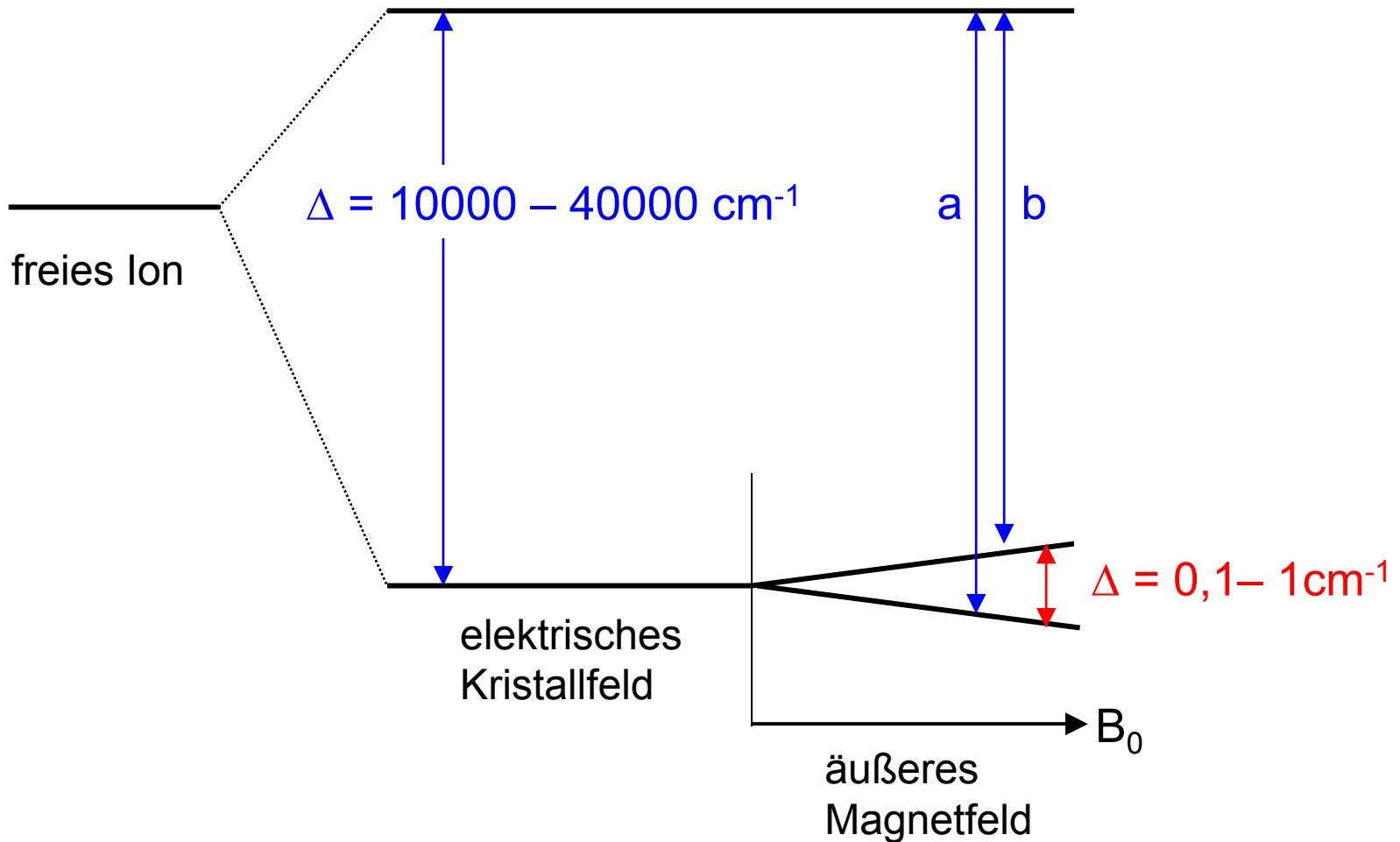


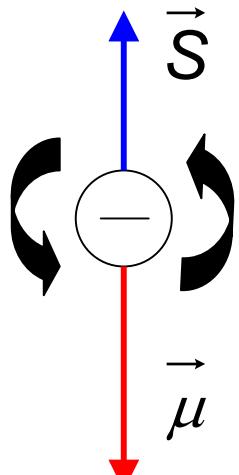
Einfluss eines äußeren Magnetfeldes



Spin und magnetisches Moment von Elektronen und Kernen

Elektron

$$|\vec{S}| = \hbar \sqrt{S(S+1)}$$



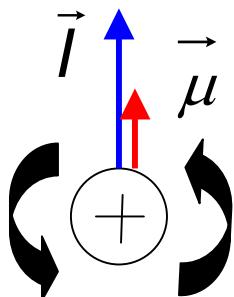
$$\vec{\mu}_e = -g_e \beta \vec{S}$$

$$\beta = e\hbar / 4\pi mc$$

$$|\vec{\mu}_e| = 658 |\vec{\mu}_p|$$

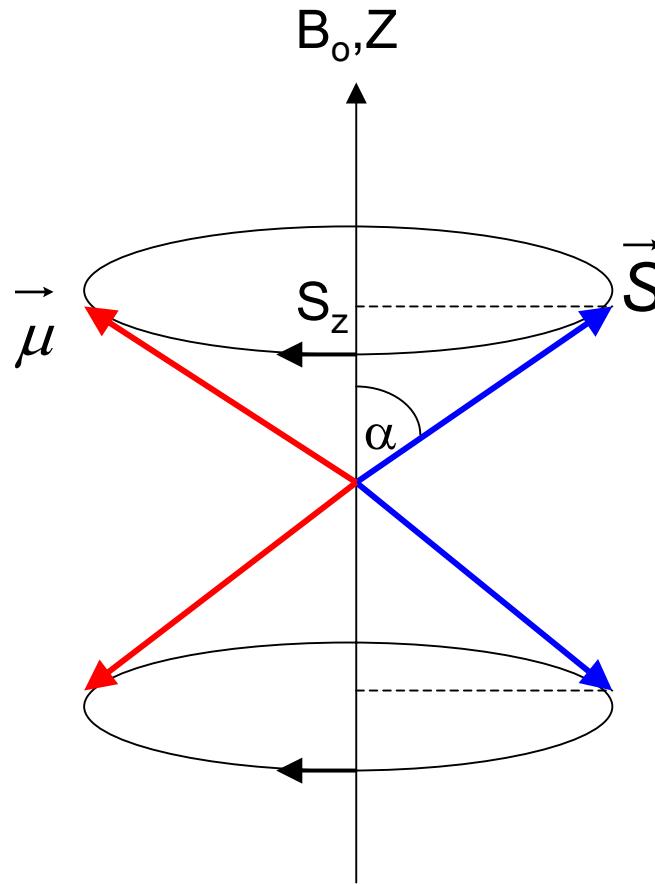
Proton

$$|\vec{I}| = \hbar \sqrt{I(I+1)}$$



$$\vec{\mu}_p = -g_p \beta_p \vec{I}$$

Elektron im Magnetfeld



$$S_z = \cos \alpha |\vec{S}| = \pm 1/2$$

Energie von Elektronen im äußeren Magnetfeld

Freies Elektron

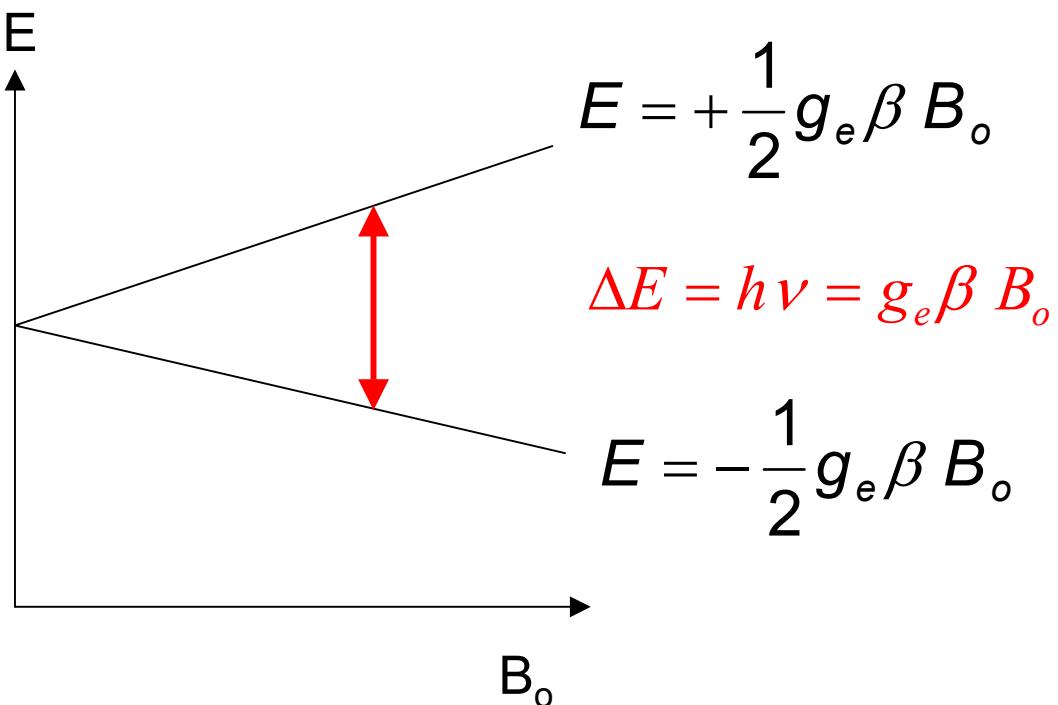
$$E = -\vec{\mu} \cdot \vec{B}$$

$$H\Psi = E\Psi$$

$$H = g_e \beta \vec{S} \cdot \vec{B}$$

$$H = g_e \beta S_z B_o$$

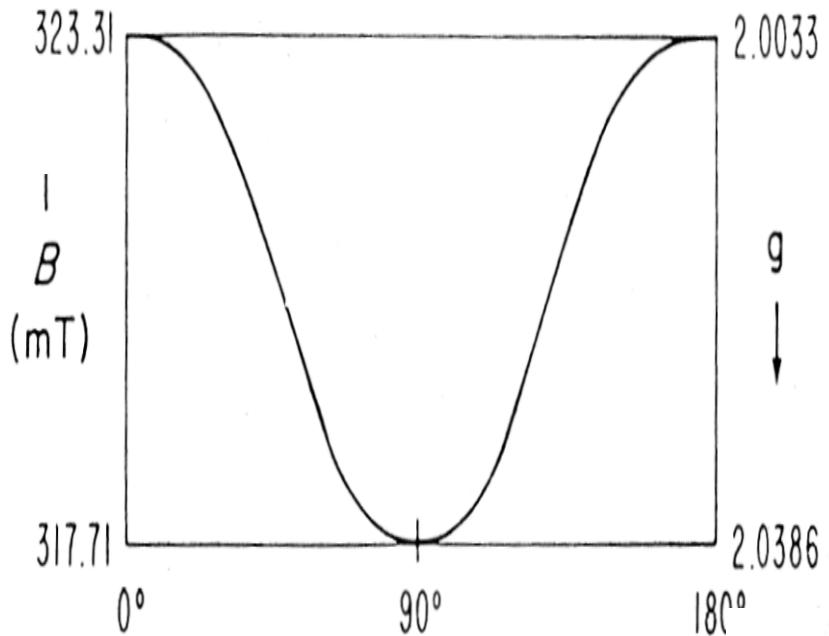
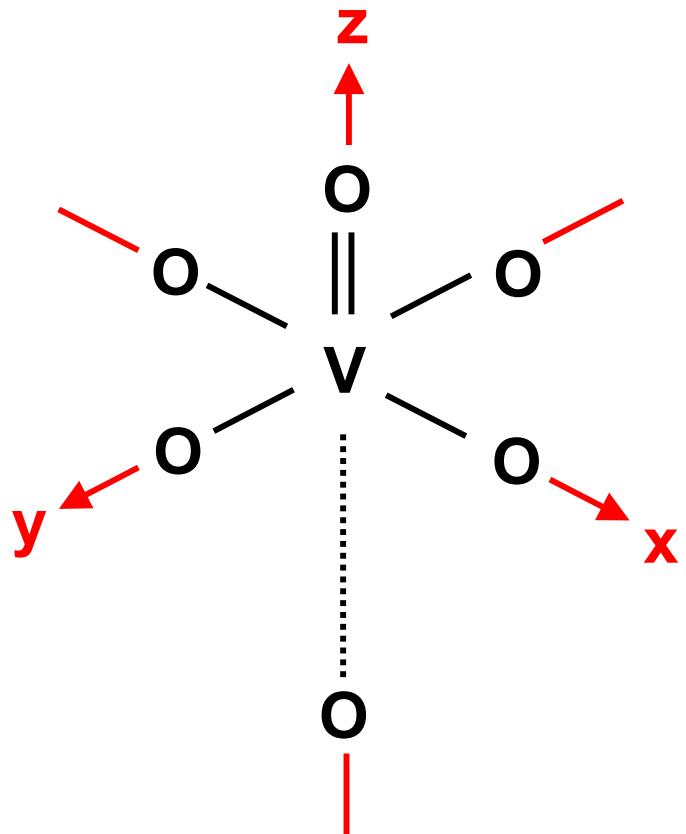
$$E = g_e \beta m_s B_o$$



Elektron in einem Atom

