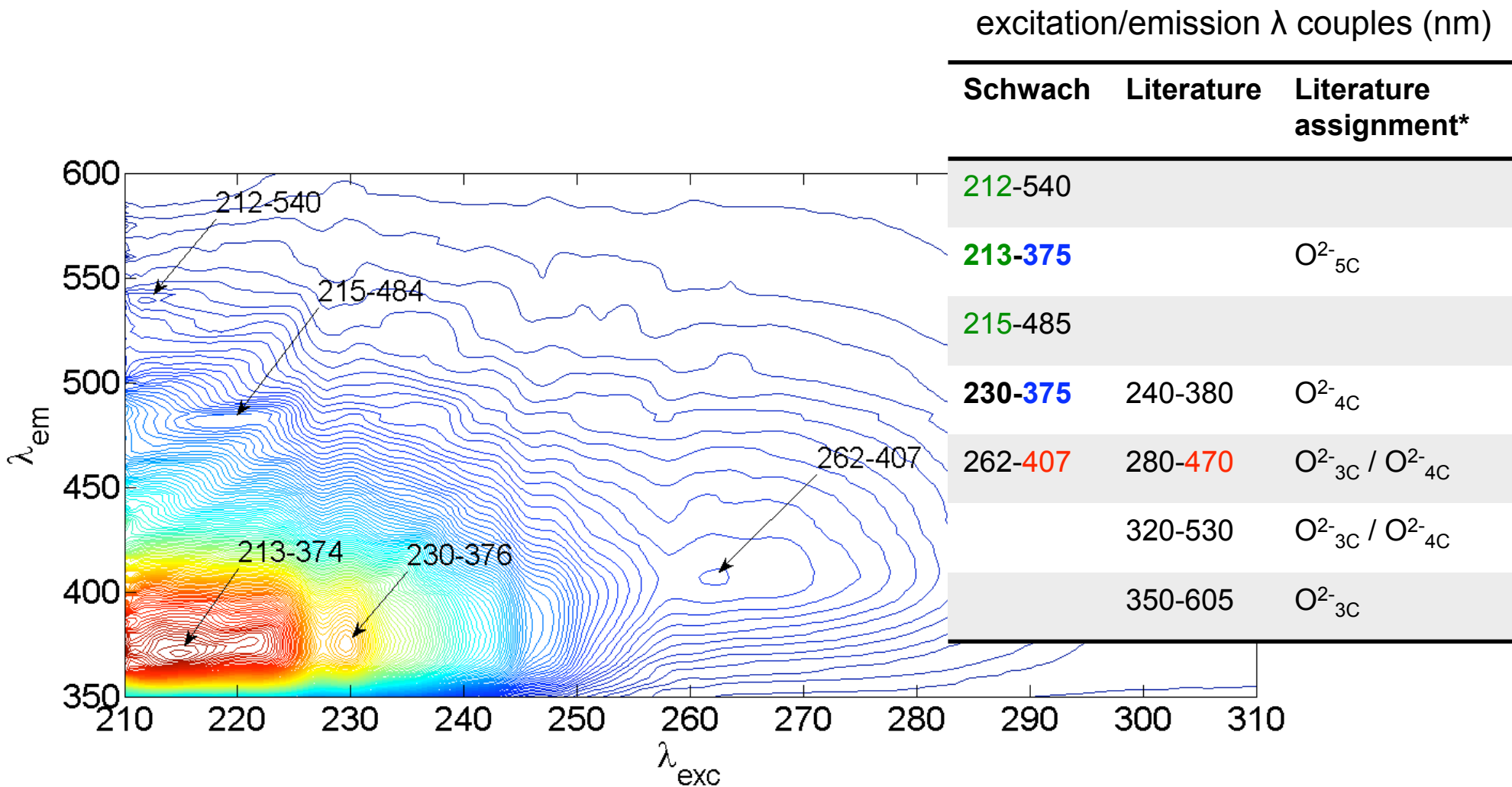
# Insulating oxides – typical catalyst supports



Measurement P. Schwach

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

# Photolumuminescence spectrum of MgO



MgO 14565, Measurement P. Schwach

\*C. Chizallet, J. Phys. Chem. C 112 (2008) 16629.

