Advanced Inorganic Chemistry (AIC)

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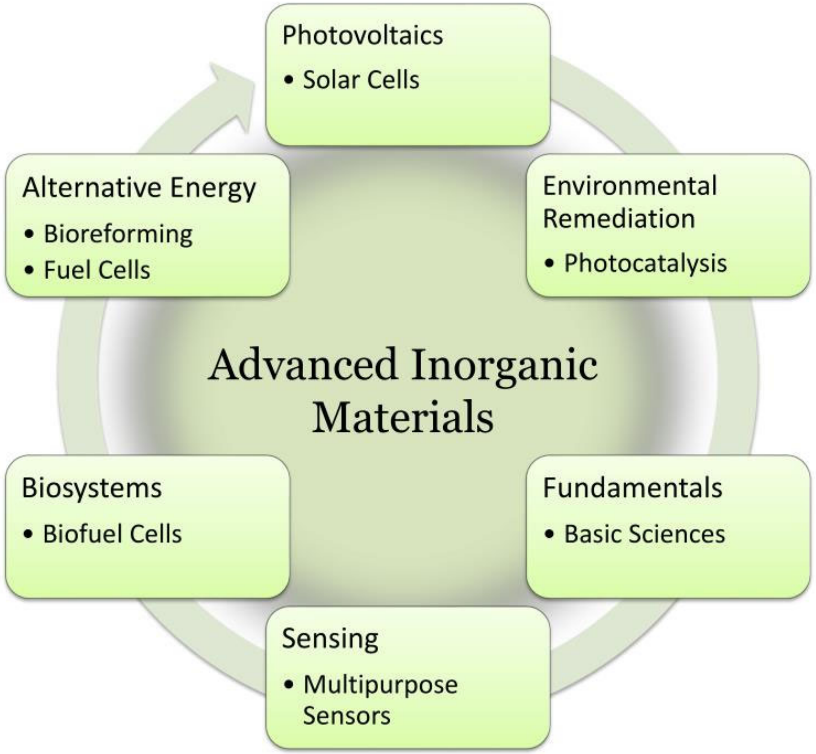

Advanced Inorganic Materials

Photovoltaics
- Solar Cells

Environmental Remediation
- Photocatalysis

Fundamentals
- Basic Sciences

Sensing
- Multipurpose Sensors

Biosystems
- Biofuel Cells

Alternative Energy
- Bioreforming
- Fuel Cells

„The time will come when diligent research over long periods will bring to light things, which now lie hidden" (Lucius Anneaus Seneca, Romain dramatist and philosopher, 4 BC - 65 AD)

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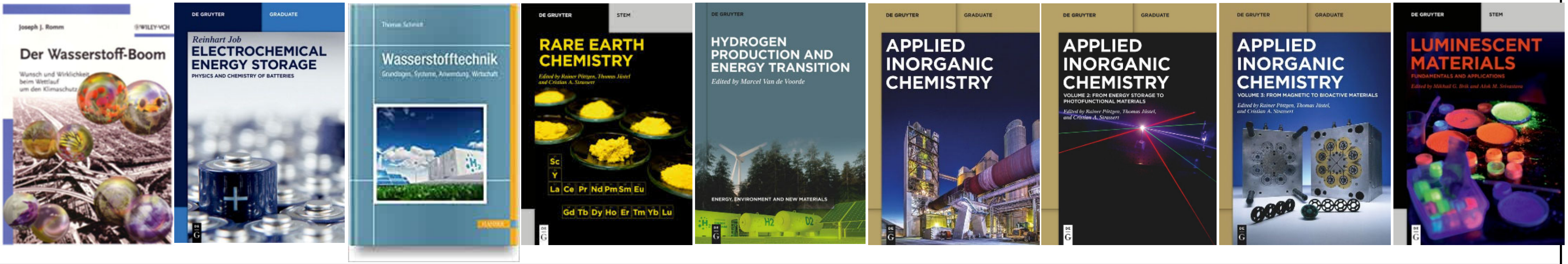
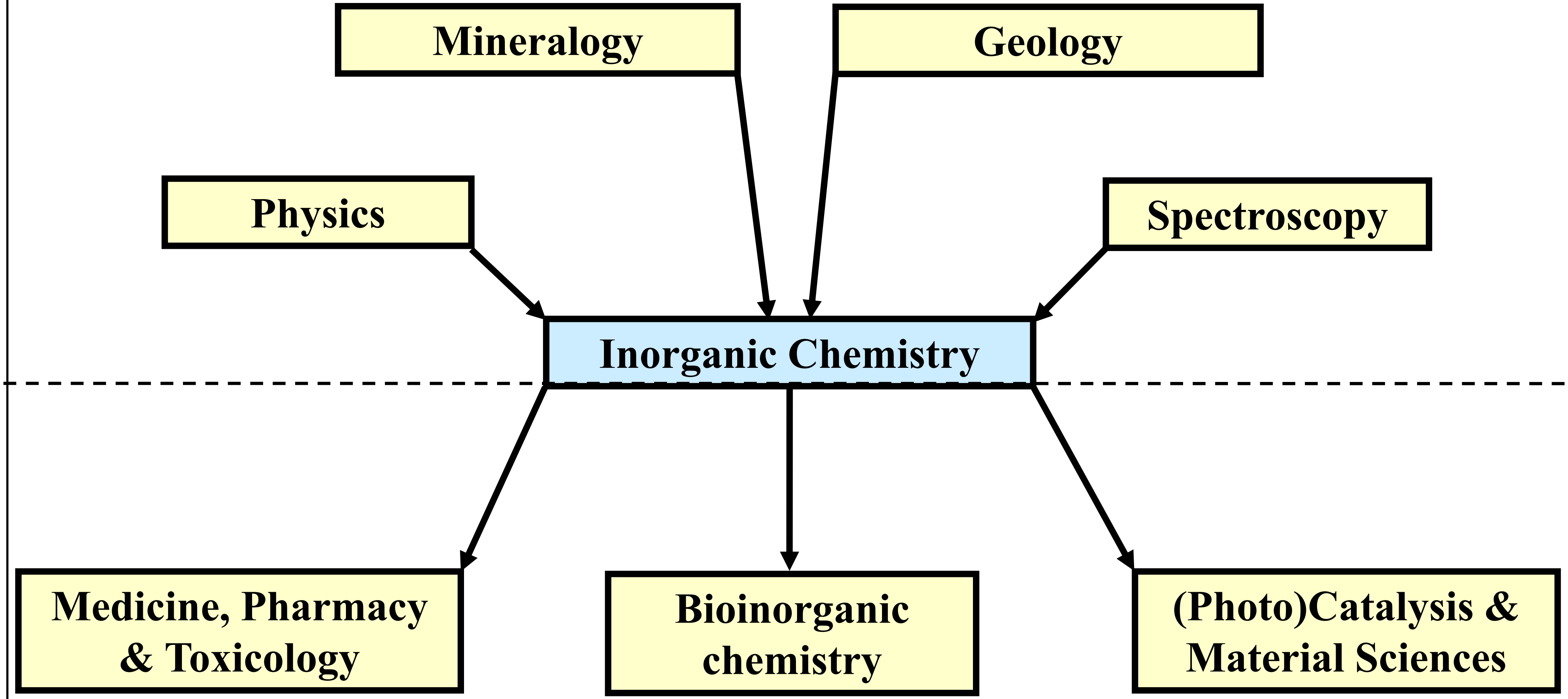


1. Role of Inorganic Chemistry

A Highly Interdisciplinary Science at the Verge of Biology, Geology, Physics, and many other Disciplines



Mineralogy

Geology

Physics

Spectroscopy

Inorganic Chemistry

Medicine, Pharmacy & Toxicology

Bioinorganic chemistry

(Photo)Catalysis & Material Sciences

1. Role of Inorganic Chemistry

A Highly Interdisciplinary Science at the Verge of Biology, Geology, Physics, and many other Disciplines

Astrophysics	Fusion of Elements	From H to He to metals
Astrochemistry	Compounds in the universe	Inorganic molecules
Geochemistry	Compounds of Earth´s body	Mineral, gemstone, and ore formation
Atmosphere chemistry	Gases	N_2, O_2, O_3, CO, CO_2, …
Biochemistry	“Materials” and Catalysts	$CaCO_3$, SiO_2, $Ca_3(PO_4)_2$ metallo enzymes
Technology	Ceramics, glass, crystals	Al_2O_3, SiO_2, Si, (In,Ga)N

2. Cosmo and Astrochemistry

Definition

Astrochemistry studies molecules anywhere in the universe/cosmos

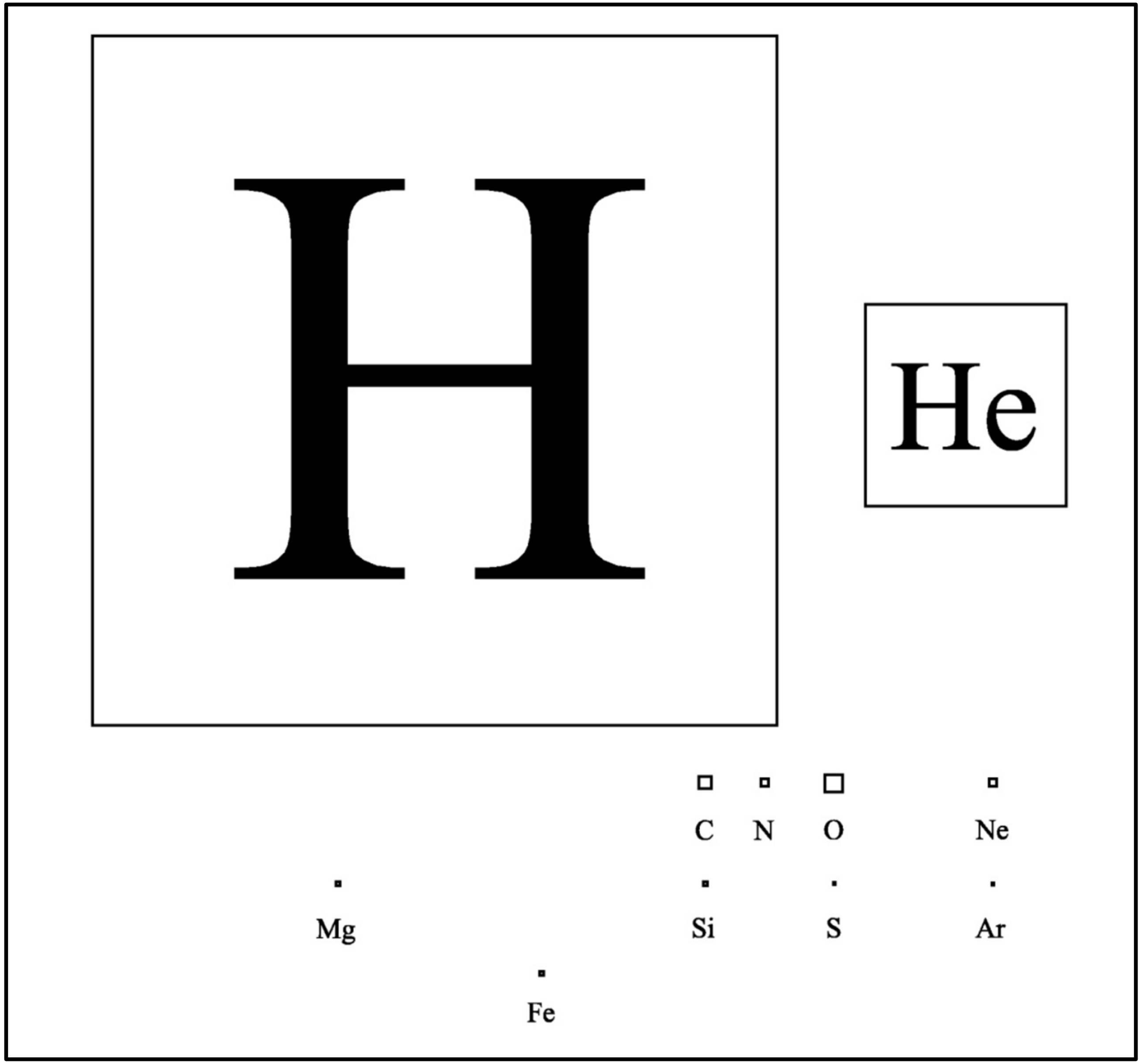
- **how are they formed**
- **decomposed**
- **how complex can they get**
- **how does molecular composition vary from location to location**
- **use them as tracer of physical conditions (temperature, density, radiation, gravity, …..)**
- **how do molecules in space relate to life as we know it (→ astrobiology)**

2. Cosmo and Astrochemistry

The Astronomers PTOE

Cosmic Abundances

Element	Ratio	Occurrence
$_1H$	1.0	H_2, H_2O
$_2He$	0.1	inert
$_6C$	$3 \cdot 10^{-4}$	CO, CO_2
$_7N$	$1 \cdot 10^{-4}$	N_2
$_8O$	$7 \cdot 10^{-4}$	CO, CO_2
$_{10}Ne$	$8 \cdot 10^{-5}$	inert
$_{12}Mg$	$3 \cdot 10^{-5}$	Dust
$_{14}Si$	$3 \cdot 10^{-5}$	Dust
$_{16}S$	$2 \cdot 10^{-5}$	SO, H_2S
$_{26}Fe$	$4 \cdot 10^{-6}$	Dust



2. Cosmo and Astrochemistry

From Plasms to Solids

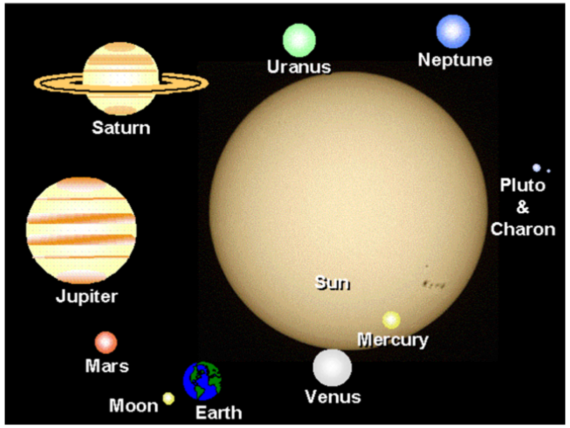
t = 3 min, $T_{CBR} \sim 1 \cdot 10^9$ K　　p = H core = H^+ = HII
$2n + 2p$ = He core = He^{2+}

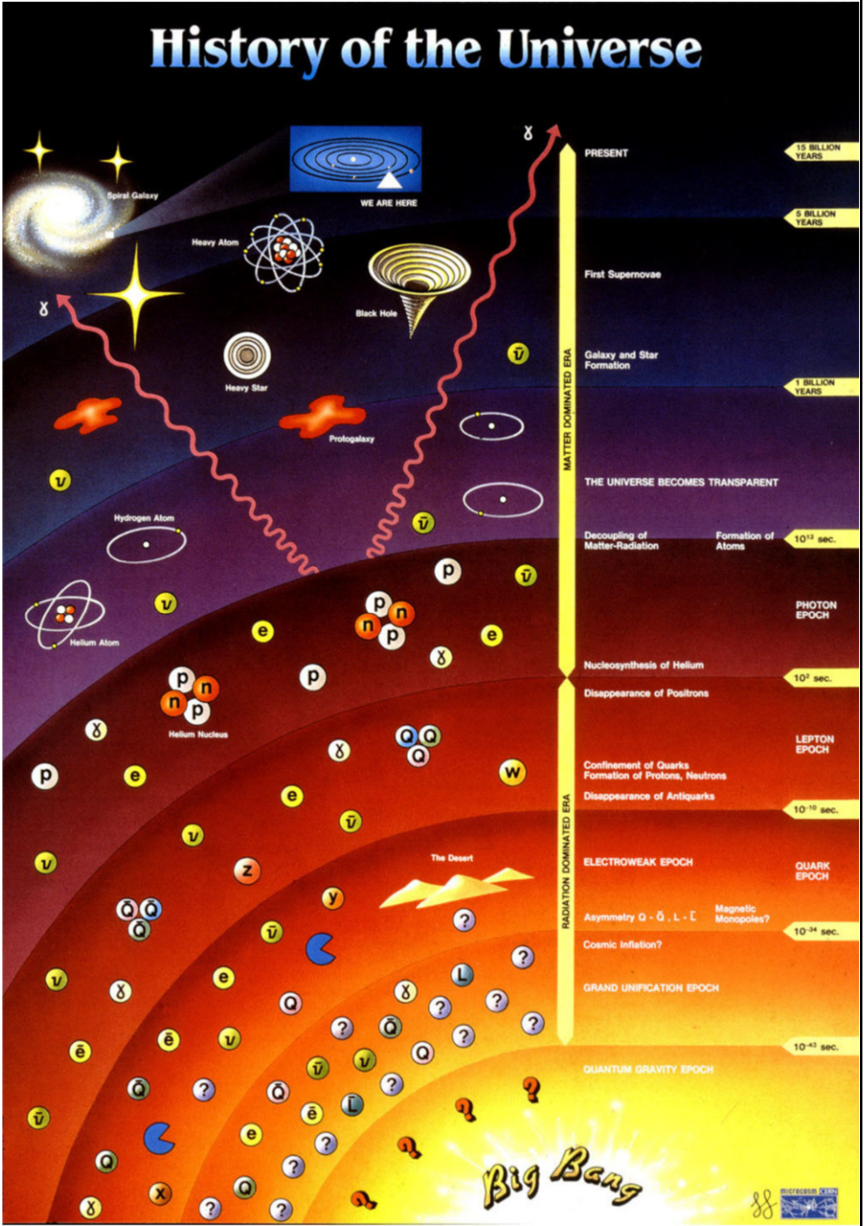
t = 300,000 y, $T_{CBR} \sim 3000$ K　　$H^+ + e^- \rightarrow H$ = HI
(recombination age)　　$He^{2+} + 2\,e^- \rightarrow He$ = HeI

t = $1 \cdot 10^9$ y, $T_{CBR} \sim 20$ K　　Stellar fusion → Fe/Ni
(1st generation stars and galaxies, Nature 602 (2022) 58)
Supernovae → Cu … Lr

t = $5 \cdot 10^9$ y, $T_{CBR} = 3$ K
(milky way formation and
2nd gen. stars with planets)

t = $13.8 \cdot 10^9$ y, $T_{CBR} = 2.726$ K





The First Atoms

Primordial relative abundances in the isotropic universe

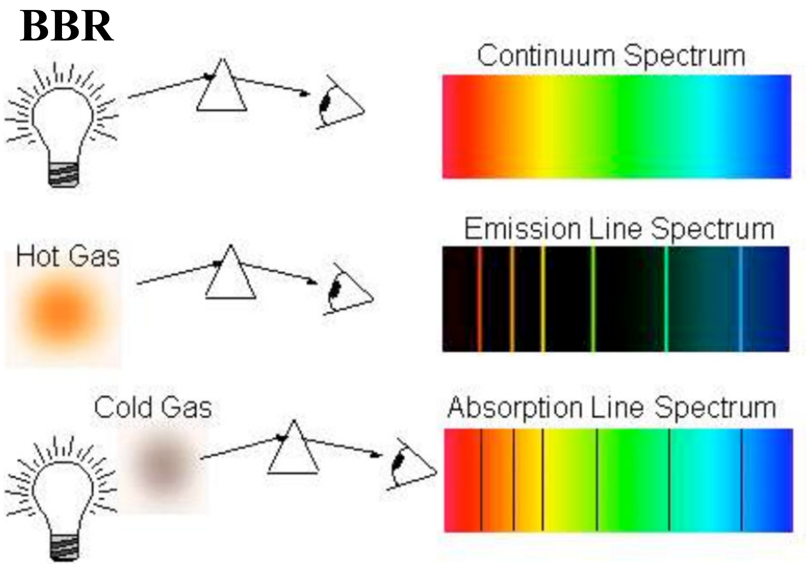
- $n(^{4}He)/n(H) = 0.083$
- $n(D)/n(H) = 2.7 \cdot 10^{-5}$
- $n(^{7}Li)/n(H) = 1.7 \cdot 10^{-10}$
- $n(^{3}He)/n(H) \sim 0.3 \cdot 10^{-5}$

These nuclei recombined with electrons in the cooling universe

(with z = red-shift, $T_{CBR} = (1 + z)$ K)

- $He^{2+} \rightarrow He^{+} \rightarrow He$ $z \sim 6000 – 2700$, T = 20,000 – 10,000 K, t ~ 18,000 - 78,000 y
  ($I_{He} = 24.6$ eV)
- $H^{+} \rightarrow H$ $z \sim 1100$, T ~ 4000 K , t ~ 370,000 y
  ($I_{H} = 13.6$ eV)
- $Li^{+} \rightarrow Li$ $z \sim 500 - 400$, T ~ 1900 - 1500 K, t ~ 1.4 - 1.9 My
  ($I_{Li} = 5.4$ eV)

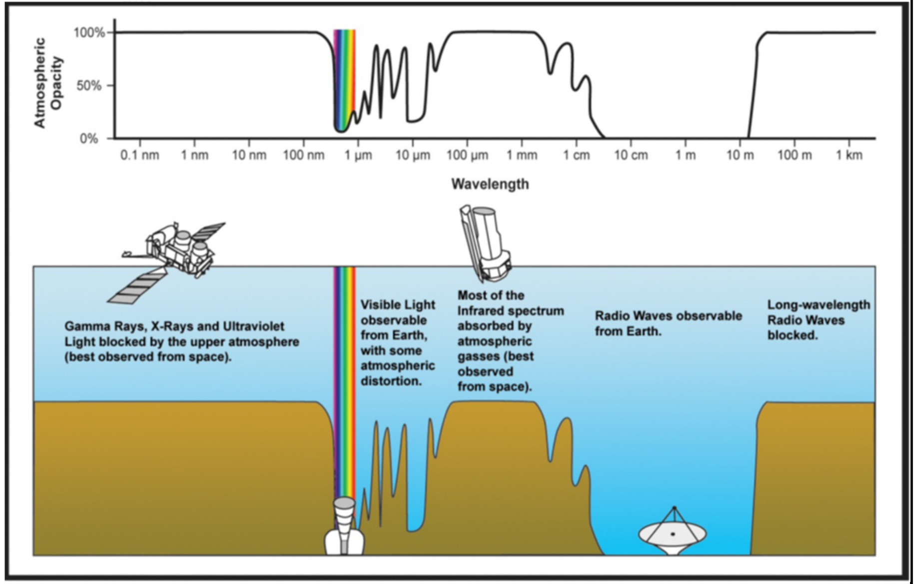
Observation Methods - Overview



$E_{total} = E_{electr.} + E_{vibr.}$(molecules) + $E_{rot.}$(gas + liquids)

Observation by absorption and/or emission spectra

Limitation by Earth's atmosphere (affected mainly by the absorption lines of H_2O, CO_2, O_2, O_3 & CH_4)



1st window	VIS 300-900 nm	$E_{electronic}$
2nd window	IR 1-5 µm	$E_{vibration}$
3rd window	MW 0.35-1.3 mm	$E_{rotation}$
4th window	Radiow. 0.1-10 m	Hyperfine transitions

2. Cosmo and Astrochemistry

Observation Methods - HI

Neutral hydrogen (HI): $1s^1 \rightarrow$ G.S.: $n = 1$
Hyperfine structure transition
at 21 cm (1.42 GHz) due to (SS-coupling)

- Predicted in 1944 by van de Hulst
- Discovered in 1951 by Ewen&Purcell
- Used for distribution and kinematics of the neutral gas in the Milky Way

Fine structure transition (LS-splitting)

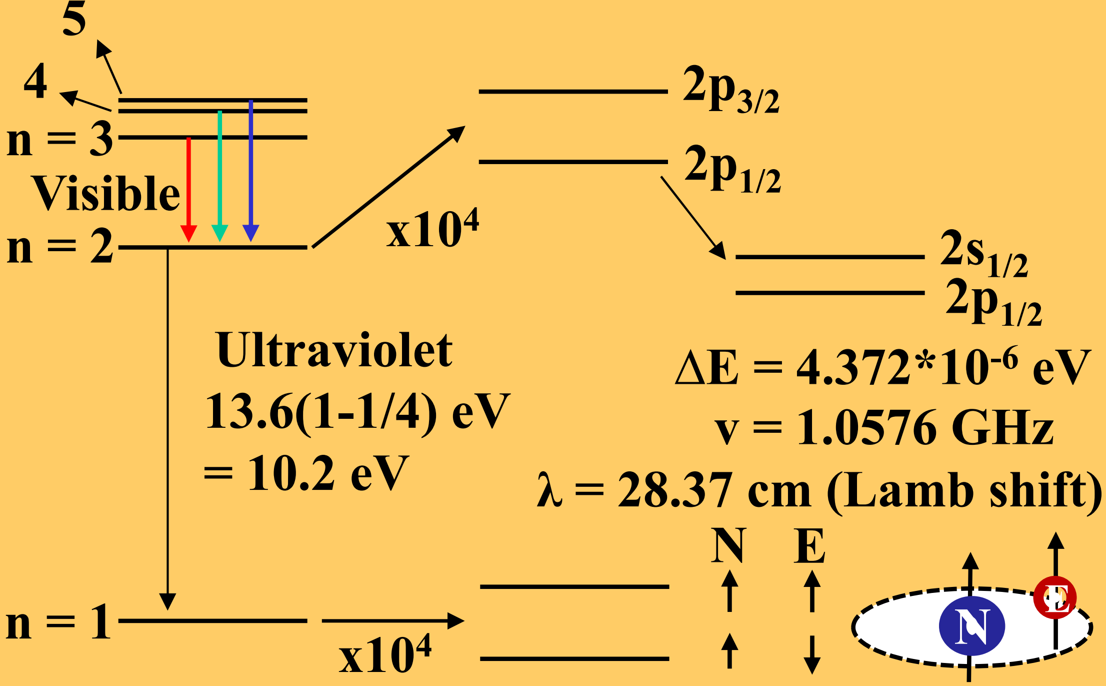
$^2p_{3/2} - {}^2p_{1/2}$ 28.37 cm (1.06 GHz)

Balmer series transitions in the VIS

5-2	434.047 nm
4-2	486.133 nm
3-2	656.272 nm

Neutral Hydrogen (HI) energy levels

Visible: $\Delta E = 4.5 \cdot 10^{-5}$ eV (< thermal energy)
$4.5 \cdot 10^{-5}$ eV = $3/2\ k_BT$ at 0.35 K
$\nu = 10.9$ GHz Doppler broadening ~ 4 GHz
$\lambda = 2.8$ cm barely resolvable



Ultraviolet
13.6(1-1/4) eV
= 10.2 eV

$\Delta E = 4.372 \cdot 10^{-6}$ eV
$\nu = 1.0576$ GHz
$\lambda = 28.37$ cm (Lamb shift)

$$E_n = \frac{-13.6\ z^2}{n^2}\ \text{eV}$$

$\Delta E = 5.9 \cdot 10^{-6}$ eV
$\nu = 1.42$ GHz
$\lambda = 21$ cm

2. Cosmo and Astrochemistry

Term Symbols: Description of Electronic States in Multiple-Electron-Atoms

Orbital angular momentum $L = |\Sigma l_i|$

$\lvert M_L \rvert$	0	1	2	3	4	5	6	7	8	9	…
	S	P	D	F	G	H	I	K	L	M	…

Spin angular momentum $S = \Sigma s_i$

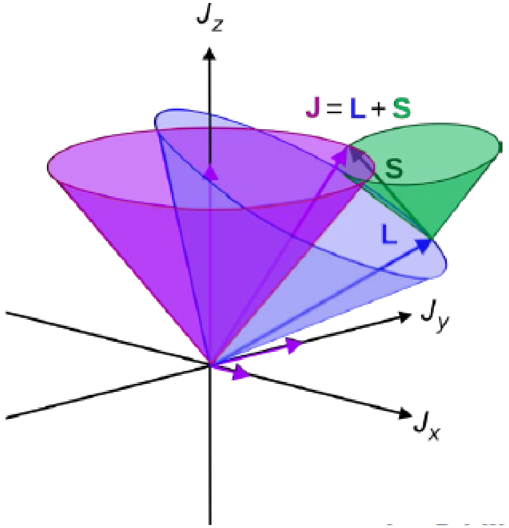
$\lvert M_S \rvert$	0	$^1/_2$	1	$^3/_2$	2	$^5/_2$	…
2S+1	1	2	3	4	5	6	…
	Singlet	Doublet	Triplet	Quartet	Quintet	Sextet	…

$$\boxed{^{2S+1}L}$$

Total angular momentum $J = |L - S|, \; ….. \; |L + S|$ results from different orientations of L and S towards each other

⇒ Russell-Saunders (RS) coupling

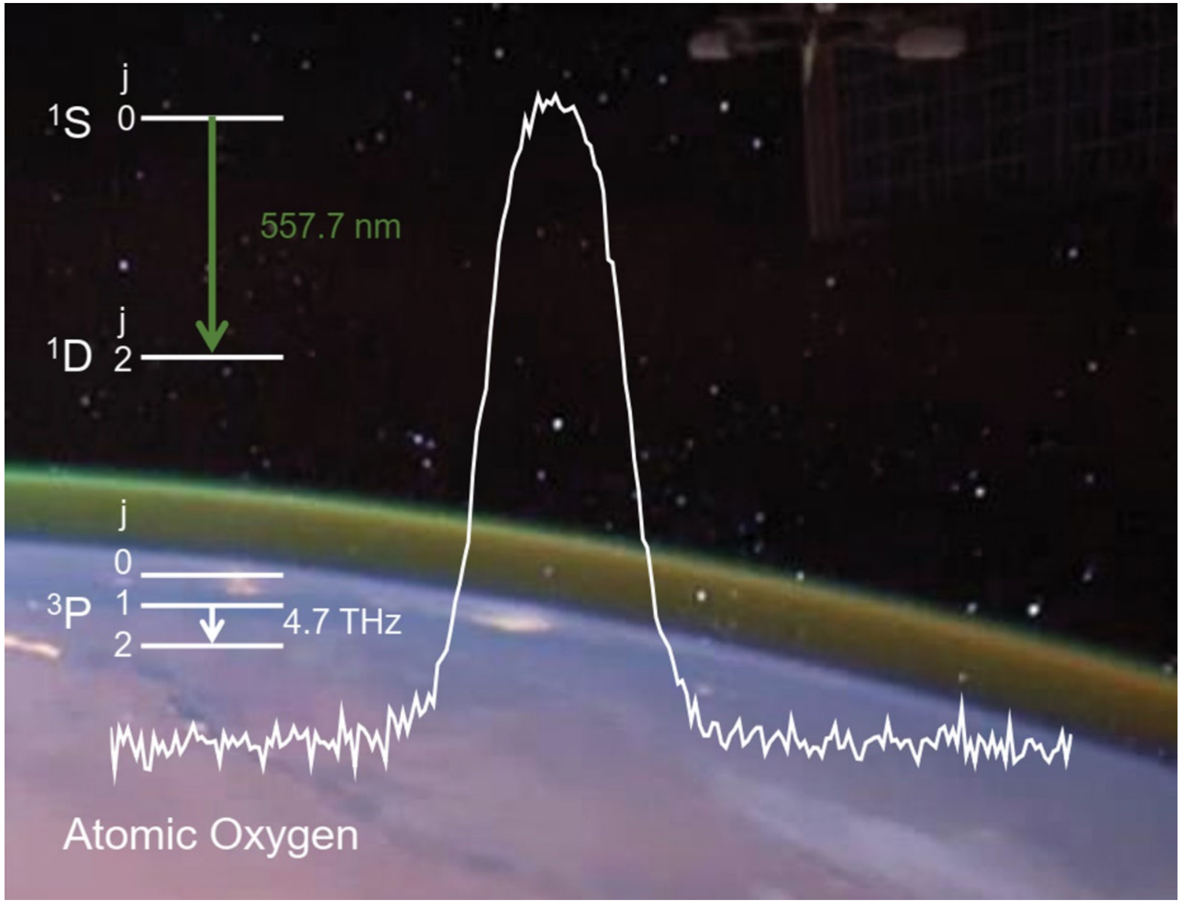
$$\boxed{^{2S+1}L_J}$$



http://upload.wikimedia.org/wikipedia/commons/thumb/3/30/LS_coupling.svg/2000px-LS_coupling.svg.png

2. Cosmo and Astrochemistry

Observation Methods - OI



Lit.: Direct measurements of atomic oxygen in the mesosphere and lower thermosphere using terahertz heterodyne spectroscopy, H. Richter et al., Communications Earth & Environment 2 (2021) 19

Neutral Oxygen (OI): [He]$2s^22s^4$
S = 1, L = 1 (P), J = 0, 1, 2 → G.S.: $^3P_2$
Green emission line is caused by the 557.7 nm transition of atomic oxygen (→ aurora borealis, aurora australis)

Fine structure transitions (LS-splitting)
$^3P_1$ - $^3P_2$
at 62.5 µm (4.75 THz, width: 170 MHz)
(image taken by astronauts aboard ISS)
$^3P_0$ - $^3P_1$
at 145.6 µm (2.06 THz)

In addition: Yellow emission of neutral Na (NaI) at 589.0 and 589.6 nm (G.S.: $^2S_{1/2}$)

Observation Methods - OI: Microstates and Term Symbol for the $2p^4$ Configuration

$L = 2 \qquad M_L = -2, -1, 0, 1, 2$

$S = 1 \qquad M_S = -1, 0, 1$

$$\boxed{\text{Number \#} = \frac{n!}{e!h!}}$$

with e = electrons, h = holes, n = maximal number of e^- in shell

$M_L = 2$ and $M_S = 0 \Rightarrow {}^1D$

L =	+2	+1	0	-1	-2
S = 0	X	X	X	X	X

$M_L = 1$ and $M_S = 1 \Rightarrow {}^3P$

L =	+1	0	-1
S = +1	X	X	X
S = 0	X	X	X
S = -1	X	X	X

$M_L = 0$ and $M_S = 0 \Rightarrow {}^1S$

L =	0
S = 0	X

Hund's rules (3 different ones)

1st S as high as possible

2nd L as high as possible

3rd Hund's rule for J:
J = |L + S| most stable for shells filled more than half

⇒ Energetic order $2p^4$ configuration ${}^3P < {}^1D < {}^1S$

2. Cosmo and Astrochemistry

Observation Methods - H_2 emission spectrum

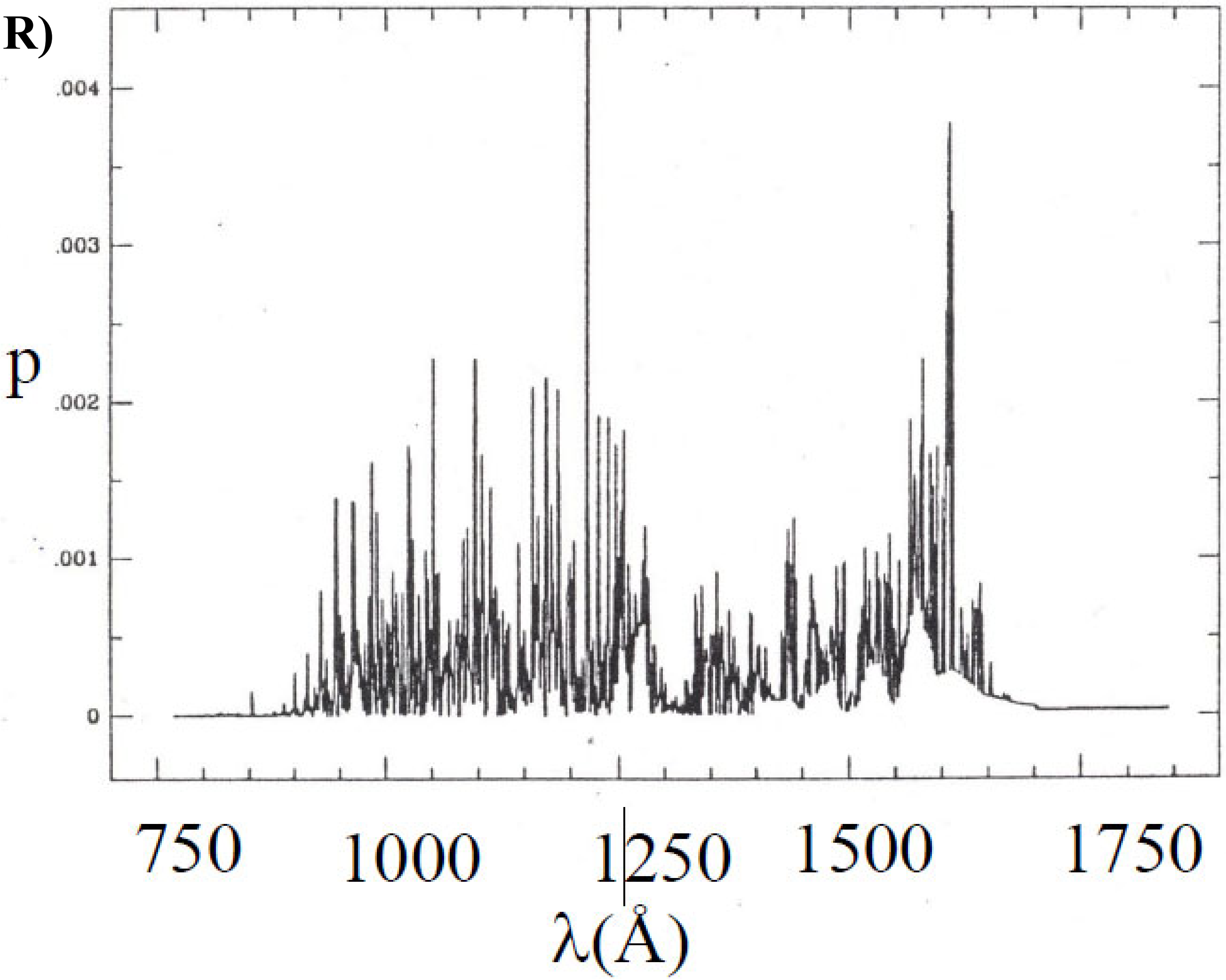
Excitation by cosmic radiation (CR)

- $H_2 + CR \rightarrow H_2^+ + e^{-*}$
- $H_2^+ + e^{-*} \rightarrow H_2^* + e^-$
- $H_2^* \rightarrow H_2 + h\nu$

VUV emission spectrum between 90 and 170 nm, similar for HD and D_2 (lamps)

References

- **Prasad & Tarafdar 1983**
- **Gredel et al. 1987**



2. Cosmo and Astrochemistry

Observation Methods - Vibrational Spectra

Vibrations of diatomic molecules are described by the Morse potential (anharmonic)

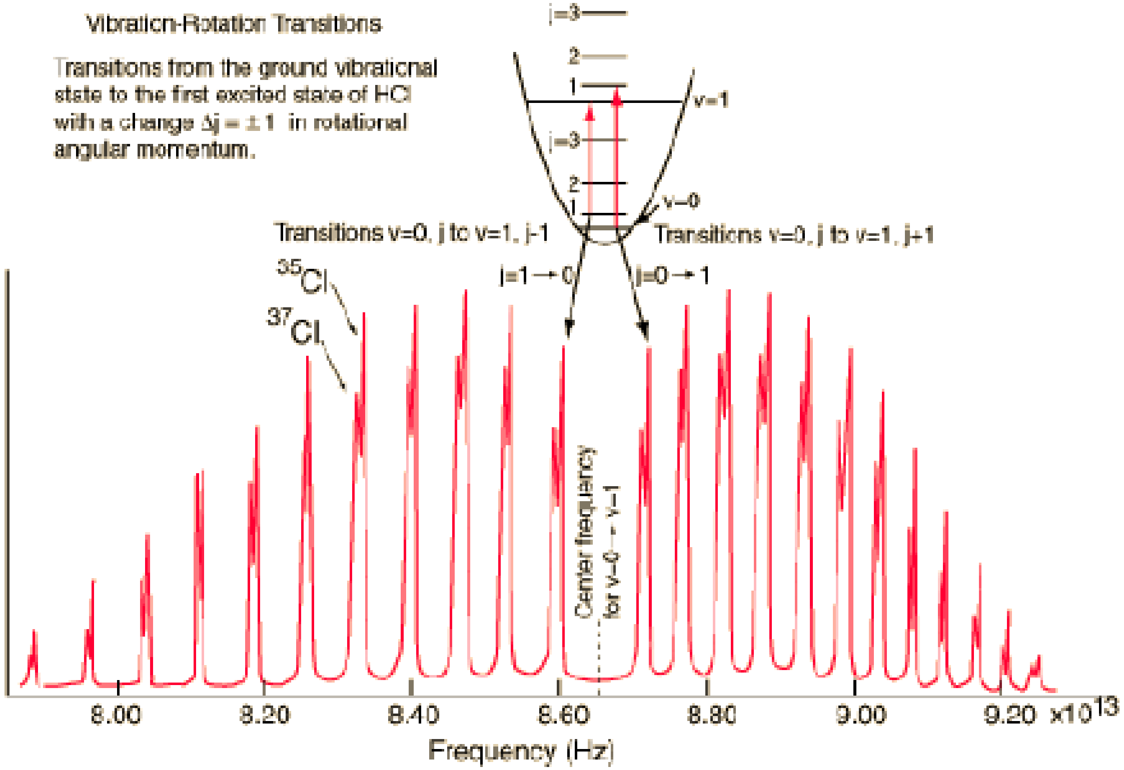
Energy states: $E(\nu) = (\nu + ½)\hbar\omega - (\nu + ½)\chi_e\hbar\omega$

Example: $^{35/37}Cl_2$

with

- $\nu = 0, 1, 2, 3, \ldots$
- $\omega = \sqrt{}(k/\mu)$
- reduced mass $\mu = m_1 * m_2 / m_1 + m_2$
- k is the force constant for the bond
- $\chi_e = \hbar\omega / 4D_e$ = anharmonicity constant
- D_e = depth of the potential energy minimum

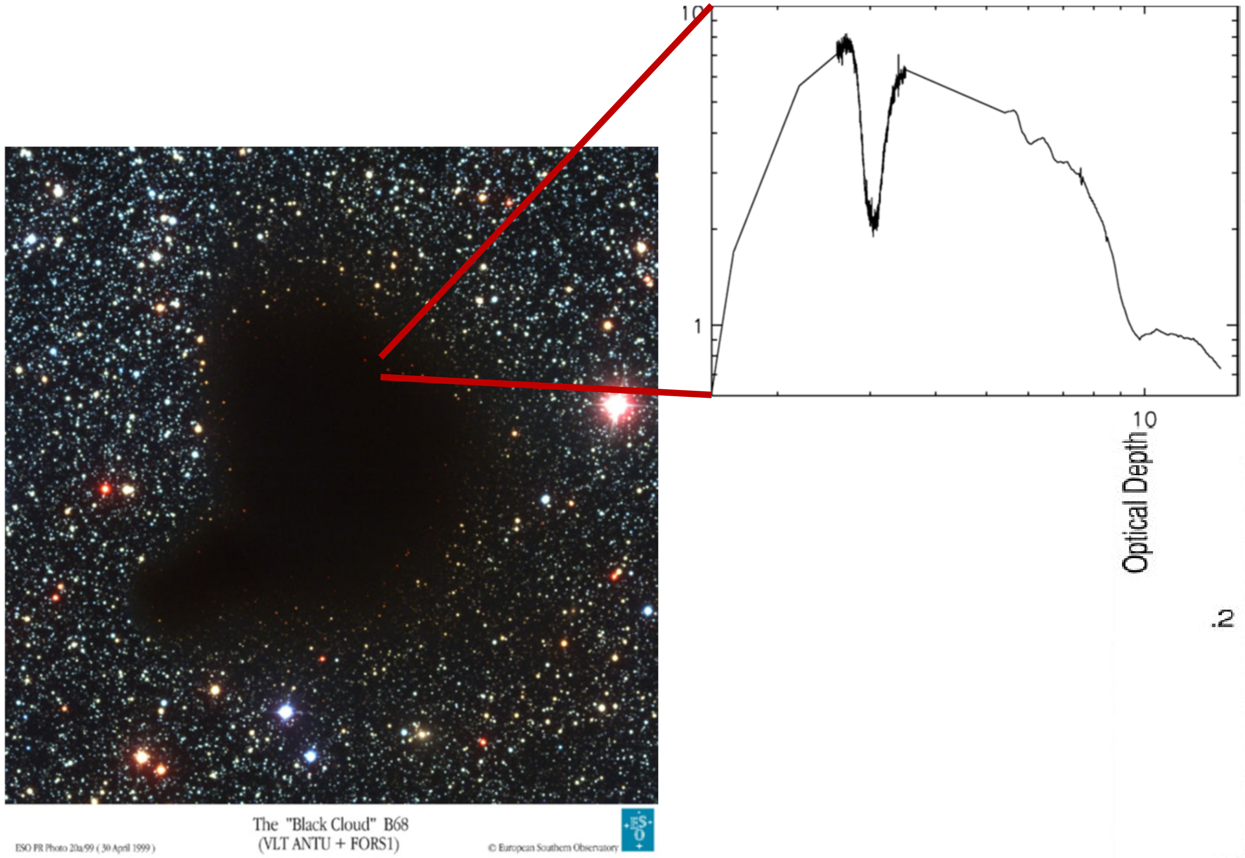
Selection rule: $\Delta\nu = \pm 1$



2. Cosmo and Astrochemistry

Observation Methods - Vibrational Spectra

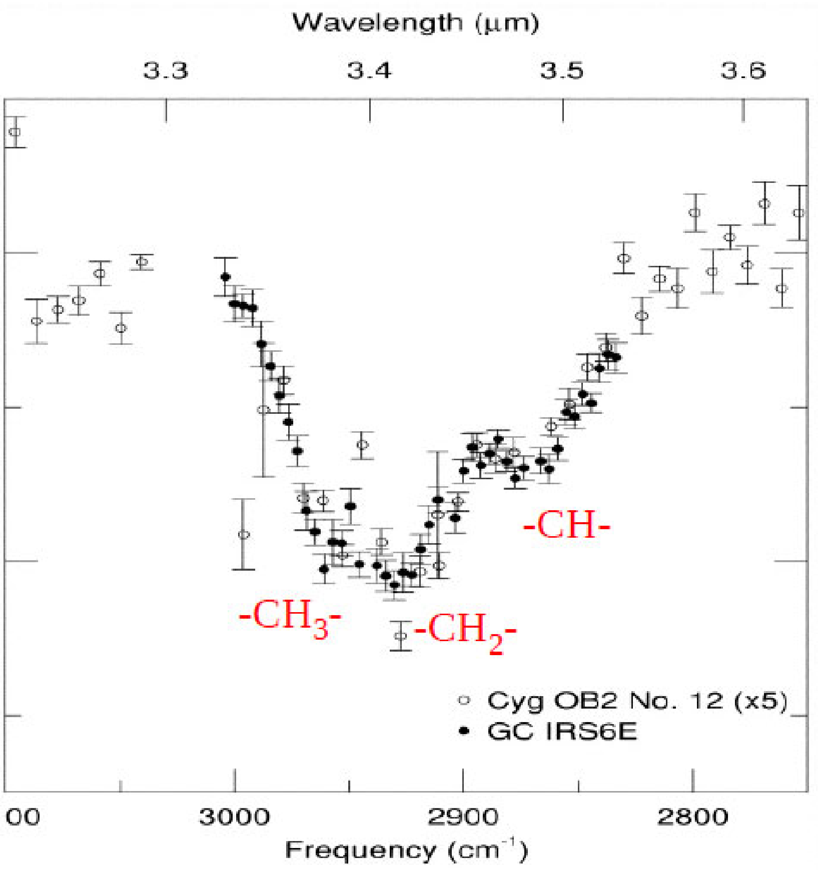
Detection of hydrocarbons by extinction of background star spectrum



The "Black Cloud" B68
(VLT ANTU + FORS1)

ESO PR Photo 20a/99 (30 April 1999)

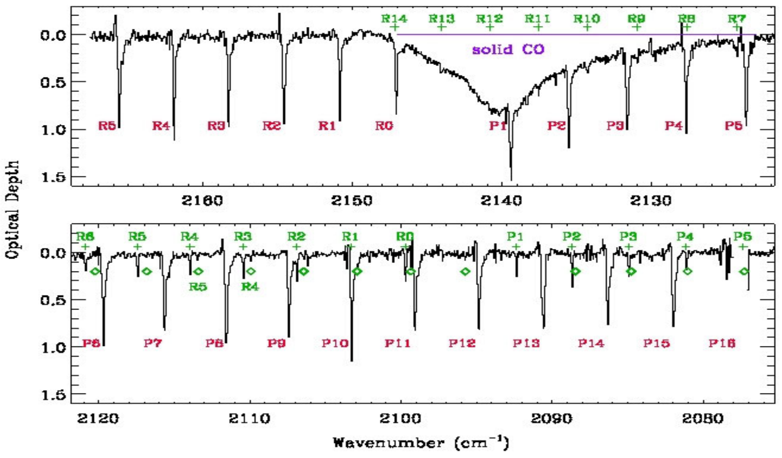
© European Southern Observatory



2. Cosmo and Astrochemistry

Observation Methods - Rotational Spectra

Example: CO (carbon monooxide)



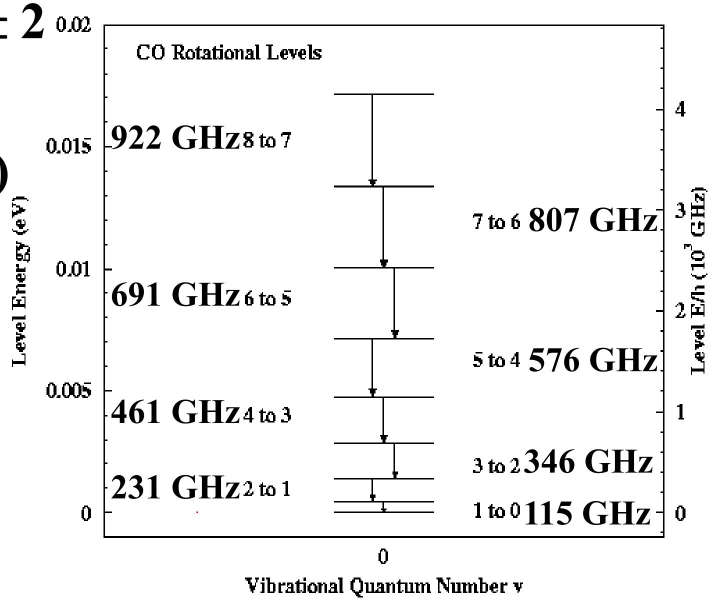
a) Linear rigid rotor (e.g. C≡O, H-C≡N, H-C≡C-C≡N)

Energy states: $E(J) = BJ(J + 1)$

- with $J = 0, 1, 2, \ldots$
- $B = \hbar/2I$, I is the momentum of inertia
- Rotational constant B is large for light molecules
- Selection rules: electric dipole $\Delta J = \pm 1$, quadrupole $\Delta J = \pm 2$

b) Symmetric top with 2 rotational axes (e.g. NH_3, $CH_3C≡CH$)

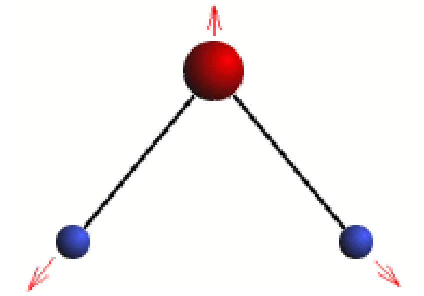
- $E(J,K) = BJ(J + 1) + (A - B)K^2$
- $J = 0, 1, 2, \ldots$; $K = 0, \pm 1, \pm 2, \ldots, \pm J$
- $B = \hbar/2I$, $A = \hbar/2I$
- Selection rules $\Delta J = 1$, $\Delta K = 0$



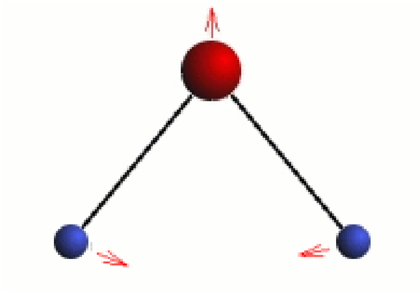
2. Cosmo and Astrochemistry

Observation Methods - Molecular Structures Helps the Detection

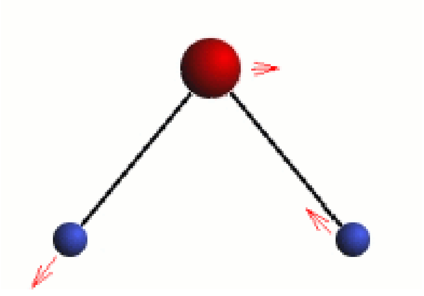
H_2O vibrational modes



symmetric stretch v_1

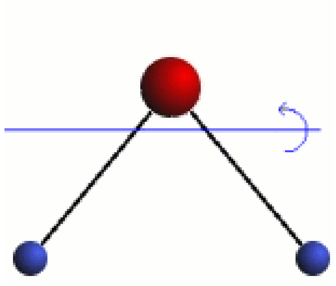


bend v_2

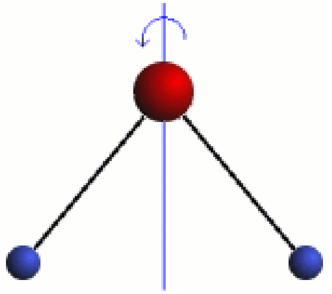


asymmetric stretch v_3

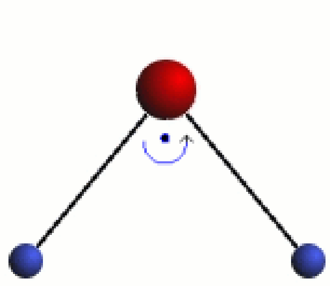
H_2O rotational modes



rotation axis A

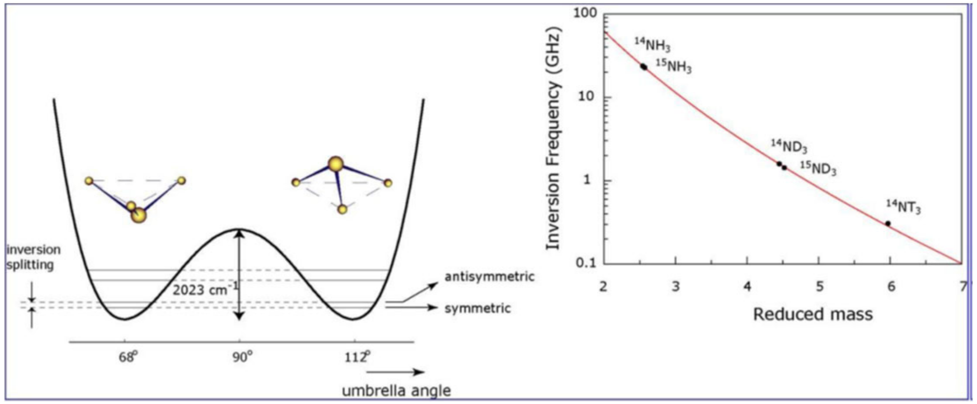


rotation axis B



rotation axis C

The inversion transition of NH_3 also causes a “molecular band” at $\lambda = 1.2$ cm (25 GHz) that helps its detection (NH_3 hail on Jupiter)



2. Cosmo and Astrochemistry

The First Molecules

Conditions in various astrophysical environments

• Interstellar medium	$T_{kin} \sim 10\text{-}100$ K	$n \sim 10^2\text{-}10^8$ cm^{-3}
• Protoplanetary disks	$T_{kin} \sim 10\text{-}1000$ K	$n \sim 10^4\text{-}10^{14}$ cm^{-3}
• Circumstellar shells of evolved stars	$T_{kin} \sim 300\text{-}3000$ K	$n < 10^{14}$ cm^{-3}
• Earth atmosphere at sea level (1 bar)	$T_{kin} \sim 300$ K	$n \sim 3 \cdot 10^{19}$ cm^{-3}
• For comparison: UHV apparatus ($1 \cdot 10^{-12}$ bar)		$n \sim 3 \cdot 10^{7}$ cm^{-3}

Typical timescales

• Collisional time	~1 month at 10 K, 10^4 cm^{-3} → kinetic gas theory (mean free path l)
• Chemical time	>10^4 - 10^5 years
• Lifetime of a cloud	~10^6 - 10^7 years
• Star formation period	~10^5 - 10^6 years

$$\boxed{l = \frac{\bar{u}}{\sqrt{2} * \sigma^2 * \bar{u} * \pi * \frac{N}{V}} = \frac{1}{\sqrt{2} * \sigma^2 * \pi * \frac{N}{V}} = \frac{kT}{\sqrt{2} * \sigma^2 * p * \pi}}$$

Chemical reactions are slow, but yet many molecules have been evolved after 10^{10} years

2. Cosmo and Astrochemistry

The First Molecules

Bonding energies of some molecules in space, first detection year in brackets

Formula	Chemical Name	Bond energy [eV]	Absorption at
OH (1963)	Hydroxyl	4.41	18 cm (1.67 GHz)
H_2^+	Dihydrogencation	2.77	
H_2 (#1) ↔ 2 H·	Dihydrogen	4.48	21.1 cm (1.42 GHz)
CH_4	Methane	4.49	124 nm
NH_3 (1968)	Ammonia	4.58	1.26 cm (23.7 GHz)
H_2O (1969)	Water	5.11	1.3 cm (22.0 GHz)
O_2	Dioxygen	5.11	
CO_2	Carbon dioxide	5.50	
CN	Cyanogen	7.77	
N_2	Dinitrogen	9.71	91.6 nm
C_2H_2	Acetylene	10.07	
CO (1970, #2)	Carbon monoxide	11.16	0.26 cm (115 GHz)

2. Cosmo and Astrochemistry

The First Molecules

Chemistry in the early universe was complicated by a large number of possible quantum states owing to collisions and interaction with the CBR

Lit.: Coppola et al. 2011, ApJS 193, 7

Formation started at z ~ 2000 (t = 1000 y), likely resulted in helium compounds, for example by radiative association

- $He^+ + He \rightarrow He_2^+ + h\nu$
- $H^+ + He \rightarrow HeH^+ + h\nu$ **(bond order according to MO theory = 0.5)**

Once H_2^+ ions and H_2 molecules are available, also the following reactions can produce HeH^+

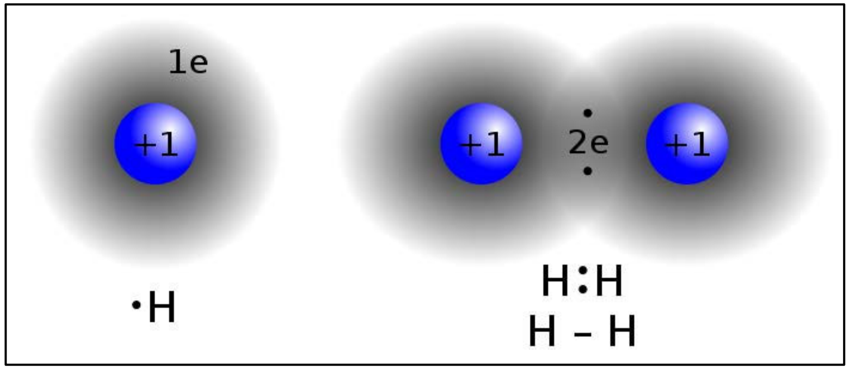
- $H_2^+ + He \rightarrow H + HeH^+$
- $H_2 + He^+ \rightarrow H + HeH^+$

Dihydrogen formation?

$H + H \leftrightarrow H_2^* \rightarrow H_2 + h\nu$ **inefficient, since dissociation is faster than relaxation!**

2. Cosmo and Astrochemistry

The First Molecules



Dihydrogen formation by

a) radiative association and charge transfer

$H + H^+ \rightarrow H_2^+ + h\nu$

$H_2^+ + H \rightarrow H_2 + H^+$ **fast reaction, i.e. the abundance of H_2^+ remains low**

b) catalytic electron attachment

$H + e^- \rightarrow H^- + h\nu$

$H^- + H \rightarrow H_2 + e^-$

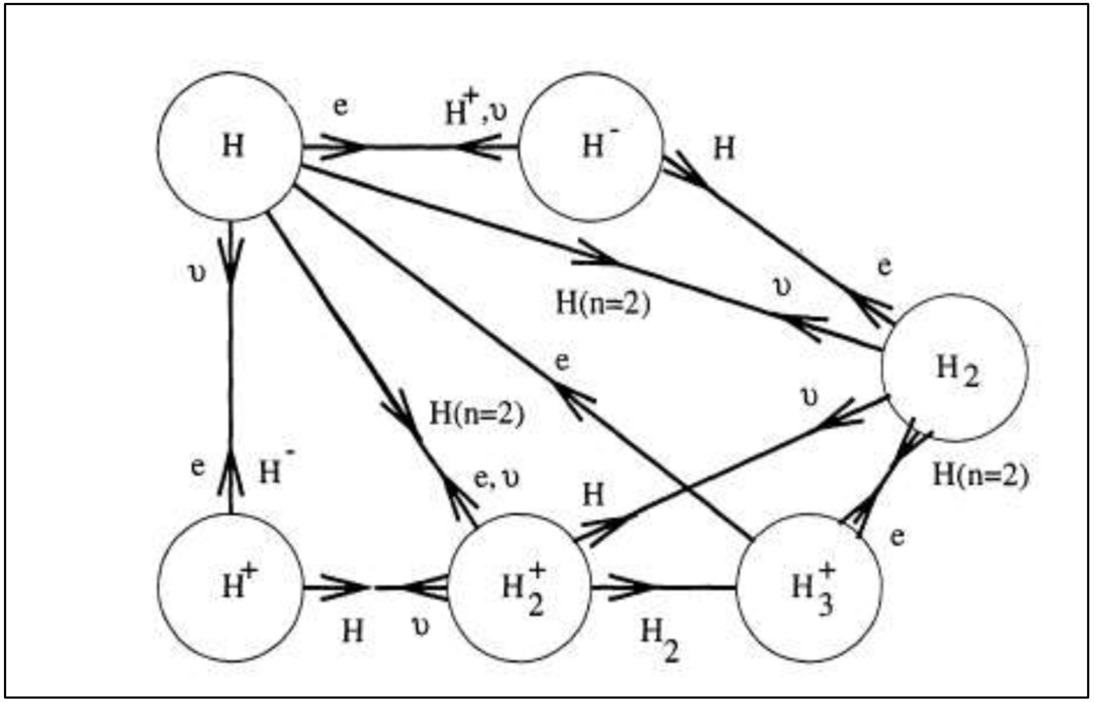
Formed H_2 is mainly dissociated in collisions

$H_2 + H \rightarrow 3\ H$

H_3^+ formation

$H_2 + H^+ \rightarrow H_3^+ + h\nu$

$H_2 + H_2^+ \rightarrow H_3^+ + H$ **(http://h3plus.uiuc.edu)**



2. Cosmo and Astrochemistry

The First Molecules: Deuterium and Lithium chemistry

Deuterium compounds by

a) radiative association and charge transfer

$D^+ + H \rightarrow HD^+ + h\nu$

$HD^+ + H \rightarrow HD + H^+$

b) charge transfer and deuteration of H_2

$D^+ + H \rightarrow D^+ + H$

$D^+ + H_2 \rightarrow HD + H^+$

Lithium compounds by

a) radiative association

$Li^+ + H \rightarrow LiH^+ + h\nu$

b) radiative association and charge transfer

$Li + H^+ \rightarrow LiH^+ + h\nu$

$LiH^+ + H \rightarrow LiH + H^+$

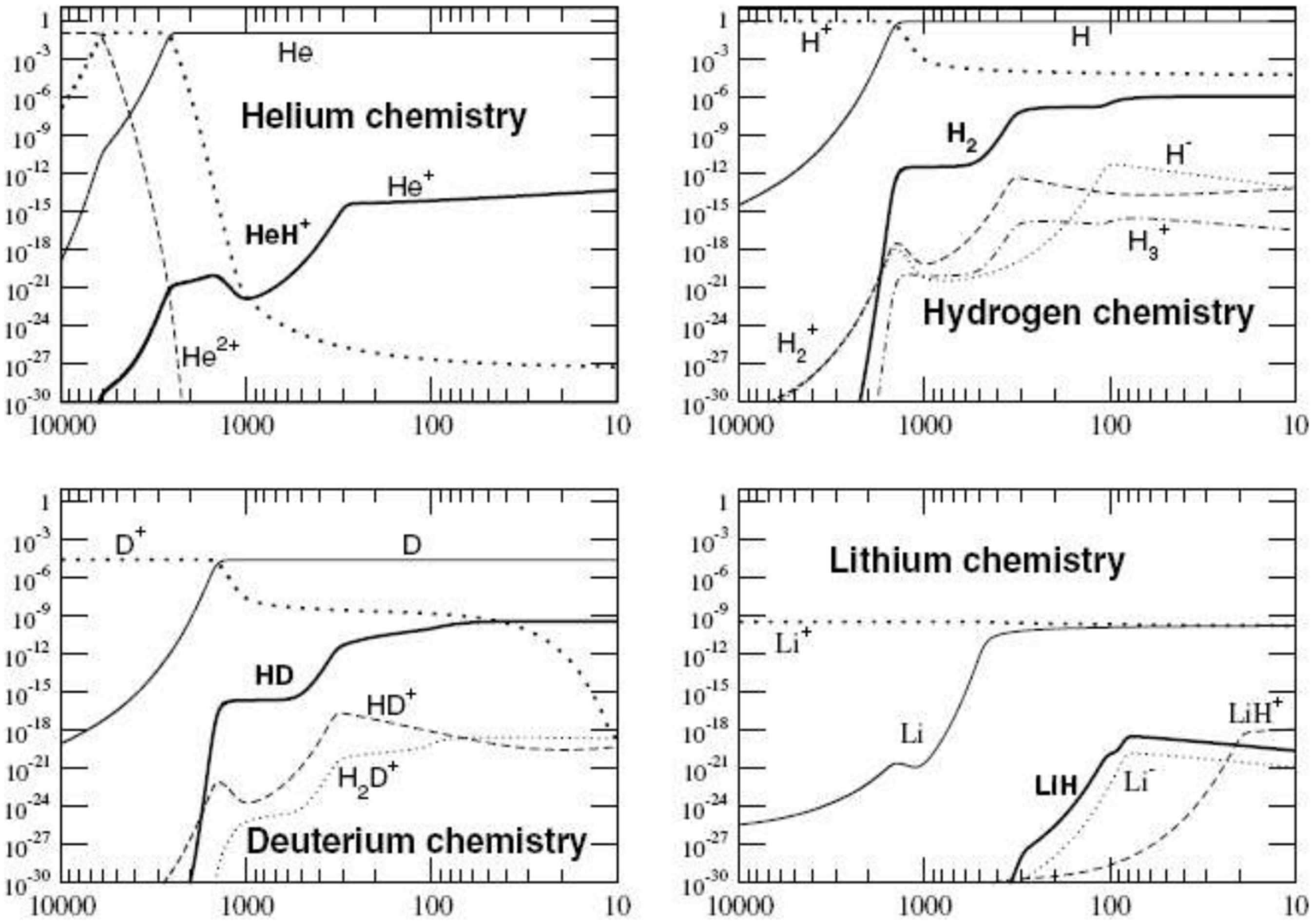
Both processes are faster than radiative association between Li and H

2. Cosmo and Astrochemistry

The First Molecules: Summary

Red-shift z	cosmic age
10	480 My
100	16 My
1000	0.47 My
10000	8389 y
100000	96.5 y

https://www.vttoth.com/CMS/cosmology-calculator



Abundances today (z = 0)

H = 1

He = 0.1

Rest << 0.1

Fractional abundances at z = 10 (480 My) after Big Bang according to Puy & Pfenniger, 2006

HeH^+	H_2	HD	LiH
$4.6 \cdot 10^{-14}$	$1.13 \cdot 10^{-6}$	$3.67 \cdot 10^{-10}$	$2.53 \cdot 10^{-20}$

2. Cosmo and Astrochemistry

Formation of "Molecules of Life" in the Milky Way

Metallicity [Fe/H] =

$$\lg(N_{Fe}/N_H) - \lg(N_{Fe}/N_H)_\odot$$

$$(N_{Fe}/N_H)_\odot = 1/31000 \sim 0.16\ \%$$

Requirements

1. **Fusion of metals in 1st generation stars**
2. **Development of stars with high metallicity [Fe/H]**
3. **Feedback of fused elements to interstellar medium (ISM) by SN or massive star winds**

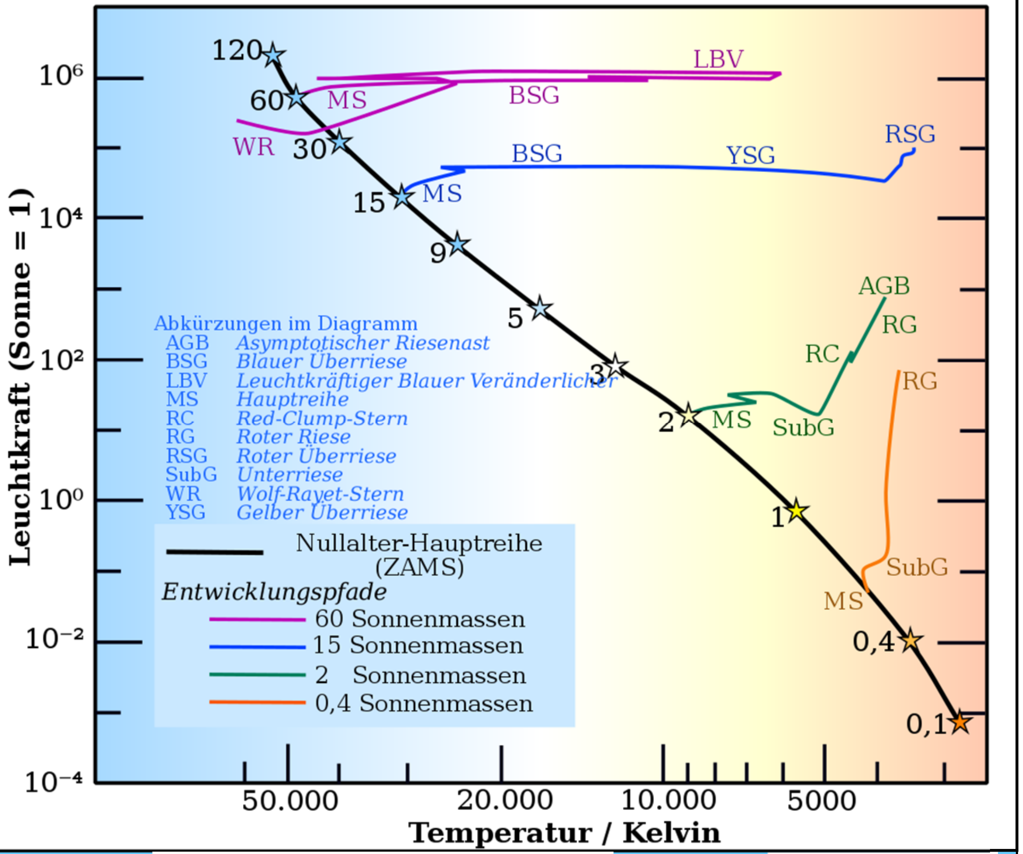
Asymptotic Giant Branch (AGB) stars show tremendous mass loss into ISM by star winds

Supernova (SN) types by the emission spectrum

Ia **Thermal runaway of a white dwarf due to mass accretion (→ standard candles)**

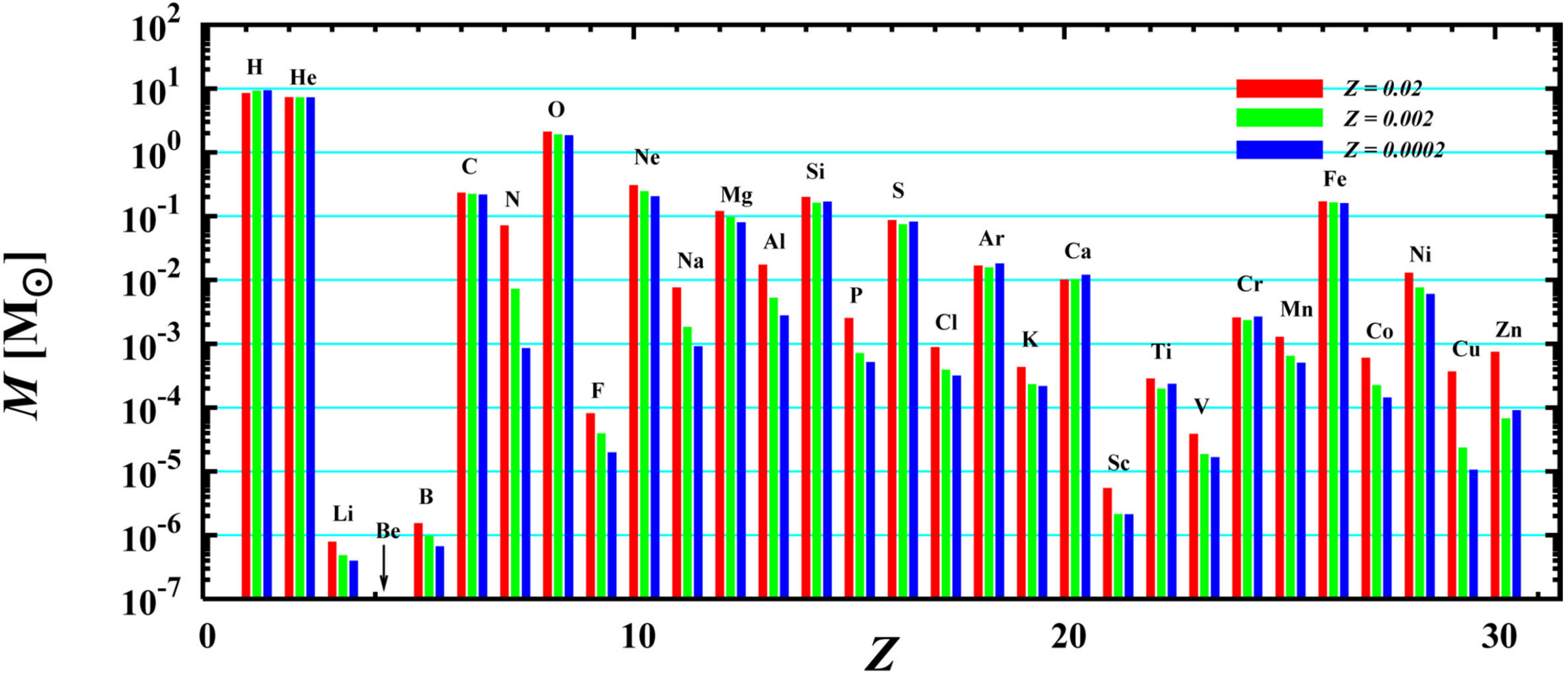
Ib **Stellar core collapse of massive stars**