$$H = \beta \vec{B} \cdot (\vec{L} + g_e \vec{S}) + \lambda \vec{L} \cdot \vec{S} = \beta \vec{B} \cdot g \cdot \vec{S}$$

g - Anisotropie des ESR-Spektrums von VO²⁺

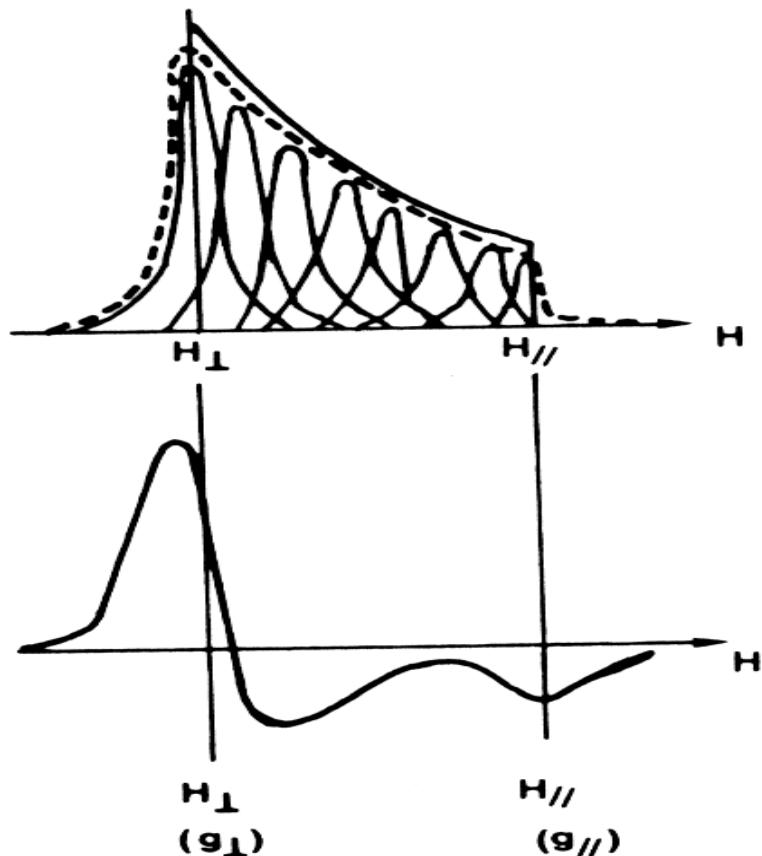
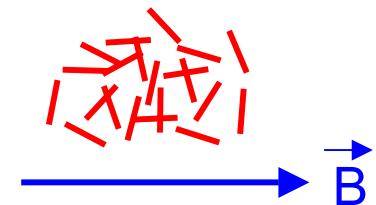


$$g_{\text{eff}}^2 = g_{\parallel}^2 \cos^2 \Theta + g_{\perp}^2 \sin^2 \Theta$$

$$H = \beta [g_{\perp}(B_x \hat{S}_x + B_y \hat{S}_y) + g_{\parallel} B_z \hat{S}_z] = \beta \vec{B} \cdot \hat{g} \cdot \hat{S}$$

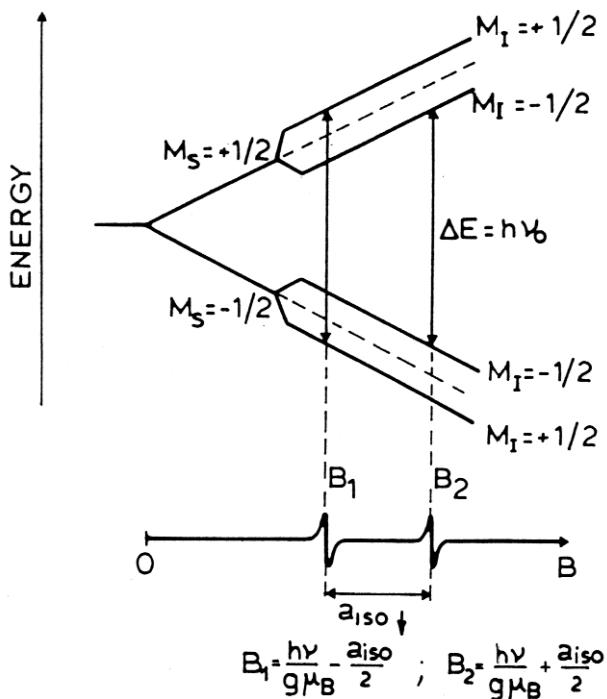
Pulver-ESR-Spektrum

Summe über alle möglichen Orientierungen der magnetischen Achsen von VO^{2+} gegenüber \vec{B}



Kopplung von Elektronen- und Kernspin

$$S = \frac{1}{2}, I = \frac{1}{2}$$



Beispiel:

H-Atom

$$a_{iso} = 50,68 \text{ mT}$$

Anzahl der Hyperfeinlinien:

$$(2I_1 + 1) (2I_2 + 1) \dots (2I_n + 1)$$

Bei Kopplung mit n äquivalenten Kernen:

$$(2nl + 1)$$

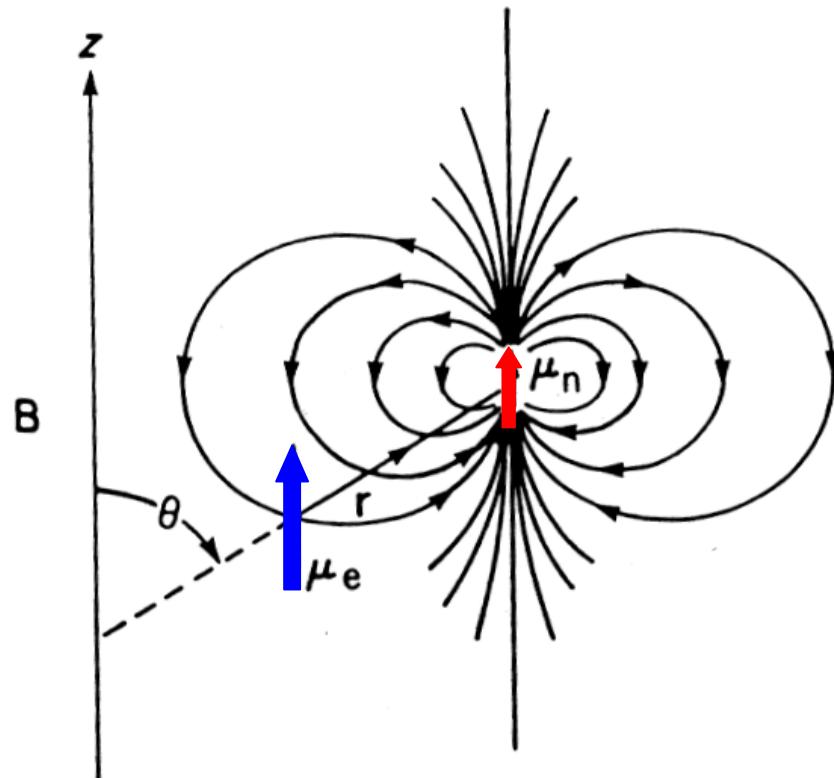
$$A_{iso} = \frac{2\mu_0}{3} g\beta_e g_n \beta_n |\psi(0)|^2$$