# Semiconductor oxides – supports and bulk catalysts

TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, ZnO, SnO

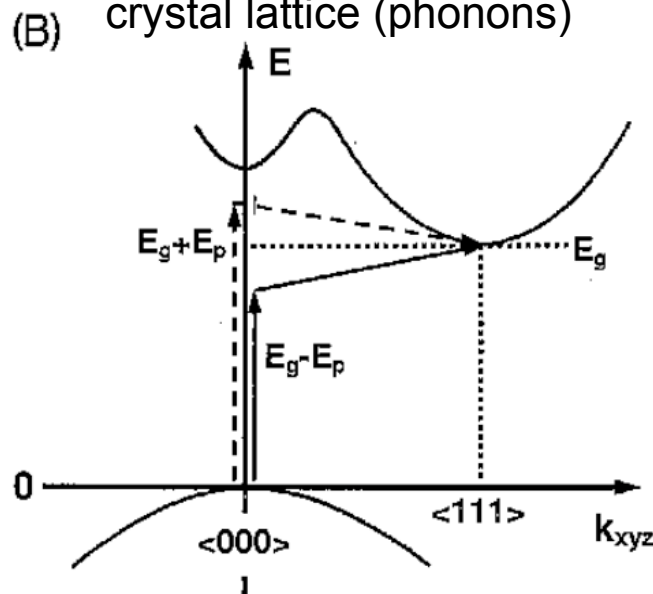
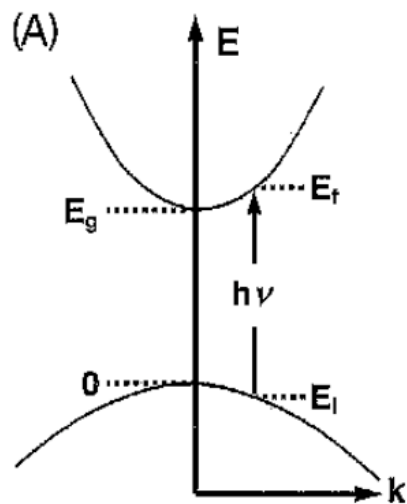
Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>

(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  $k = \langle 000 \rangle$  and  $k = \langle 111 \rangle$ . 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:

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

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

$x = h\nu = \text{photon energy (eV)}$

$x @ y = 0 = B = E_g$

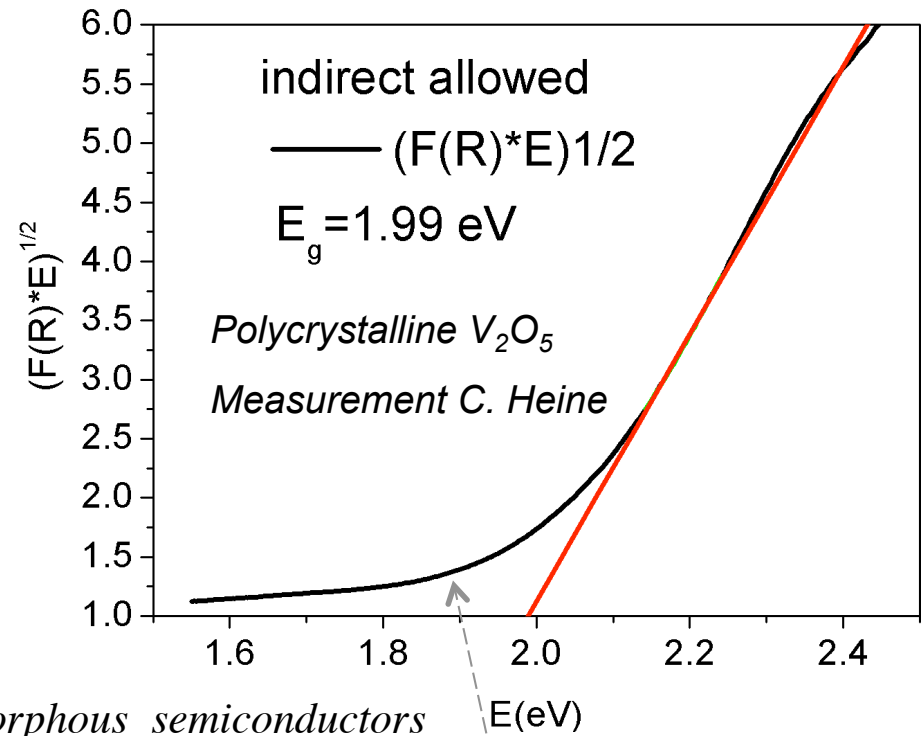
$\eta$  in crystalline semiconductors:

