

Strukturaufklärung in der molekularen anorganischen Chemie

7. Elektronische Struktur

Elektronische Struktur von H


In sphärischen Koordinaten:

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi)$$

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi$$

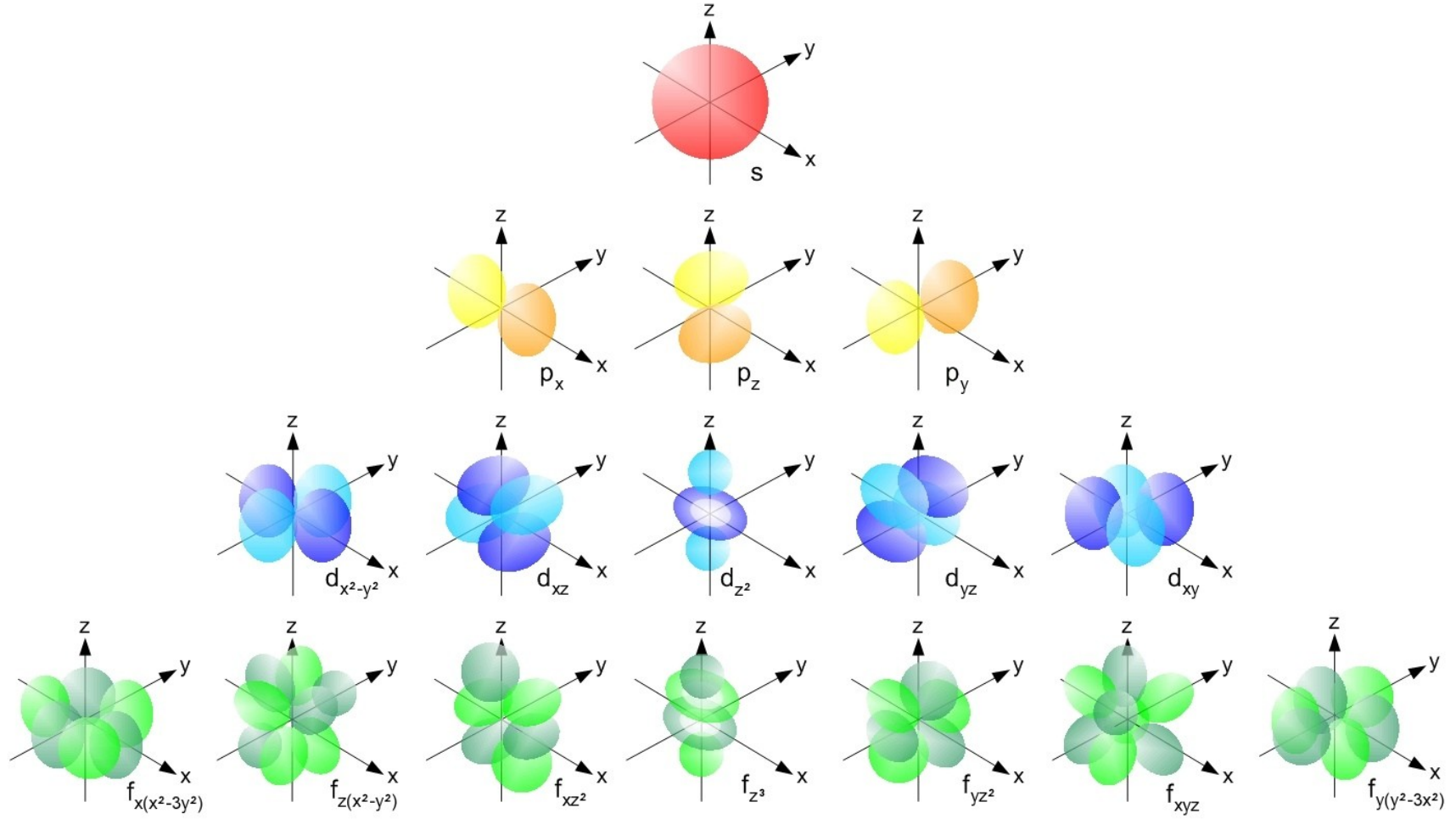
Lösungen:

$$\psi_{n\ell m}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0^*} \right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) Y_\ell^m(\theta, \varphi) \quad \left(\rho = \frac{2r}{na_0^*} \quad a_0^* = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \right)$$

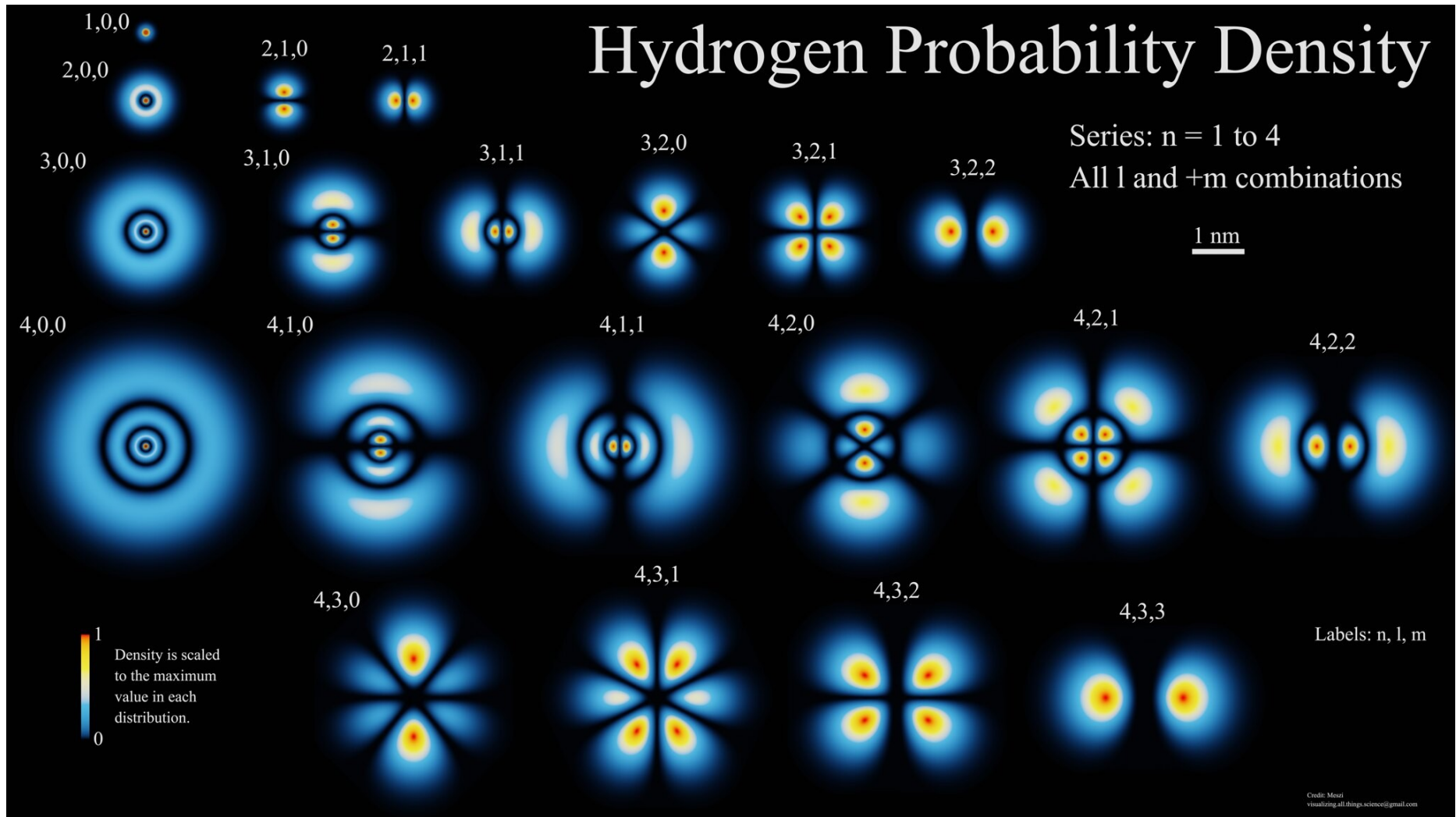

$$E_n = -\frac{Z^2}{2n^2} \text{ hartrees}$$

$$\text{Rydberg (1890): } \frac{1}{\lambda} = \mathcal{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad n_1 = 1, 2, 3, \dots, n_2 > n_1$$

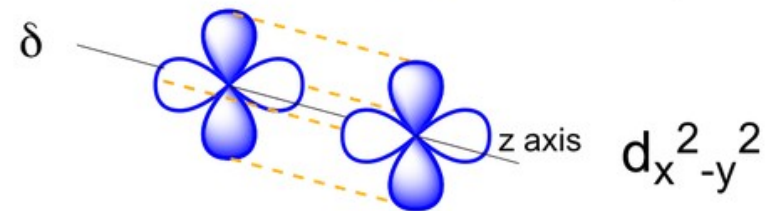
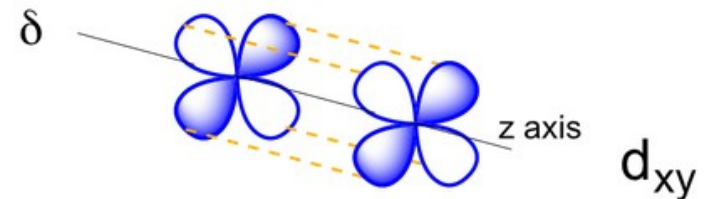
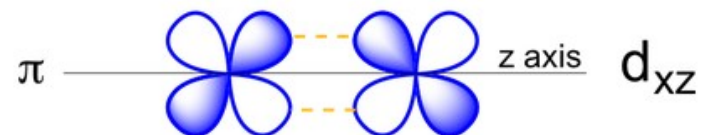
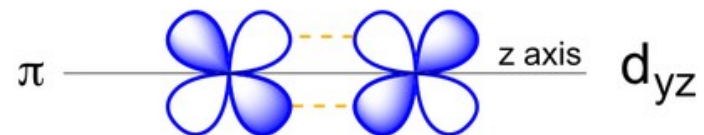
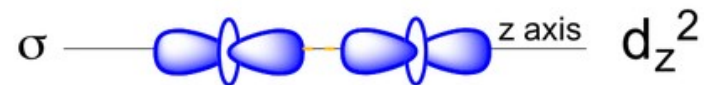
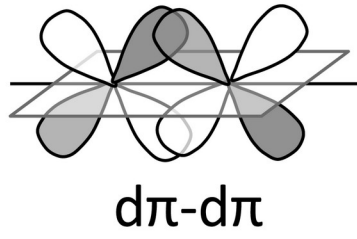
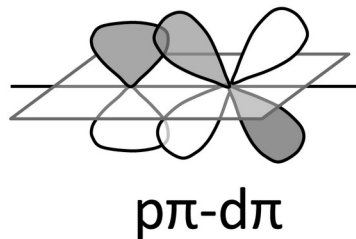
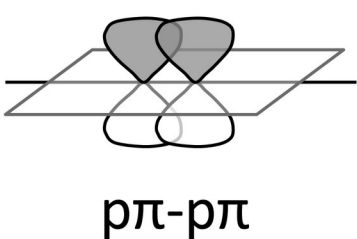
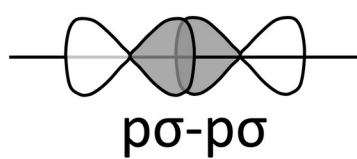
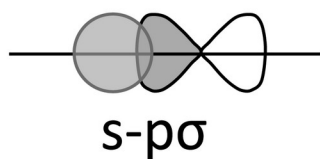
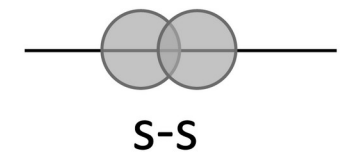
H Orbitale



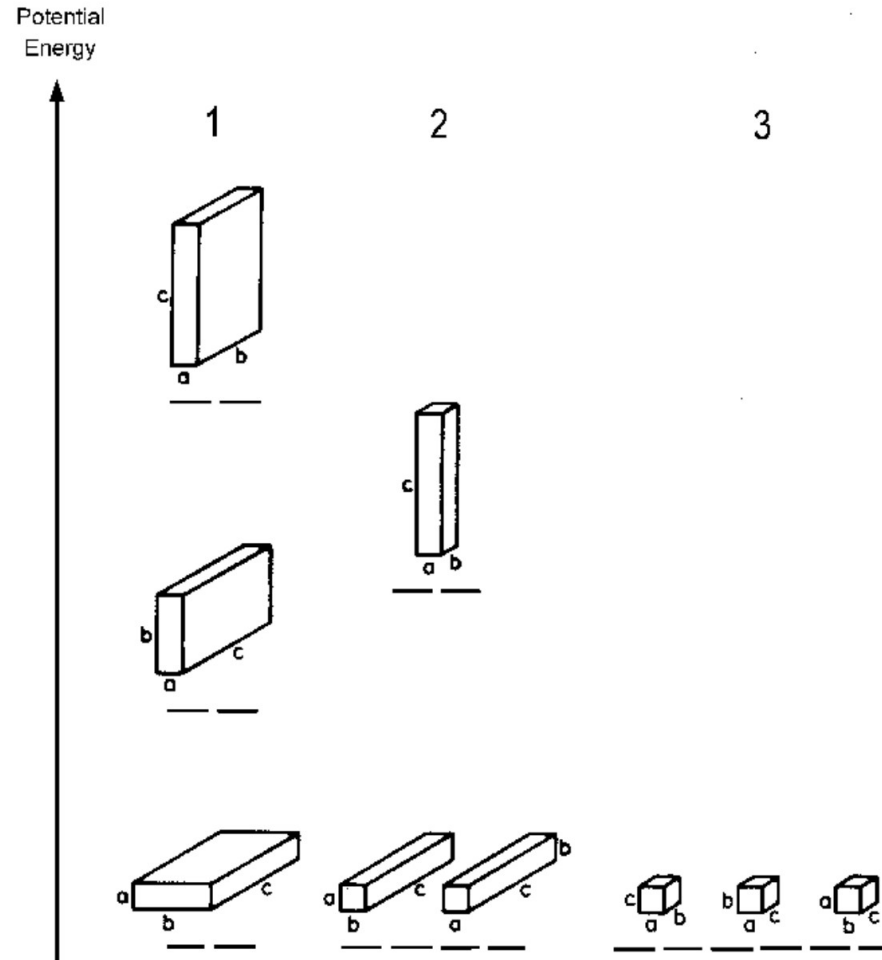
H Orbitale mit R.-Komponente



Moleküle



Symmetrie und Entartung



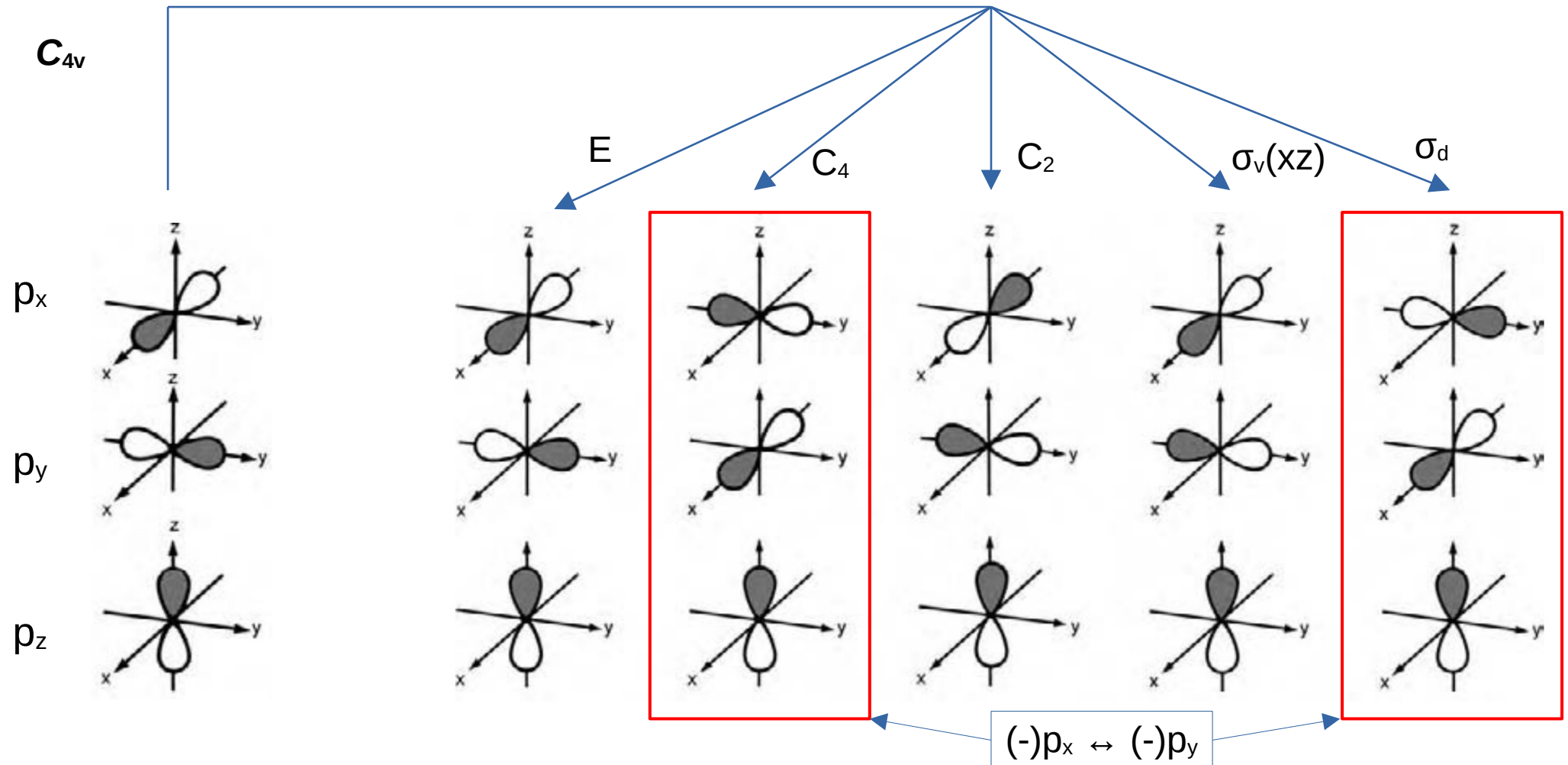
Symmetrie und Entartung

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y) (R_x, R_y)$	(xz, yz)

p-Orbitale

d-Orbitale

Symmetrie und Entartung: grafisch



Symmetrie und Entartung: mathematisch

Basis: p_x, p_y, p_z

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_4 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_4^3 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