II **Stellar core collapse of very massive stars > 40-50 sun masses**



2. Cosmo and Astrochemistry

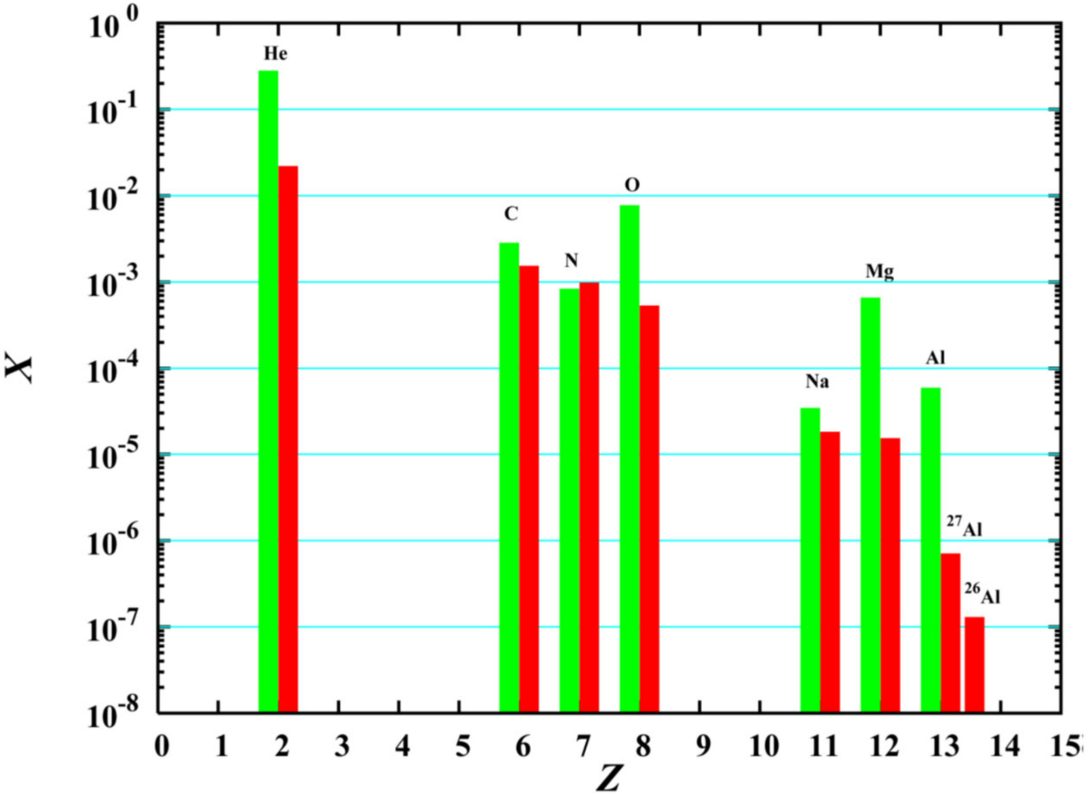
Feedback of elements to ISM up to Zn due to Supernovae Type II

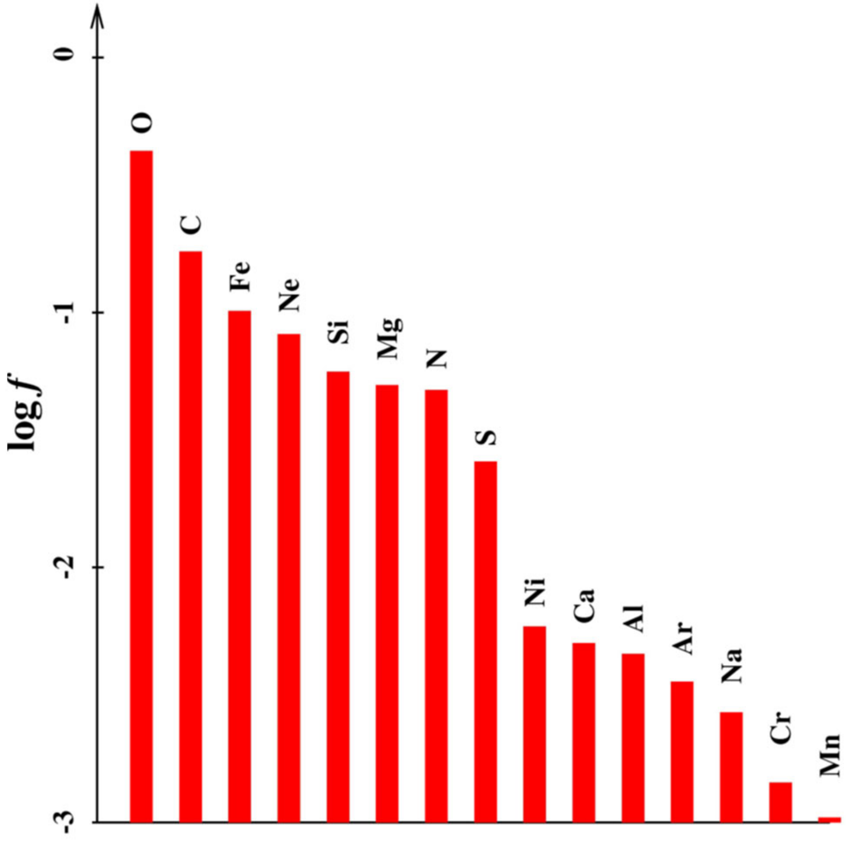


2. Cosmo and Astrochemistry

Feedback of elements to ISM up to Zn due to Supernovae Type II

Most of the elements of life formed (except Se, Mo, W) → Bioinorganic chemistry





2. Cosmo and Astrochemistry

Formation of Water

C/1995 O1
(Hale-Bopp), 1997

Requirements

1. Fusion of Oxygen in 1st generation stars
2. Feedback of fused elements to interstellar medium (ISM)

Reaction sequence initiated by Cosmic Ray Photoionisation (CRP)

- $H_2 + CRP \rightarrow H_2^+ + e^-$
- $H_2^+ + H_2 \rightarrow H_3^+ + H\bullet$
- $H_3^+ + O \rightarrow OH^+ + H_2$
- $OH^+ + H_2 \rightarrow H_2O^+ + H\bullet$
- $H_2O^+ + H_2 \rightarrow H_3O^+ + H\bullet$

Gas halo of solar comet Hale-Bopp

- Simple neutral molecules: H_2O, HDO, CO, CO_2, H_2S, SO, SO_2, OCS, CS, NaCl, NH_3
- Radicals: OH, CN, NH_2, NH, C_3, C_2
- Hydrocarbons, nitriles, amides: HCN, DCN, CH_3CN, HNC, HC_3N, HNCO, C_2H_2, C_2H_6 CH_4, NH_2CHO
- Molecular cations: H_2O^+, H_3O^+, HCO^+, CO^+

Water formation step

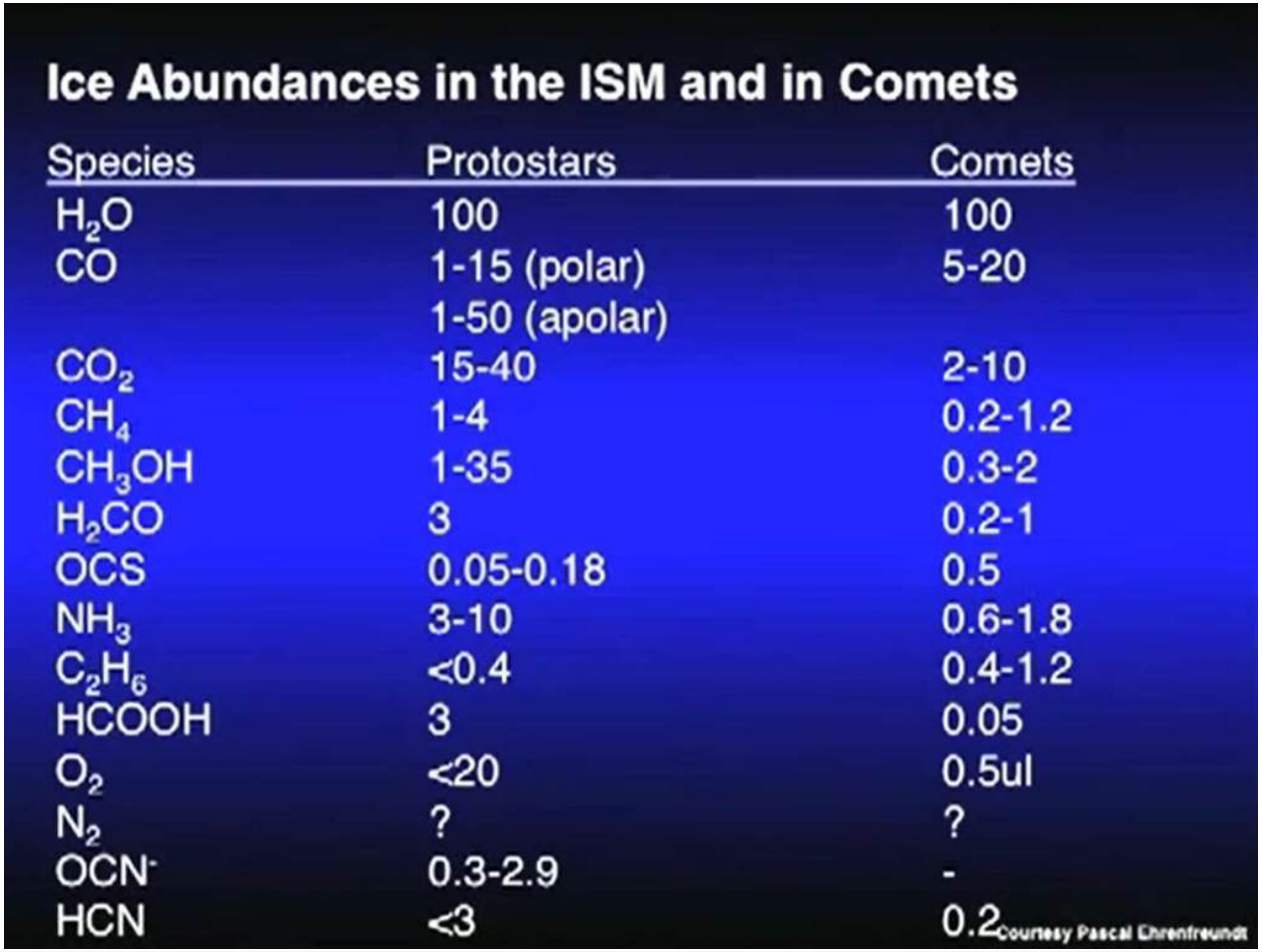
- $H_3O^+ + e^- \rightarrow H_2O + H$ or $OH + 2\,H$ or $OH + H_2$

Water accumulation onto rocky planets, e.g. by comet impacts

2. Cosmo and Astrochemistry

Formation of Water

Ice is quite abundant and a very good solvent for (in)organic molecules and thus chemistry



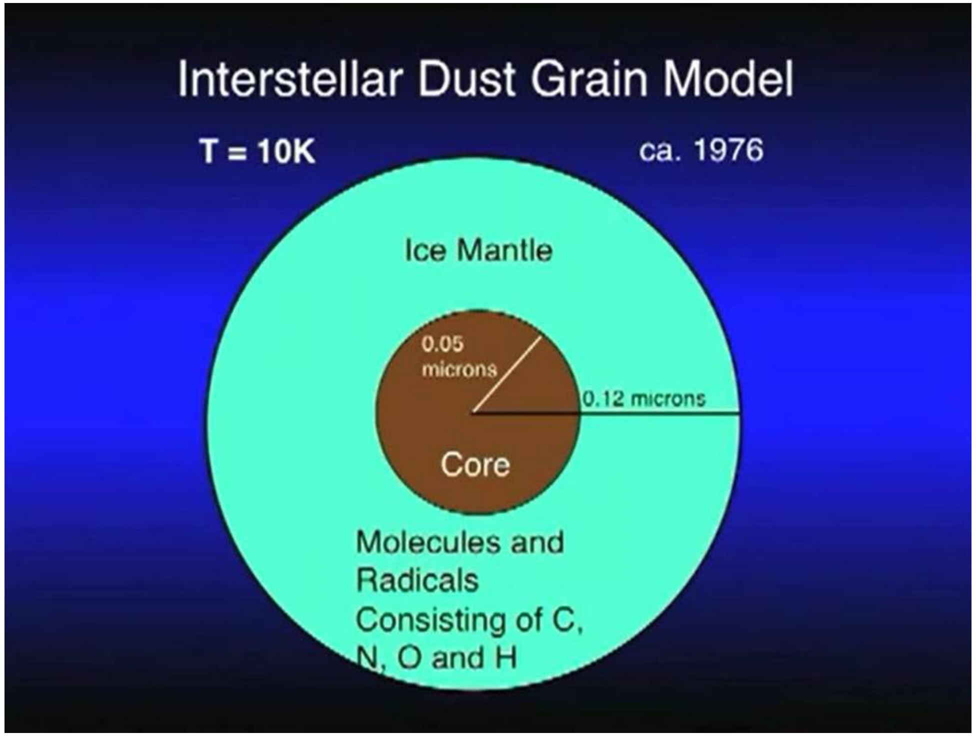
Ice Abundances in the ISM and in Comets

Species	Protostars	Comets
H_2O	100	100
CO	1-15 (polar) 1-50 (apolar)	5-20
CO_2	15-40	2-10
CH_4	1-4	0.2-1.2
CH_3OH	1-35	0.3-2
H_2CO	3	0.2-1
OCS	0.05-0.18	0.5
NH_3	3-10	0.6-1.8
C_2H_6	<0.4	0.4-1.2
HCOOH	3	0.05
O_2	<20	0.5ul
N_2	?	?
OCN^-	0.3-2.9	-
HCN	<3	0.2

Courtesy Pascal Ehrenfreundt

2. Cosmo and Astrochemistry

Formation of Complex Molecules



Starting from ionized carbon:

$C^+ + H_2 \rightarrow CH_2^+$

$CH_2^+ + H_2 \rightarrow CH_3^+ + H\bullet$

$CH_3^+ + H_2 \rightarrow CH_5^+ + H_2$

$CH_3^+ + O \rightarrow HCO^+ + H_2$

$CH_5^+ + e^- \rightarrow CH_3\bullet + H_2$

$CH_3\bullet + O \rightarrow H_2CO$ (methanal) $+ H\bullet$

$CH_3OH_2^+ + e^- \rightarrow CH_3OH$ (methanol) $+ H\bullet$

Lit.: Luca et al. 2002, Geppert et al. 2006

2. Cosmo and Astrochemistry

Formation of Complex Molecules

Coupling carbon with oxygen chemistry

CO is the second most common molecule in the ISM → high stability (1072 kJ/mol, #1!)

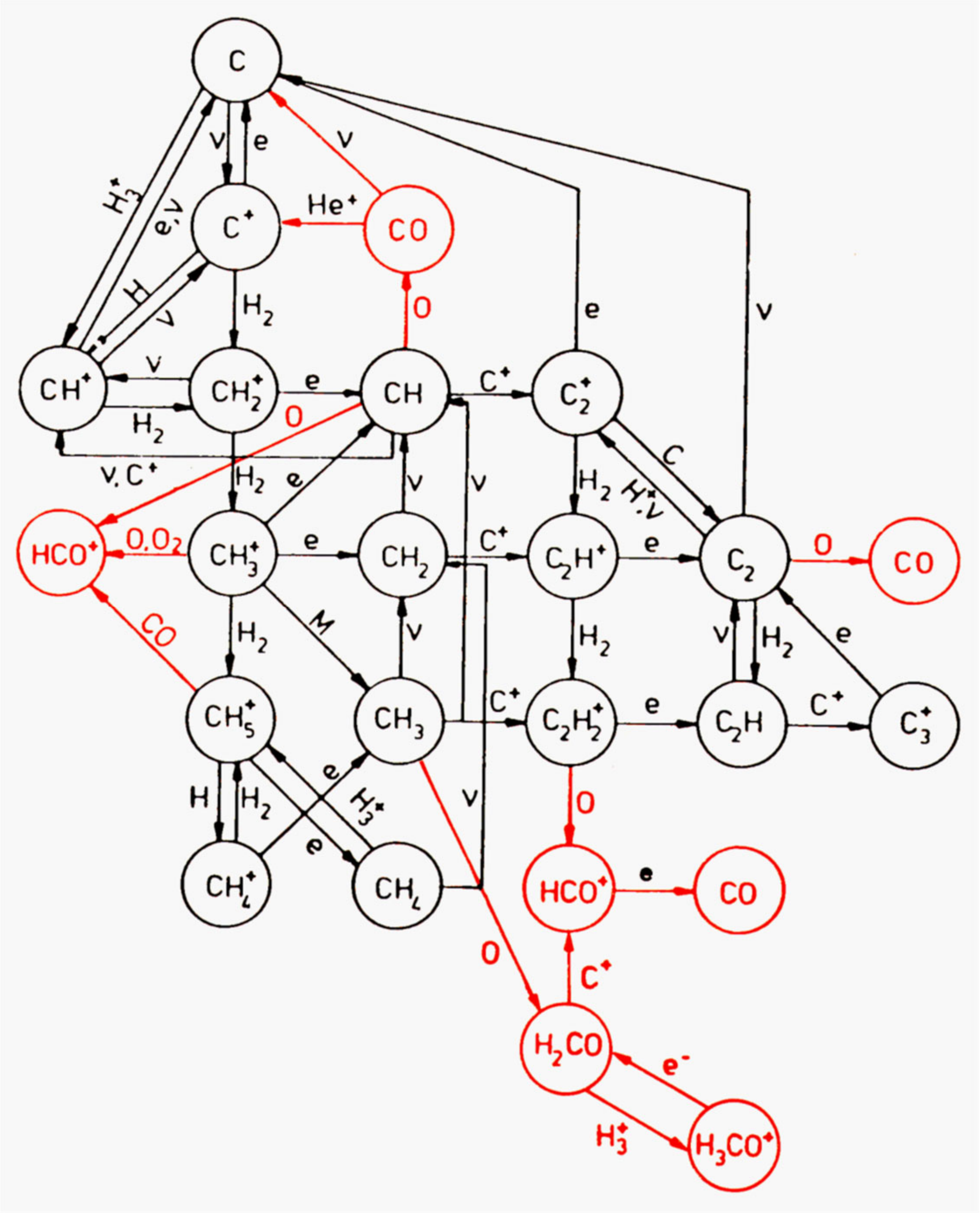
Most common ISM species:
H_2 + CO → synthesis gas → many products

e.g. 2 H_2 + CO → CH_3OH (methanol)

Need for heterogeneous catalysts

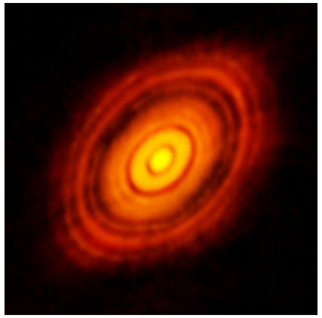
→ interstellar dust particles

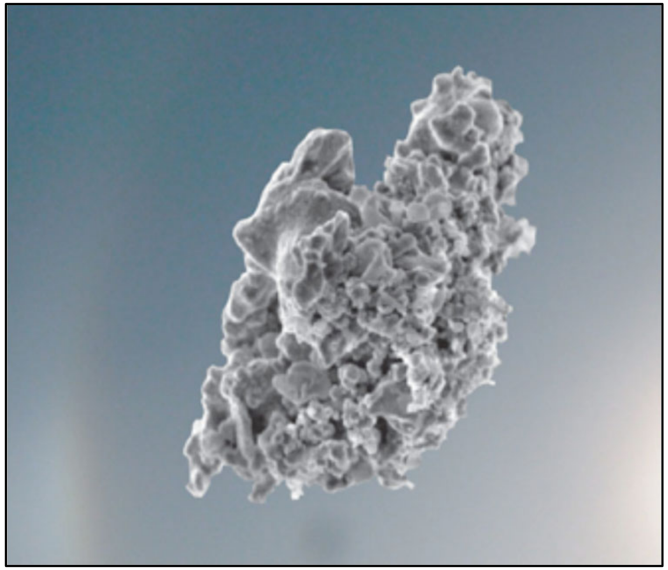
Coupling to Nitrogen via $NH_3/N_2/N_2H^+$ results in CN/HCN formation



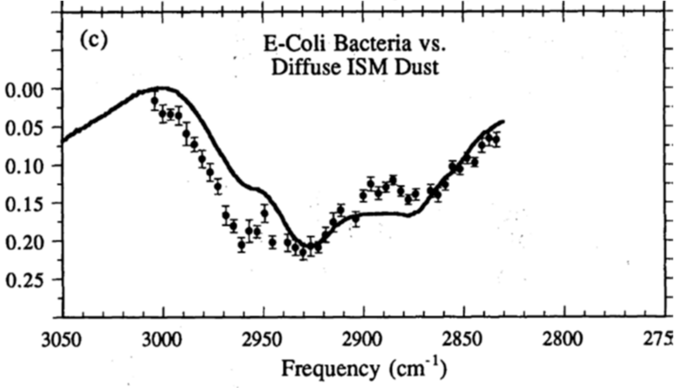
2. Cosmo and Astrochemistry

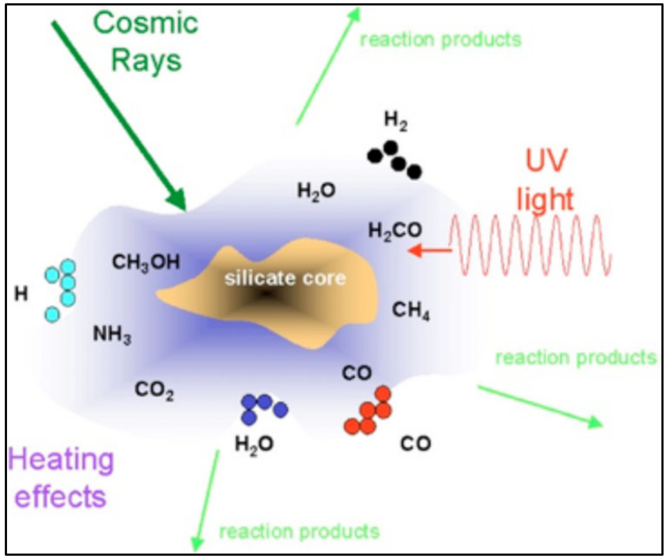
Interstellar Dust





- Formed in AGB stars & grow in the ISM and circumstellar medium (CSM)
- Typical size ~ 0.01-1 µm
- Silicate core, with refractory materials (most of Si, Mg, Fe)
- Carbonaceous material (~ 30% of O, ~ 60% of C), PAHs
- Abundance ~ 10^{-12} with respect to H_2
- $T_{kin} < 150$ K: condensation of gas → icy mantles around the dust particles
- Dust particles serve as heterogenous catalysts for several organic reactions induced by radiation at low temperature



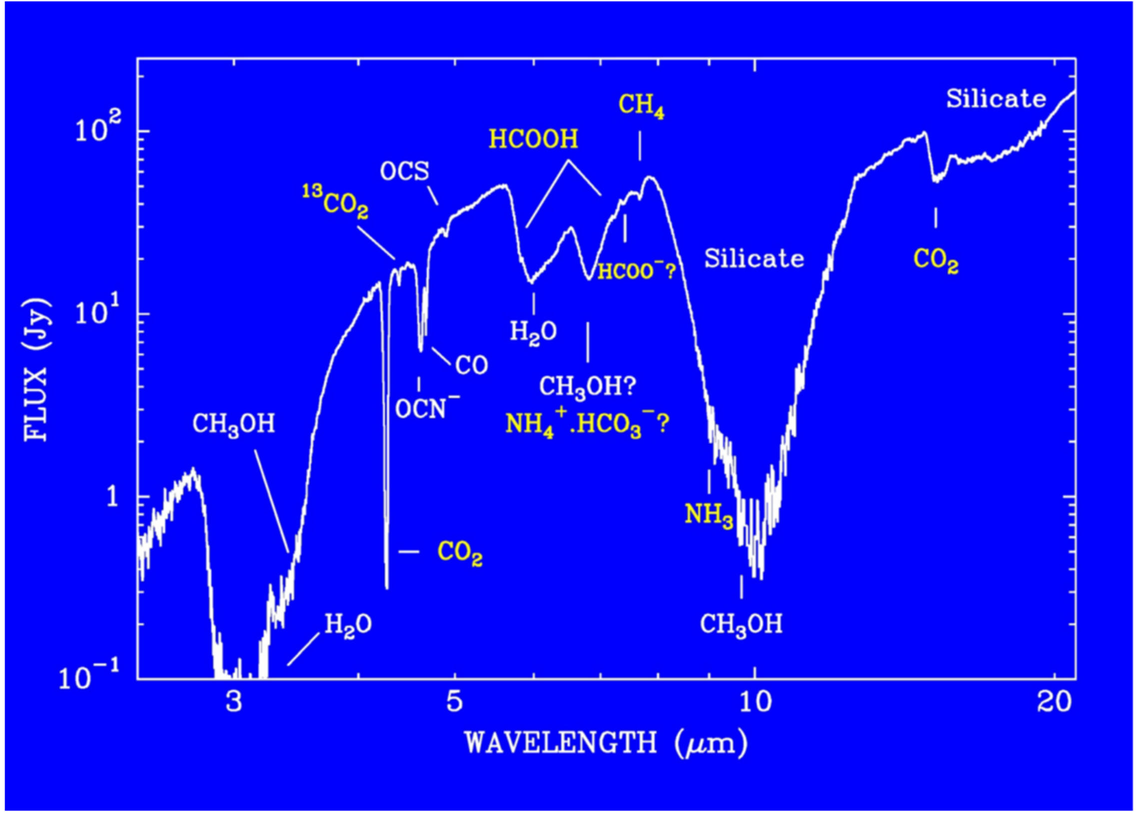


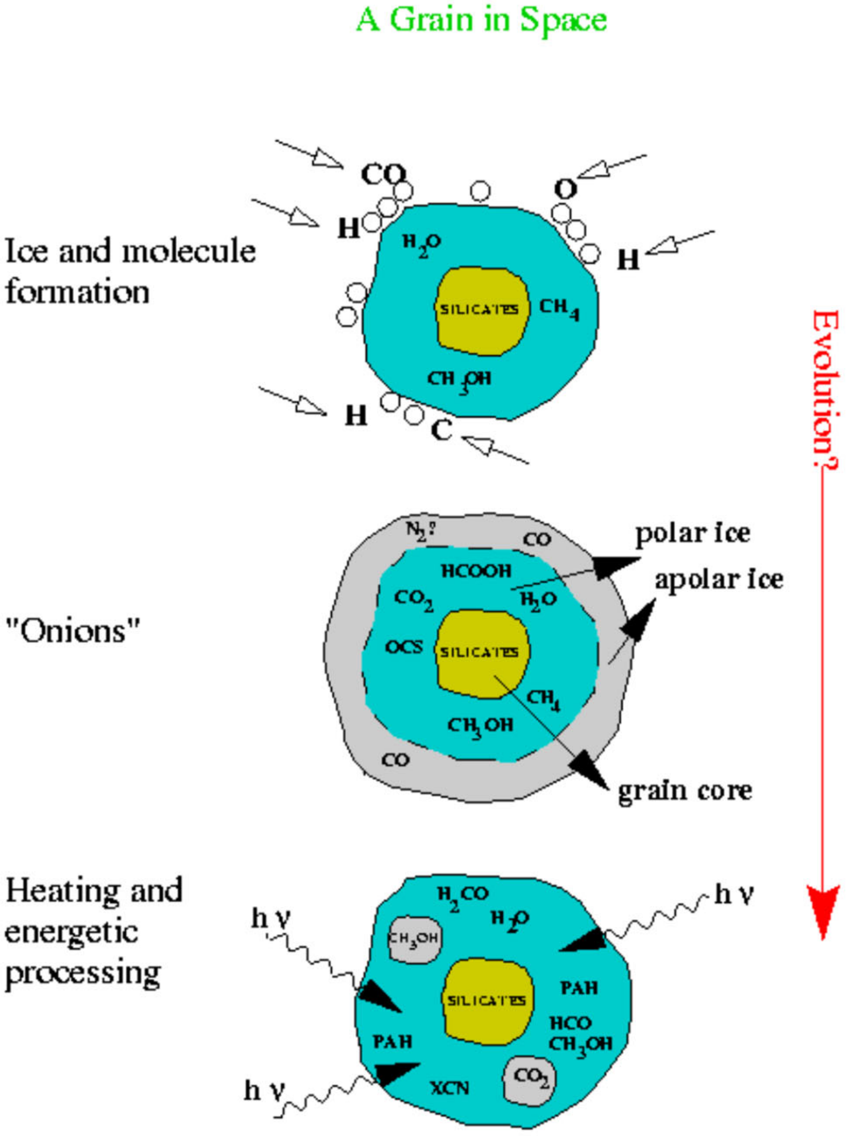
2. Cosmo and Astrochemistry

Interstellar Dust: Location of Chemical Evolution

Formation of complex organic molecules, amino acids, and even peptides

IR spectrum of interstellar dust

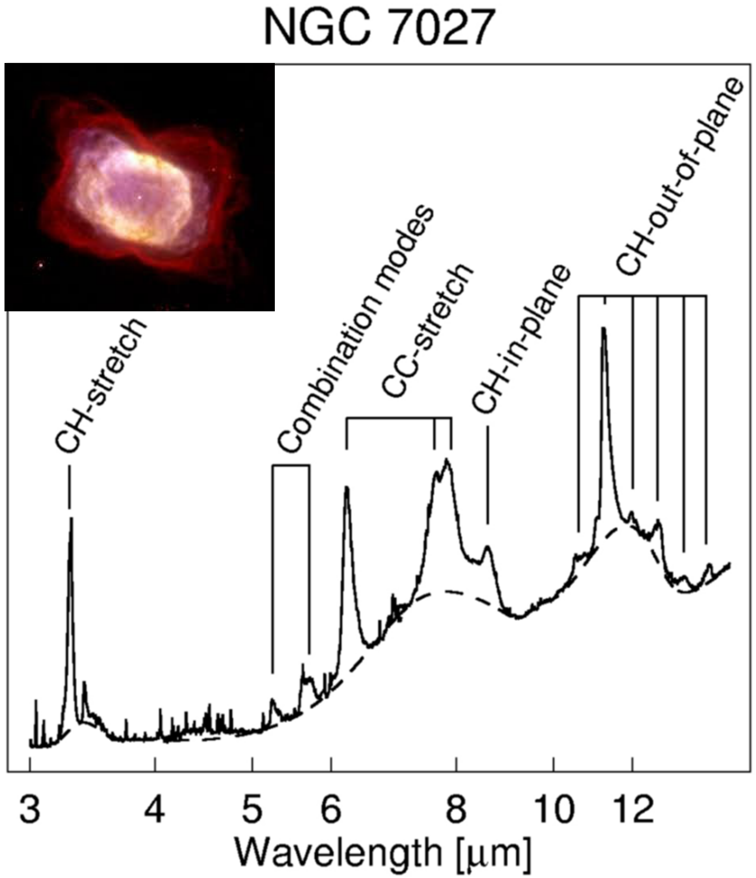


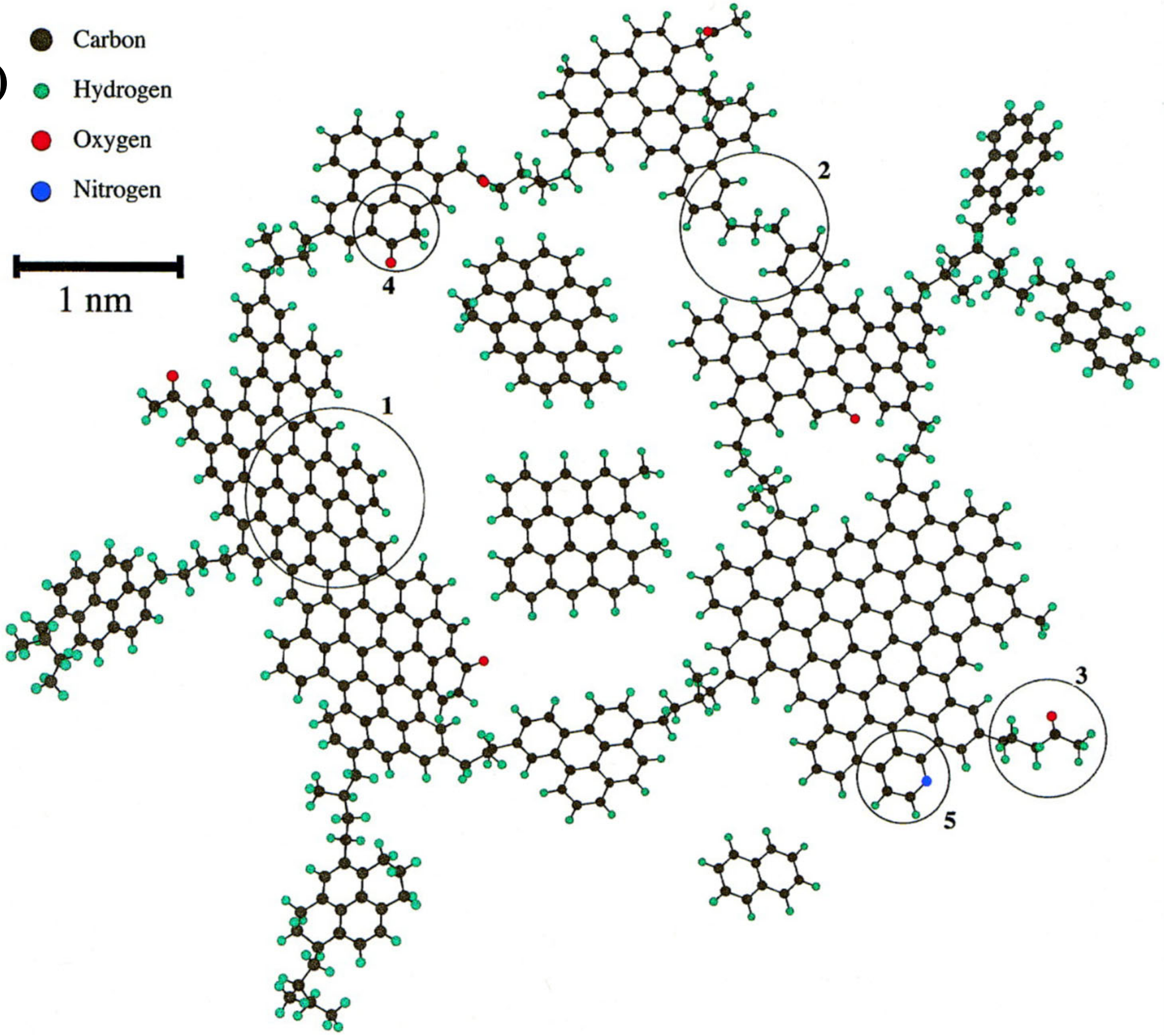


2. Cosmo and Astrochemistry

Formation of Complex Molecules

PolyAromatic Hydrocarbons (PAHs) observed throughout the universe, e.g. in NGC7027, a planetary nebula

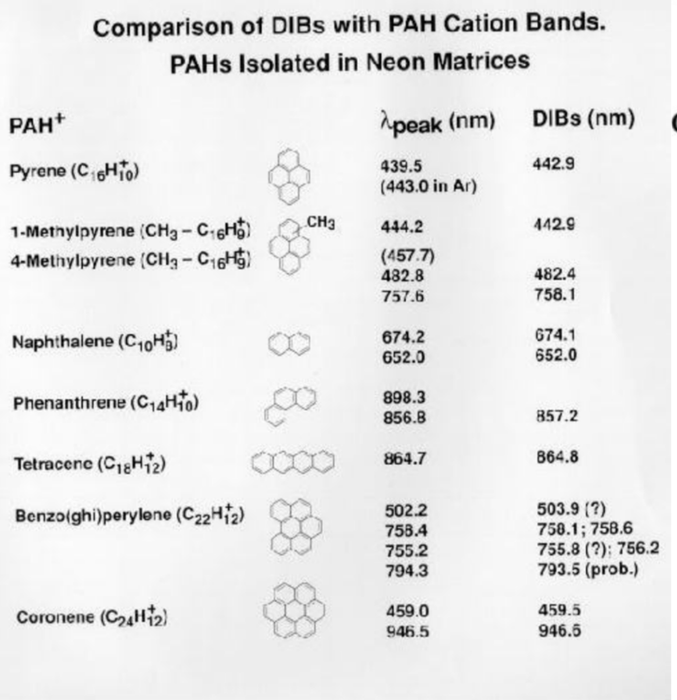




2. Cosmo and Astrochemistry

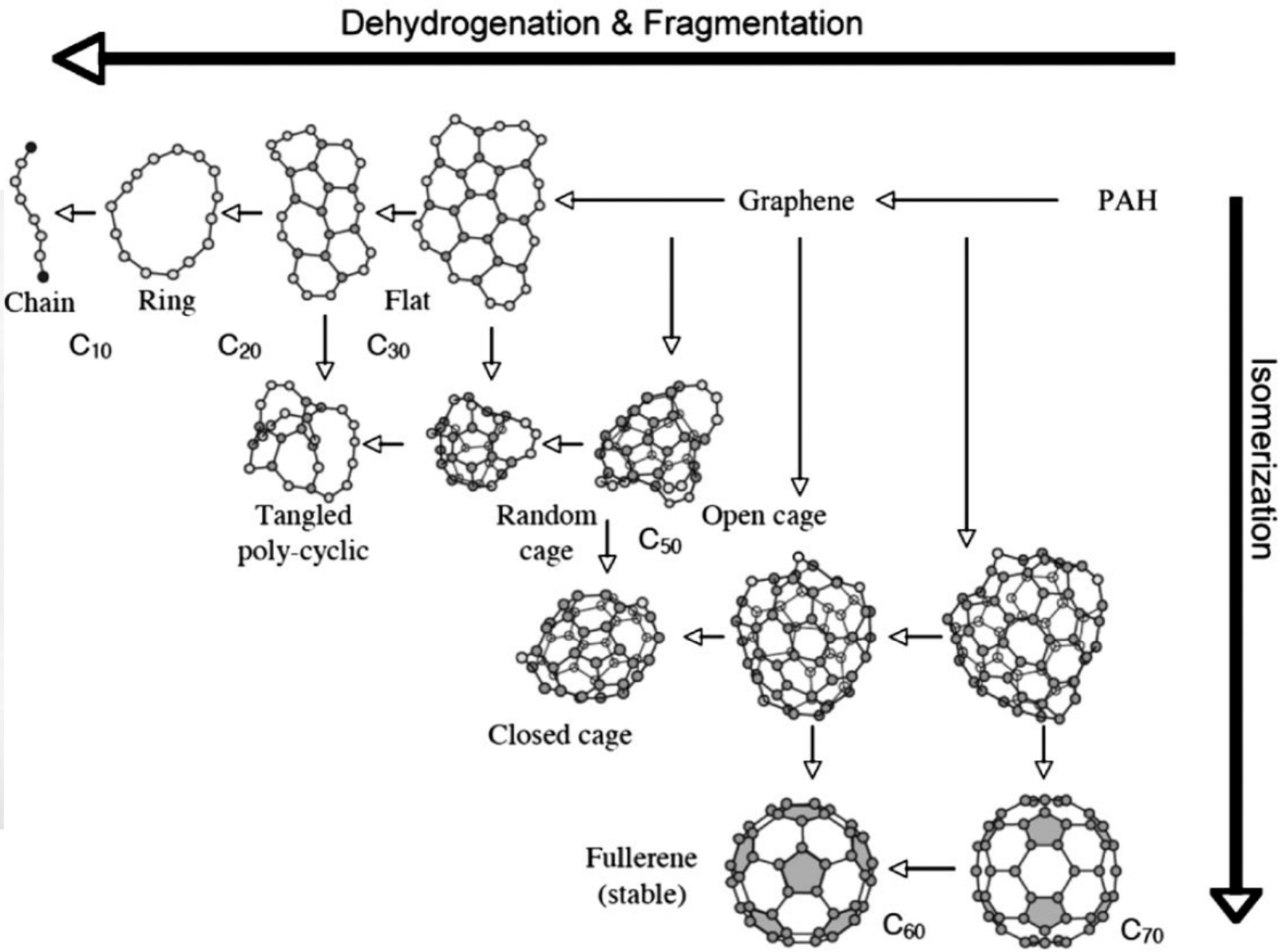
Formation of Complex Molecules

Top-down chemistry by fragmentation of PAHs



Comparison of DIBs with PAH Cation Bands.
PAHs Isolated in Neon Matrices

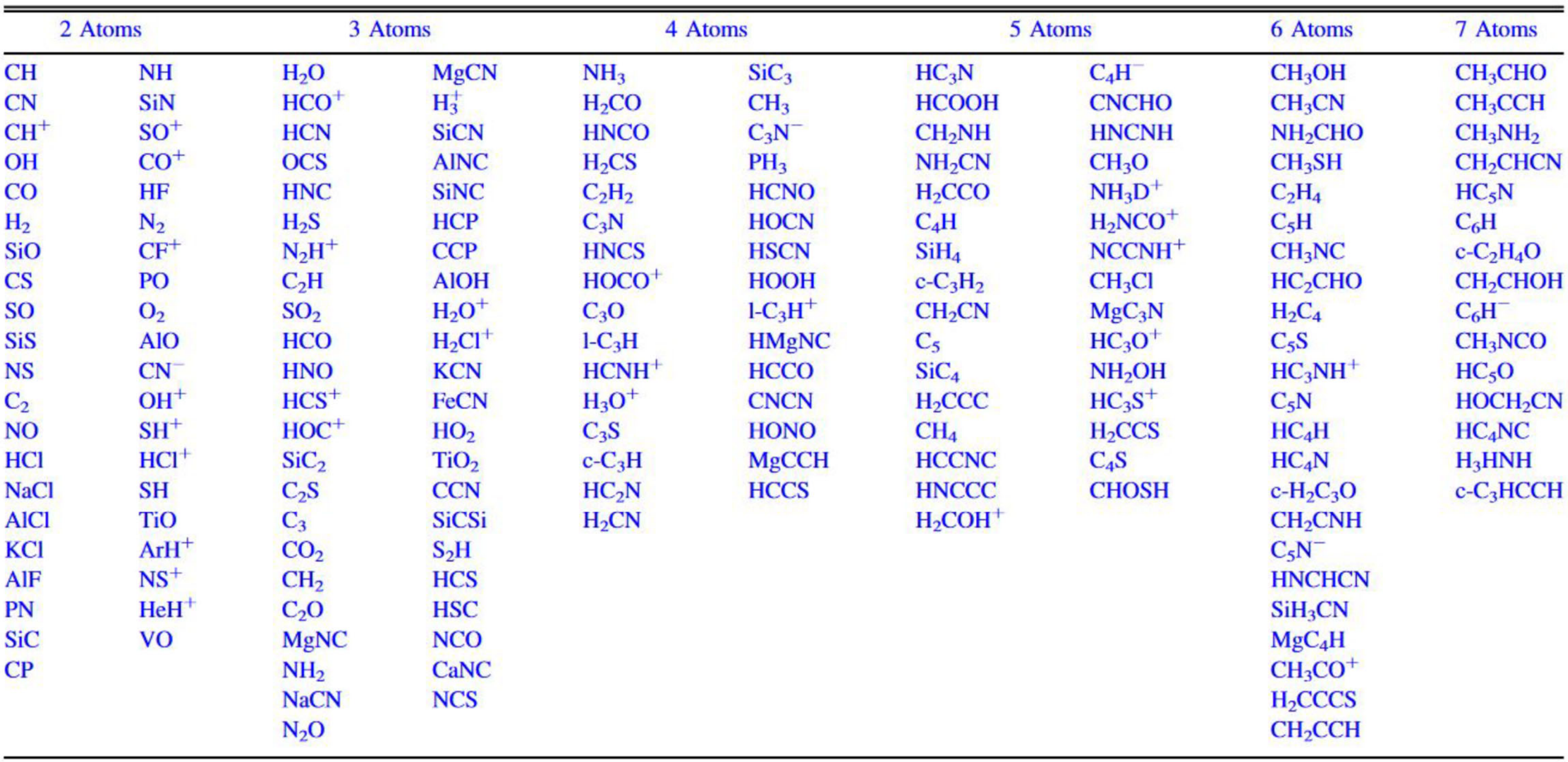
PAH^+	λ_{peak} (nm)	DIBs (nm)
Pyrene ($C_{16}H_{10}^+$)	439.5 (443.0 in Ar)	442.9
1-Methylpyrene ($CH_3 - C_{16}H_9^+$)	444.2	442.9
4-Methylpyrene ($CH_3 - C_{16}H_9^+$)	(457.7) 482.8 757.6	 482.4 758.1
Naphthalene ($C_{10}H_8^+$)	674.2 652.0	674.1 652.0
Phenanthrene ($C_{14}H_{10}^+$)	898.3 856.8	 857.2
Tetracene ($C_{18}H_{12}^+$)	864.7	864.8
Benzo(ghi)perylene ($C_{22}H_{12}^+$)	502.2 758.4 755.2 794.3	503.9 (?) 758.1; 758.6 755.8 (?); 756.2 793.5 (prob.)
Coronene ($C_{24}H_{12}^+$)	459.0 946.5	459.5 946.5



Formation of the Bucky balls C_{60} & C_{70}, graphenes, as well as rings and chains of carbon

2. Cosmo and Astrochemistry

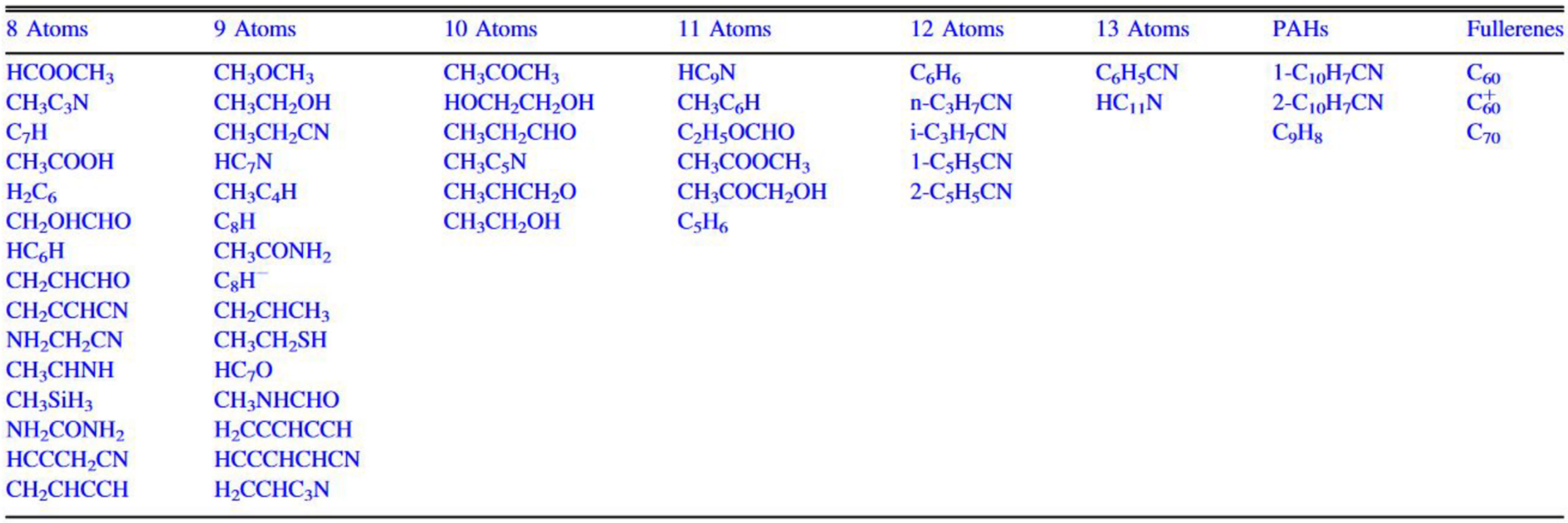
Molecules Detected until Today > 200 with 2 or more Atoms



2 Atoms		3 Atoms		4 Atoms		5 Atoms		6 Atoms	7 Atoms
CH	NH	H_2O	$MgCN$	NH_3	SiC_3	HC_3N	C_4H^-	CH_3OH	CH_3CHO
CN	SiN	HCO^+	H_3^+	H_2CO	CH_3	$HCOOH$	$CNCHO$	CH_3CN	CH_3CCH
CH^+	SO^+	HCN	$SiCN$	$HNCO$	C_3N^-	CH_2NH	$HNCNH$	NH_2CHO	CH_3NH_2
OH	CO^+	OCS	$AlNC$	H_2CS	PH_3	NH_2CN	CH_3O	CH_3SH	CH_2CHCN
CO	HF	HNC	$SiNC$	C_2H_2	$HCNO$	H_2CCO	NH_3D^+	C_2H_4	HC_5N
H_2	N_2	H_2S	HCP	C_3N	$HOCN$	C_4H	H_2NCO^+	C_5H	C_6H
SiO	CF^+	N_2H^+	CCP	$HNCS$	$HSCN$	SiH_4	$NCCNH^+$	CH_3NC	c-C_2H_4O
CS	PO	C_2H	$AlOH$	$HOCO^+$	$HOOH$	c-C_3H_2	CH_3Cl	HC_2CHO	CH_2CHOH
SO	O_2	SO_2	H_2O^+	C_3O	l-C_3H^+	CH_2CN	MgC_3N	H_2C_4	C_6H^-
SiS	AlO	HCO	H_2Cl^+	l-C_3H	$HMgNC$	C_5	HC_3O^+	C_5S	CH_3NCO
NS	CN^-	HNO	KCN	$HCNH^+$	$HCCO$	SiC_4	NH_2OH	HC_3NH^+	HC_5O
C_2	OH^+	HCS^+	$FeCN$	H_3O^+	$CNCN$	H_2CCC	HC_3S^+	C_5N	$HOCH_2CN$
NO	SH^+	HOC^+	HO_2	C_3S	$HONO$	CH_4	H_2CCS	HC_4H	HC_4NC
HCl	HCl^+	SiC_2	TiO_2	c-C_3H	$MgCCH$	$HCCNC$	C_4S	HC_4N	H_3HNH
$NaCl$	SH	C_2S	CCN	HC_2N	$HCCS$	$HNCCC$	$CHOSH$	c-H_2C_3O	c-C_3HCCH
$AlCl$	TiO	C_3	$SiCSi$	H_2CN		H_2COH^+		CH_2CNH	
KCl	ArH^+	CO_2	S_2H					C_5N^-	
AlF	NS^+	CH_2	HCS					$HNCHCN$	
PN	HeH^+	C_2O	HSC					SiH_3CN	
SiC	VO	$MgNC$	NCO					MgC_4H	
CP		NH_2	$CaNC$					CH_3CO^+	
		$NaCN$	NCS					H_2CCCS	
		N_2O						CH_2CCH	

2. Cosmo and Astrochemistry

Molecules Detected until Today > 200 with 2 or more Atoms



8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	13 Atoms	PAHs	Fullerenes
$HCOOCH_3$	CH_3OCH_3	CH_3COCH_3	HC_9N	C_6H_6	C_6H_5CN	1-$C_{10}H_7CN$	C_{60}
CH_3C_3N	CH_3CH_2OH	$HOCH_2CH_2OH$	CH_3C_6H	n-C_3H_7CN	$HC_{11}N$	2-$C_{10}H_7CN$	C_{60}^+
C_7H	CH_3CH_2CN	CH_3CH_2CHO	C_2H_5OCHO	i-C_3H_7CN		C_9H_8	C_{70}
CH_3COOH	HC_7N	CH_3C_5N	CH_3COOCH_3	1-C_5H_5CN			
H_2C_6	CH_3C_4H	CH_3CHCH_2O	CH_3COCH_2OH	2-C_5H_5CN			
CH_2OHCHO	C_8H	CH_3CH_2OH	C_5H_6				
HC_6H	CH_3CONH_2						
CH_2CHCHO	C_8H^-						
CH_2CCHCN	CH_2CHCH_3						
NH_2CH_2CN	CH_3CH_2SH						
CH_3CHNH	HC_7O						
CH_3SiH_3	CH_3NHCHO						
NH_2CONH_2	$H_2CCCHCCH$						
$HCCCH_2CN$	$HCCCHCHCN$						
CH_2CHCCH	H_2CCHC_3N						

- **Ordinary molecules: NH_3, H_2O, H_2CO, CH_3OH, CH_3CH_2OH, ….**
- **Exotic molecules: HCO^+, N_2H^+, HCCCCCCCN, …. (rare on earth but not in space)**
- **For most molecules, also isotopologs detected, e.g. ^{13}C, ^{18}O, ^{15}N**
- **Deuterated molecules are also very abundant→ higher stability (OLED materials)**

Lit.: Brett A. McGuire, ApJS 259 (2022) 30, Census of ISM, CSM & exoplanetary molecules

2. Cosmo and Astrochemistry

Probiotic Astrochemistry at Dust Particles

Activation by photolysis reactions

$H_2O + h\nu \rightarrow$ •OH + •H

$H_2 + O$

$CH_3OH + h\nu \rightarrow$ •CH_3 + •OH

CH_3O• + •H

•CH_2OH + •H

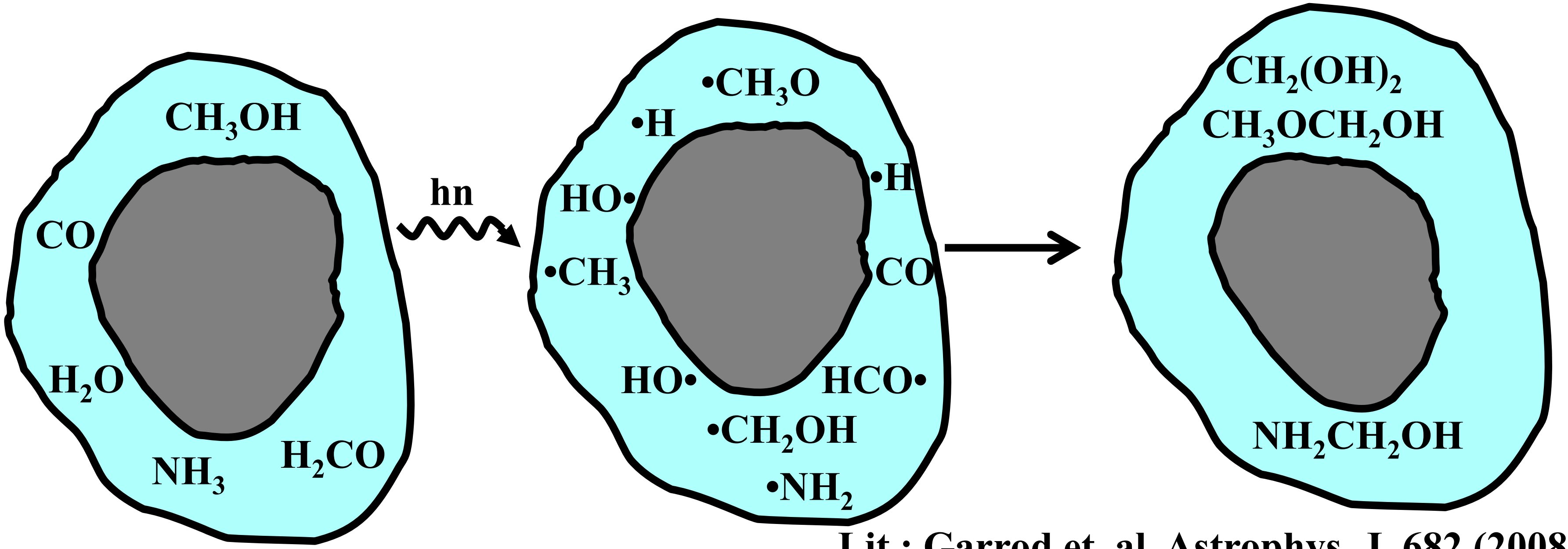
$NH_3 + h\nu \rightarrow$ •NH_2 + •H

Radical-Radical recombination reactions

•CH_2OH + •OH $\rightarrow$ $CH_2(OH)_2$

CH_3O• + •CH_2OH $\rightarrow$ CH_3OCH_2OH

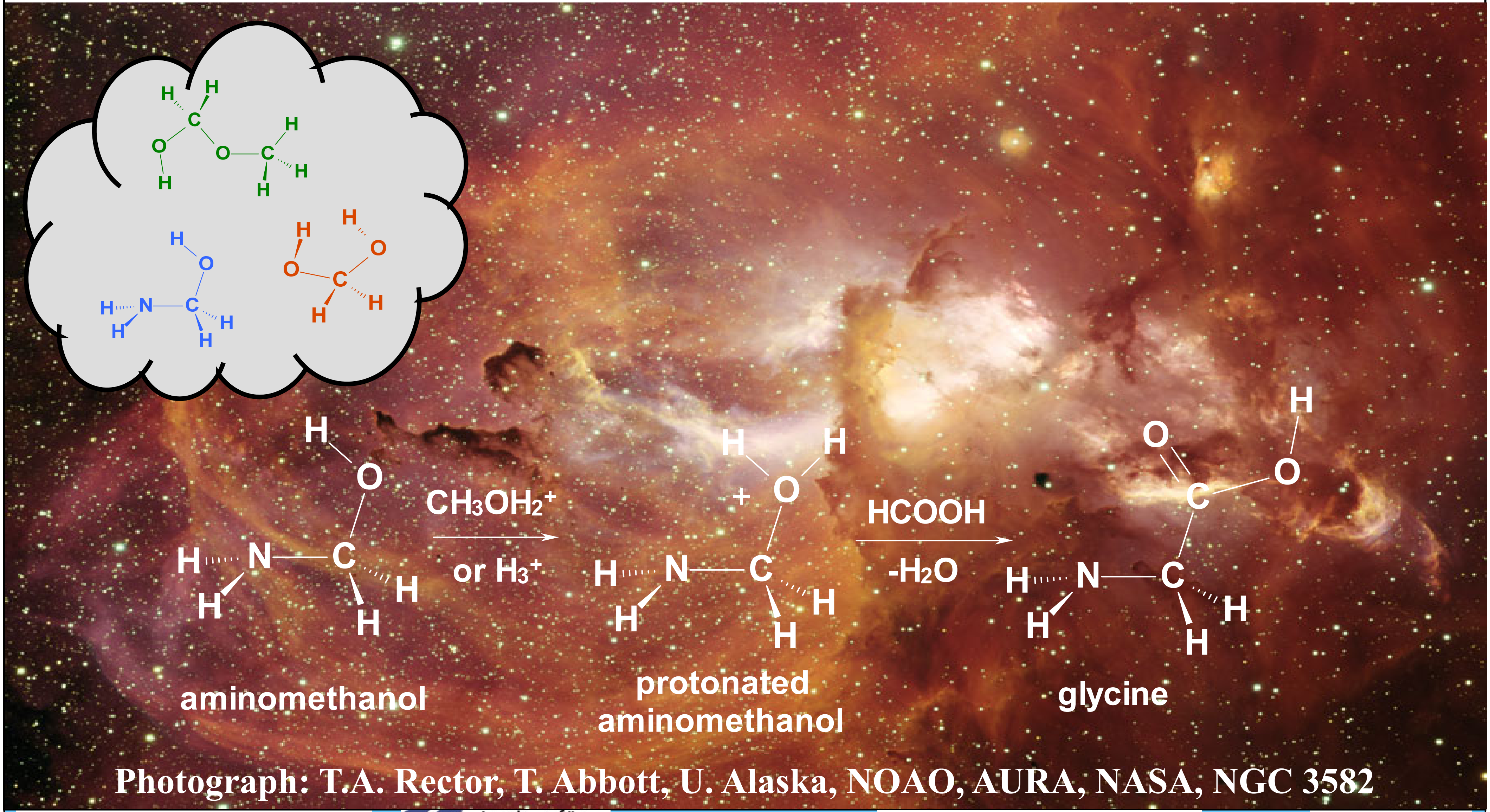
•CH_2OH + •NH_2 $\rightarrow$ NH_2CH_2OH (aminomethanol)



Lit.: Garrod et. al. Astrophys. J. 682 (2008) 283-302

2. Cosmo and Astrochemistry

Probiotic Astrochemistry in Free Space: Conversion of Aminomethanol to Glycin

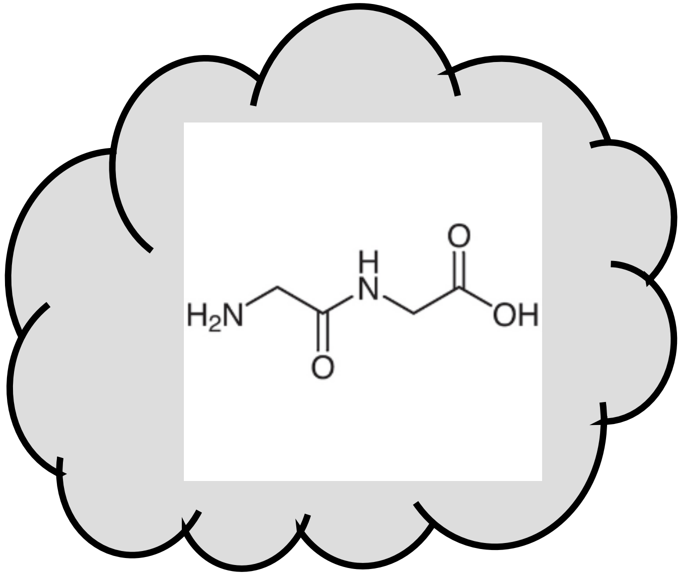


Photograph: T.A. Rector, T. Abbott, U. Alaska, NOAO, AURA, NASA, NGC 3582

2. Cosmo and Astrochemistry

Probiotic Astrochemistry in Free Space

Formation of peptides in space without condensation reaction at dust particles of the interstellar medium (ISM), T ~ 10-20 K:



$C + NH_3 \rightarrow H + C\text{-}NH_2$ (at dust particle surfaces)

$HC\text{-}NH_2 + CO \rightarrow O{=}C{=}HC\text{-}NH_2$ (aminoketene)

$O{=}C{=}HC\text{-}NH_2 + H_2O \rightarrow HOOC\text{-}CH_2\text{-}NH_2$ (glycine)

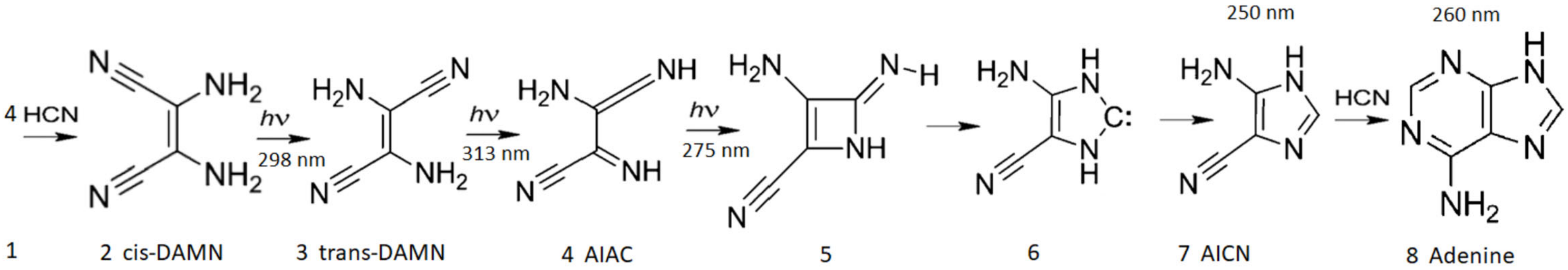
$O{=}C{=}HC\text{-}NH_2 + HOOC\text{-}CH_2\text{-}NH_2 \rightarrow HOOC\text{-}CH_2\text{-}NH\text{-}CO\text{-}CH_2\text{-}NH_2$ (glycylglycine)

→ Oligo-/polypeptides formed in space → panspermia = fertilization of planets from space?

2. Cosmo and Astrochemistry

Probiotic Astrochemistry in Free Space

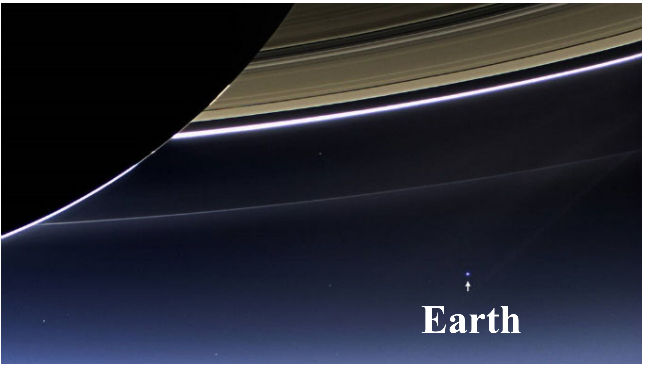
Formation of Adenine (a DNA nucleobase) by photochemistry

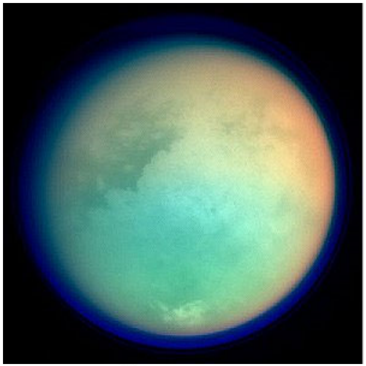


Lit.: arXiv:2007.00618v3 [physics.bio-ph] 23 Dec 2020

2. Cosmo and Astrochemistry

Probiotic Astrochemistry on Planets/Moons: Titan (d = 5153 km, T_e~82 K, T_{eff}~94 K)



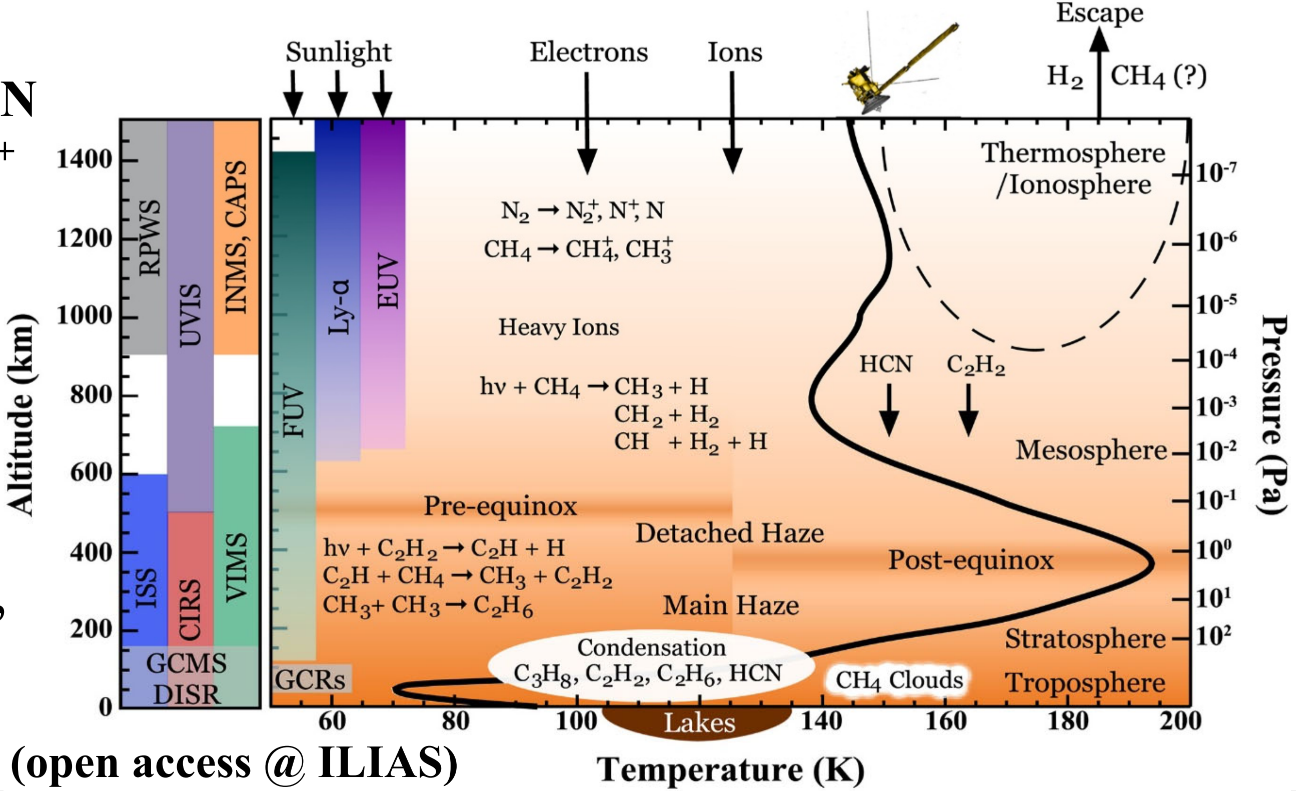


Distance to the sun = 9.546 AU = $1.428 \cdot 10^9$ km
Atmosphere: p = 1.5 bar, CH_4, N_2, hydrocarbons
Temperature increase by the greenhouse effect ~ 15% (Earth ~ 13%)

Photo- and radiolysis products by dissociation: C_2H_2, C_2H_4, C_2H_6, HCN or ionisation: $C_2H_5^+$, $HCNH^+$, $C_4N_5^+$

React to benzene, more complex organic molecules (100 - 350 u) & negative organic ions (20 - 8000 u)

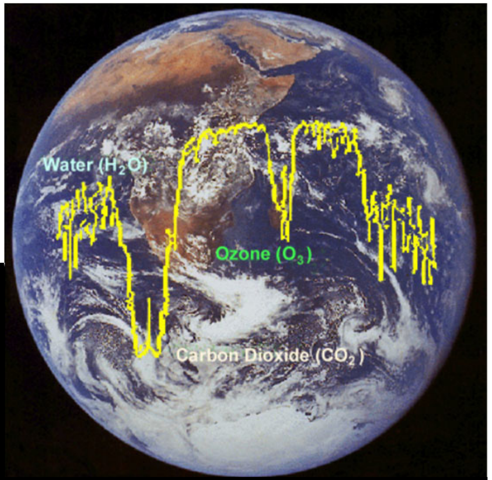
Tholins (yellow-red-brown) in haze comprising complex org. molecules, e.g. polyacrylonitrile



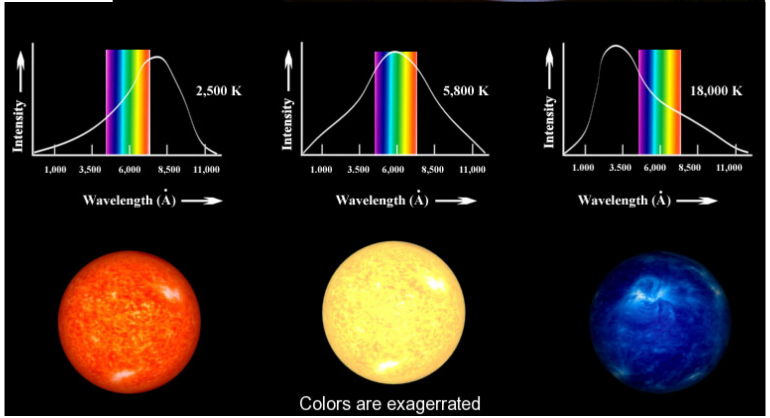
Lit.: JGR Planets 122, 3 (2017) 432-482 (open access @ ILIAS)

2. Cosmo and Astrochemistry

Evolution of (intelligent) Life on Planets/Moons: Requirements

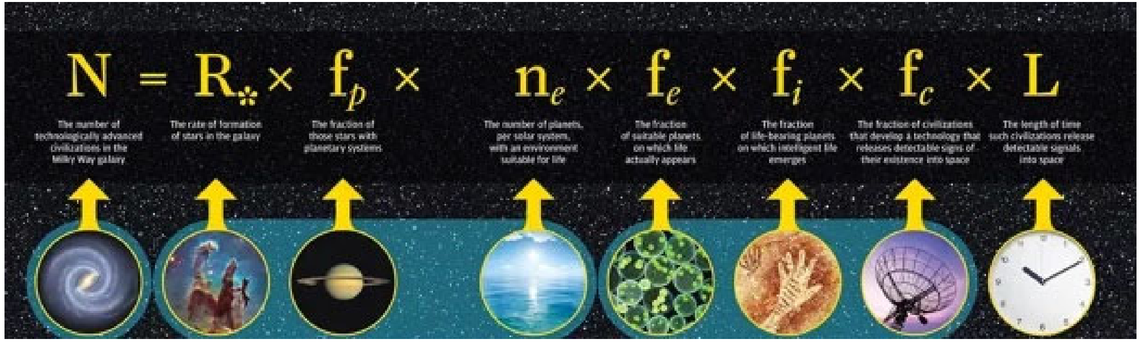


- Earth size planet/moon in habitable zone → atmosphere, liquid H_2O
- Partner body to stabilise the inclination of rotation axis → a moon?
- Suitable colour temperature → K or G stars ~ 4000 - 6000 K for life maintaining photochemistry → O_3 formation, PS
- No tidal locking of rotation → limited tidal momentum loss
- Limited probability of impacts → Right position in the milky way and presence of large outer planets (Jupiter)
- Magnetic field → liquid Fe/Ni core with convection
- Carbonate-silicate cycle → thin planetary crust to enable long-term continental drift and volcanism
- Lifetime of star and stability/width of habitable zone
- Suitable metallicity [Fe/H] of the star to enable sufficiently dense O_3 layer



Intelligent civilisations in the milky way?