$\eta = 1/2$  direct - allowed

$\eta = 3/2$  direct - forbidden

$\eta = 2$  indirect - allowed

$\eta = 3$  indirect - forbidden



$\eta = 2$  amorphous semiconductors

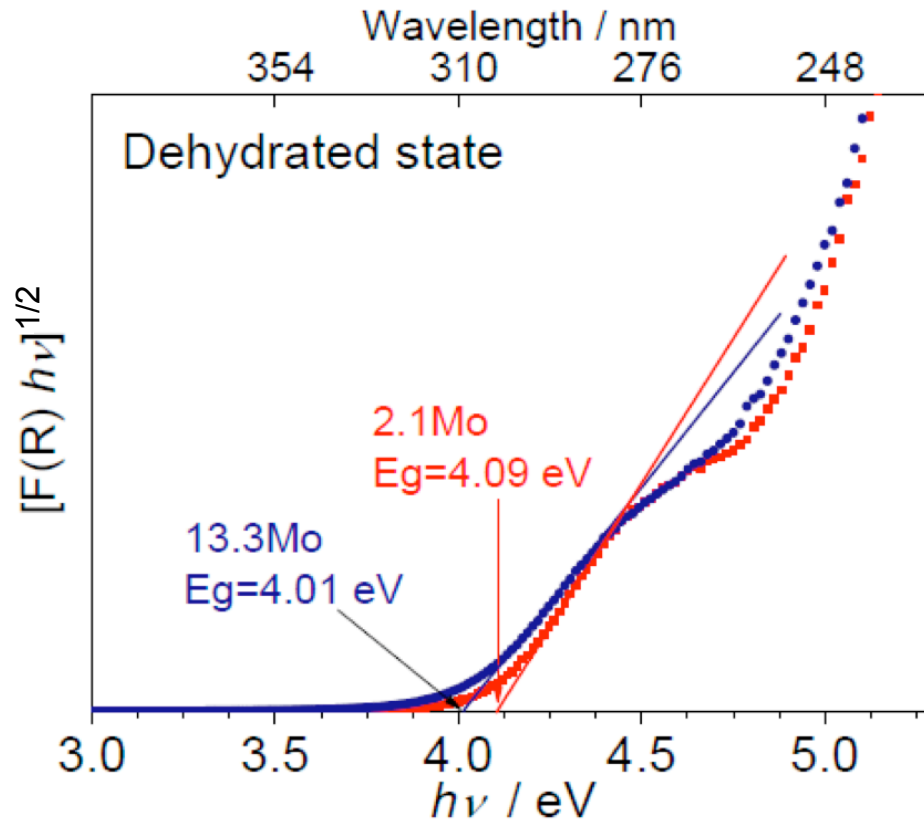
$\alpha$ ...absorption coefficient in transmission – use  $F(R)$  in DRS

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

$$K \propto F(R_\infty) \text{ if } S = \text{const.}$$

Urbach tail  
“fluctuations in the band gap”