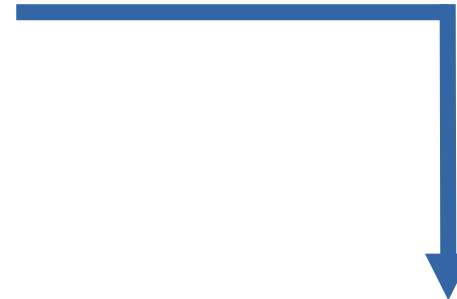
$$\sigma_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_d = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma'_d = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

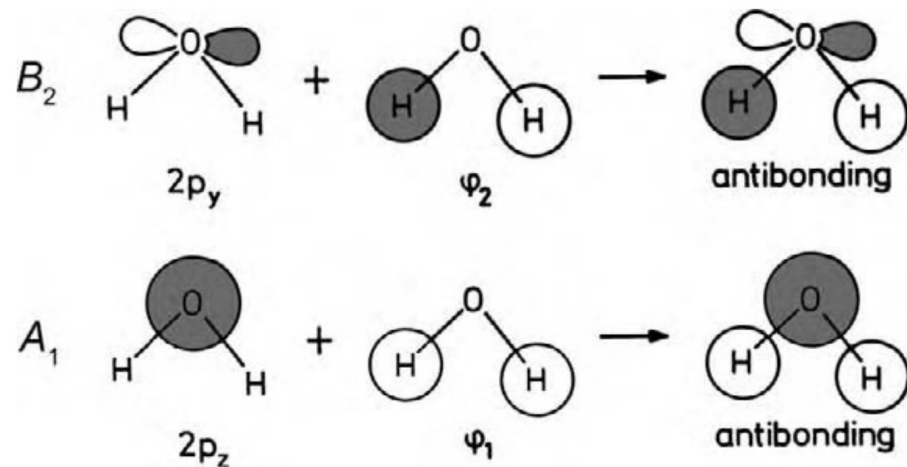
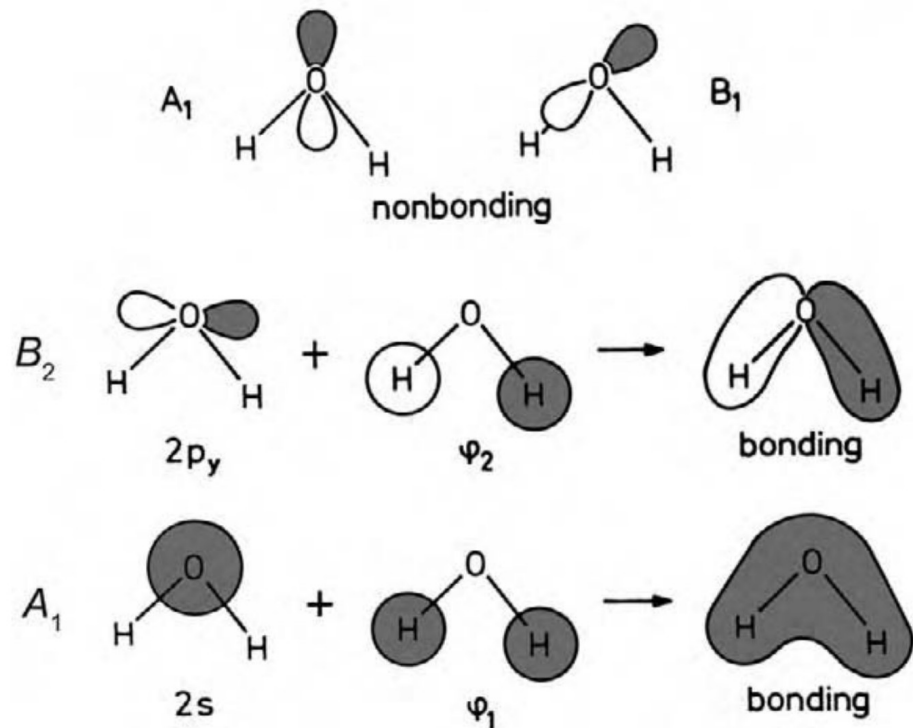
Irreduzible Darstellungen,
Charaktere:



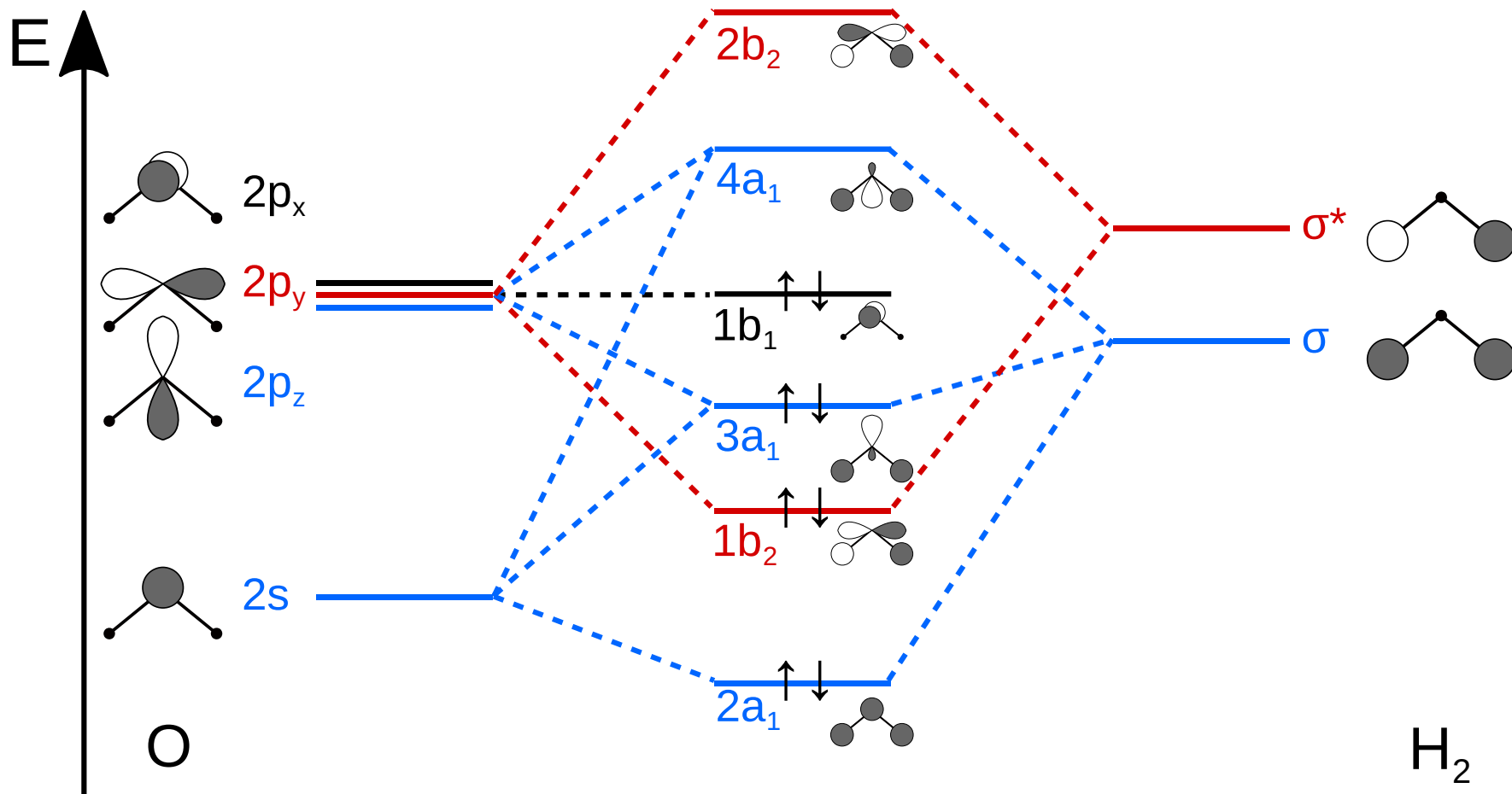
	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
p_z	1	1	1	1	1	A_1
(p_x, p_y)	2	0	-2	0	0	E

Moleküle: MOs von H₂O

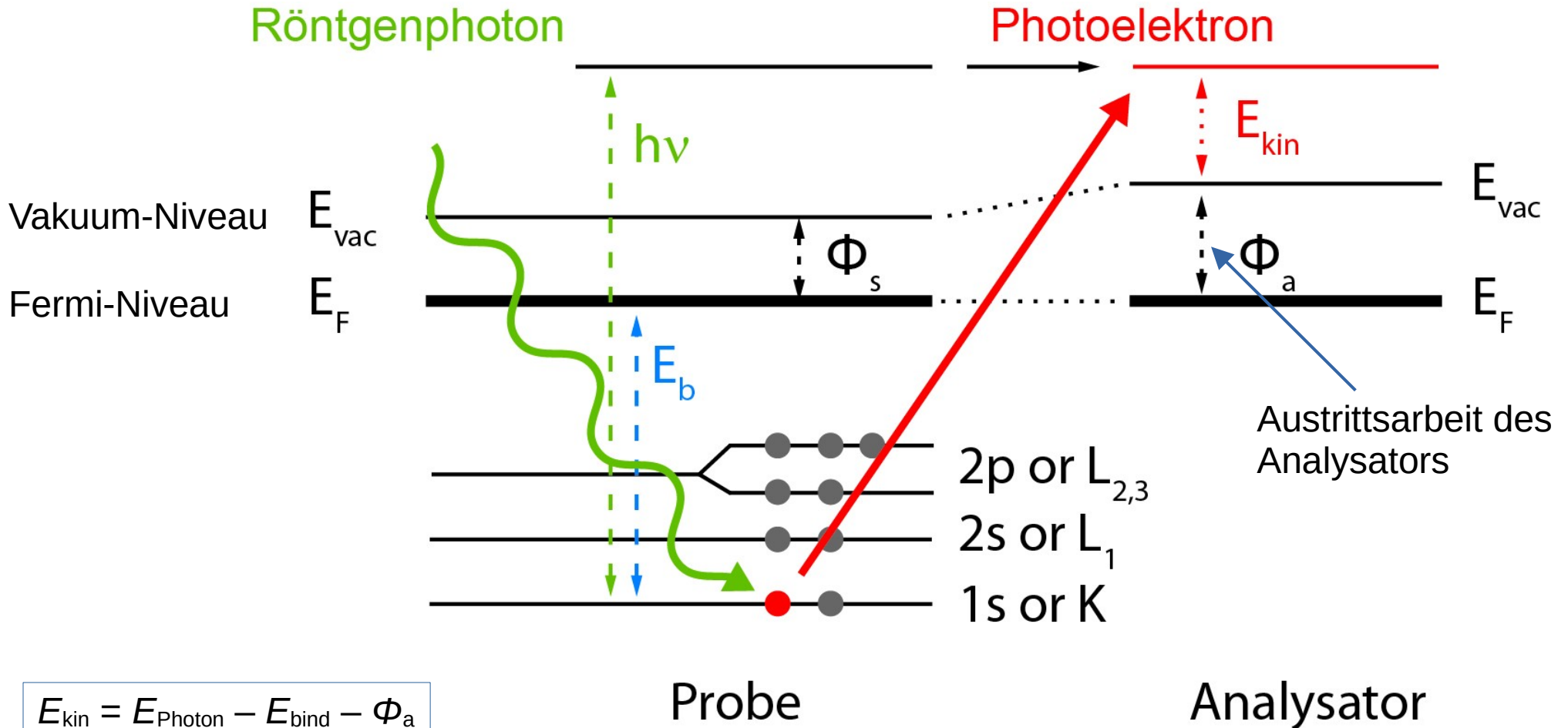
(s. Vorlesung Symmetrie)



H₂O: MO Energie-Diagramm

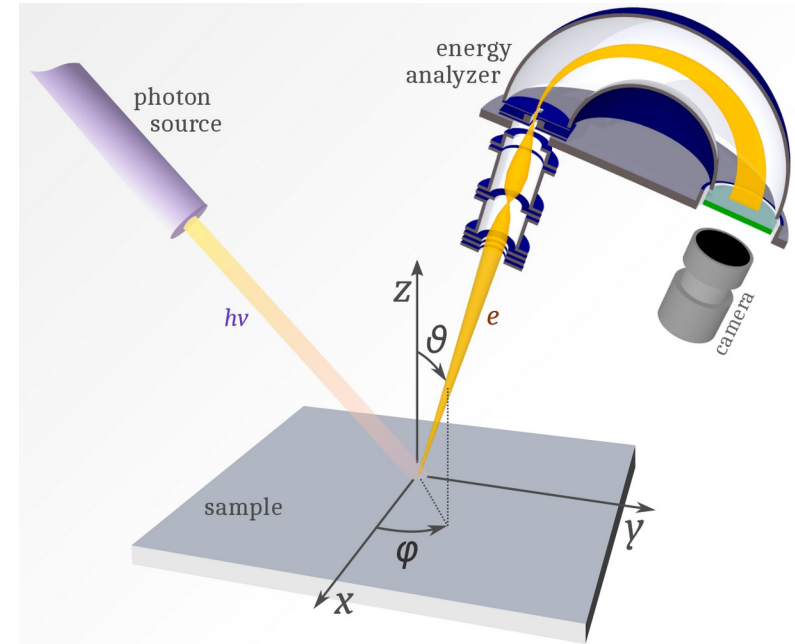


Photoelektronen-Spektroskopie



$$E_{kin} = E_{Photon} - E_{bind} - \Phi_a$$

XPS- und UPS-Spektroskopie



Röntgenphotoelektronenspektroskopie, XPS:
 $E \sim 1000 \text{ eV}$

Ultravioletphotoelektronenspektroskopie, UPS:
 $E \sim 10 - 100 \text{ eV}$

XPS, UPS

γ -ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmwave	mm-wave	Micro-wave	Radio-wave
$\leftarrow < 0.1 \text{ \AA}$	5 \AA	100 \AA 10 nm	2000 \AA	200 nm	400 nm	700 nm	2500 nm	25 \mu m		1 mm		10 cm \rightarrow
	$> 10^9$	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400		10		0.1
	1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8		0.12		1.2×10^{-3}
	120 000	2400	120	6	3	1.7	0.5	0.05		0.001		0.00001
	3×10^{19}	6×10^{17}	3×10^{16}	1.5×10^{15}	7.5×10^{14}	4×10^{14}	1.2×10^{14}	1.2×10^{13}		3×10^{11}		3×10^9
												$\nu / \text{ Hz}$

UPS: ~10 bis ~100 eV

XPS: ~ 1000 eV

XPS, UPS

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Streuung/Diffraktion
- Resonanzmethode
- Elektrische Methode
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (/Dichte)
- (Elektrische) Dipolmomente