Anisotropie der Hyperfeinkopplung von VO²⁺

Kopplung von \vec{S} und \vec{l}

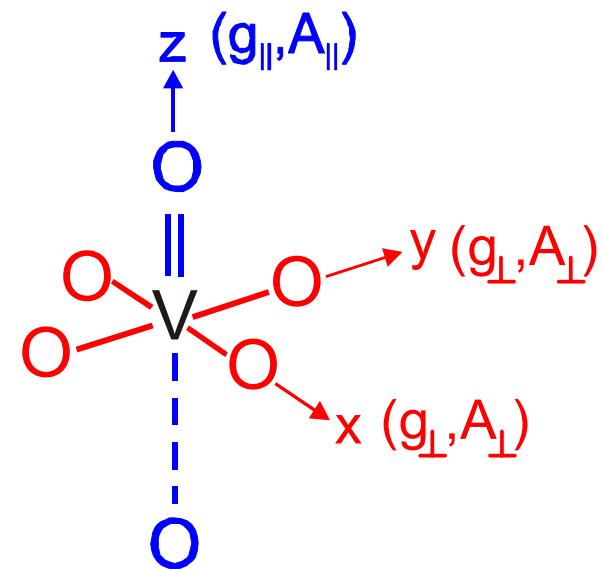
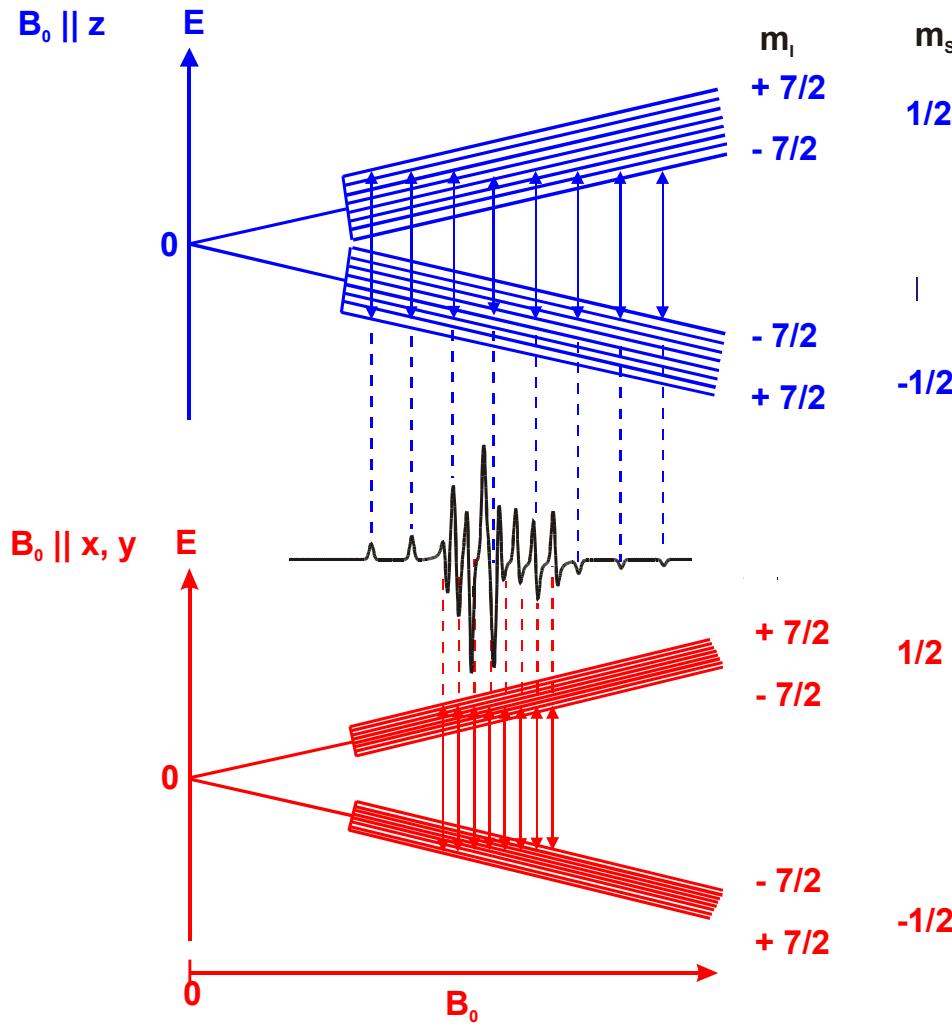
für V: $I = 7/2$

Aufspaltung jedes
Elektronenniveaus in
 $(2I + 1) = 8$
Hyperfeinniveaus



$$E_{dipolar} = -\frac{\mu_0}{4\pi} \frac{3\cos^2\theta - 1}{r^3} \mu_{nz} \mu_{ez}$$

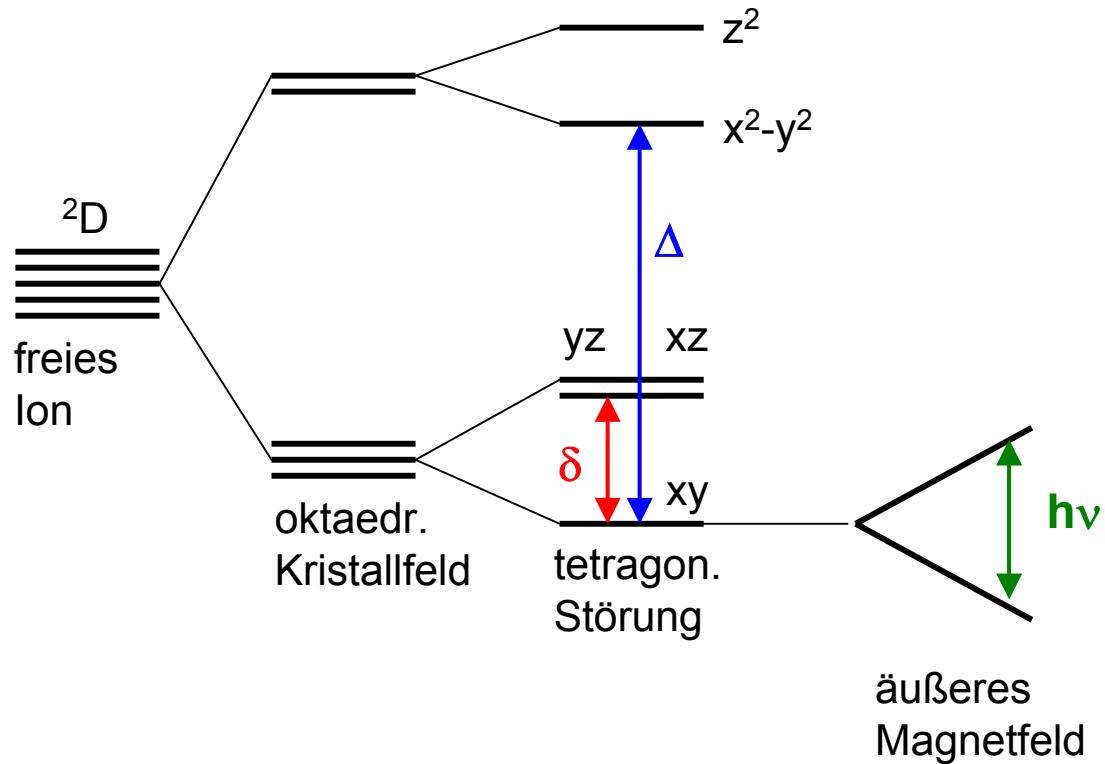
Pulver-ESR-Spektrum von VO²⁺



$$\Delta m_s = \pm 1$$

$$\Delta m_l = 0$$

Abhangigkeit des V⁴⁺-ESR-Spektrums von der Koordinationsgeometrie (oktaedrisch, VO²⁺)



$$g_{||} = g_e - 8\lambda/\Delta$$

$$g_{\perp} = g_e - 2\lambda/\delta$$

fur $\text{VOSO}_4 \cdot 5 \text{ H}_2\text{O}$

$$g_{||} = 1,878$$

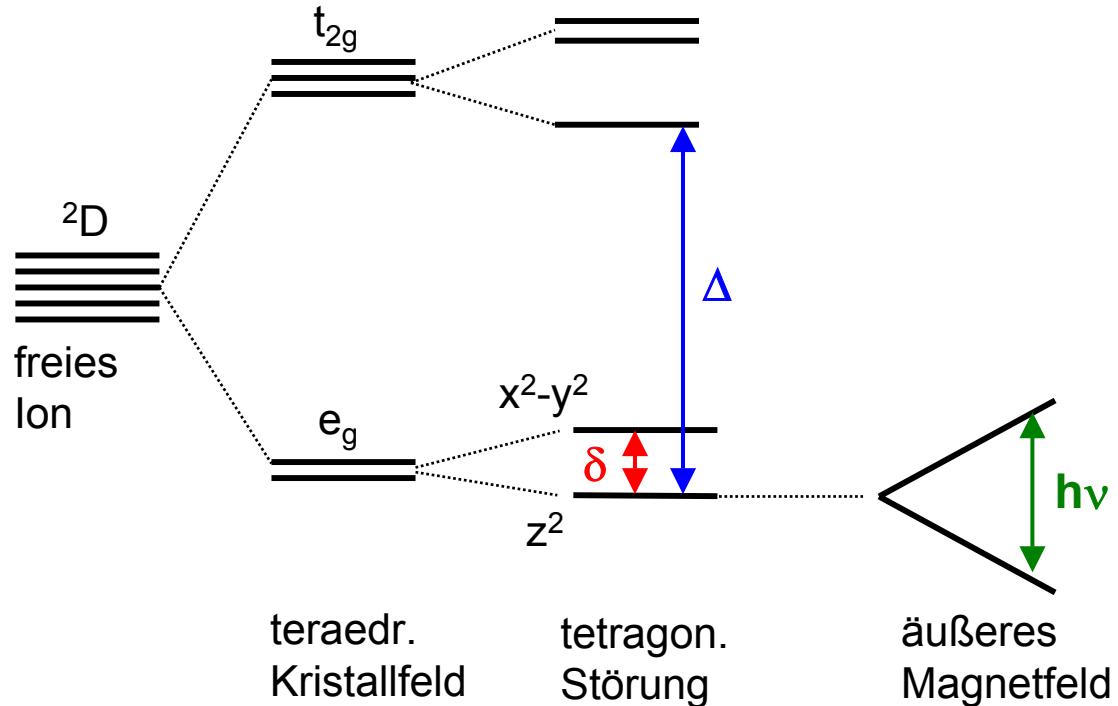
$$\delta = 12900 \text{ cm}^{-1}$$

$$\lambda (\text{V}^{4+}) = 250 \text{ cm}^{-1}$$

$$g_{\perp} = 1,963$$

$$\Delta = 16100 \text{ cm}^{-1}$$

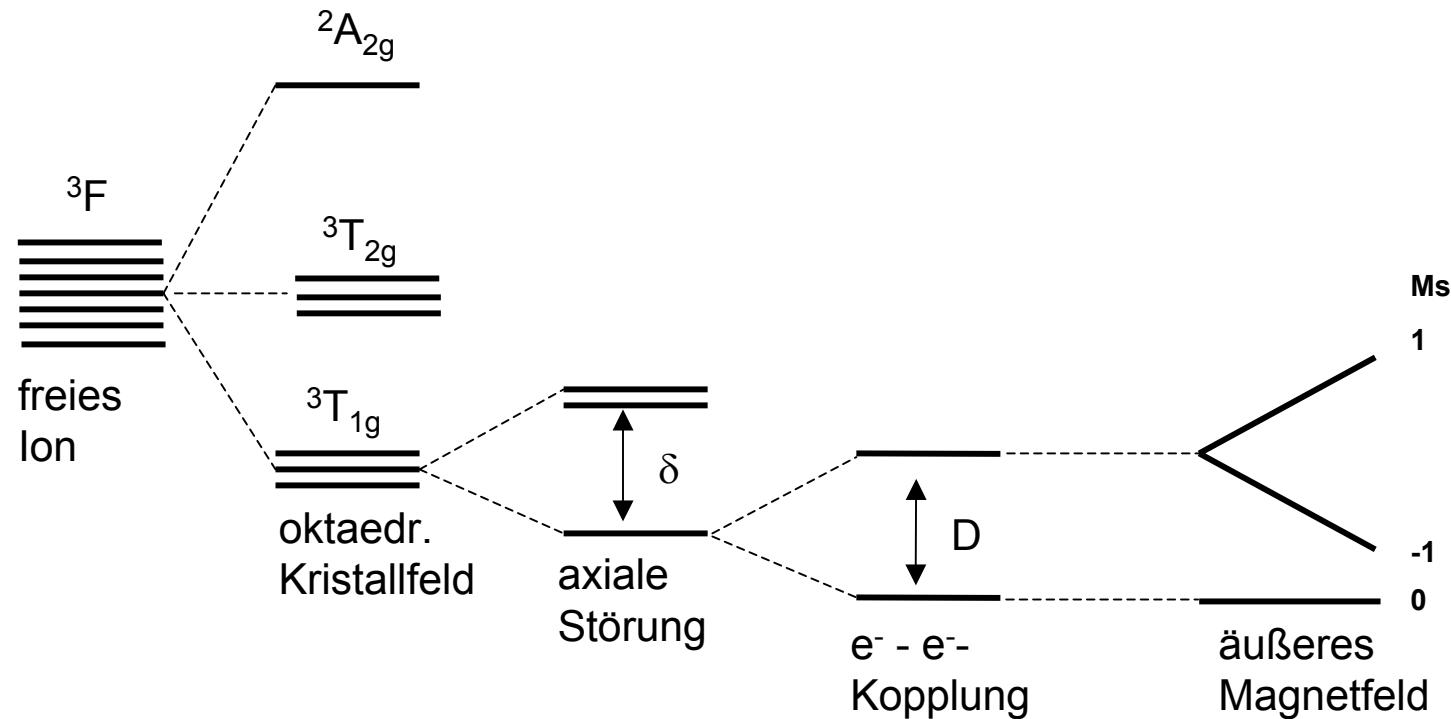
Abhangigkeit des V⁴⁺-ESR-Spektrums von der Koordinationsgeometrie (tetraedrisch)