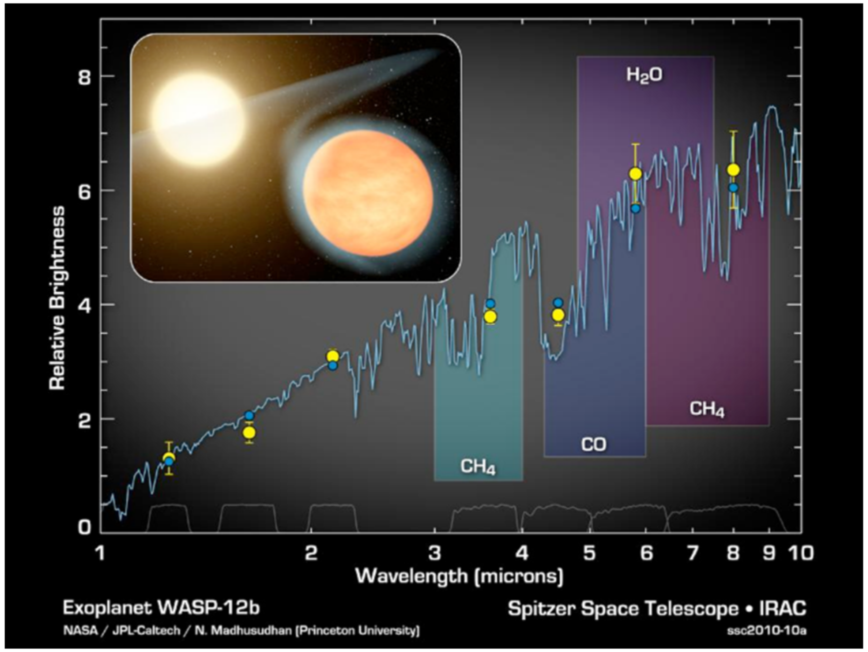
Drake equation (Green Bank, WV, USA, 1961)



2. Cosmo and Astrochemistry

Summary

- The universe is isotropic → Chemistry takes place at any corner of the space!
- Galaxies (d ~ 100 kly) are systems, where gas/dust is accumulated, which fosters chemistry
- Chemistry occurs at low pressure and temperature: kinetic control of formed products
- Many products do not fulfil octet rule and/or are radicals
- Number of known molecules presently grow exponentially
- The importance of gas/grain interaction has become increasingly evident through observations of very cold cores (depletion) and star forming regions (shock waves)
- At present astrochemical research is a joint effort of theorists, observers, i.e. radio astronomers, and laboratory workers
- Molecules of life are presently detected onto exoplanets by Spitzer, JWST etc.…
- Dimethyl sulphide (DMS) „the smell of the coast“ was discovered by JWST onto exoplanet K2-18b in a distance of ~ 120 ly
- Life in space is probable → search for biomarker, e.g. O_2, O_3, H_2O, CH_4, CO, DMS, amino acids, …



Exoplanet WASP-12b

NASA / JPL-Caltech / N. Madhusudhan (Princeton University)

Spitzer Space Telescope • IRAC

ssc2010-10a

3. Symmetry and Group Theory

Application Areas of Group Theory in Chemistry

Quantum Chemistry

- Computational efforts of quantum chemical calculations simplified, e.g. by an Hamilton Operator with same symmetry as the system
- SALCs (symmetry adapted linear combination of atom orbitals) useful in MO- and LF-theory
- Theory of maintenance of orbital symmetry (→ Woodward-Hoffmann-Rules in organic chemistry)

Spectroscopy

- IR-Spectroscopy: IR- and/or Raman activity
- Presence of quadrupole and octupole moment can be taken from character table of molecule
- NMR-Spectroscopy: Protons, which are by a mirror operation chemical equivalent yield in NMR spectra the same chemical shift

Physical Properties

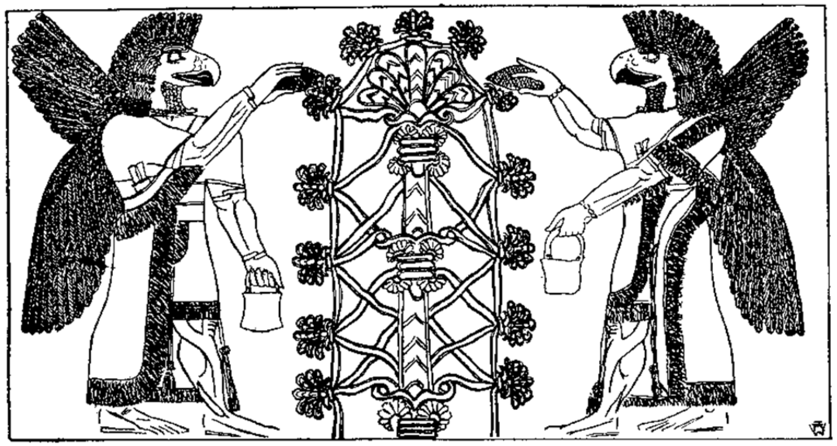
- Permanent dipole moments can be predicted from the type of point group

Chirality & Optical Activity

- Molecules without rotating mirror axis S_n are chiral and thus optical active, e.g. brome-chlor-iod-methane. Molecules with a rotating mirror axis S_n are not optical active, even if they have chiral centres as e.g. meso compounds. Chiral catalysts in enantioselective synthesis comprise ligands with C_2-symmetry in order to produce defined complexes

3. Symmetry and Group Theory

Symmetry in Arts and Nature



Sumerian Art „Eagle man“

„Oskar Lafontaine“

Bird

Taj Mahal

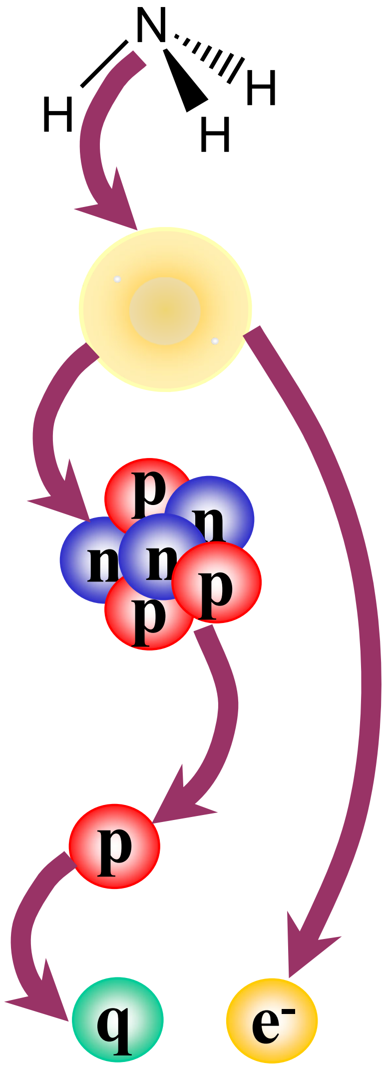
Symmetry is] an invention of the Italian architectsin the worst age of an attempted revival of Classical art”. James Fergusson (1849, p. 399)

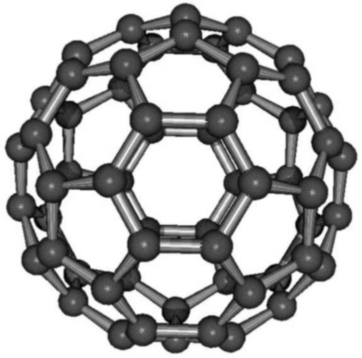
Butterfly

Crystal twins

3. Symmetry and Group Theory

Symmetry in Physics and Chemistry





10^{-9} m Chemistry → VSEPR, space groups, …

10^{-10} m Atom physics → Charge, parity & time reversal symmetry

Particles **Antiparticles**

10^{-14} m

$$\begin{pmatrix}\nu_e\\ e^-\end{pmatrix}\begin{pmatrix}\nu_\mu\\ \mu^-\end{pmatrix}\begin{pmatrix}\nu_\tau\\ \tau^-\end{pmatrix}\quad \textbf{Leptons}\quad \begin{pmatrix}\bar{\nu}_e\\ e^+\end{pmatrix}\begin{pmatrix}\bar{\nu}_\mu\\ \mu^+\end{pmatrix}\begin{pmatrix}\bar{\nu}_\tau\\ \tau^+\end{pmatrix}$$

10^{-15} m

10^{-19} m

$$\begin{pmatrix}u^{+\frac{2}{3}}\\ d^{-\frac{1}{3}}\end{pmatrix}\begin{pmatrix}c^{+\frac{2}{3}}\\ s^{-\frac{1}{3}}\end{pmatrix}\begin{pmatrix}t^{+\frac{2}{3}}\\ b^{-\frac{1}{3}}\end{pmatrix}\quad \textbf{Quarks}\quad \begin{pmatrix}\bar{u}^{-\frac{2}{3}}\\ \bar{d}^{+\frac{1}{3}}\end{pmatrix}\begin{pmatrix}\bar{c}^{-\frac{2}{3}}\\ \bar{s}^{+\frac{1}{3}}\end{pmatrix}\begin{pmatrix}\bar{t}^{-\frac{2}{3}}\\ \bar{b}^{+\frac{1}{3}}\end{pmatrix}$$

3. Symmetry and Group Theory

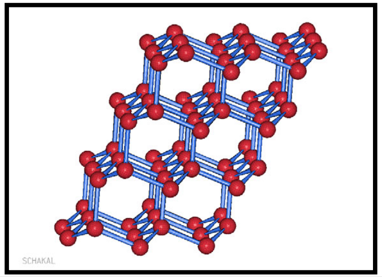
Symmetry - Some History

- **The universe is the totality of four elements, viz.** **Energy Matter → $E = mc^2$**
  Space Time → spacetime

- **Empedokles (495 - 435 BC, Sicily) → First formulated the 4 Element theory**

Element	**Quality**	**God**	**Season**	**Polyhedron**	**Universe**
Fire	**hot and dry**	**Zeus**	**Summer**	**Tetrahedron** 	**Energy**
Earth	**cold and dry**	**Hera**	**Autumn**	**Hexahedron** 	**Matter**
Air	**hot and wet**	**Hades**	**Spring**	**Octahedron** 	**Space**
Water	**cold and wet**	**Nestis**	**Winter**	**Icosahedron** 	**Time**

- **1611 Johannes Kepler Snowflake structure**
- **1849 Auguste Bravais Bravais lattices**
- **1912 Max von Laue Proof of lattice structure**



3. Symmetry and Group Theory

Symmetry Elements and Operations

Greek: Συμ μετρια, lat.: sum metria, dt. Ebenmaß, engl.: evenness

Definitions

- **A symmetry element is a geometric object, e.g. a plane, line (axis), or point**

- **Symmetry operations are movements (reflection, rotation, inversion) carried out with respect to the known symmetry elements. To possess a symmetry operation, an object must appear indistinguishable before/after performing the symmetry operation**

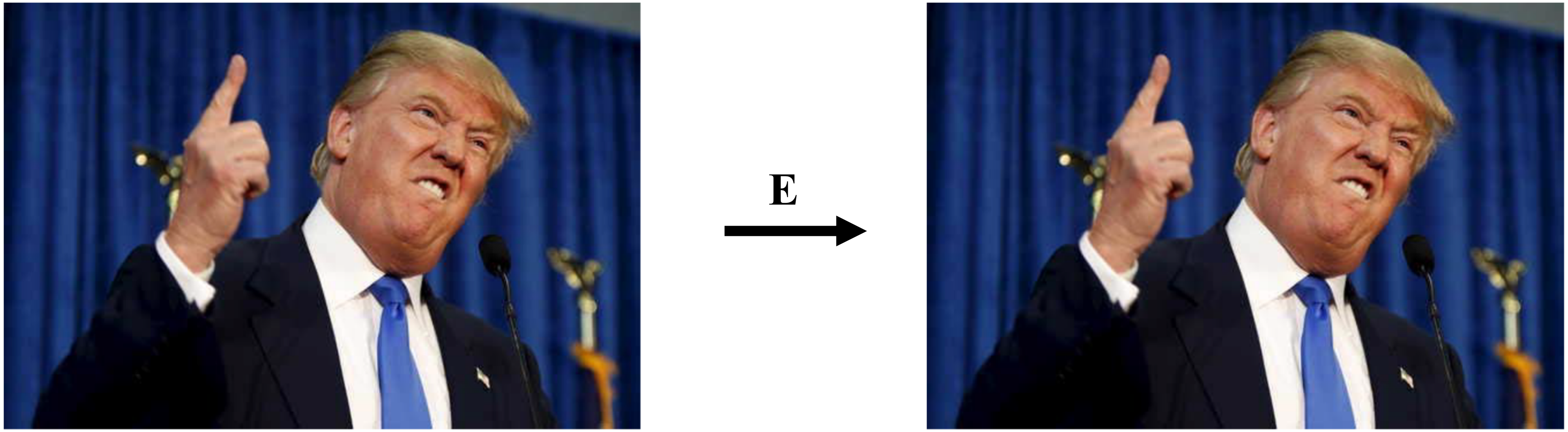
Symmetry element	Symmetry operations
mirror plane	reflection in the plane
proper axis	rotation about the axis
improper axis	rotation, followed by reflection in a plane perpendicular to axis
center of inversion	inversion of all atoms through center

5 operations exists:
Reflection (σ), proper rotation (C_n), improper rotation (S_n), inversion (i), and identity (E)

3. Symmetry and Group Theory

Symmetry Operations: Identity (E)

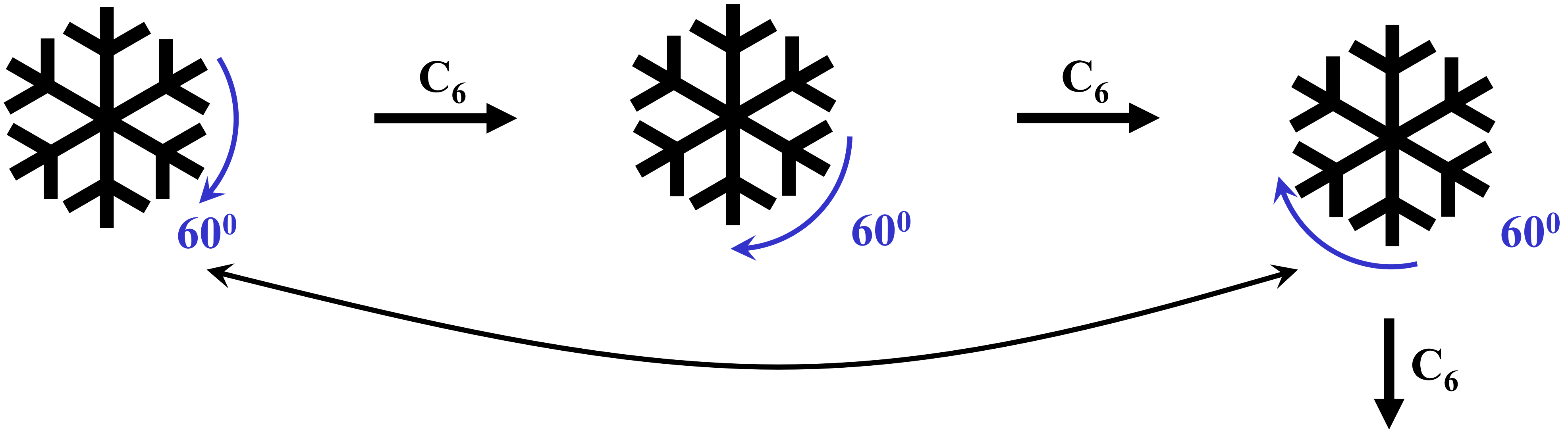
- The “do nothing” operation (the simplest operation)
- Mathematically equivalent to multiplying by 1 (neutral element)
- All kind of objects have E



3. Symmetry and Group Theory

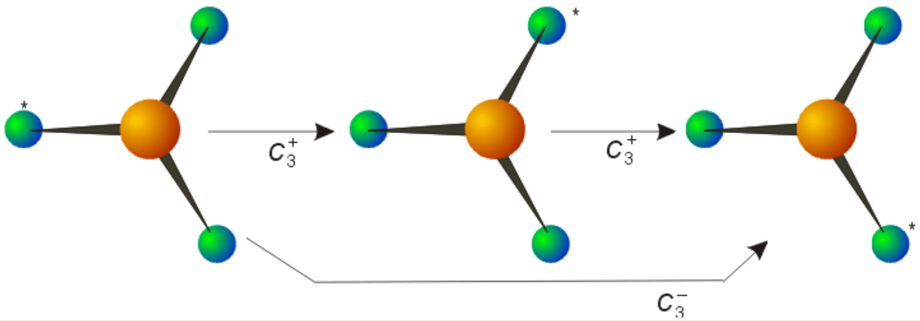
Symmetry Operations: Proper Rotations (C_n)

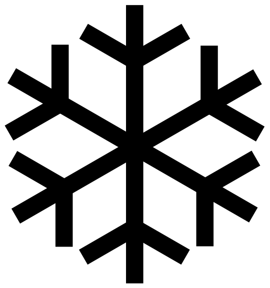
- Clockwise (+1) or counter clockwise (-1) rotation of $2\pi/n$ (360°/n) about an axis



- Multiplication of operations $C_6 \times C_6 = C_6^2 = C_3$

- NH_3 has a c_3 axis



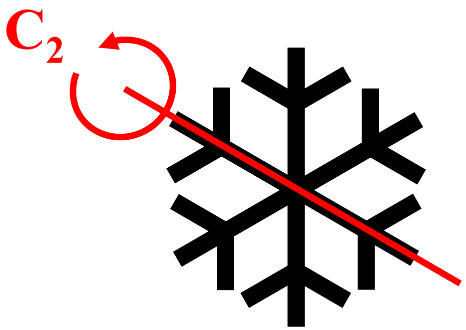


$C_6 \times C_6 \times C_6 = C_6^3 = C_2$

3. Symmetry and Group Theory

Symmetry Operations: Proper Rotations (C_n)

- A clockwise rotation of 2π/n (360°/n) about an axis
- The rotation axis with the largest n is called the highest order or principal axis (the C_6 axis in the case of our snowflake)
- Some objects have rotations that are perpendicular to the principal axis
- An object with a C_n axis must have zero or n perpendicular C_2 axes
- The snowflake has coincident C_6, C_3, and C_2 axes plus six orthogonal C_2 axes



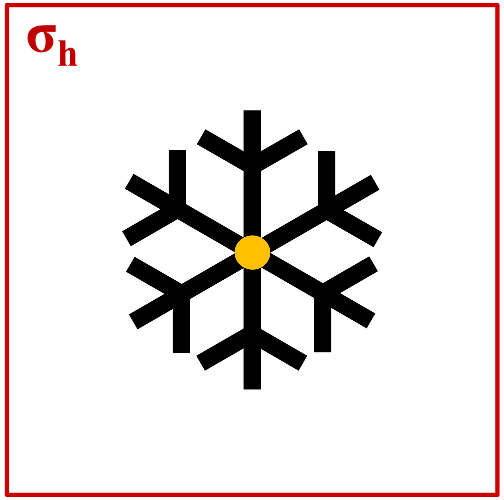
3. Symmetry and Group Theory

Symmetry Operations: Reflection Operation (σ)

- An internal reflection thru a plane of symmetry within an object
- A horizontal mirror plane (σ_h) is perpendicular to the principal axis

Conclusions

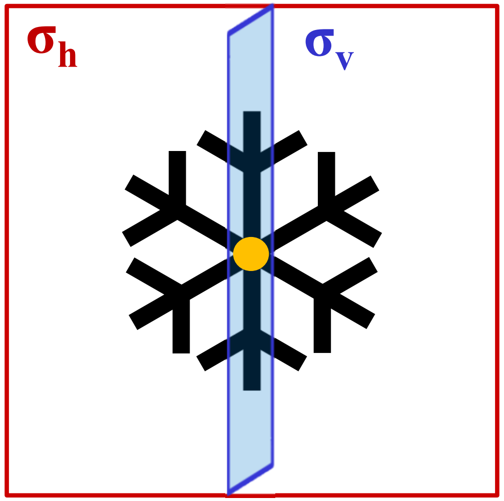
- $\sigma^n = E$ when n is even (0, 2, …)
- $\sigma^n = \sigma$ when n is odd (1, 3, …)

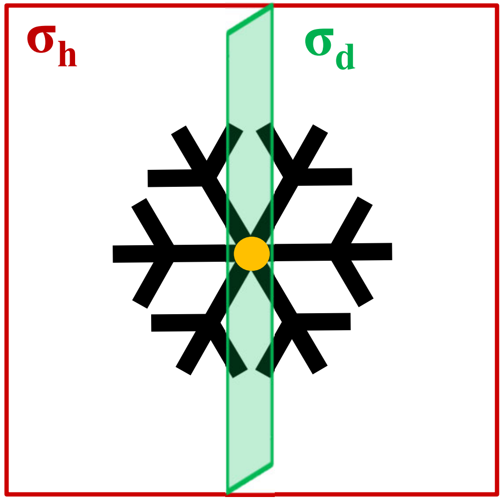


3. Symmetry and Group Theory

Symmetry Operations: Reflection Operation (σ)

- An internal reflection (σ) thru a plane of symmetry within an object
- $\sigma^n = E$ when n is even (0, 2, …)
- $\sigma^n = \sigma$ when n is odd (1, 3, …)
- A horizontal mirror plane (σ_h) is perpendicular to the principal axis
- Vertical (σ_v) and dihedral (σ_d) mirror planes are parallel to the principal axis
- $\# \sigma_v + \# \sigma_d = 0$ or n
- The snowflake has 1 σ_h, 3 σ_v and 3 σ_d mirror planes

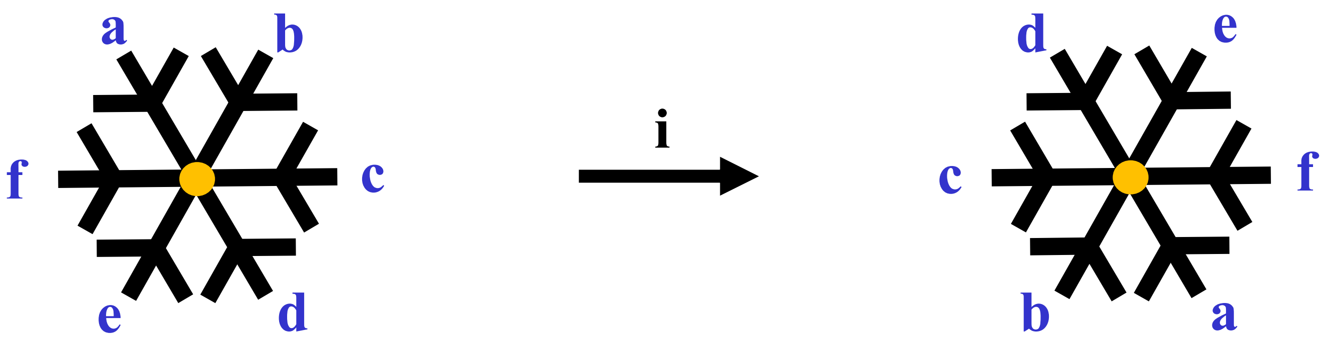




3. Symmetry and Group Theory

Symmetry Operations: Inversion Operation (i)

- each point is moved along a straight line through the center of the object (the inversion center) to a point an equal distance from the center
- In other words: $(x, y, z) \rightarrow (-x, -y, -z)$ for all points
- An object can have zero or one inversion center
- The snowflake has an inversion center
- Rule: $i^n = E$ when n is even, $i^n = i$ when n is odd



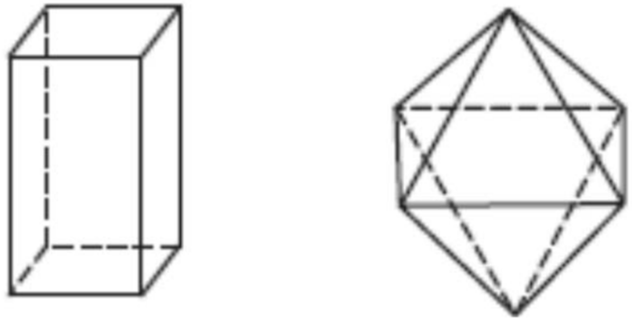
Cat’s Eye Nebula, a 3000 y old supernova remnant

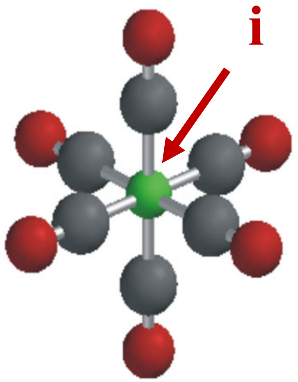
3. Symmetry and Group Theory

Symmetry Operations: Inversion Operation (i)

Octahedra, boxes, squares, rectangles, and parallelograms have an inversion center, but tetrahedra, triangles, and pentagons do not

Inversion center

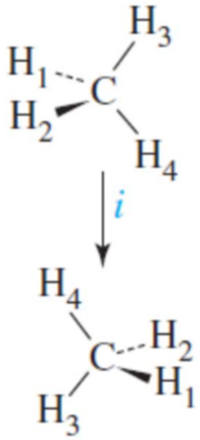




$[W(CO)_6]$

No inversion center

Echinodermata (starfish etc…)



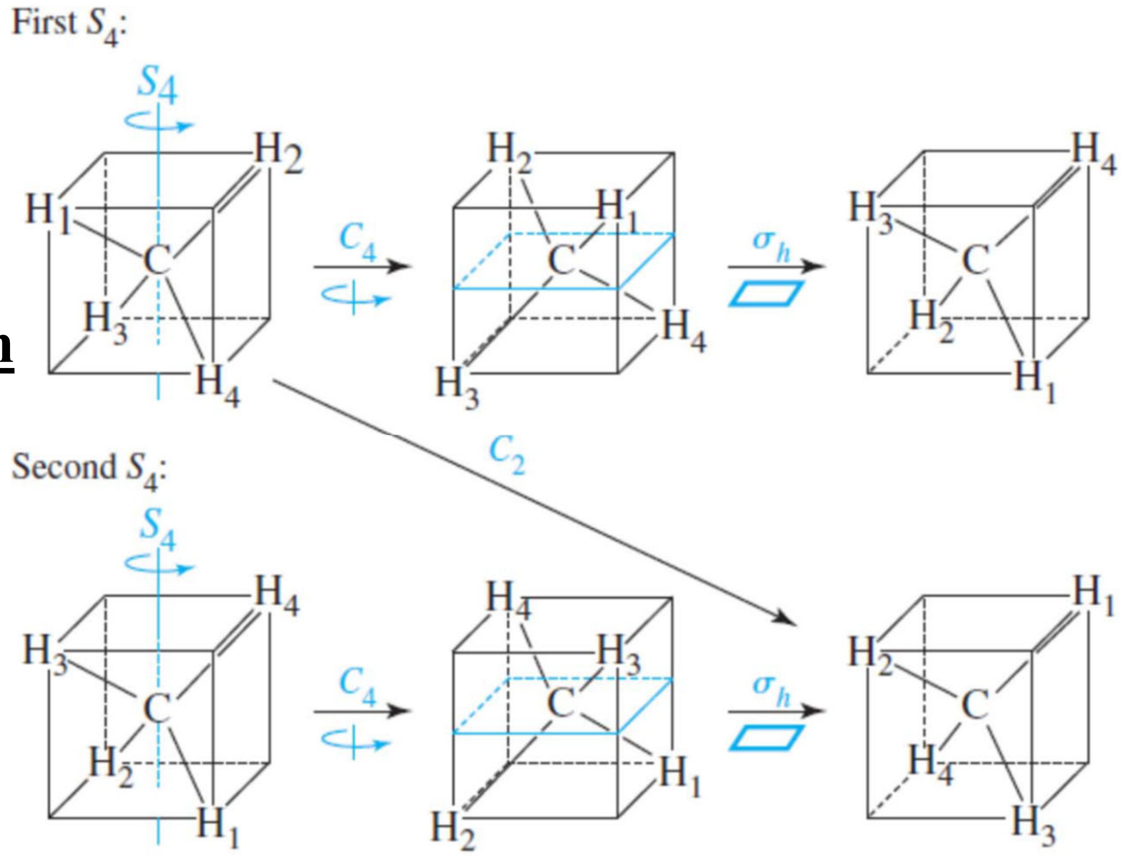
No center of inversion

3. Symmetry and Group Theory

Symmetry Operations: Improper Rotation Operation (S_n)

Definition: Rotation about an axis followed by a reflection in a plane perpendicular to the rotation axis (roto-reflection)

Example: S_4 operation in methane



<u>Rotation angle / symmetry operation</u>

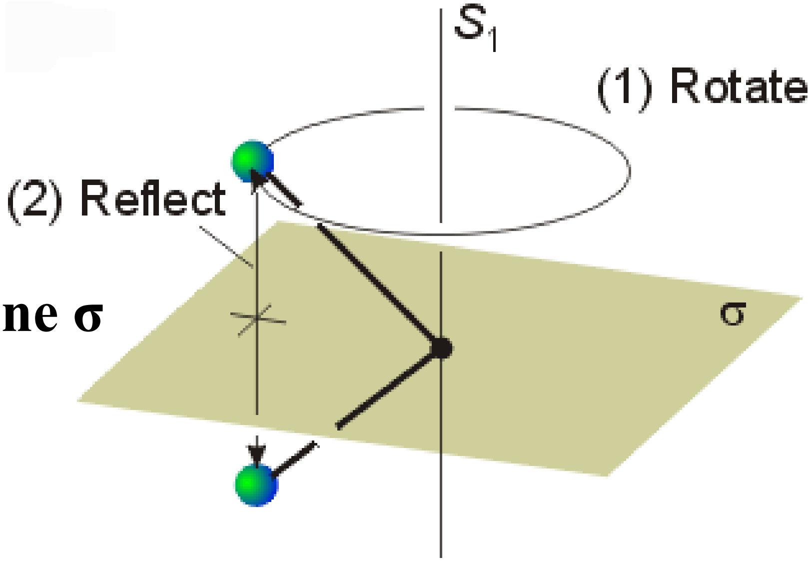
90 °C	S_4^1
180 °C	$S_4^2 \equiv C_2$
270 °C	S_4^3
360 °C	$S_4^4 \equiv E$

3. Symmetry and Group Theory

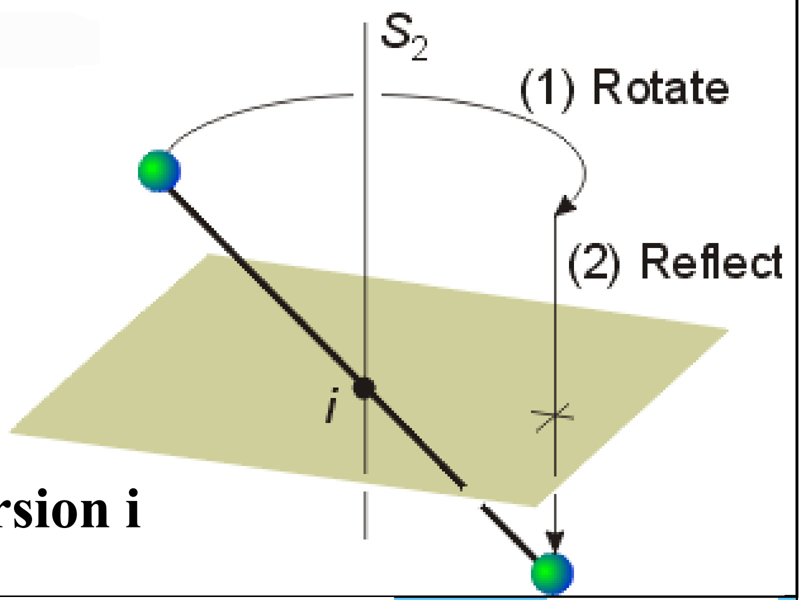
Symmetry Operations: Improper Rotation Operation (S_n)

Redundancies

- An S_1 axis doesn’t exist, since it is a mirror plane σ

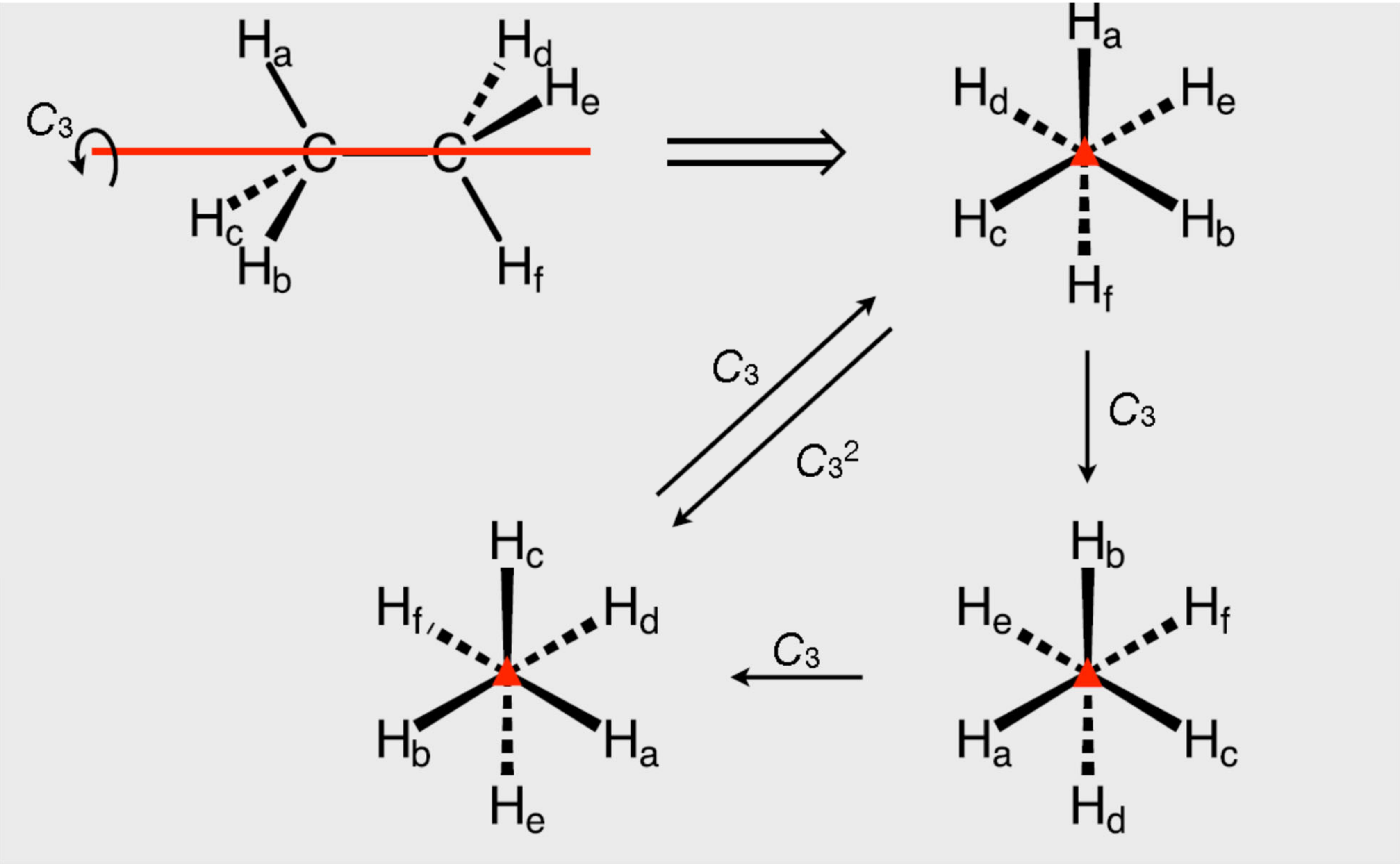


- An S_2 axis doesn’t exist, since it is a center of inversion i



3. Symmetry and Group Theory

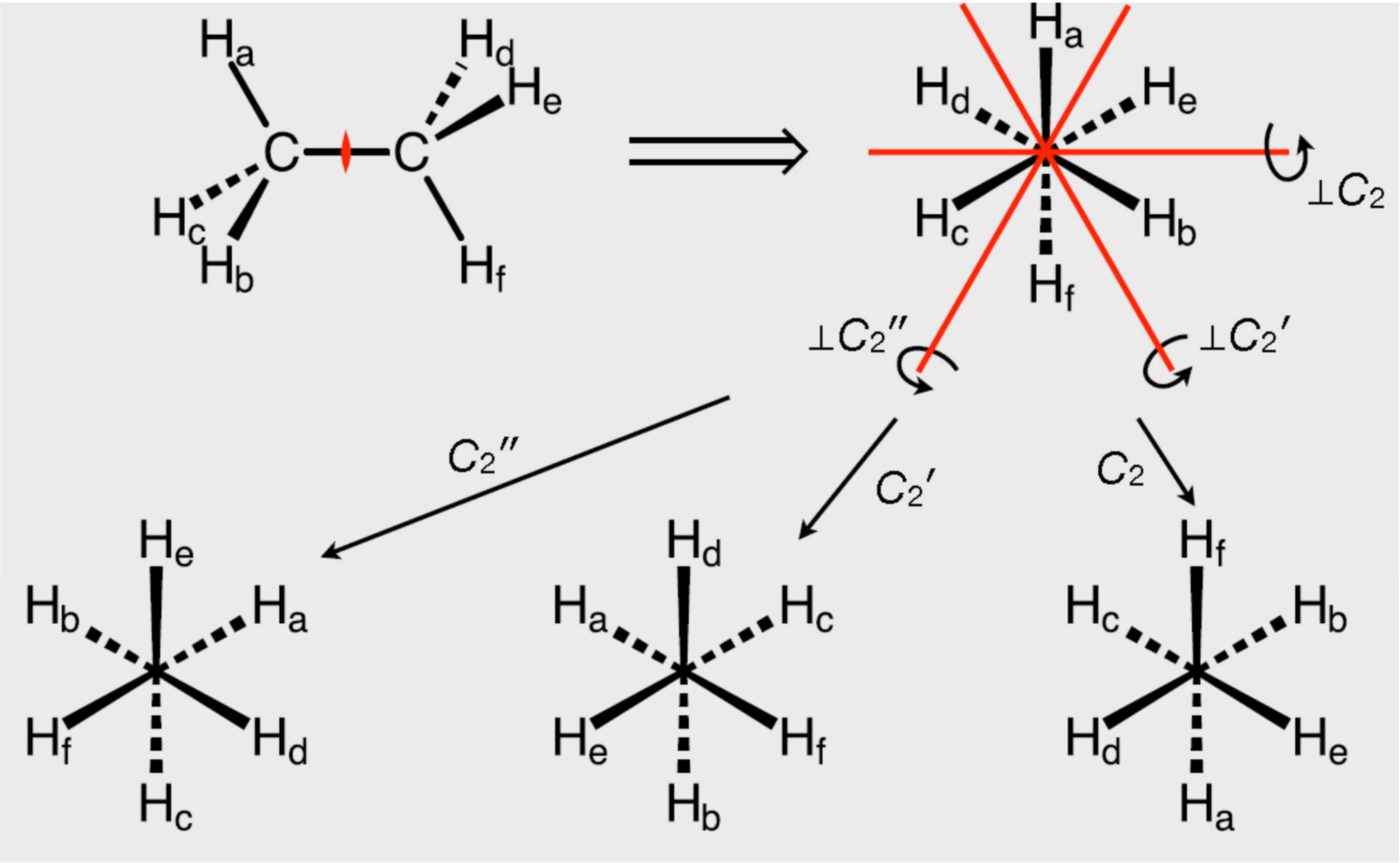
Symmetry in Molecules: Example Staggered Ethane



Staggered ethane has e.g. the following three symmetry operations: E, C_3, and C_3^2

3. Symmetry and Group Theory

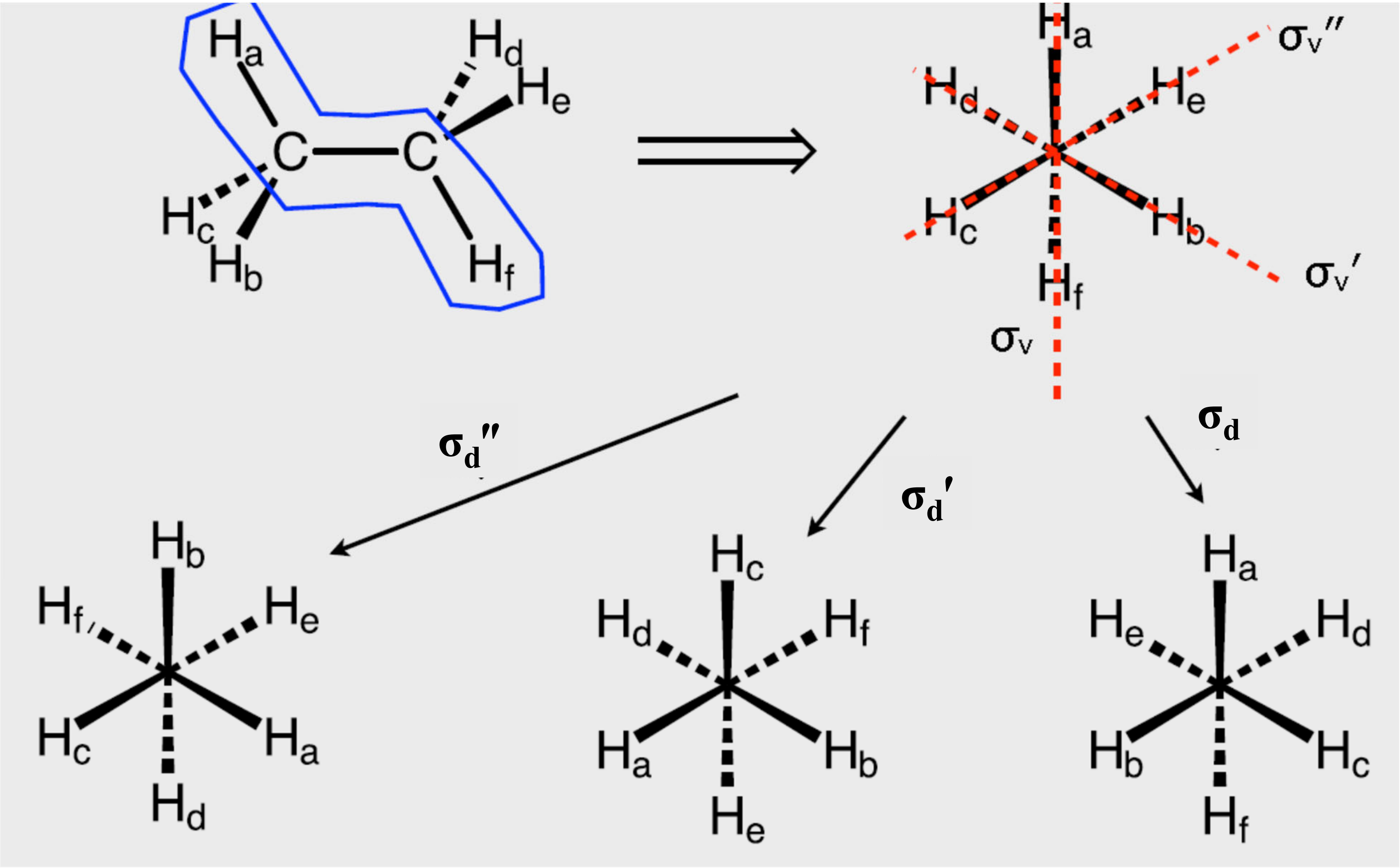
Symmetry in Molecules: Example Staggered Ethane



Three more operations: C_2, C_2', and C_2''

3. Symmetry and Group Theory

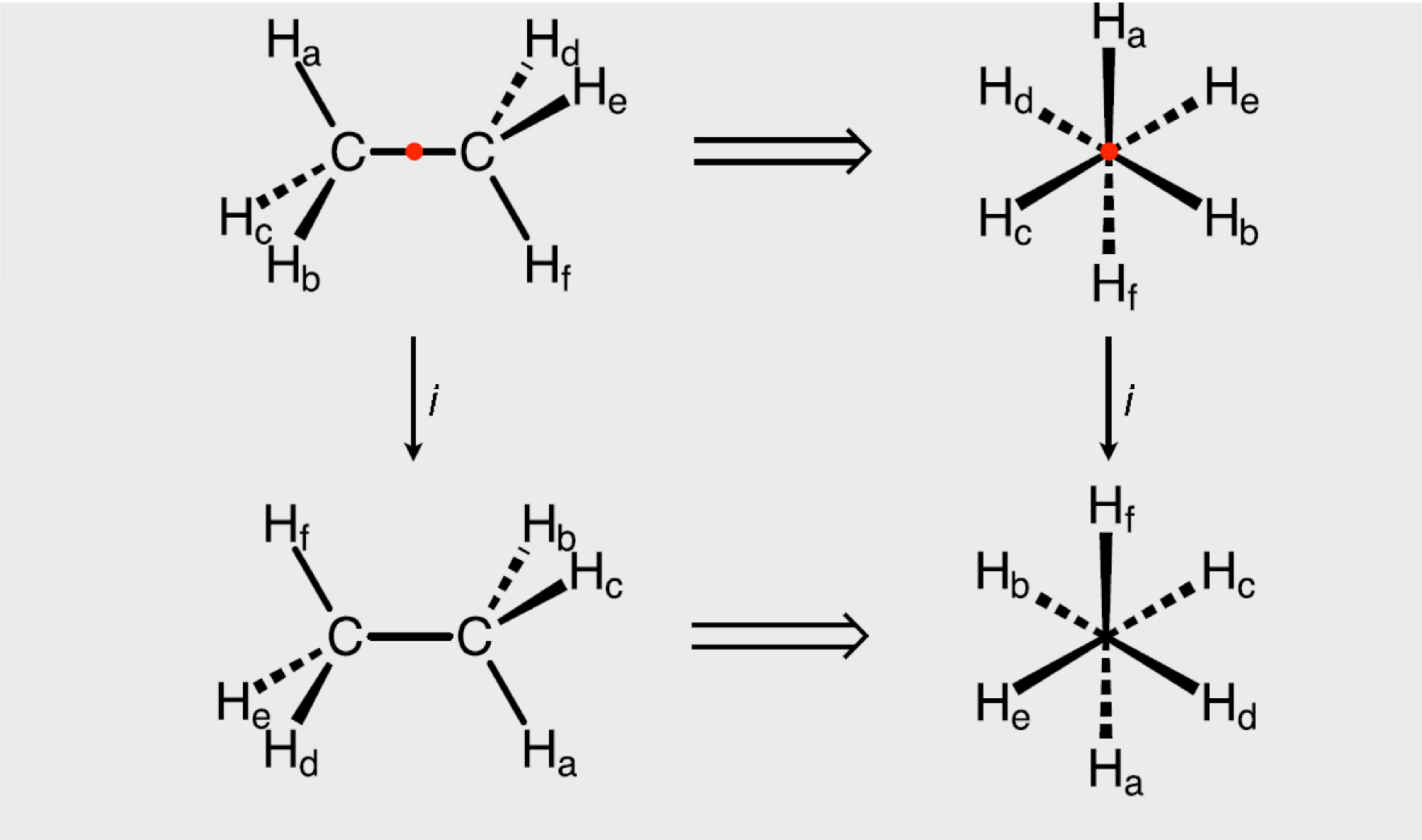
Symmetry in Molecules: Example Staggered Ethane



Three more operations: Reflections σ_d, σ_d', and σ_d'', but no σ_h

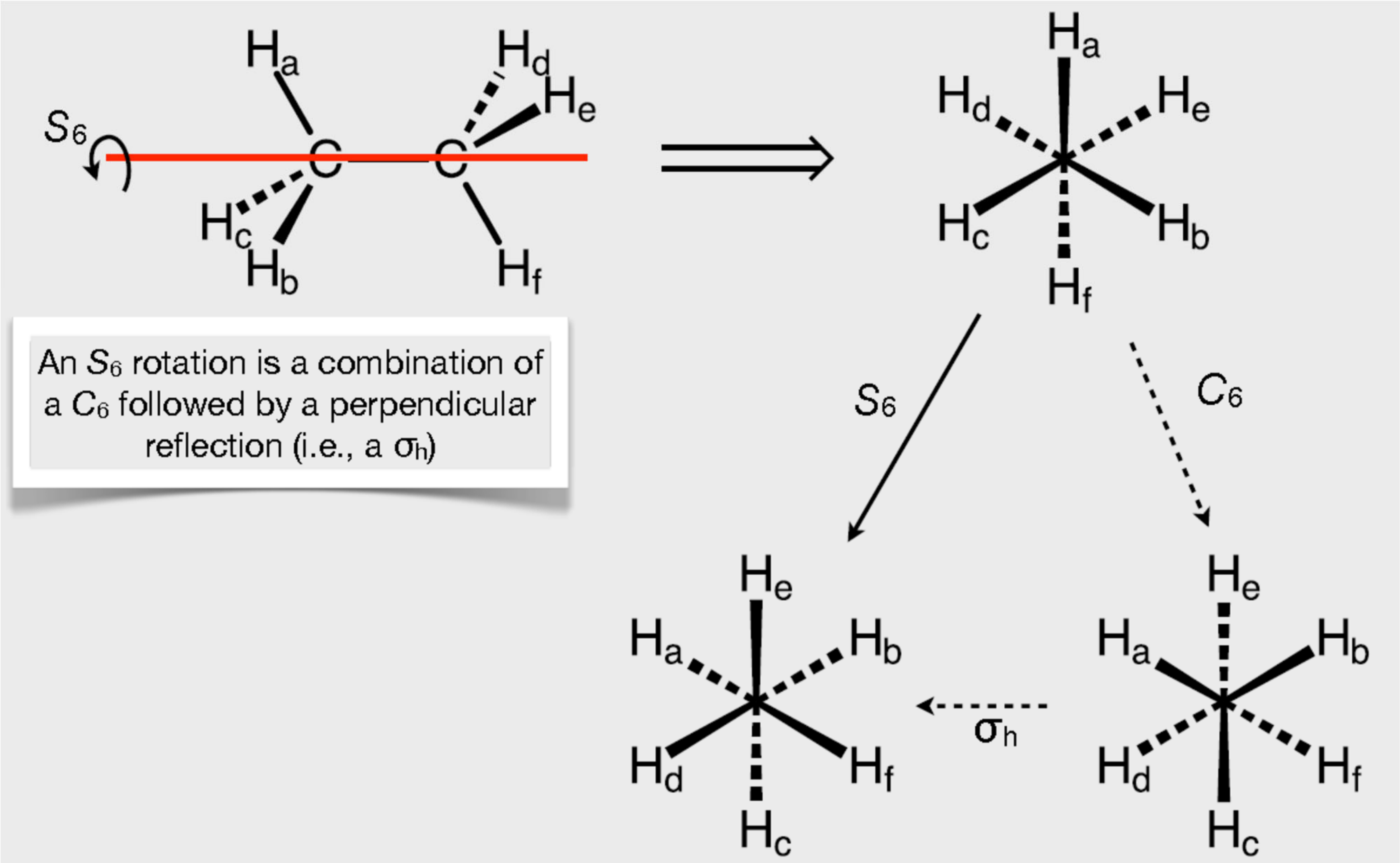
3. Symmetry and Group Theory

Symmetry in Molecules: Example Staggered Ethane



Staggered ethane also has an inversion center that lies at the midpoint

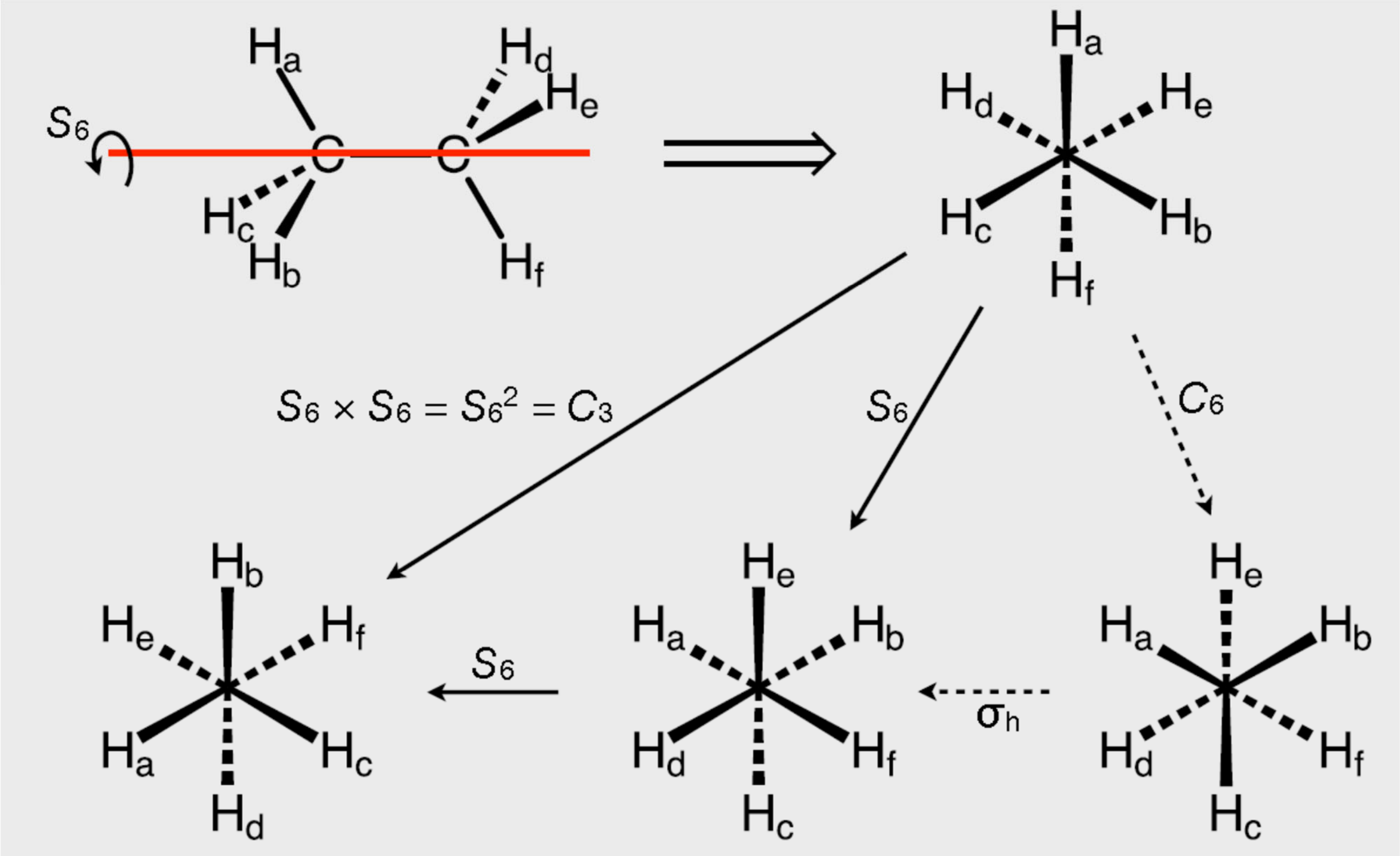
Symmetry in Molecules: Example Staggered Ethane



An S_6 rotation is a combination of a C_6 followed by a perpendicular reflection (i.e., a σ_h)

Staggered ethane also has an improper rotation axis, which is an S_6 (S_{2n}) axis

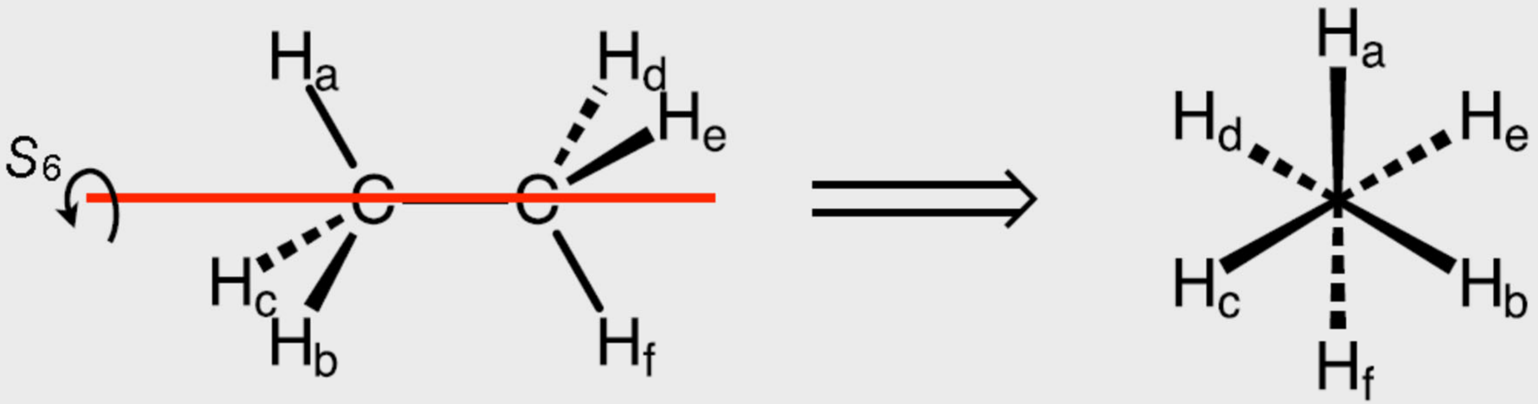
Symmetry in Molecules: Example Staggered Ethane



The S_6 (S_{2n}) axis that is coincident with the C_3 axis

3. Symmetry and Group Theory

Symmetry in Molecules: Example Staggered Ethane



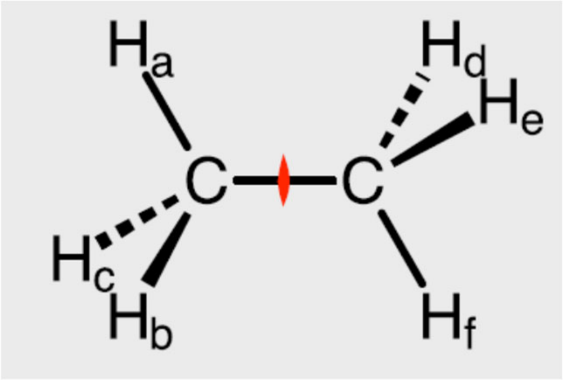
S_6 operation	equivalent operation
S_6	S_6
S_6^2	C_3
S_6^3	i
S_6^4	C_3^2
S_6^5	S_6^5
S_6^6	E

Several redundancies for the unique improper rotations exist:
→ The improper rotations add only two unique operations

3. Symmetry and Group Theory

Symmetry in Molecules: Example Staggered Ethane in Summary

Operation type	Number of operations
Identity	1
Rotations	5 (2 C_3 + 3 C_2)
Reflections	3 (3 σ_d)
Inversion	1
Improper Rotations	2 (S_6 + S_6^5)
Total h	12



These 12 symmetry operations describe completely and without redundancy the symmetry properties of the staggered ethane molecule!

- **The complete set of symmetry operations possessed by an object defines its point group. For example, the point group of staggered ethane is D_{3d}**
- **The total number of operations is called the order (h) of a point group. The order is always an integer multiple of n of the principal axis**
- **For staggered ethane: h = 4n (4 × 3 = 12)**

3. Symmetry and Group Theory

Symmetry Elements and Operations: Summary

- Elements are imaginary points, lines, or planes within the object

- Operations are movements that take an object between equivalent configurations - indistinguishable from the original configuration, although not necessarily identical to it

- For molecules one use “point” symmetry operations, which include rotations, reflections, inversion, improper rotations, and the identity. At least one point remains stationary in a point operation

- Some symmetry operations are redundant, e.g. $S_6^2 \equiv C_3$, in these cases, the convention is to list the simpler operation

- Symmetry is a fundamental property in physics, chemistry & biology (preferences) from elementary particles to spacetime

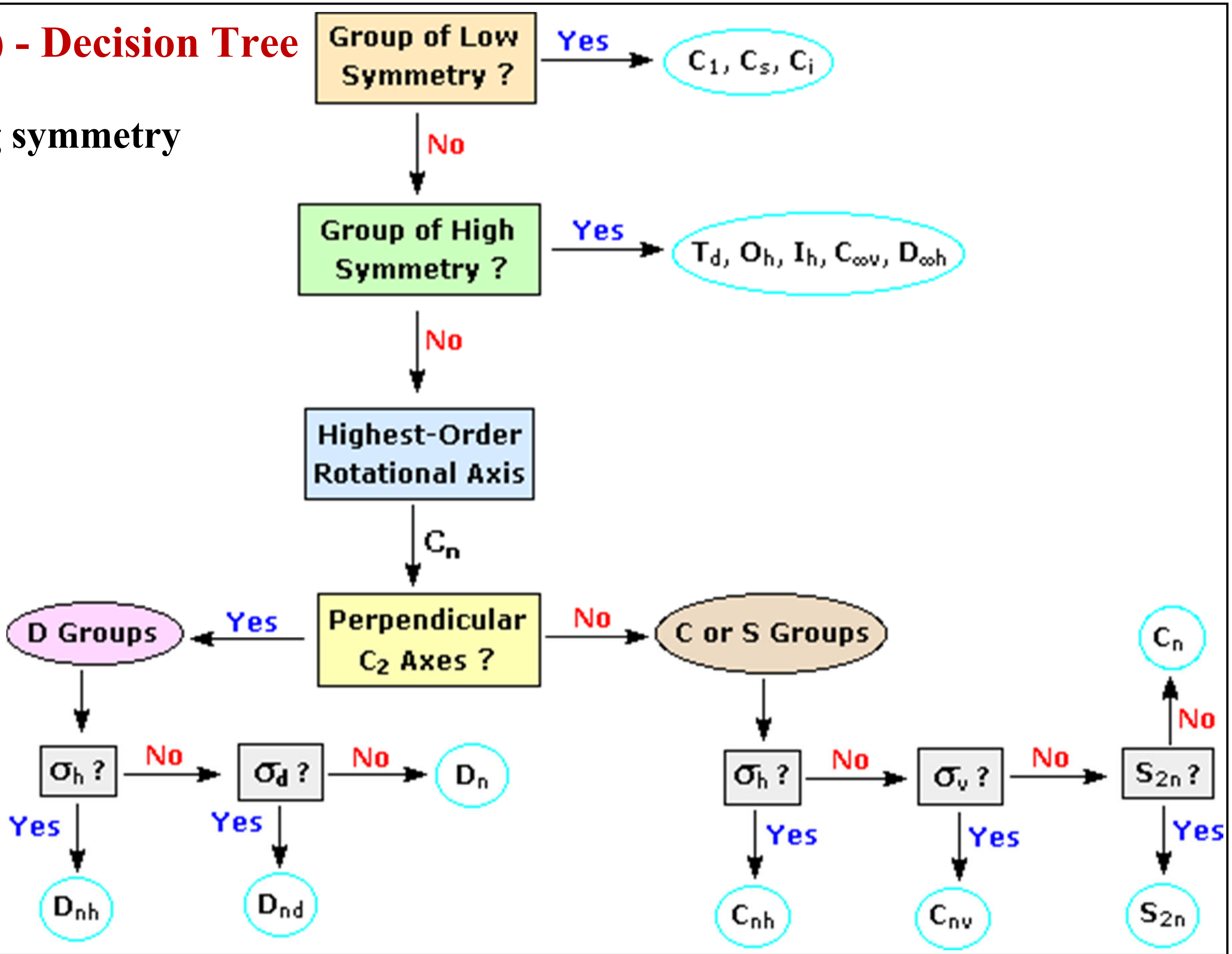
Zebrafinch

3. Symmetry and Group Theory

Point Groups (PGs) - Decision Tree

In order of increasing symmetry

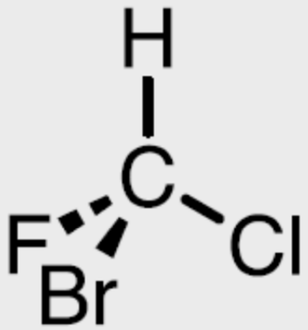
C_1
C_s
C_i
C_n
S_n
C_{nv}
C_{nh}
D_n
D_{nh}
D_{nd}
$C_{\infty v}$
$D_{\infty h}$
T_d
O_h
I_h
K_h



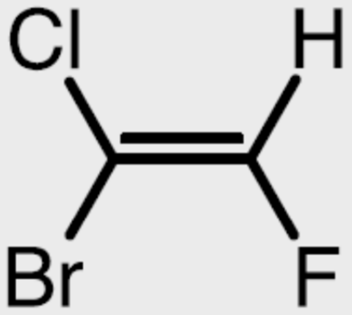
3. Symmetry and Group Theory

Point Groups of Low Symmetry

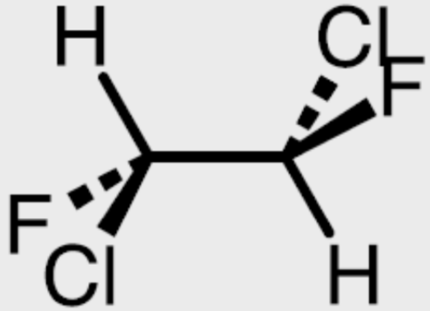
C_1
(E)
h = 1

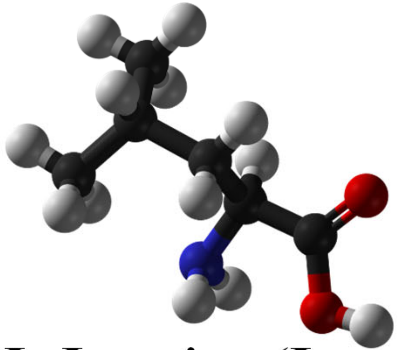


C_s
(E, σ_h)
h = 2



C_i
(E, i)
h = 2





L-Leucine (Leu, L) and all amino acids except glycine → Symmetry is broken in biological evolution!

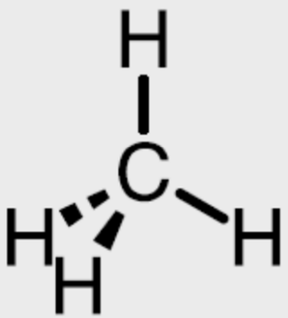
3. Symmetry and Group Theory

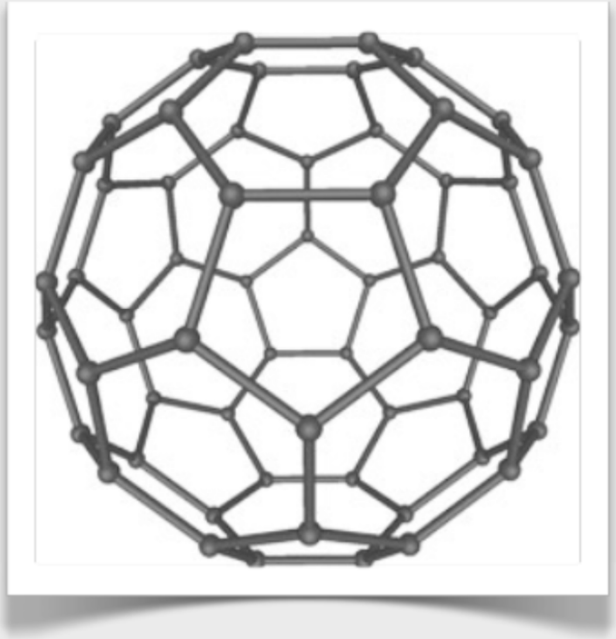
Point Groups of High Symmetry

T_d
$(E, 8C_3, 3C_2, 6S_4, 6\sigma_d)$
$h = 24$

O_h
$(E, 8C_3, 6C_2, 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d)$
$h = 48$

I_h
$(E, 12C_5, 12C_5^2, 20C_3, 15C_2, i, 12S_{10}, 12S_{10}^3, 20S_6, 15\sigma)$, $h = 120$





Buckminster fullerene (C_{60})

Tetrahedra

Octahedra, Cube

Dodecahedra, Icosahedra

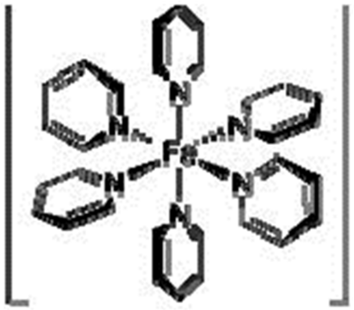
3. Symmetry and Group Theory

Point Groups of High Symmetry

- In addition to T_d, O_h, and I_h, there are corresponding point groups that lack the mirror planes (T, O, and I)
- Adding an inversion center to the T point group gives the T_h point group

Point group	Symmetry operations	Total number of symmetry operations h
K_h	all	∞
I_h	$E, 12C_5, 12C_5^2, 20C_3, 15C_2, i, 12S_{10}, 12S_{10}^3, 20S_6, 15\sigma$	120
I	$E, 12C_5, 12C_5^2, 20C_3, 15C_2$	60
O_h	$E, 8C_3, 6C_2, 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$	48
O	$E, 8C_3, 6C_2, 6C_4, 3C_2$	24
T_d	$E, 8C_3, 3C_2, 6S_4, 6\sigma_d$	24
T	$E, 4C_3, 4C_3^2, 3C_2$	12
T_h	$E, 4C_3, 4C_3^2, 3C_2, i, 4S_6, 4S_6^5, 3\sigma_h$	24

Example for a molecule with point group T_h: $[Fe(py)_6]^{2+}$



3. Symmetry and Group Theory

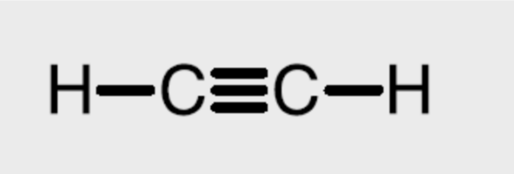
Point Groups of High Symmetry

These point groups have a C_∞ axis as the principal rotation axis

$C_{\infty v}$
$(E, 2C_\infty\varphi, \ldots, \infty\sigma_v)$
$h = \infty$

Hydrogen cyanide
$H\text{-}C{\equiv}C\text{-}X$, CO, NO, COS
$(X = F, Cl, Br)$

$D_{\infty h}$
$(E, 2C_\infty\varphi, \ldots, \infty C_2, i, 2S_\infty\varphi, \infty\sigma_v)$
$h = \infty$



Acetylene
N_2, O_2, F_2, Cl_2, Br_2, I_2, CO_2, N_3^-, C_3^{4-}

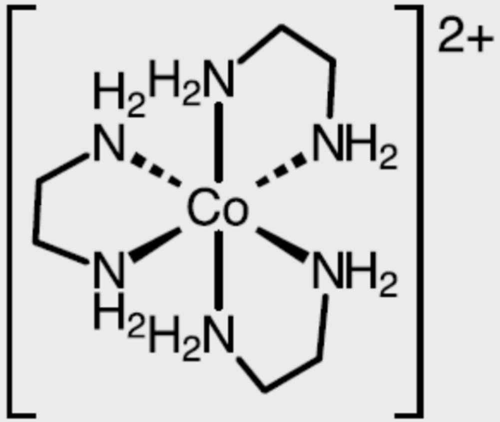
3. Symmetry and Group Theory

D Point Groups

These point groups have nC_2 axes perpendicular to a principal axis (C_n)

D_n
(E, (n-1)C_n, n⊥C_2)

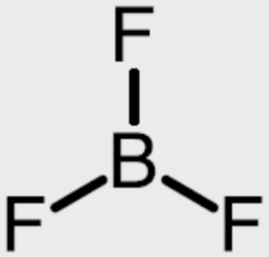
trisethylendiamincobalt(II)



D_3
(E, 2C_n, 3⊥C_2)
h = 6

D_{nh}
(depends on n, with h = 4n)

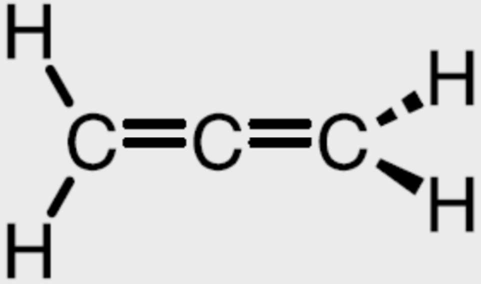
bortrifluoride



D_{3h}
(E, 2C_3, 3C_2, σ_h, 2S_3, 3σ_v)
h = 12

D_{nd}
(depends on n, with h = 4n)

allene (propadiene)



D_{2d}
(E, 2S_4, C_2, 2C_2’, 2σ_d)
h = 8

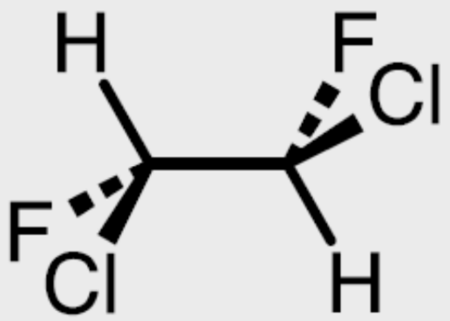
3. Symmetry and Group Theory

C Point Groups

These point groups have a principal axis (C_n) but no $\perp C_2$ axes

C_n
(E, (n-1)C_n)

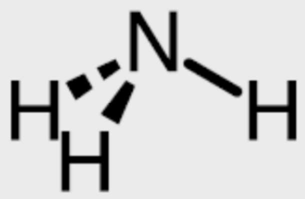
1,2-dichlor-1,2-fluor-ethane



C_2
(E, C_2)
h = 2

C_{nv}
(E, (n-1)C_n, nσ_v)

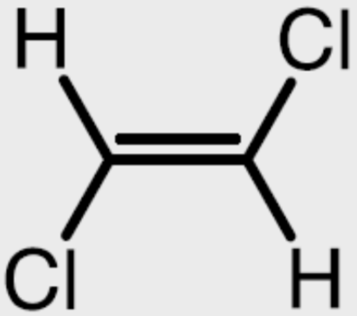
ammonia



C_{3v}
(E, 2C_3, 3σ_v)
h = 6

C_{nh}
(depends on n, with h = 2n)

1,2-Dichlorethylene



C_{2h}
(E, C_2, i, σ_h)
h = 4

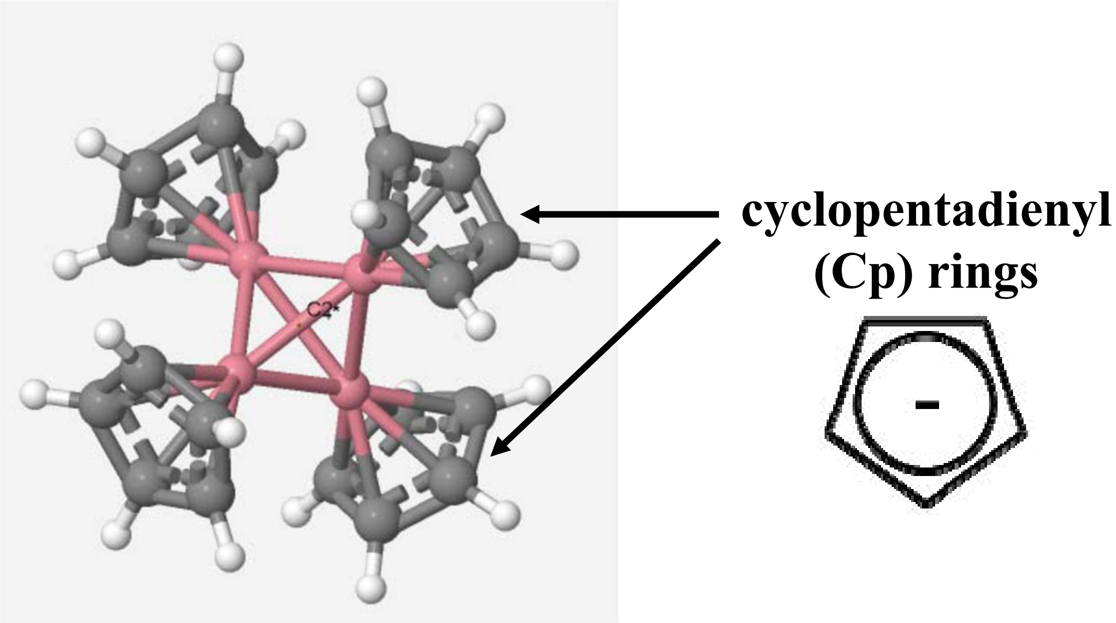
3. Symmetry and Group Theory

S Point Groups

If an object has a principal axis (C_n) and an S_{2n} axis but no $\perp C_2$ axes and no mirror planes, it falls into an S_{2n} group

S_{2n} depends on n, with h = 2n

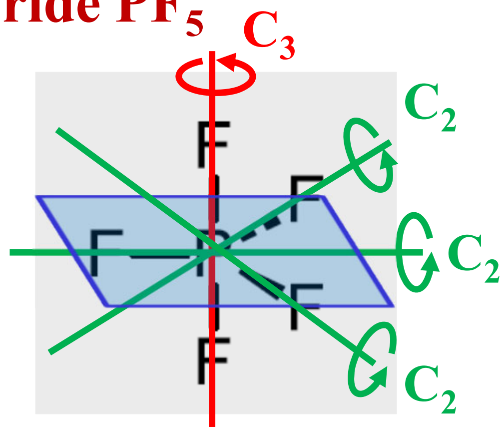
Example: Tetracobalttetracyclopentadienyl (Co_4Cp_4)



S_4 (E, S_4, C_2, S_4^3), h = 4

3. Symmetry and Group Theory

Example: Phosphorous Pentafluoride PF_5



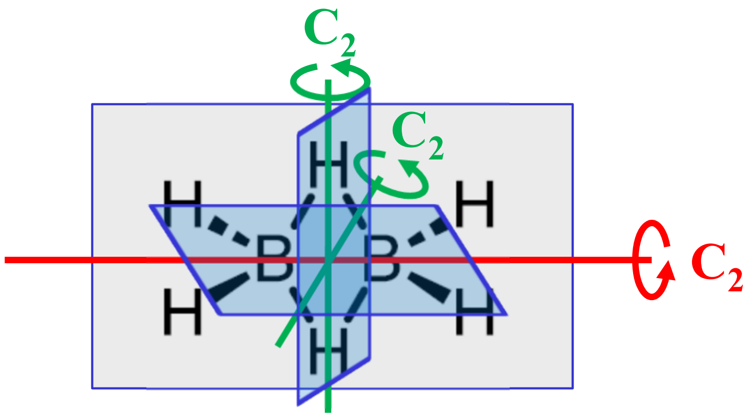
Does it belong to one of the low- or high-symmetry point groups?	NO
Find the principal axis!	C_3
Does it have perpendicular C_2 axes?	YES, three
PF_5 must be D_3, D_{3d}, or D_{3h}!	
Is there a horizontal mirror plane?	YES

The horizontal mirror plane is defined by the P atom and the 3 equatorial fluorine atoms

→ Point group: D_{3h} (E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$), $h = 12$

3. Symmetry and Group Theory

Example: Diborane $(BH_3)_2$

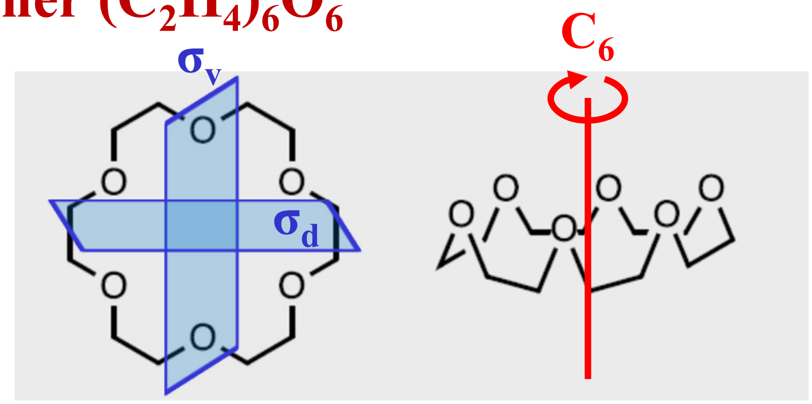


Does it belong to one of the low- or high-symmetry point groups?	NO
Find the principal axis!	C_2
Does it have perpendicular C_2 axes?	YES, two
BH_3 must be D_2, D_{2d}, or D_{2h}!	
Is there a horizontal mirror plane? Each one is perpendicular to one of the three C_2 axes	YES, three

→ Point group: D_{2h} (E, $3C_2$, $3\sigma_h$, i), h = 4

3. Symmetry and Group Theory

Example: 18-Crown-6-Ether $(C_2H_4)_6O_6$



Does it belong to one of the low- or high-symmetry point groups?	NO
Find the principal axis!	C_6
Does it have perpendicular C_2 axes?	NO
Is there a horizontal mirror plane?	NO

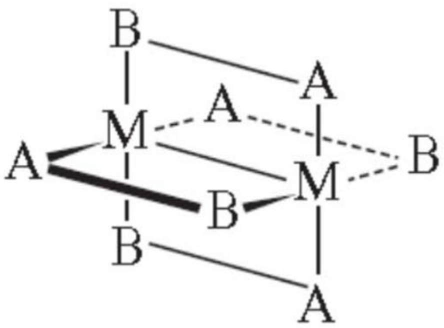
But there are vertical and dihedral mirror planes. The vertical mirror planes contain two O atoms and are parallel to the C_6 axis. The dihedral mirror planes bisect opposite C–C bonds

→ Point group: C_{6v} (E, $2C_6$, $2C_3$, C_2, $3\sigma_v$, $3\sigma_d$), $h = 12$

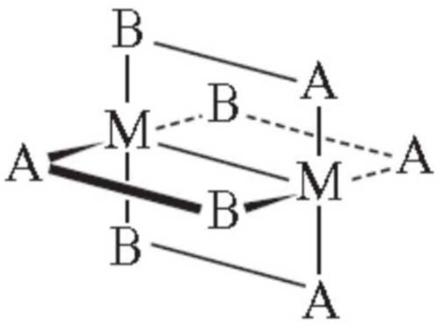
3. Symmetry and Group Theory

Exercise: Apply the decision tree on the left to determine the point groups of such 4 molecule

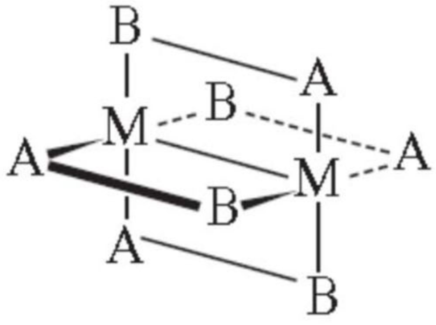
A:



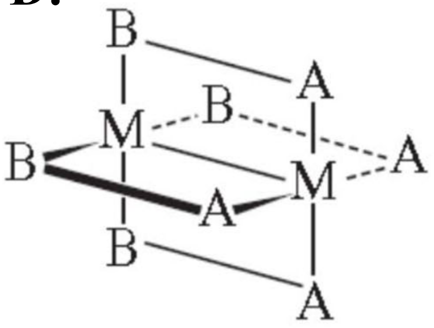
B:

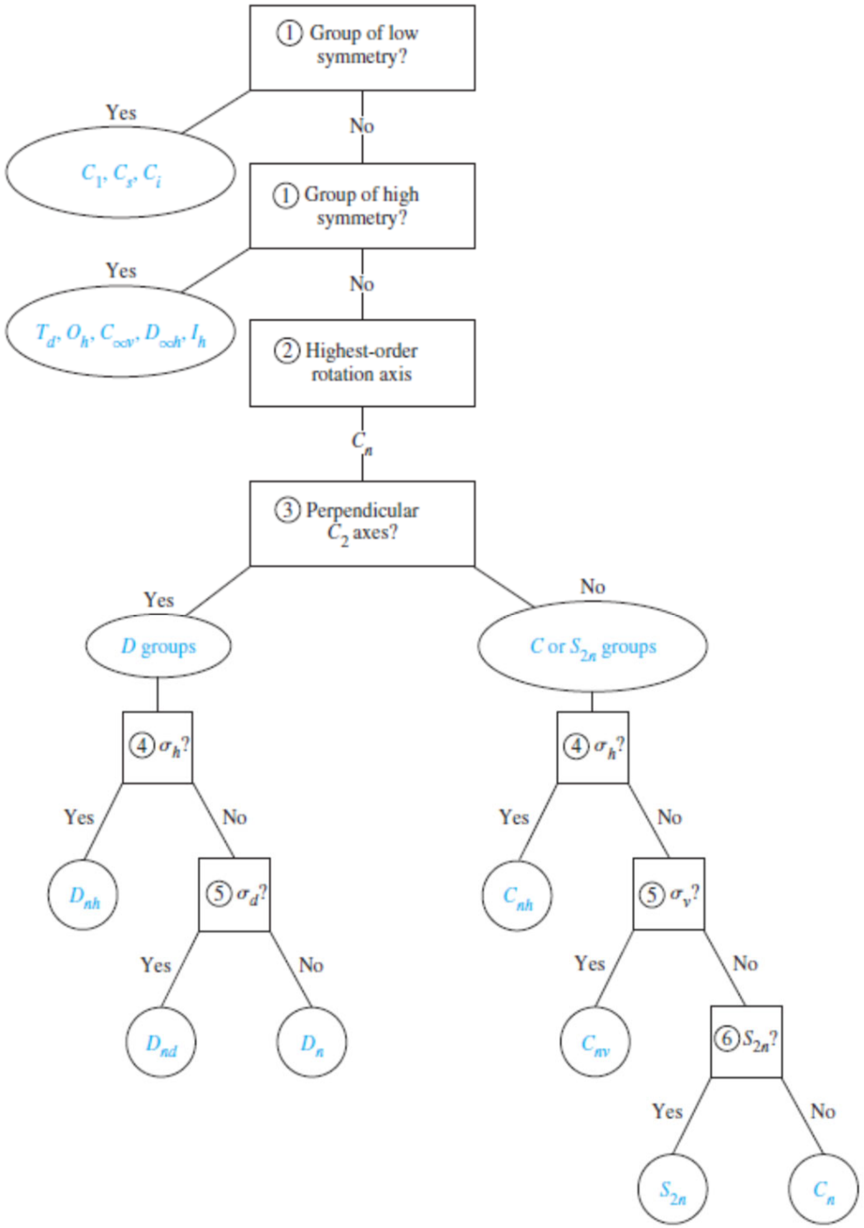


C:



D:





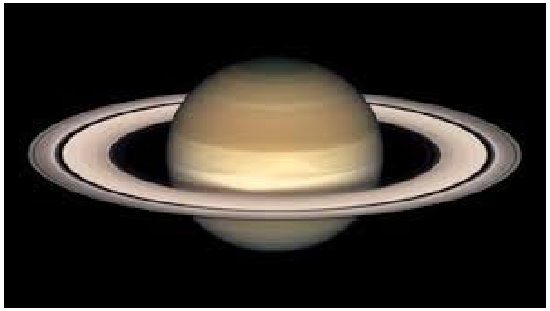
3. Symmetry and Group Theory

Point Group of a Tennis Ball and Celestial Objects

Sphere with point group K_h? NO!