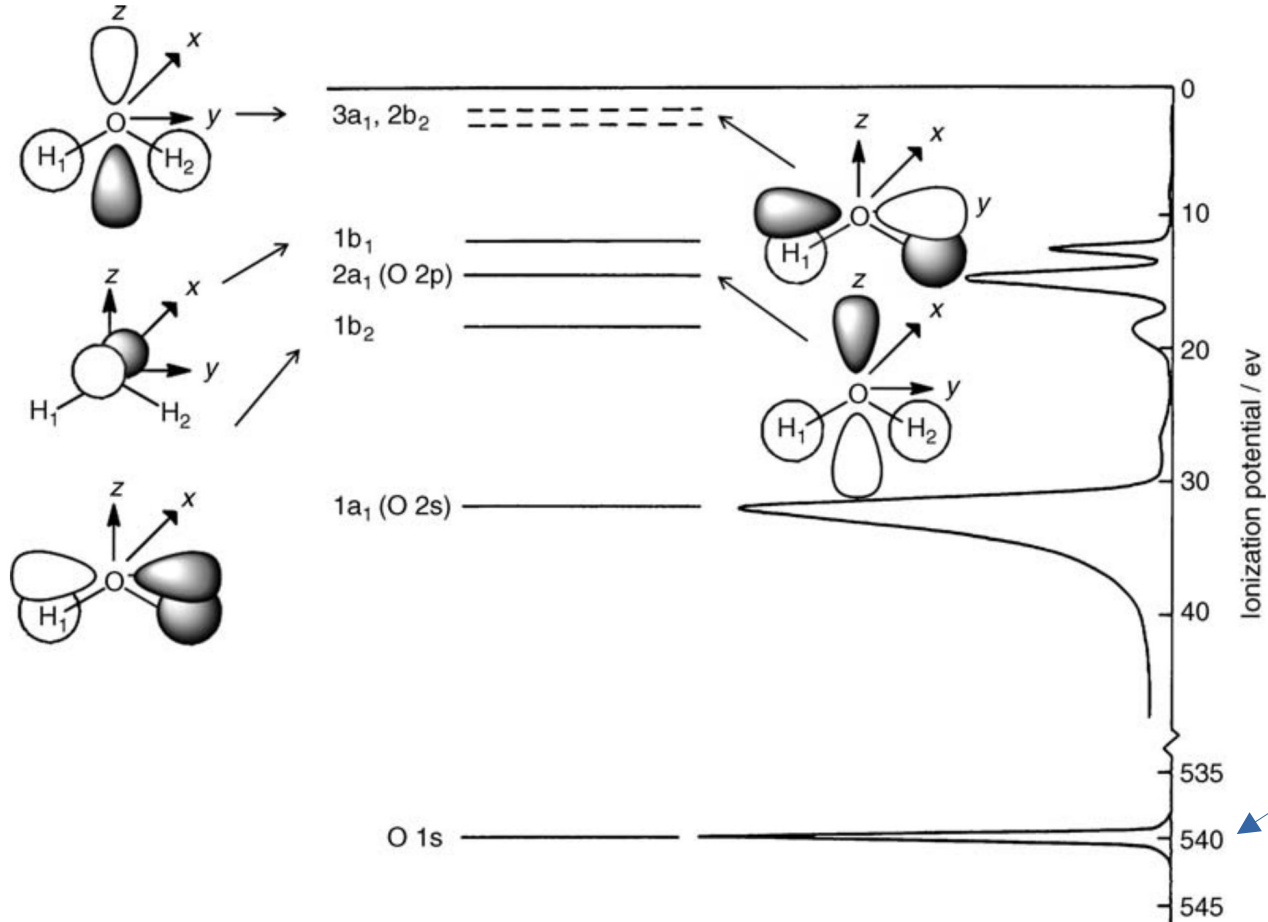
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

Photoelektronen-Spektrum: H₂O



K-edge:

C ≈ 285 eV

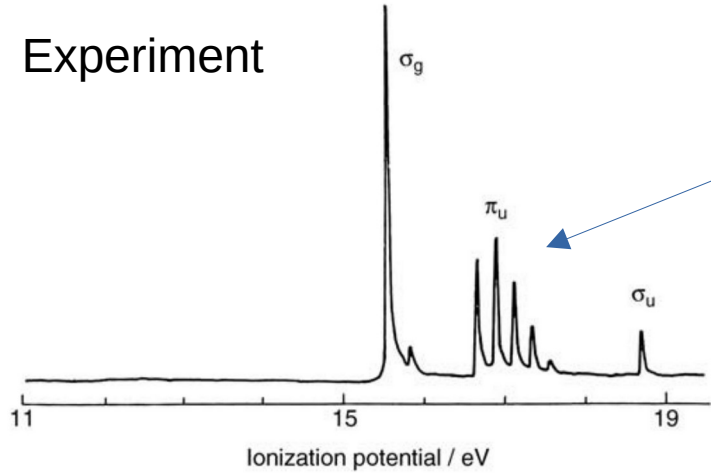
N ≈ 400 eV

O ≈ 530 eV

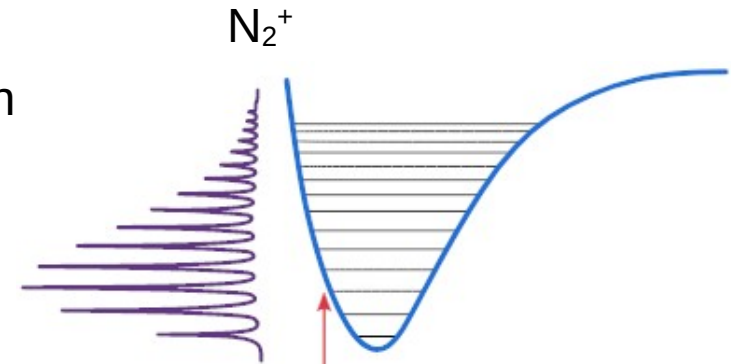
Entspricht dem
K-edge in
Röntgen-
Nahkanten-
Absorptions-
Spektroskopie

UPS von N₂

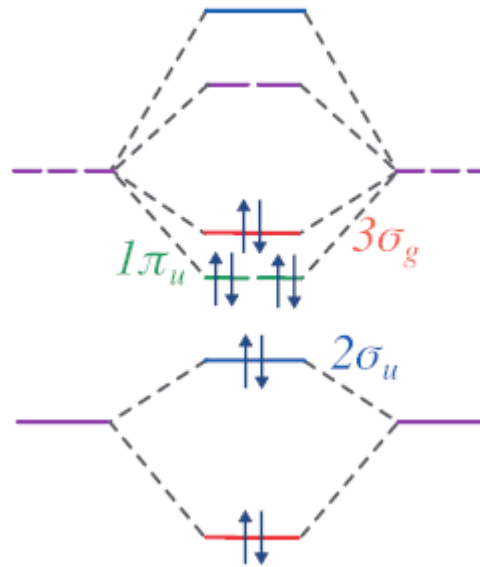
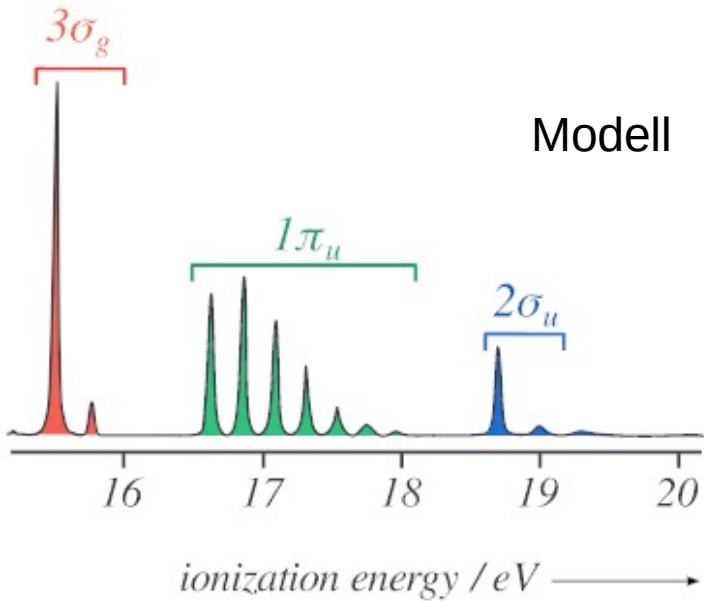
Experiment



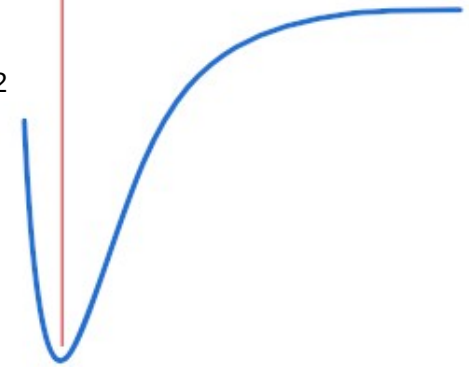
Vibrationsprogression



Modell



N₂



UV/Vis

γ -ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmwave	mm-wave	Micro-wave	Radio-wave
$< 0.1 \text{ \AA}$	5 \AA	100 \AA	2000 \AA	2000 \AA	0.7 \mu m	2.5 \mu m	25 \mu m			1 mm		10 cm
		10 nm	200 nm	400 nm	700 nm	2500 nm						
$> 10^9$	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400			10		0.1
1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8			0.12		1.2×10^{-3}
$120\,000$	2400	120	6	3	1.7	0.5	0.05			0.001		0.00001
3×10^{19}	6×10^{17}	3×10^{16}	1.5×10^{15}	7.5×10^{14}	4×10^{14}	1.2×10^{14}	1.2×10^{13}			3×10^{11}		3×10^9

rot	$\approx 790\text{--}630$
orange	$\approx 630\text{--}580$
gelb	$\approx 580\text{--}560$
grün	$\approx 560\text{--}480$
blau	$\approx 480\text{--}420$
violett	$\approx 420\text{--}390$

λ : $\sim 200 \text{ nm}$ bis $\sim 800 \text{ nm}$

τ : $\sim 6 \times 10^{-16}$ bis $\sim 3 \times 10^{-15}$ Sek

UV/Vis

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- (Elektrische) Dipolmomente

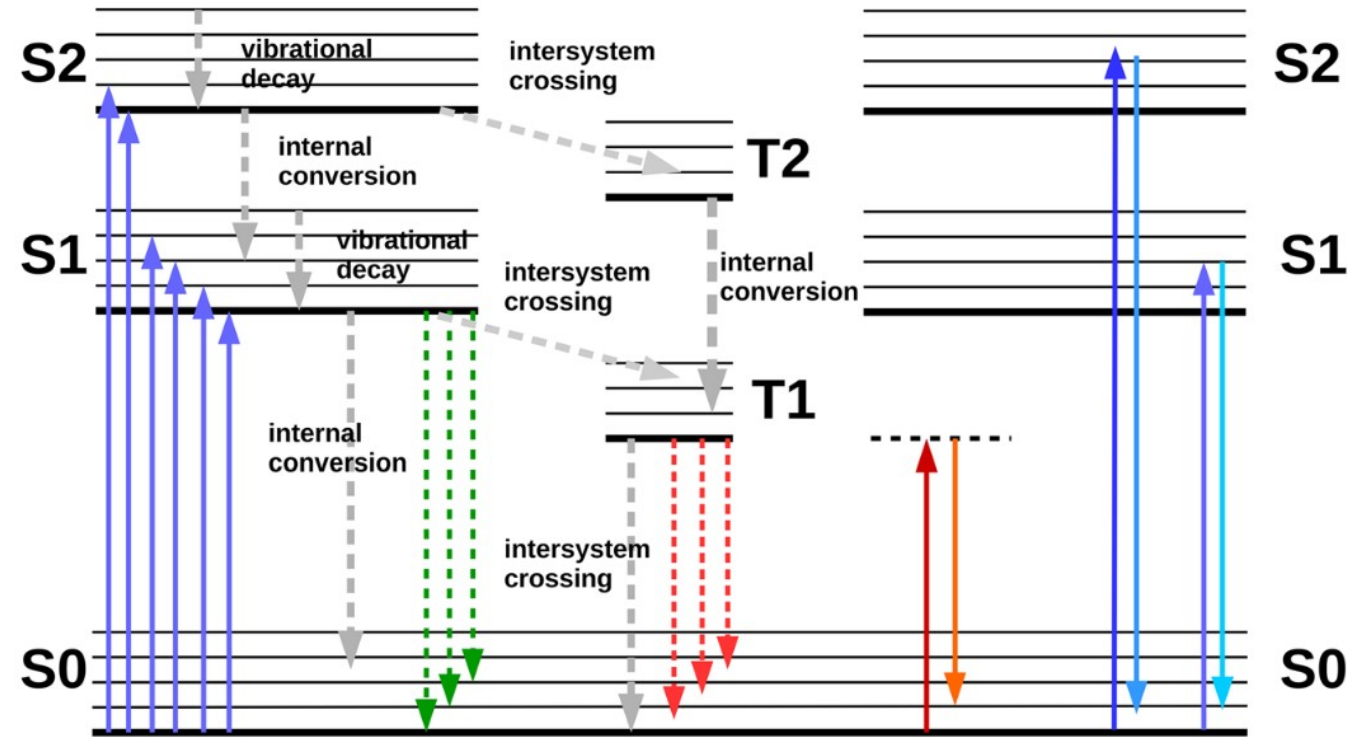
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

Jabłoński-Diagramm



Absorption: 10^{-15} Sek.

Internal Conversion: $10^{-14} - 10^{-11}$
(Innere Umwandlung)

Vibr.-Relaxation: $10^{-13} - 10^{-10}$

Fluoreszenz: $10^{-9} - 10^{-7}$

Intersystem Crossing: $10^{-10} - 10^{-5}$

Phosphoreszenz: $10^{-3} - 10^2$

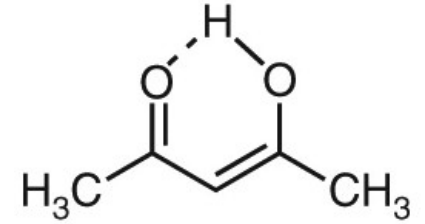
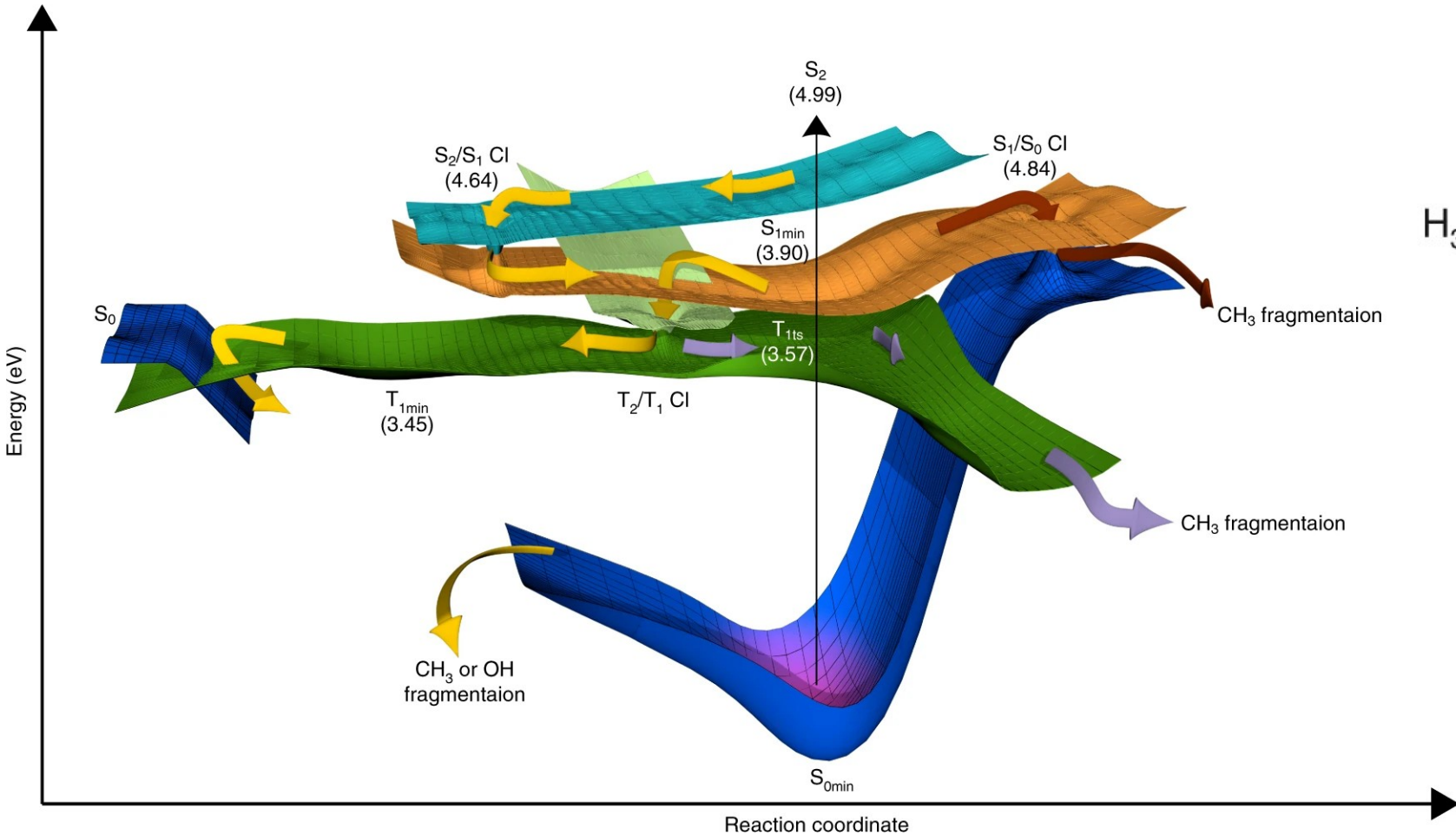
Absorption