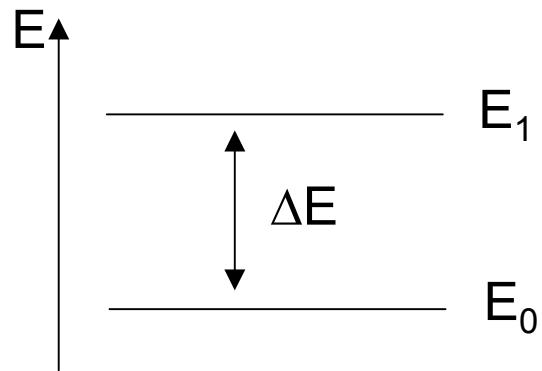
$$g_{\parallel} = g_e$$
$$g_{\perp} = g_e - 6\lambda/\delta$$

$\Delta E \approx h/2\pi\tau \rightarrow$ kurze Relaxationszeiten, groe Linienbreiten

EPR von V³⁺ (d²)



Intensität von EPR-Signalen

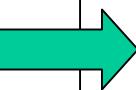


$$N(E) \sim N \cdot e^{-E/kT}$$

$$I \sim \frac{N_1}{N_0} = e^{-(E_1 - E_0)/kT}$$

$$= e^{\Delta E/kT} \approx 1 - \Delta E/kT$$

$$I \sim \frac{N_1}{N_0} \approx 1 - \frac{g\beta B_o}{kT}$$



im X-Band ca. 0,999

vorteilhaft: Messung bei
tiefen T und großem B_0

Temperaturabhängigkeit der Signalintensität

$$\vec{M} \approx N_v \vec{\mu}$$

$$I \sim \chi_m = \frac{M \cdot \mu_m}{B}$$

$$M = \frac{N_v \mu^2 B}{3kT} \text{ (therm. Gleichgewicht)}$$

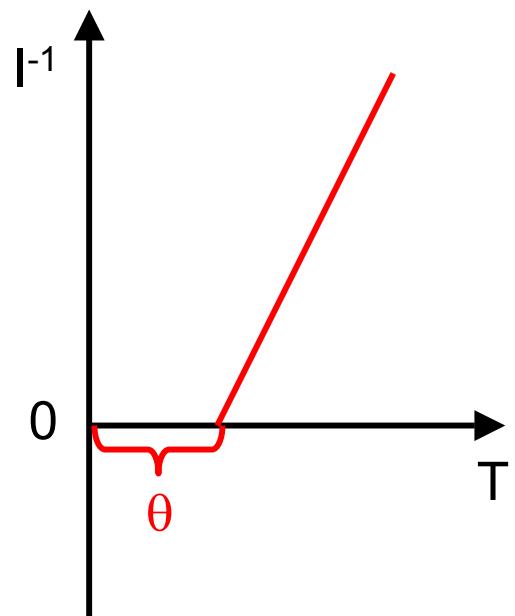
$$I \sim \chi_m = \frac{N_v g^2 \beta^2 S(S+1) \mu_m}{3k} \cdot \frac{1}{T}$$

$$\boxed{\chi_m = \frac{C}{T}}$$

Curie

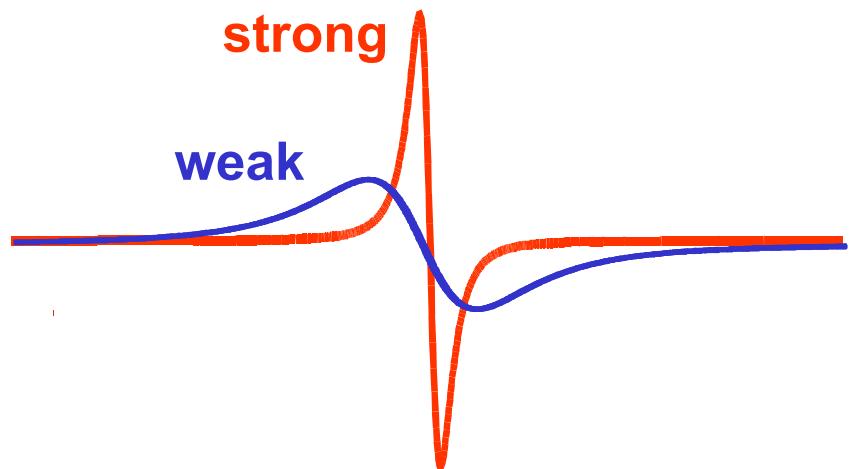
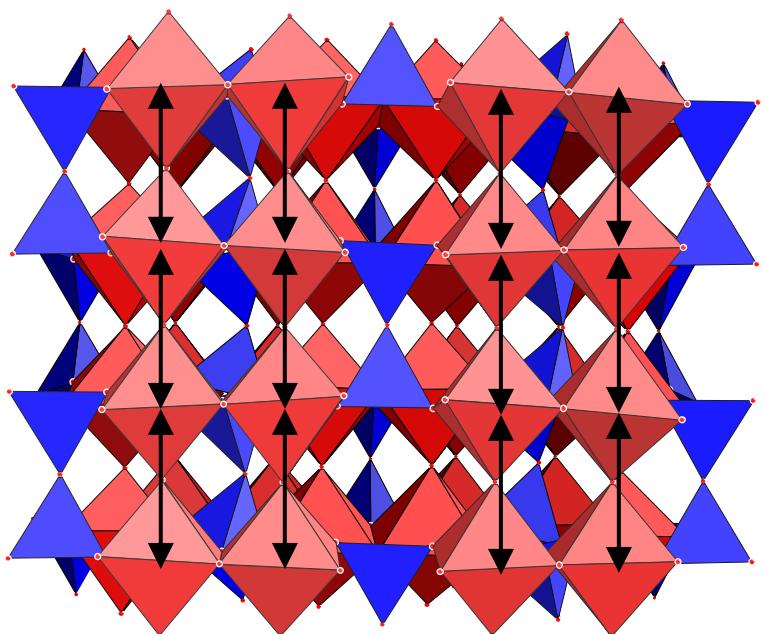
$$\boxed{\chi_m = \frac{C}{T - \Theta}}$$

Curie - Weiß



Magnetische Wechselwirkung von VO²⁺ in (VO)₂P₂O₇

Spin-spin exchange



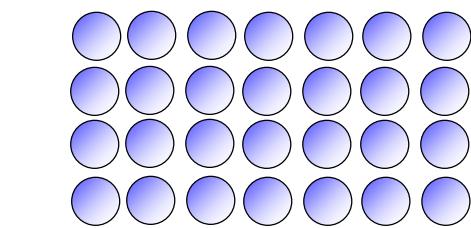
Measure of exchange efficiency:

ΔE – exchange energy

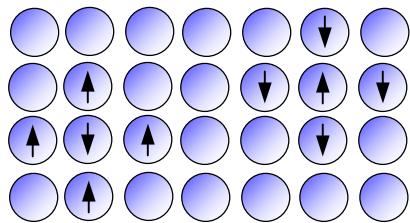
J – exchange integral
(when crystal structure is known)

$$J = \frac{\Delta E}{2zS_i(S_i + 1)}$$

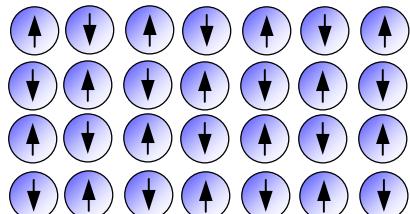
Exchange Energy ΔE derived by the cluster model



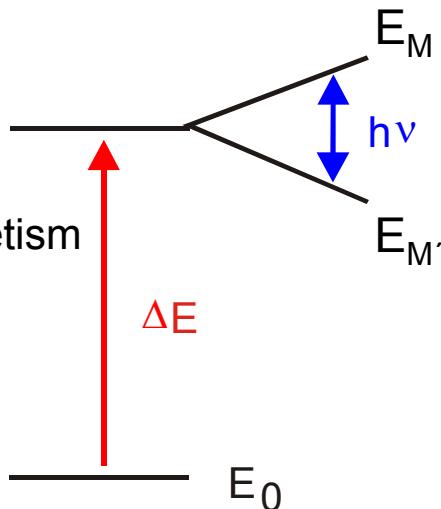
$T \gg T_N \rightarrow$ pure paramagnetism
no clusters