Structure of surface breaks symmetry

D_{2d} (E, 2S_4, C_2, 2C_2', 2σ_d)



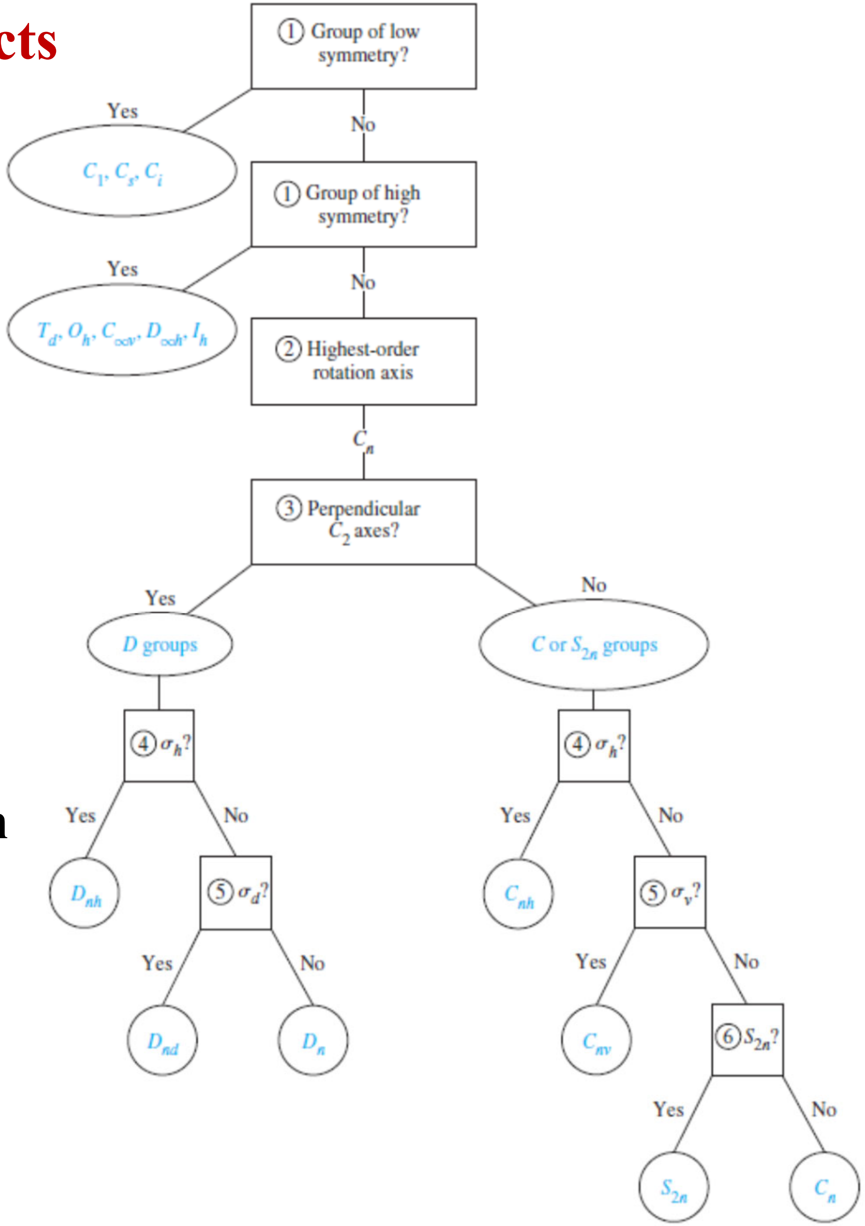
rotation period: 10 h 14 min

d(equatorial) = 120536 km

d(polar) = 108728 km

Rotation breaks symmetry

C_s (E, σ_h)

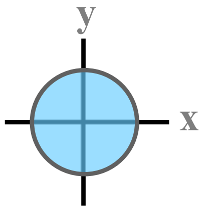


3. Symmetry and Group Theory

Point Group of Atom Orbitals → Orbitals belong to High Symmetry Point Groups

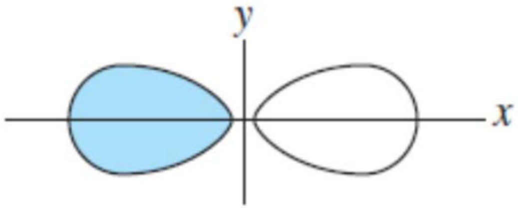
Electron density distribution with lowest energy!

s-orbitals



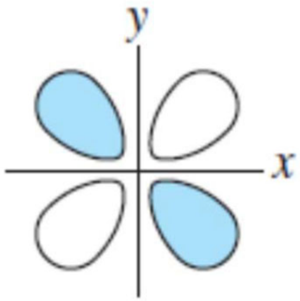
K_h

p-orbitals (p_x)



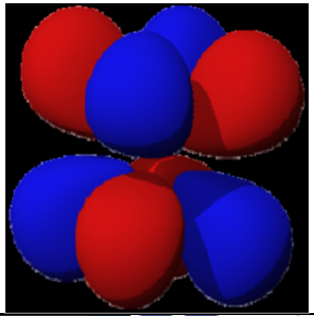
$C_{\infty v}$

d-orbitals (d_{xy})



D_{2h}

f-orbitals (f_{xyz})



T_d

3. Symmetry and Group Theory

Properties of Mathematical Groups

A point group is an example of an algebraic structure called a group, a collection of elements that obey certain algebraic rules!

The 4 key rules that define a group are

1. Each group contains an identity operation that commutes with all other members of the group and leaves them unchanged: $EA = AE = A$

2. Each operation has an inverse operation that yields the identity when multiplied together. For example, in C_{3v} ($E, 2C_3, 3\sigma_v$): $\sigma_v\sigma_v = E$ and $C_3C_3^2 = E$

3. The product of any two operations in the group must also be a member of the group.
For example, in C_{4v} ($E, 2C_4, C_2, 2\sigma_v, 2\sigma_d$): $C_4C_4 = C_2$, $C_4\sigma_v = \sigma_d$, $\sigma_d\sigma_v = C_4$

4. The associative law of multiplication holds: $A(BC) = (AB)C$

Matrices and Matrix Multiplications (Revisited…..)

A matrix is an array of numbers, viz. A_{ij}

$$\begin{array}{cc} & \text{columns} \\ \text{Rows} & \begin{pmatrix} -1 & 4 & 3 \\ -8 & -1 & 7 \\ 2 & 4 & 1 \end{pmatrix} \end{array}$$

column matrix

$$\begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$$

row matrix

$$\begin{bmatrix} 1 & 2 & 3 & 4 \end{bmatrix}$$

To multiply two matrices, add the products, element by element, of each row of the first matrix with each column in the second matrix:

1st

$$\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \times \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} = \begin{pmatrix} (1x1)+(2x3) & (1x2)+(2*4) \\ (3x1)+(4x3) & (3x2)+(4x4) \end{pmatrix} = \begin{pmatrix} 7 & 10 \\ 15 & 22 \end{pmatrix}$$

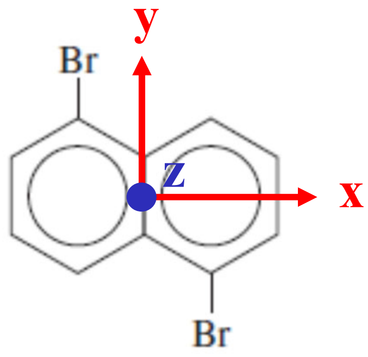
2nd

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \times \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 1 \\ -2 \\ 6 \end{bmatrix}$$

3. Symmetry and Group Theory

Transformation Matrices

Approach: Each symmetry operation can be represented by a 3×3 matrix that shows how the operation transforms a set of *x*, *y*, and *z* coordinates



1,5-dibromonaphthalene

Example: Point group C_{2h} (E, C_2, i, σ_h)

1,5-Dibromnaphthalene
1,2-Dichlorethylene
Oxalic acid

Operation

C_2 (rotation at z-axis) **new coordinates** **t.m.** **old coordinates** **new in terms of old**

transformation matrix (t.m.)

x‘ = -x
y‘ = -y
z‘ = z

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

i (inversion at centre)

x‘ = -x
y‘ = -y
z‘ = -z

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

3. Symmetry and Group Theory

Representations of Groups

The set of four transformation matrices forms a matrix representation of the C_{2h} point group

$$E: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad C_2: \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad i: \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \sigma_h: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

These matrices combine in the same way as the operations in the group, e.g.

$$C_2 \times C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

The sum of the numbers along each matrix diagonal (the character) gives a shorthand version of the matrix representation, called Γ:

C_{2h}	E	C_2	i	σ_h
Γ	3	-1	-3	1

Γ (gamma) is the reducible representation, i.e. it can be further simplified!

3. Symmetry and Group Theory

Irreducible Representations

The transformation matrices can be reduced to their simplest units (1×1 matrices in this case) by block diagonalization with translation vectors x, y, z:

$$E: \begin{array}{cc} \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix} & \begin{array}{c} x \\ y \\ z \end{array} \end{array} \quad C_2: \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix} \quad i: \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [-1] \end{pmatrix} \quad \sigma_h: \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [-1] \end{pmatrix}$$

Now a table of the characters of each 1×1 matrix for each operation can be set up:
„A“ means symmetric with regard to rotation about the principle axis, „B“ means anti-symmetric with regard to rotation about the principle axis, u = ungerade, g = gerade

irreducible representations R

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x
B_u	1	-1	-1	1	y
A_u	1	1	-1	-1	z
Γ	3	-1	-3	1	

The three rows (labeled B_u, B_u, and A_u) are irreducible representations of the C_{2h} point group. They cannot be simplified further. Their characters sum yield Γ (gamma).

3. Symmetry and Group Theory

Irreducible Representations

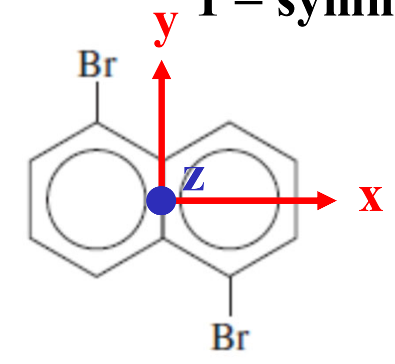
The characters (1, -1) in the table indicate how each irreducible representation transforms with each operation:

----------------- symmetry operations -----------------

irreducible representations R

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x
B_u	1	-1	-1	1	y
A_u	1	1	-1	-1	z

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither



1,5-dibromonaphthalene

A_u transforms like the z-axis:

E → no change
C_2 → no change
i → inverted
σ_h → inverted

Therefore: A_u has the same symmetry as z in point groups C_{2h}

3. Symmetry and Group Theory

Irreducible Representations

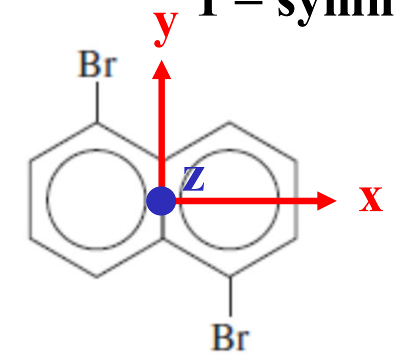
The characters (1, -1) in the table indicate how each irreducible representation transforms with each operation:

----------------- symmetry operations -----------------

irreducible representations R

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x
B_u	1	-1	-1	1	y
A_u	1	1	-1	-1	z

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither



1,5-dibromonaphthalene

B_u transforms like the x- or y-axis:

E → no change
C_2 → inverted
i → inverted
σ_h → no change

Therefore: The two B_u representations are exactly the same

3. Symmetry and Group Theory

Irreducible Representations

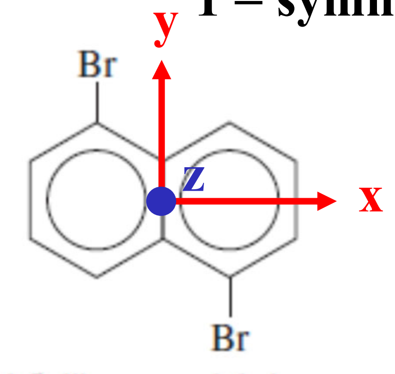
The characters (1, -1) in the table indicate how each irreducible representation transforms with each operation:

----------------- symmetry operations ------------------

irreducible representations R

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x, y
A_u	1	1	-1	-1	z

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither



1,5-dibromonaphthalene

The two B_u representations are thus merged to avoid redundancies

3. Symmetry and Group Theory

Character Tables

List of the complete set of irreducible representations (rows) and symmetry classes (columns) of a point group:

symmetry classes

irreducible representations R

C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

The first column gives the Mulliken label for the representation

- A or B = 1×1 representation that is symmetric (A) or anti-symmetric (B) to the principal axis
- E = 2×2 representation (character under the identity E will be 2)
- T = 3×3 representation (character under the identity E will be 3)
- For point groups with inversion symmetry, the representations are labelled with a subscript g (gerade) or u (ungerade) to denote symmetric or anti-symmetric with respect to inversion
- If present, number subscripts refer to the symmetry of the next operation class after the principle axis. For symmetric use subscript 1 and for anti-symmetric use subscript 2

3. Symmetry and Group Theory

Character Tables

List of the complete set of irreducible representations (rows) and symmetry classes (columns) of a point group:

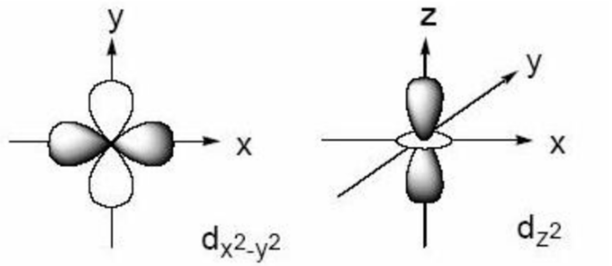
symmetry classes

irreducible representations R

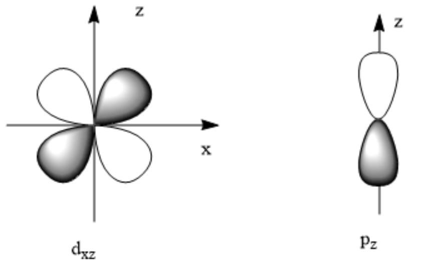
C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

The last two columns give functions (with an origin at the inversion center) that belong to the given representation:

The $d_{x^2-y^2}$ and d_{z^2} orbitals are A_g



The d_{xz}, d_{yz} orbitals are B_g and the p_z orbital is A_u



3. Symmetry and Group Theory

Properties of Character Tables

irreducible representations R

C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

- **The total number of symmetry operations is the order (h)** **h = 4 for point group C_{2h}**
- **Operations belong to the same class if they are identical within coordinate systems accessible by a symmetry operation. One class is listed per column**
- **# irreducible representations = # classes (character tables are square!)**
- **One representation is totally symmetric (all characters = 1)**
- **h is related to the characters (χ) in the following two ways:**

$$\boxed{h = \Sigma\, [\chi_i(E)]^2} \qquad \boxed{h = \Sigma\, [\chi_i(R)]^2}$$

where i and R are indices for the representations and the symmetry operations.

- **Irreducible representations are orthogonal:** $\Sigma \chi_i(R)\chi_j(R) = 0$ **with** $i \neq j$

3. Symmetry and Group Theory

Properties of Character Tables

irreducible representations R

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{3N} (H_2O)	9	-1	1	3		

The number of species N of the four irreducible representations can be calculated by

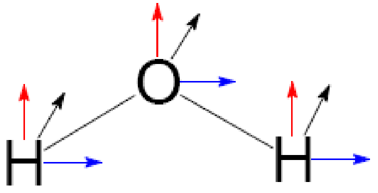
$\boxed{N = 1/h\Sigma\chi_r^x\chi_i^x n^x}$ with

h = total number of symmetry operations

n = number of operation in symmetry class x

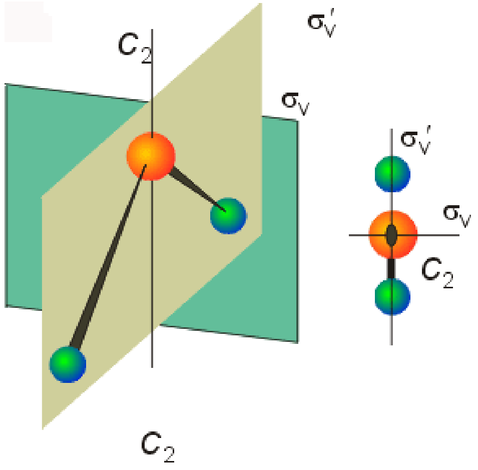
χ_r^x = Character of reducible representation in symmetry class x

χ_i^x = Character of irreducible representation in symmetry class x

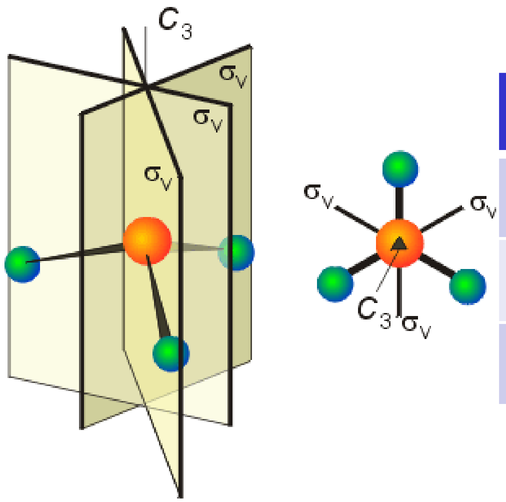


$$A_1 = \tfrac{1}{4}[(9)(1)(1) + (-1)(1)(1) + (1)(1)(1) + (3)(1)(1)] = 3$$
$$A_2 = \tfrac{1}{4}[(9)(1)(1) + (-1)(1)(1) + (1)(-1)(1) + (3)(-1)(1)] = 1$$
$$B_1 = \tfrac{1}{4}[(9)(1)(1) + (-1)(-1)(1) + (1)(1)(1) + (3)(-1)(1)] = 2$$
$$B_2 = \tfrac{1}{4}[(9)(1)(1) + (-1)(-1)(1) + (1)(-1)(1) + (3)(1)(1)] = 3 \quad \rightarrow \quad \Gamma_9 = 3A_1 + A_2 + 2B_1 + 3B_2 = 9$$

Character Tables C_{2v} (e.g. H_2O) and C_{3v} (e.g. NH_3)

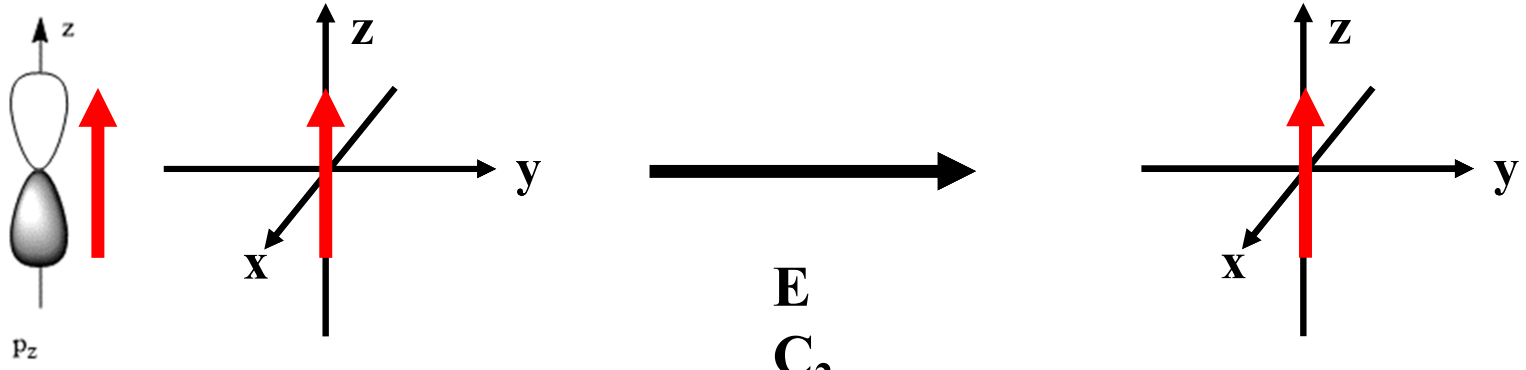


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz



C_{3v}	E	$2C_3$	$3\sigma_v$	linear	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	x, y, R_x, R_y	x^2-y^2, xy, xz, yz

Character Table C_{2v} - p_z Orbital has the Same Symmetry as the Translation Vector z

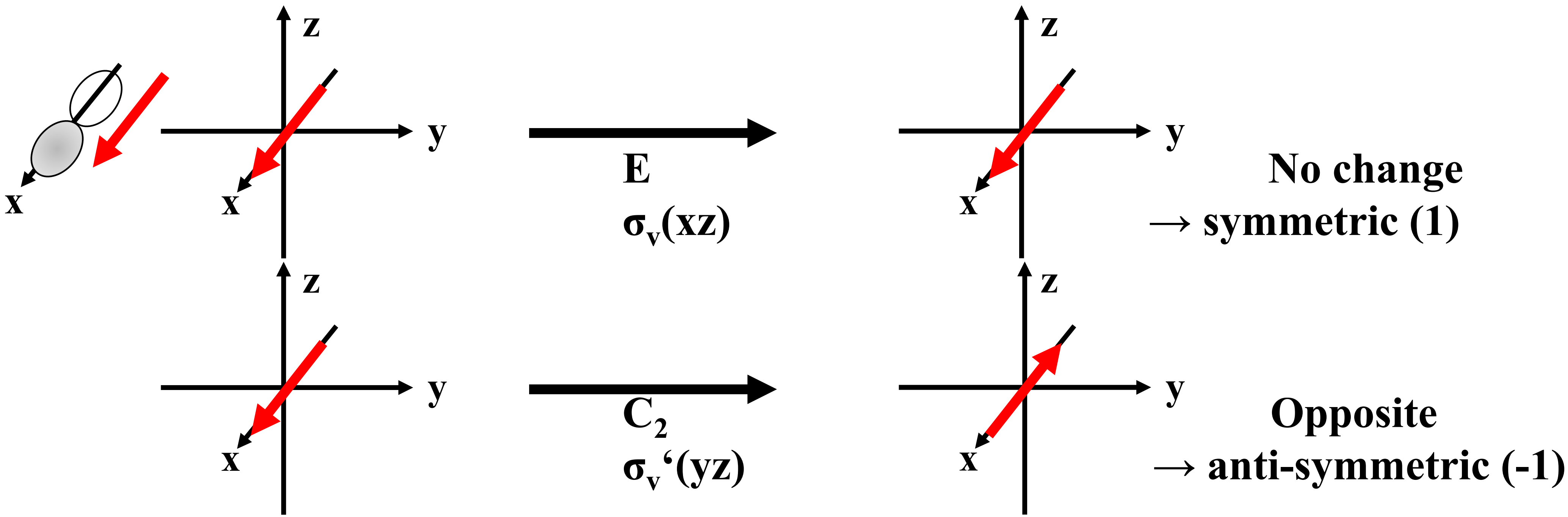


E
C_2
$\sigma_v(xz)$
σ_v‘(yz)   No change → symmetric (character = 1)

C_{2v}	E	C_2	$\sigma_v(xz)$	σ_v‘(yz)	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

3. Symmetry and Group Theory

Character Table C_{2v} - p_x Orbital has the Same Symmetry as the Translation Vector x



E
$\sigma_v(xz)$

No change
→ symmetric (1)

C_2
$\sigma_v'(yz)$

Opposite
→ anti-symmetric (-1)

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

3. Symmetry and Group Theory

Summary

- Each molecule (ion, body) belongs to a point group, which is a full set of symmetry operations that describes the molecule's overall symmetry
- One can use a flow chart (decision tree) to assign point groups
- Character tables show how the complete set of irreducible representations of a point group transforms under all of the symmetry classes of that group
- The tables contain all of the symmetry information in convenient form, while the characters are 1 = symmetric (unchanged), -1 = anti-symmetric (inverted), or 0 = neither
- Irreproducible presentation are A = symmetric or B = anti-symmetric with regard to rotation about the principle axis, and with u = ungerade or g = gerade to denote symmetric or anti-symmetric with respect to inversion
- One can use character tables to understand bonding and spectroscopy

Further reading: F.A. Cotton, Chemical Applications of Group Theory, 3rd edition, 1990

3. Symmetry and Group Theory

Application Areas of Group Theory

1. Predicting the polarity of molecules

- A molecule cannot have a permanent dipole moment if it

a) has a center of inversion	trans-Dichlorethylene
b) belongs to any of the D point groups	CO_2 or BF_3
c) belongs to the cubic groups T or O	CH_4 or SF_6

- A permanent dipole moment is only observed for molecules with point group C_{nv} or C_2 — H_2O, NH_3

The dipole moment itself is invariant under all symmetry operations

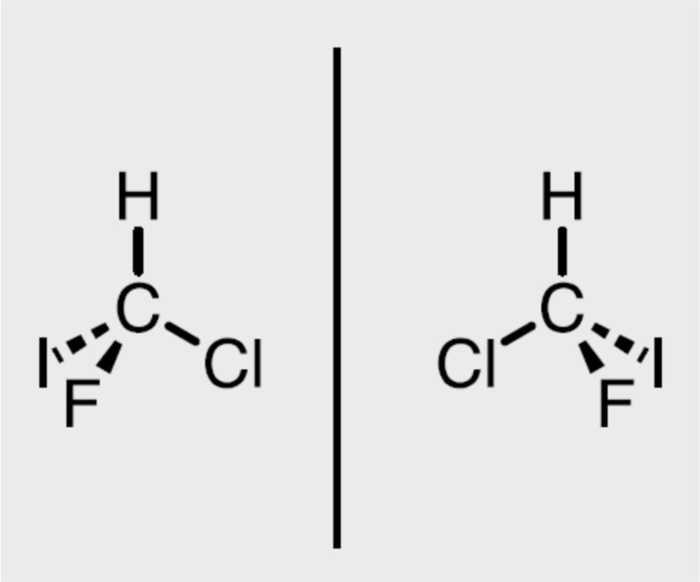
3. Symmetry and Group Theory

Application Areas of Group Theory

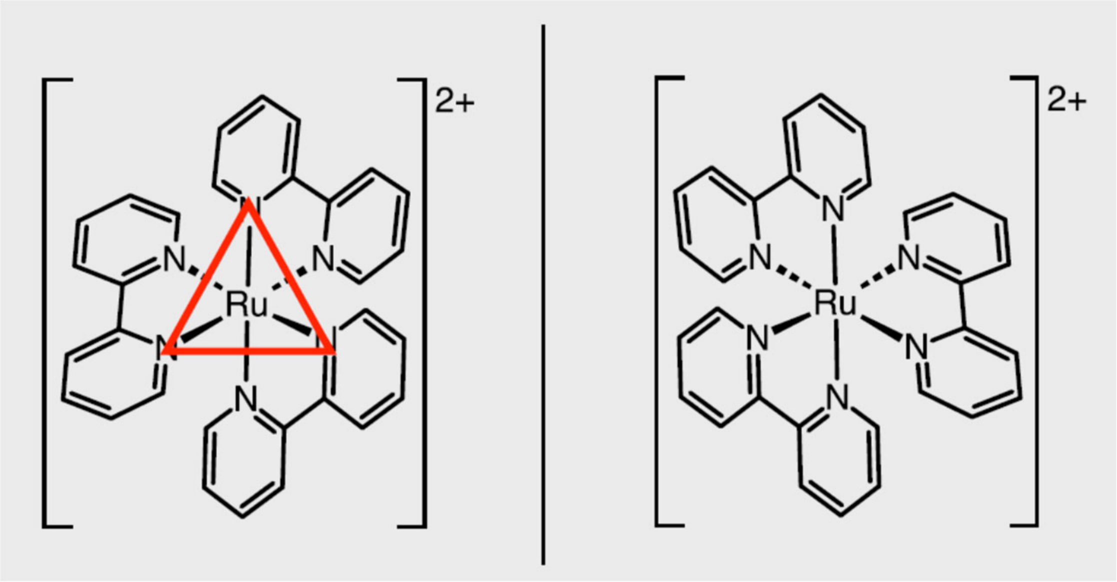
2. Identification of chirality and thus optical activity

- To be chiral, a molecule must lack an improper rotation axis
- In other words, for a molecule to be chiral it must be in the C_1, C_n, or D_n point groups (remember that $\sigma = S_1$, $i = S_2$, and $S^2_{2n} = C_n$)

C_1



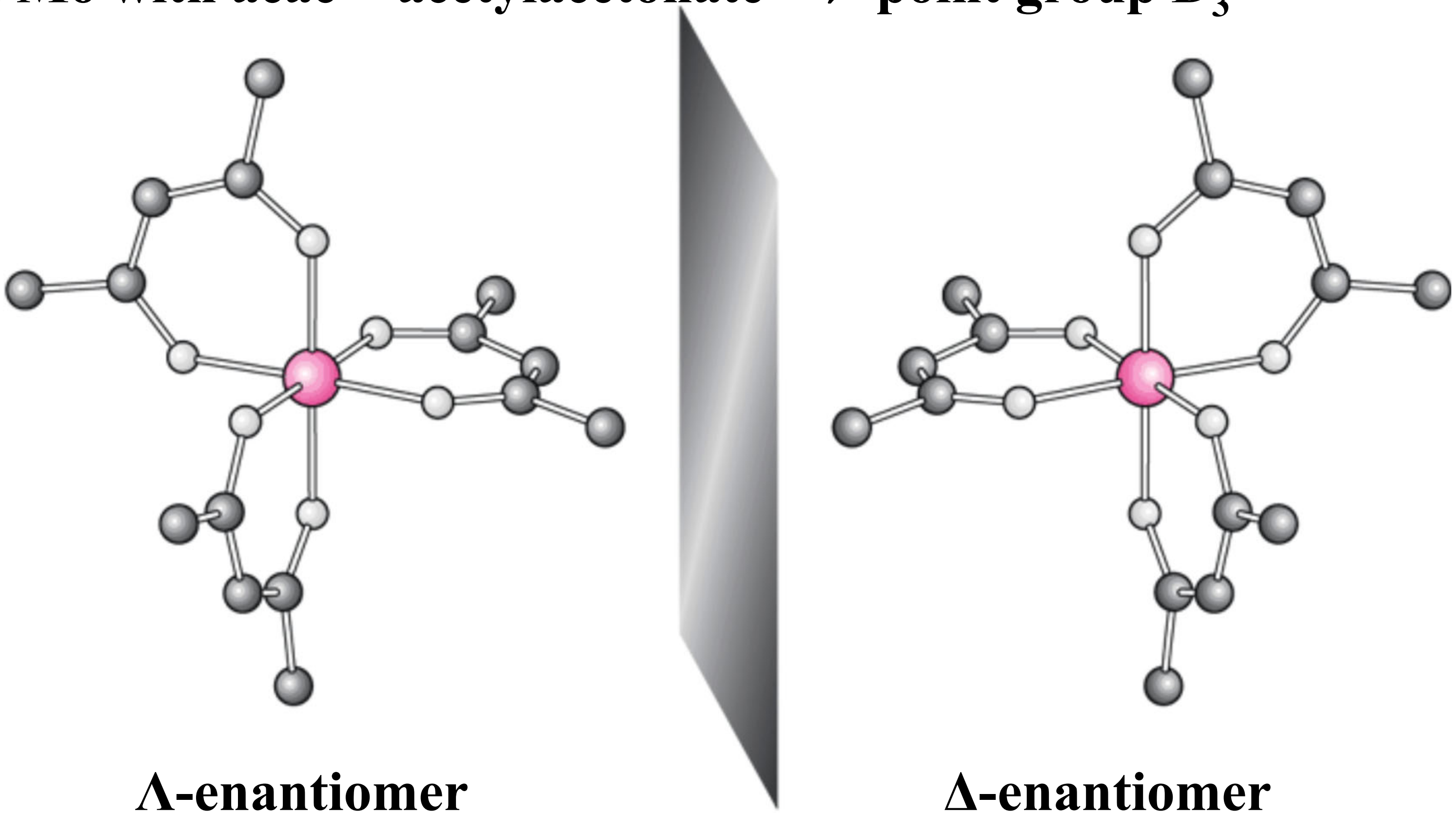
D_3



3. Symmetry and Group Theory

Application Areas of Group Theory

2. Identification of chirality and thus optical activity, e.g. $[M^{III}(acac)_3]^0$ with M = Cr, Mn, Fe, Co, Mo with acac = acetylacetonate → point group D_3



Λ-enantiomer **Δ-enantiomer**

Note: If a molecule is not superimposable on its mirror image, it is said to be chiral!

3. Symmetry and Group Theory

Application Areas of Group Theory

3. Predicting the orbitals used in σ bonds: Group theory can be used to predict which orbitals on a central atom can be mixed to create hybrid orbitals

4. Predicting the orbitals used in molecular orbitals (MOs). Molecular orbitals result from the combining or overlap of atomic orbitals, and they encompass the entire molecule → Chapter MO Theory

5. Derivation of the 32 crystallographic point groups from the infinite number of molecular point groups (see next slide)

The universe is an enormous direct product of representations of symmetry groups,
Steven Weinberg, US Physicist, 1933-2021

3. Symmetry and Group Theory

Application Areas of Group Theory

The seven crystal systems and the 32 crystallographic point groups

Crystal system	Point groups Hermann-Mauguin	Point groups Schoenflies
Triclinic	1, -1	C_1, C_i
Monoclinic	2, m, 2/m	C_2, C_s, C_{2h}
Orthorhombic	2 2 2, m m 2, m m m	D_2, C_{2v}, D_{2h}
Tetragonal	4, -4, 4/m, 4 2 2	C_4, S_4, C_{4h}, D_4
	4 m m, 4 m, 4/m m m	C_{4v}, D_{2d}, D_{4h}
Trigonal	3, -3, 3 2, 3 m, -3 m	C_3, C_{3i}, D_3, C_{3v}, D_{3d}
Hexagonal	6, -6, 6/m, 6 2 2	C_6, C_{3h}, C_{6h}
	6 m m, -6 m 2, 6/m m m	D_6, C_{6v}, D_{3h}, D_{6h}
Cubic	2 3, m 3, 4 3 2, -4 3 m, m 3 m	T, T_h, O, T_d, O_h

Point groups K_h, I_h, $C_{\infty v}$, $D_{\infty h}$ do not enable crystallographic point groups, i.e. all macroscopic crystals can be subdivided into these 32 crystallographic point groups

3. Symmetry and Group Theory

Application Areas of Group Theory

6. IR and Raman spectra can be interpreted by using symmetry

- **Molecular motion includes translations, rotations and vibrations. The total number of degrees of freedom (types of molecular motion) is equal to 3N, where N is the number of atoms in the molecule**

- **Of the 3N types of motion, three represent molecular translations in the x, y, or z directions. Linear molecules have two rotational degrees of freedom, and non-linear molecules have three rotational degrees of freedom**

- **For linear molecules, the number of molecular vibrations:** $3N-3-2 = 3N-5$

- **For non-linear molecules, the number of molecular vibrations:** $3N-3-3 = 3N-6$

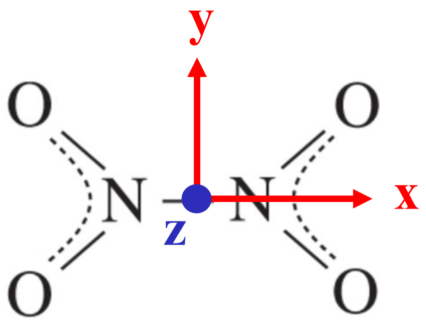
3. Symmetry and Group Theory

Application Areas of Group Theory

Example: N_2O_4 (dimeric NO_2)

- For nonlinear molecules, the number of vibrational modes is 3N - 6, whereas N is the number of atoms and 3N the number of degrees of freedom

- Consider N_2O_4, which belongs to point group D_{2h}



- Each atom can move in three dimensions (3)

- If all atoms move the same amount in the same direction the molecule moves, which is a translation, not a vibration, which accounts for three degrees of freedom

- Molecule can also rotate around the three orthogonal axes, which accounts for three (3) more degrees of freedom

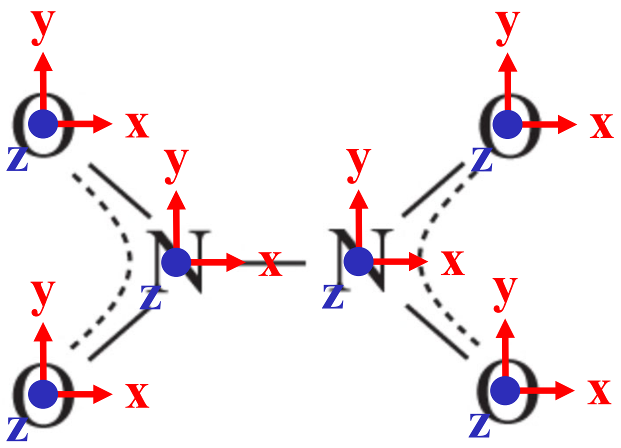
- So for N_2O_4 we predict that there will be 3N - 6 = 12 vibrational modes!

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: N_2O_4 (dimeric NO_2)

One can use character tables to determine the symmetry of all 18 motions and then assign them to translations, rotations, or vibration. Determination of which vibrations are IR or Raman active



Algorithm

1. Assign x, y, z coordinates to each atom

2. Determine how each axis transforms for every class of symmetry operation in the group:

- **If an atom moves, the character for all of its axes is 0**
- **If an atom is stationary and the axis direction is unchanged, its character is 1**
- **If an atom is stationary and the axis direction is reversed, its character is -1**

3. Sum the characters in each symmetry class to determine the reducible representation Γ

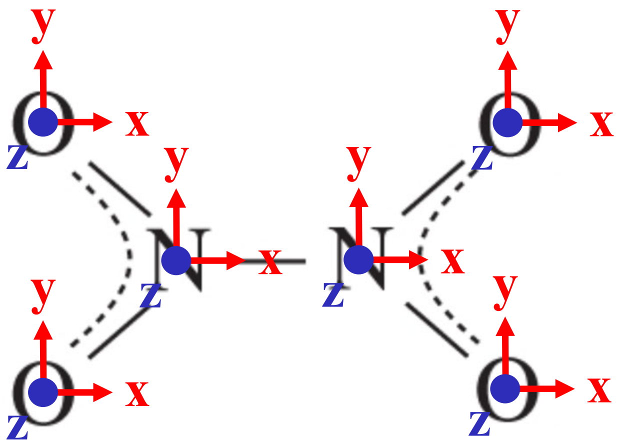
3. Symmetry and Group Theory

Application Areas of Group Theory

Example: N_2O_4 (dimeric NO_2) → Reducible representation Γ

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)
Γ	18	0	0	-2	0	6	2	0

E:	all 18 axes unchanged	→ $\chi = 18$
$C_2(z)$:	all atoms move	→ $\chi = 0$
$C_2(y)$:	all atoms move	→ $\chi = 0$
$C_2(x)$:	oxygens move N's x unchanged N's y,z reversed	→ $\chi = -2$
i:	all atoms move	→ $\chi = 0$
σ(xy):	z axes reversed x, y axes unchanged	→ $\chi = 6$
σ(xz):	oxygens move N's x,z unchanged N's y reversed	→ $\chi = 2$
σ(yz):	all atoms move	→ $\chi = 0$



Γ is the reducible representation for all motions of N_2O_4

3. Symmetry and Group Theory

Application Areas of Group Theory

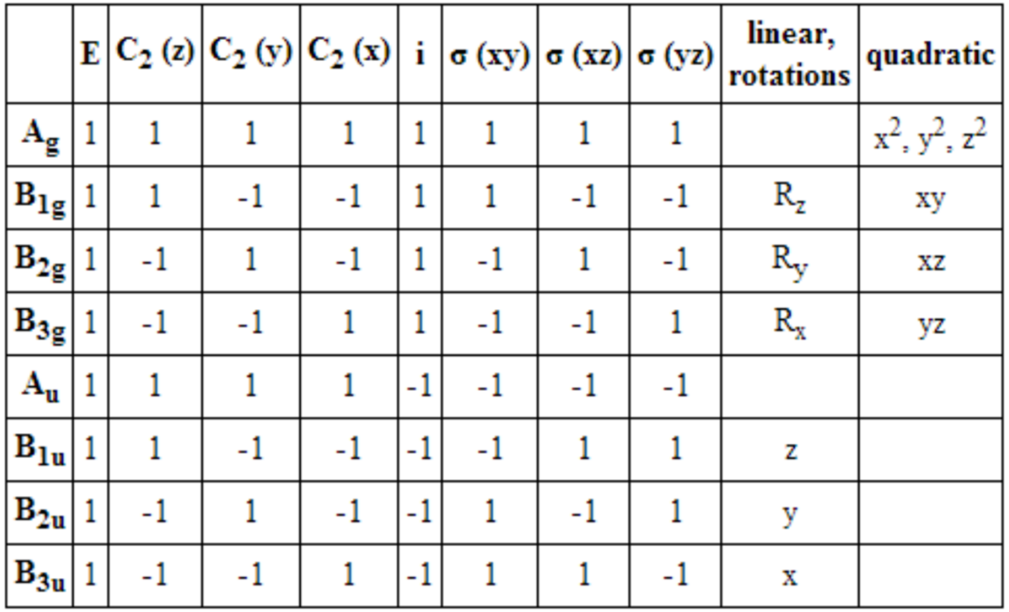
Example: N_2O_4 (dimeric NO_2)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)
Γ	18	0	0	-2	0	6	2	0

4. Now reduce Γ to a number N of irreducible representations of a given type upon using the character table and the following property of groups: $N = 1/h\Sigma\chi_r^x\chi_i^x n^x$ with h = order

$N(A_g) = 1/8*[18+0+0-2+0+6+2+0] = 3$
$N(B_{1g}) = 1/8*[18+0+0+2+0+6-2+0] = 3$
$N(B_{2g}) = 1/8*[18+0+0+2+0-6+2+0] = 2$
$N(B_{1u}) = 1/8*[18+0+0+2+0-6+2+0] = 2$
$N(B_{3g}) = 1/8*[18+0+0-2+0-6-2+0] = 1$
$N(A_u) = 1/8*[18+0+0-2+0-6-2+0] = 1$
$N(B_{2u}) = 1/8*[18+0+0+2+0+6-2+0] = 3$
$N(B_{3u}) = 1/8*[18+0+0-2+0+6+2+0] = 3$

Character table for D_{2h} point group



	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

→ $\Gamma = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: N_2O_4 (dimeric NO_2)

$\Gamma = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$

5. Finally, use the character table to subtract the translations and rotations, leaving the representations corresponding to the vibrations

Translations (x, y, z) = $B_{1u} + B_{2u} + B_{3u}$

Rotations (R_x, R_y, R_z) = $B_{1g} + B_{2g} + B_{3g}$

→ Vibrational modes (all that remain) =
$3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

→ These are the symmetries of the 12 vibrational modes of N_2O_4

Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

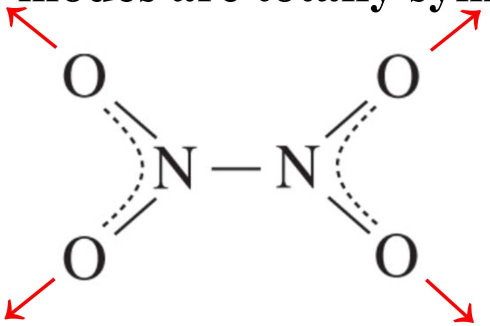
3. Symmetry and Group Theory

Application Areas of Group Theory

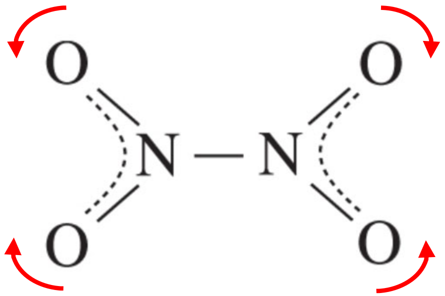
Example: N_2O_4 (dimeric NO_2)

Vibrational modes = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

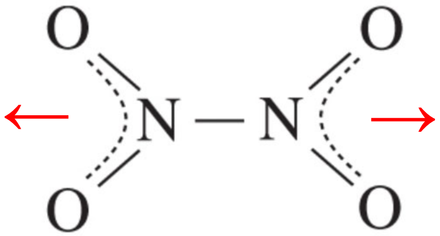
Using the character table, one can guess how these modes might look like, e.g. the three A_g modes are totally symmetric:



NO_2 symmetric stretch



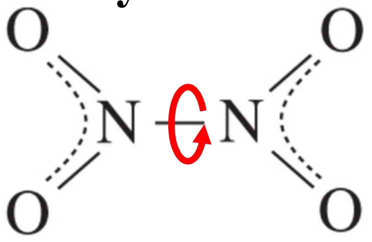
NO_2 symmetric bend



N-N stretch

The A_u mode is symmetric w.r.t C_2 but antisymmetric with respect to σ and i:

Neither a change in dipole moment nor in polarizibility is observed



3. Symmetry and Group Theory

Application Areas of Group Theory

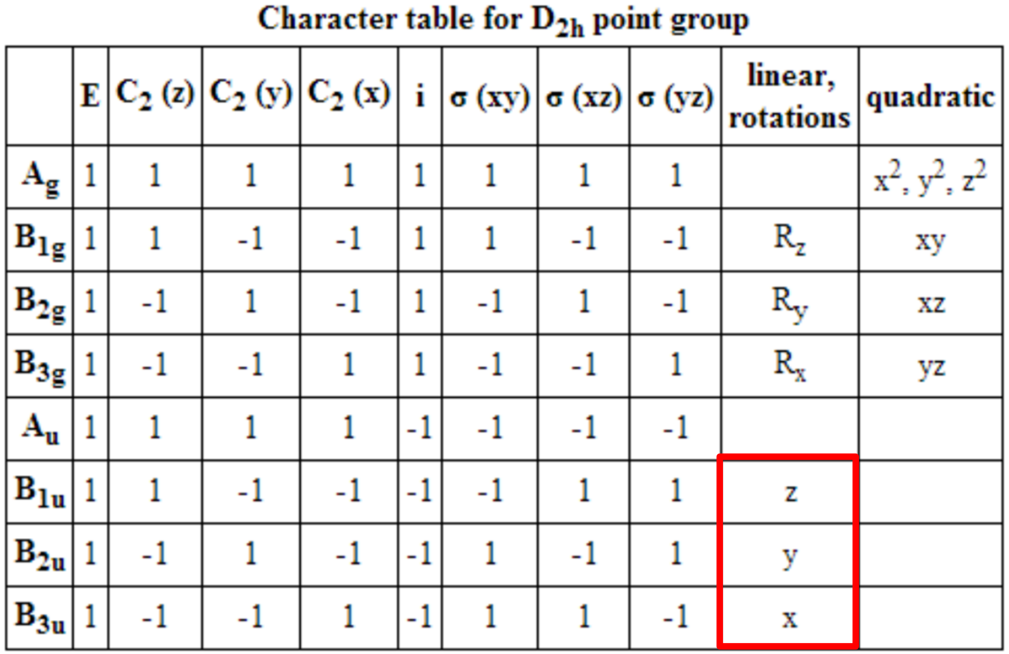
Example: N_2O_4 (dimeric NO_2)

The character table tells us whether the vibrational modes are IR active and/or Raman active

To be IR active (allowed), the vibration must change the dipole moment of the molecule
→ Only irreducible representations with x, y, or z symmetry do this

All 12 N_2O_4 vibrations:
$3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

IR active are $B_{1u} + 2B_{2u} + 2B_{3u}$



Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: N_2O_4 (dimeric NO_2)

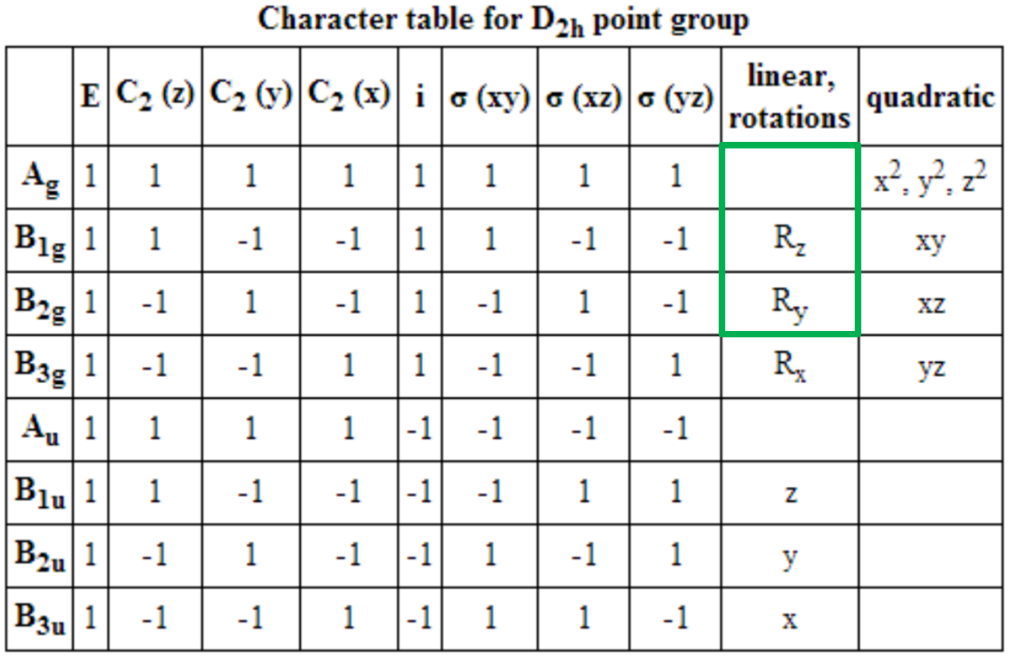
The character table tells us whether the vibrational modes are IR active and/or Raman active

To be Raman active (allowed), the vibration must change the polarizability of the molecule → Only irreducible representations that transform like the binary products of x, y, and z, i.e., xy, xz, yz, x^2, y^2, z^2 or their linear combinations do this

All 12 N_2O_4 vibrations:
$3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

Raman active are $3A_g + 2B_{1g} + B_{2g}$

Note that the A_u mode is IR and Raman silent



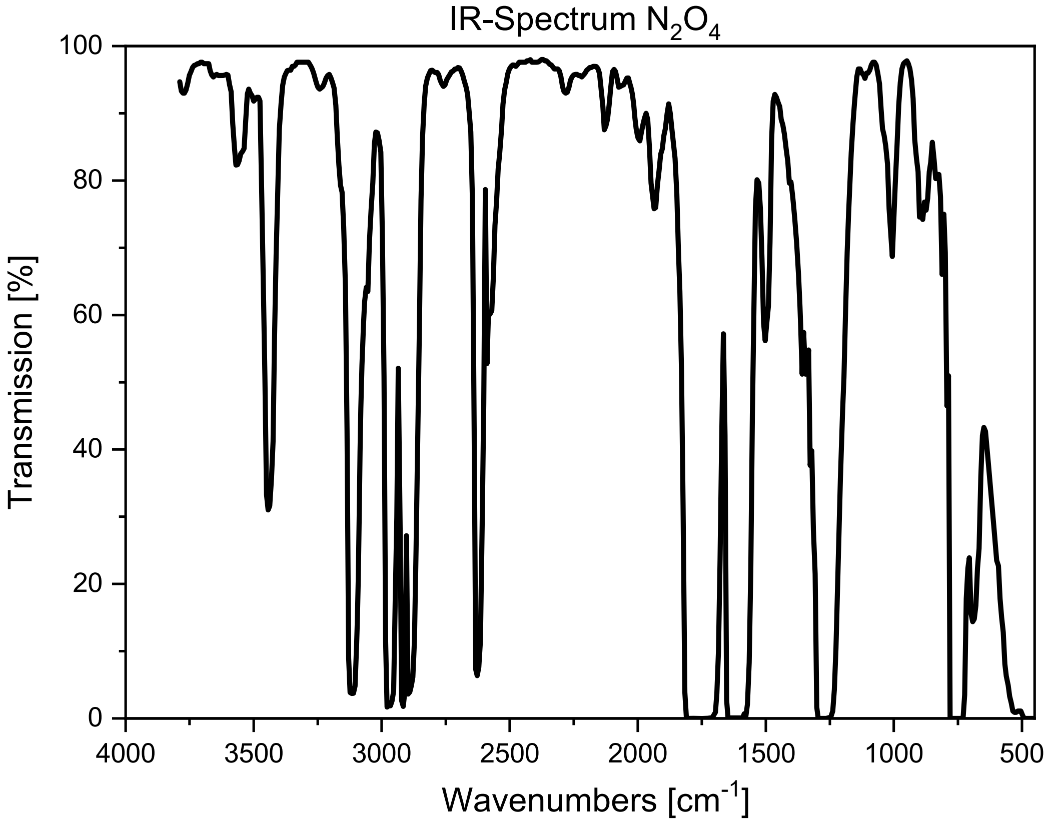
Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

3. Symmetry and Group Theory

Application Areas of Group Theory

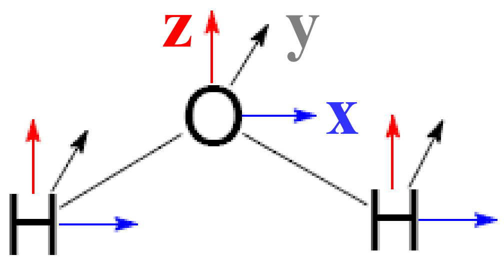
Example: N_2O_4 (dimeric NO_2) → Recorded IR spectrum shows more than 5 bands



Origin: Beyond the fundamental vibrations overtones and combination vibrations appear!

3. Symmetry and Group Theory

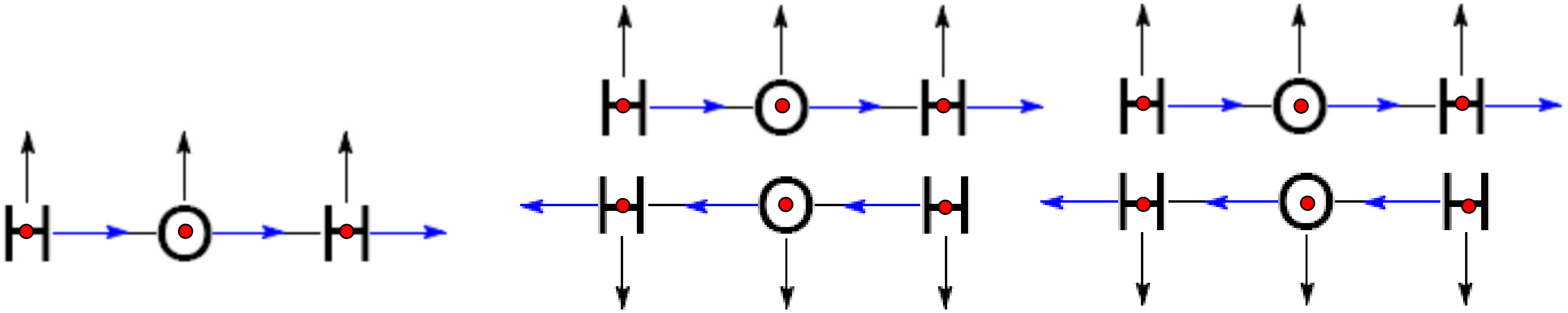
Application Areas of Group Theory



Example: H_2O (non-linear molecule) → C_{2v} with N = 3

To obtain Γ_{red} for all molecular motion, we must consider the symmetry properties of the three cartesian coordinates on all atoms of the molecule
The molecule lies in the xz plane. The x axis is drawn in blue, and the y axis is drawn in black. The red arrows indicate the principle z axis

Derivation of the reducable character for C_2 operation around the principle axis (z):



z-coordinate **x-coordinate** **y-coordinate**

The character for the C_2 operation will be +1 (z axis on oxygen), -1 (y axis on oxygen), and -1 (x axis on oxygen) = -1

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: H_2O (non-linear molecule) → C_{2v} with N = 3

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{3N} (H_2O)	9	-1	1	3		

A_1 = ¼[(9)(1)(1) + (-1)(1)(1) + (1)(1)(1) + (3)(1)(1)] = 3
A_2 = ¼[(9)(1)(1) + (-1)(1)(1) + (1)(-1)(1) + (3)(-1)(1)] = 1
B_1 = ¼[(9)(1)(1) + (-1)(-1)(1) + (1)(1)(1) + (3)(-1)(1)] = 2
B_2 = ¼[(9)(1)(1) + (-1)(-1)(1) + (1)(-1)(1) + (3)(1)(1)] = 3

→ $\Gamma_9 = \Gamma_{3N}(H_2O) = 3A_1 + A_2 + 2B_1 + 3B_2 = 9$

Note that there are 9 modes of motion, which include vibrations, rotations, and translations

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: H_2O (non-linear molecule) → C_{2v} with N = 3

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{3N} (H_2O)	9	-1	1	3		

Translations have the same symmetry properties as the x, y, and z vectors, i.e. with the irreducible representations A_1, B_1, and B_2

$\rightarrow \Gamma_{translation}(H_2O) = A_1 + B_1 + B_2 = 3$

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: H_2O (non-linear molecule) → C_{2v} with N = 3

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{3N} (H_2O)	9	-1	1	3		

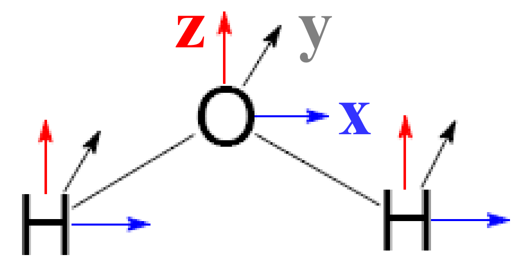
Rotations have the same symmetry properties as the linear R_x, R_y, and R_z vectors, i.e. with the irreducible representations A_2, B_1, and B_2

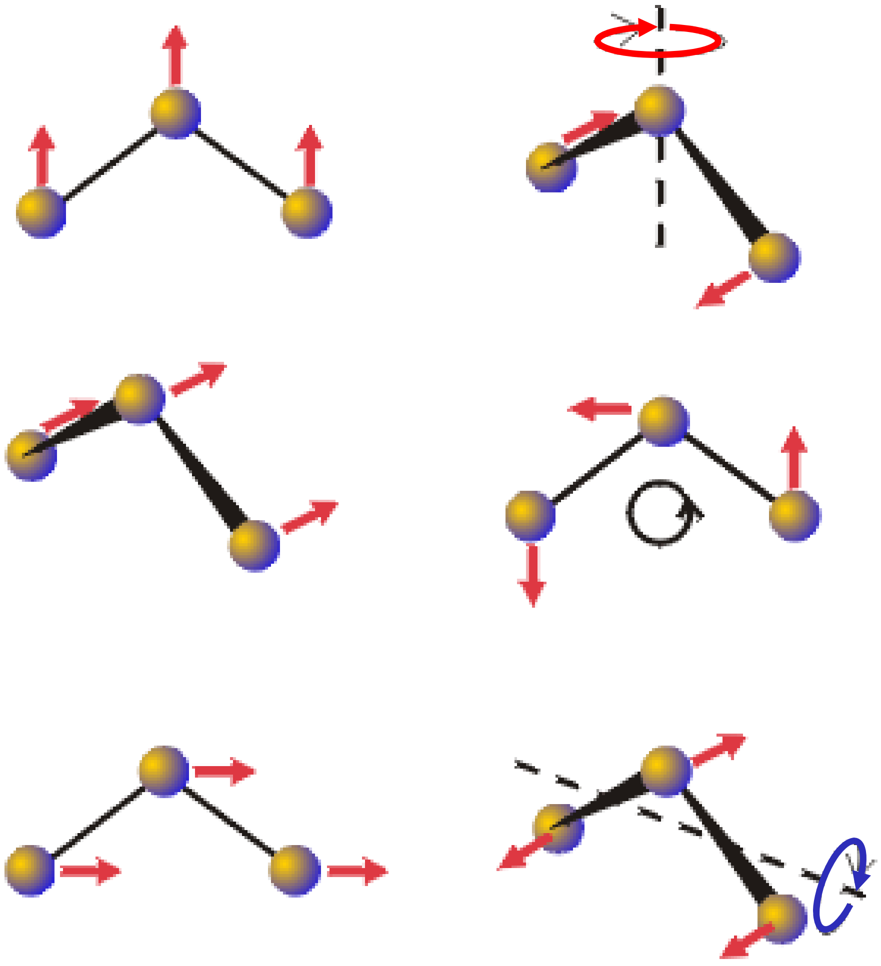
$\rightarrow \Gamma_{rotation}(H_2O) = A_2 + B_1 + B_2 = 3$

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: H_2O (non-linear molecule) → C_{2v} with $N = 3$





Translation z

Rotation R_z

Translation y

Rotation R_y

Translation x

Rotation R_x

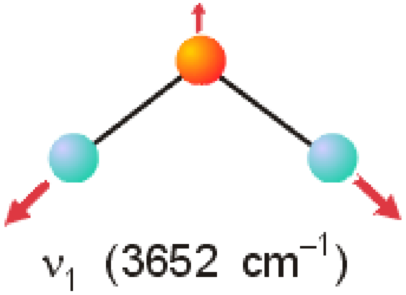
3. Symmetry and Group Theory

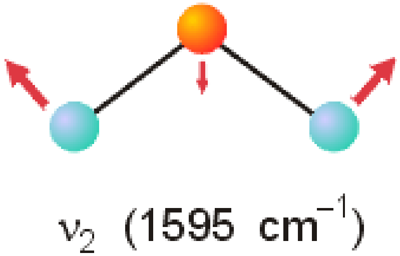
Application Areas of Group Theory

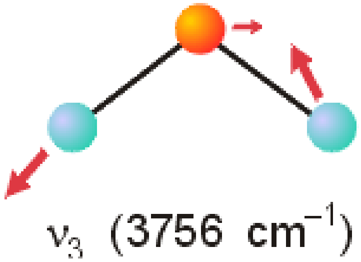
Example: H_2O (non-linear molecule) → C_{2v} with N = 3

$$\Gamma_{vibration}(H_2O) = (3A_1 + A_2 + 2B_1 + 3B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2)$$
$$= 2A_1 + B_1$$
$$= 3$$

- **Two vibrations are symmetric with respect to all symmetry operations of the group**
  A_1 symmetric stretch ν_1
  A_1 bend ν_2
- **One vibration is asymmetric with respect to rotation and reflection perpendicular to the molecular plane**
  B_1 asymmetric stretch ν_3


ν_1 (3652 cm^{-1})


ν_2 (1595 cm^{-1})


ν_3 (3756 cm^{-1})

3. Symmetry and Group Theory

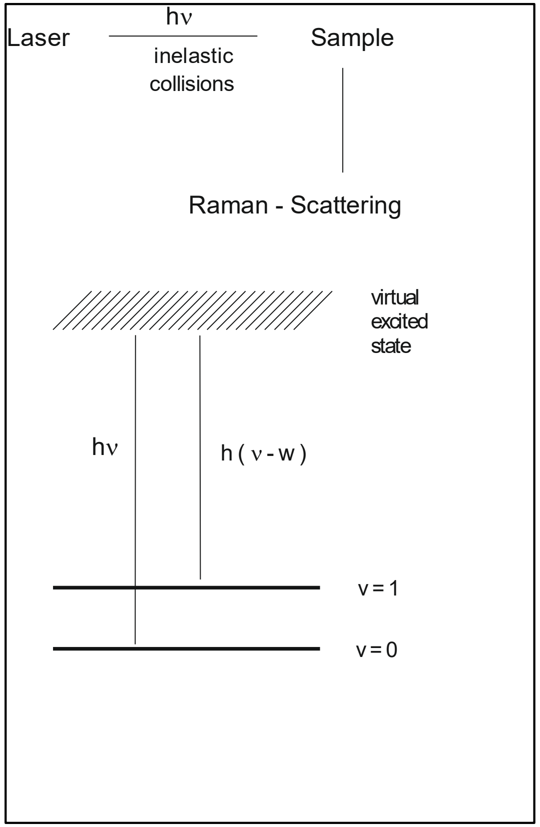
Application Areas of Group Theory

Example: H_2O (non-linear molecule) → C_{2v} with N = 3

For a molecular vibration to be observable in the infrared spectrum (IR active), it must change the dipole moment of the molecule. The dipole moment vectors have the same symmetry properties as cartesian coordinates → x, y, and z

Raman spectroscopy measures the wavelengths of radiation (in the IR range) scattered by a molecule. Certain molecular vibrations will cause the frequency of the scattered radiation to be less than the frequency of the incident radiation

For a molecular vibration to be observable in the Raman spectrum (Raman active), it must change the polarizability of the molecule. The polarizability has the same symmetry properties as the quadratic functions → xy, yz, xz, x^2, y^2, and z^2



3. Symmetry and Group Theory

Application Areas of Group Theory

Example: H_2O (non-linear molecule): C_{2v} with N = 3

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{3N} (H_2O)	9	-1	1	3		

Both vibrations with A_1 symmetry have z as a basis function, so they are IR active. They also have quadratic basis functions, so they are Raman active two of water as well. This will result in two bands (at different frequencies) in the IR and Raman spectrum.