# Semiconductor oxides – small surface domains



*MoO<sub>x</sub>/SBA-15, K. Amakawa, to be submitted*

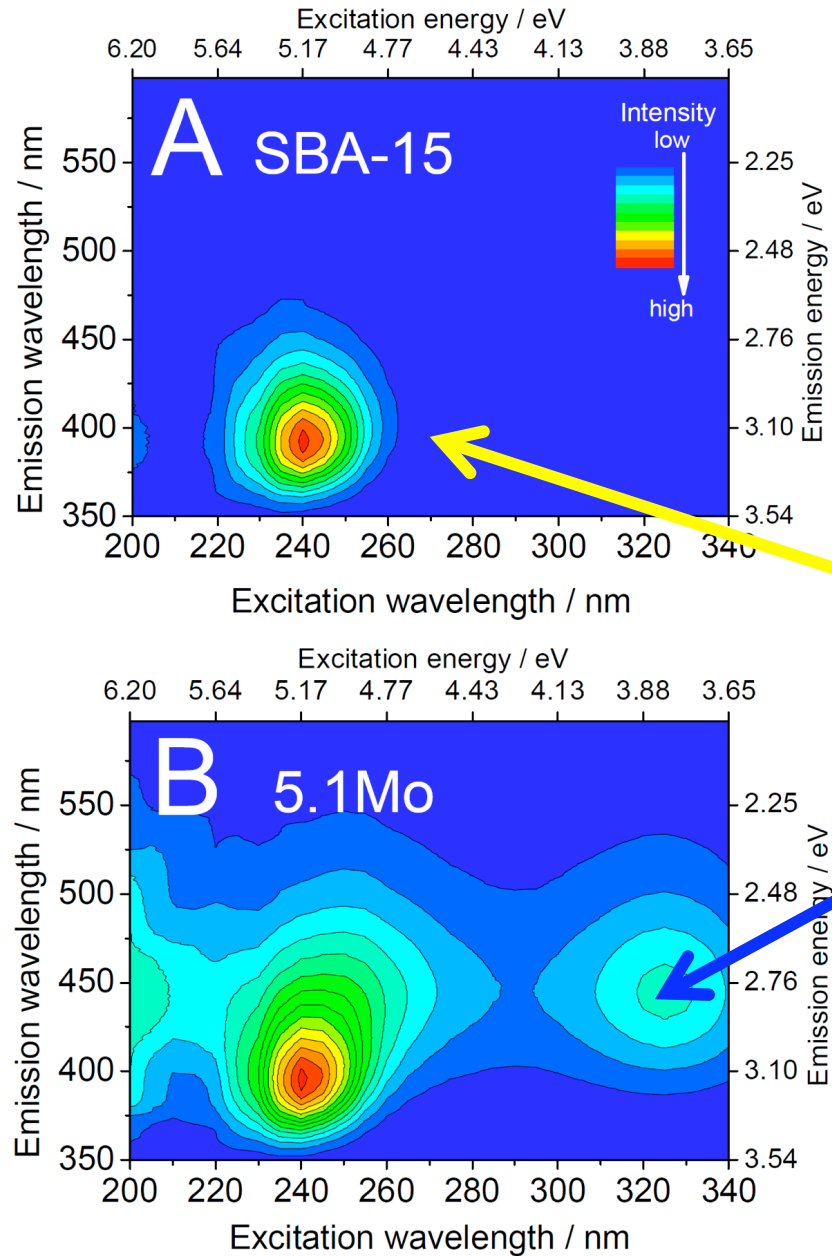
$E_g$  of **three-dimensional** particles depends on

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

## Supported metal oxides

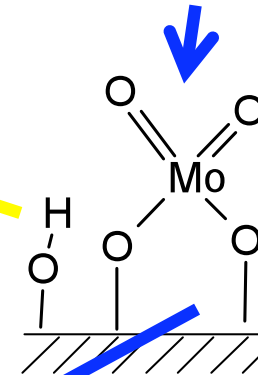
- For small  $M_xO_y$  surface domains, the band theory does not apply, but analysis has shown that the broad distribution of energy levels in surface clusters can be treated like bands
- Spectrum requires deconvolution when different clusters are present

# UV-vis and Photolumuminescence spectra of Mo/SiO<sub>2</sub>



sampling time period of  $0.05 < t < 0.5$  ms

330 / 445 nm  
3.76 / 2.79 eV



( $T_1$ :  $\text{Mo}^{5+}-\text{O}^-$ )

( $S_0$ :  $\text{Mo}^{6+}=\text{O}^{2-}$ )