$T > T_N \rightarrow$ short range order
within clusters
EPR signal



$T < T_N \rightarrow$ antiferromagnetic
long range order
no EPR signal



Cluster Model

K. Dräger, Z. Naturforsch. A 32 (1977) 163

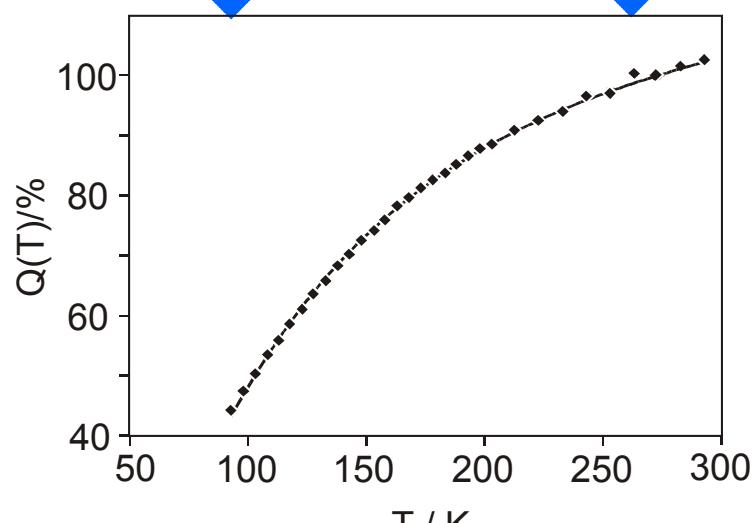
$$\Delta N = N_0 \frac{h\nu}{kT} \frac{\exp [-\Delta E/kT]}{1 + (2S+1) \exp [-\Delta E/kT]}$$

$$Q^*(T) = \frac{T \Delta N(T)}{T_R \Delta N(T_R)}$$

$$Q(T) = \frac{T I(T)}{T_R I(T_R)}$$

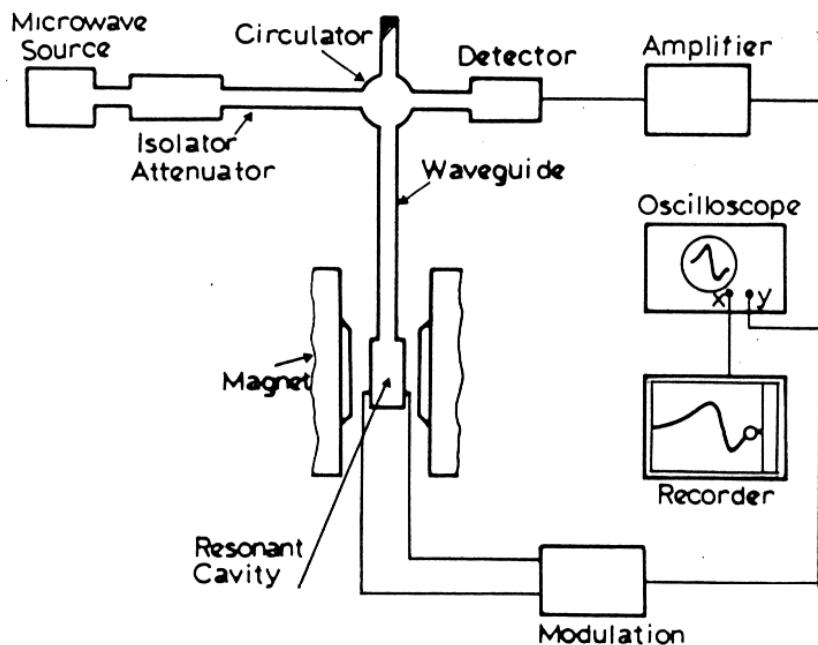
Model function

EPR intensities

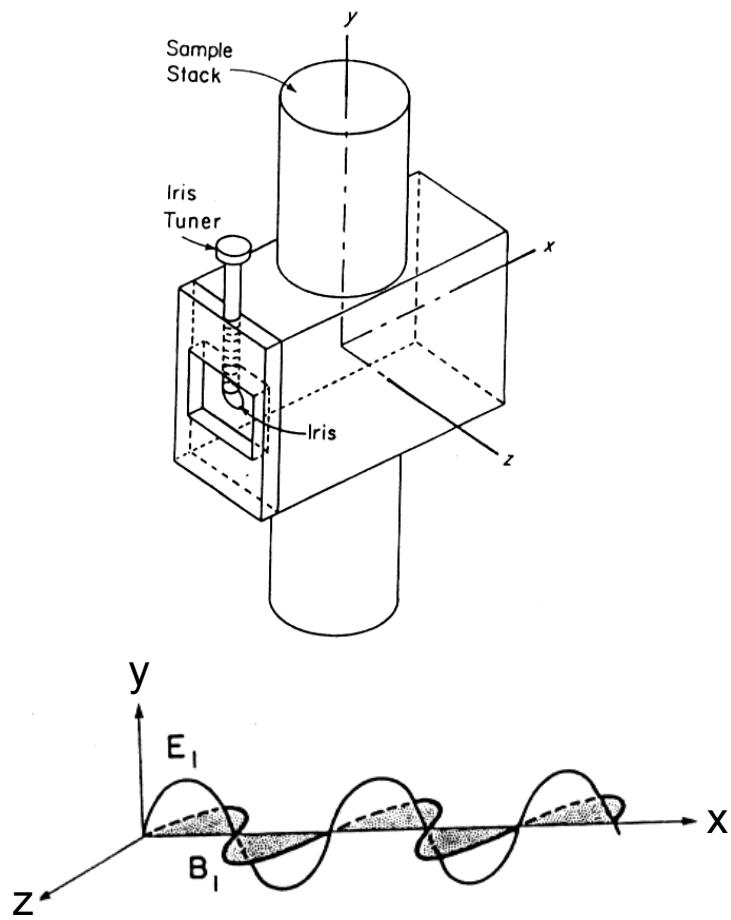


EPR – apparatus Details

Spektrometer-Aufbau



Rechteck-Hohlraumresonator

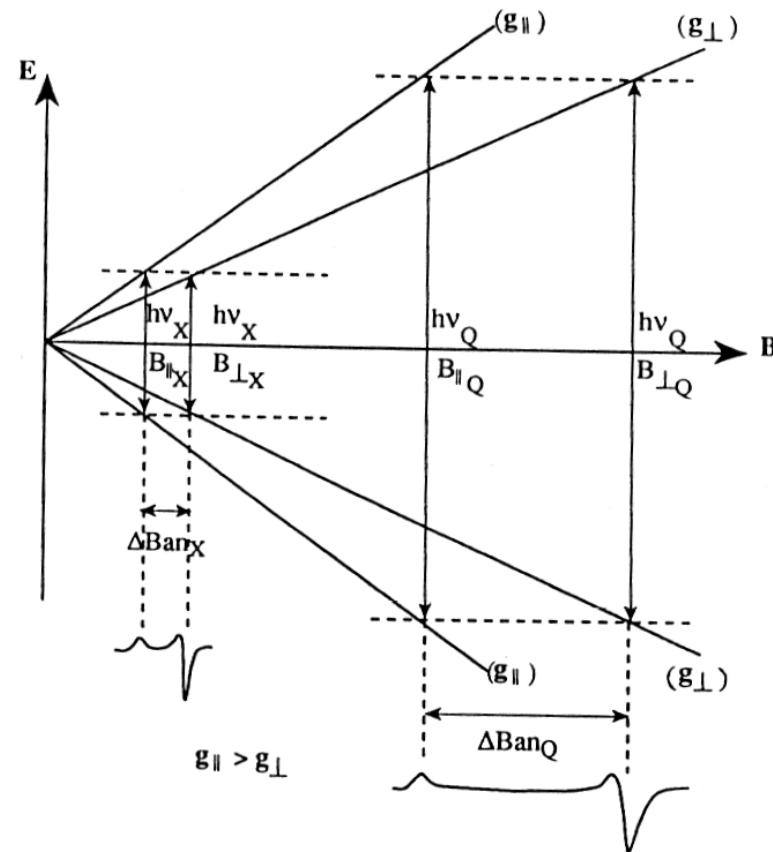


Einfluss der Mikrowellenfrequenz

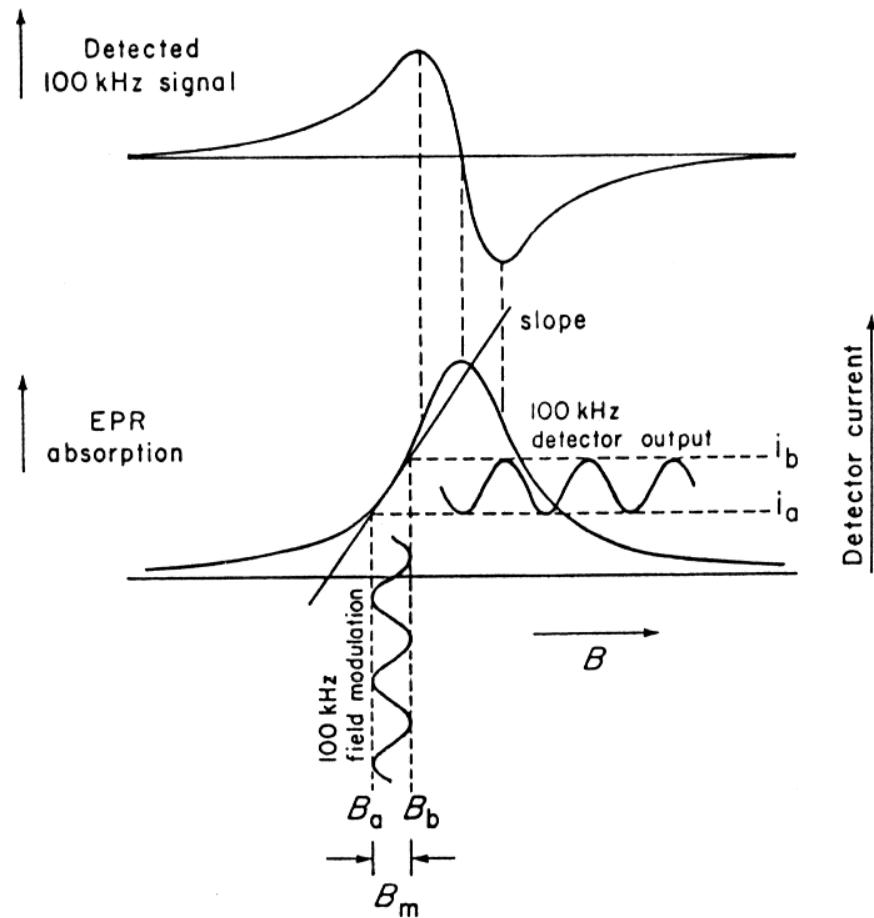
Band	ν / GHz	B_R / mT	λ / cm
L	1,5	54	19,9
S	3,0	111	9,3
X	9,5	350	2,9
K	25,0	890	1,1
Q	35,0	1250	0,8
W	95,0	3400	0,3