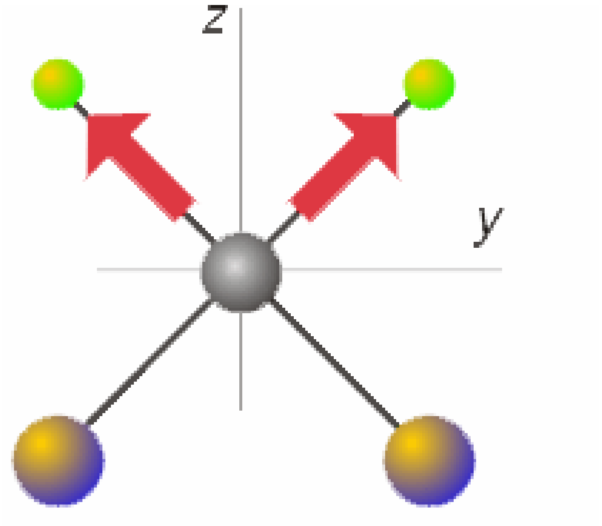
The vibration with B_1 symmetry has x and xz as basis functions. This vibration will be both IR active and Raman active. It will appear as a band (at same frequency) in both spectra.

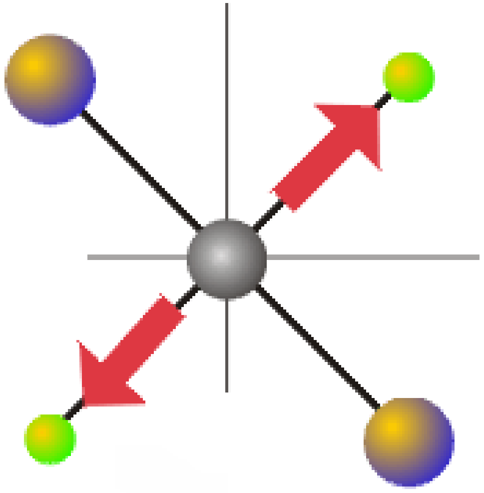
Both the IR and Raman spectra should show three different absorption bands.

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: cis- and trans-[M(CO)$_2$L$_2$] (square-planar molecules) → C$_{2v}$ or D$_{2h}$



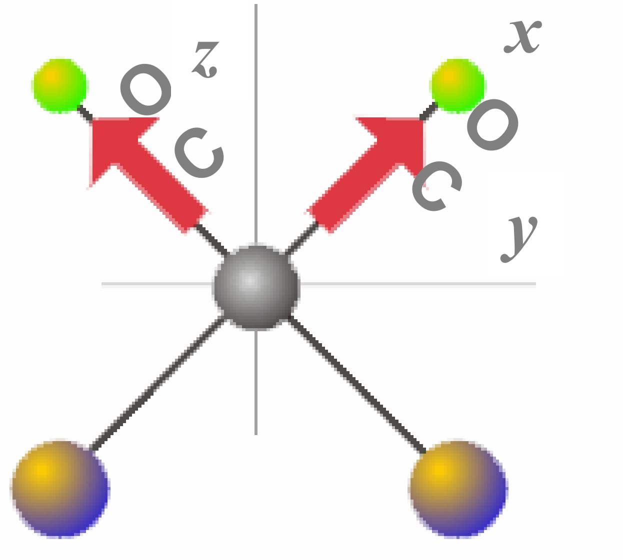


cis-isomer (C$_{2v}$) **trans-isomer (D$_{2h}$)**

Is vibrational spectroscopy able to distinguish between the cis- and trans-isomer?

3. Symmetry and Group Theory

Application Areas of Group Theory



Example: cis-$[M(CO)_2L_2] \rightarrow C_{2v}$

Determine reducible representations Γ_{CO} of the C≡O bonds in each molecule

$\chi = 1$ if unchanged for 2 CO

$\chi = 0$ if reversed for 2 CO

cis-isomer(C_{2v})

C_{2v}	E	C_2	$\sigma_v(xz)$	σ_v'(yz)	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ(CO)	2	0	2	0		

Γ_{CO} reduces to $A_1 + B_1$

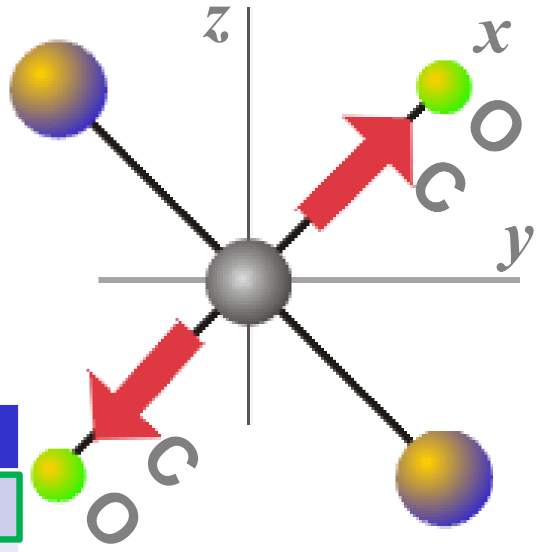
A_1 is a symmetric stretch, and B_1 is an asymmetric stretch, both are IR and Raman active

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: trans-$[M(CO)_2L_2] \rightarrow D_{2h}$

Determine reducible representations Γ_{CO} of the C≡O bonds in each molecule



trans-isomer(D_{2h})

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)	linear	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	
Γ(CO)	2	0	0	2	0	2	2	0		

Γ_{CO} reduces to $A_g + B_{3u}$ whereby A_g is a symmetric stretch (basis x^2, y^2, and z^2) and thus Raman active, while B_{3u} is an asymmetric stretch (basis x) and thus IR active

3. Symmetry and Group Theory

Application Areas of Group Theory

Example: cis- and trans-$[M(CO)_2L_2]$ (square-planar molecules) → C_{2v} or D_{2h}

Exclusion rule:
If a molecule has a center of symmetry (i), none of its modes of vibration can be both infrared and Raman active

The cis- and trans-isomers of the square planar complex $[ML_2(CO)_2]$ can be easily distinguished by vibrational spectroscopy

The cis-isomer has absorption bands that are observed in both the IR and Raman spectra, whereas the trans-isomer with a center of symmetry (i) does not.

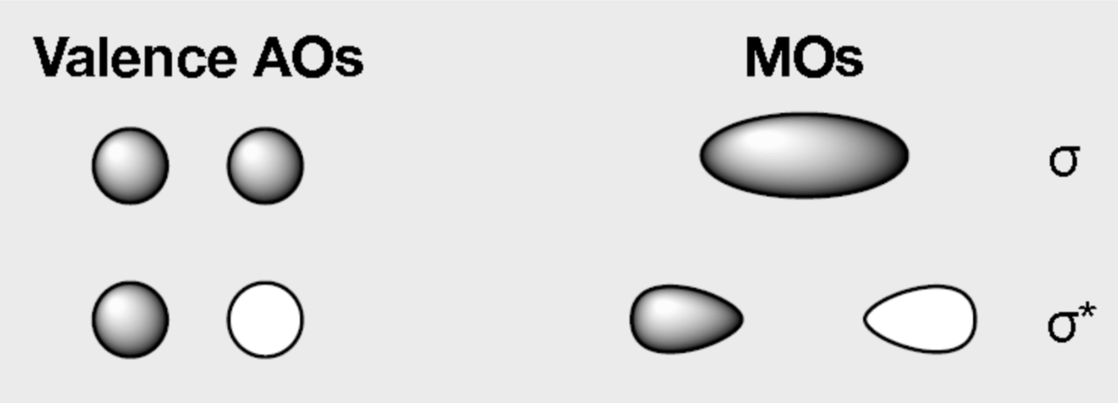
4. Molecular Orbital (MO) Theory

MO Theory is an Approach to Understanding the Electronic Structure of Molecules

- **MO theory assumes that the valence electrons of the atoms within a molecule become the valence electrons of the entire molecule**

- **Molecular orbitals are constructed by taking linear combinations of the valence orbitals of atoms within the molecule**

Consider H_2: 1s-1s



- **Symmetry allow to treat more complex molecules by helping to determine which AOs combine to yield MOs**

4. Molecular Orbital (MO) Theory

The Most Common Approach to Approximating MOs is the Linear Combination of Atomic Orbitals (LCAO) Method

$$\psi_n = \sum_i c_{ni}\phi_i = c_{n1}\phi_1 + c_{n2}\phi_2 + c_{n3}\phi_3 + \cdots$$

with ϕ_i = Valence AOs of the atoms that make up the molecule

c_{ni} = Weighting factors that tell how much of each AO is in the MO

Three conditions must be fulfilled for AOs to interact and form MOs:

- The AOs must have the same symmetry
- The AOs must have similar energy
- The AOs must have spatial overlap

Like any physical model, the LCAO MO theory provides only an approximation to the exact electronic structure of molecules

4. Molecular Orbital (MO) Theory

MO Mathematics for Diatomic Molecules

Example: Two atoms A and B with a single atomic orbital, viz. ϕ_1 and ϕ_2 A-B

Each MO may be written as an LCAO $\psi = c_1\phi_1 + c_2\phi_2$

The probability density is given by the square of the wavefunction

$$\psi^2 = (c_1\phi_1 + c_2\phi_2)^2 = c_1^2\phi_1^2 + c_2^2\phi_2^2 + 2c_1c_2\phi_1\phi_2$$

$$\int\psi^2 d\tau = \underbrace{c_1^2\int\phi_1^2 d\tau}_{\text{probability of finding the electron close to atom A}} + \underbrace{c_2^2\int\phi_2^2 d\tau}_{\text{probability of finding the electron close to atom B}} + \underbrace{2c_1c_2\int\phi_1\phi_2 d\tau}_{\text{overlap term, important between the atoms}}$$

4. Molecular Orbital (MO) Theory

MO Mathematics for Diatomic Molecules

$$\int\psi^2 d\tau = \underbrace{c_1^2\int\phi_1^2 d\tau}_{=1} + \underbrace{c_2^2\int\phi_2^2 d\tau}_{=1} + \underbrace{2c_1c_2\int\phi_1\phi_2 d\tau}_{=S}$$

Therefore, one can simplify the integral probability density to

$$\int\psi^2 d\tau = c_1^2 + c_2^2 + 2c_1c_2S$$

if the individual AOs are normalized:

$\int \phi_1^2 d\tau = 1$ **and** $\int \phi_2^2 d\tau = 1$

$\Rightarrow$ **100% probability of finding the electron somewhere for each free atom**

4. Molecular Orbital (MO) Theory

MO Mathematics for Diatomic Molecules

For two identical AOs on identical atoms, the electrons are equally shared

$\psi = c_1\phi_1 + c_2\phi_2$ **with** $c_1^2 = c_2^2 \Rightarrow c_1 = \pm c_2$

Thus we have two MOs obtained from two AOs of the equal atoms

$\psi_+ = c_{+,1}(\phi_1 + \phi_2)$ $\psi_- = c_{-,1}(\phi_1 - \phi_2)$

After normalisation by setting $\int\psi_+^2 d\tau = 1$ **and** $\int\psi_-^2 d\tau = 1$ **with**

$c_{+,1}^2 + c_{+,1}^2 + 2c_{+,1}c_{+1}S = 1 \Rightarrow 2c_{+,1}^2 + 2c_{+,1}^2S = 1 \Rightarrow 2(1+S) = 1/c_{+,1}^2 \Rightarrow c_{+,1} = 1/[2(1+S)]^{1/2}$

$c_{-,1}^2 + c_{-,1}^2 - 2c_{-,1}c_{-1}S = 1 \Rightarrow 2c_{-,1}^2 - 2c_{-,1}^2S = 1 \Rightarrow 2(1-S) = 1/c_{-,1}^2 \Rightarrow c_{-,1} = 1/[2(1-S)]^{1/2}$

one obtain $\psi_+ = 1/[2(1+S)]^{1/2}(\phi_1 + \phi_2)$ $\psi_- = 1/[2(1-S)]^{1/2}(\phi_1 - \phi_2)$

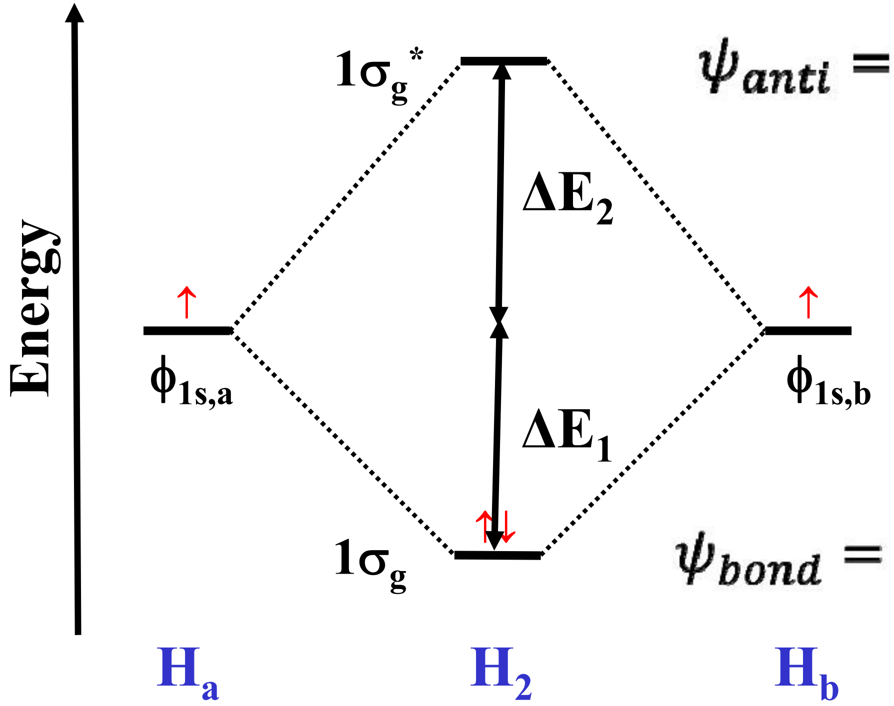
bonding wavefunction **antibonding wavefunction**

where S is the overlap integral $S = \int\phi_1\phi_2 d\tau$ **with** $0 \leq S \leq 1$

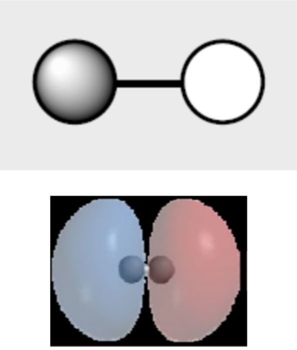
4. Molecular Orbital (MO) Theory

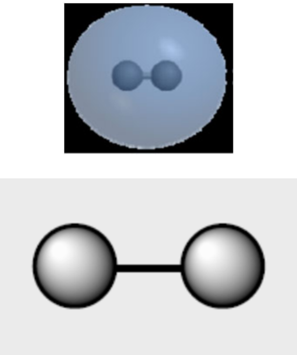
LCAO MO Diagram for H_2

Two 1s atomic orbitals combine to create one bonding and one antibonding molecular orbital



$$\psi_{anti} = \frac{1}{[2(1-S)]^{1/2}}(\phi_{1sa} - \phi_{1sb})$$





$$\psi_{bond} = \frac{1}{[2(1+S)]^{1/2}}(\phi_{1sa} + \phi_{1sb})$$

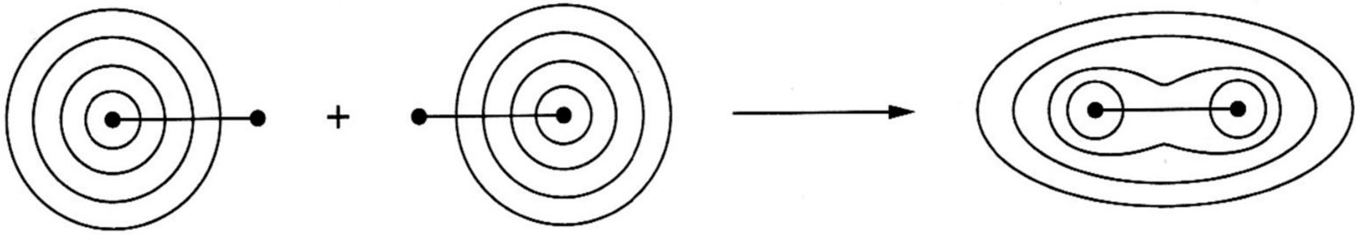
$\Delta E_2 > \Delta E_1$ → the antibonding orbital is always somewhat more antibonding than the bonding orbital is bonding

4. Molecular Orbital (MO) Theory

MOs for H_2

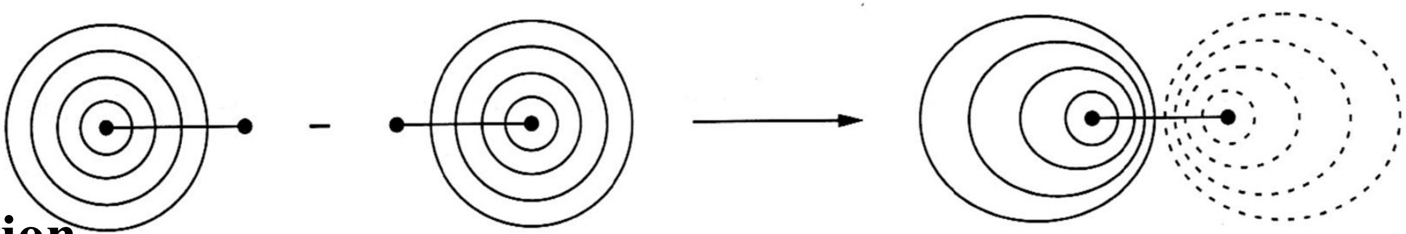
$$\psi_+^2 = 1/[2(1+S)](\phi_1^2 + \phi_2^2 + 2\phi_1\phi_2)$$

ψ_+



- in phase combination
- constructive interference
- large e^- density in the internuclear region (bonding)
- an electron in this MO lowers the molecule’s energy

ψ_-

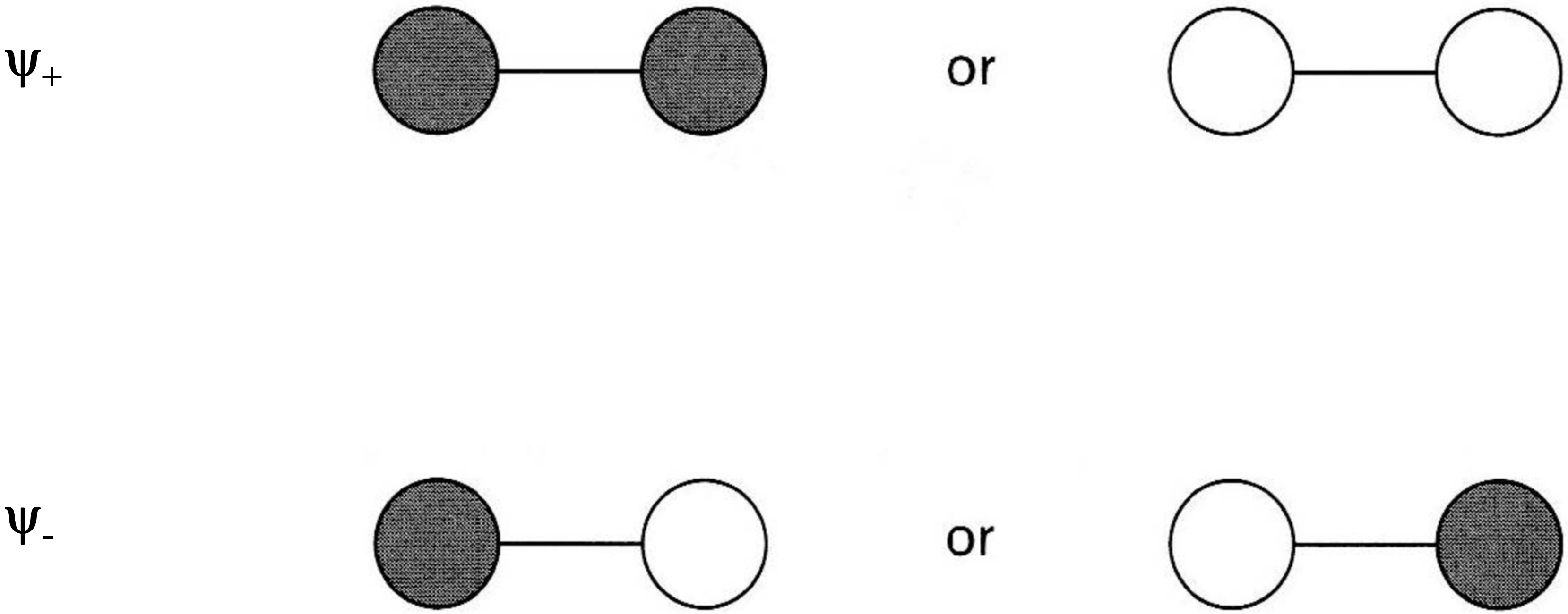


- out of phase combination
- destructive interference
- small e^- density in the internuclear region (antibonding)
- nodal plane between atoms
- an electron in this MO raises the molecule’s energy

$$\psi_-^2 = 1/[2(1+S)](\phi_1^2 + \phi_2^2 - 2\phi_1\phi_2)$$

4. Molecular Orbital (MO) Theory

Schematic representations of the MOs

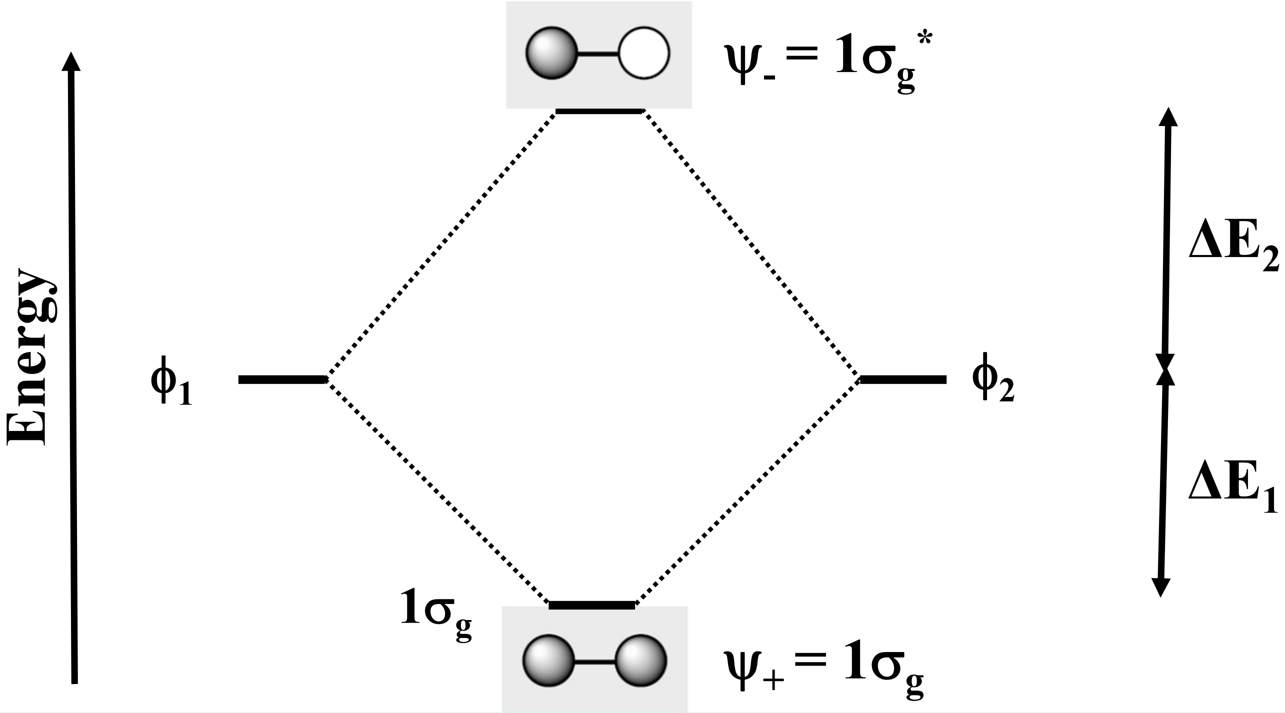


- The shading indicates sign of the respective AO
- The size of AO reflects the magnitude of its coefficient in the MO

4. Molecular Orbital (MO) Theory

Basic Rules of MO Theory: Rule #1

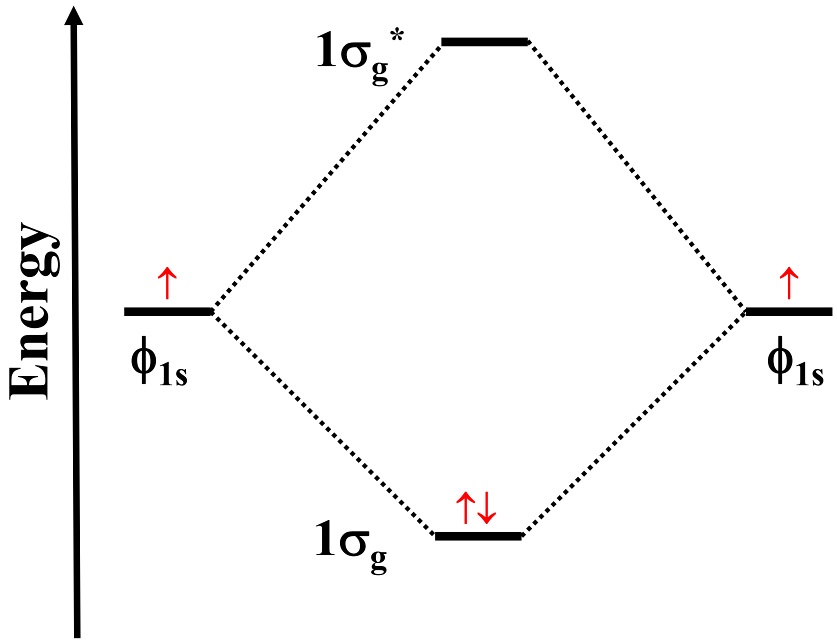
- **The interaction of *n* AOs leads to the formation of *n* MOs. If *n* = 2, one MO is bonding and one antibonding**
- **The bonding orbital is more stable than the lower-energy AO**
- **The antibonding orbital is less stable than the higher-energy AO**
- **The bonding orbital is stabilized less than the antibonding orbital is destabilized → $\Delta E_2 > \Delta E_1$**



4. Molecular Orbital (MO) Theory

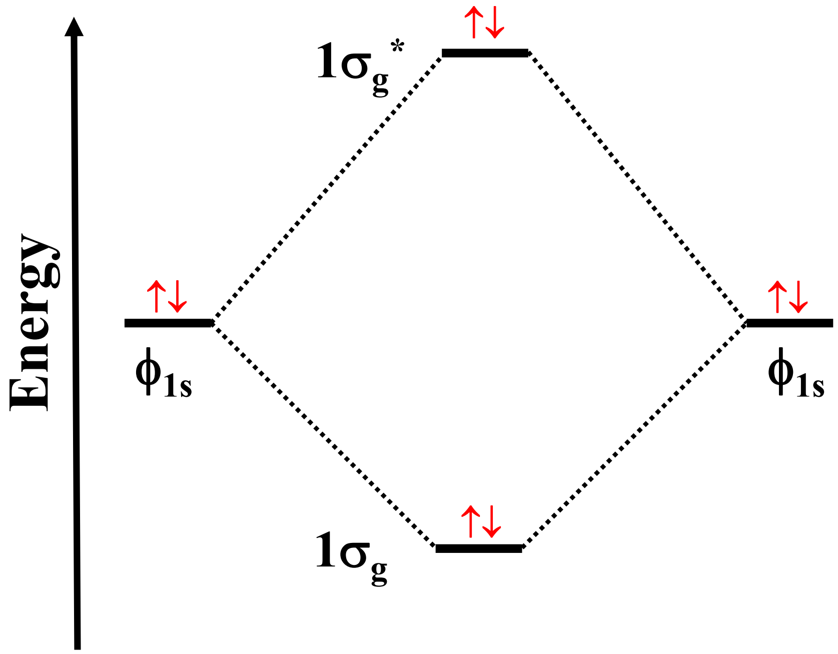
Stability of H_2 and He_2

Dihydrogen H_2



Bond order = 1.0

Dihelium He_2



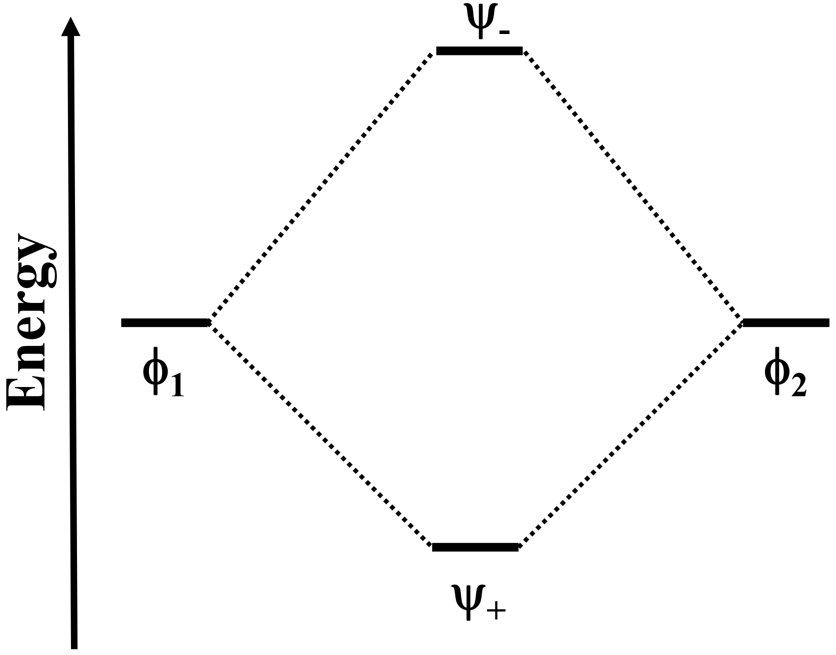
Bond order = 0.0 (instable)

Bond order BO = ½[(# of bonding e^-) – (# of antibonding e^-)]

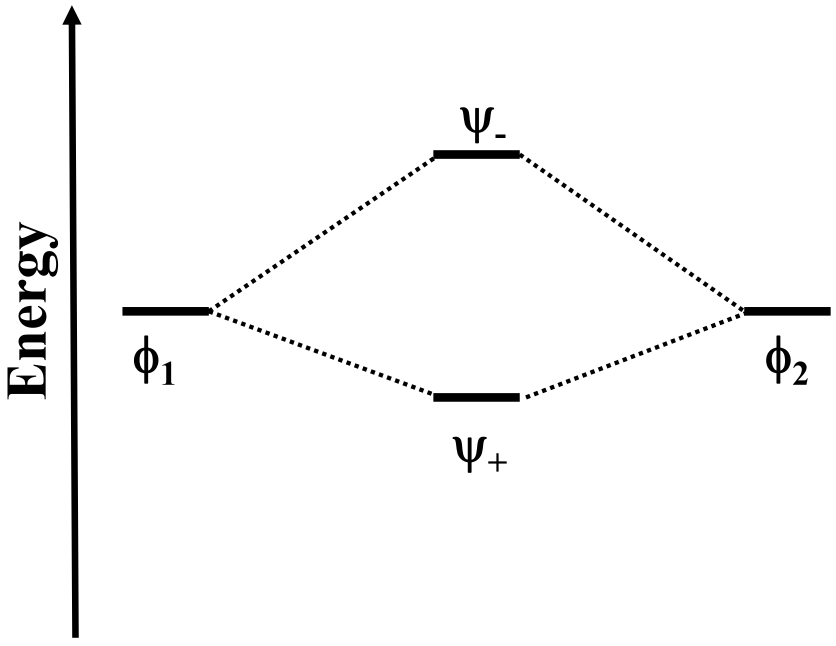
4. Molecular Orbital (MO) Theory

Basic Rules of MO Theory: Rule #2

If the AOs are degenerate, their interaction is proportional to the overlap integral S



large overlap



small overlap

$$S = \int \phi_1 \phi_2 d\tau \quad \text{with } 0 \le S \le 1$$

The larger the degree of overlap the stronger the bonding/antibonding character is

4. Molecular Orbital (MO) Theory

Basic Rules of MO Theory: Rule #3

Orbitals must have the same symmetry (same irreducible representations, chapter 3) to have non-zero overlap:

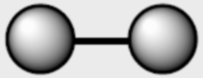
$$S = \int \phi_1 \phi_2 d\tau \quad \text{with } 0 \leq S \leq 1$$

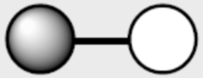
- **If $S \neq 0$, then bonding and antibonding MOs result**
- **$S = 0$ if orbitals have different irreducible representations**
- **If the overlap integral S between two orbitals centered on two different atoms is zero, then there is no interaction between them**
- **If an orbital has $S = 0$ with all other orbitals in the molecule, then it is a 100% non-bonding orbital**

4. Molecular Orbital (MO) Theory

MOs: Overlap and Type

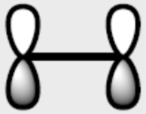
The bonding nature of an orbital interaction is defined by the relative orbital phasing

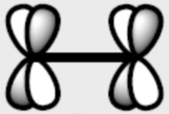

bonding


anti-bonding

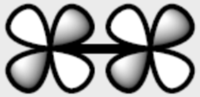
The type of bonding is defined by the number of nodes parallel to the bond

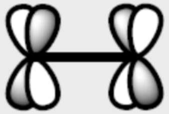

σ or σ-bonding


π

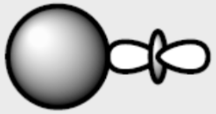

δ

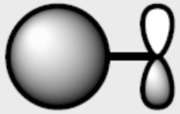

σ* or σ-anti-bonding

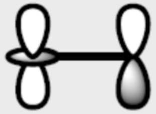

π*


δ*

Interactions between different types of orbitals is okay as long as there is net overlap


σ


non-bonding


non-bonding

Nodes	Type	#
0	σ	1
1	π	2
2	δ	2

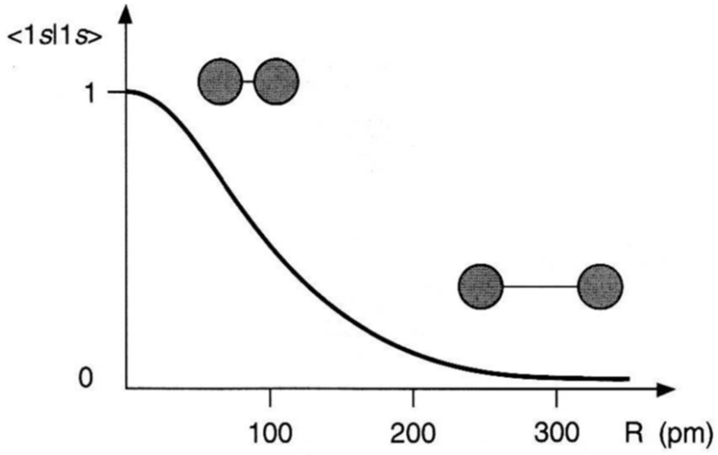
5fold bonds feasible!

4. Molecular Orbital (MO) Theory

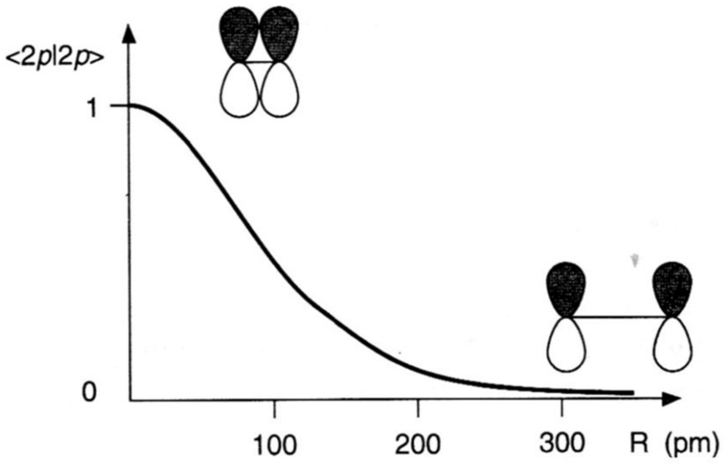
MOs: The extent of overlap depends on the internuclear separation, the nature of the orbitals involved (s, p, or d), and their relative orientation

(Remarks: f-orbitals do not undergo bond formation, r(H) = 53 pm, r(H_2) = 74 pm)

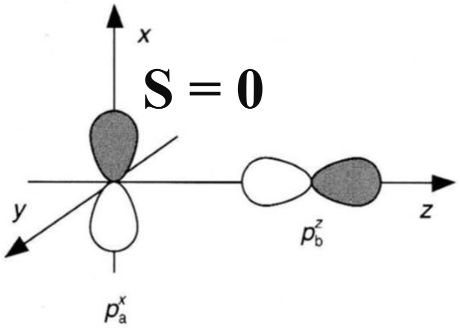
a) 1s-1s overlap: σ-bond

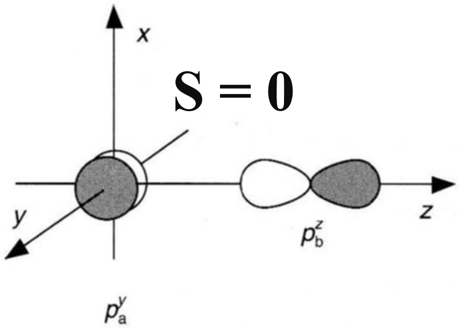


b) 2p-2p overlap (parallel): π-bond



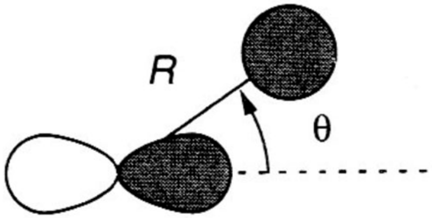
c) 2p-2p overlap (perpendicular) have zero overlap by symmetry





4. Molecular Orbital (MO) Theory

MOs: The extent of overlap depends on the internuclear separation, the nature of the orbitals involved (s, p, or d), and their relative orientation

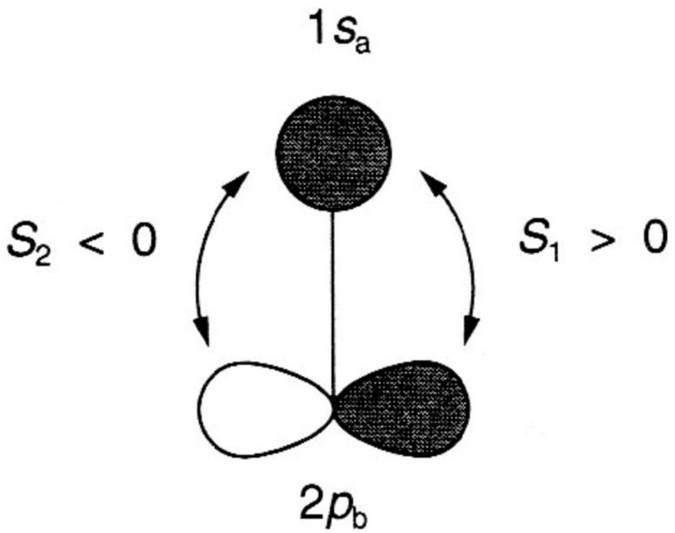


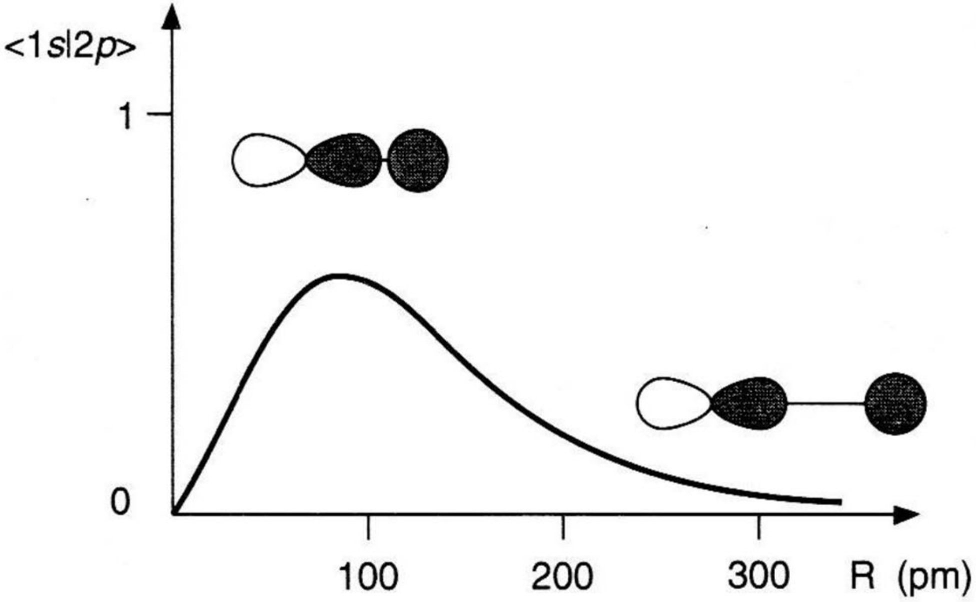
d) 1s-2p overlap depends on the angle θ

overlap $S = c \cdot \cos\theta$ with $c = \langle 1s|2p \rangle$

$\theta = 90° \rightarrow \cos\theta = 0 \rightarrow S = 0$

$\theta = 0° \rightarrow \cos\theta = 1 \rightarrow 0 \leq S \leq 1$





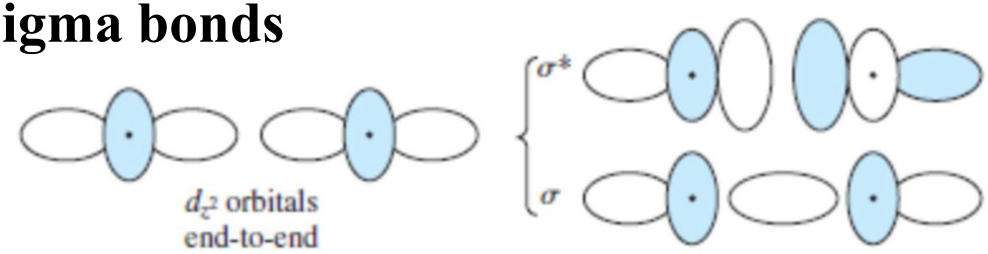
4. Molecular Orbital (MO) Theory

MOs: The extent of overlap depends on the internuclear separation, the nature of the orbitals involved (s, p, or d), and their relative orientation

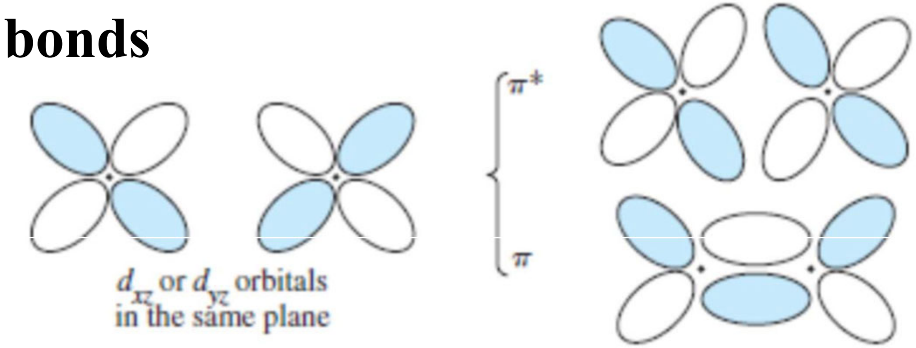
e) Involvement of d-orbitals

zero overlap by symmetry

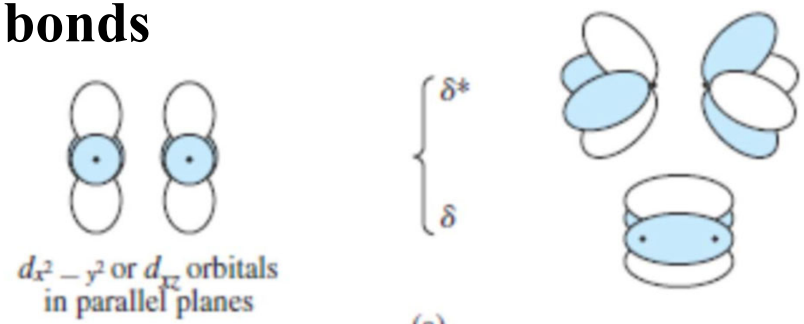
sigma bonds



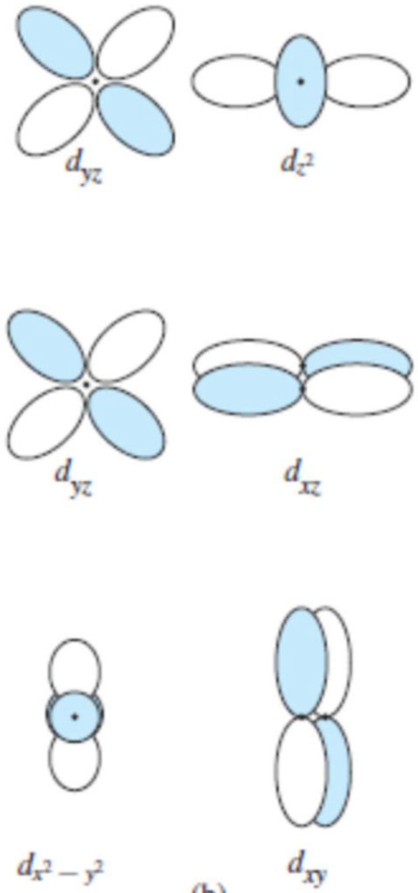
pi bonds



delta bonds



(a)



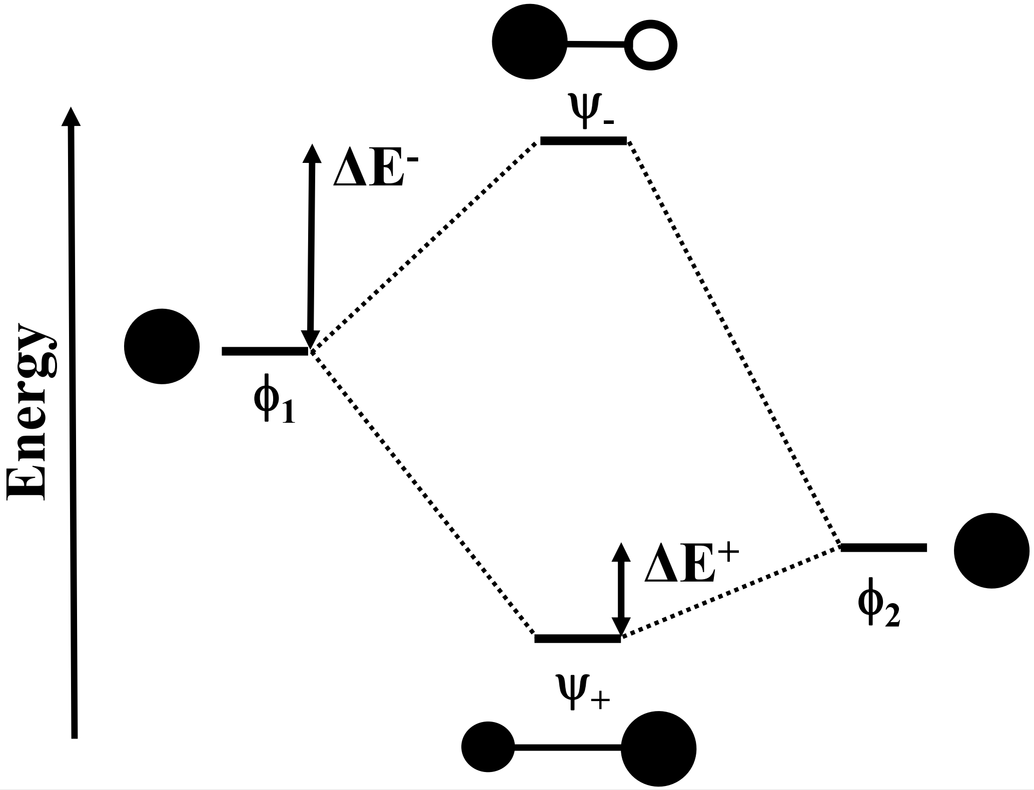
(b)

→ d-orbitals enable triple bonds

4. Molecular Orbital (MO) Theory

Basic Rules of MO Theory: Rule #4

If the AOs are non-degenerate, their interaction is proportional to $S^2/\Delta E$, where ΔE is the energy separation between the AOs. In this case the bonding orbital is mostly localized on the atom with the deeper lying AO, usually the more electronegative atom. The antibonding orbital is mostly localized on the atom with the higher AO



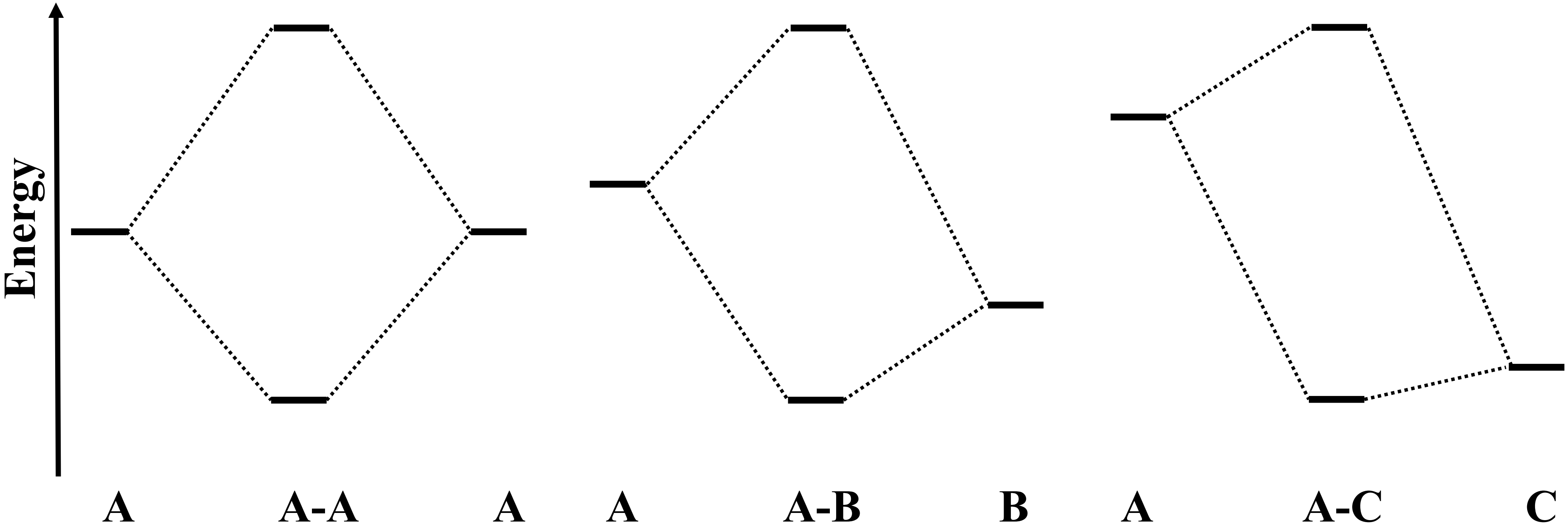
$$\psi = c_1\phi_1 + c_2\phi_2 \qquad \text{with } c_1^2 \neq c_2^2$$

Orbitals with $\Delta E > 12\text{-}14$ eV have essentially zero interaction, i.e. do not undergo bond formation

4. Molecular Orbital (MO) Theory

Basic Rules of MO Theory: Rule #4

Extent of interaction depends on ΔE between AOs

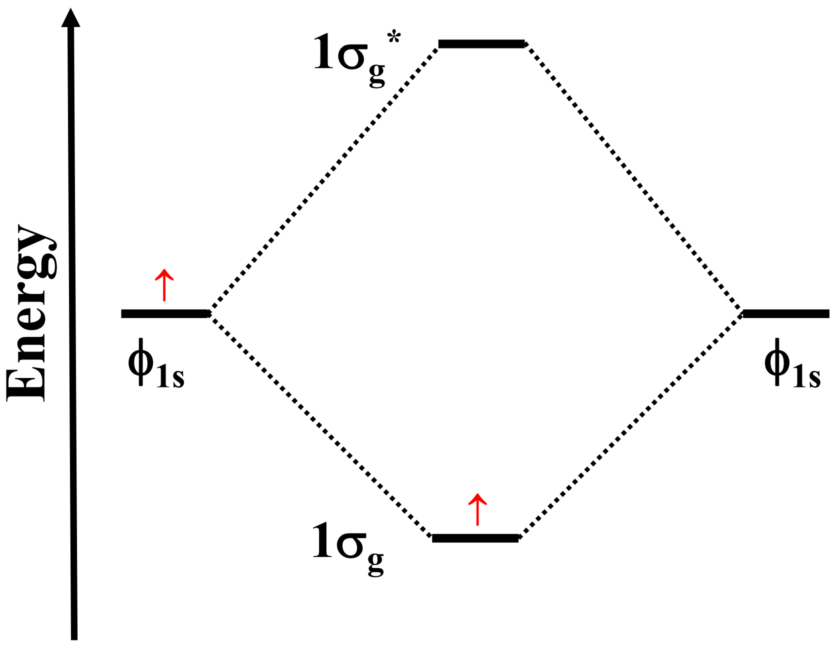


Equal energies Non polar covalent bonds	unequal energies polar covalent bonds	very unequal energies ionic bonds

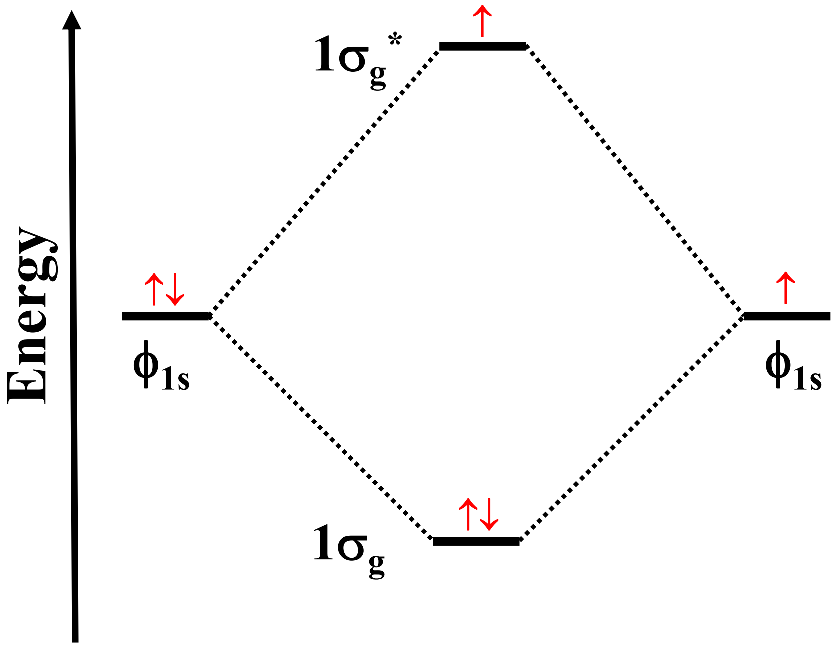
4. Molecular Orbital (MO) Theory

Homonuclear Diatomic Molecules

H and H interaction, e.g. H_2^+



He and He interaction, e.g. He_2^+



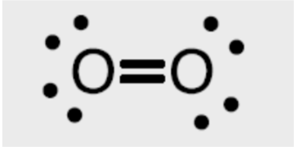
Species	bond order	
H_2^-	0.5	isoelectronic to
H_2	1.0	isoelectronic to
H_2^+	0.5	isoelectronic to

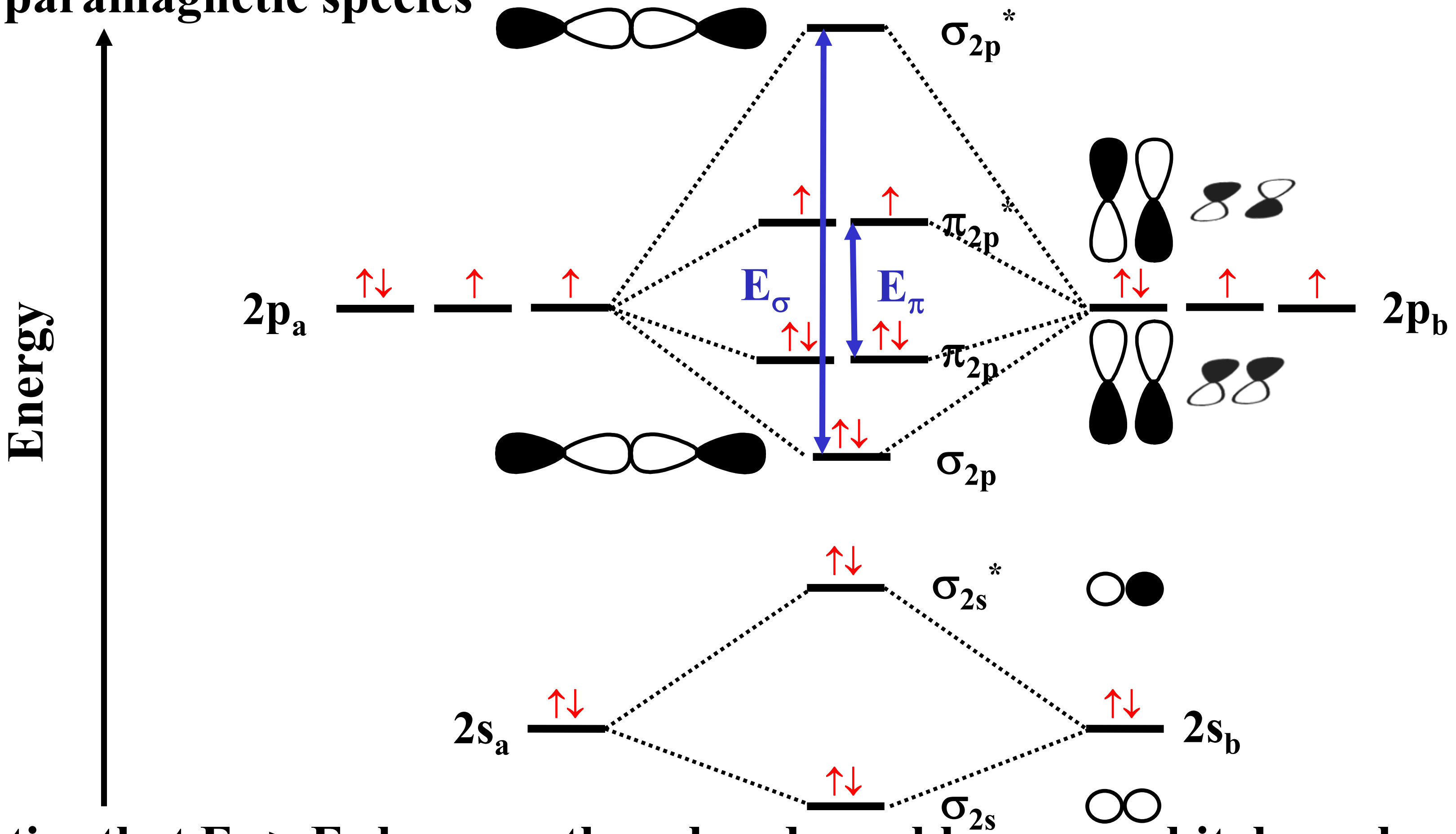
Species	bond order
He_2^+	0.5
He_2^{2+}	1.0
He_2^{3+}	0.5

4. Molecular Orbital (MO) Theory

Homonuclear Diatomic Molecules

The Lewis bond dot structure predicts the wrong electronic situation for O_2, since it is a paramagnetic species

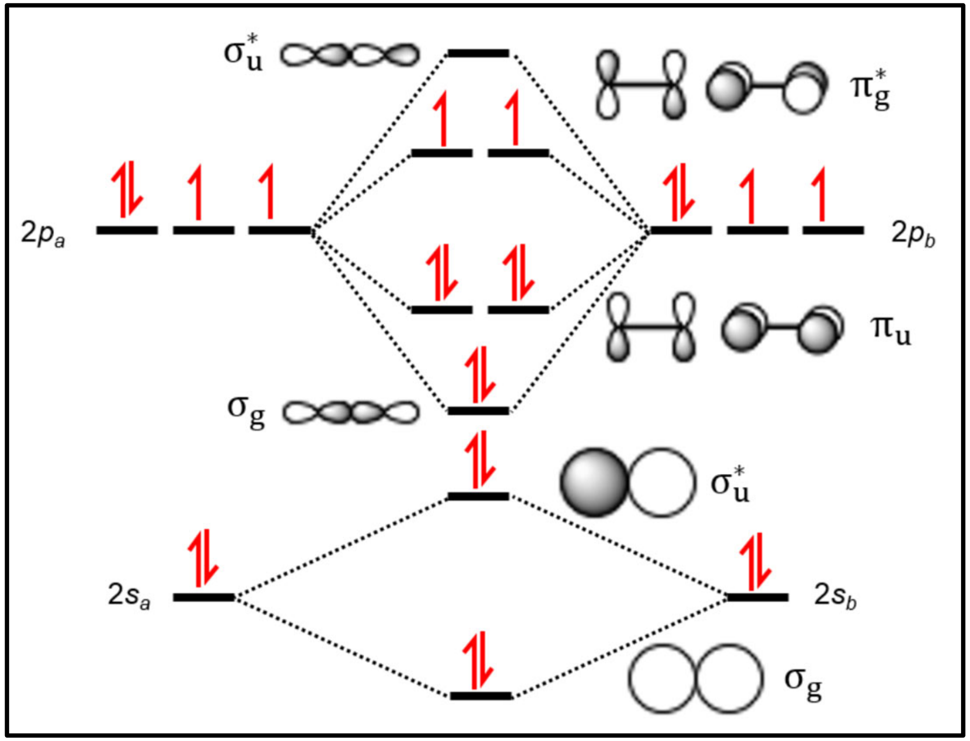




Notice that $E_\sigma > E_\pi$ because the σ bonds enable more orbital overlap than π bonds

4. Molecular Orbital (MO) Theory

Homonuclear Diatomic Molecules



Similar to atoms, one can write a molecular electron configuration for dioxygen species

Species	configuration	bond length [pm]
O_2^+	$\sigma^2\sigma^{*2}\sigma^2\pi^4\pi^*$	112
O_2	$\sigma^2\sigma^{*2}\sigma^2\pi^4\pi^{*2}$	120
O_2^-	$\sigma^2\sigma^{*2}\sigma^2\pi^4\pi^{*3}$	128
O_2^{2-}	$\sigma^2\sigma^{*2}\sigma^2\pi^4\pi^{*4}$	149

Calculation of the bond order (BO)

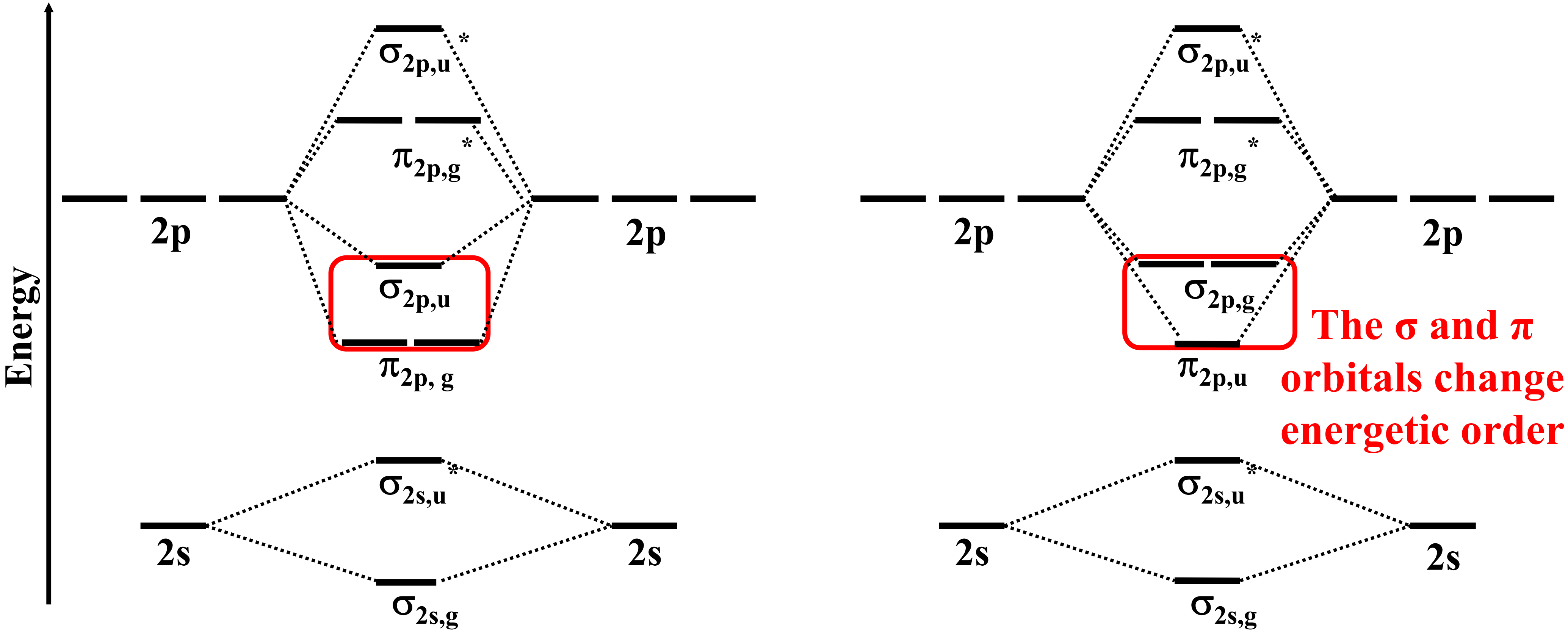
$$BO(O_2) = ½[(\#\text{ of bonding } e^-) – (\#\text{ of antibonding } e^-)] = ½[(8-4)] = 2$$

LCAO MO theory also predicts (correctly) that molecular oxygen has two unpaired electrons and is thus a diradical. It also correctly describes the effect of oxidation or reduction on the bond length

4. Molecular Orbital (MO) Theory

Orbital Mixing

- Orbitals of similar but unequal energies can interact if they have same symmetry
- The 2s and $2p_z$ orbitals form MOs with the same symmetry (σ_g and σ_u)
- sp mixing causes the σ_g and σ_u MOs to be pushed apart in energy

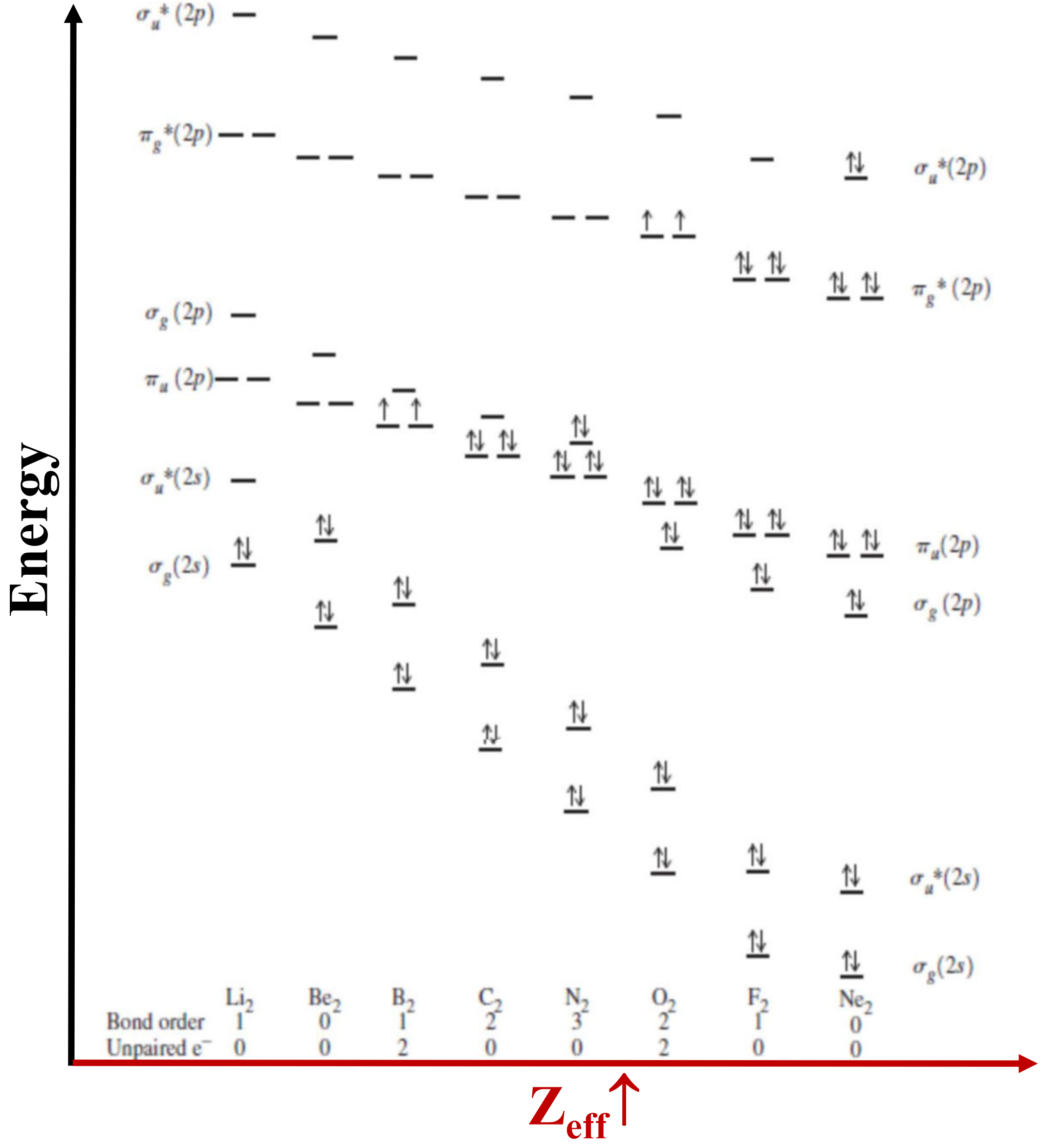


The σ and π orbitals change energetic order

4. Molecular Orbital (MO) Theory

Orbital Mixing

The size of the effect depends on the 2s-2p energy distance

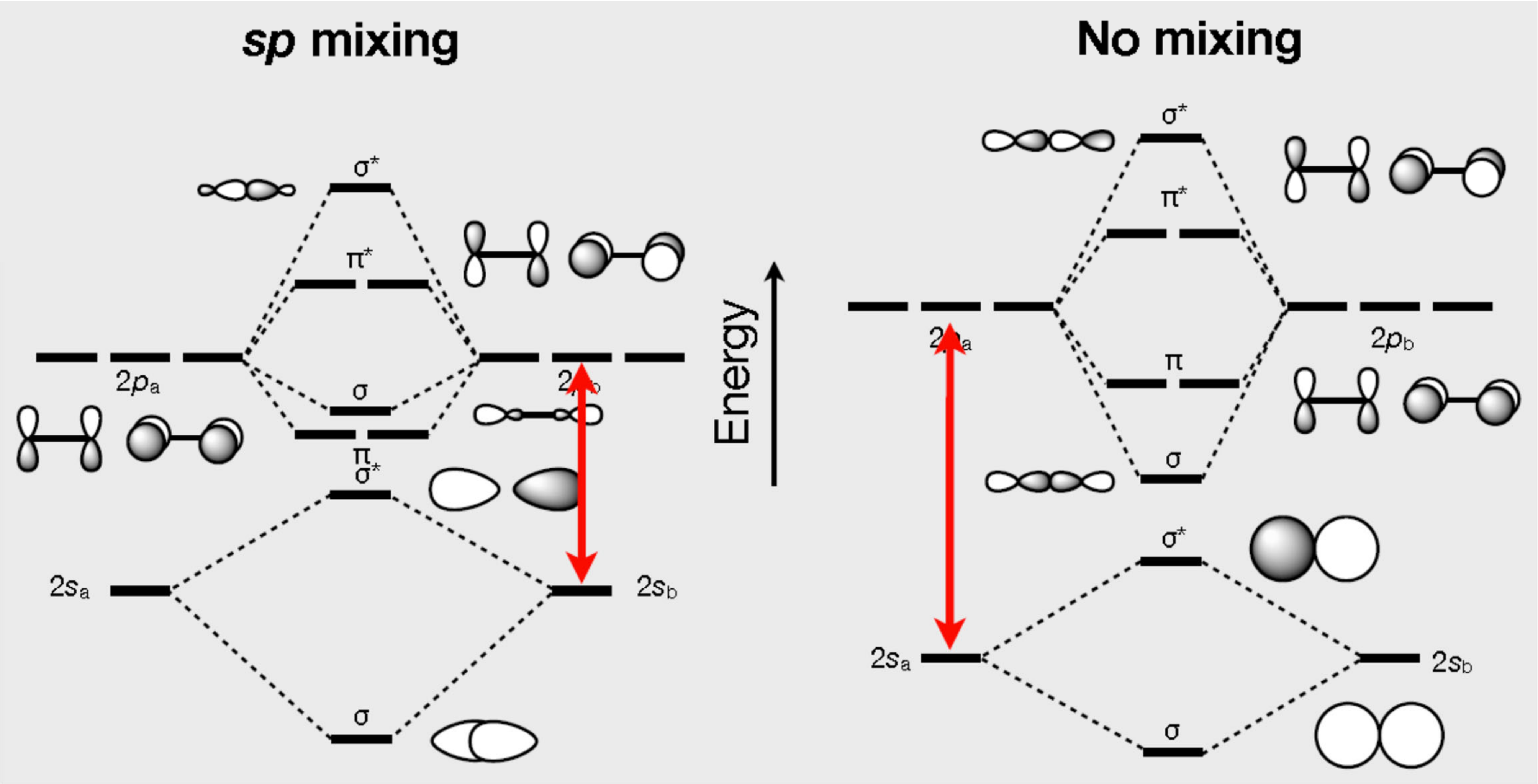


small Z_{eff} = small energy difference = large sp mixing

large Z_{eff} = large energy difference = small sp mixing

4. Molecular Orbital (MO) Theory

The MO energy level diagram of homonuclear diatomic molecules depends on the amount of sp mixing and thus on the atomic number due to the E-field increase