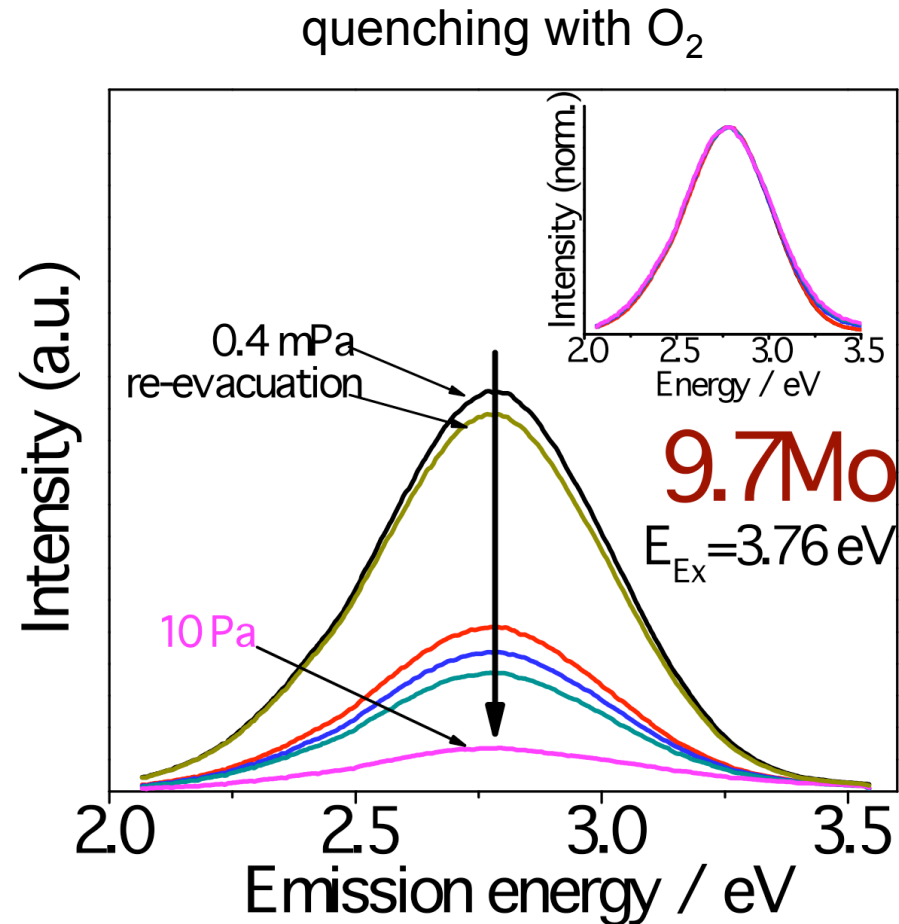
*M. Anpo et al., Journal of the American Chemical Society 111 (1989) 8791.*