$$\Delta E = h\nu = g_e \beta B_o$$

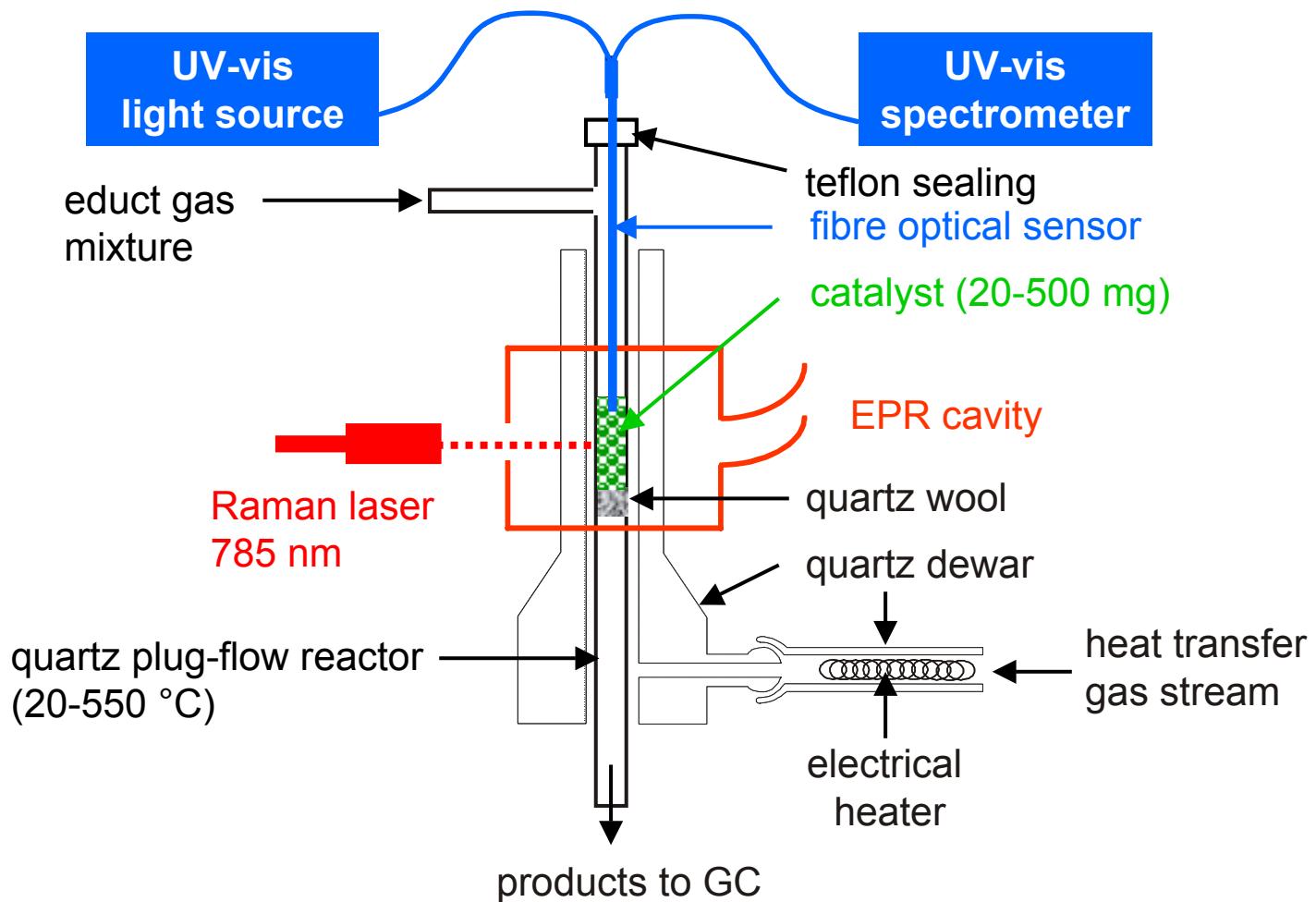
$$H = \beta \vec{B} \cdot \hat{g} \cdot \hat{S} + \hat{S} \cdot \hat{A} \cdot \hat{I} + \hat{S} \cdot \hat{D} \cdot \hat{S}$$



Feld-Modulation und Signalform



Operando-EPR/UV-vis/Raman-Kopplung am ACA



Anwendungsbeispiel I

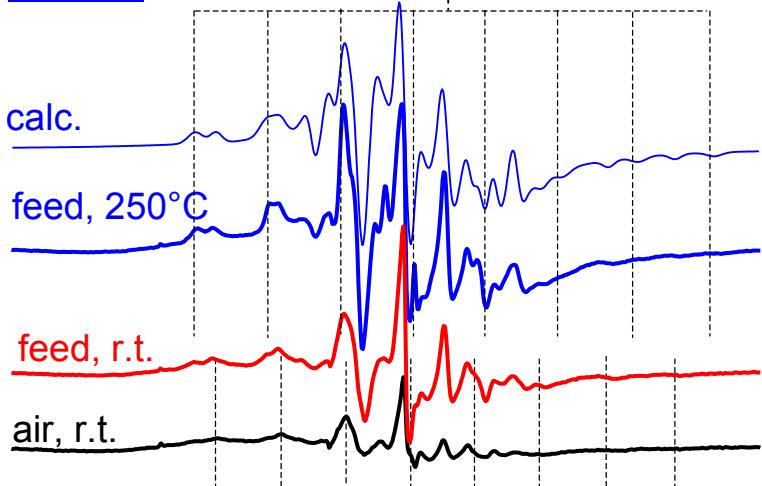
Oxidative Dehydrierung von Propan an
einem 6 % V/TiO₂ – Trägerkatalysator



6% V/anatase (2.2% sulfate)
8.3 % C₃H₈, 8.3 % O₂ / N₂ up to 250°C

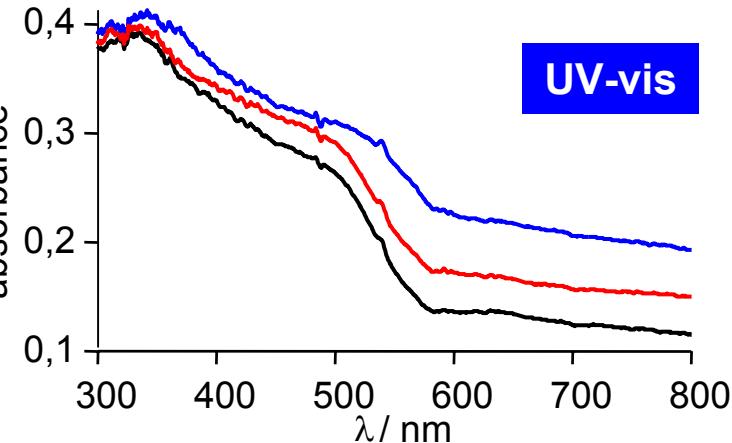
EPR

$g_{\parallel} = 1.925$, $A_{\parallel} = 199.2$ G

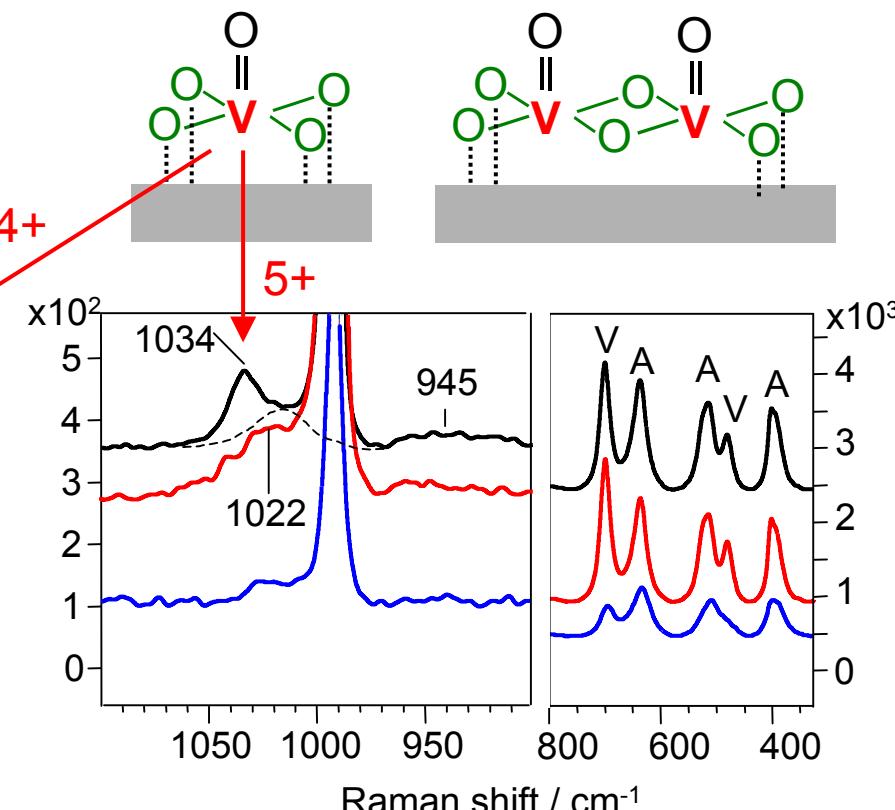


$g_{\parallel} = 1.983$, $A_{\parallel} = 176.3$ G

UV-vis

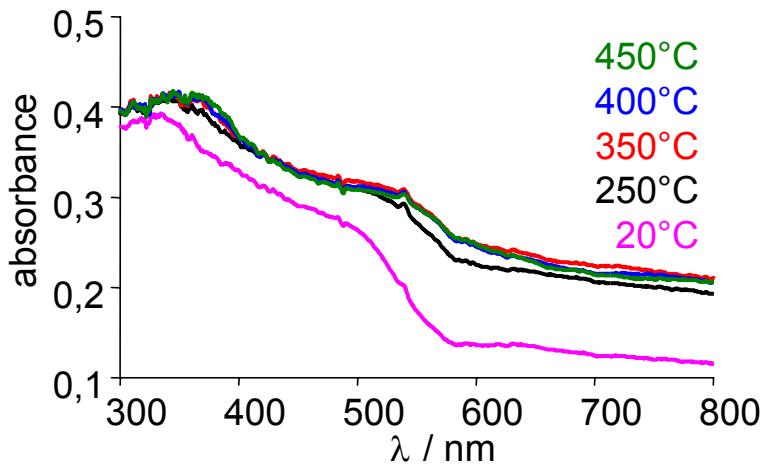


Raman

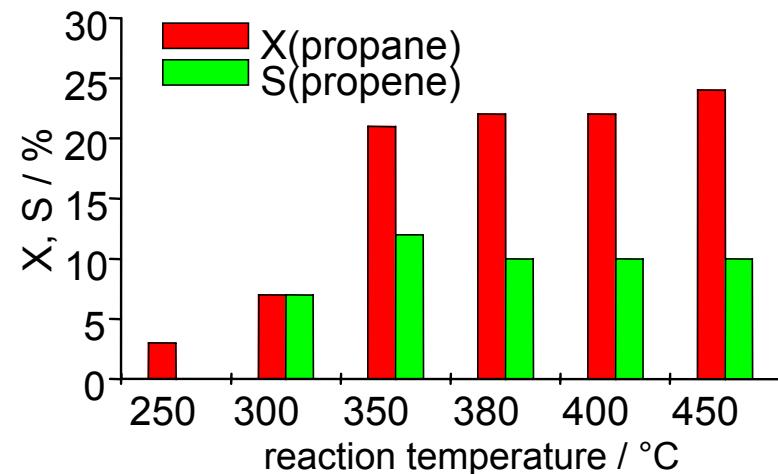


8.3 % C₃H₈, 8.3 % O₂ / N₂ at 250 – 450 °C

UV-vis



catalysis

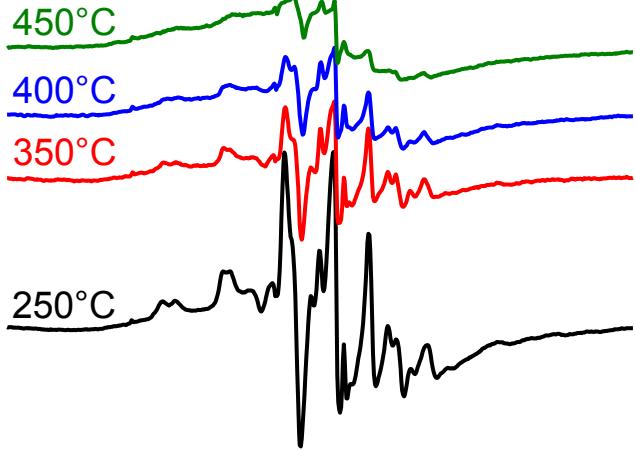


V reduction almost completed above 250°C

Selectivity increases with V reduction

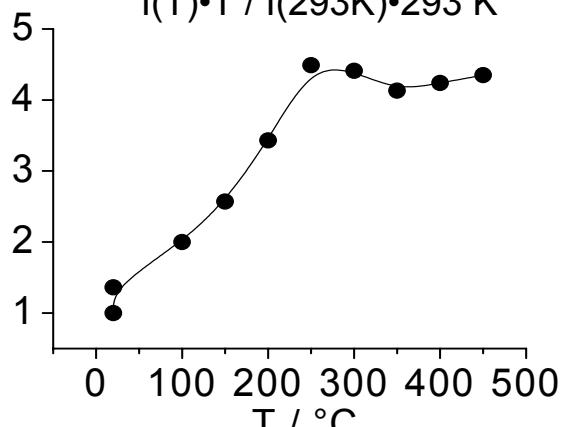
8.3 % C₃H₈, 8.3 % O₂ / N₂ at 250 – 450 °C