Li_2, Be_2, B_2, C_2, N_2

O_2, F_2, Ne_2

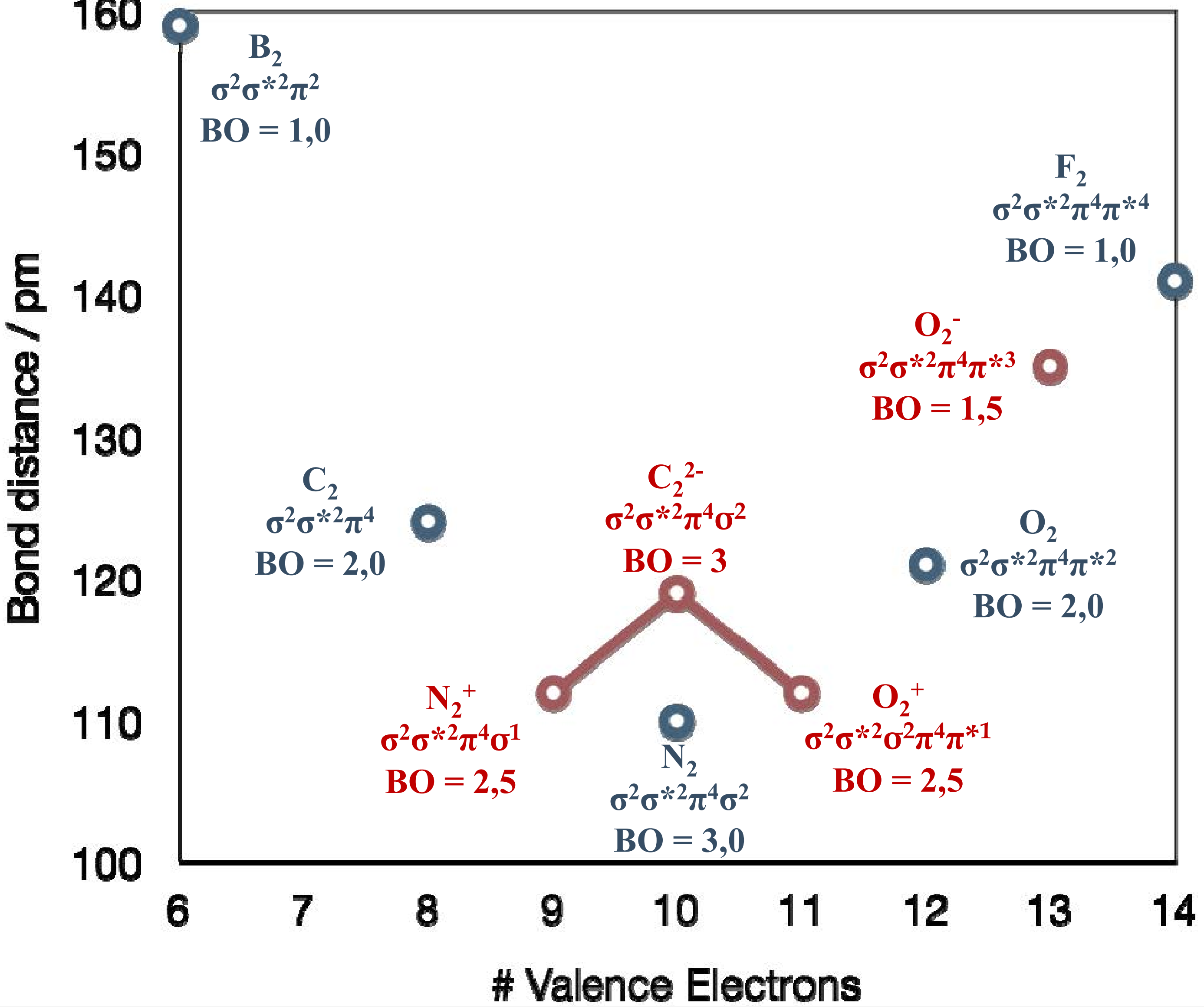
4. Molecular Orbital (MO) Theory

The MO bond order is the main factor controlling the internuclear distance

Bond length range:

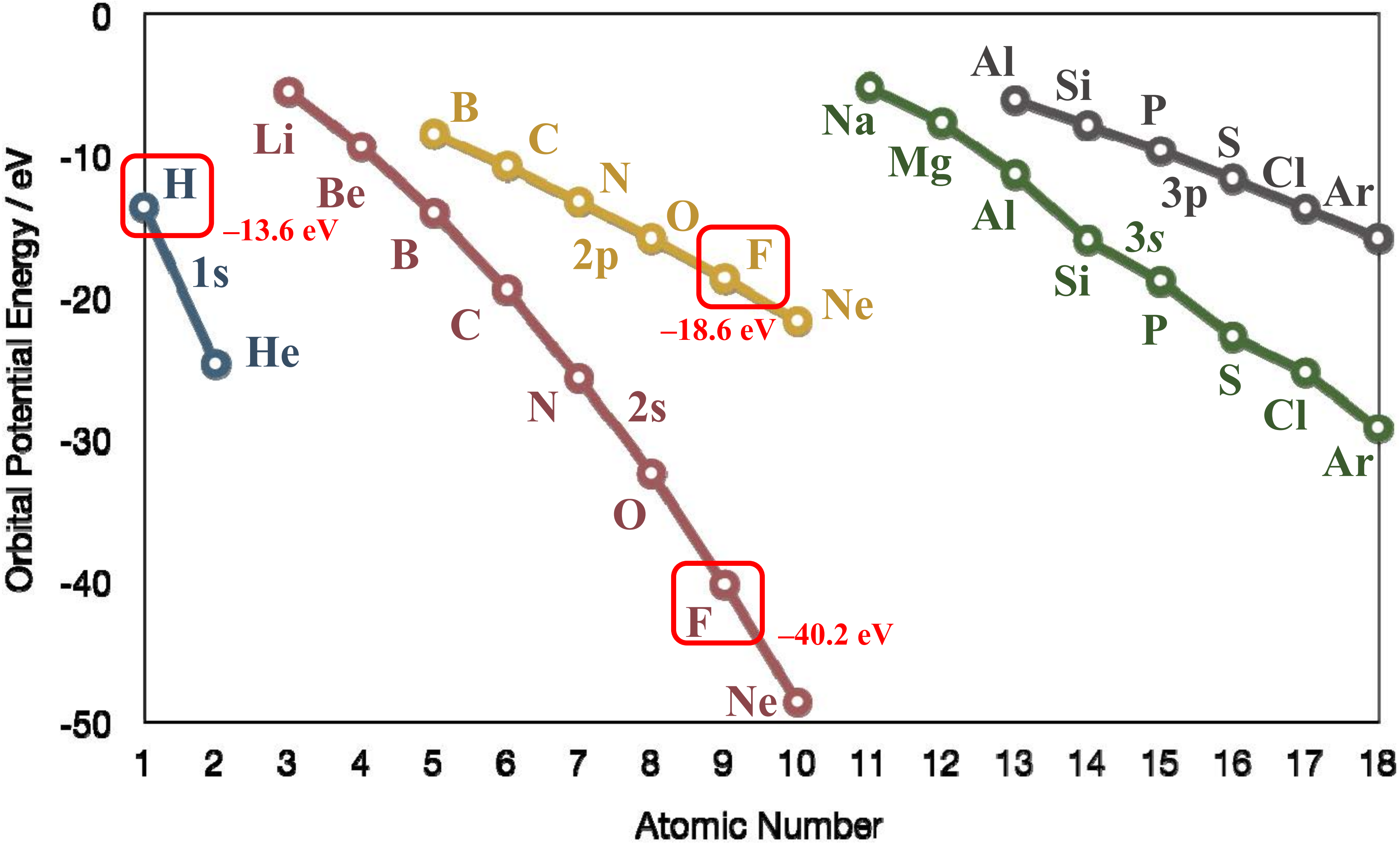
74 pm (H_2) -

~ 400 pm ($La_{11}Hg_{45}$)



4. Molecular Orbital (MO) Theory

Relative AO Energies for the Construction of MO Diagrams (obtained from UPS = Ultraviolet Photoelectron Spectroscopy Experiments)



4. Molecular Orbital (MO) Theory

UPS = Ultraviolet Photoelectron Spectroscopy (0 - 50 eV, compare: XPS > 100 eV)

UPS spectral lines originate from electrons in the valence band

$E_{kin} = h\nu - E_B - \Theta$

$\Rightarrow E_B = h\nu - E_{kin} - \Theta$

with Θ = known work function of the detector

$h\nu$ = energy of the incident UV photons

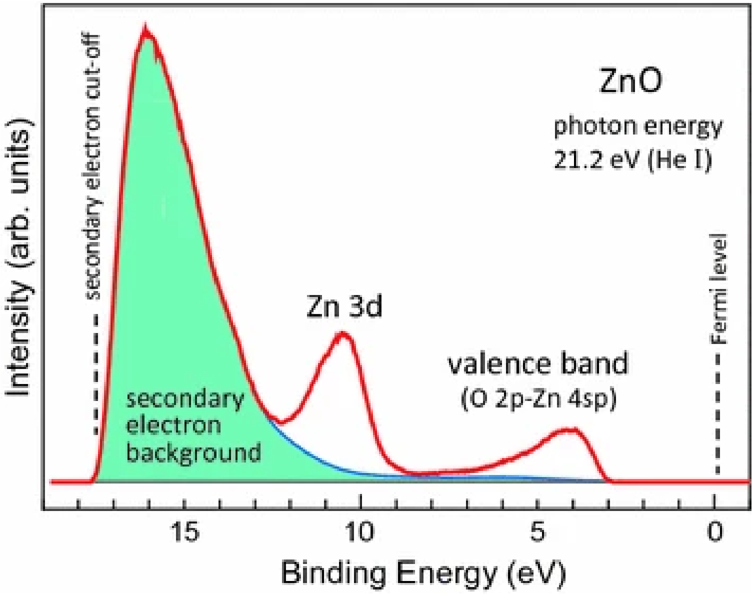
E_{kin} = kinetic energy of photoelectrons

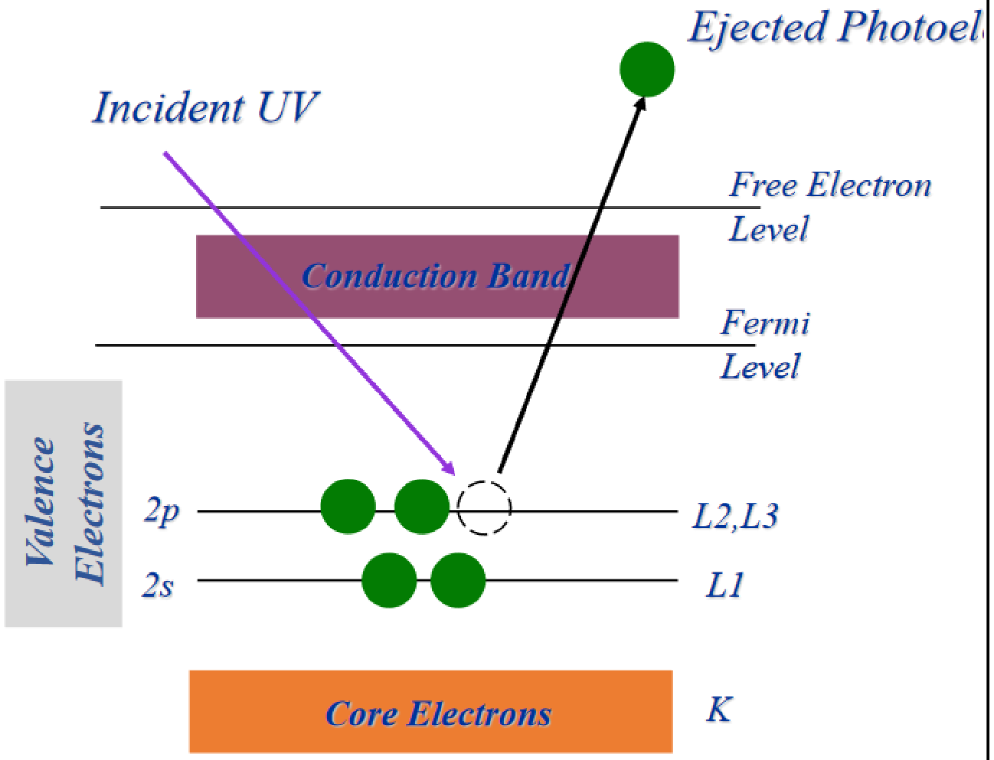
E_B = binding energy

UV photons originate from differentially pumped He discharge lamp

- **HeI 21.2 eV**
- **HeII 40.8 eV**

UPS Spectrum of a ZnO Layer

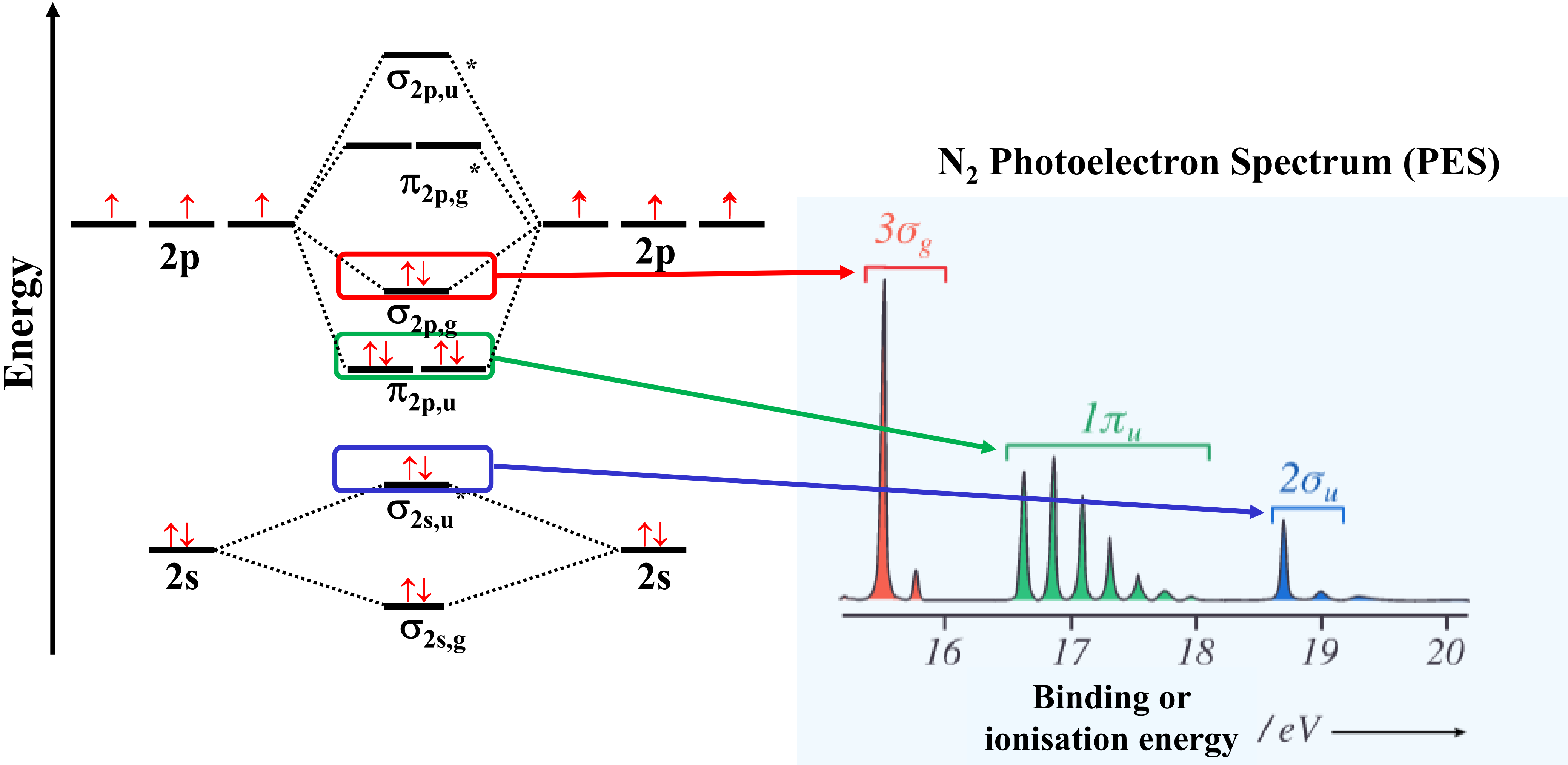




4. Molecular Orbital (MO) Theory

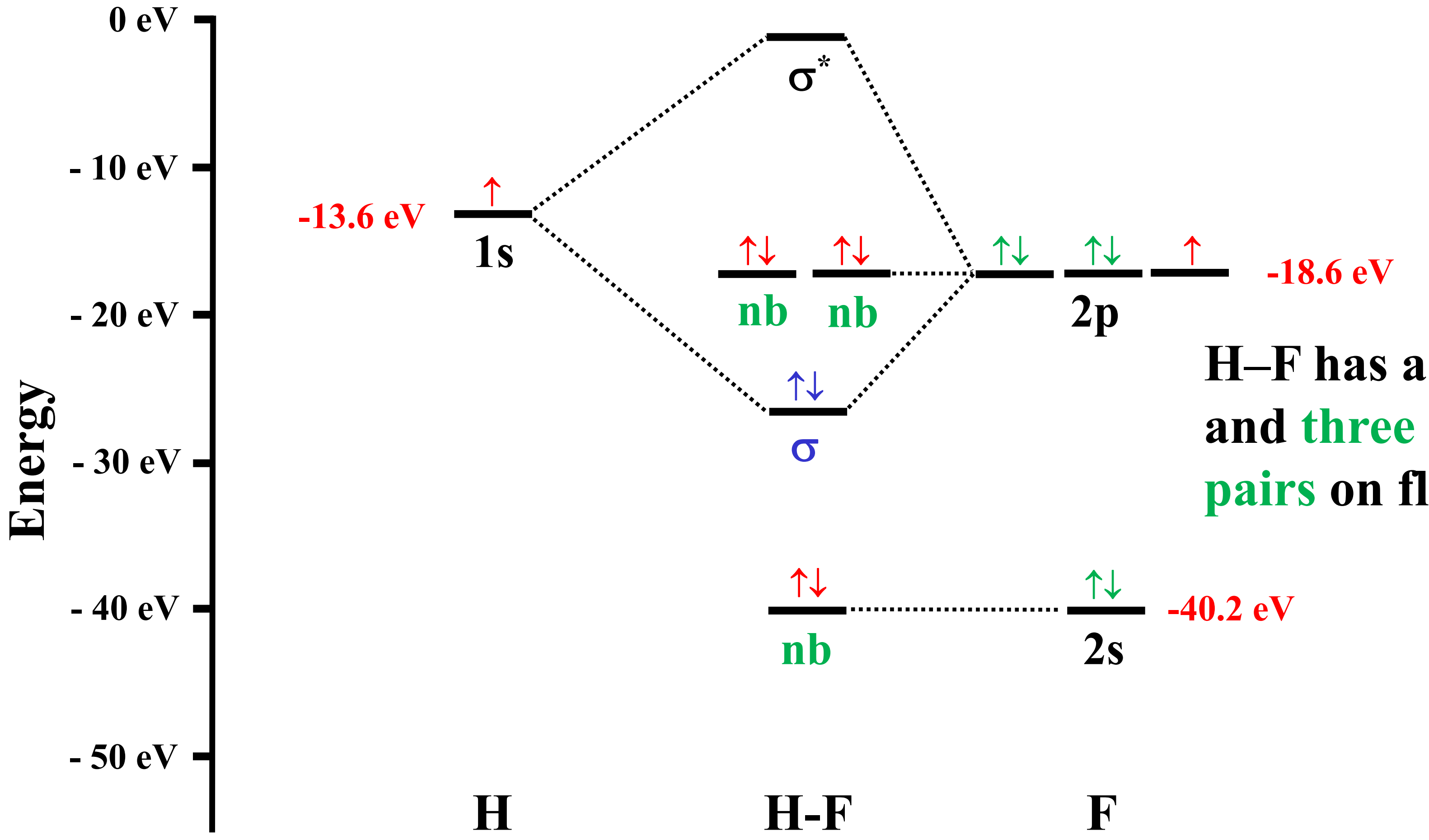
UPS = Ultraviolet Photoelectron Spectroscopy (0 - 50 eV, compare: XPS > 100 eV)

Example: N_2 UPS Spectrum and its relation to the MOs (Lit.: J. Chem. Phys. 62 (1975) 1447)



4. Molecular Orbital (MO) Theory

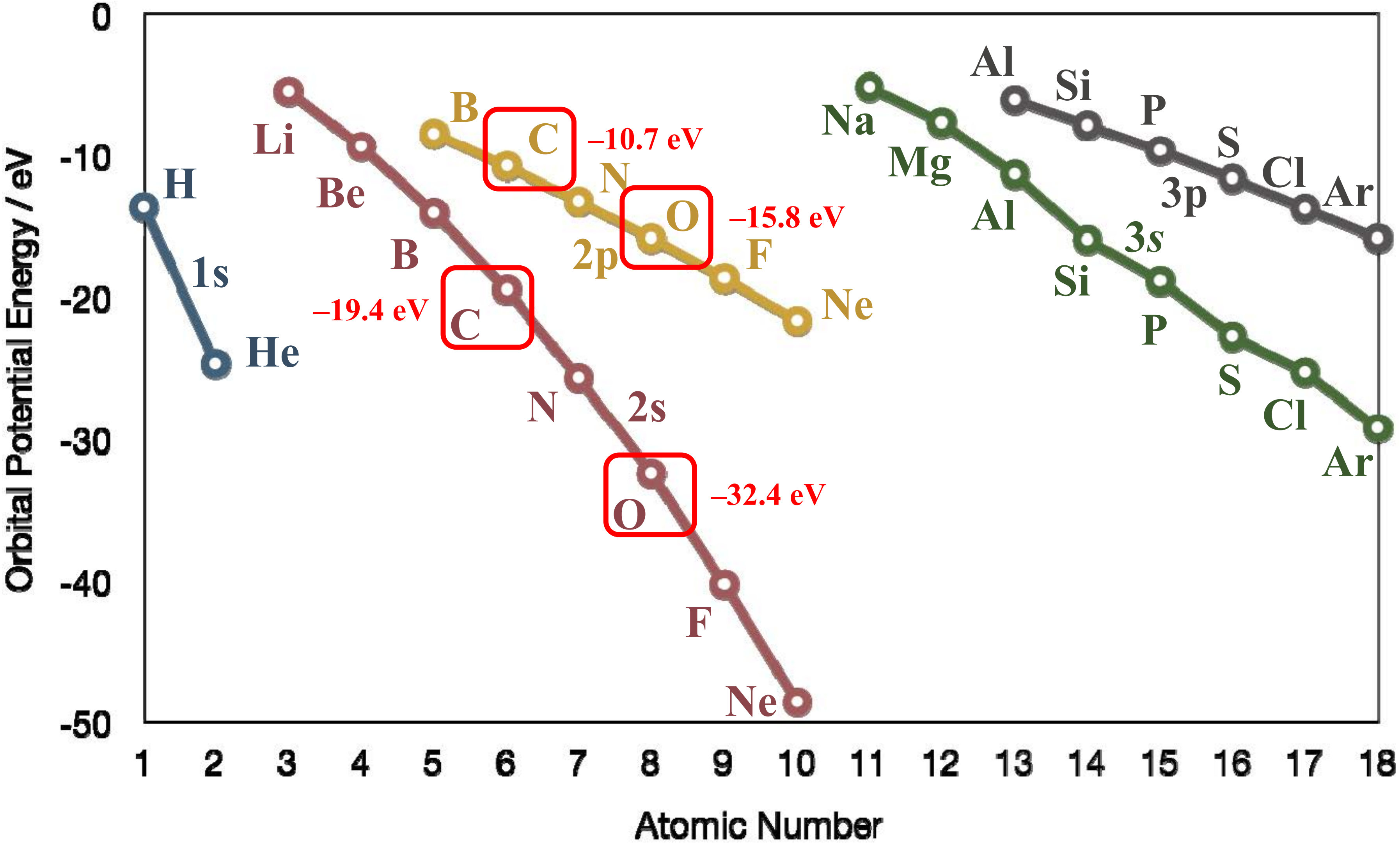
Homonuclear Diatomic Molecules: HF → The AO Energies foster that the 1s Orbital of Hydrogen Interacts with a 2p Orbital of Fluorine. The F 2s is Nonbonding (nb)



H–F has a single σ bond and three lone electron pairs on fluorine atom

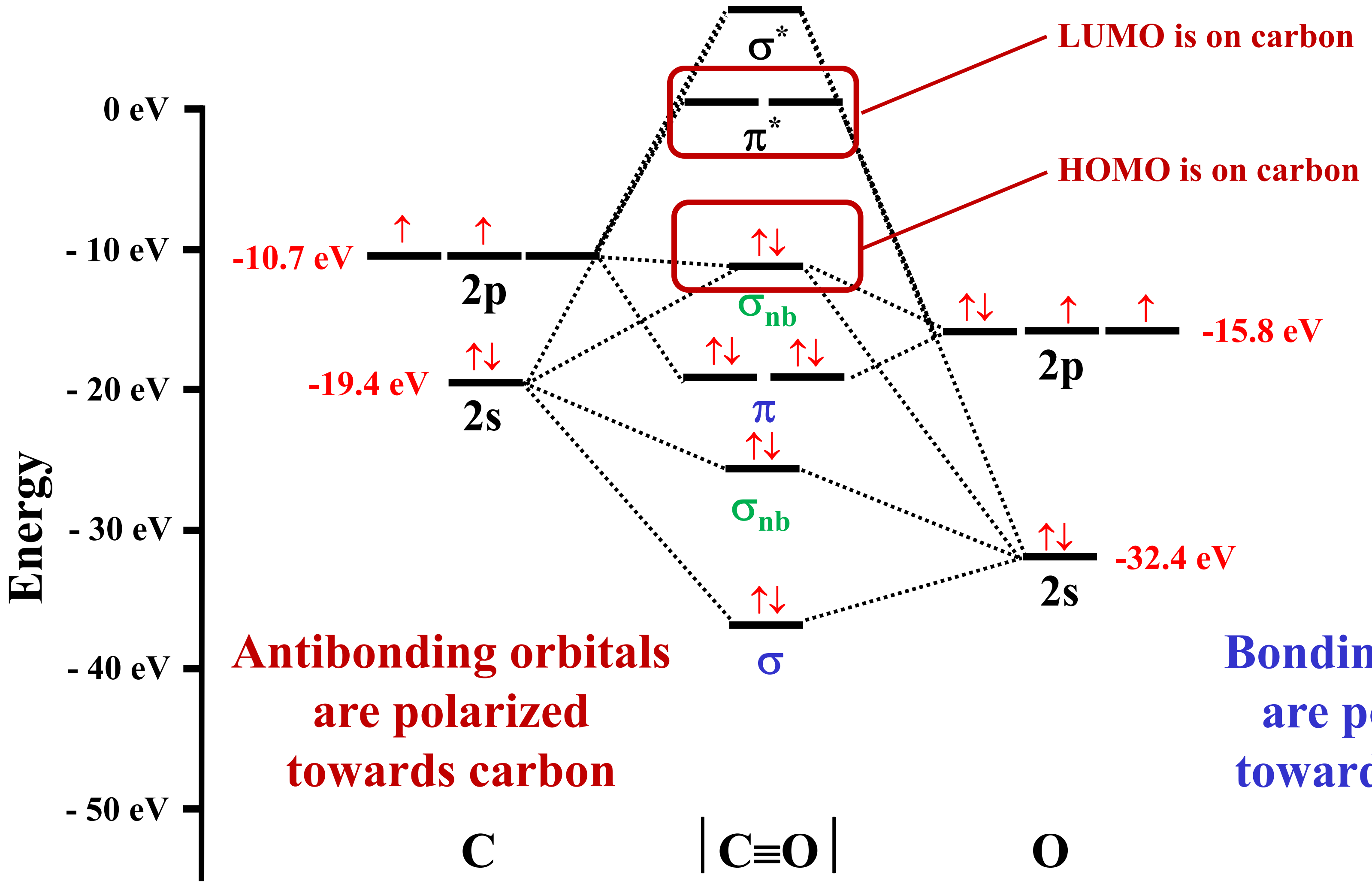
4. Molecular Orbital (MO) Theory

Relative AO Energies for the Construction of MO Diagrams (obtained from UPS = Ultraviolet Photoelectron Spectroscopy Experiments)



4. Molecular Orbital (MO) Theory

Homonuclear Diatomic Molecules: CO → The AO Energies foster the Formation of a Triple Bond. HOMO and LUMO are mostly Located on Carbon!



Antibonding orbitals are polarized towards carbon

Bonding orbitals are polarized towards oxygen

Coordination of CO occur via lone pair on carbon, as well as a nucleophilic attack

4. Molecular Orbital (MO) Theory

Summary (so far)

- **LCAO-MO Theory is a simple method for predicting the approximate electronic structure of molecules**
- **Atomic orbitals must have the proper symmetry and energy to interact towards the formation of molecular orbitals**
- **Ultraviolet Photoelectron Spectroscopy (UPS) provides useful information on the absolute energies of atomic orbitals**
- **Symmetry will permit to treat larger molecules in the framework of the LCAO-MO theory**

4. Molecular Orbital (MO) Theory

MOs for Larger Molecules: „Algorithm“

1. Determine point group of molecule, if it is linear, use D_{2h} and C_{2v} instead of $D_{\infty h}$ or $C_{\infty v}$

2. Assign x, y, z coordinates (z axis is the principal axis, if non-linear the y axes of outer atoms point to central atom

3. Find the characters of the reducible representation for the combination of valence orbitals on the outer atoms. Treat s, p_x, p_y, p_z, and so on separately (as for vibrations, orbitals that change position = 0, orbitals that do not change = 1; and orbitals that remain in the same position but change sign = -1)

4. Find the irreducible representations, they correspond to the symmetry of group orbitals, also called Symmetry Adapted Linear Combinations (SALCs) of the orbitals

5. Find AOs on central atom with the same symmetry

6. Combine AOs from central atom with those group orbitals of same symmetry and similar energy to make the MO diagram

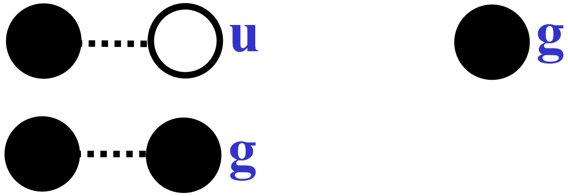
4. Molecular Orbital (MO) Theory

Linear H_3^+ which is the Simplest Multi-atom Molecule by Inspection

General procedure for simple molecules that contain a central atom →
Build group orbitals using the outer atoms, then interact the group orbitals with the central atom orbitals to construct the MOs

$$[\mathrm{H{-}H{-}H}]^+ \rightarrow [\mathrm{H \cdot H}] + [\mathrm{H}^+]$$

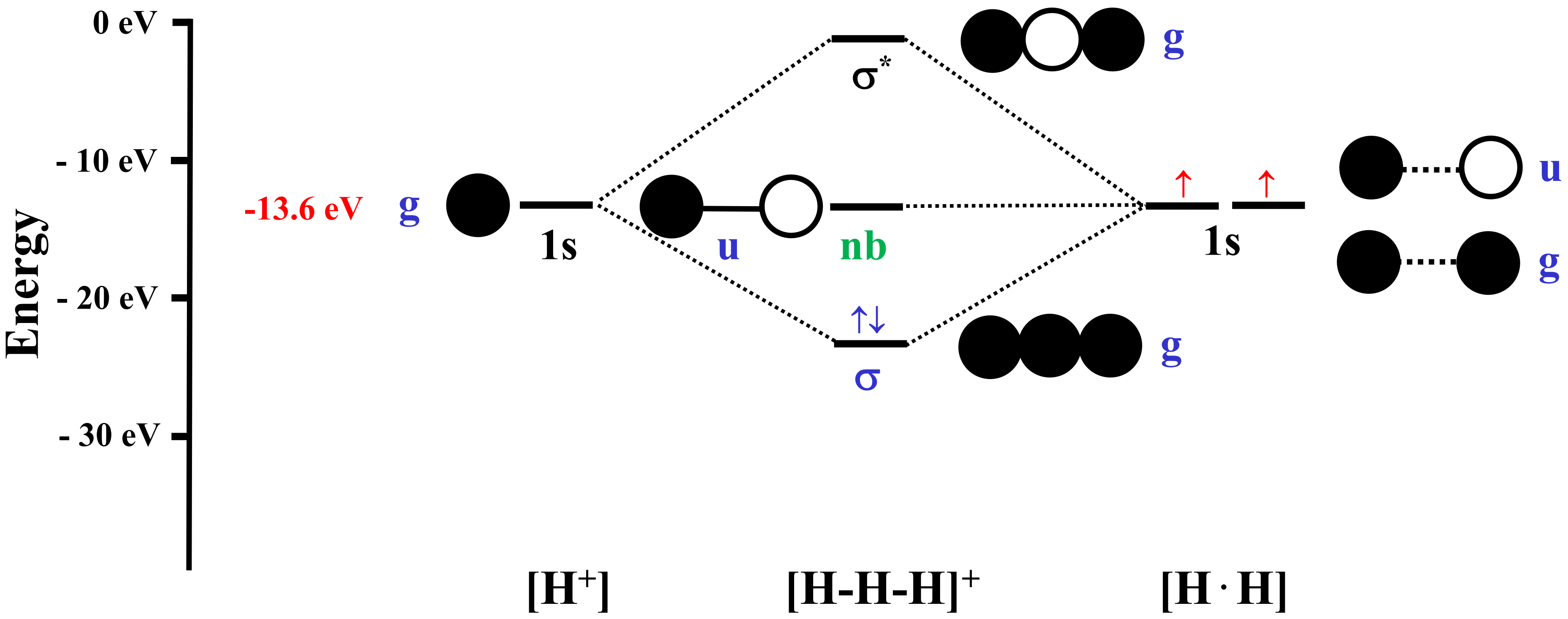
linear molecule — group of outer atoms — central atom



Only group orbitals and central atom orbitals with the same symmetry and similar energy will interact

4. Molecular Orbital (MO) Theory

Linear H_3^+: g Orbitals Interact, while u Orbital is Nonbonding



Open 3-center-2-electron bond (see chapter boranes, lecture "Inorg. Chemistry I")

4. Molecular Orbital (MO) Theory

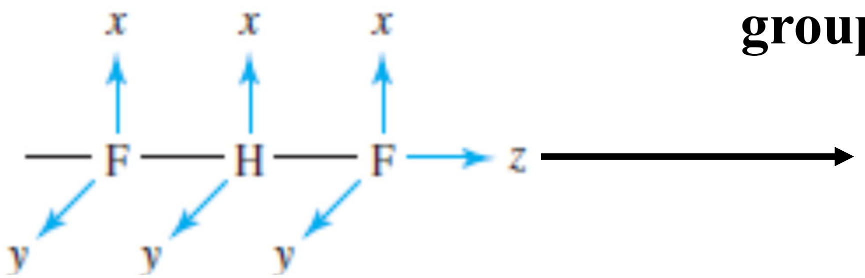
Linear HF_2^-: Involve the 2s and 2p Orbitals of the two Fluorine Atoms (8 AOs in total). Use Point Group D_{2h} instead of $D_{\infty h}$

$[F\text{-}H\text{-}F]^- \rightarrow [F \cdot F] + [H^-]$

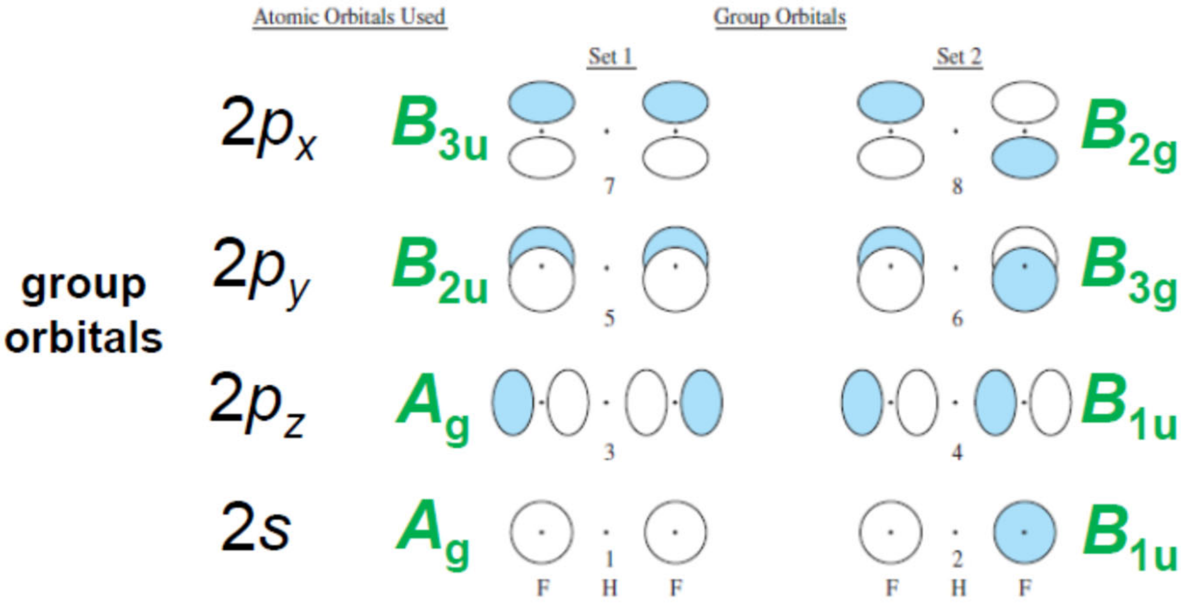
group of outer atoms

central atom

● A_g



principle z-axis



4. Molecular Orbital (MO) Theory

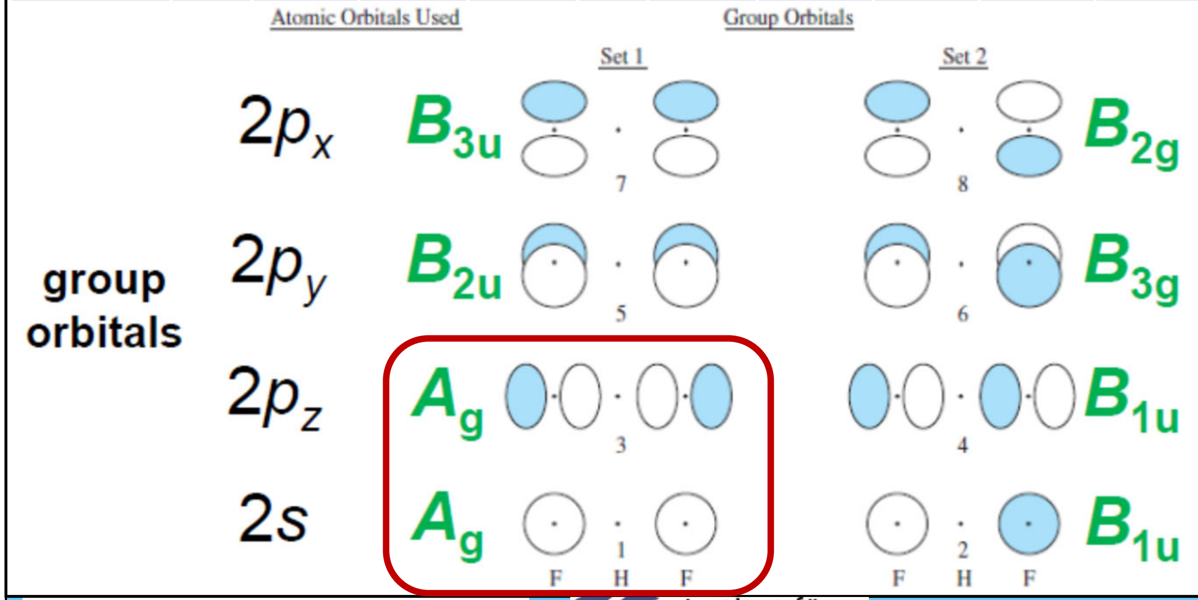
Linear HF_2^-: Involve the 2s and 2p Orbitals of the two Fluorine Atoms (8 AOs in total). Use Point Group D_{2h} instead of $D_{\infty h}$

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)	linear	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

$[H^-]$

central atom

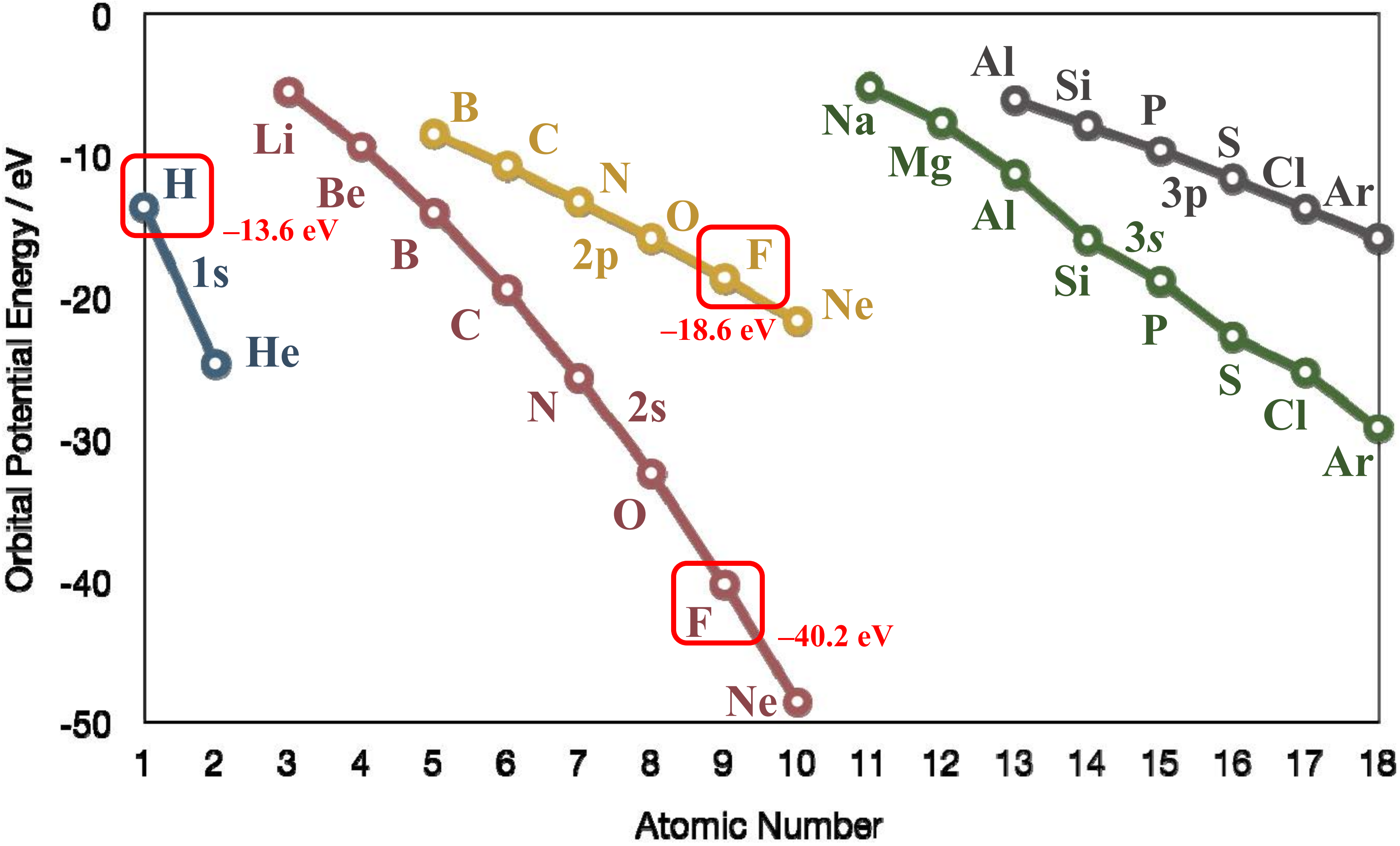
● A_g



The central atom has the proper symmetry to interact solely with group orbitals #1 and #3!

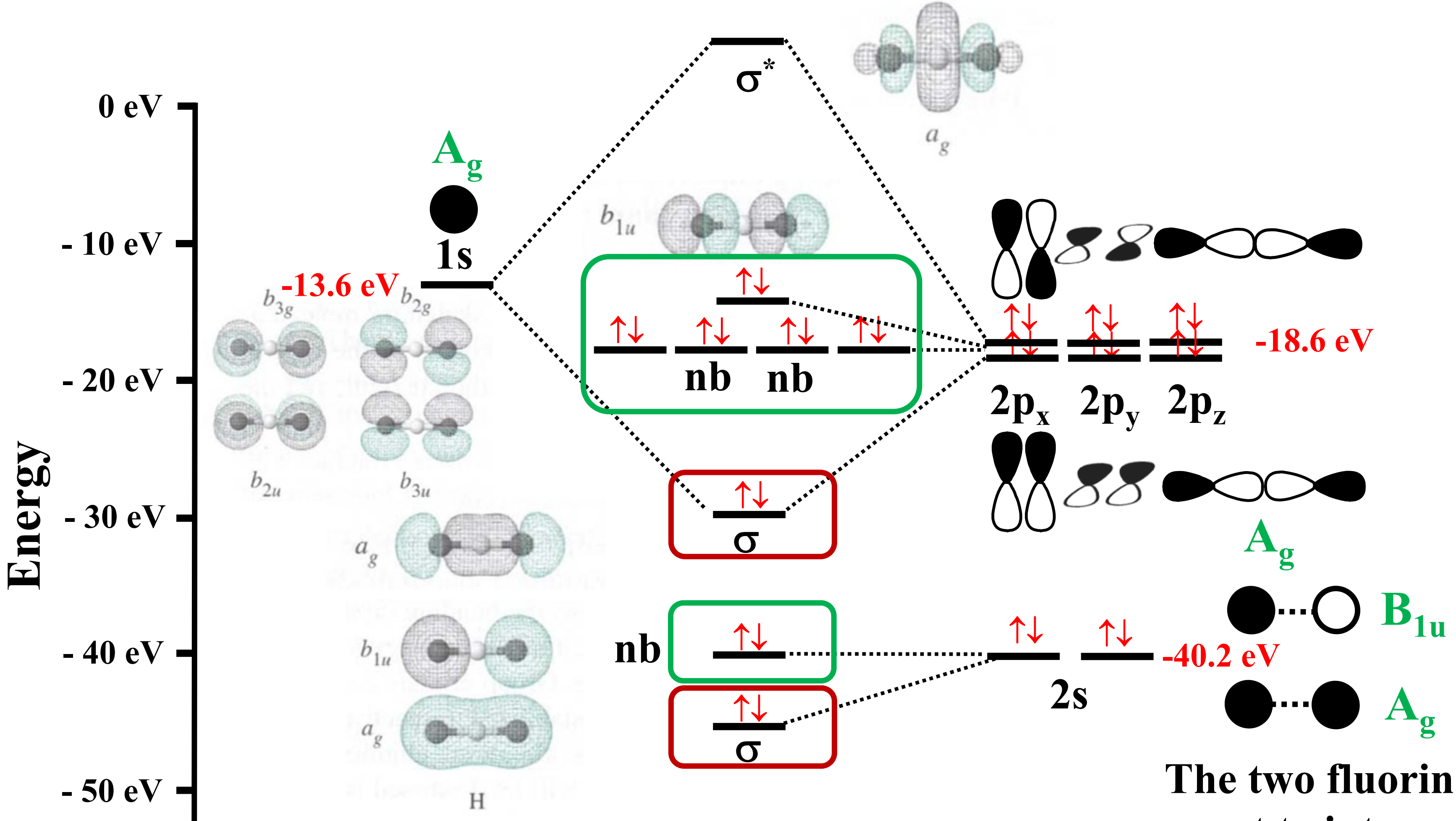
4. Molecular Orbital (MO) Theory

The F 2s Orbital is Very Deep in Energy and will be Essentially Nonbonding



4. Molecular Orbital (MO) Theory

F 2s orbitals are too deep in energy to interact, leaving an interaction (σ) only with group orbital 3. Some sp mixing occurs between a_g and b_{1u} MOs.



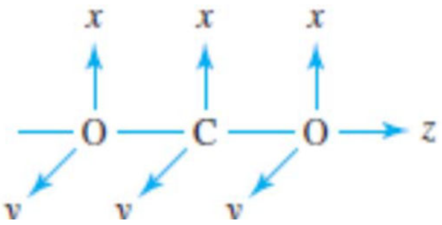
The two fluorines are too far apart to interact directly → orbital overlap S is very small

MO model of HF_2^- yields < 2 bonds and > 6 lone pairs

4. Molecular Orbital (MO) Theory

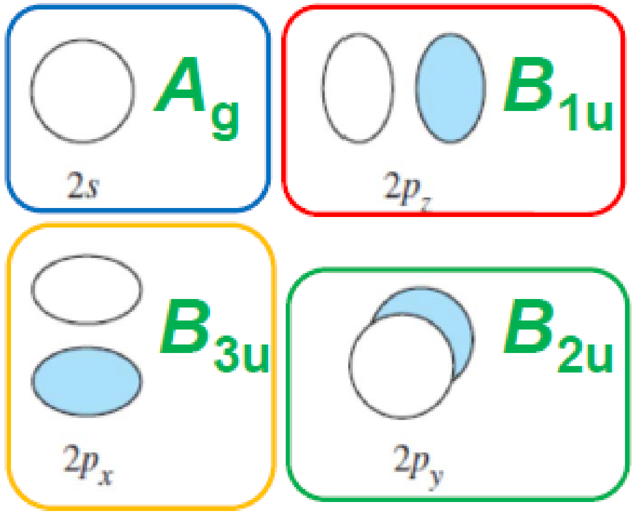
CO_2: This molecule is also linear. Here all three atoms have 2s and 2p orbitals to be considered. Again, the point group D_{2h} instead of $D_{\infty h}$ will be used

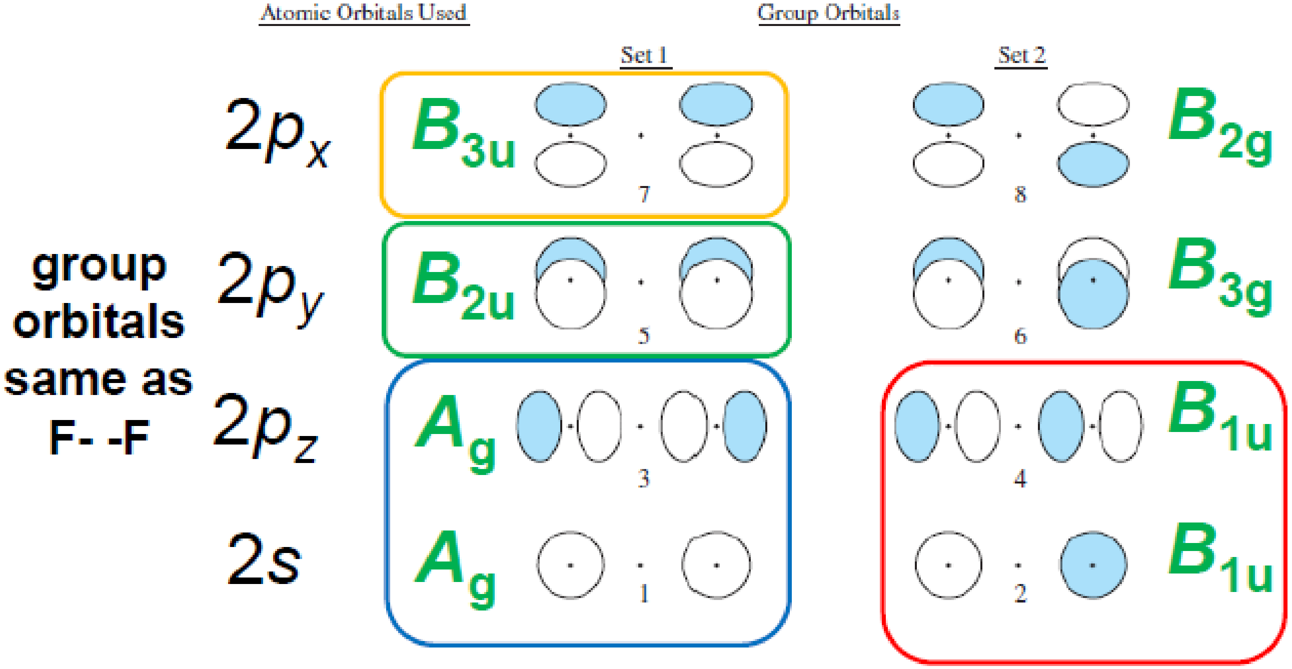
O=C=O → [O · O] + [C]



group of outer atoms

central atom

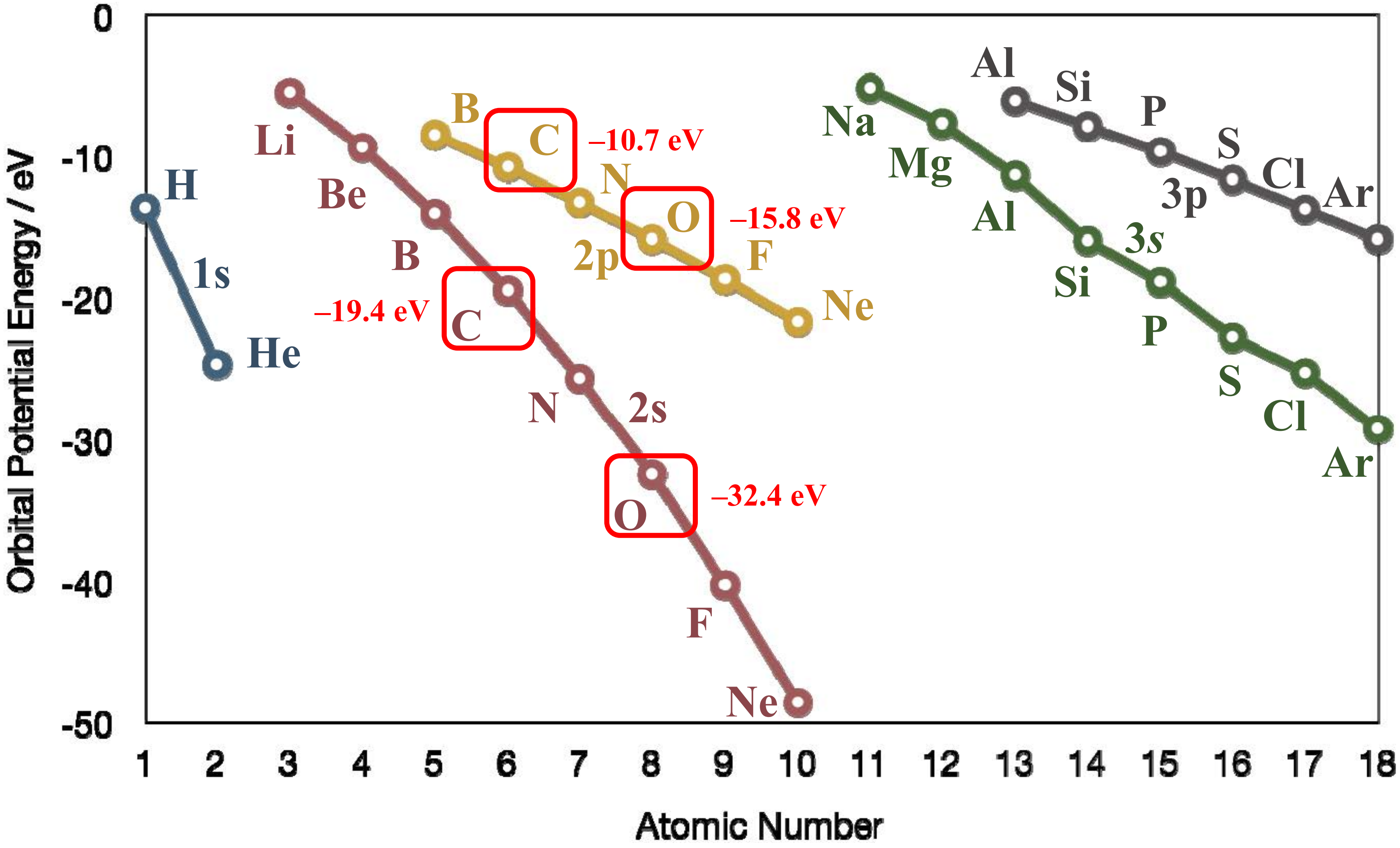




carbon has 4 AOs to be considered

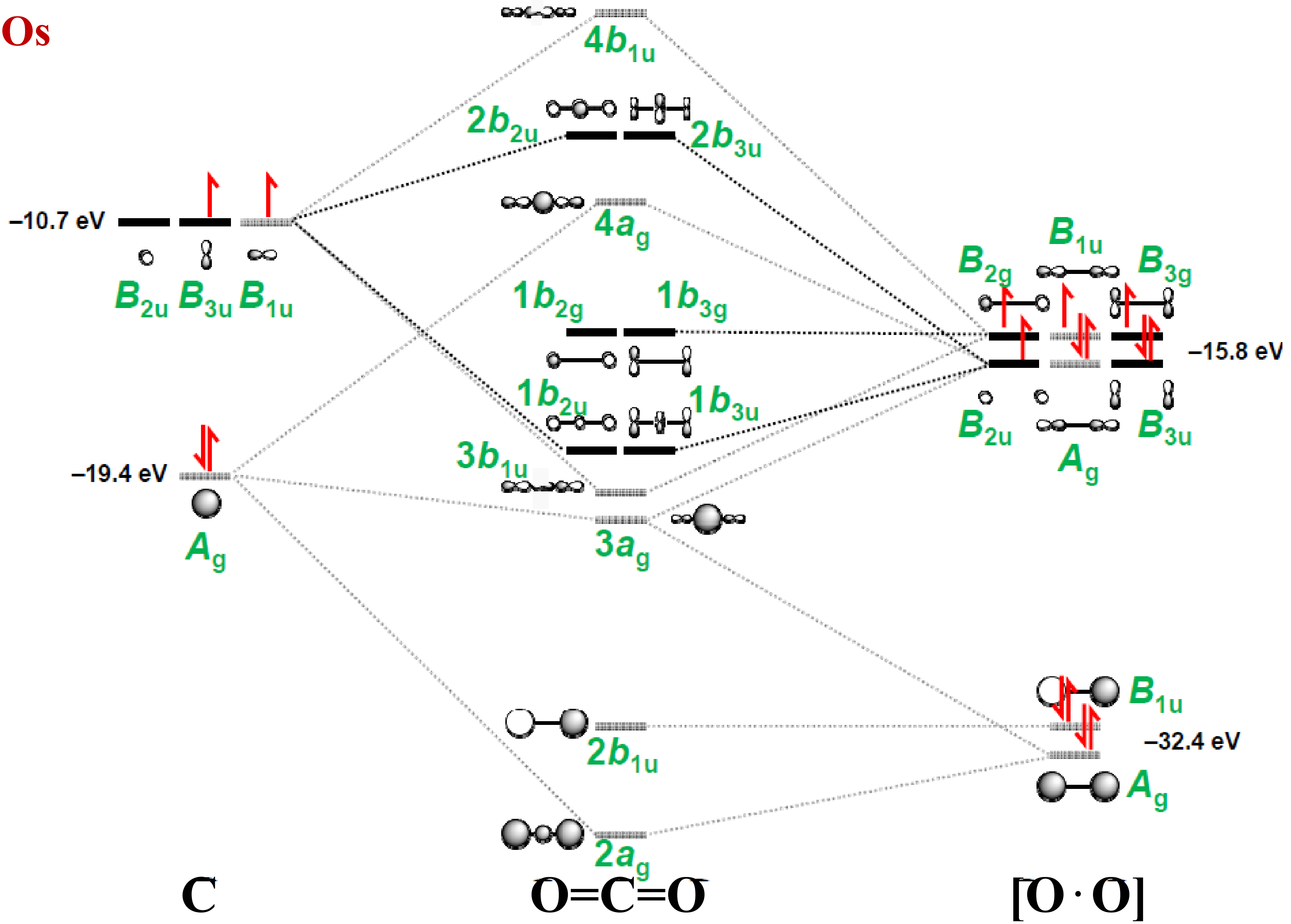
4. Molecular Orbital (MO) Theory

CO_2: The O 2s Orbital is Deep in Energy, but yet able to interact with C 2s



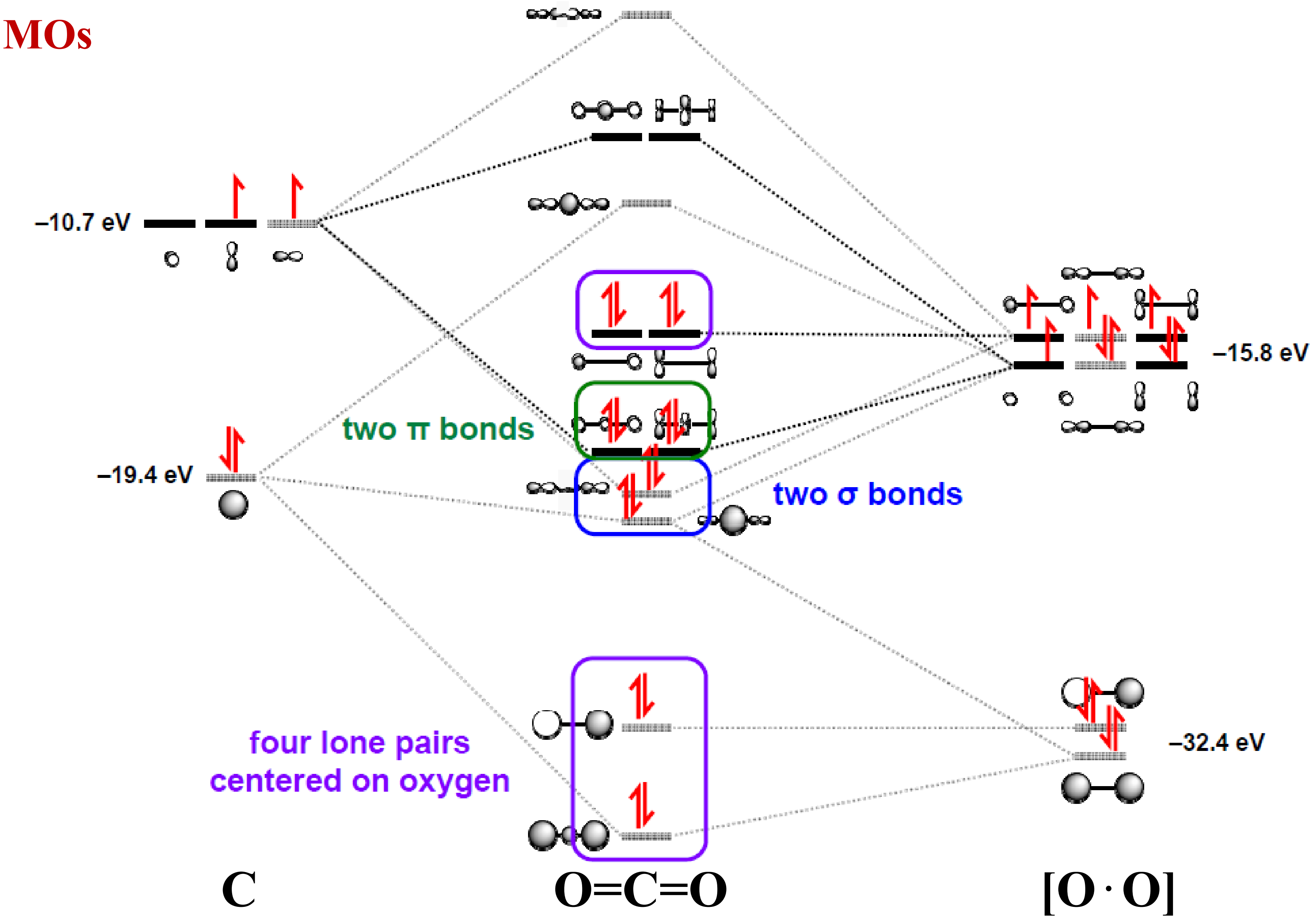
4. Molecular Orbital (MO) Theory

CO_2 MOs



4. Molecular Orbital (MO) Theory

CO_2 MOs

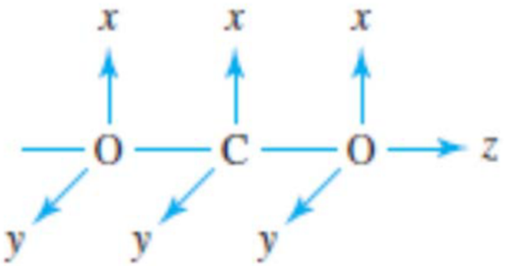


4. Molecular Orbital (MO) Theory

Way to CO_2 MOs by Using Reducible Representations

1. Determine point group → $D_{\infty h}$ but use D_{2h} (this is called descending in symmetry)

2. Take D_{2h} character table



3. Determine reducible representions for orbitals of outer atoms (2 O)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)	linear	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	
Γ_{2s}	2	2	0	0	0	0	2	2		
Γ_{2pz}	2	2	0	0	0	0	2	2		
Γ_{2px}	2	-2	0	0	0	0	2	-2		
Γ_{2py}	2	-2	0	0	0	0	-2	2		

4. Molecular Orbital (MO) Theory

Way to CO_2 MOs by Using Reducible Representations

4. Determine group orbital symmetries by reducing each Γ (order h = 8)

$N = 1/h\, \Sigma n^x \chi_r^x \chi_i^x$

$$\begin{matrix}\text{\# of irreducible} \\ \text{representations} \\ \text{of a given type}\end{matrix} = \frac{1}{\text{order}} \sum_R \left(\begin{matrix}\text{\# of} \\ \text{operations} \\ \text{in the class}\end{matrix} \times \begin{matrix}\text{character of} \\ \text{reducible} \\ \text{representation}\end{matrix} \times \begin{matrix}\text{character of} \\ \text{irreducible} \\ \text{representation}\end{matrix} \right)$$

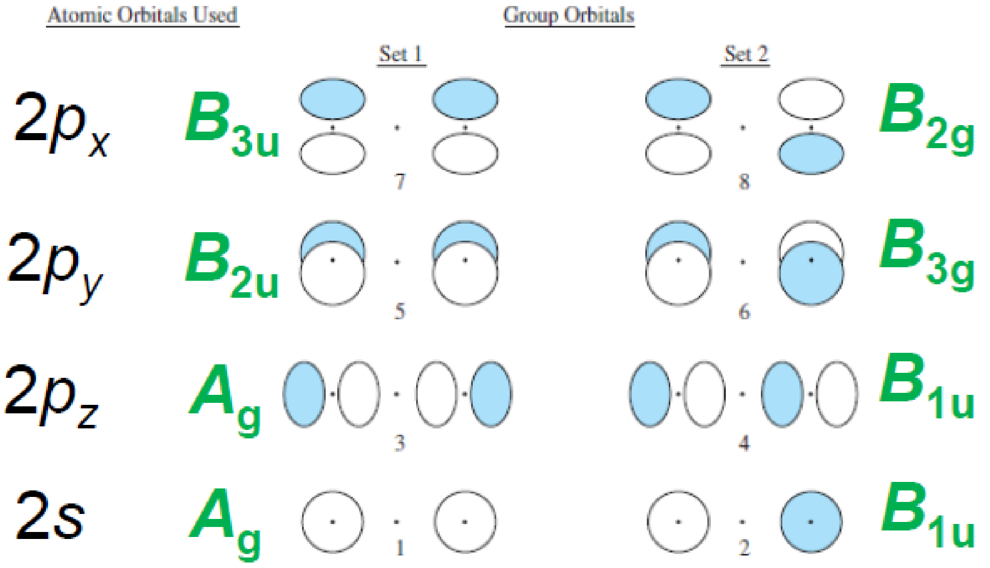
Result

$\Gamma_{2px} = B_{2g} + B_{3u}$

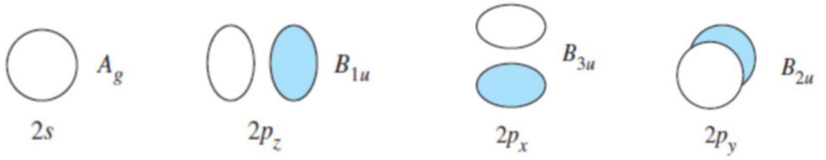
$\Gamma_{2py} = B_{3g} + B_{2u}$

$\Gamma_{2pz} = A_g + B_{1u}$

$\Gamma_{2s} = A_g + B_{1u}$



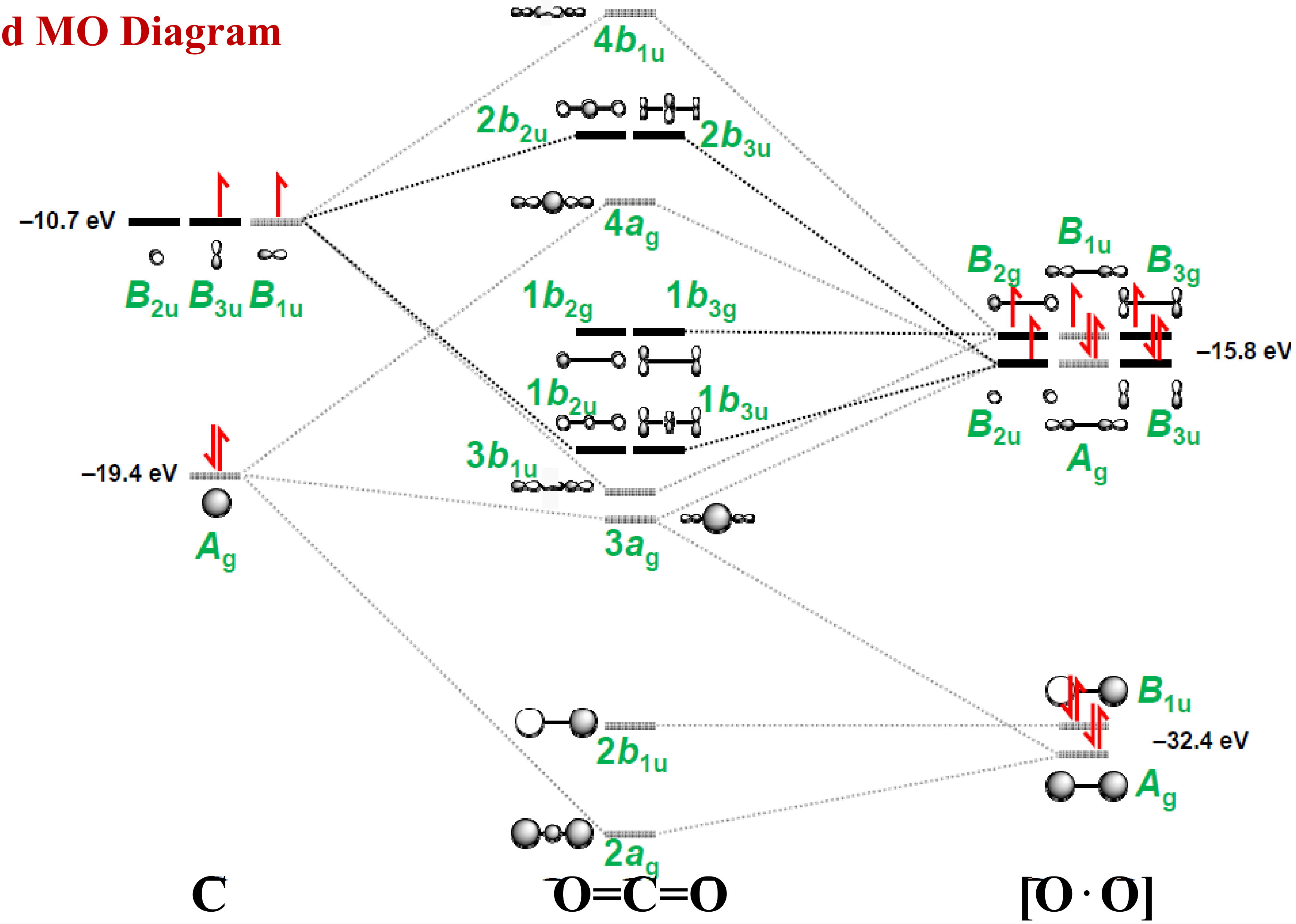
These are the same group orbital symmetries as obtained by inspection



5. Find matching orbitals on central atom C

4. Molecular Orbital (MO) Theory

6. Build MO Diagram

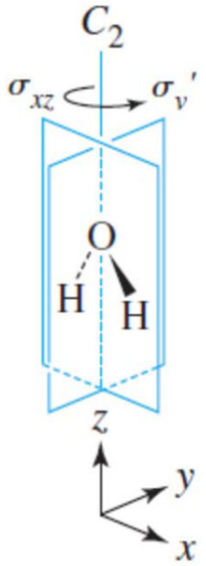


4. Molecular Orbital (MO) Theory

H_2O: This Molecule is Bent → MOs by Using Reducible Representations

1. Determine point group → C_{2v}

2. Take C_{2v} character table



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{1s}	2	0	2	0		

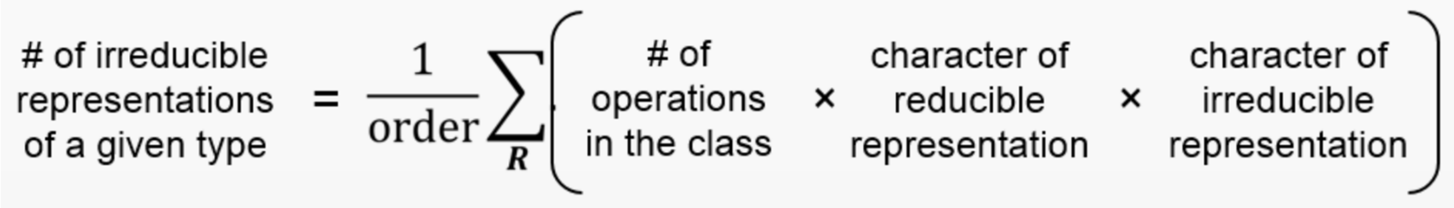
3. Determine reducible representations for orbital of outer atoms (2 H)

4. Molecular Orbital (MO) Theory

H_2O: This Molecule is Bent → MOs by Using Reducible Representations

4. Determine group orbital symmetries by reducing each Γ (order h = 8)

$N = 1/h\ \Sigma n^x \chi_r{}^x \chi_i{}^x$



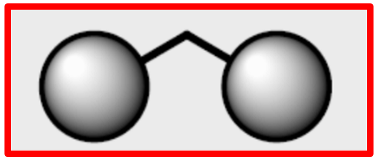
$$\text{\# of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_R \left(\text{\# of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

Result

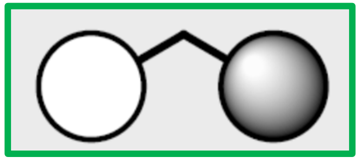
$\Gamma_{1s} = A_1 + B_1$

These hydrogen orbitals look like

A_1

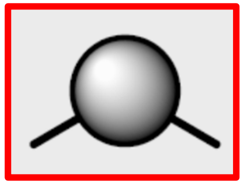


B_2



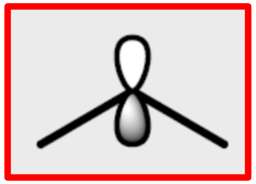
5. Find matching orbitals on central atom O