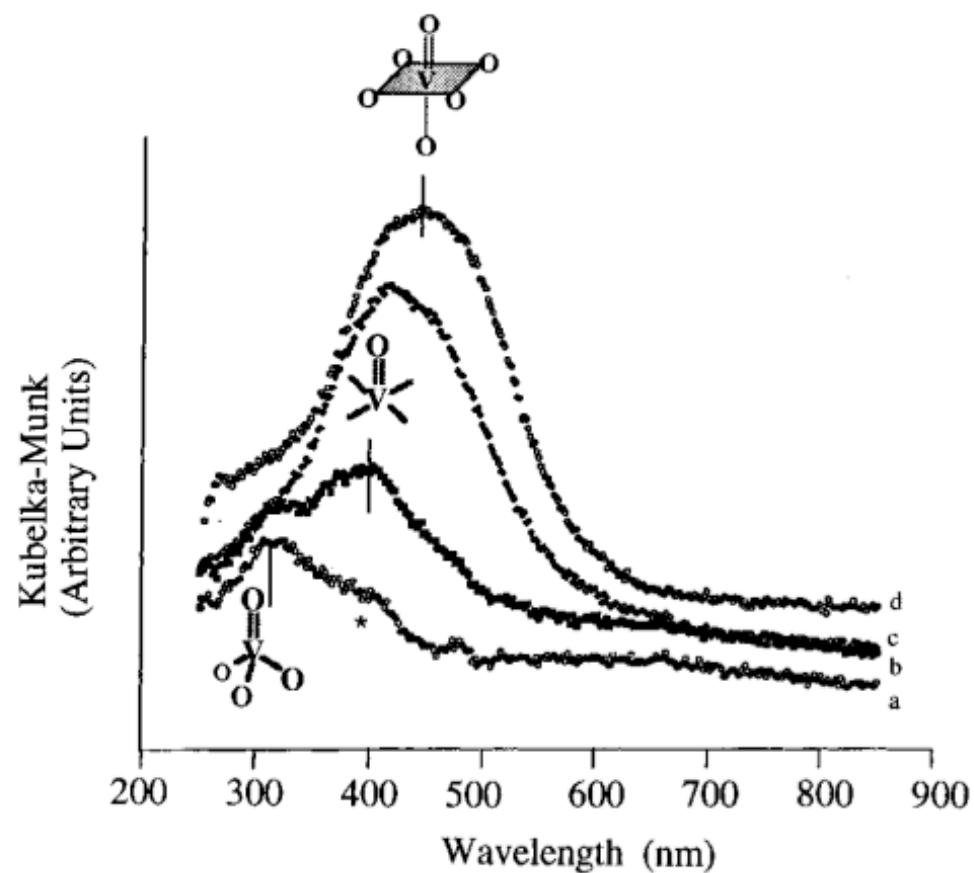
# Discrimination of bulk and surface species

Selective quenching with gas phase molecules

Molecules with widely spaced vibrational levels are able to accept the electronic energy and quench the fluorescence/phosphorescence