EPR

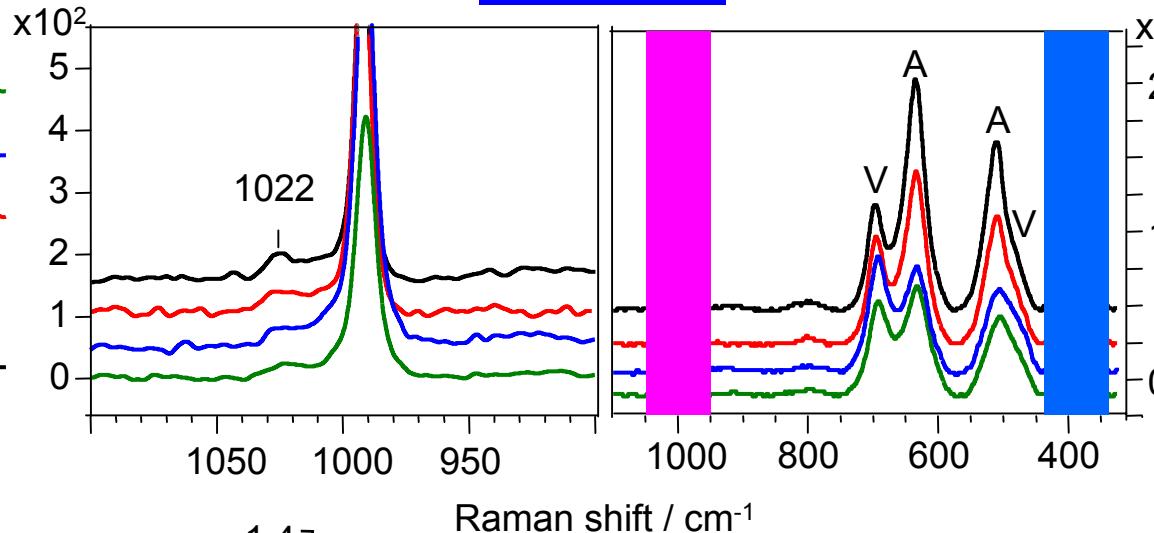


Normalized total EPR intensity

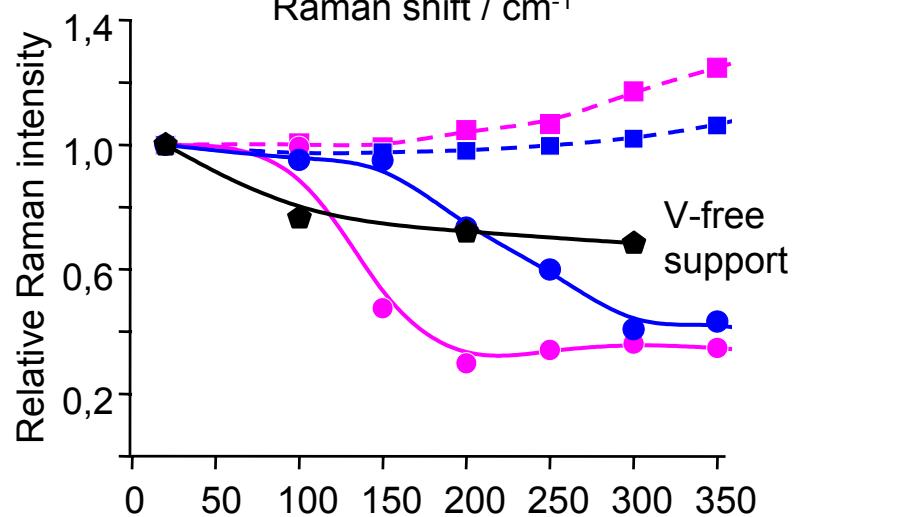
$$I(T) \cdot T / I(293K) \cdot 293 K$$



Raman

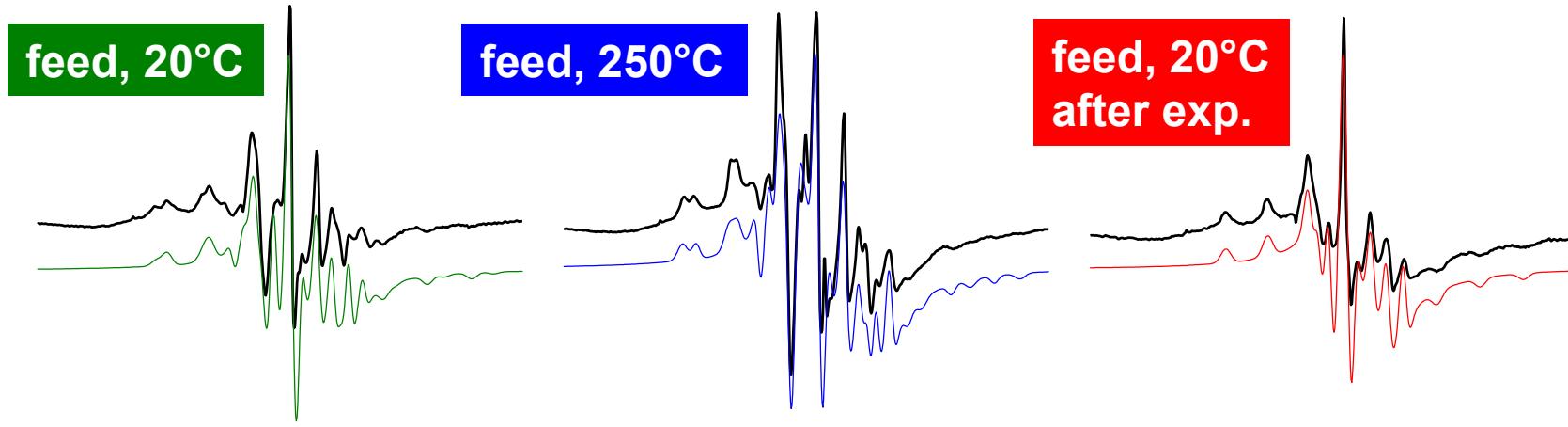


Raman shift / cm⁻¹



V-free
support

Nature of two different isolated VO^{2+}



$\Delta g_{||}/\Delta g_{\perp}$



A	B
2.16	4.00
180.1	199,2
0.85	0.87
1	0.4

$A_{||}/G$

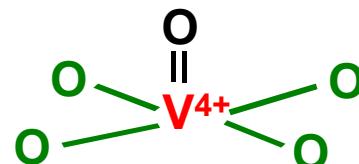
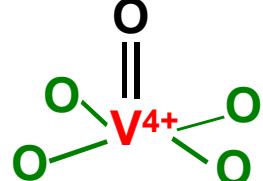