A_1



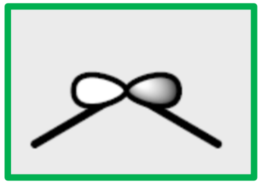
2s

A_1



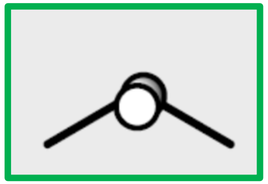
$2p_z$

B_1



$2p_x$

B_2

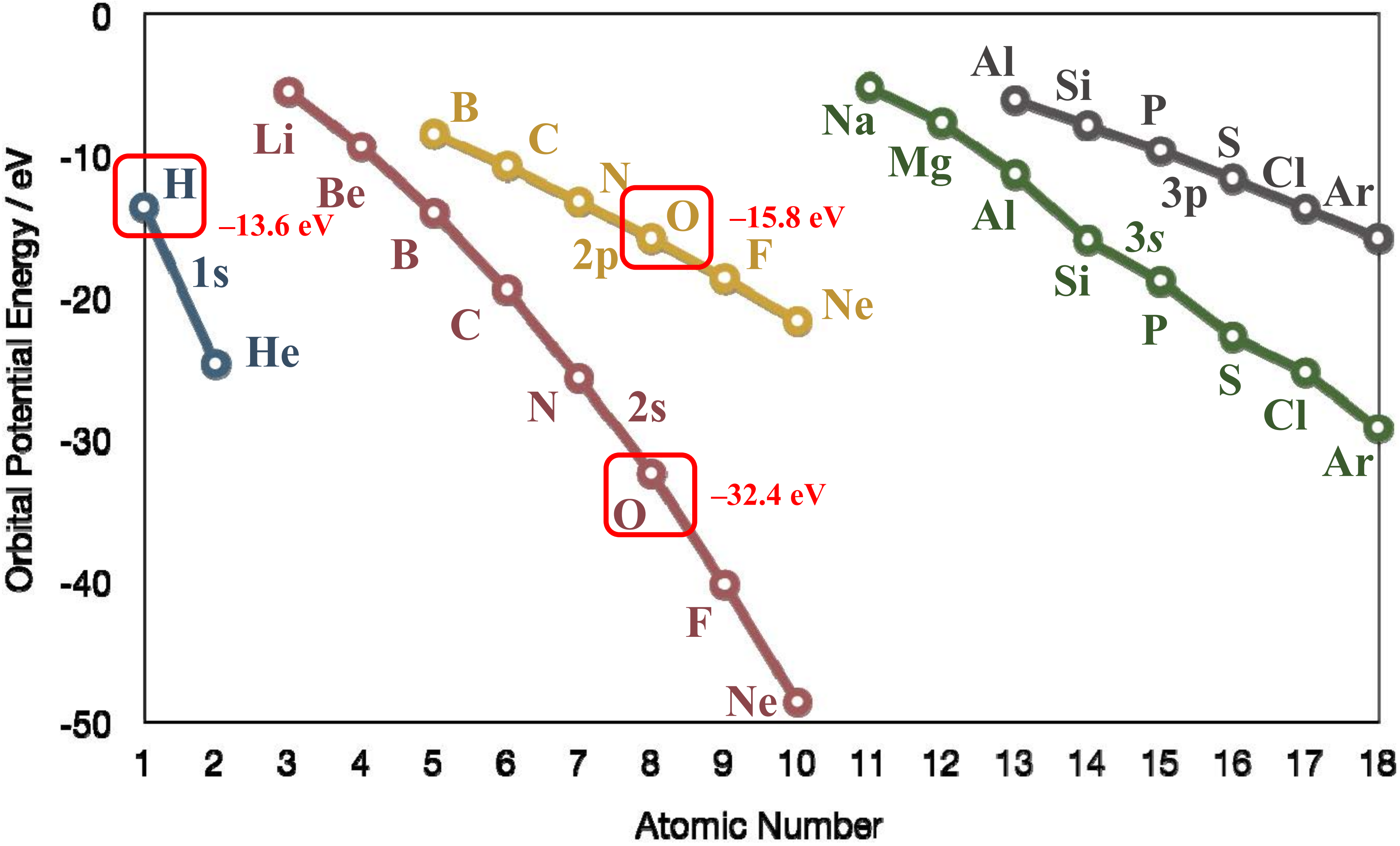


$2p_y$

6. Build MO diagram → six MOs, while the O $2p_y$ totally nonbonding

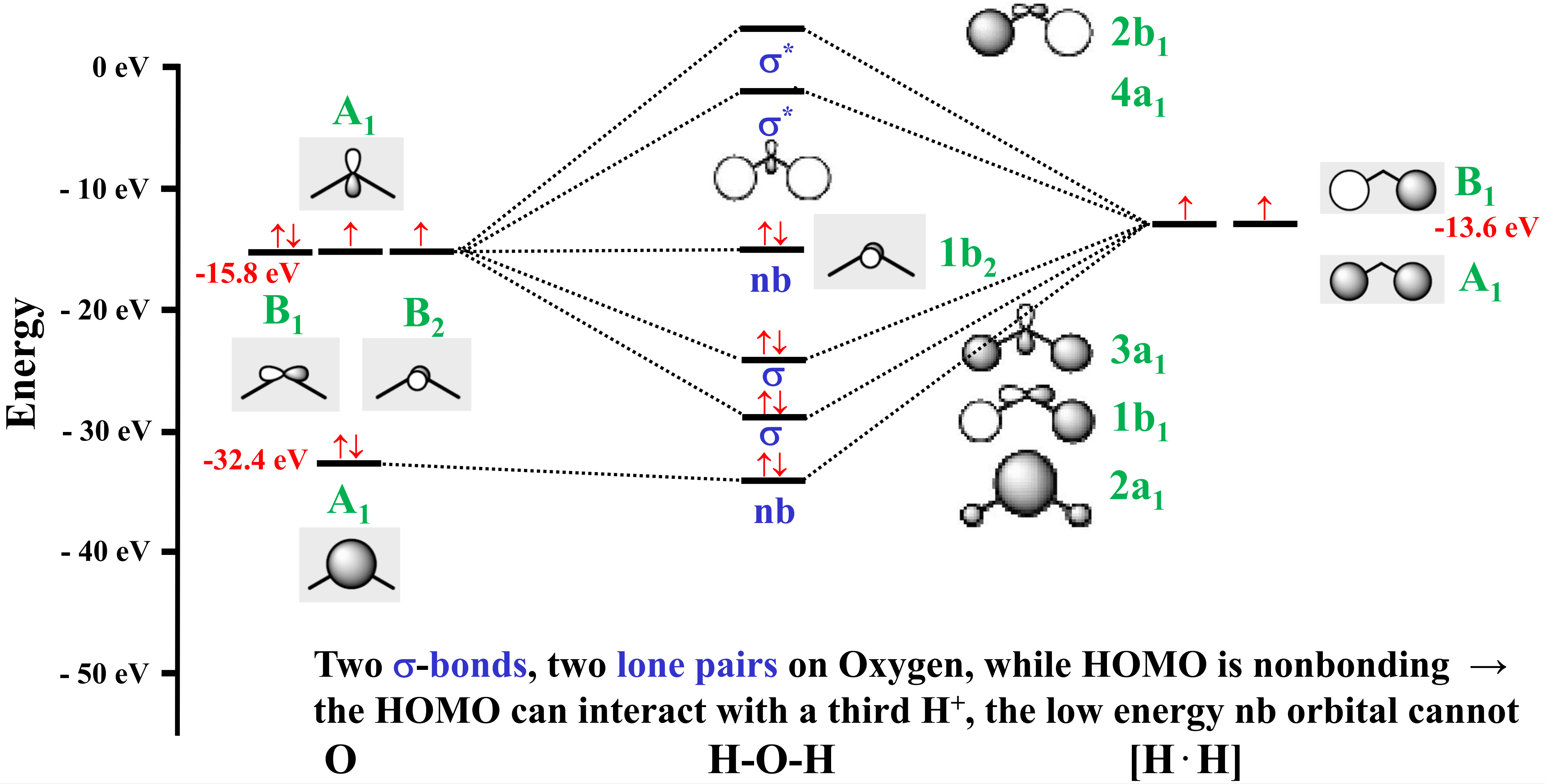
4. Molecular Orbital (MO) Theory

Based on the Large ΔE it is Obvious that O 2*s* is almost Nonbonding



4. Molecular Orbital (MO) Theory

With Orbital Shapes, Symmetries, and Absolute Energies Determined the MO Diagram can be sketched

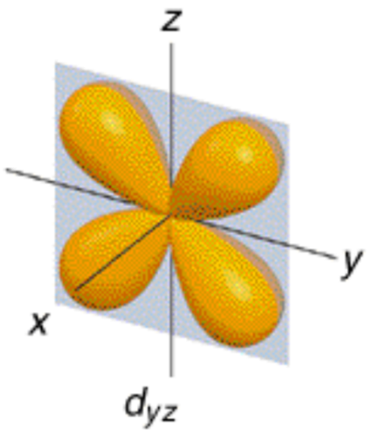


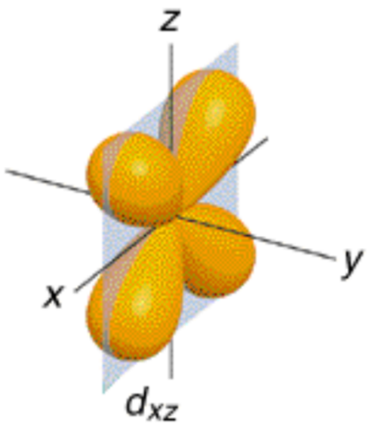
Two σ-bonds, two lone pairs on Oxygen, while HOMO is nonbonding → the HOMO can interact with a third H^+, the low energy nb orbital cannot

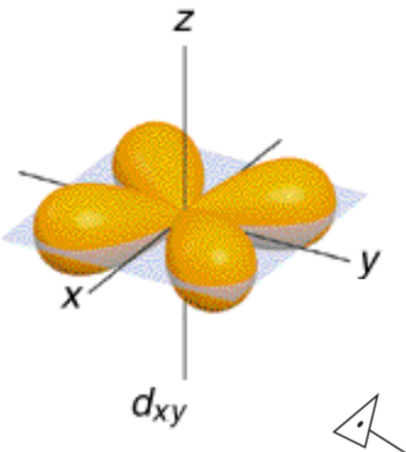
4. Molecular Orbital (MO) Theory

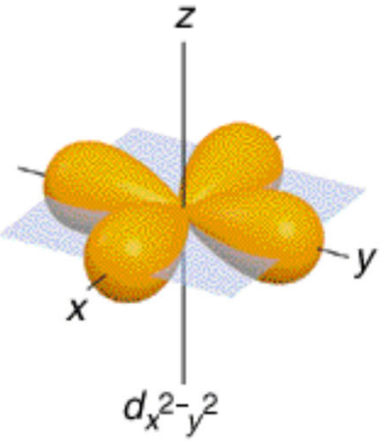
MOs for Molecules Comprising d-Orbitals

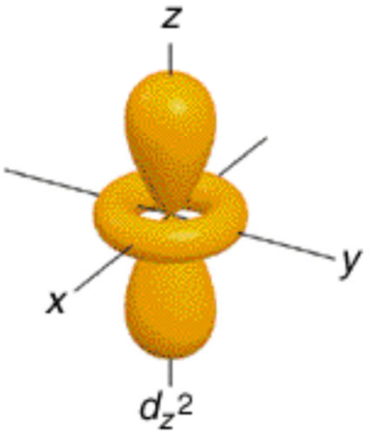
l = 2 → 2l + 1 = 5 d-orbitals per shell → 10 electrons → 10 3d-, 4d-, and 5d-elements

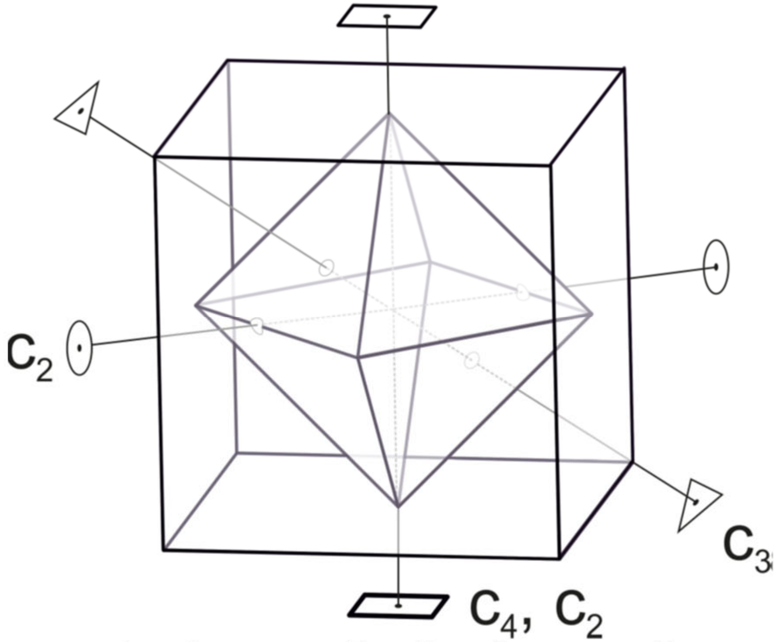








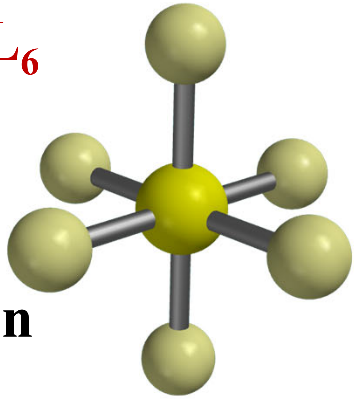




d-orbitals can undergo σ-, π-, or δ-bonding → mostly in octahedral complexes

4. Molecular Orbital (MO) Theory

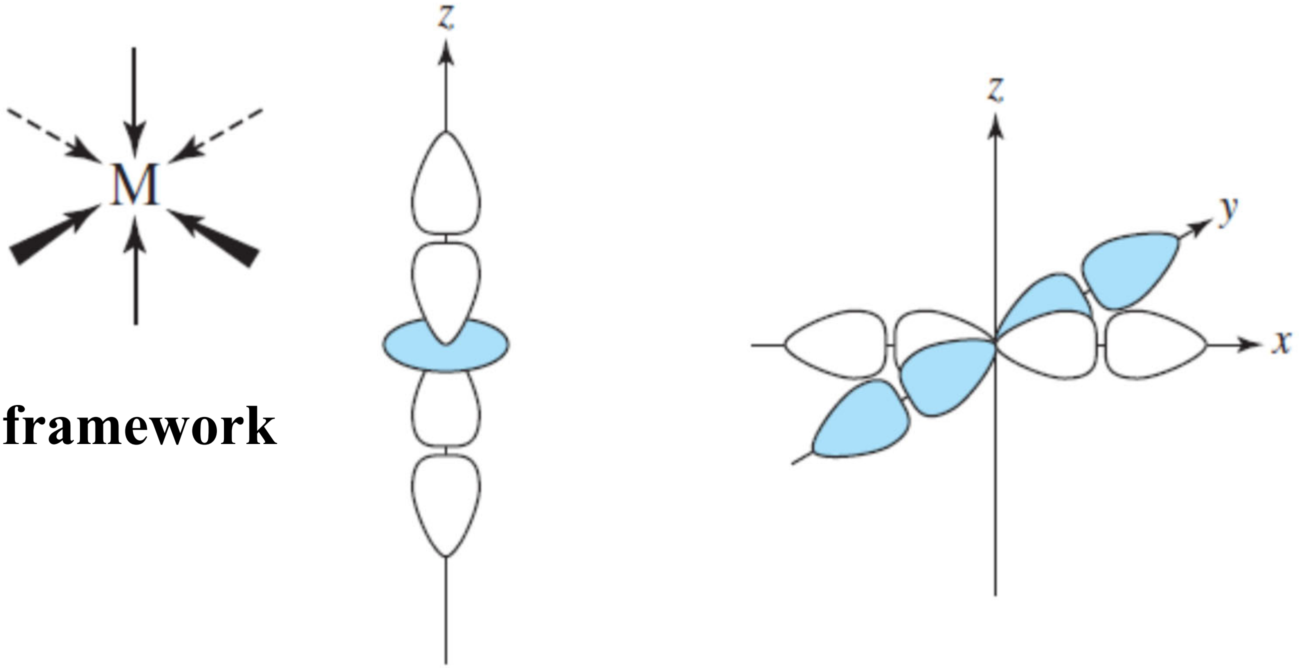
Octahedral Molecules → AlF_6^{3-}, SiF_6^{2-}, PF_6^{-}, SF_6, metal complexes ML_6



1. Determine point group → O_h

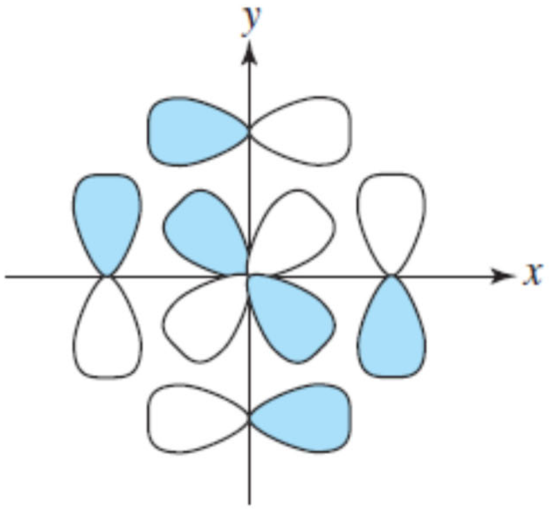
2. The six ligands can interact with the central atom in a σ- or π-fashion

σ-framework



Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital

Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital



Pi bonding interaction between four ligand orbitals and metal d_{xy} orbital

4. Molecular Orbital (MO) Theory

Octahedral Molecules → AlF_6^{3-}, SiF_6^{2-}, PF_6^-, SF_6, metal complexes ML_6

3. Determine reducible representations for M-L sigma bonds

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$2z^2-x^2-y^2$, x^2-y^2
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	R_x, R_y, R_z	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		xy, xz, yz
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x, y, z	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		
Γ_σ	6	0	0	2	2	0	0	0	4	2		

4. Determine group orbital symmetries:

$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$ → six group orbitals L_6 in total

4. Molecular Orbital (MO) Theory

Octahedral Molecules → AlF_6^{3-}, SiF_6^{2-}, PF_6^{-}, SF_6, metal complexes ML_6

5. Find symmetry matches with central atom: $\Gamma_\sigma = A_{1g} + E_g + T_{1u}$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$2z^2-x^2-y^2$, x^2-y^2
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	R_x, R_y, R_z	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		xy, xz, yz
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x, y, z	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		
Γ_σ	6	0	0	2	2	0	0	0	4	2		

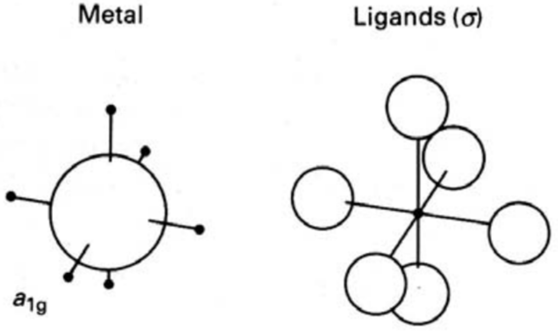
Reading off the character table, it turns out that the group orbitals match the metal s orbital (A_{1g}), the metal p orbitals (T_{1u}), and the d_{z^2} and $d_{x^2-y^2}$ metal d orbitals (E_g) to yield bonding / antibonding combinations. The remaining three metal d orbitals are T_{2g} and σ-nonbonding!

4. Molecular Orbital (MO) Theory

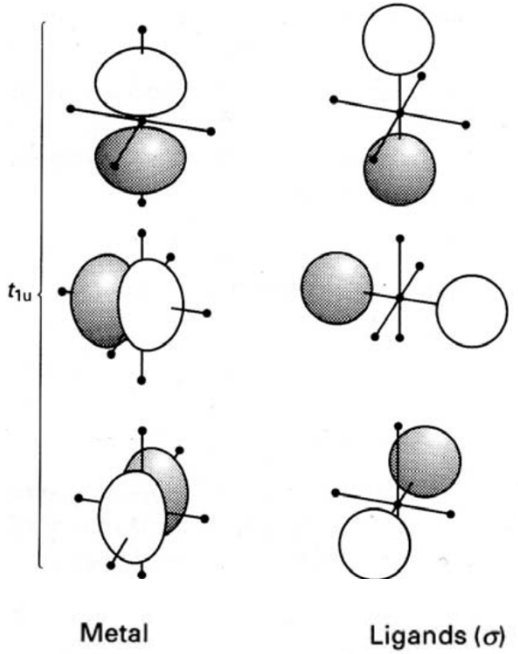
Octahedral Molecules → AlF_6^{3-}, SiF_6^{2-}, PF_6^{-}, SF_6, metal complexes ML_6

L_6 Symmetry Adapted Linear Combinations (SALCs)	Symmetry label
$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$	A_{1g} (non-degenerate)
$\sigma_1 - \sigma_3$; $\sigma_2 - \sigma_4$; $\sigma_5 - \sigma_6$	T_{1u} (triply degenerate)
$\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$; $2\sigma_6 + 2\sigma_5 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4$	E_g (doubly degenerate)

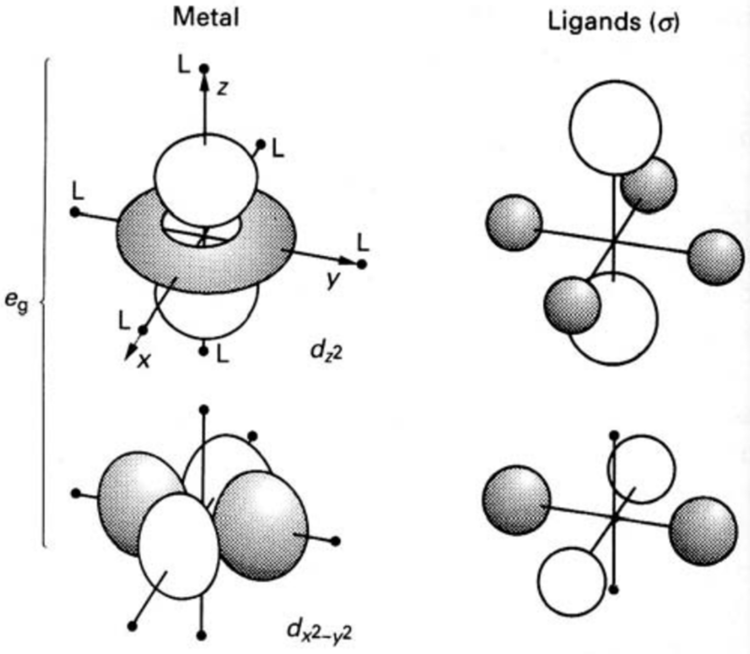
A_{1g} (non-degenerate)



T_{1u} (triply degenerate)



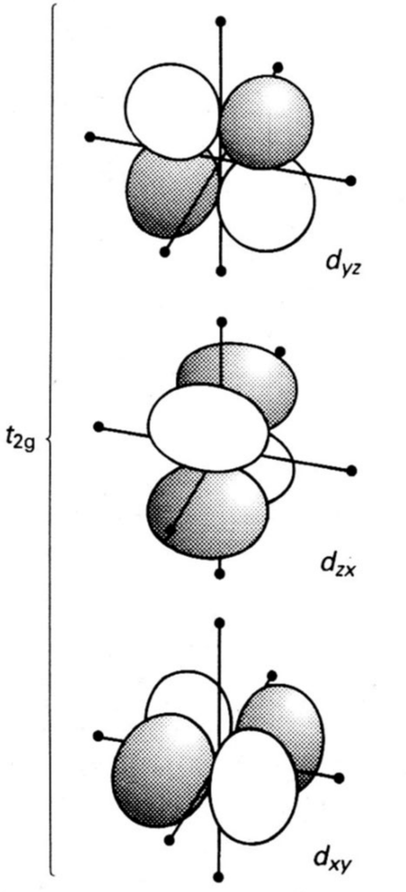
E_g (doubly degenerate)

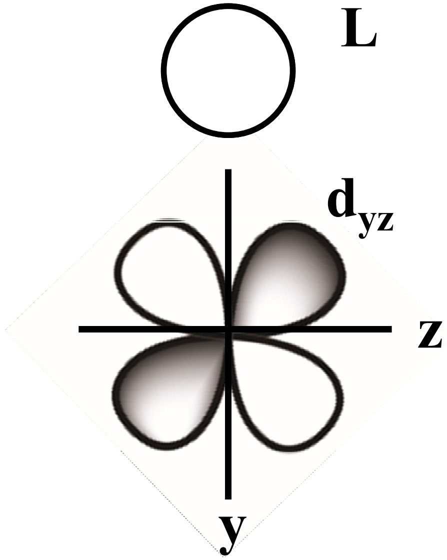


4. Molecular Orbital (MO) Theory

Octahedral Molecules → AlF_6^{3-}, SiF_6^{2-}, PF_6^-, SF_6, metal complexes ML_6

There is no combination of ligand σ orbitals with the symmetry of the metal T_{2g} orbitals, so these do not participate in σ bonding:





T_{2g} orbitals cannot form sigma bonds with the L_6 set

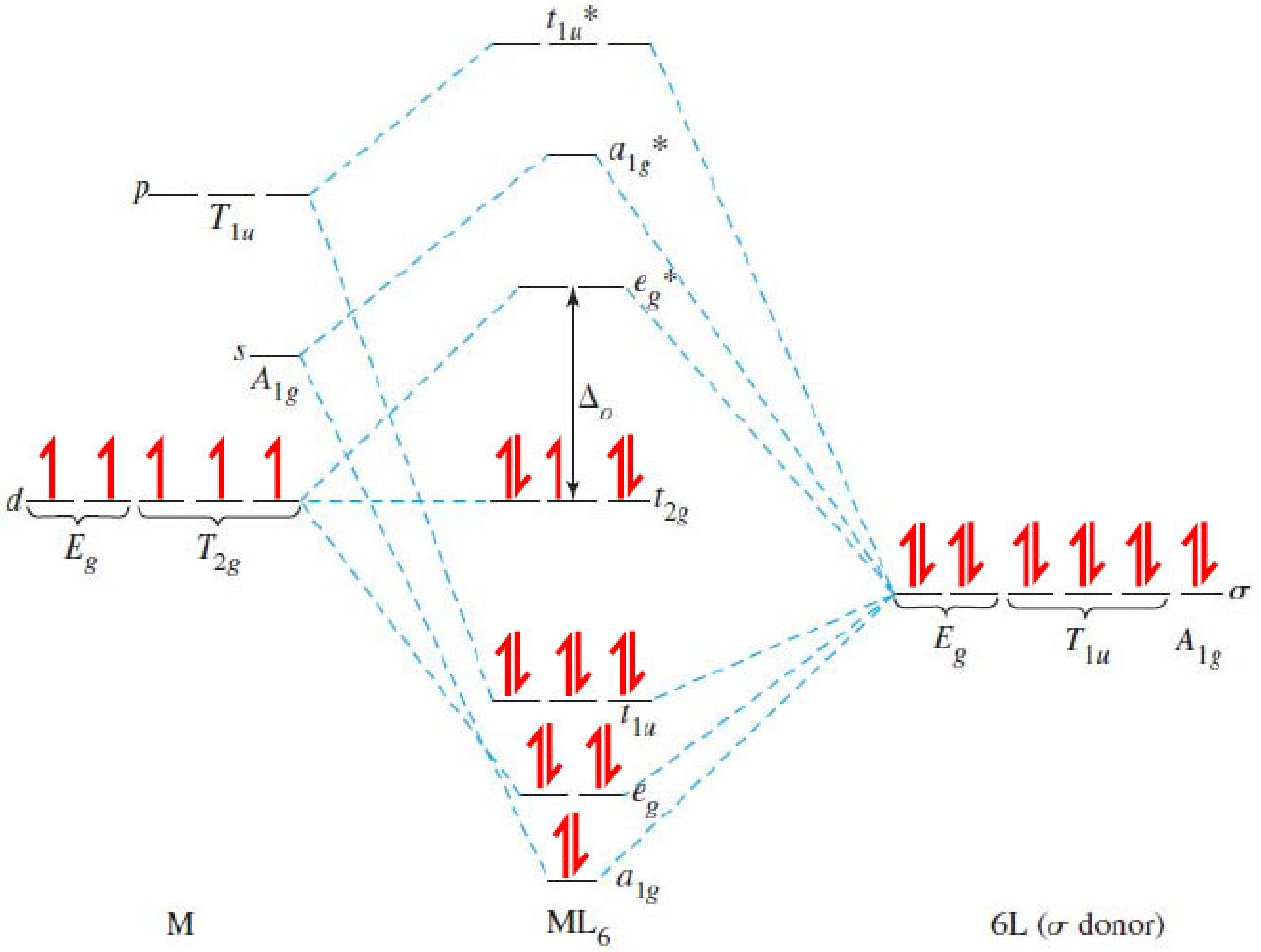
→ Orbital overlap S = 0

T_{2g} are thus non-bonding

4. Molecular Orbital (MO) Theory

Octahedral Molecules → AlF_6^{3-}, SiF_6^{2-}, PF_6^{-}, SF_6, metal complexes ML_6

6. Build MO diagram for σ-bonding in ML_6 complexes with O_h symmetry



4. Molecular Orbital (MO) Theory

Summary

- MO diagrams can be built from group orbitals and central atom orbitals by considering orbital symmetries and energies
- The symmetry of group orbitals is determined by reducing a reducible representation of the orbitals under consideration. This approach is used only when the group orbitals are not obvious by inspection
- MOs for the following molecules were derived
  Homonuclear diatomics, HF, CO, H_3^+, FHF^-, CO_2, H_2O, and σ-ML_6
- MO diagrams can correctly explain some physical properties and reactivity of molecules and complexes

5. Marcus Theory

Goal and History

Goal

- Theory of reaction kinetics of electron transfer (ELT) or atom transfer (AT)
- Electron exchange between a donor (D) and an acceptor (A) without a major change in structure

$$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$$

- Compare: Energy transfer (ET) → photochemistry or PL

$$D + A \xrightarrow{h\nu} D^* + A \rightarrow D + A^*$$

History

- Published 1956 by Rudolph Arthur Marcus (*1923)
- 1992: Nobel Prize for Chemistry

Literature

- R.A. Marcus, The Nobel Prize in Chemistry 1992, 1992, 69-92
- R.A. Marcus, The Journal of Chemical Physics 1956, 24(5), 966-978

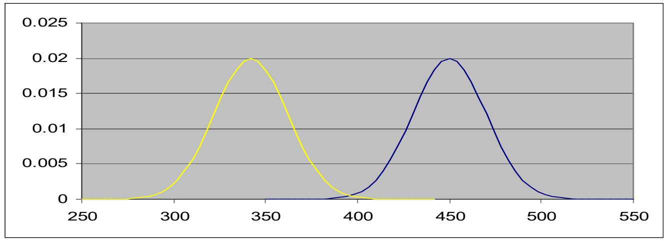
5. Marcus Theory

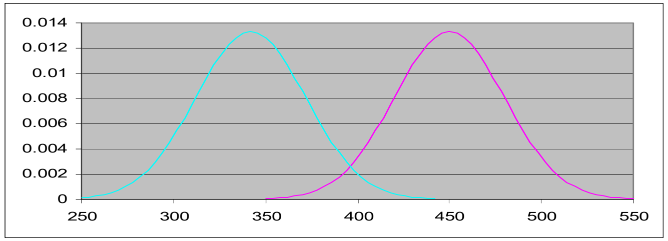
Energy Transfer – Some Basics

- Isoelectronic energy transfer/migration via chemical species → photosynthesis
- No breaking or making of novel bonds
- Franck-Condon-Principal:
  - ET is faster (~10^{-15} s) than movement of the nucleus (~10^{-13} s) or solvent, i.e. coordination of nucleus doesn't change during ET processes

  ⇒ transition state yet possible due to thermal fluctuation of the solvent

  ⇒ necessary configuration change by polarisation and/or vibrations
- Thermal fluctuations
  - random deviations from average state in an equilibrium
  - increase in size and frequency if temperature rises
- Efficiency increases with overlapping of the emission spectrum of D^* with the absorption spectrum of A





5. Marcus Theory

Energy Transfer: $D^* + A \rightarrow D + A^* \Rightarrow$ quenching of D* depends on concentr. of A

Dexter energy transfer: short distances (up to ca. 1 nm) → „Transfer“ of electrons

Förster energy transfer: longer distances (up to ca. 10 nm) → Coulomb interaction

$\tau = 1/(k_r + k_{nr})$

k_r= radiation processes

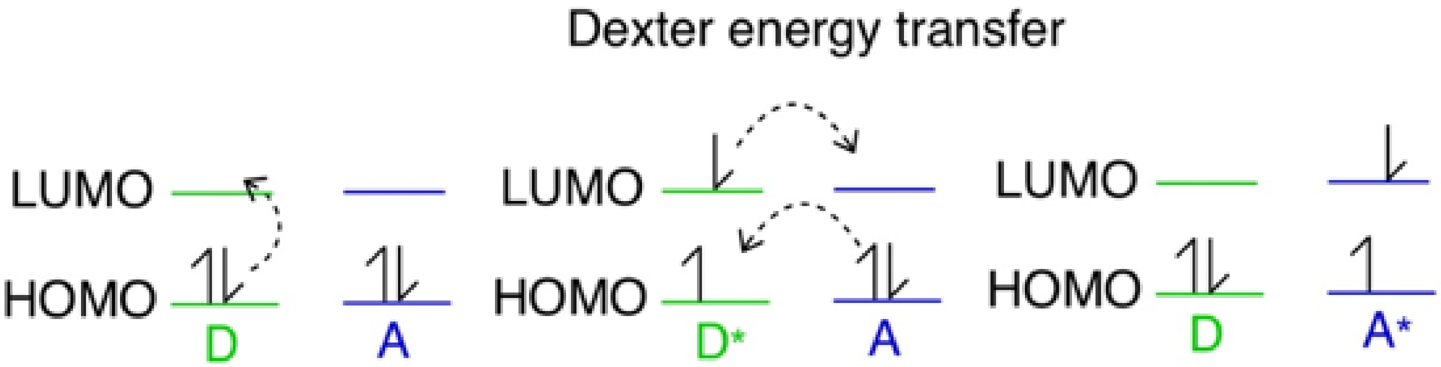
$\Rightarrow$ assumed to be temp.-independent

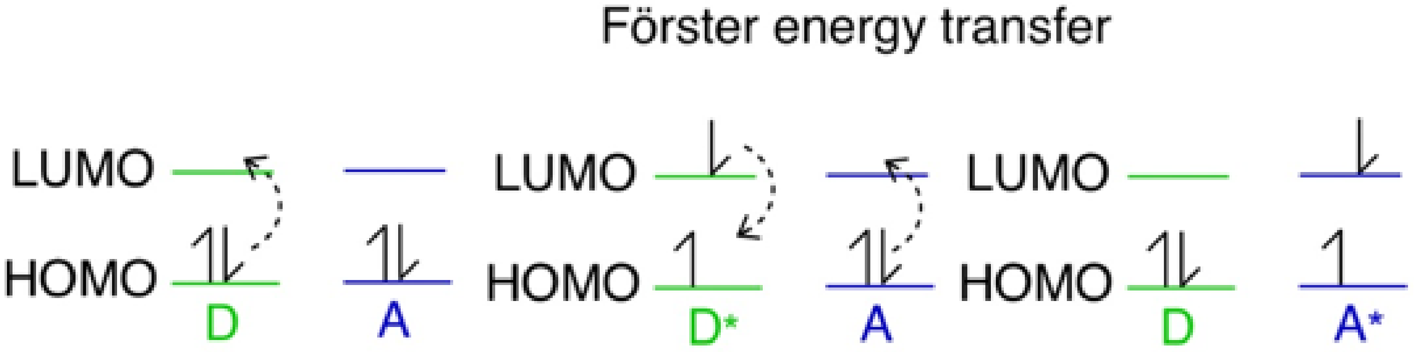
k_{nr} = radiationless processes (quenching)

$\Rightarrow$ may depend on temp.

$k_{ET} = 1/\tau_1 - 1/\tau_0$

τ_1 and τ_0: lifetimes of the excited state with and without quencher



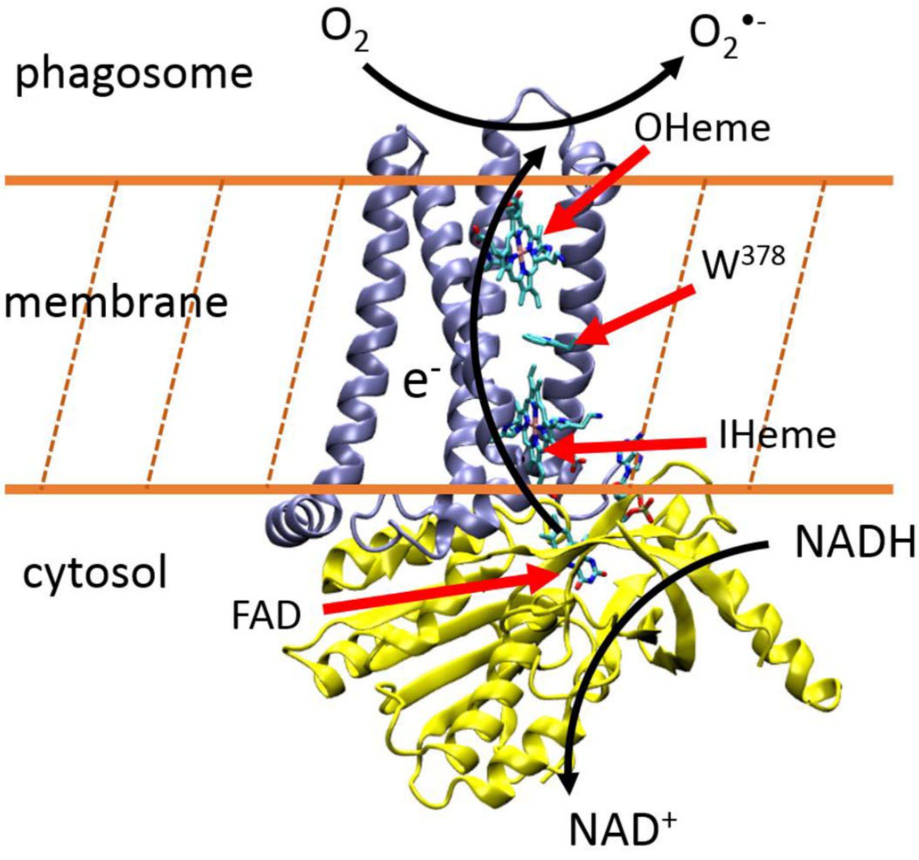


5. Marcus Theory

Electron Transfer

Oxidation and reduction (redox) reactions are defined by the change of the oxidation state of two interacting species

→ Acceptor (A) and Donor (D) species



An effective change in the oxidation state can occur via a pure electron transfer (ELT or ET)

$$A^{(n+1)+} + D^{m+} \rightleftharpoons A^{n+} + D^{(m+1)+}$$

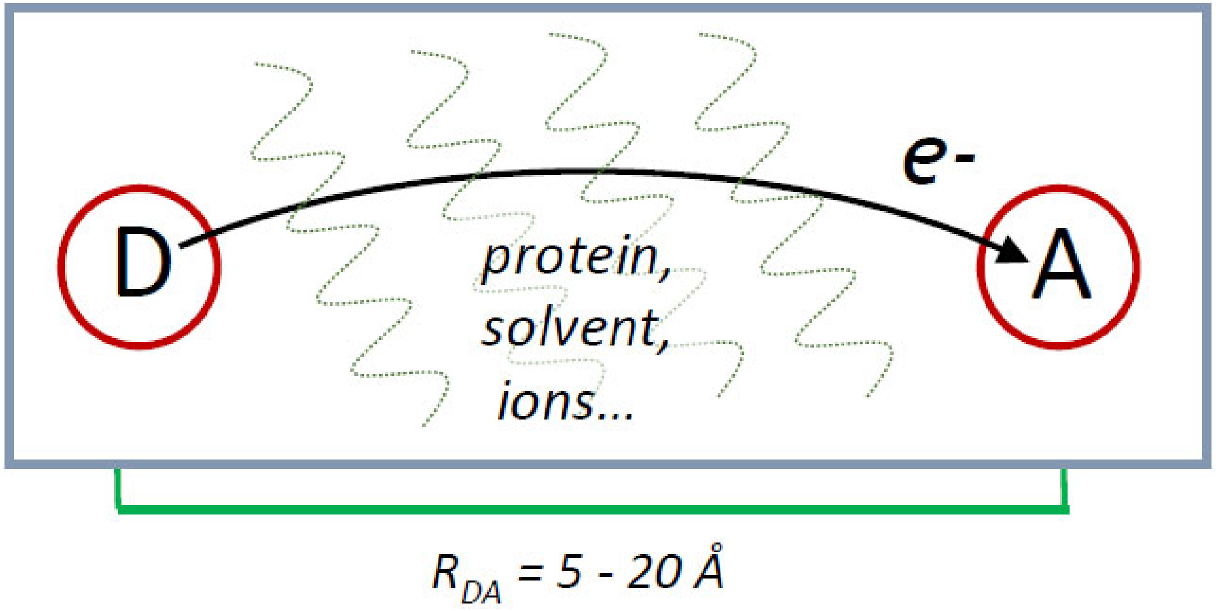
or by an atom transfer (AT)

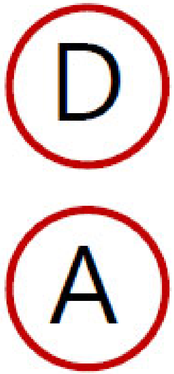
$$AX_n^- + X^- \rightleftharpoons AX_{n+1}^{2-}$$

5. Marcus Theory

Electron Transfer – Applications in Biology and Medicine

- Damages to biomolecules, e.g. DNA, by ionizing radiations: cancer treatment
- Respiratory chain of bacteria or in mitochondria of Eukarya
- Photosynthesis: photoreactive centers
- Enzymatic catalysis: oxidoreductases
- Bio-electrochemical system and bioinspired artificial systems



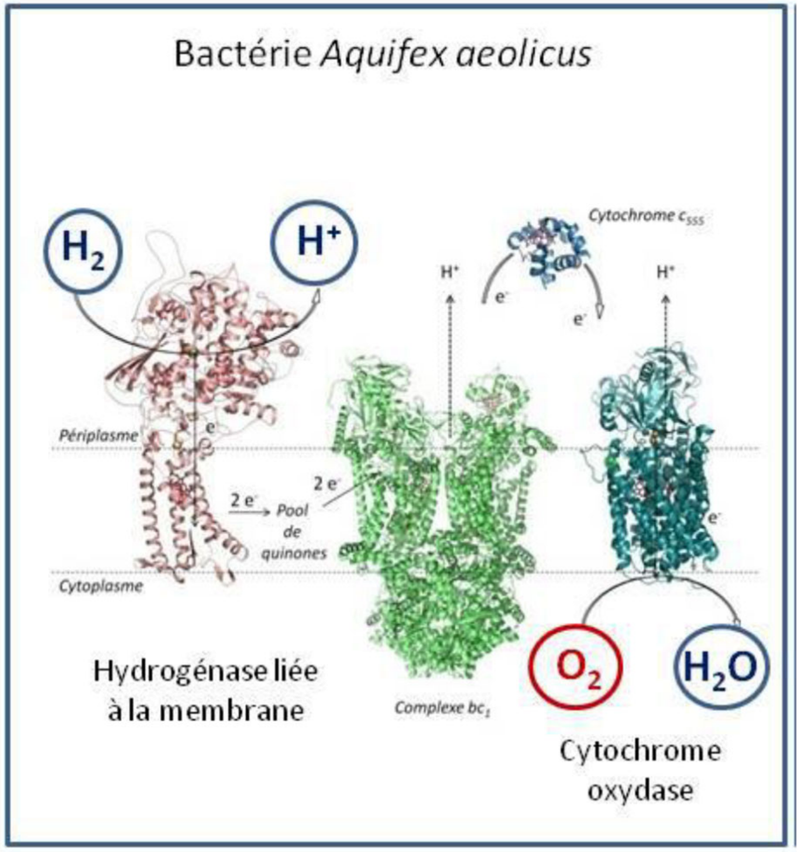


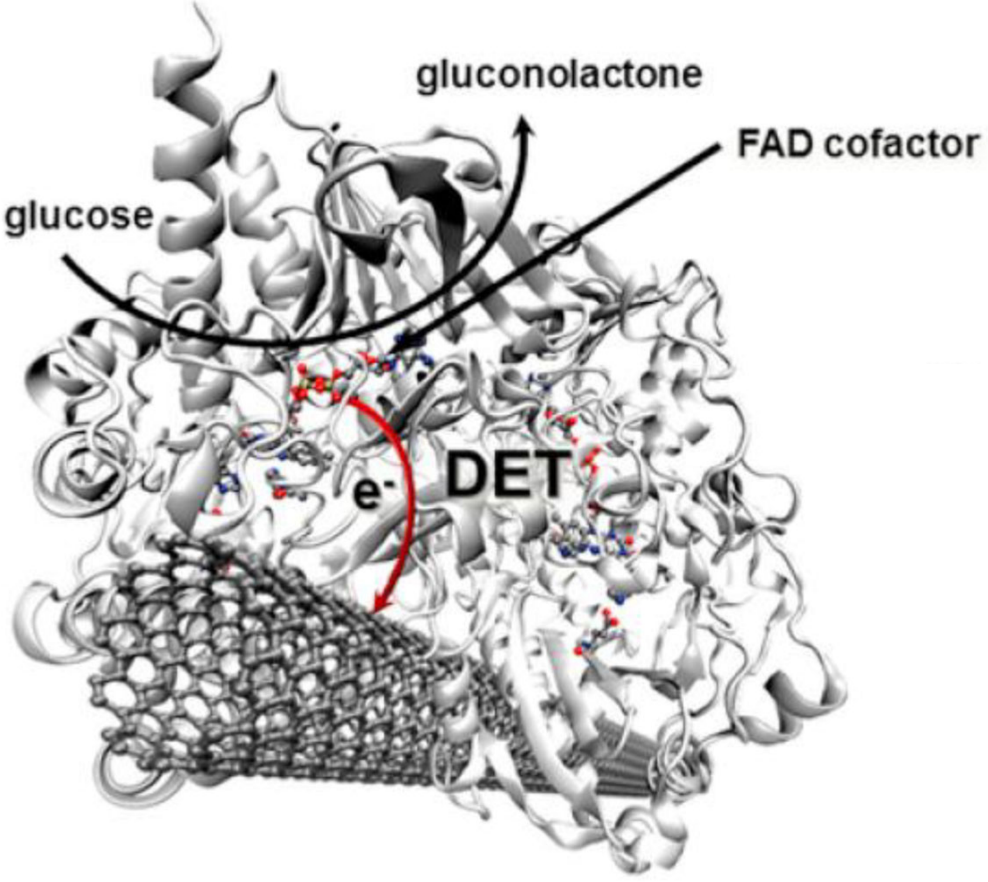
Organic co-factors
quinones
flavins
amino acid residues

“Inorganic” co-factors
hemes (Fe)
chlorophyls (Mg)
blue copper centers (Cu)
iron-sulphur centers (Fe)

5. Marcus Theory

Electron Transfer – Application for Biology Fuel Cells





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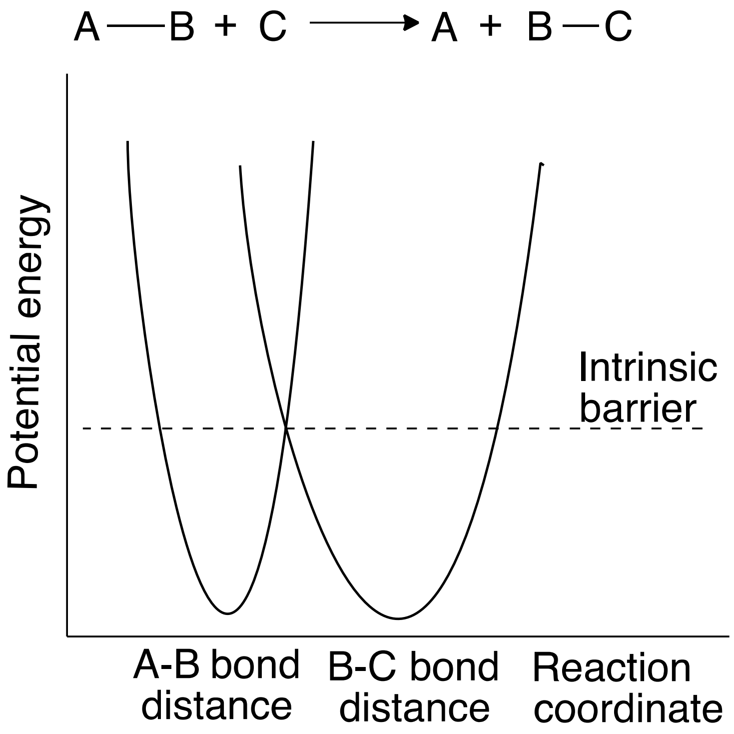
S. Cosnier et al., J Power Sources 325 (2016) 252

5. Marcus Theory

Application to Redox Reactions in Solvents

- **Electron transfer (ELT) = non-radiative transition through the tunnel effect**
  - $MnO_4^-(aq) + 8\ H^+ + 5\ Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O$
  - $CrO_4^{2-}(aq) + 8\ H^+ + 3\ Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + 3\ Fe^{3+}(aq) + 4\ H_2O$
- **Atom transfer (AT) = Transfer of an atom, e.g. H^+ or O^{2-}, along a reaction coordinate over an intrinsic barrier**
  - $ClO^-(aq) + NO_2^-(aq) \rightarrow Cl^-(aq) + NO_3^-(aq)$



- **Reaction rates of the transfer**
  - **spans over several ten potencies**
  - **depend on size of molecule/complex/ion**
  - **access by UV spectroscopy**

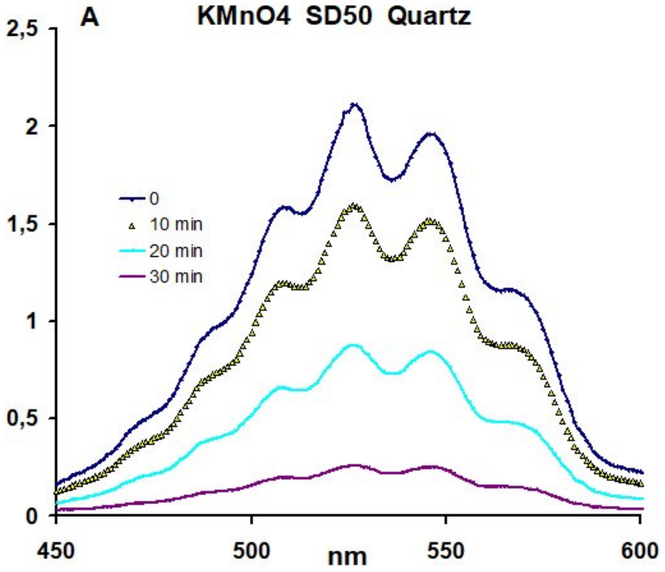
- **1st order** rate = $k[A]$ with $[k] = s^{-1}$
- **2nd order** rate = $k[A][B]$ with $[k] = l mol^{-1} s^{-1}$

5. Marcus Theory

Application to Redox Reactions in Solvents

Example: $MnO_4^-(aq) + 8\ H^+ + 5\ Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O$

Determination of $[MnO_4^-]$ by absorption spectroscopy



Results

- Reaction rate = k[A][B] with $[k] = lmol^{-1}s^{-1}$
- Strong dependency on pH value

Assumptions

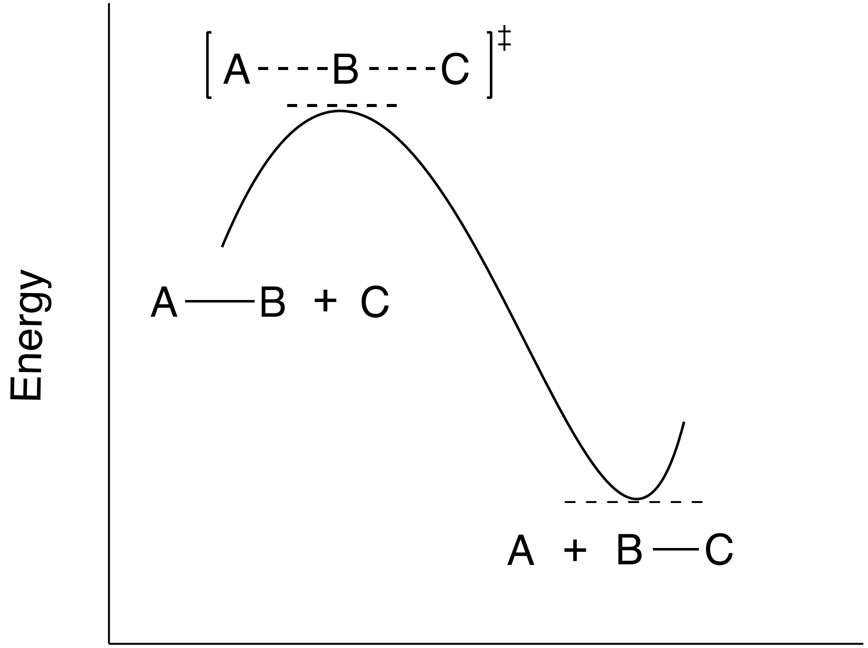
- At the rate determining reaction step solely two particles are involved
  $MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow MnO_4^{2-}(aq) + Fe^{3+}(aq)$
- All other reaction steps are fast
  $MnO_4^{2-}(aq) + 8\ H^+ + 4\ e^- \rightarrow \rightarrow \rightarrow \rightarrow Mn^{2+}(aq) + 4\ H_2O$

5. Marcus Theory

Background

Transition State Theory (TST)

- **Developed by Henry Eyring in the 1930s**
- **Describes reaction rates focusing on the geometry of transition state at the top of the energy barrier**
- **Effective for describing bond breakage followed by bond formation**



Transition State Theory: effective in describing bond formation/bond cleavage

Eyring equation
(k = rate constant)

$$\boxed{k = \frac{k_B \cdot T}{h} \cdot e^{\frac{-\Delta G^{\#}}{RT}}}$$

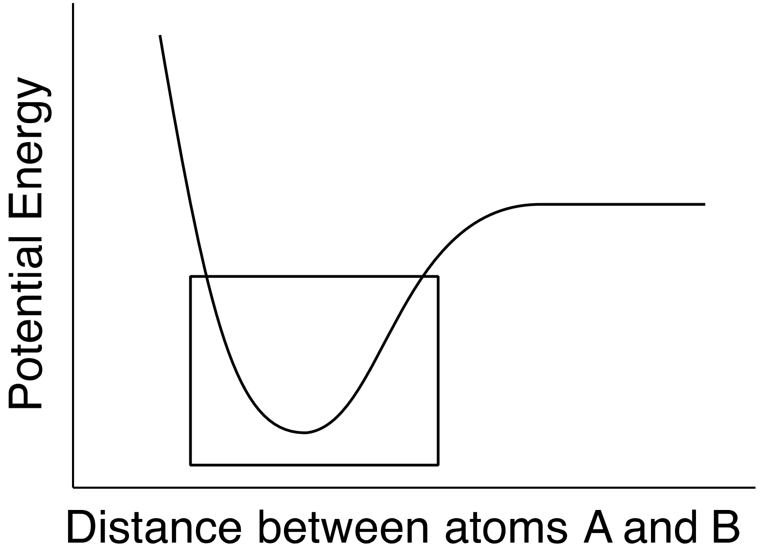
Limitations

Reactions that do not involve bond breakage/formation, i.e. electron transfer reactions, involve little nuclear movement in the transition state
→ rate of electron transfer is much faster than rate of molecular vibrations
→ TST fails and this necessitates a different model

5. Marcus Theory

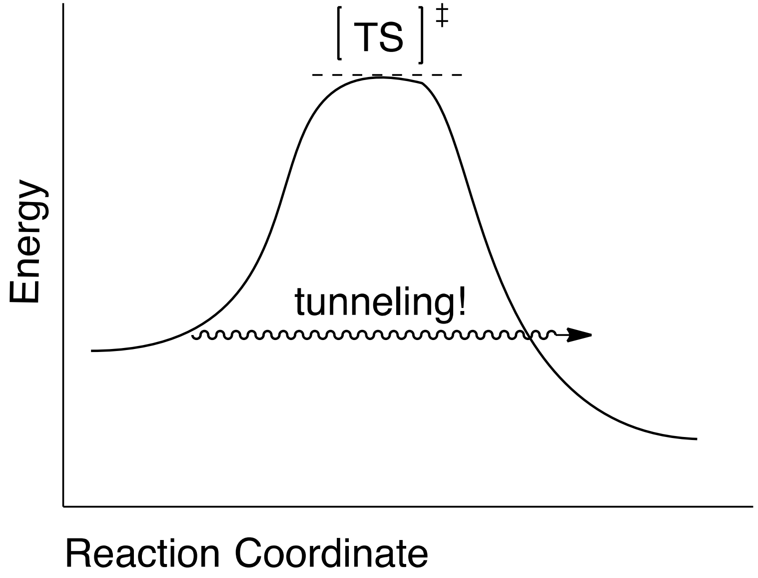
Background

Morse potential: It describes the potential energy as a function of bond distance. The Marcus theory focuses on a parabolic approximation of the boxed fraction ~ harmonic oscillator



Morse potential for A-B

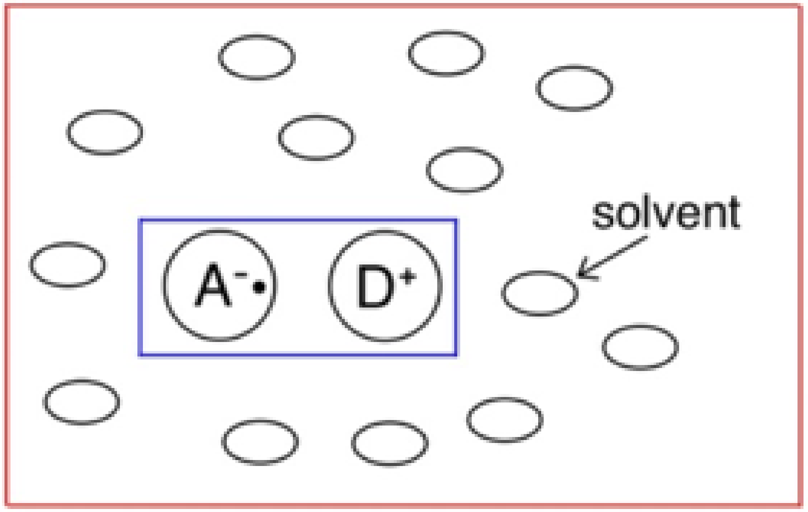
Franck-Condon principle: In an electronic transition between two reactants, the solvent molecules do not have time to rearrange; thus, the atomic configuration and total energy of the system remain the same; only the electronic state changes

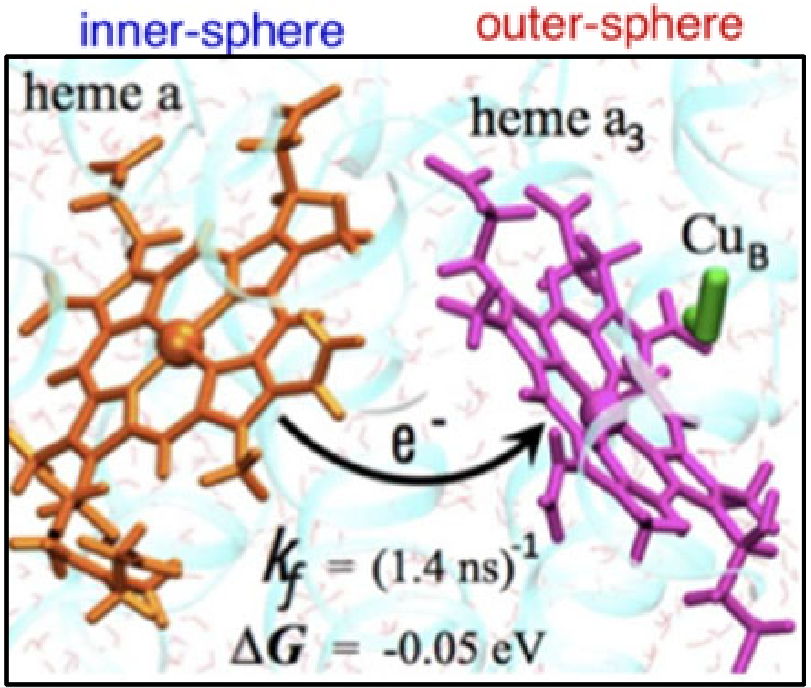


Quantum tunneling: Some small particles (electrons, H^+, Li^+, …..) can tunnel through energy barriers rather than going over them. This complicates free energy calculations

5. Marcus Theory

Inner Sphere and Outer Sphere Reactions





- Inner sphere
    - redox reaction between a donor and an acceptor via a bridging ligand, i.e. via a covalent linkage
    - at least one of the complexes needs to be labile to allow the bridge to form
    - bonds are broken and formed (see TST)

- Outer sphere
    - electron transfer occurs between complexes or molecules that do not undergo structural changes
    - no new bonds are broken or formed
    - strong impact of solvent
    - Long-range ELTs in biology are all of the outer-sphere type

5. Marcus Theory

Outer Sphere Reactions

$A^{(n+1)+}L_x \quad + \quad B^{m+}L_y \quad \rightleftharpoons \quad A^{n+}L_x \quad + \quad B^{(m+1)+}L_y$

oxidant is reduced **reductant is oxidised**

Mechanism

1. Formation of the precursor complex

$A^{(n+1)+}L_x + B^{m+}L_y \rightleftharpoons [A^{(n+1)+}L_x\cdots B^{m+}L_y]$ k_0 **precursor complex**

2. Activation/reorganisation of precursor complex, electron transfer, and relaxation to successor complex

$[A^{(n+1)+}L_x\cdots B^{m+}L_y] \rightarrow [A^{n+}L_x\cdots B^{(m+1)+}L_y]$ k_{ET} **successor complex**

3. Dissociation of successor complex

$[A^{n+}L_x\cdots B^{(m+1)+}L_y] \rightarrow A^{n+}L_x + B^{(m+1)+}L_y$ k_{diss} **products P**

5. Marcus Theory

Outer Sphere Reactions

Example:

$[Co(NH_3)_6]^{3+}$ + $[Cr(H_2O)_6]^{2+}$ $\rightleftharpoons$ $[Co(NH_3)_6]^{2+}$ + $[Cr(H_2O)_6]^{3+}$

$[Ar]3d^6$ l.s.: inert | $[Ar]3d^4$ h.s.: labile | $[Ar]3d^7$ h.s. | $[Ar]3d^3$

Formation of the precursor complex

$A^{(n+1)+}L_x + B^{m+}L_y \rightleftharpoons [A^{(n+1)+}L_x{\cdots\cdots}B^{m+}L_y]$ k_0 precursor complex

Dependency of k_0

- Dielectric constant of the solvent → eluotropic series
- Radius of the ions +
- Charge of the ions → ion charge density ….. ☺

K_0 can be calculated upon using the Debye-Hückel theory (see below)

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Outer Sphere Reactions

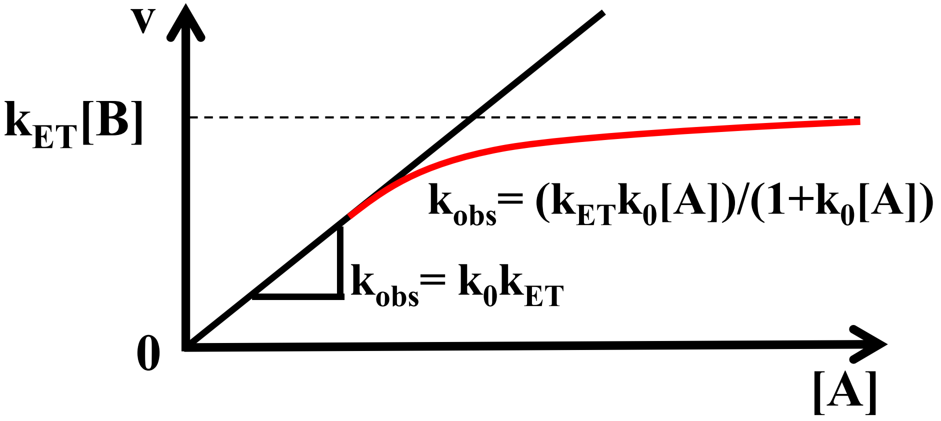
The mechanism thus involves an upstream equilibrium
→ Michaelis-Menten-Kinetics for reactions of a substrate A at an enzyme B

$k_0 >> k_{ET}$ ($k_{catalysis}$)

Reaction rate $v = d[P]/dt = (k_{ET}k_0[A])/(1+k_0[A])\ [B] = k_{obs}\ [B]$

Kinetic measurements are mostly done under pseudo 1st order conditions: One component in excess, e.g. the substrate in biocatalysis:

$k_0[A] >> 1$ $v = k_{ET}[B]$ 1st order
$k_0[A] << 1$ $v = k_0k_{ET}[A][B]$ 2nd order



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Outer Sphere Reactions

The problem of kinetic measurements is that k_{obs} is determined and a change cannot traced back to a change of k_0 or k_{ET}

The interest is focused on k_{ET}, since this is important for catalysis and biocatalysis

Experiments are performed at large [A], to obtain saturation of the formation of the precursor complex

But: If k_0 is small, e.g. for ions with same charge, which strongly repell each other, [A] cannot adjusted largely enough due to experimental (concentration) limitation

Calculation of k_0 required!

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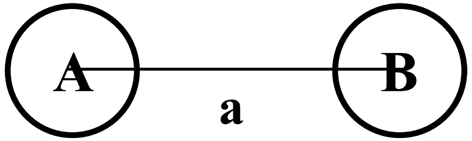
Outer Sphere Reactions - Calculation of k_0 by the Eigen-Fuoss Equation

$$k_0 = 4\pi N_A a^3/3000 \cdot \exp(-U(a)/k_B T)$$



with N_A = Avogadro constant

k_B = Boltzmann constant

a = minimum distance of approach between the complexes in solution

$U(a) = z_1 z_2 e^2/\varepsilon a(1+\chi a)$

z = ion charge

ε = dielectric constant

$\chi = [8\pi N_A e^2 I/1000\varepsilon k_B T]^{1/2}$

I = Ion strength

Requirement: x-ray structure of the precursor complex known

$k_0 = 10^{-3} – 10^{-1}$ for equally charged ions (calculation required)

$k_0 = 10^3 – 10^4$ for oppositely charged ions (experimental determination feasible)

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Outer Sphere Reactions: Thermodynamic Driving Force $\Delta G^0 = -nF\Delta E^0$

Examples

a) Self exchange reaction between isotopes: $\Delta G^0 = 0$, $\Delta G^{\neq} = ?$

$[Co^*(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightleftharpoons [Co^*(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$

[Ar]3d^7 h.s. [Ar]3d^6 l.s. [Ar]3d^6 l.s. [Ar]3d^7 h.s.

$k_{11} = 1.0 \cdot 10^{-9}\ M^{-1}s^{-1}$ (at RT)
large reorganisation
$E^0 = 0.058\ V\ [Co(NH_3)_6]^{2+/3+}$

$[Ru^*(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \rightleftharpoons [Ru^*(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$

[Kr]4d^6 l.s. [Kr]4d^5 l.s. [Kr]4d^5 l.s. [Kr]4d^6 l.s.