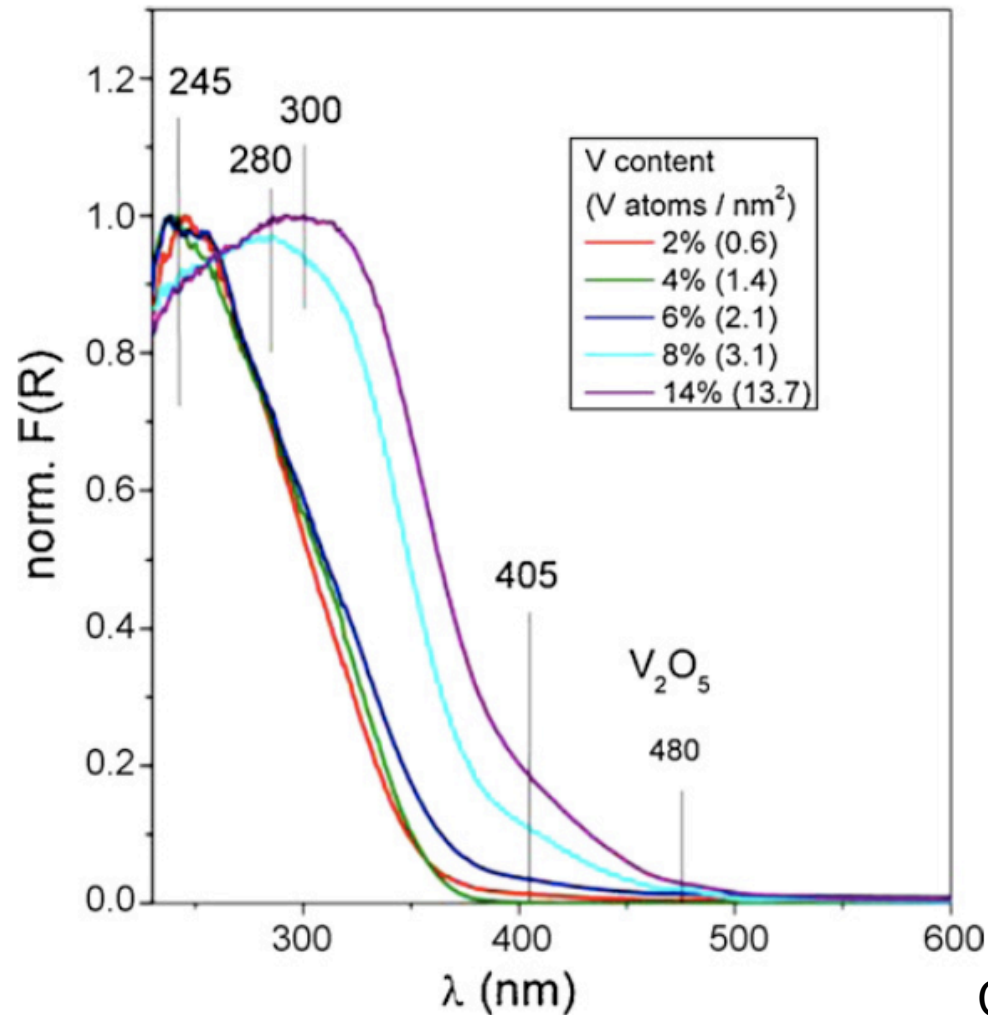
## Highly dispersed species - LMCT



**Figure 5.** Evolution of UV-vis spectra as a function of hydration time (under ambient conditions) for the V/MCM-48/0.05 sample: (a) time 0; (b) 10 min; (c) 30 min; (d) 2 h.

The transition energy decreases as the coordination number increases

# Highly dispersed species - LMCT



Isolated and polymerized  $V_xO_y$  ?

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

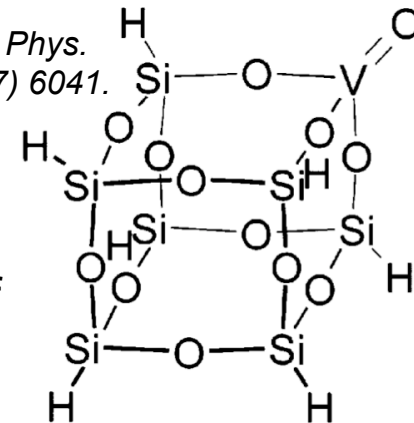
**TABLE 4: Band Maxima and Edge Energies of V-Reference Compounds**

compounds	band max. (nm)	$E_g$ (eV)	molecular structure <sup>a</sup>
$V_2O_5$	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.*