Fluore-
-szenz

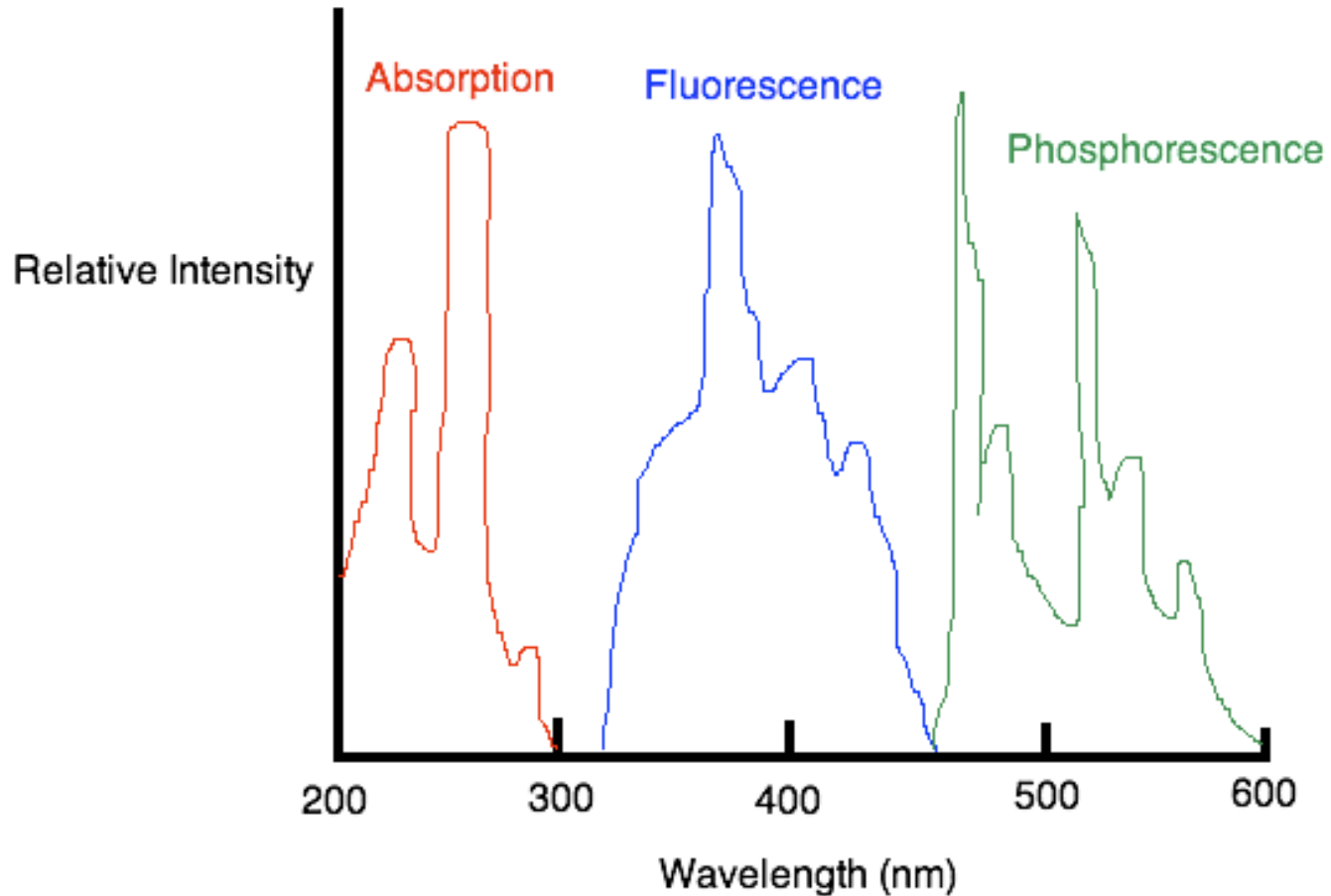
Phospho-
-reszenz

Raman Scattering
Normal Resonance

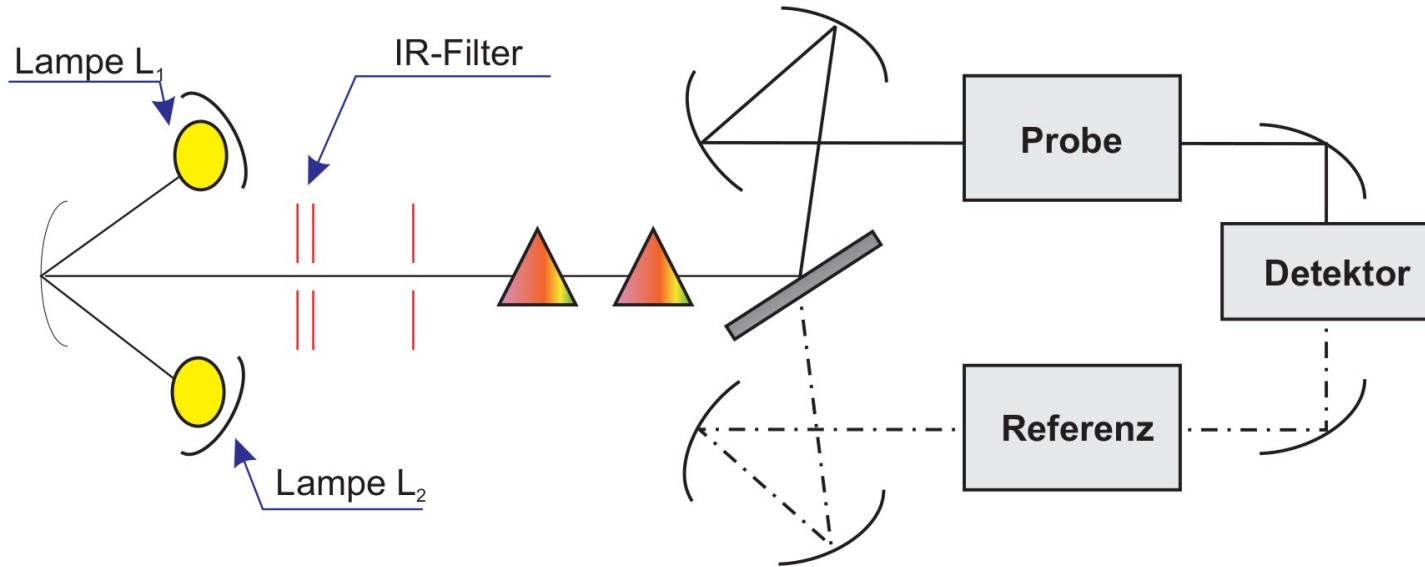
Beispiel: Photodynamik von Acetylaceton



Wellenlängen



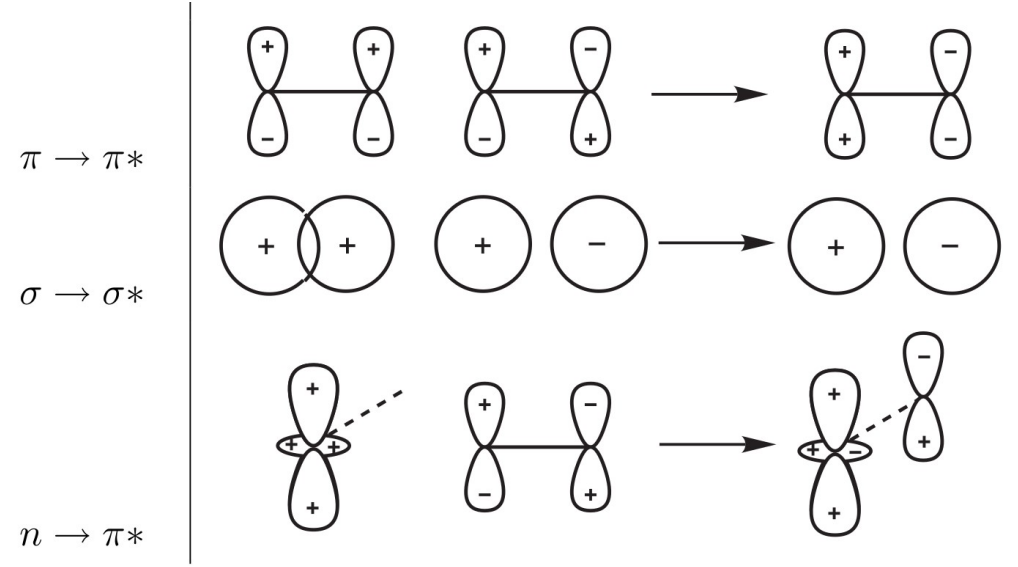
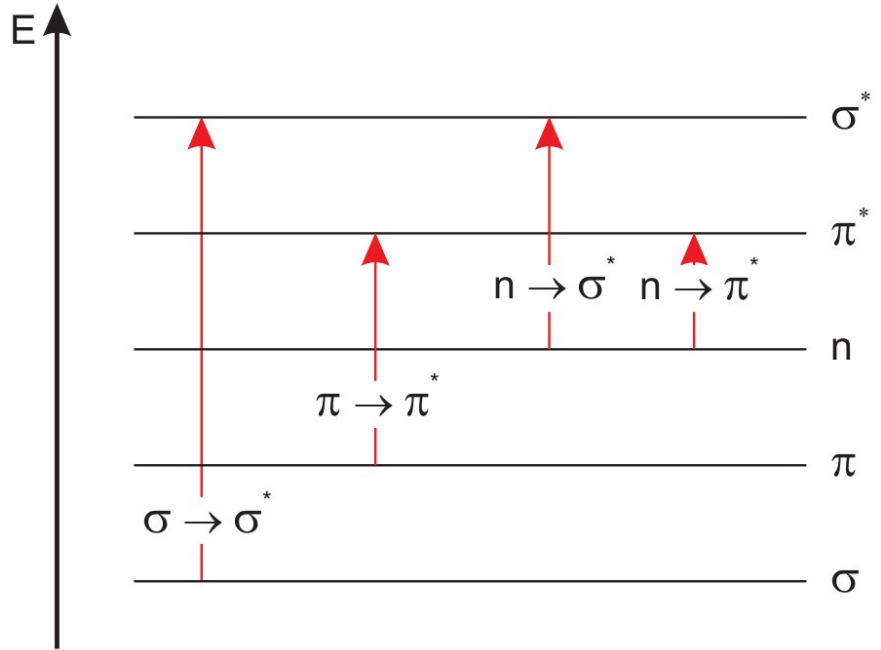
UV/Vis-Photometer



Lambert-Beer'sche Gesetz:
$$E_{\lambda} = \log_{10} \left(\frac{I_0}{I_1} \right) = \varepsilon_{\lambda} \cdot c \cdot d$$

Extinktionskoeffizient
Stoffmengenkonzentration
Schichtdicke

Übergänge



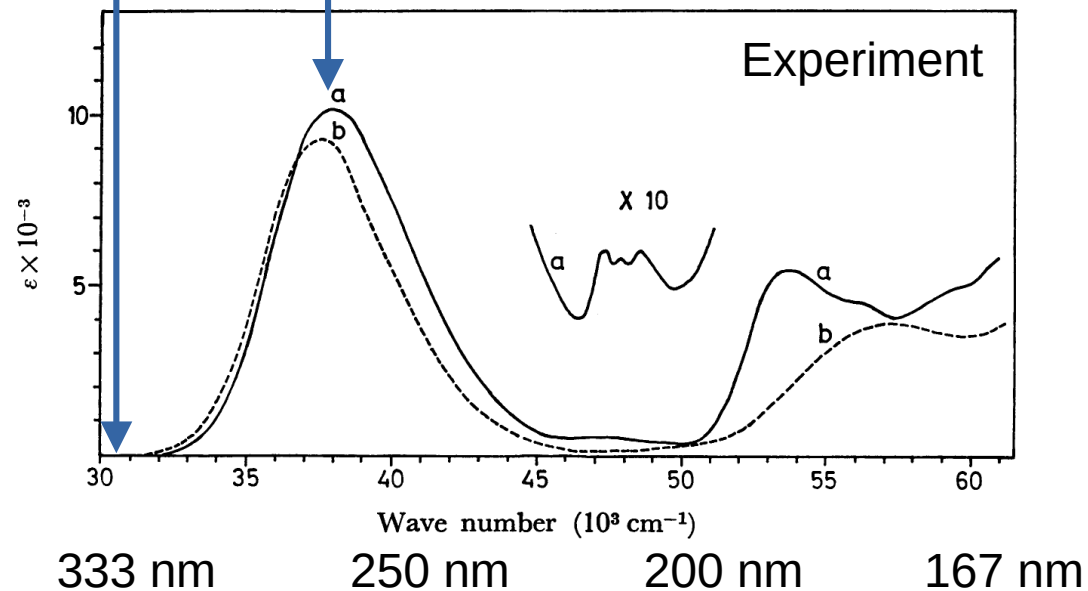
- Spin-Verbot
(\rightarrow erlaubt $\Delta S = 0$)
- Symmetrie-Verbot (g, u)
(\rightarrow erlaubt zwischen Orbitalen ungleicher Parität)

$\sigma \rightarrow \sigma^*$:	voll symmetrie-erlaubt	$\epsilon = 10^3 - 10^4$	$\lambda < 200nm$
$\pi \rightarrow \pi^*$:	voll symmetrie-erlaubt	$\epsilon = 10^3 - 10^5$	$\lambda > 200nm$
$n \rightarrow \pi^*$:	partiell erlaubt	$\epsilon = 1 - 10^3$	$\lambda > 250nm$
$n \rightarrow \sigma^*$:	partiell erlaubt		$\lambda > 200nm$

Beispiel: Acetylaceton

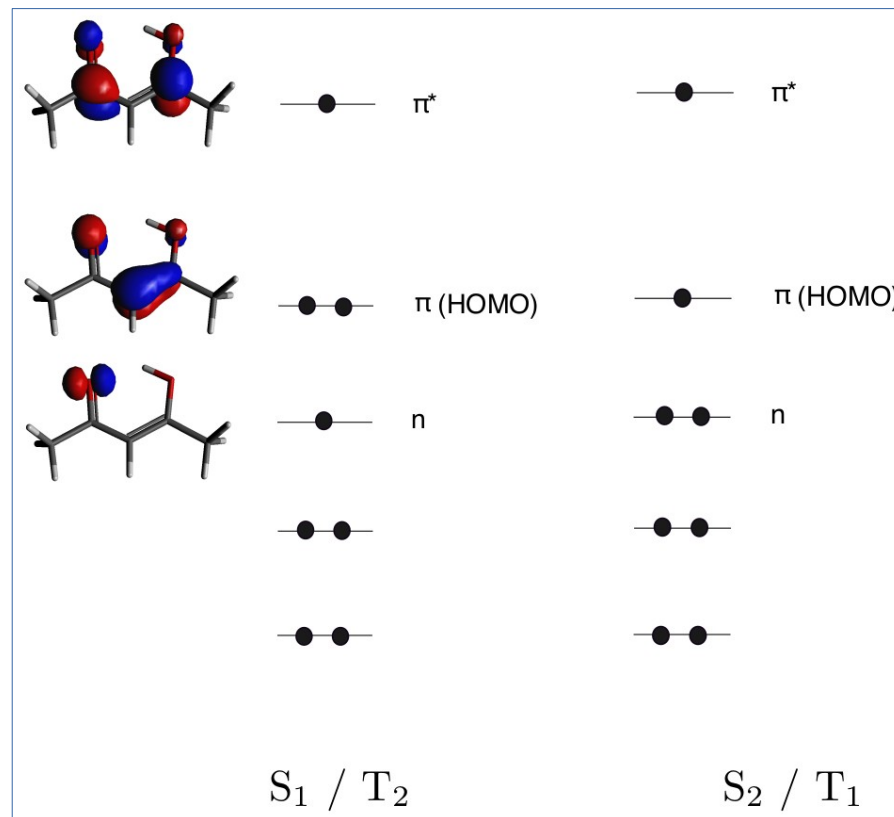
$S_1 (n, \pi^*) \leftarrow S_0$

$S_2 (\pi, \pi^*) \leftarrow S_0$



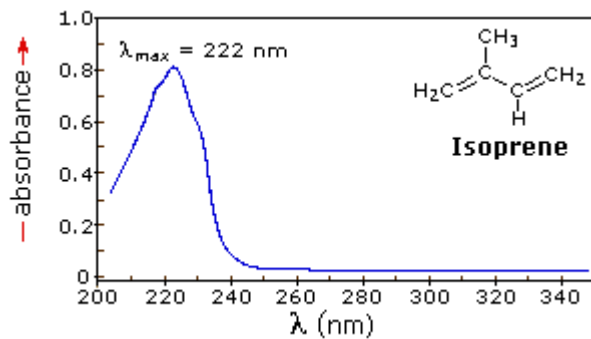
Nakanishi et al., *Bull. Chem. Soc. Jpn.*
1977, 50, 2255–2261.