β_2^{*2}

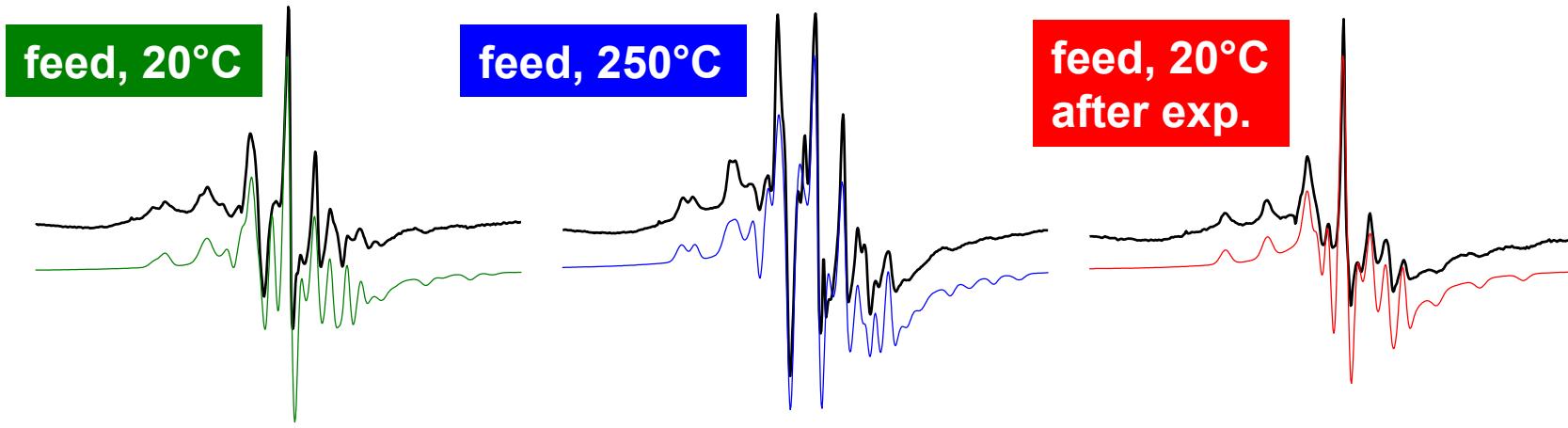
I_{rel}

A	B
2.13	4.00
176.3	199.2
0.82	0.86
1	1.2

A	B
2.02	-
175.8	-
0.83	-
1	-



Nature of two different isolated VO^{2+}



$\Delta g_{||}/\Delta g_{\perp}$

A	B
2.16	4.00
180.1	199,2
1	0.4

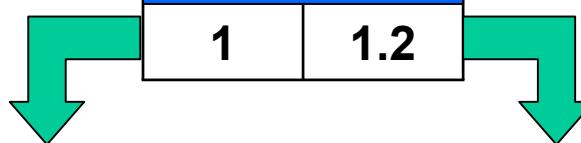
$A_{||}/G$

A	B
2.13	4.00
176.3	199.2
1	1.2

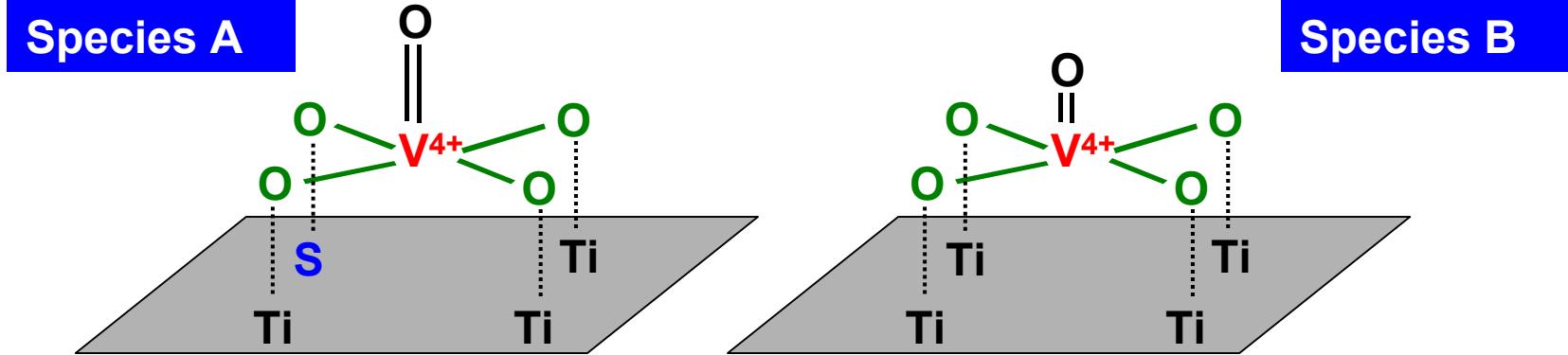
β_2^{*2}

A	B
2.02	-
175.8	-
1	-

I_{rel}



Influence of sulfate

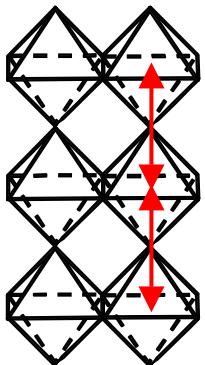


- on sulfate-free anatase only species B observed
A. Brückner et al., *Z. Anorg. Allg. Chem.* **631**, 60, 2005
- hints for bonding of VO^{2+} and/or VO^{3+} to SO_4 also from FTIR and thermal analysis
- sulfate might stabilize VO^{2+} as active species on the surface
 - prevents reduction to V^{3+}
 - prevents agglomeration
 - prevents diffusion into the bulk of the support

Anwendungsbeispiel II

**Struktur und Reaktivität ungeträgerter
Vanadiumpyrophosphate**

Permanent disorder and catalytic performance in differently calcined $(\text{VO})_2\text{P}_2\text{O}_7$



$$J = \frac{\Delta E}{2zS_i(S_i + 1)}$$

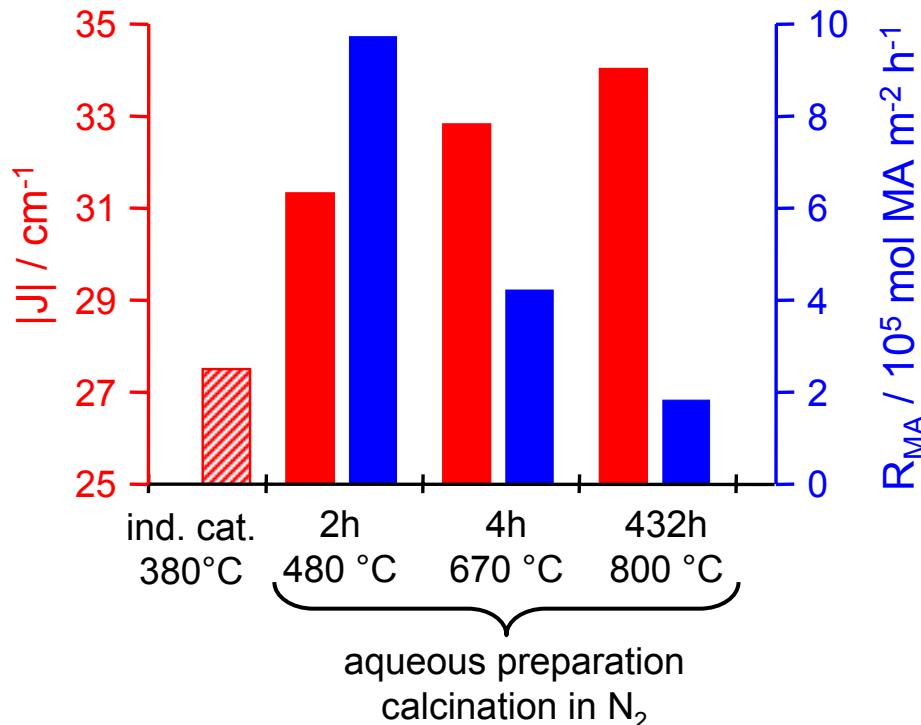
J values from susceptibility measurements:

-30.6 cm⁻¹

J. W. Johnson et al., *J. Am. Chem. Soc.* 106 (1984) 8123.

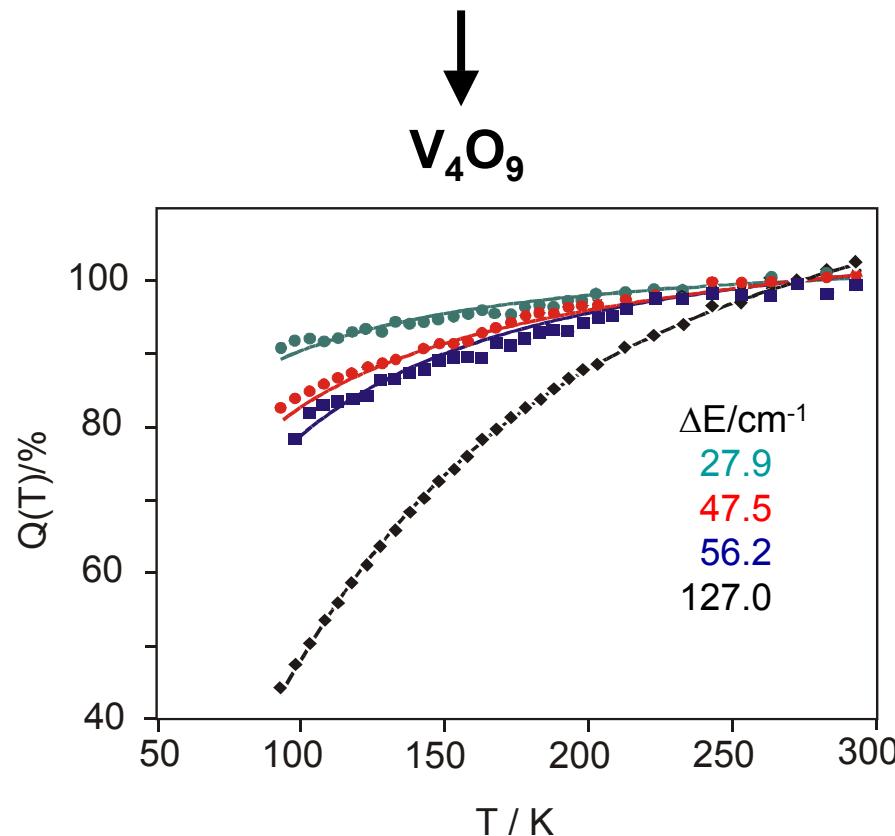
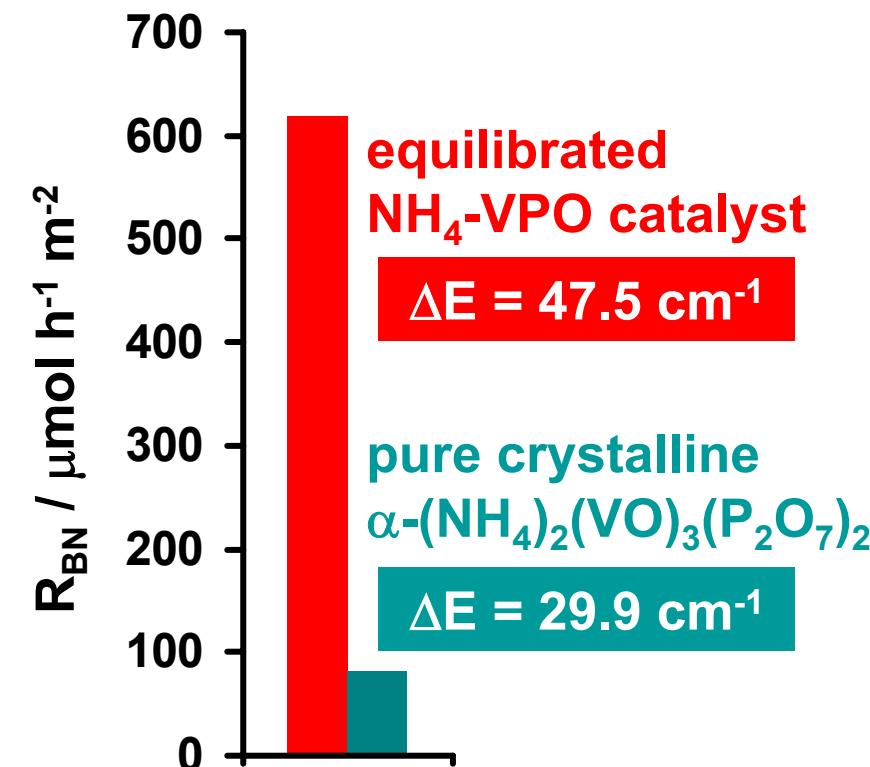
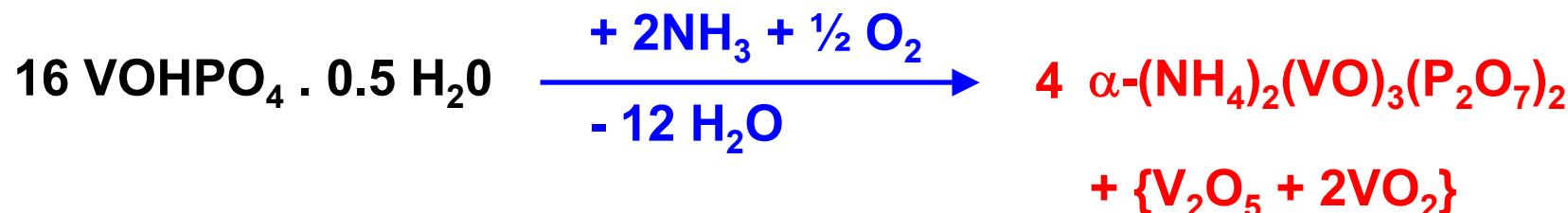
-29.9 cm⁻¹

M. E. Leonowicz et al., *J. Solid State Chem.* 56 (1985) 370.



- the weaker spin-spin exchange (low $|J|$), the higher structural disorder
- the higher structural disorder, the higher the MA yield

Identifying active phases by spin-spin exchange in toluene ammoxidation



Toluene → benzonitrile over $(\text{NH}_4)_2(\text{VO})_3(\text{P}_2\text{O}_7)_2$

Electronic changes evidenced by spin-spin exchange

51 % air + 7.4 % NH_3 + 40 % $\text{H}_2\text{O} \pm 1.6\% \text{CH}_3\text{-C}_6\text{H}_4\text{-R}$