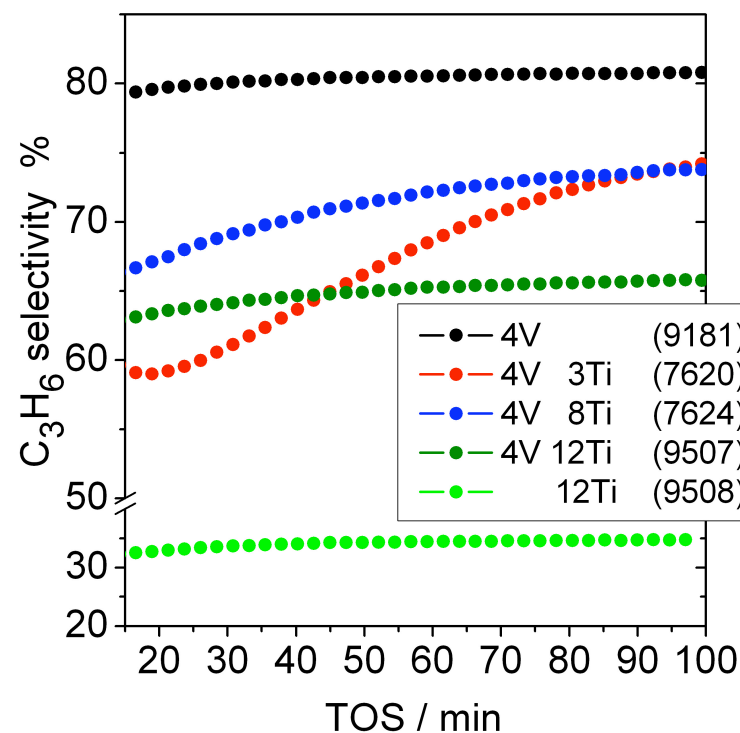
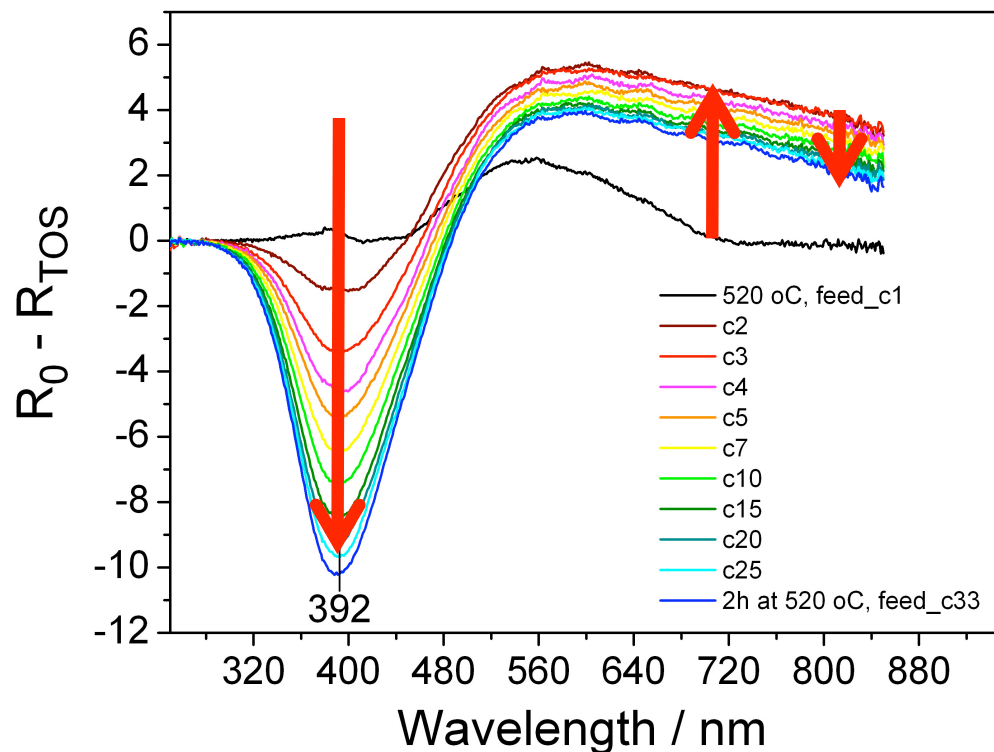
*Rozanska et al., J. Phys. Chem. C 111 (2007) 6041.*

Computational chemistry required for interpretation of spectra



# In-situ UV-vis: propane oxidation on V/SiO<sub>2</sub>

Reaction conditions: T=793K; n<sub>C<sub>3</sub>H<sub>8</sub></sub>: n<sub>O<sub>2</sub></sub>: n<sub>He</sub> = 1:1:5; v = 7 ml/min; m<sub>cat</sub> = 20-30 mg



Analysis of changes in the spectrum in parallel with product analysis by gas chromatography or mass spectrometry allows conclusions about structure-function relationships

# Outline



1. Spectroscopic techniques and data analysis
2. Types of electron transitions and relevance for catalyst/precursor characterization
3. Conclusions

## Conclusions



- UV-vis-NIR spectroscopy and Photoluminescence spectroscopy are useful techniques for the characterization of heterogeneous catalysts and their precursors with respect to local and solid state structure
- The methods provide information about, e.g., oxidation state, coordination number, coordination geometry, nature of chemical bonding, degree of condensation, particle size and band gap
- Theory is necessary for interpretation of the spectra
- UV-vis-NIR and Photoluminescence spectroscopy are complementary methods that emphasize different aspects of the studied materials
- The measurements are comparatively cheap and easy
- UV-vis-NIR spectroscopy can be performed in-situ or under operation
- Adsorption of probe molecules and the dynamic of photocatalytic processes (not shown) can be studied by photoluminescence spectroscopy

## 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. J.L.G. Fierro (Ed.), “Metal Oxides – Chemistry and Applications”, Taylor&Francis, Boca Raton, 2006.

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Philipp Grüne

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Thank you for your attention!