Modell



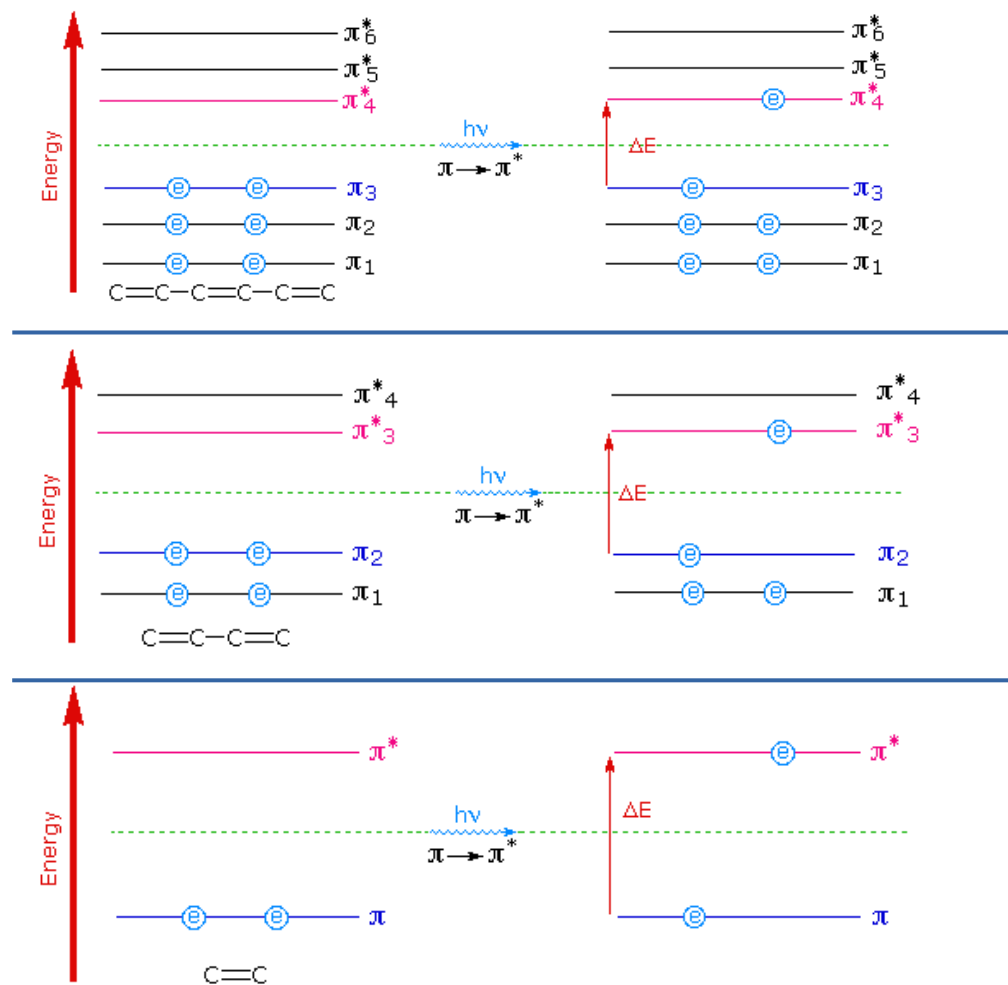
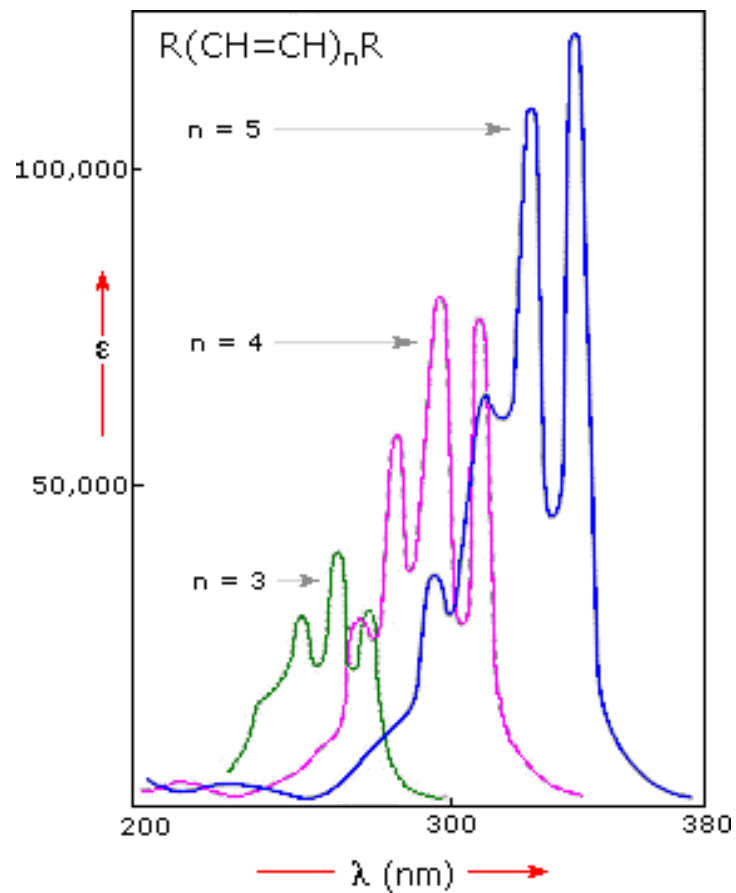
Ponzi et al., *Molecules* 2022, 27, 1811.

UV/Vis Chromophore

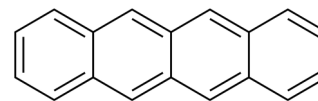
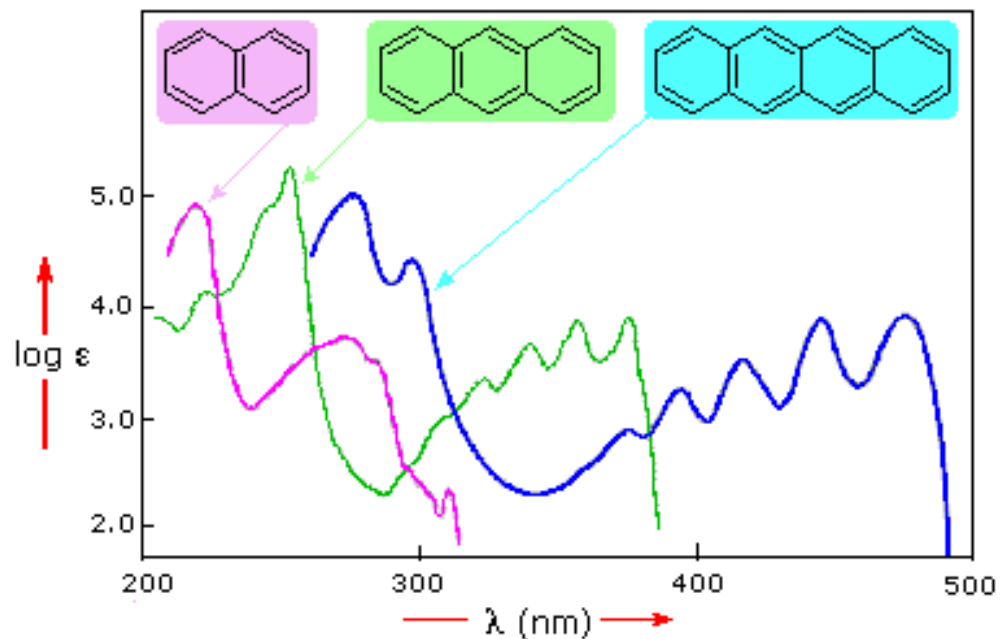
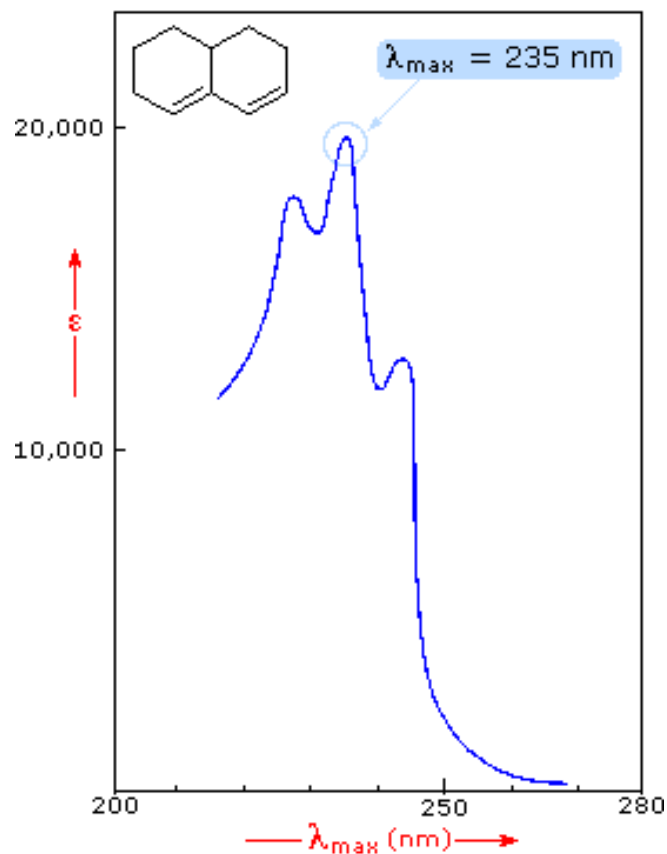


Chromophore	Example	Excitation	λ_{\max} , nm	ϵ	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C \equiv C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X	X=Br X=I	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

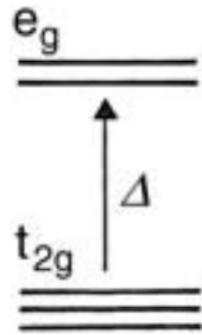
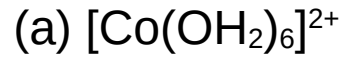
Konjugation



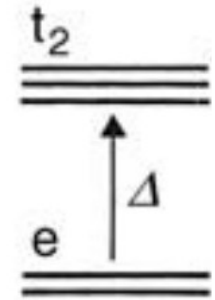
Konjugation



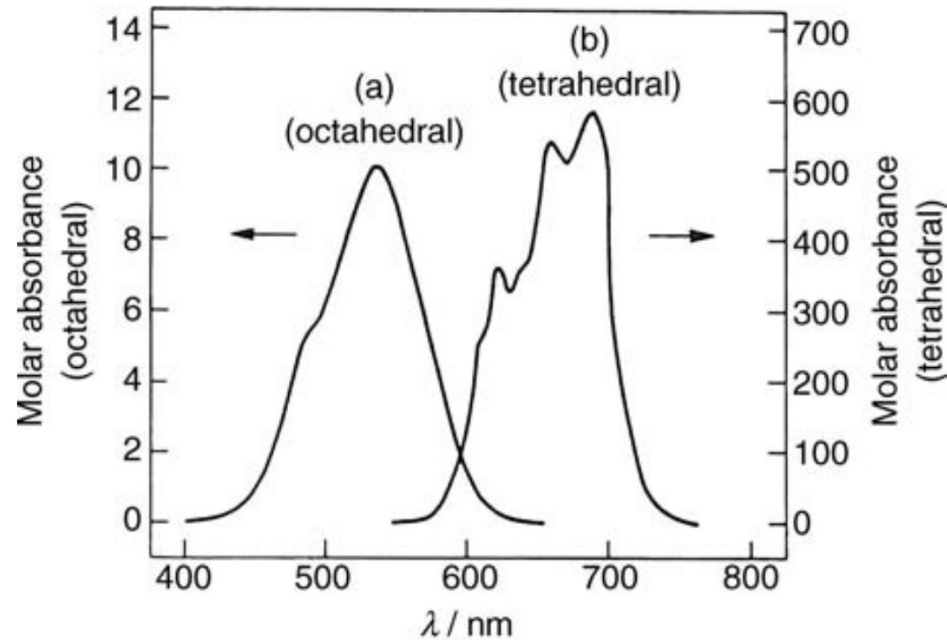
Me-Komplexe



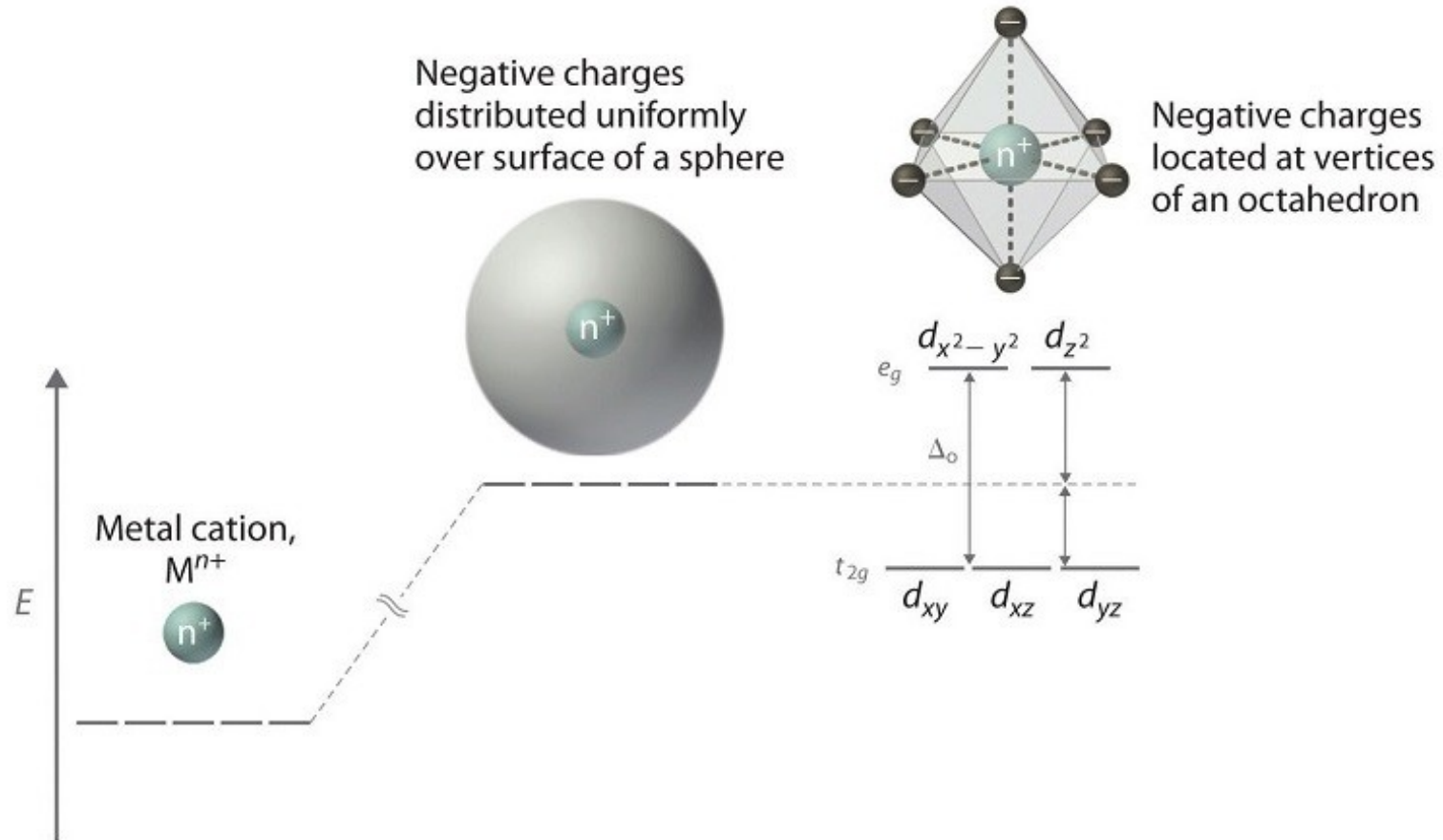
(a) O_h



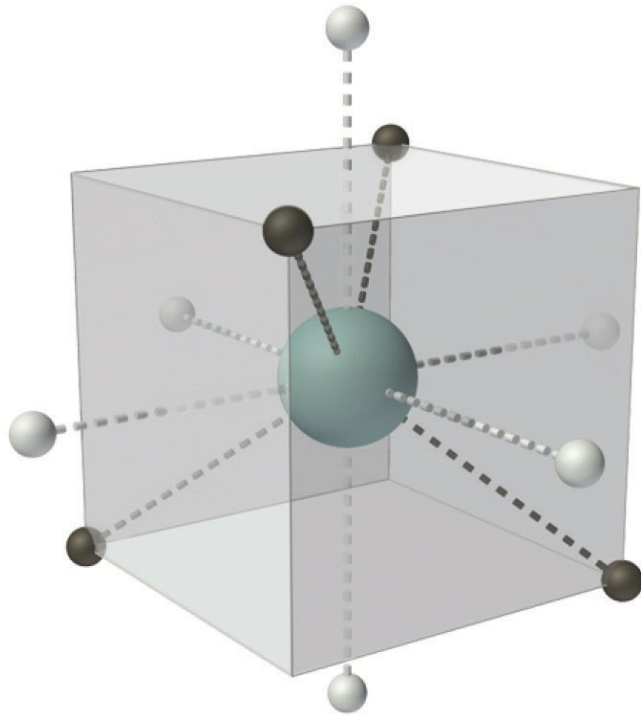
(b) T_d



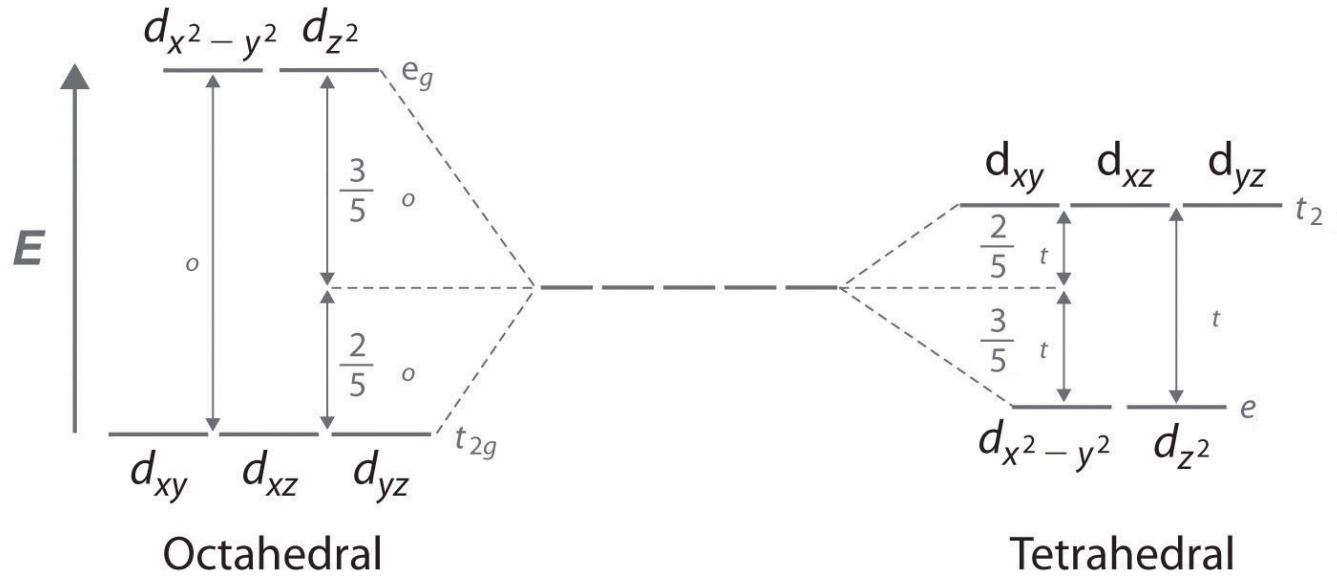
Kristallfeld- und Ligandenfeldtheorie



Kristallfeld- und Ligandenfeldtheorie



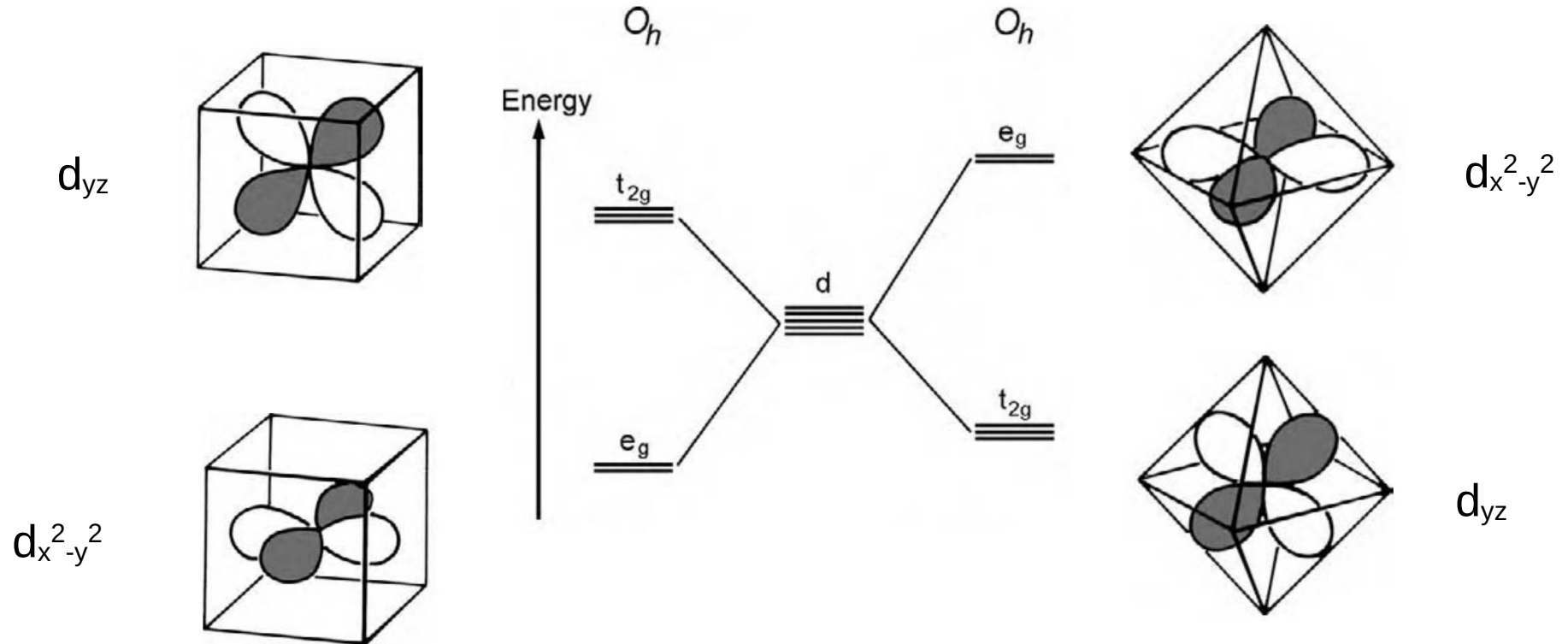
(a)



(b)

Ligandenfeldtheorie: grafisch

Abstoßungen Orbitale ↔ Liganden (in Ecken)



Jahn-Teller-, Pseudo-Jahn-Teller- und Renner-Teller-Effekte



Hermann Arthur Jahn
(1907 – 1979)



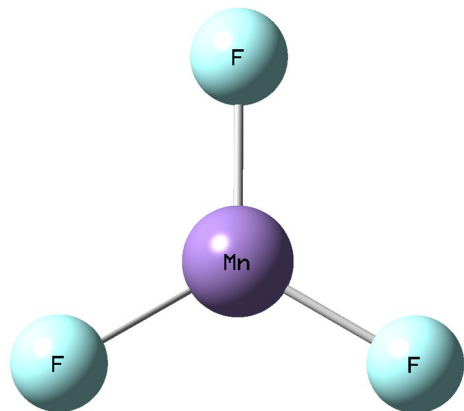
Edward Teller
(1908 – 2003)



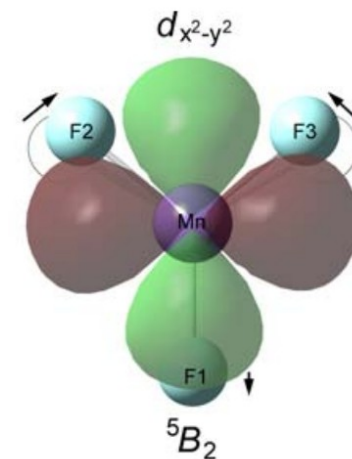
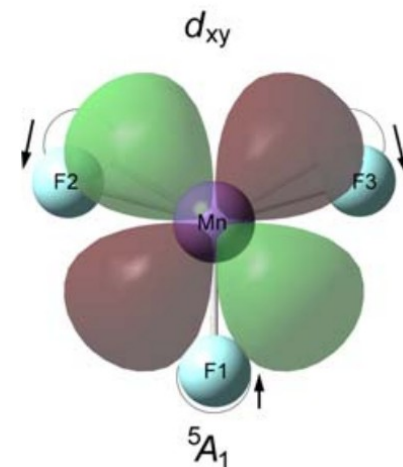
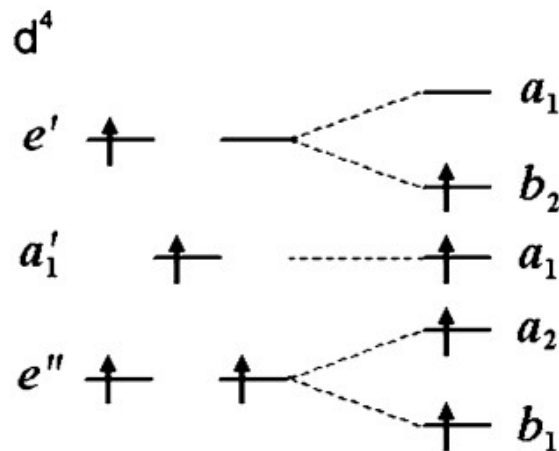
Rudolf Renner
(1909 – 1991)

Jahn-Teller-Effekt

MnF₃ (Mn⁰: [Ar] 3d⁵ 4s²)



High-spin (Quintet!)
(Hundsche Regel!)

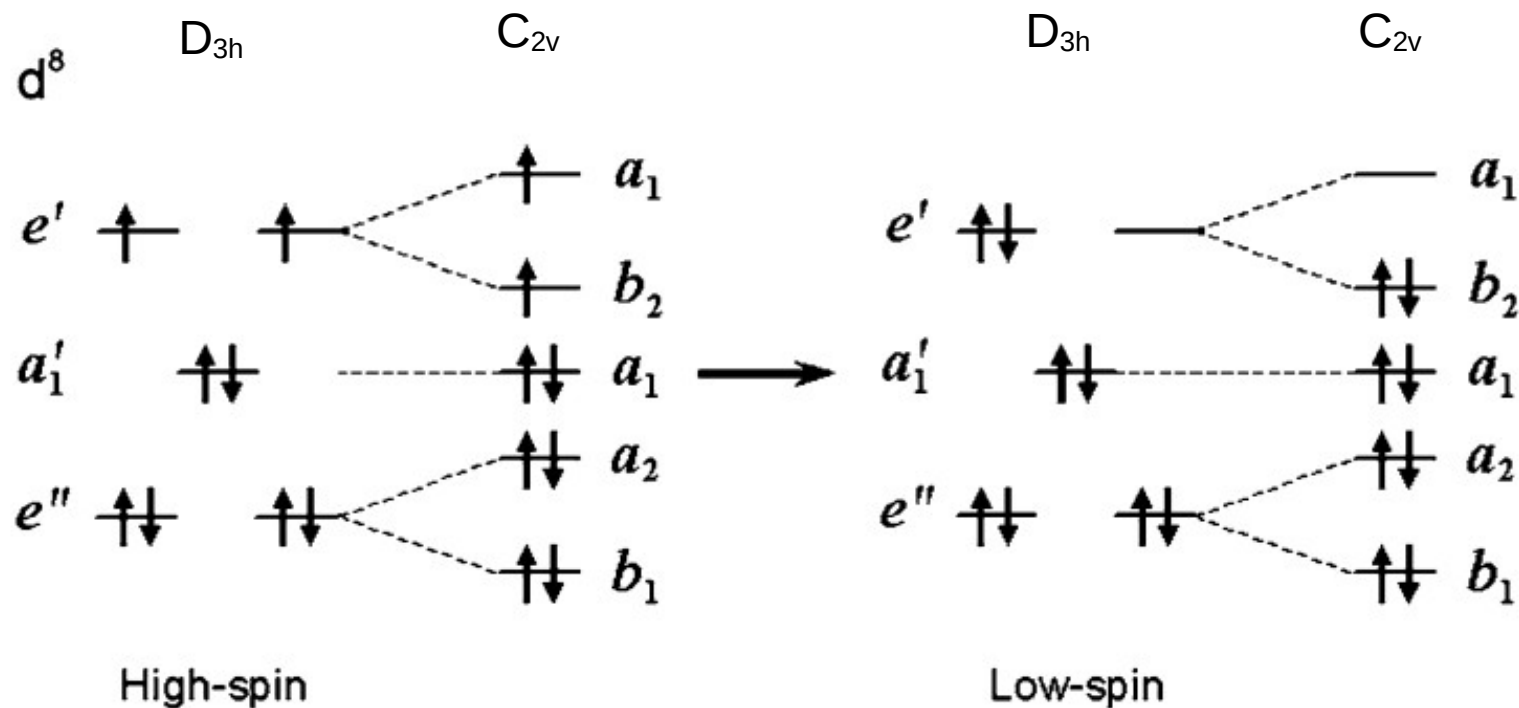


GED: $r_g(\text{Mn-F1})=1.728(14) \text{ \AA}$
 $r_g(\text{Mn-F2})=1.754(14) \text{ \AA}$
 $\alpha(\text{F1-Mn-F2})=106.4(9)^\circ$

(Hargittai, 1997)

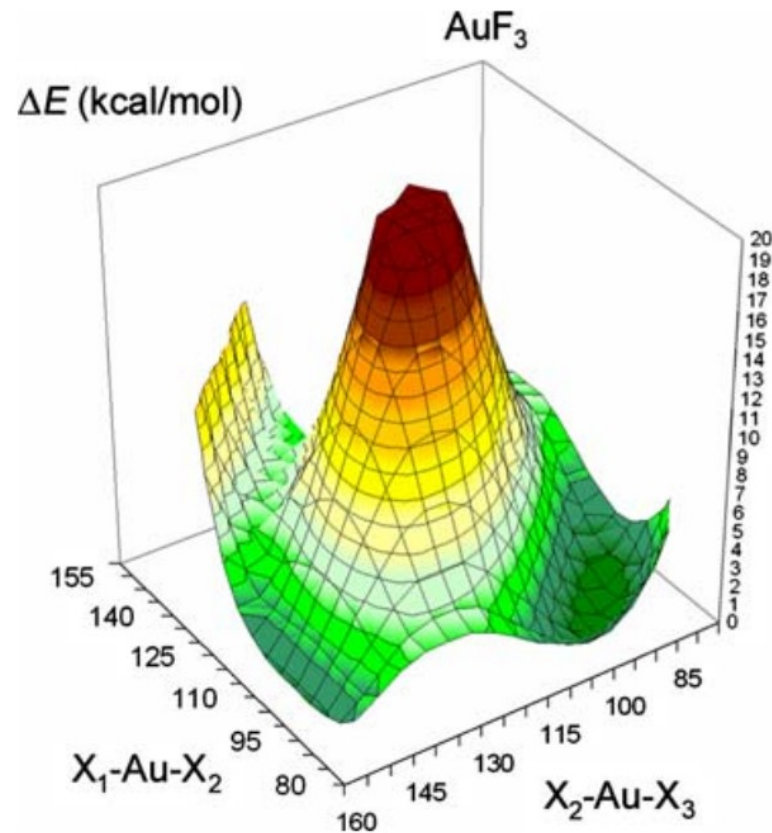
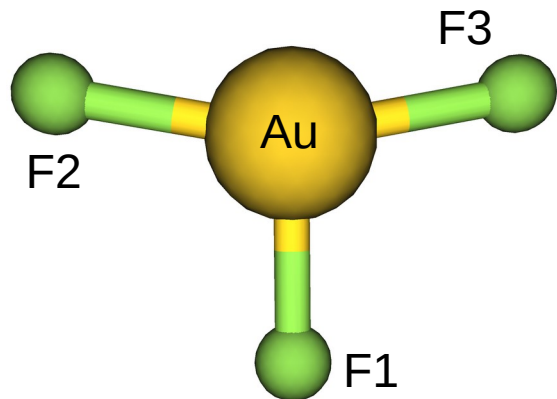
Jahn-Teller-Effekt: AuF₃

AuF₃ (Au⁰: [Xe] 4f¹⁴ 5d¹⁰ 6s¹)



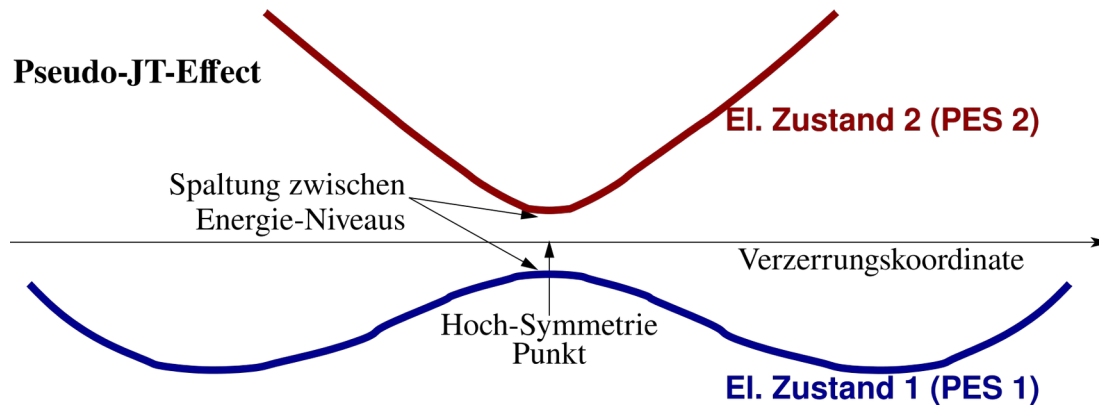
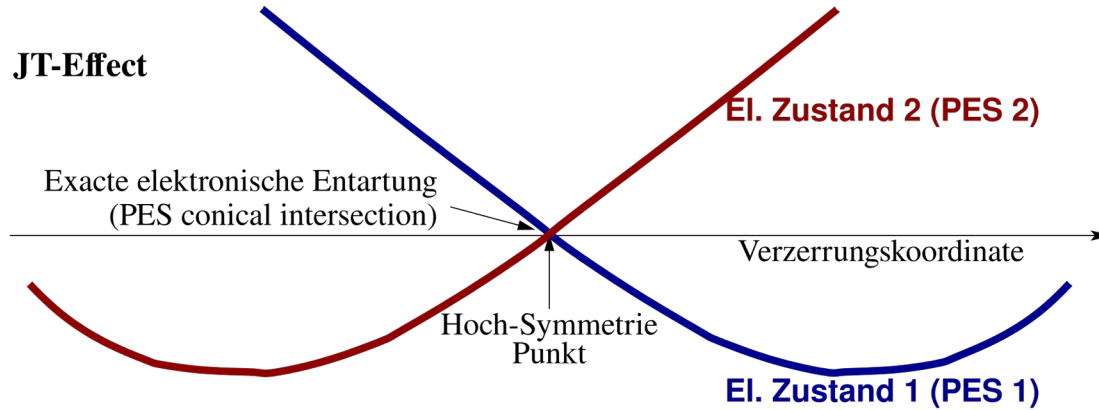
„Low-spin“ is niedriger in Energie!

Jahn-Teller-Effekt: AuF₃



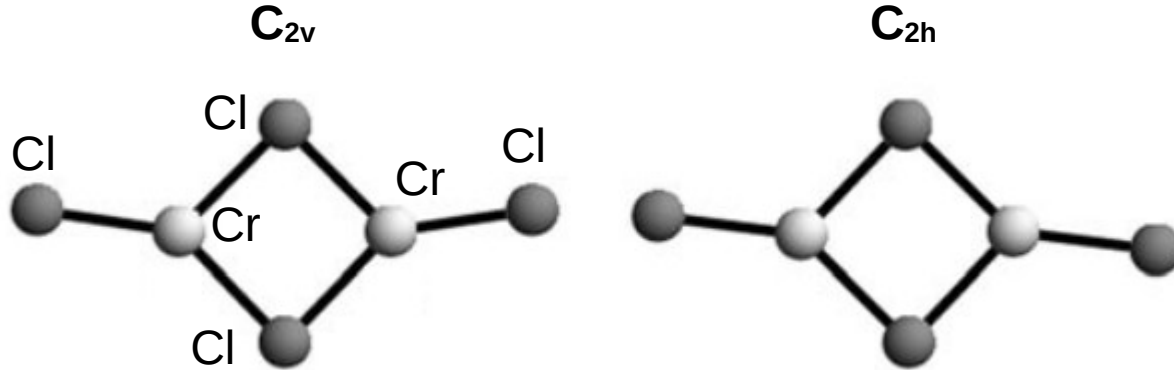
GED: $r_g(\text{Au-F1})=1.893(12) \text{ \AA}$
 $r_g(\text{Au-F2})=1.913(8) \text{ \AA}$ (Réffy, 2000)
 $\alpha(\text{F1-Au-F2})=102.5(1.9)^\circ$

Pseudo-Jahn-Teller-Effekt



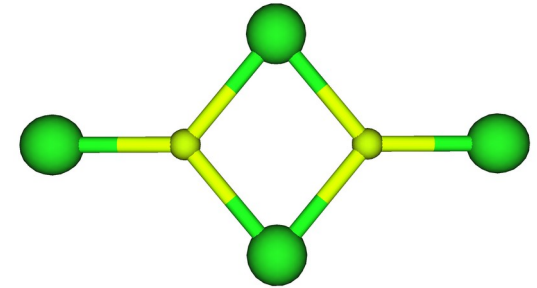
Pseudo-Jahn-Teller-Effekt: Cr_2Cl_4

Rechnungen und GED (Vest, 2008):



(Nur 0.024 eV zwischen Nonet und Singlet in C_{2v} !)
(Nur 0.001 eV zwischen C_{2h} und C_{2v})

Normalerweise ohne Verzerrung D_{2h}



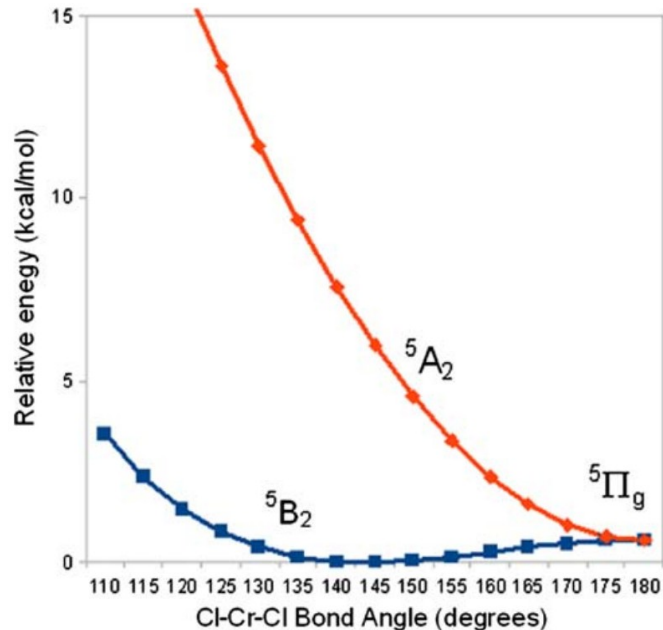
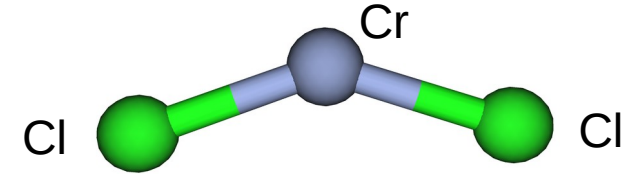
(experimentell f. Be_2Cl_4 , Mg_2Cl_4)

Renner-Teller-Effekt

Für lineare Strukturen in 2-fach-entarteten E-Zuständen!

CrCl_2 (Cr^0 : $[\text{Ar}] 3d^5 4s^1$)

GED und Rechnungen (Vest, 2008)



Electronic state	ΔE	$r(\text{Cr}-\text{Cl})$	$\angle \text{Cl}-\text{Cr}-\text{Cl}$	Method
$5B_2$	0	2.193	146.7	CASSCF(16,15)
	0	2.194	167.0	CCSD(T)
	0	2.193	146.7	B3LYP
$5\Pi_g$	7.2	2.198	180	CASSCF(16,15)
	3.1	2.194	180	CCSD(T)
	1.9	2.198	180	B3LYP
$5\Sigma_g$	26.6	2.239	180	CASSCF(16,15)
	14.0	2.240	180	CCSD(T)
	15.1	2.239	180	B3LYP
		2.196(20) ^b	149(9.5)	Electron diffraction ^a

Rovibronische Spektren

Silicium Borid SiB, Emissionsspektren (Brazier, 2007)

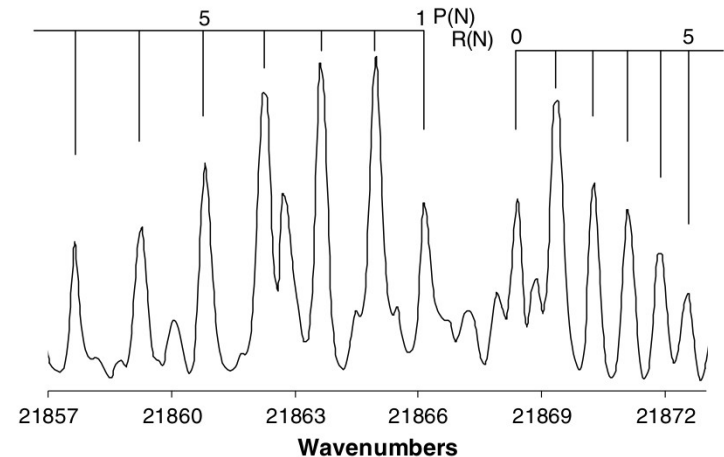
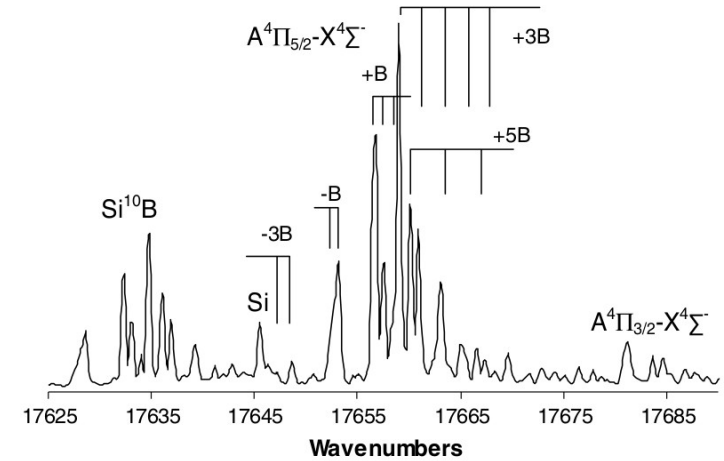
Für Si¹¹B [cm⁻¹]:



Level	Energy	B
$X^4\Sigma^- (v=0)$	0	0.5786(13)
$X^4\Sigma^- (v=1)$	739.021(25)	0.5760(15)
$X^4\Sigma^- (v=2)$	1467.244(24)	0.5723(11)
$X^4\Sigma^- (v=3)$	2184.874(23)	0.5712(9)
$A^4\Pi (v=0)$	18432.090(42)	0.6489(12)
$D^4\Sigma^- (v=0)$	23334.525(19)	0.5377(11)

Bindungslängen (Å):

State	r_0
$X^4\Sigma^-$	1.920
$A^4\Pi$	1.813
$D^4\Sigma^-$	1.992

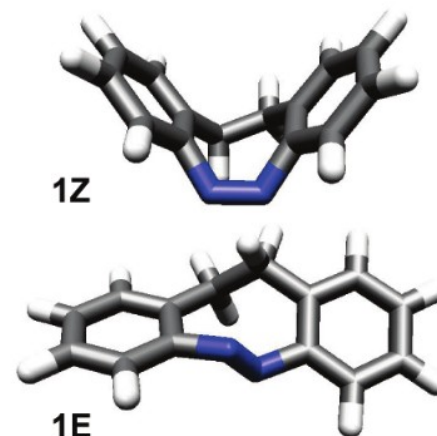
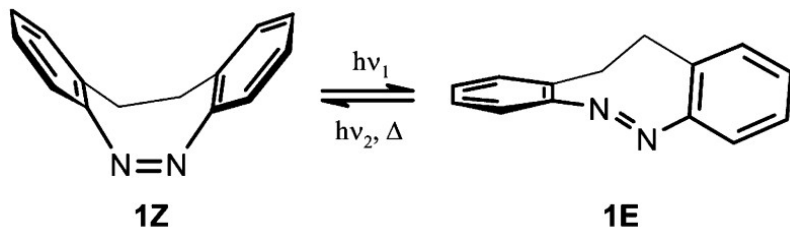


Molekül(e) des Tages

Highly Efficient Reversible Z–E Photoisomerization of a Bridged Azobenzene with Visible Light through Resolved S₁(nπ*) Absorption Bands

Ron Siewertsen,[†] Hendrikje Neumann,[†] Bengt Buchheim-Stehn,[‡] Rainer Herges,^{*,‡} Christian Näther,[§] Falk Renth,^{*,†} and Friedrich Temps^{*,†}

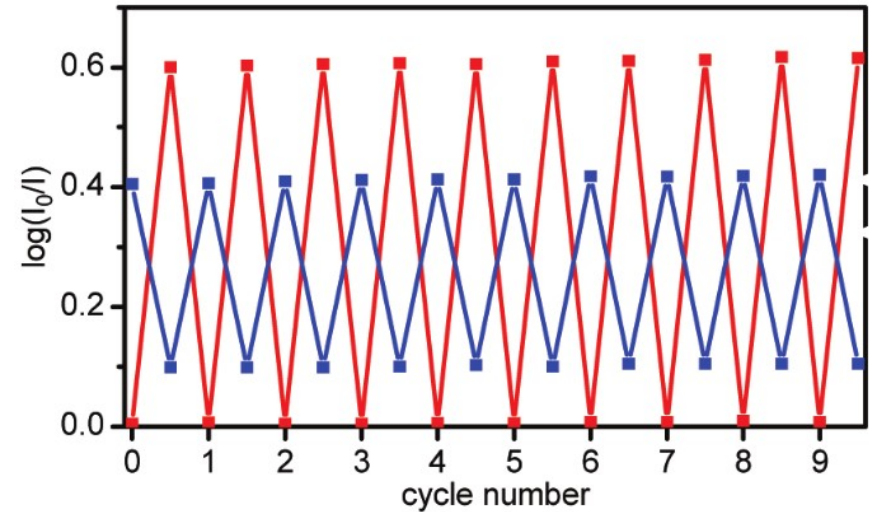
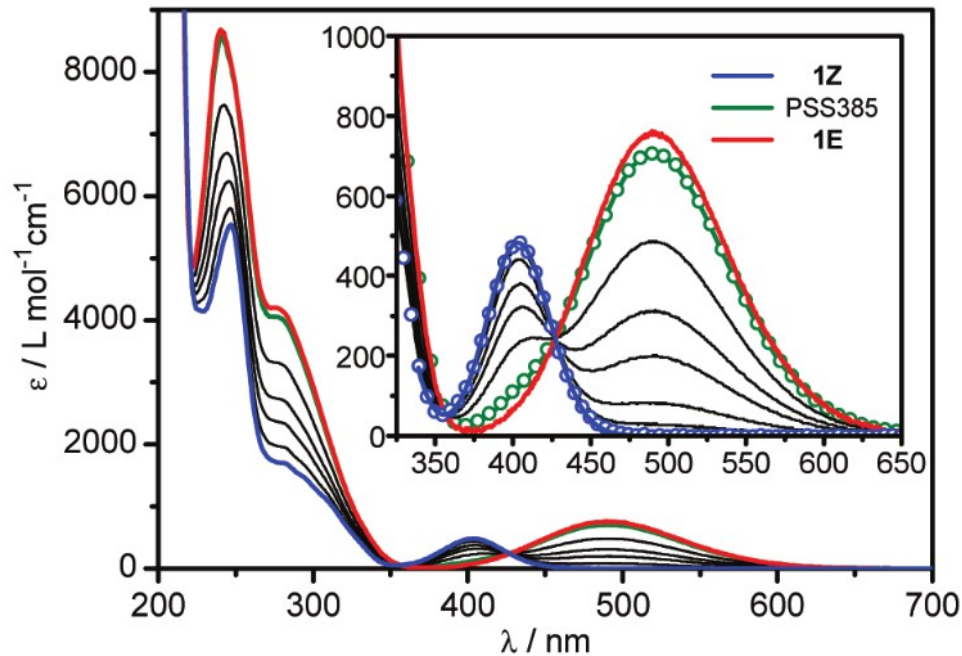
Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24098 Kiel, Germany, and Otto Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, D-24098 Kiel, Germany, and Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 6-7, D-24098 Kiel, Germany



Photoisomerisierung: UV/Vis-Spektren

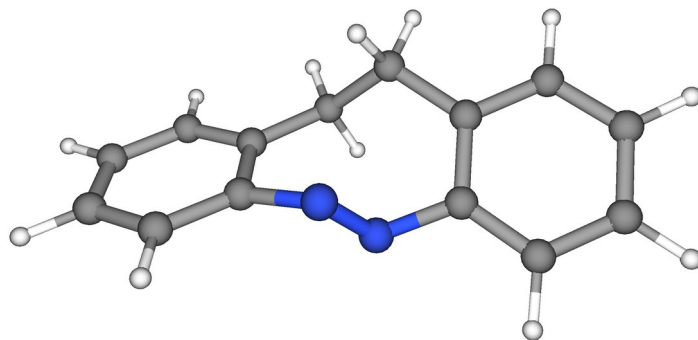
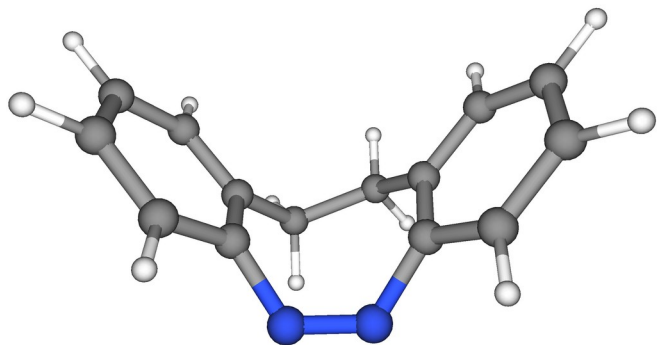
Bestrahlung $\lambda=370$ nm: Z \rightarrow E

Bestrahlung $\lambda=520$ nm: E \rightarrow Z (oder thermisch)



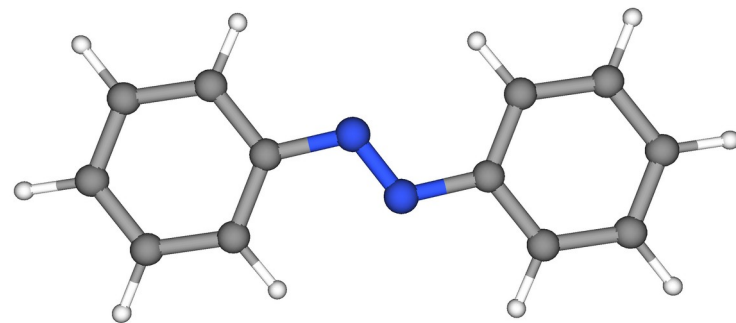
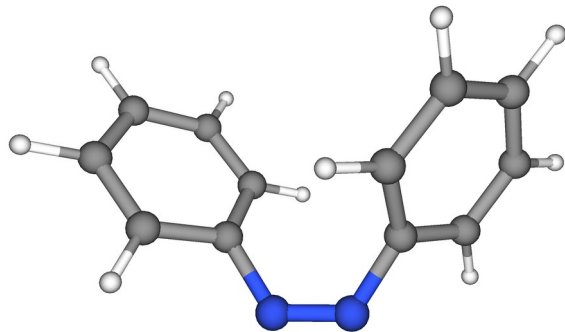
Bei $\lambda_1=400$ nm (blau) und $\lambda_2=490$ nm (rot)

Theoretische Interpretation: Geometrie

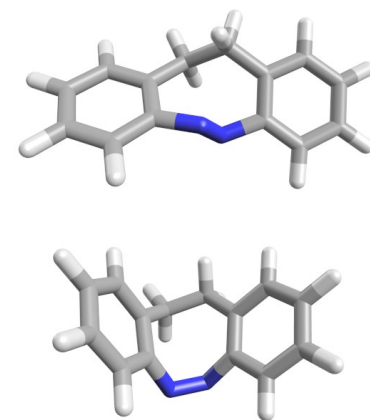
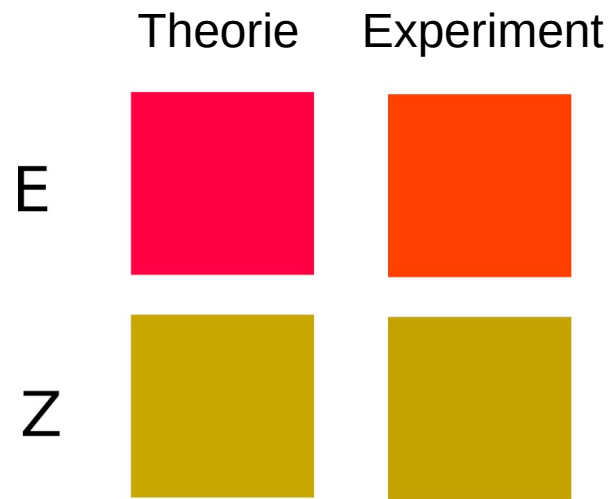
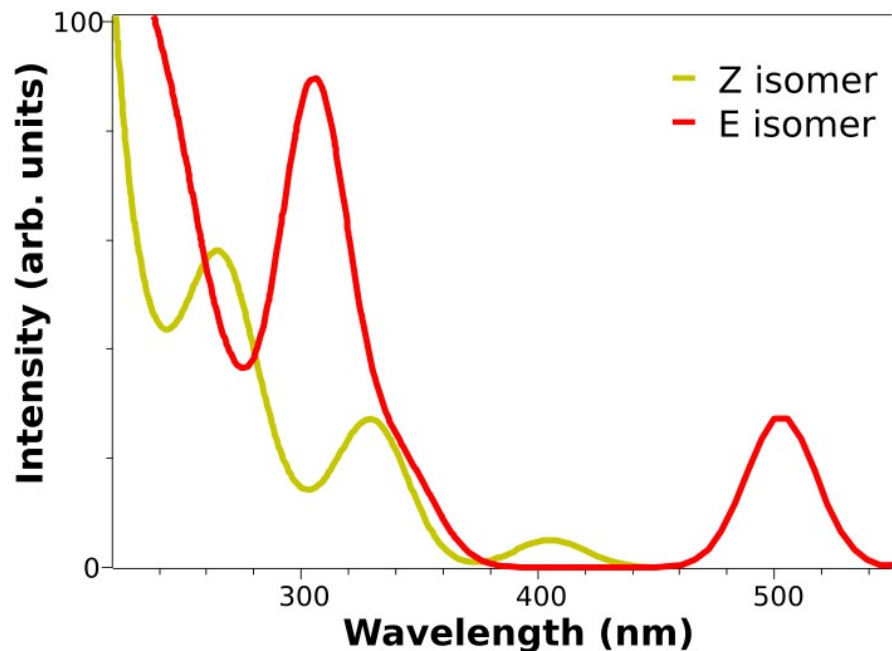


$\Delta E = +7.5$ kcal/mol
(Ungewöhnlich!)

Typisch ist Z-Isomer
höher in Energie,
wie z.B.:
 $\Delta E = +12.5$ kcal/mol



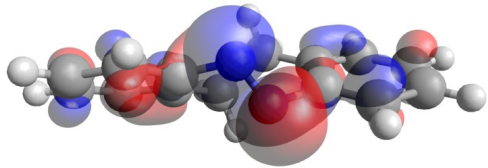
Theoretische Interpretation: TD-DFT



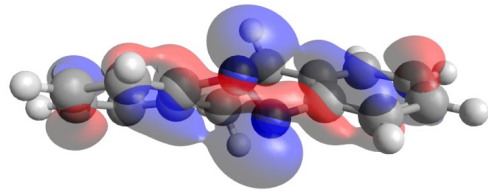
Theoretische Interpretation: Übergänge

E-Isomer:

S1 state n- π^*

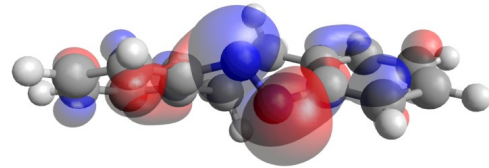


LUMO π^*

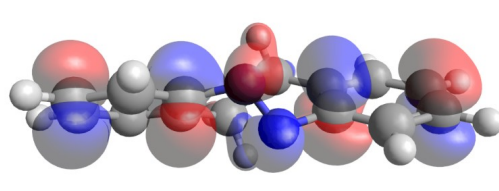


HOMO n

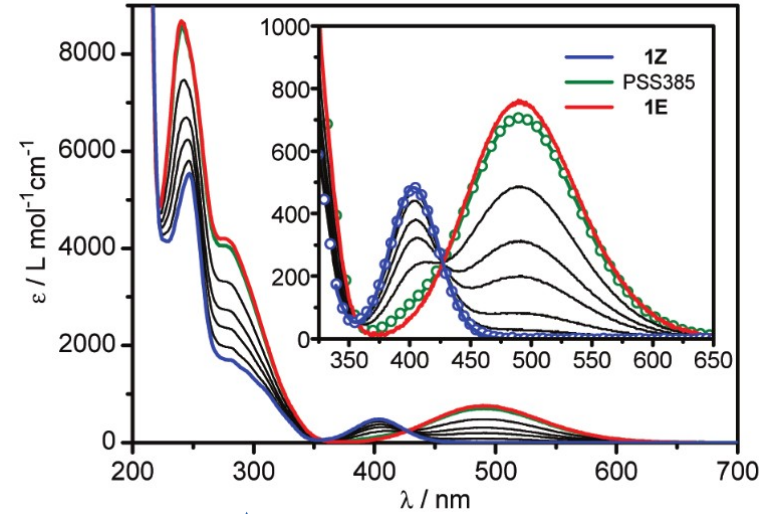
S2 state π - π^*



LUMO π^*



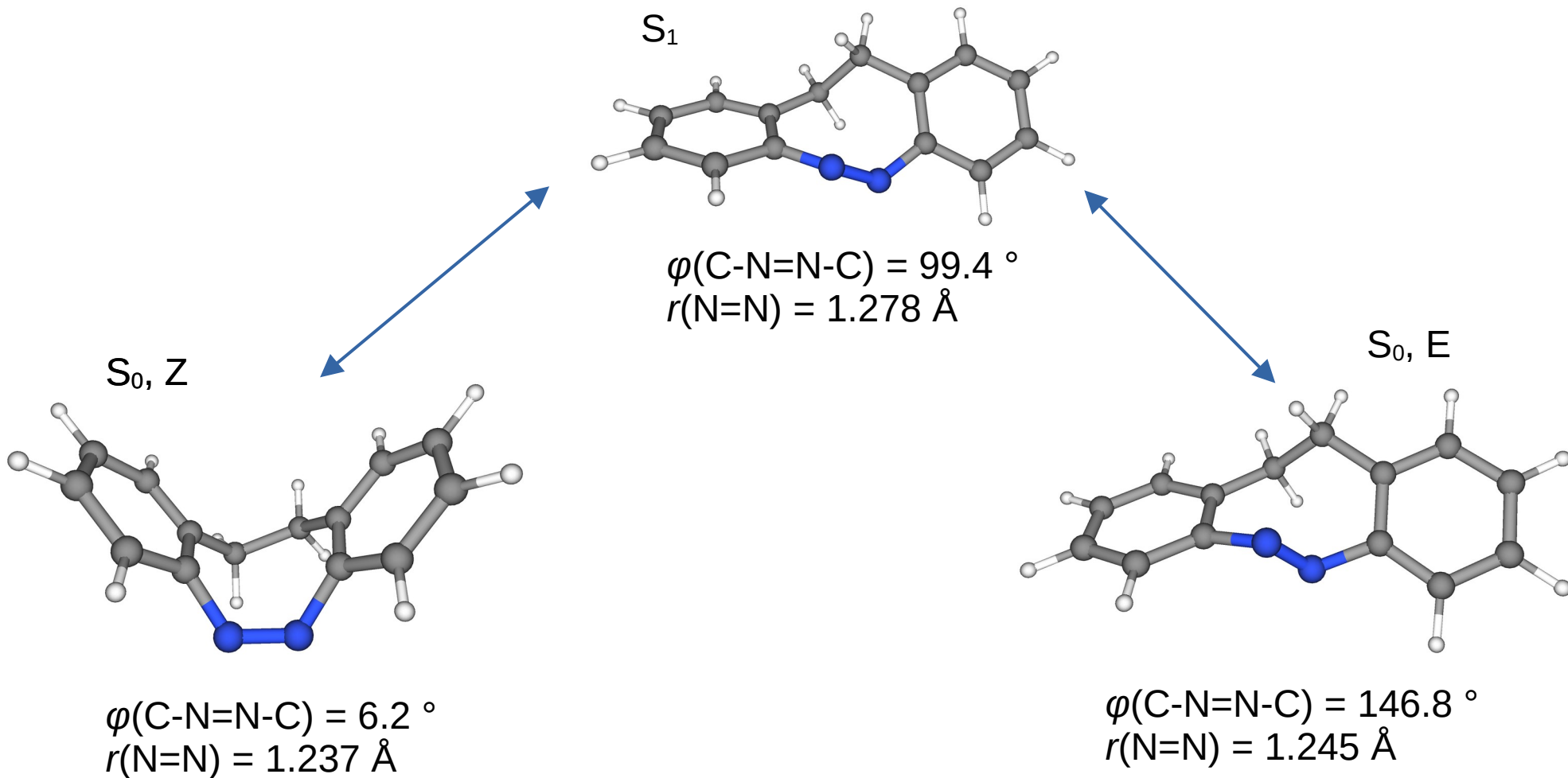
HOMO-1 π



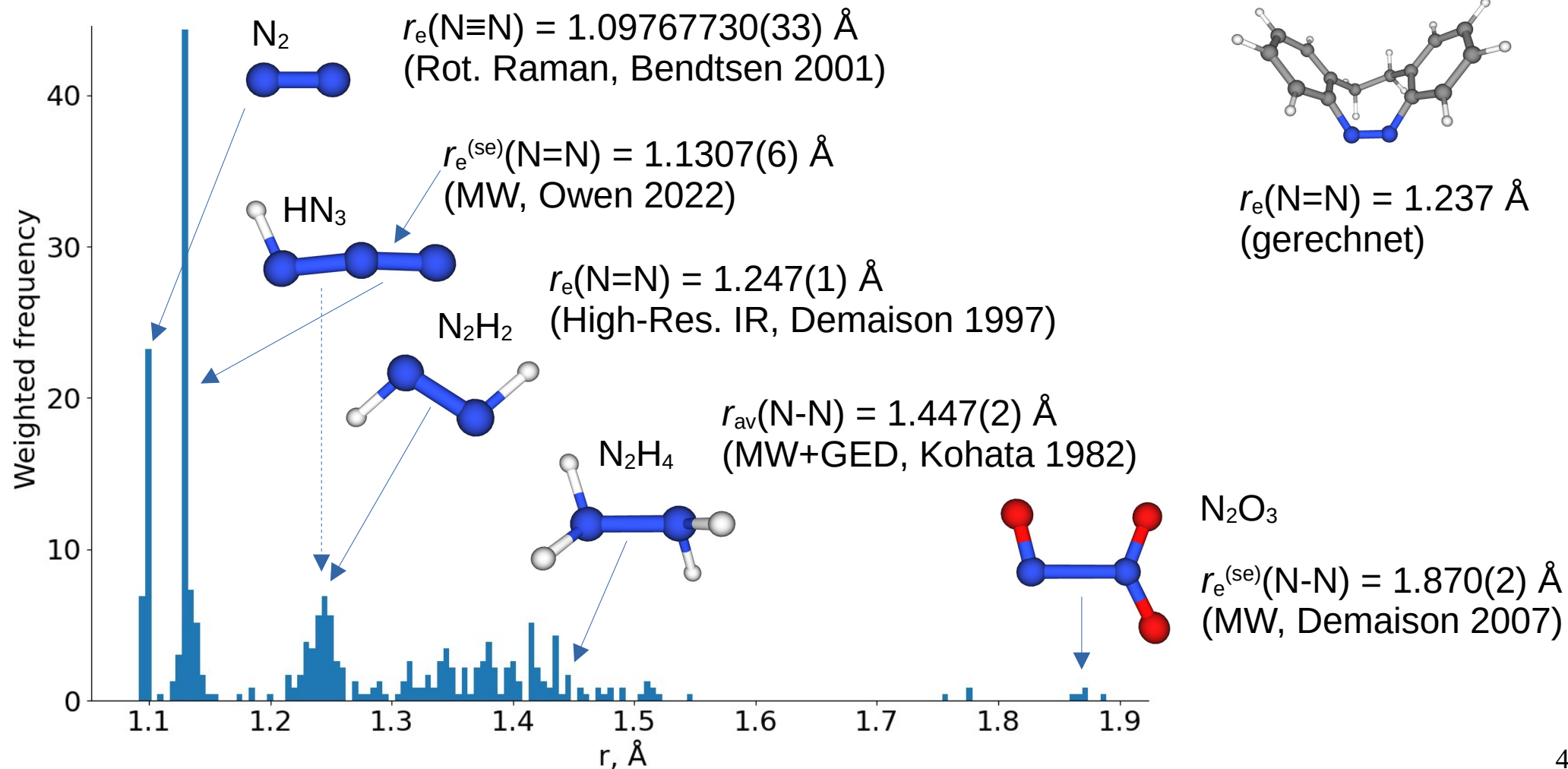
Z und E
 S_2 (π - π^*)

Z E
 S_1 (n- π^*)

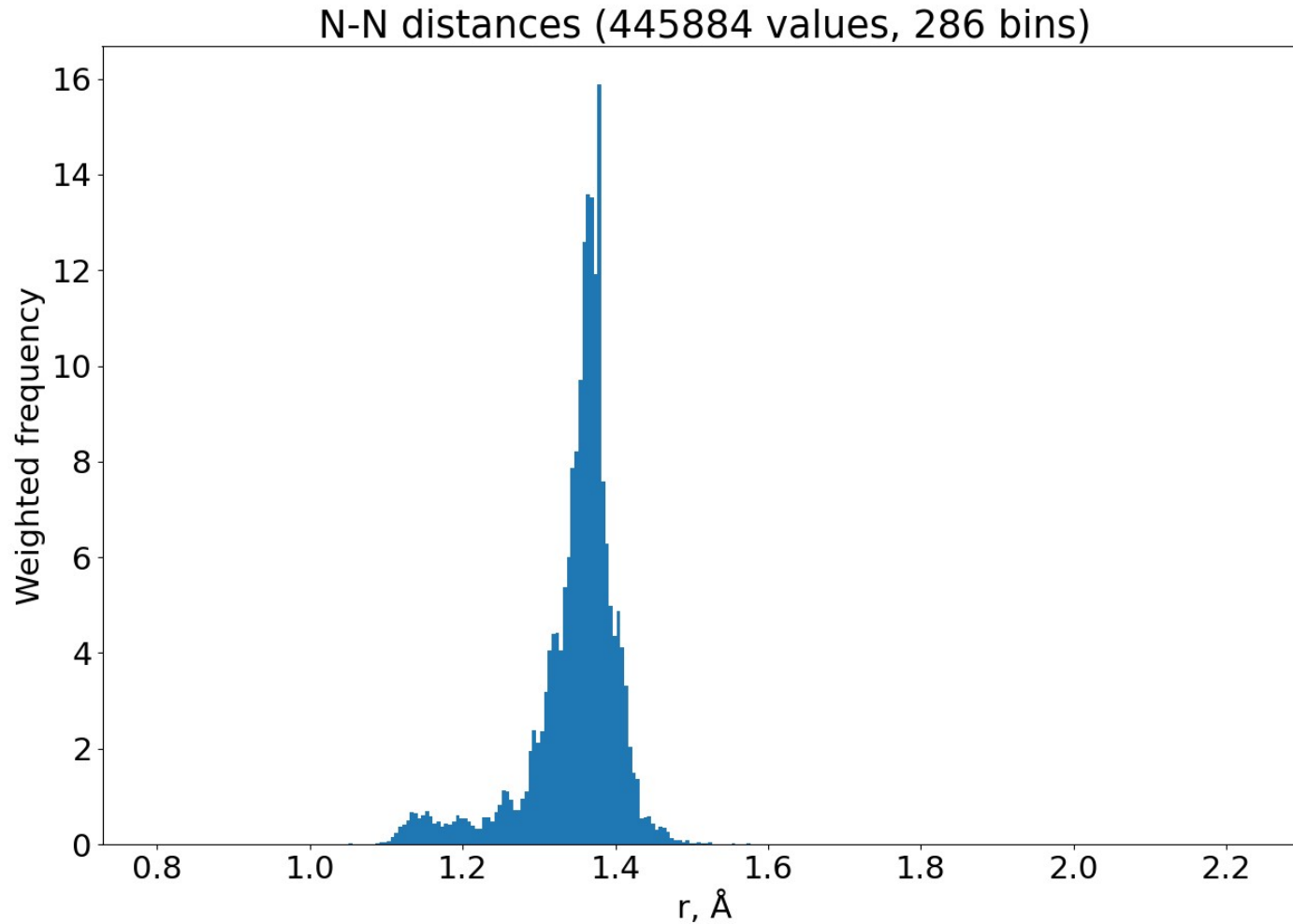
Theo. Interpretation: Photoisomerisierung



$r(\text{N}\sim\text{N})$, Gasphase MOGADOC



$r(N\sim N)$, Kristalle CSD



Quellen/Literatur

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Franck-Condon-Prinzip