$k_{11} = 6.7 \cdot 10^{3}\ M^{-1}s^{-1}$ (at RT)
little reorganisation
$E^0 = 0.051\ V\ [Ru(NH_3)_6]^{2+/3+}$

$[V^*(H_2O)_6]^{2+} + [V(H_2O)_6]^{3+} \rightleftharpoons [V^*(NH_3)_6]^{2+} + [V(H_2O)_6]^{3+}$

[Ar]4d^3 [Ar]3d^2 [Ar]3d^2 [Ar]3d^3

$k_{22} = 3.0 \cdot 10^{3}\ M^{-1}s^{-1}$ (at RT)
little reorganisation
$E^0 = -0.225\ V\ [V(H_2O)_6]^{2+/3+}$

b) Cross reaction: $\Delta G^0 \neq 0$, $\Delta G^{\neq} = ?$

$[Ru(NH_3)_6]^{3+} + [V(H_2O)_6]^{2+} \rightleftharpoons [Ru(NH_3)_6]^{2+} + [V(H_2O)_6]^{3+}$

[Kr]4d^5 l.s. [Ar]3d^3 [Kr]4d^6 l.s. [Ar]3d^2

$k_{12} = 1.3 \cdot 10^{3}\ M^{-1}s^{-1}$ (at RT)
moderate reorganisation
$E^0 = -0.255\ V$: $K_{12} = 1.5 \cdot 10^5$

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Outer Sphere Reactions: Correlation between ΔG^0 & $\Delta G^{\neq}$ → Marcus Cross Relation

Transfer rate: $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$ while k_{11} and k_{22} are listed self-exchange reaction rates

with $f_{12} = (\log k_{12})^2/4\log(k_{11}k_{22}/z^2)$ and $K_{12} = k_{12}/k_{-12}$

Assumption $f_{12} = 1$

$\Rightarrow$ $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$

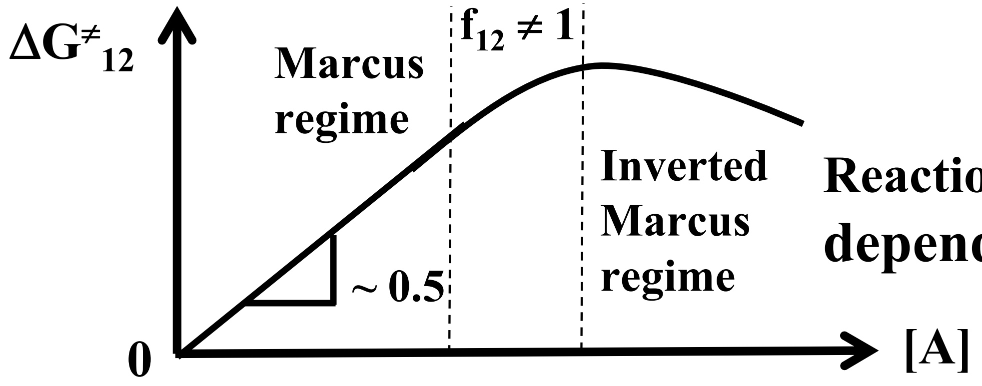
$\Rightarrow$ $\ln k_{12} = 0.5\ln k_{11} + 0.5\ln k_{22} + 0.5\ln K_{12}$

van't Hoff equation: $\Delta G^0 = -RT\ln K = -F\Delta E^0$

$\Rightarrow$ $\Delta G^{\neq}_{12} = 0.5\Delta G^{\neq}_{11} + 0.5\Delta G^{\neq}_{22} + 0.5\Delta G^0_{12}$

$\Rightarrow$ $\Delta G^{\neq}_{12} \sim 0.5\Delta G^0_{12}$

"Linear free energy relation (LFER)"



Reactions are so fast, that the reaction rate is not dependent on $\Delta G^{\neq}_{12}$ anymore, but diffusion limited

5. Marcus Theory

Outer Sphere Reactions: Determination of the self-exchange reaction rates k_{11}, k_{22}

a) By isotope marking (and quenching by precipitation): $\Delta G^0 = 0 \rightarrow K_{11} = k_{11}/k_{-11} = 1$

$[^{60}Co^*(NH_3)_6]^{2+} + [^{59}Co(NH_3)_6]^{3+} \rightleftharpoons [^{60}Co^*(NH_3)_6]^{3+} + [^{59}Co(NH_3)_6]^{2+}$

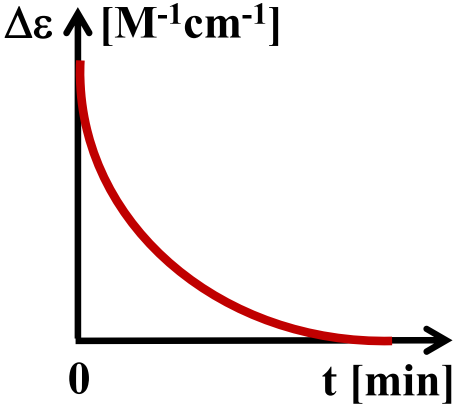
→ Precipitation of Co^{3+} as $[Co^{III}(NH_3)_6][Fe^{III}(CN)_6]\downarrow$

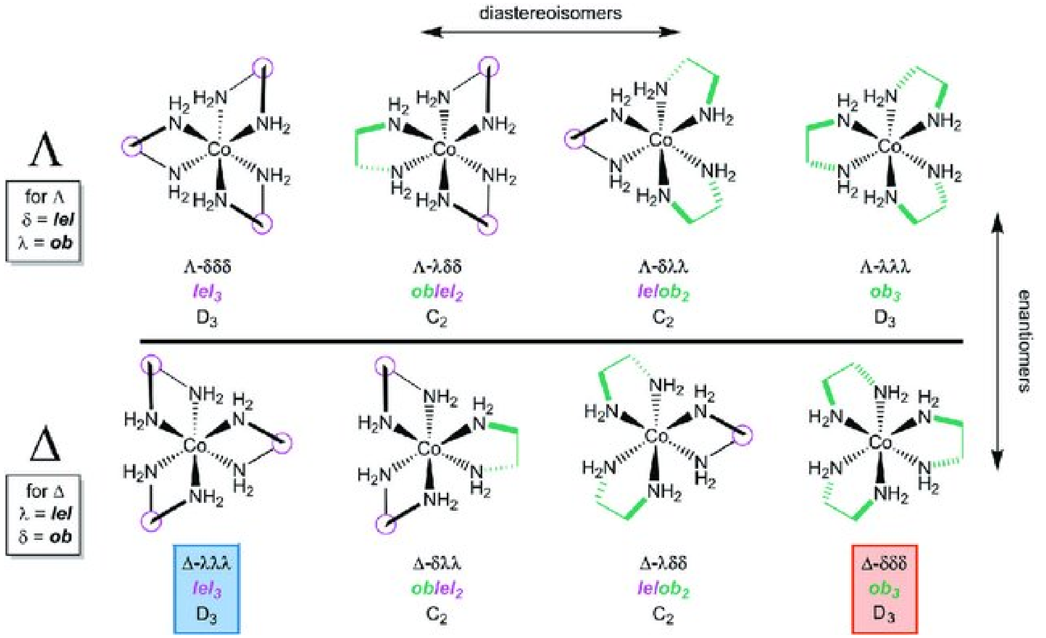
→ Determination of the change in radioactivity of the precipitate

b) By circular dichroism (CD) spectroscopy

$[\Lambda\text{-}Co^{III}(en)_3]^{3+} + [\Delta\text{-}Co^{II}(en)_3]^{2+} \rightleftharpoons [\Lambda\text{-}Co^{II}(en)_3]^{2+} + [\Delta\text{-}Co^{III}(en)_3]^{3+}$

→ Determination of the CD as function of time at abs. maximum





Complex	k_{11} [$M^{-1}s^{-1}$]
$[Fe(H_2O)_6]^{2+/3+}$	4.0
$[Fe(phen)_3]^{2+/3+}$	$1.0 \cdot 10^6$
$[V(H_2O)_6]^{2+/3+}$	$1.0 \cdot 10^{-3}$
$[Cr(H_2O)_6]^{2+/3+}$	$1.0 \cdot 10^{-9}$
$[Ru(NH_3)_6]^{2+/3+}$	$1.0 \cdot 10^5$
$[IrCl_6]^{2-/3-}$	$2.3 \cdot 10^5$

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Outer Sphere Reactions: Dependency of k_{11}, k_{22}

Octahedral Co^{3+} complexes: $[Co^*N_6]^{2+} + [CoN_6]^{3+} \rightleftharpoons [Co^*N_6]^{3+} + [CoN_6]^{2+}$

Complex	k_{11} [$M^{-1}s^{-1}$]		Δd(Co-N) [pm]	Remarks
$[Co(NH_3)_6]^{2+/3+}$	$1.0 \cdot 10^{-7}$	"slow"	25	largest bond difference of 1st TM ion redox couples
$[Co(en)_3]^{2+/3+}$	$1.0 \cdot 10^{-5}$			en = ethylendiamine
$[Co(tacn)_2]^{2+/3+}$	$1.0 \cdot 10^{-1}$		14	tacn = 1,4,7-triazacyclononane
$[Co(sep)]^{2+/3+}$	$1.0 \cdot 10^{0}$			sep = sepulchrate (macrobicyclic ligand)
$[Co(bpy)_3]^{2+/3+}$	$1.0 \cdot 10^{1}$			bpy = 1,10-bipyridine
$[Co(ttcn)_2]^{2+/3+}$	$1.0 \cdot 10^{4}$	"fast"	7	ttcn = 1,4,7-trithiocyclononane

Large reactivity differences even though same mechanism and coordination geometry

Cause: Variation of the Franck-Condon barrier

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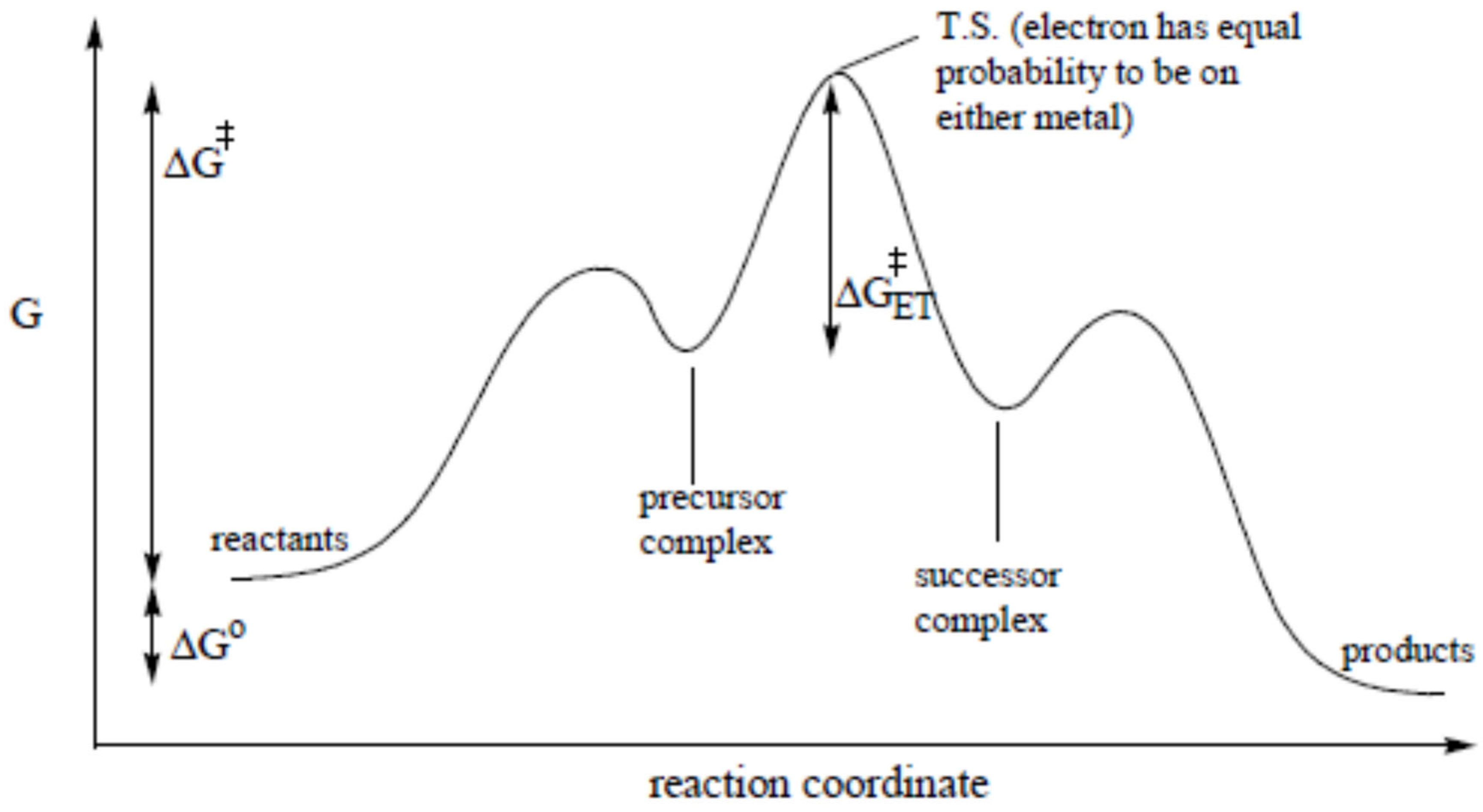
Outer Sphere Reactions: Reaction coordinate – free energy profile G - plot



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Outer Sphere Reactions: Dependency of the Activation Energy $\Delta G^{\neq}$

Contributions to the overall activation energy $\Delta G^{\neq}$

- Loss of free translational and rotational energy for the formation of the precursor complex impact on $\Delta S^{\neq}$ (< 0)
- Change of the solvate shell of the complexes upon formation of the precursor
- Electrostatic interaction between charged complexes

$$\Delta G^{\neq} = \Delta G^{\neq}_{\text{prec.}} + \Delta G^{\neq}_{0} + \Delta G^{\neq}_{i}$$

with		
	$\Delta G^{\neq}_{\text{prec.}}$	Activation energy for encounter of the reactants, including overcoming the Coulomb repulsion
	$\Delta G^{\neq}_{0}$	Activation energy needed for solvent reorganisation
	$\Delta G^{\neq}_{i}$	Activation energy required for reorganisation of bond elongation or compression to yield interacting orbitals of same energy

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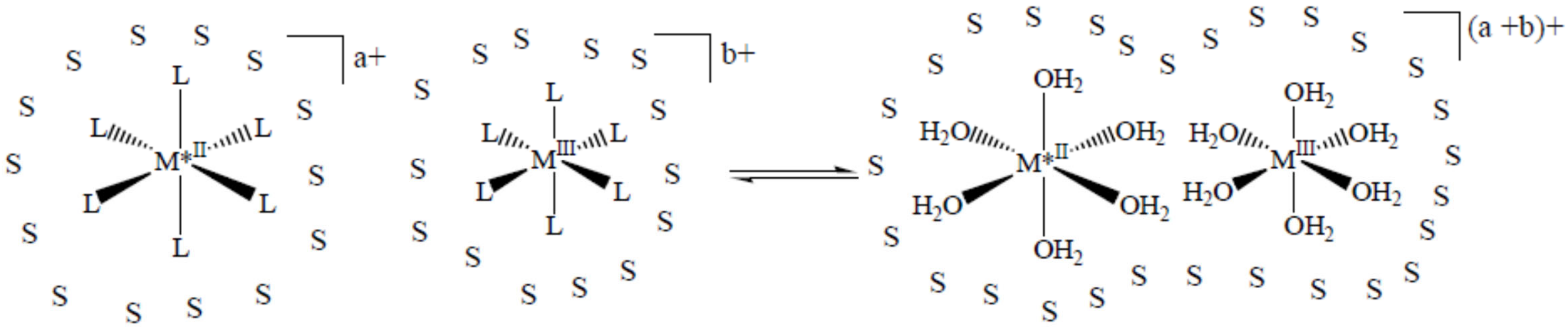
Outer Sphere Reactions: Formation of the Precursor Complex → $\Delta G^{\neq}_{prec.} + \Delta G^{\neq}_{0}$

The Effect of the Solvent

- The stronger the interaction with the solvent, the more difficult is the electron transfer
- Solvents which interact strongly with complexes (such as by Hydrogen bonding) will reduce the rate of electron transfer



precursor complex

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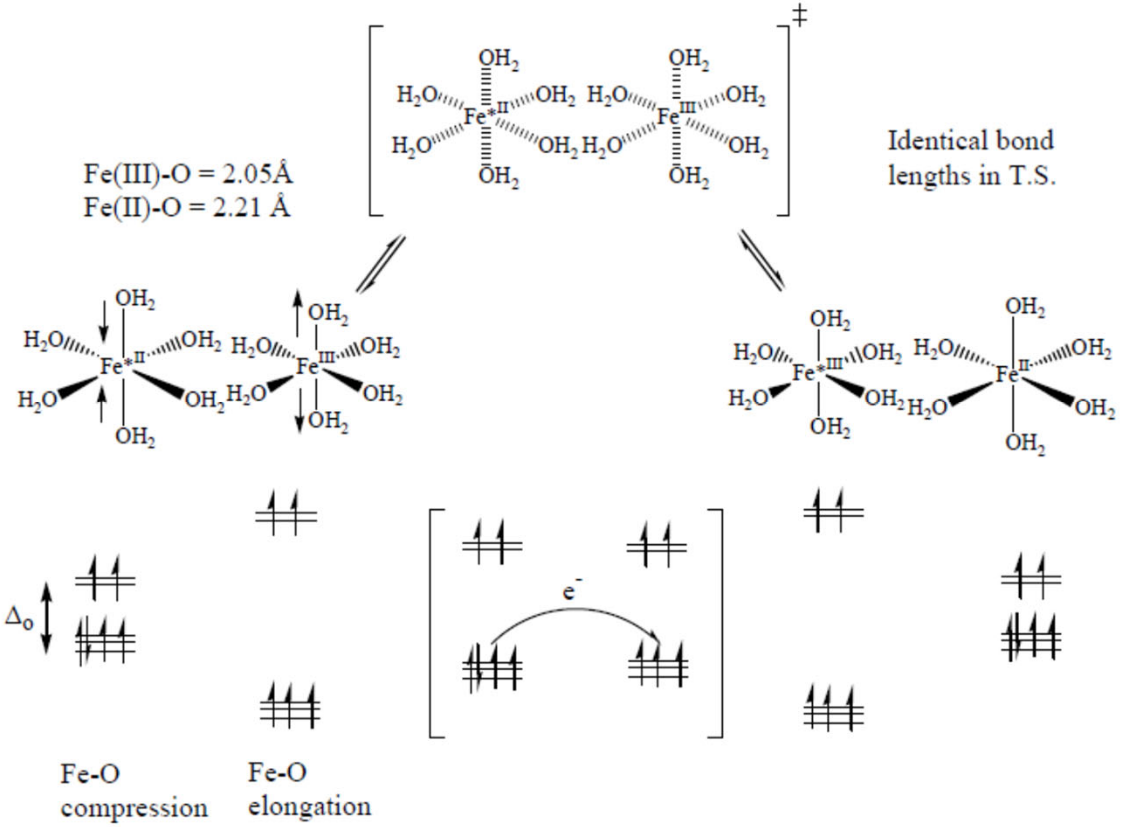
Outer Sphere Reactions: Reorganization of Bonds → $\Delta G^{\neq}_{i}$

Metal-ligand bond lengths will change once the oxidation state of the metal changes. The Franck-Condon principle states that because nuclei are much more massive than electrons, an electronic transition occurs much faster (~ 10^3) than the nuclei can respond. Complexes must adjust their M-L bond lengths prior to the electron transfer.

Example: Self-exchange reaction for $[Fe^{II/III}(H_2O)_6]^{2+/3+}$ aqua complexes

→ Fe^{III}-O and Fe^{II}-O bond length are different in the reactant, but at the transition state identical bond length make the electron transfer possible



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Outer Sphere Reactions: Reorganization of Bonds

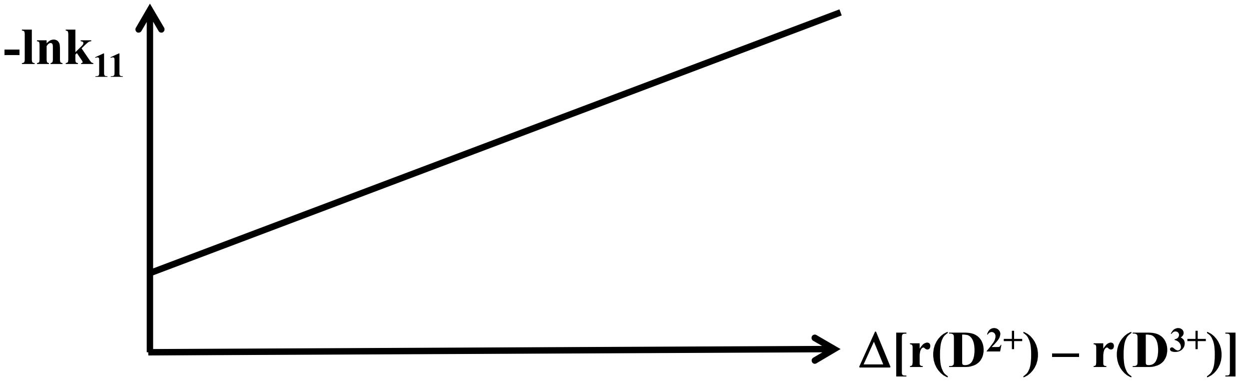
ET requires orbital overlap and occurs between orbitals of the same symmetry

Self-exchange reaction	electron configuration	k_{11} [$M^{-1}s^{-1}$]	Δr [pm]
$[Cr(H_2O)_6]^{2+/3+}$	$t_{2g}^3e_g^1/t_{2g}^3e_g^0$	$1.0 \cdot 10^{-5}$	30
$[V(H_2O)_6]^{2+/3+}$	$t_{2g}^3e_g^0/t_{2g}^2e_g^0$	$1.0 \cdot 10^{-2}$	20
$[Fe(H_2O)_6]^{2+/3+}$	$t_{2g}^4e_g^2/t_{2g}^3e_g^2$	$4.0 \cdot 10^{0}$	15
$[Ru(H_2O)_6]^{2+/3+}$	$t_{2g}^6e_g^0/t_{2g}^5e_g^0$	$4.0 \cdot 10^{3}$	5
$[Fe(phen)_3]^{2+/3+}$	$t_{2g}^6e_g^0/t_{2g}^5e_g^0$	$1.0 \cdot 10^{3}$	1

Marcus-Sutin-Hush-equation

→ Structure reactivity relation

$$-\ln k_{11} \sim \Delta[r(D^{2+}) - r(D^{3+})]$$



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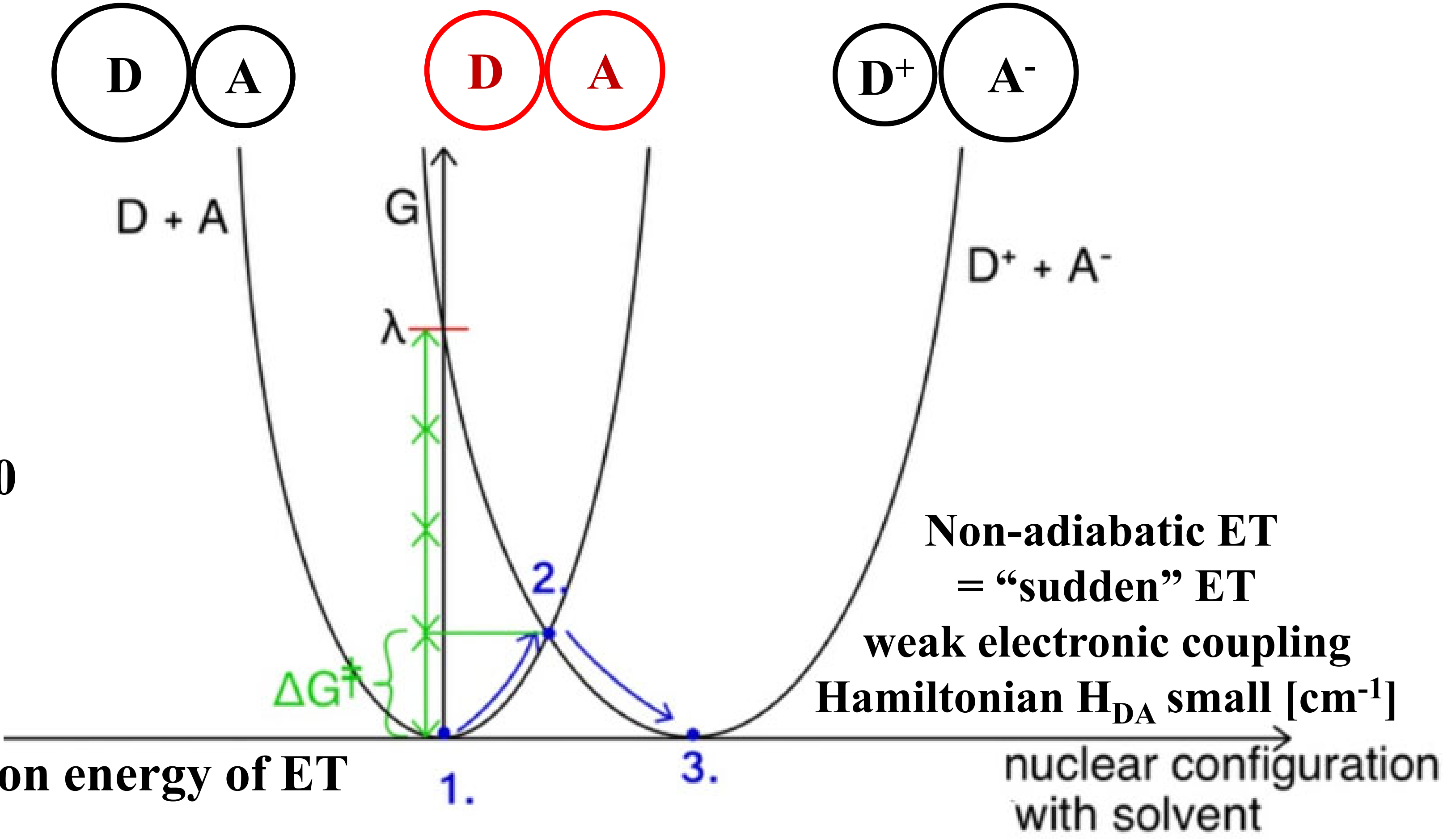
Outer Sphere Reactions: Reorganization of Bonds

2D representation of the nuclear configuration including the configuration S where electron can jump



Non-adiabatic ET
= "sudden" ET
weak electronic coupling
Hamiltonian H_{DA} small [cm^{-1}]

Example:

Self-exchange

reaction → $\Delta G^0 = 0$

$\Delta G^{\neq}$ = free activation energy of ET

λ = reorganisation energy

5. Marcus Theory

Outer Sphere Reactions: Mathematical Treatment Based on Morse Potentials

Morse potentials are used to describe the reaction coordinate. After aligning the potentials along the intrinsic barrier, the product potential is adjusted to compensate for the free energy change of the reaction. The intersection of the curves defines the energy of the transition state.

"Parabola mathematics"

$G_{DA} = nx^2$

$G_{D+A-} = m(x - a)^2 + b$; n, m = slope/steepness

- a = shift along the x-axis
- b = ΔG^0 = shift up and down along the y-axis

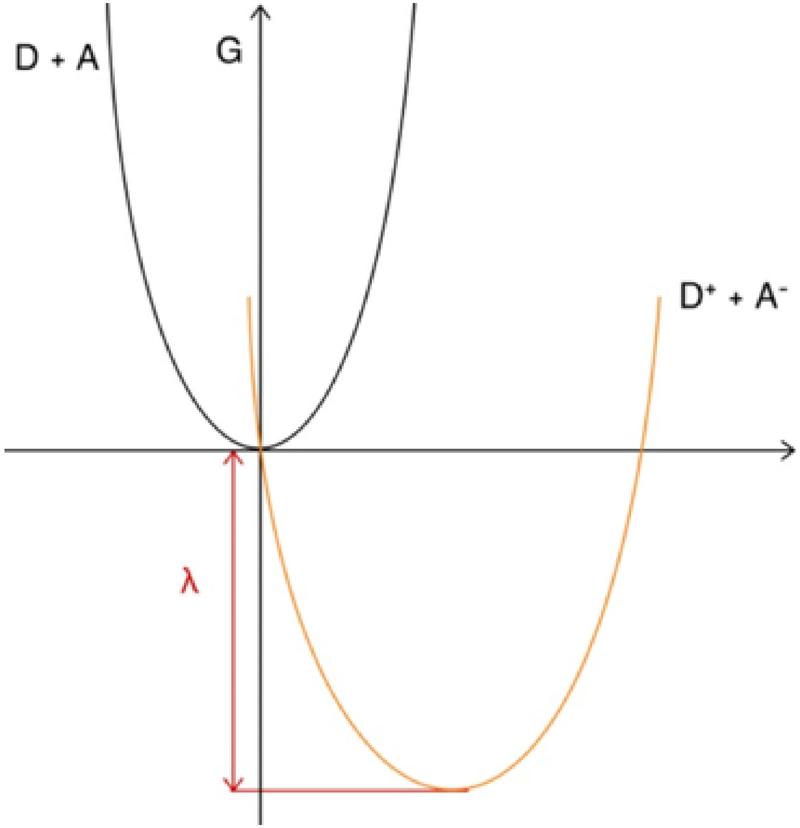
$\Rightarrow$ **four cases:**

a) $-\Delta G^0 = 0$

b) $-\Delta G^0 < -\lambda$

c) $-\Delta G^0 = \lambda$

d) $-\Delta G^0 > -\lambda$



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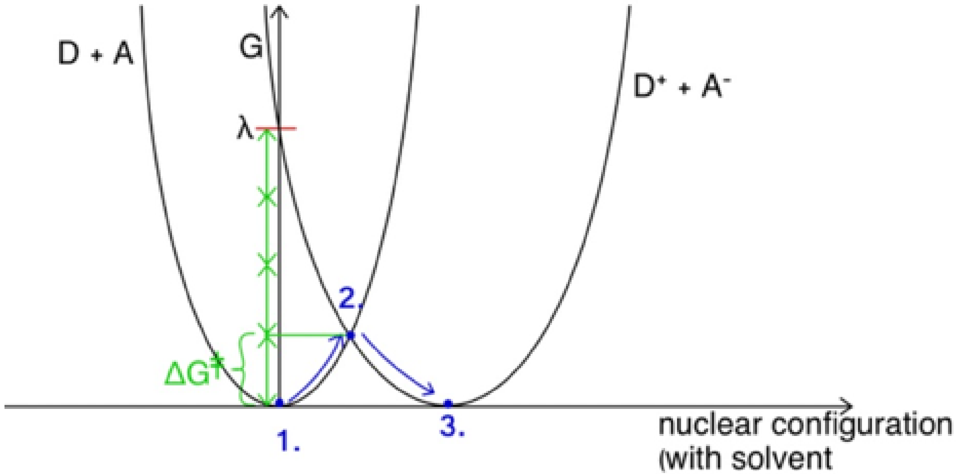
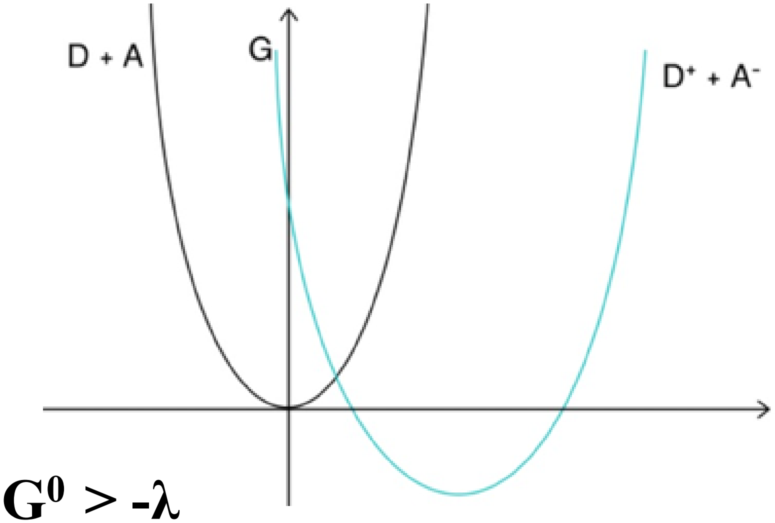
Outer Sphere Reactions: Overview of the Relation between $-\Delta G^0$ and λ

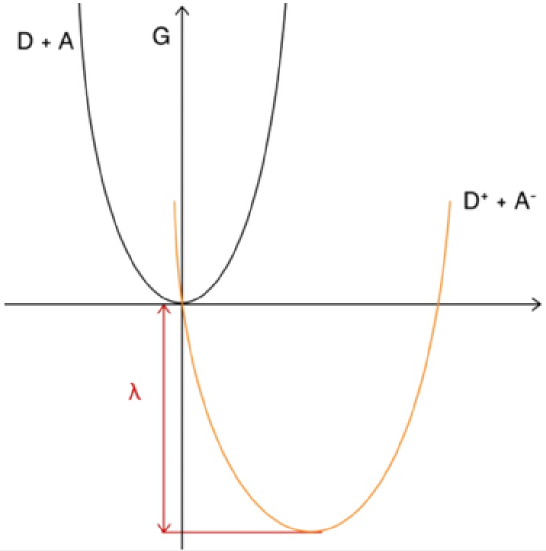
a) $-\Delta G^0 = 0$



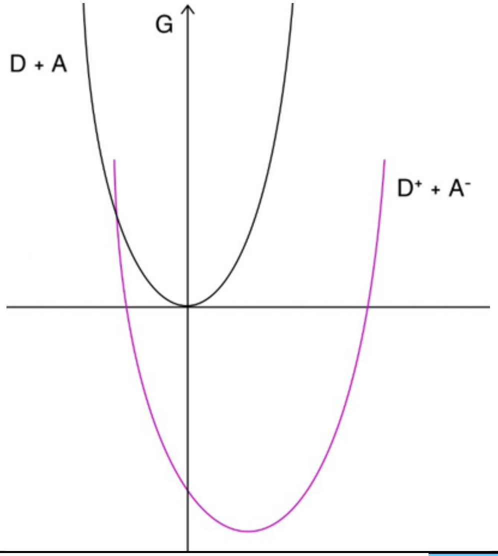
b) $-\Delta G^0 < -\lambda$



c) $-\Delta G^0 = \lambda$



d) $-\Delta G^0 > -\lambda$



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Outer Sphere Reactions: Dependency of $\lambda = \lambda_{\text{inner sphere}} + \lambda_{\text{outer sphere}}$

$\lambda_{\text{outer sphere}}$

- increases with
  - the distance between molecules
  - the dielectric constant → polarity of the solvent (eluotropic series)
- Solvent molecules orient towards created dipoles with time (rotational motion)

$\lambda_{\text{inner sphere}}$

- charge transfer absorption - charge transfer emission = 2 λ_{inner} (between 0.3 and 1 eV)
- Vibrational motions
- Can be determined by PL spectroscopy (Stokes Shift SS)
  - Small SS: PL and small reorganisation energy
  - Large SS: ET and large reorganisation energy

5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 = 0$ → Self Exchange Reactions

1^{st} Step: electron lies in minimum of G_{DA}

2^{nd} Step: electron reaches the point of intersection → cross-over at this point

3^{rd} Step: electron moves to minimum of $G_{D^+A^-}$

At the crossing point

$G_{DA} = G_{D^+A^-}$

$x^2 = (x - a)^2 + b \quad |a = \sqrt{\lambda}, b = \Delta G^0$

$\Rightarrow\ x^2 = x^2 - 2x\sqrt{\lambda} + \lambda + \Delta G^0$

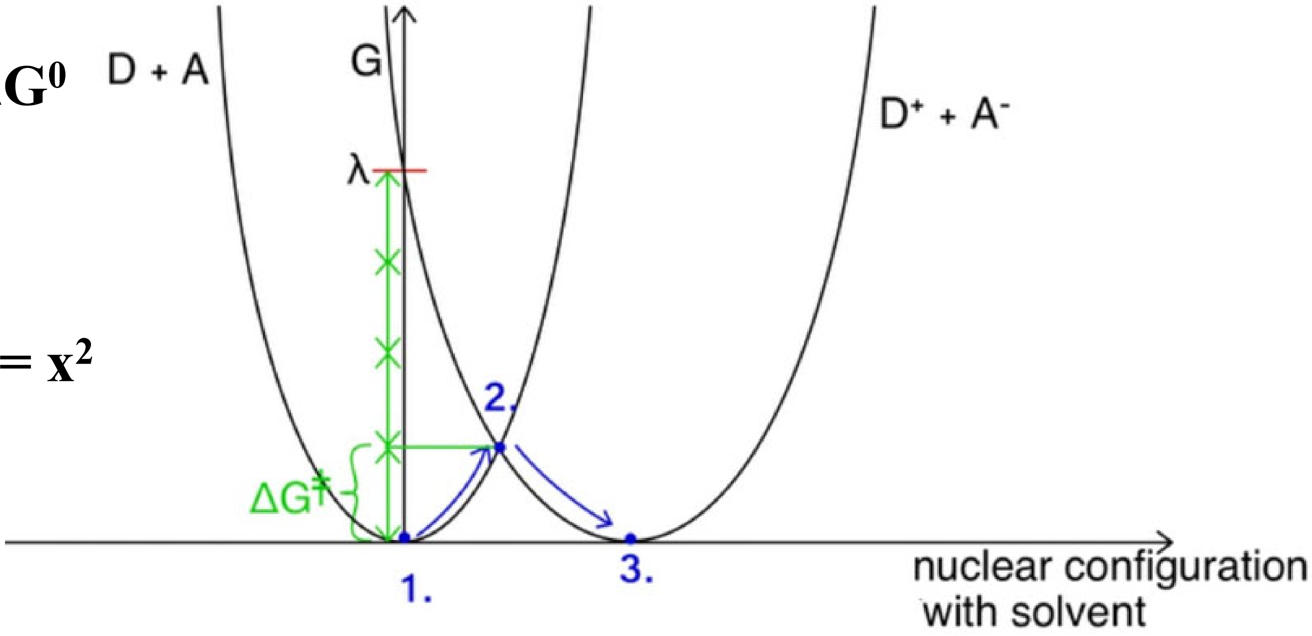
$\Rightarrow\ 0 = -2x\sqrt{\lambda} + \lambda + \Delta G^0$

$\Rightarrow\ 2x\sqrt{\lambda} = \lambda + \Delta G^0$

$\Rightarrow\ x^2 = (\lambda + \Delta G^0)^2/4\lambda \qquad |\Delta G^{\neq} = x^2$

$\Rightarrow\ \Delta G^{\neq} = (\lambda + \Delta G^0)^2/4\lambda$

If $\Delta G^0 = 0$ then $\Delta G^{\neq} = ¼\ \lambda$

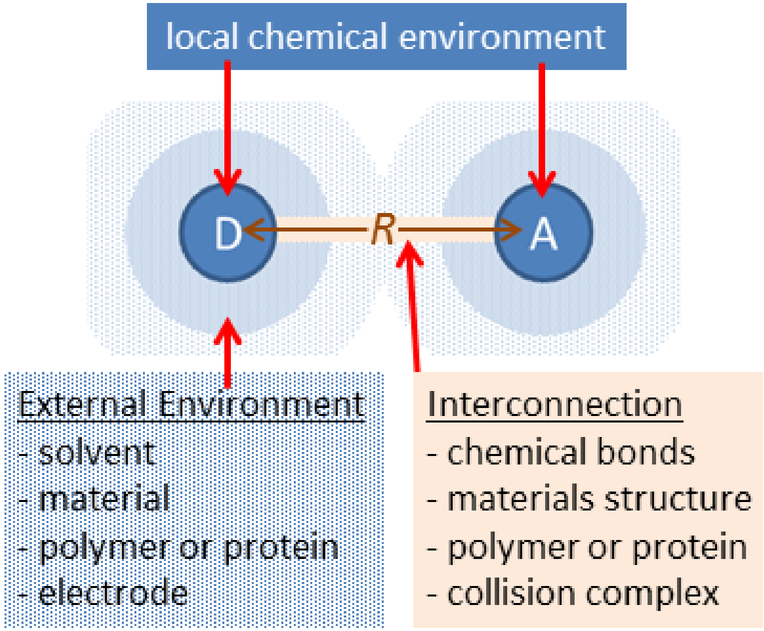


5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 \neq 0$

$$\Delta G^{\neq} = (\lambda + \Delta G^0)^2 / 4\lambda \quad \text{and} \quad k_{ET} \sim \exp[-\Delta G^{\neq} / k_B T]$$

$$k_{ET} \sim \exp[-(\lambda + \Delta G^0)^2 / 4\lambda k_B T]$$



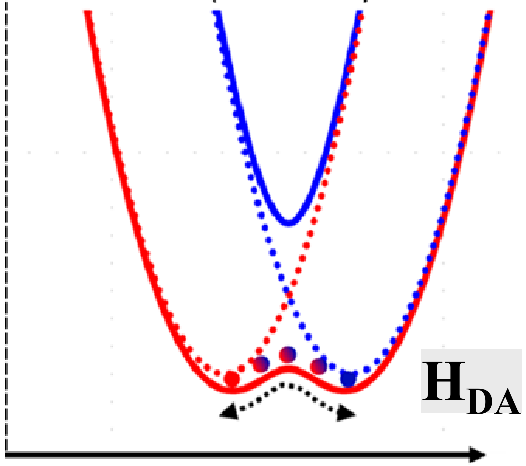
External Environment
- solvent
- material
- polymer or protein
- electrode

Interconnection
- chemical bonds
- materials structure
- polymer or protein
- collision complex

Adiabatic ET (gradual ET) developed by Noel Hush

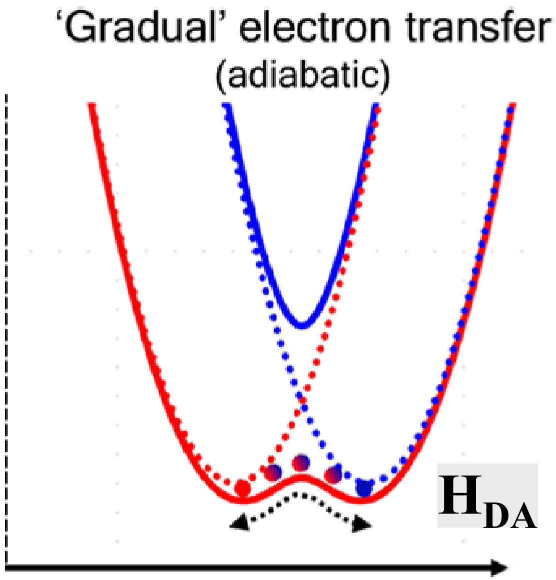
- Relevant for (artificial) photosynthesis, organic PV, OLEDs, MMCT pigments like Prussian blue
- Proportionality factor depends on donor (D) - acceptor (A) coupling H_{DA}
  - overlap of the electron wavefunctions
  - strong coupling as requirement for fast ET
  - probability of ET
  - decreases exponentially with increasing distance r

'Gradual' electron transfer (adiabatic)



5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 \neq 0$



Calculation of H_{DA}

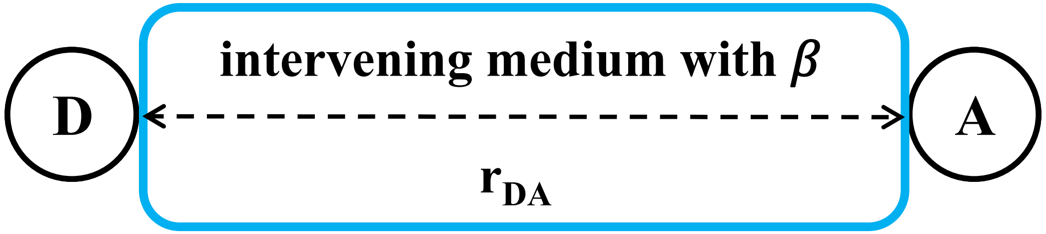
$H_{DA} = H^0_{DA}\exp(-\beta(r_c - r_0)/2)$

with

H^0_{DA} = coupling at donor-acceptor contact distance → affected by orientation effects
ß = damping factor → electron tunnelling barrier
a) through solvent: $ß = \sqrt{-2m_eE_0/\hbar^2}$
b) in optical materials (dielectrics): $ß = 1.025/n_D * \sqrt{\Delta E_0^{\neq}}$ → large in Titanates!
$\Delta E_0^{\neq}$ = absolute potential of the standard calomel electrode (4.71 eV = 4.44 eV, SHE + 0.27 eV calomel vs. SHE) + reduction potential of the donor
r_c = center-to-center donor(D)-acceptor(A) distance
r_0 = contact distance

5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 \neq 0$


D

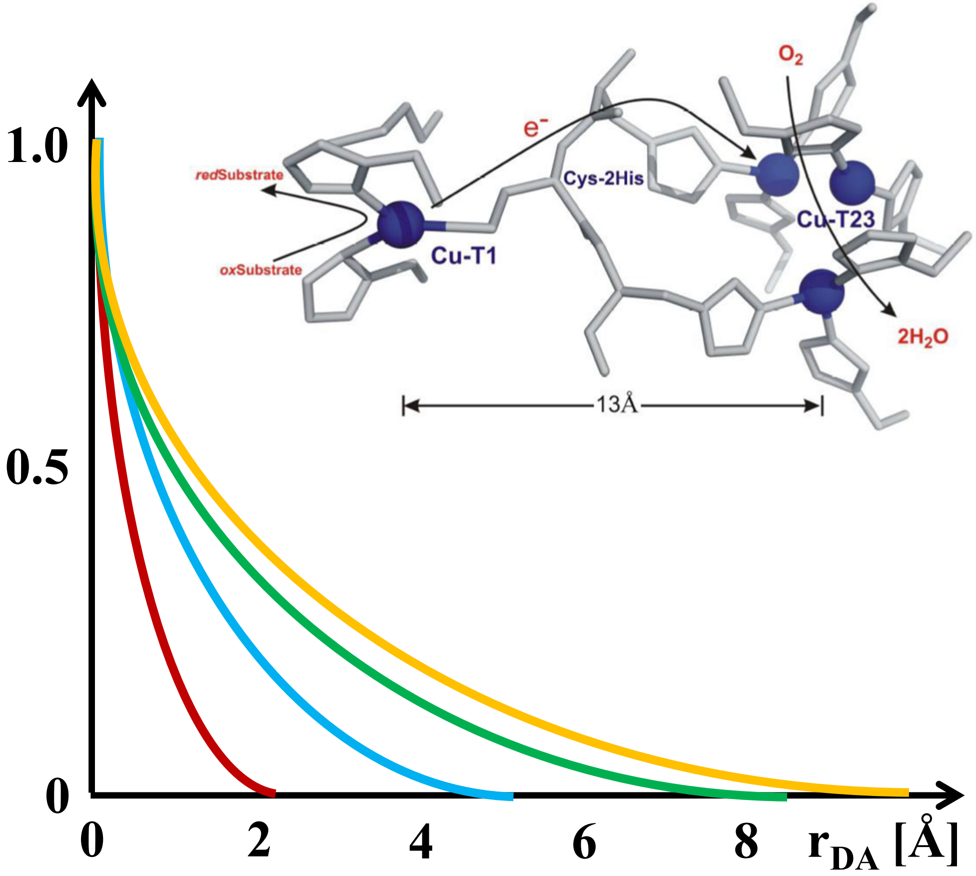
intervening medium with β

r_{DA}

A

The damping factor β from theory

Vacuum	**2.0 Å^{-1}**
Water	**0.83 Å^{-1}**
THF	**0.6 Å^{-1}**
Proteins	**0.5 Å^{-1}**



For proteins the $\sigma \rightarrow \sigma*$ band gap of the surrounding material (≈ 3 eV) $\rightarrow \beta = 0.72$

5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 \neq 0$

Adiabatic electron-transfer (strong-coupling limit)

$k_{ET} \sim H_{DA}{}^2R^2/\lambda+\Delta G^0$

- ⇒ Also relevant to the Robin-Day classification system of MMCT (chapter 6)
- ⇒ Intervalent complexes and compounds, e.g. $LFe^{II}(\mu\text{-}Cl)_3Fe^{III}L$ with L = tridentate macrocyclic ligand

Non-adiabatic electron-transfer (weak-coupling limit)

$k_{ET} = [2\pi^{3/2}/h(\lambda k_BT)^{1/2}]H_{DA}{}^2 \quad * \quad \exp[-(\lambda+\Delta G^0)^2/4\lambda k_BT]$

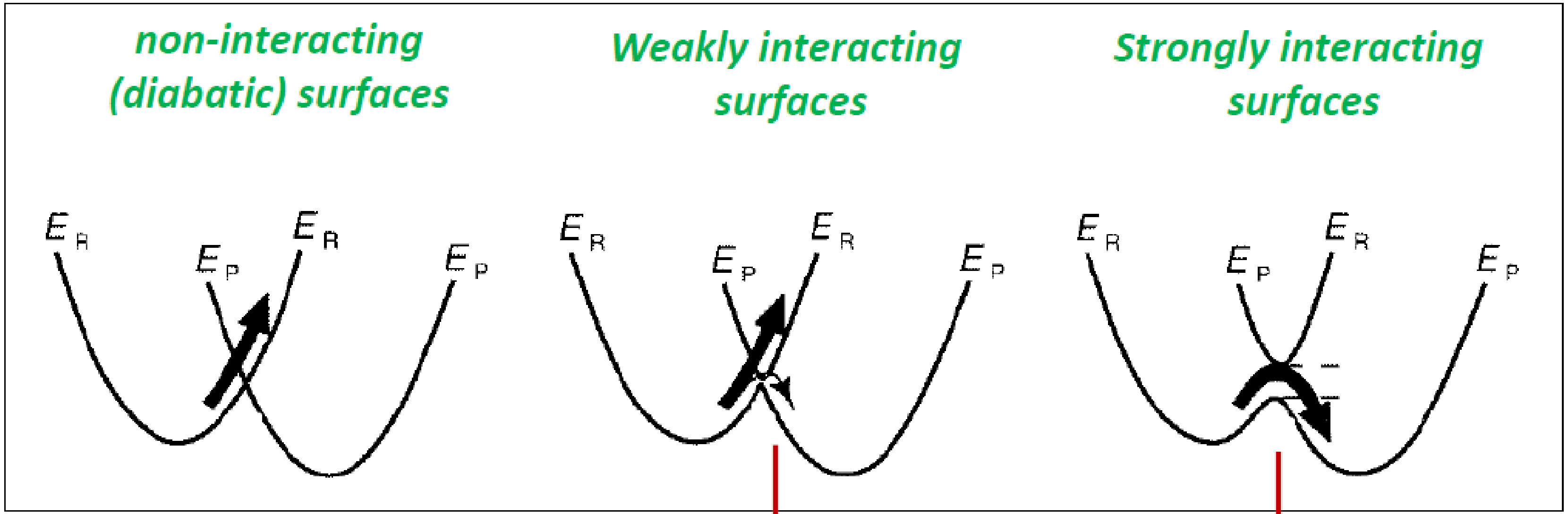
donor (D)-acceptor (A) coupling   activation energy

Widely applicable to long-range ground-state intramolecular electron transfer (ET), ET in biology, and electron transfer in conducting materials

5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 \neq 0$

Adiabatic vs. non-adiabatic electron-transfer (strong-coupling limit)



Great majority of ETs are non-adiabatic

Non-adiabatic transfer

Weak interaction = non-adiabatic dynamics
→ suitable for description of **an outer-sphere ET**

Adiabatic transfer

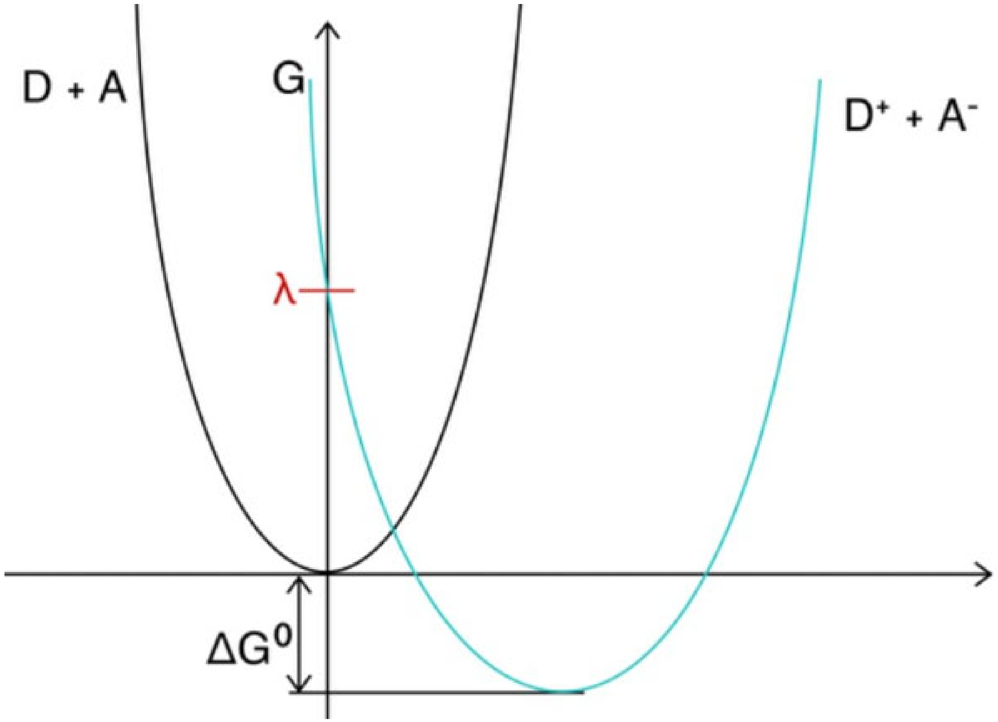
Strong interaction = adiabatic dynamics
→ may be suitable for description of **an inner-sphere ET**

5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 < 0$

- Exogenic reaction
- Common in photoinduced ET → photochemistry
- $\Delta G^0 < 0$ because of excitation energy

$$k_{ET} = 2\pi^{3/2}/h(\lambda k_B T)^{1/2} H_{DA}{}^2 * \exp[-(\lambda+\Delta G^0)^2/4\lambda k_B T]$$



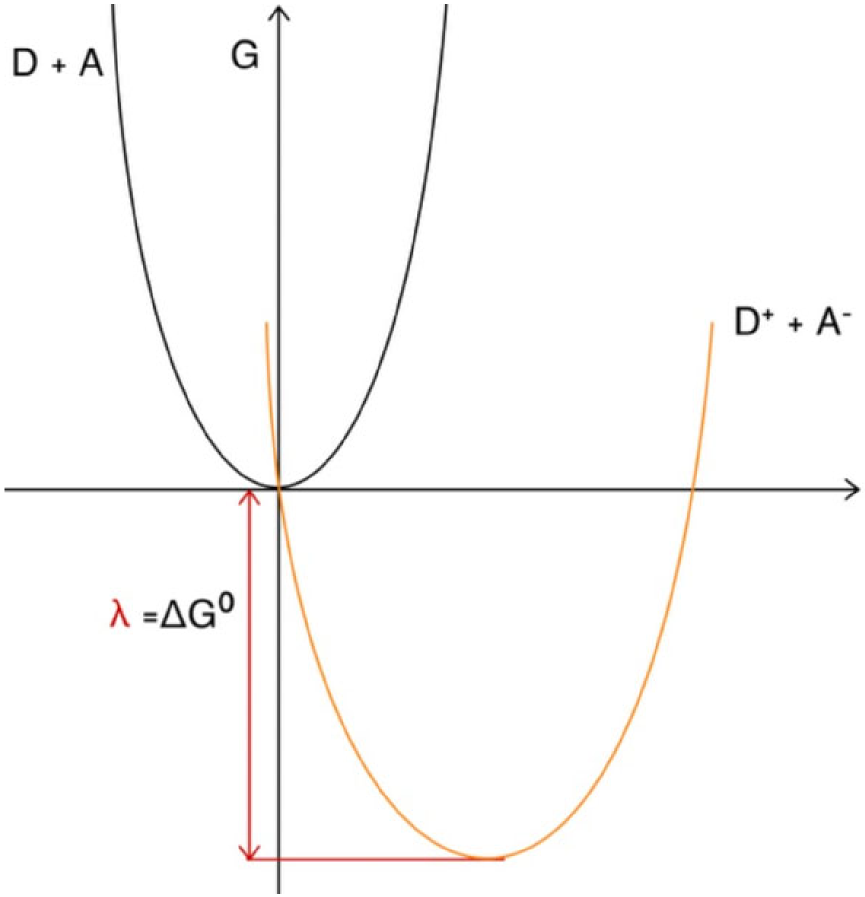
5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 = -\lambda$

No energy barrier for ET → the fastest possible ET with rates in the range of 10^{13} s^{-1}

$$k_{ET} = 2\pi^{3/2}/h(\lambda k_B T)^{1/2} H_{DA}^2 * \exp[0]$$

$$\Rightarrow k_{ET} = 2\pi^{3/2}/h(\lambda k_B T)^{1/2} H_{DA}^2$$



5. Marcus Theory

Outer Sphere Reactions with $\Delta G^0 > -\lambda$

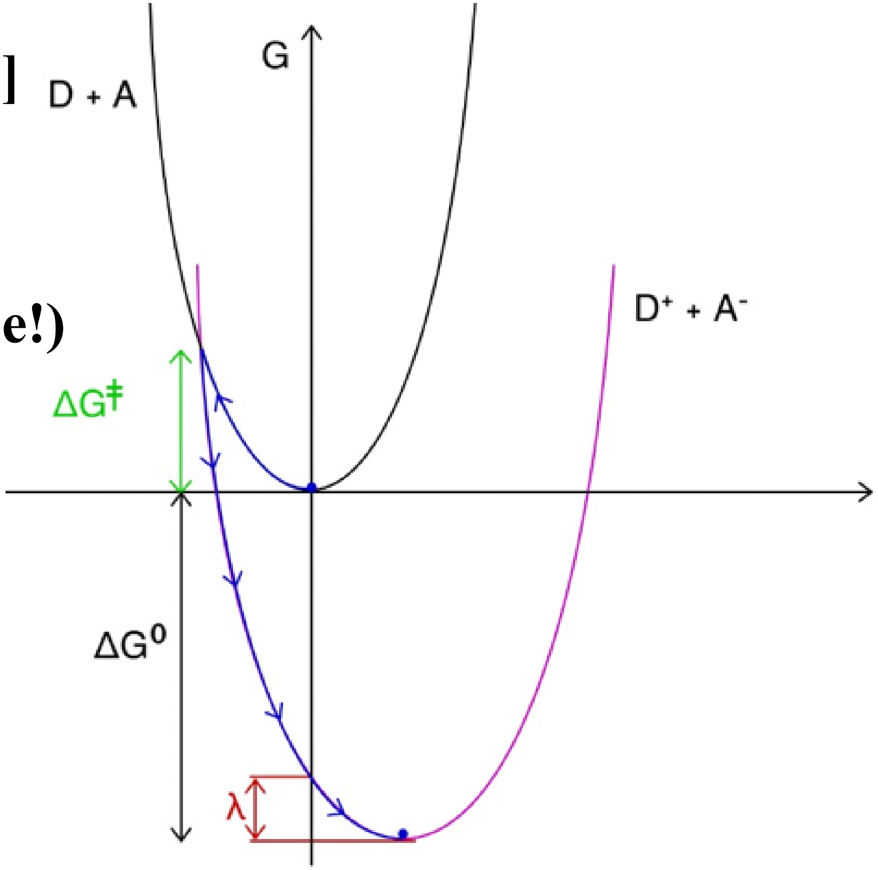
High energy barrier for ET → very slowly reactions which are very thermodynamically favourable

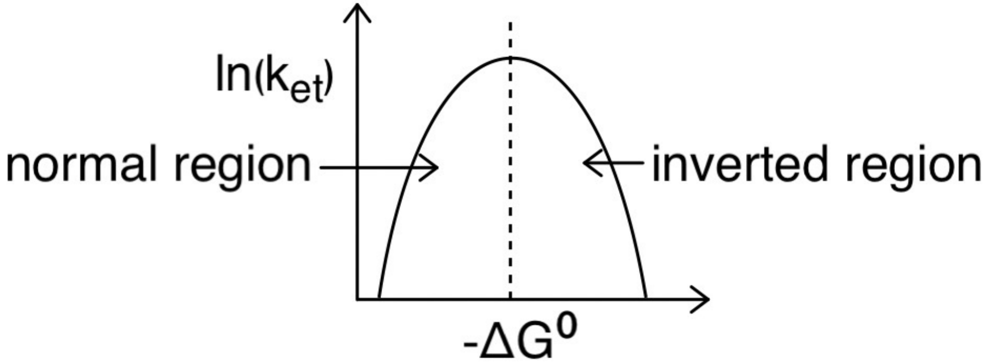
$k_{ET} = 2\pi^{3/2}/h(\lambda k_B T)^{1/2} H_{DA}{}^2 * \exp[-(\lambda+\Delta G^0)^2/4\lambda k_B T]$

→ inverted Marcus region

e.g. for charge separation in QDots (ns decay time!)

→ diffusion limited





5. Marcus Theory

Outer Sphere Reactions: Calculation of ΔG^0

$$\frac{e^2}{4\pi\varepsilon_0} = 14.4 \text{ eV Å}$$

Approximation by the Weller equation

$$\Delta G^0 = e[E^0_{D/D+} - E^0_{A/A-}] - E^* - e^2/4\pi\varepsilon_0\varepsilon_s r_c - e^2/8\pi\varepsilon_0(1/r_{D+} + 1/r_{A-})(1/\varepsilon_{EC} - 1/\varepsilon_S)$$

with
$E^0_{D/D+}$ / $E^0_{A/A-}$ = standard redox potential of the donor D / acceptor A redox couple
E^* = standard redox potential of the excited donor D*
ε_S = dielectric constant of the solvent S
→ the more polar the solvent, the higher the dielectric constant
→ the charge density influences ΔG^0

ε_{EC} = dielectric constant of the electrode/reaction
e = elementary charge
r_c = center to center distance from molecular modelling and effective ion radii
r_{D+}/r_{A-} = effective ionic radius of the donor/acceptor

5. Marcus Theory

Inner Sphere Reactions

Definition: Redox reactions, where prior to the electron transfer a substitution reaction occur → reaction rate $v = d[P]/dt = k_0k_{ET}[A][B] = k_{obs}[A][B]$

Mechanism

1. Formation of the precursor complex

$A^{III}L| + B^{II}(H_2O)_6 \rightleftharpoons [A^{III}L\text{-}B^{II}(H_2O)_5] + H_2O$ k_0 precursor complex

L = Ligand with additional free electron pair, complex $B^{II}(H_2O)_6$ must be labile

2. Electron transfer and relaxation to successor complex

$[A^{III}L\text{-}B^{II}(H_2O)_5] \rightarrow [A^{II}L\text{-}B^{III}(H_2O)_5]$ k_{ET} successor complex

3. Dissociation of successor complex (typically very fast, i.e. not relevant for the rate)

$[A^{II}L\text{-}B^{III}(H_2O)_5] + H_2O \rightarrow A^{II}L| + B^{III}(H_2O)_6$ k_{diss} without ligand transfer

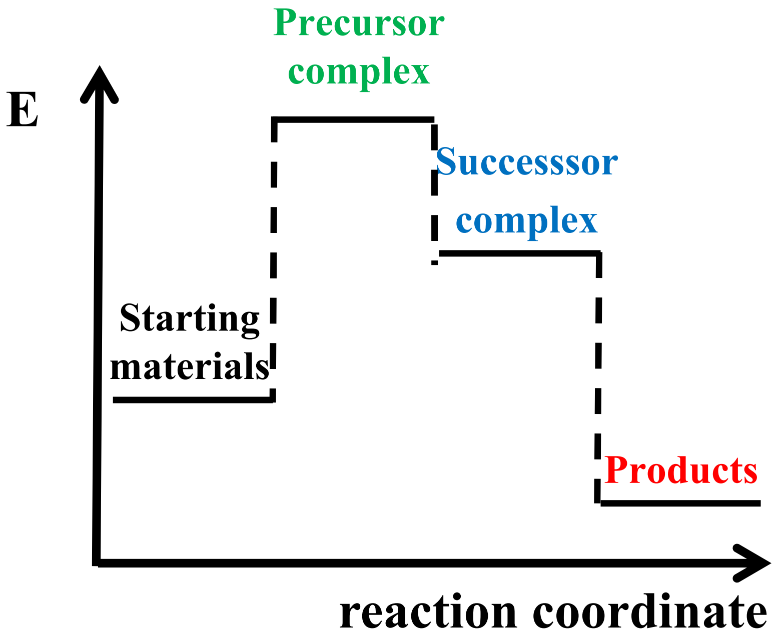
$\rightarrow A^{II}(H_2O) + B^{III}(H_2O)_5L|$ with ligand transfer

5. Marcus Theory

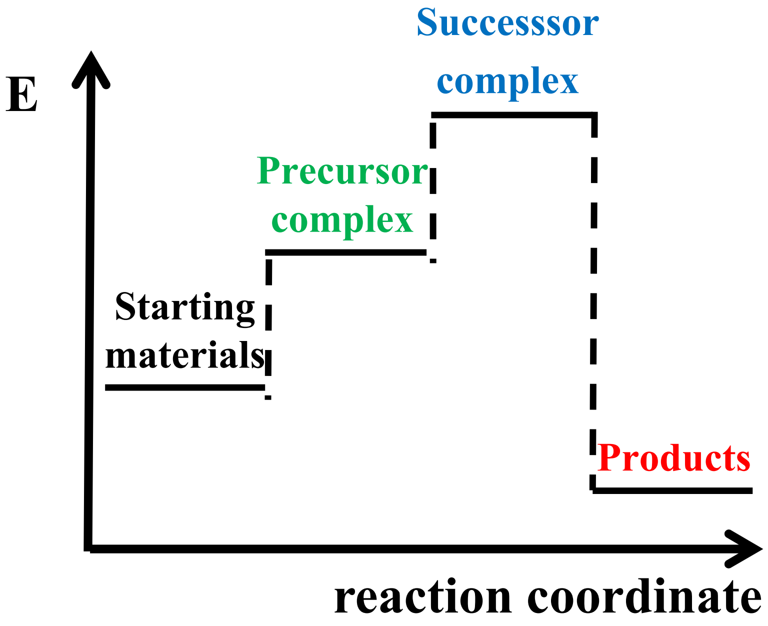
Inner Sphere Reactions

Energetics

a)



b)



The reaction rate is determined by the

a) formation of the precursor complex **b) formation of the successor complex**

5. Marcus Theory

Inner Sphere Reactions

Discovered by Henry Taube in the 1960s

$[Co^{III}Cl(NH_3)_5]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \rightleftharpoons [Co^{II}(NH_3)_5(H_2O)]^{2+} + [Cr^{III}Cl(H_2O)_5]^{2+}$

$[Co^{III}Cl(NH_3)_5]^{2+}$	$[Cr^{II}(H_2O)_6]^{2+}$	$[Co^{II}(NH_3)_5(H_2O)]^{2+}$	$[Cr^{III}Cl(H_2O)_5]^{2+}$
$[Ar]3d^6$ l.s.	$[Ar]3d^4$ h.s.	$[Ar]3d^7$ h.s.	$[Ar]3d^3$
inert	labile	labile	inert
	J.T. distorted		

The product proofs the presence of an inner sphere reaction, since for an outer sphere reaction solely the Cr^{3+} complex $[Cr^{III}(H_2O)_6]^{3+}$ would be generated

Precursor complex **Successor complex**

$[(NH_3)_5Co^{III}\text{-}Cl\text{-}Cr^{II}(H_2O)_5]^{2+} \rightarrow [(NH_3)_5Co^{II}\text{-}Cl\text{-}Cr^{III}(H_2O)_5]^{2+}$ k_{ET} **rate determining**

Further findings:

- **Transfer rate $k_{12} = k_0 \cdot k_{ET} = 4 \cdot 10^5\ M^{-1}s^{-1}$ is too fast for an outer sphere reaction**
- **Reaction of Cl* marked complex in 1 M NaCl solution do not show Cl exchange**

5. Marcus Theory

Inner Sphere Reactions

Example for a rate determining formation of the precursor complex reaction:

$$[\mathrm{Co}^{\mathrm{III}}\mathrm{X}(\mathrm{NH}_3)_5]^{2+} + [\mathrm{V}^{\mathrm{II}}(\mathrm{H}_2\mathrm{O})_6]^{2+} \rightleftharpoons [\mathrm{V}^{\mathrm{III}}(\mathrm{H}_2\mathrm{O})_5\mathrm{X}]^{2+} + [\mathrm{Co}^{\mathrm{II}}(\mathrm{H}_2\mathrm{O})_6]^{2+} + 5\ \mathrm{NH}_4^{+}$$

$[Ar]3d^6$ l.s.	$[Ar]3d^3$	$[Ar]3d^2$	$[Ar]3d^7$
inert	inert	labile	labile

Replacement of the aqua ligands is difficult, since the octahedral V^{3+} complex exhibit large CFSE = - 12 Dq_o

Transfer rate k_{12} is small and almost independent of X

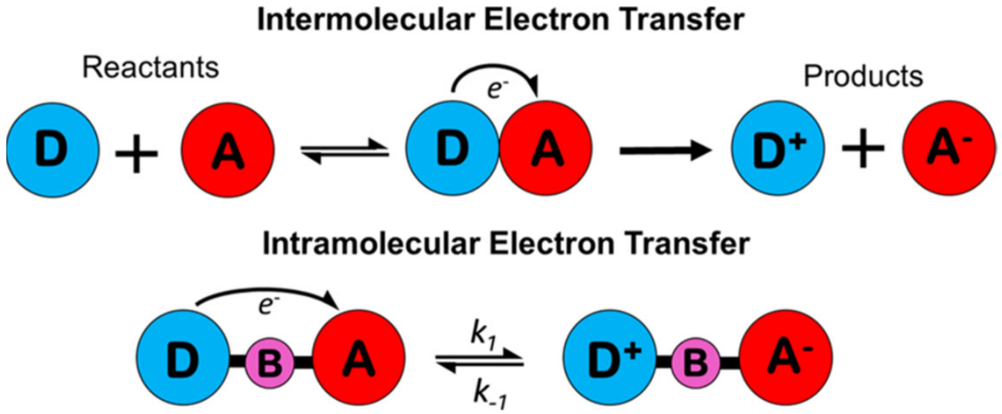
X	k_{12} $[M^{-1}s^{-1}]$
NCS^-	13
N_3^-	28

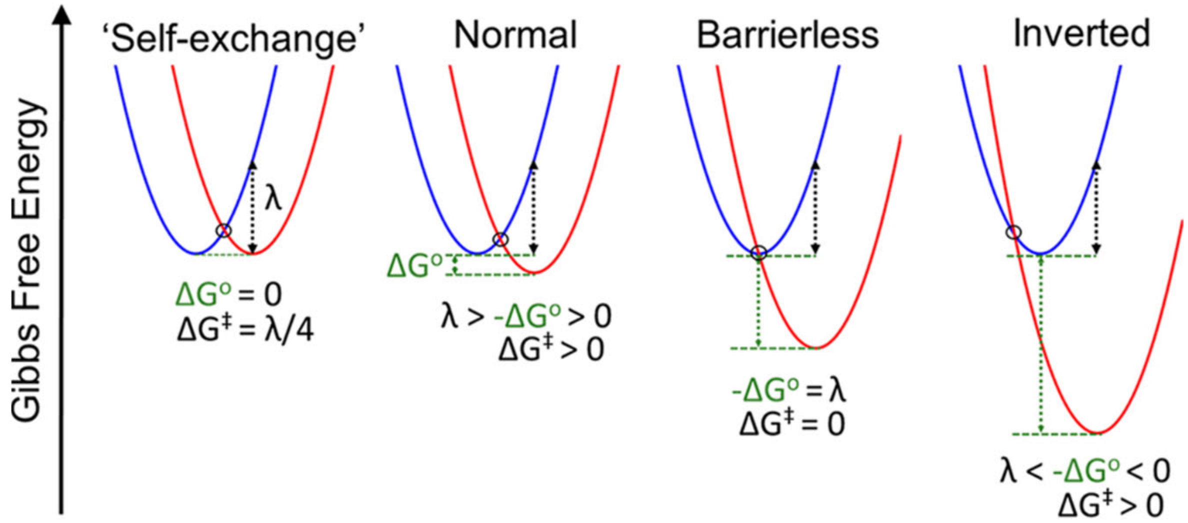
Remark: two arrangements for the bridging ligand possible

5. Marcus Theory

Summary

- Uses Morse potentials to describe redox reactions along the reaction coordinate
- Explains the rates of electron transfer reactions, which are inter- (outer sphere) or intramolecular (inner sphere)
- Marcus theory yields
  - the Gibbs free energy change ΔG°
  - the reorganization energy λ
  - electronic coupling between D and A wave functions H_{DA}
- Variation of ΔG° results in a Gaussian distribution of activation energies that give rise to Marcus normal, barrierless, and inverted kinetic behaviors
- A strong distance dependence of λ and H_{DA} exists

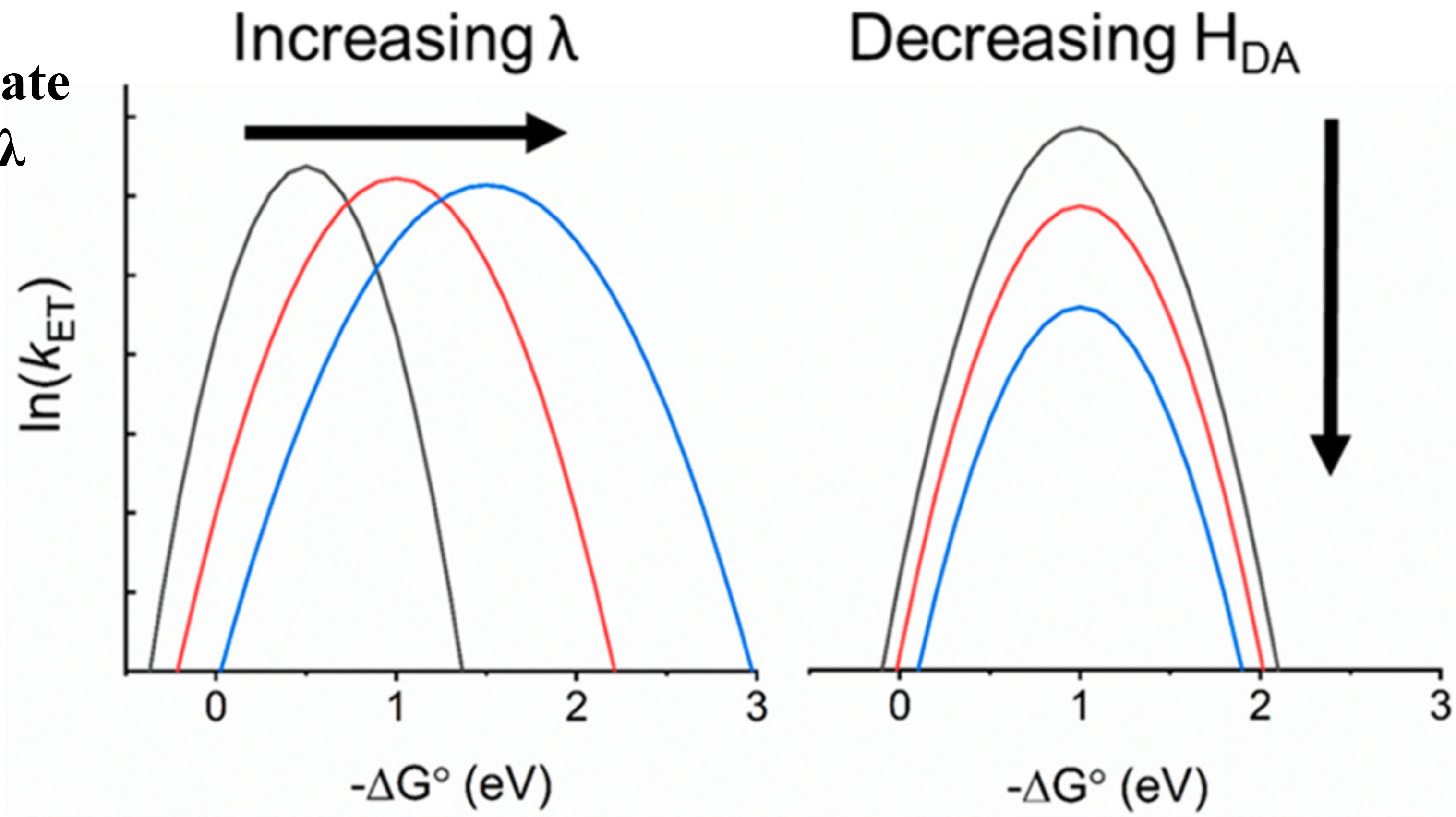




5. Marcus Theory

Summary

The electron transfer rate k_{12} or k_{ET} depends on λ and H_{DA}

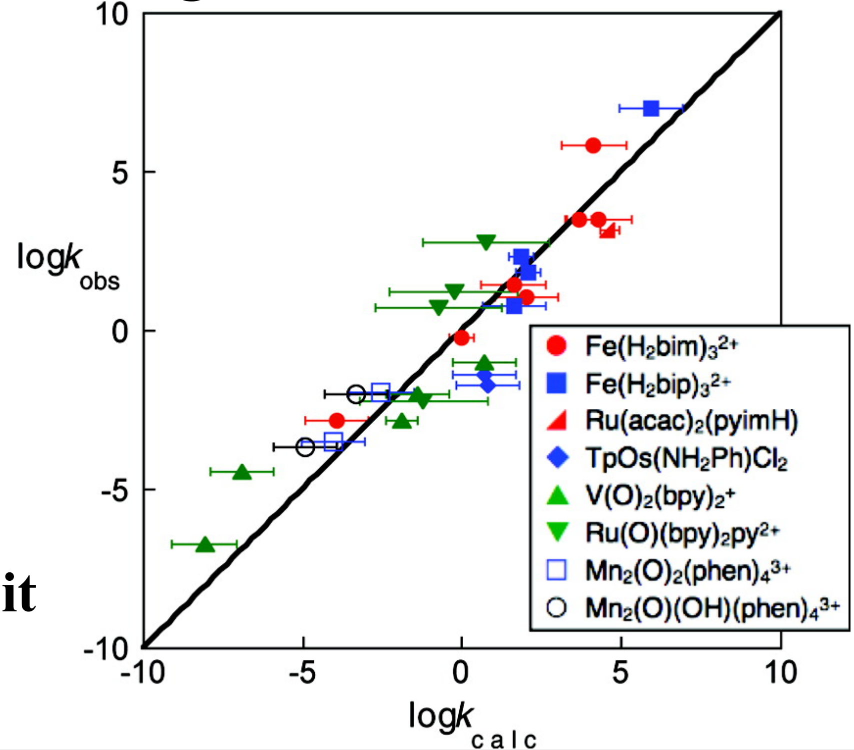


Effects of increasing reorganization energies and decreasing electronic coupling on Marcus parabolas for electron transfer. An increase in the reorganization energies forces the parabola to translate to the right. Decreases in electronic coupling cause the maximum rate constant to decrease at a fixed λ value.

5. Marcus Theory

Summary

- **The simplest form of the Marcus equation for electron transfer predicts the reaction barrier ($\Delta G^{\neq}$) from the reaction driving force (ΔG^0) and intrinsic barrier (λ) which is the energy required to reorganize the reactants and surrounding solvent without electron transfer**
- **This equation, with a few assumptions, can be rearranged to the Marcus cross relation: $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$**
- **Marcus theory can also applied to Hydrogen atom self exchange transfer reactions (HAT): $A\text{-}H + A \rightleftharpoons A + H\text{-}A$: $k_{AH/A}$**
- **The log/log plot of observed versus calculated HAT rate constant for a number of metal complexes reacting with various substrates. The diagonal line illustrates $k_{obs} = k_{calc}$. The estimated errors on $k_{calc.}$ are typically ±1 log unit**



Lit.: Mayer, J. Understanding Hydrogen Atom Transfer: From Bond Strengths to Marcus Theory, Acc. Chem. Res. 44 (2011) 36

6. Intervalence Compounds

Charge Transfer Transitions

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Ligand to Metal Charge Transfer (LMCT)

- Transfer of an electron from an orbital with primarily ligand character to one with primarily metal character → OLEDs & Sensitisation of phosphors
- Can be observed with π donor ligands or easily reducible metals

Metal to Ligand Charge Transfer (MLCT)

- Transfer of an electron from an orbital with primarily metal character to one with primarily ligand character → Emission of metallates and OLEDs
- Can be observed with π acceptor ligands

Ligand to Ligand Charge Transfer (LLCT)

- Transfer of an electron from a ligand to another ligand
- Heteroleptic complexes with aromatic ligands → OLED emission, enz. catalysis

Metal to Metal Charge Transfer (MMCT) or InterValence Charge Transfer (IVCT)

- Transfer of an electron from a metal center to another metal center
- Can be observed in intervalence compounds → Colour, quenching, e^- transport

Remark: Charge transfer transitions are spin and Laporte allowed: $\varepsilon > 1000\ M^{-1}cm^{-1}$

6. Intervalence Compounds

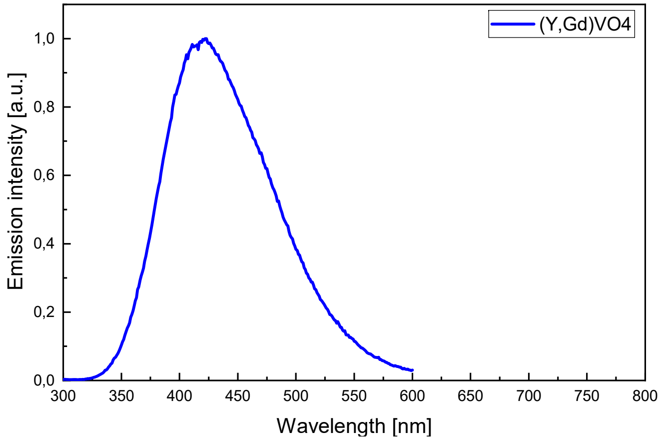
LMCT Absorption and MLCT Emission in Metallates

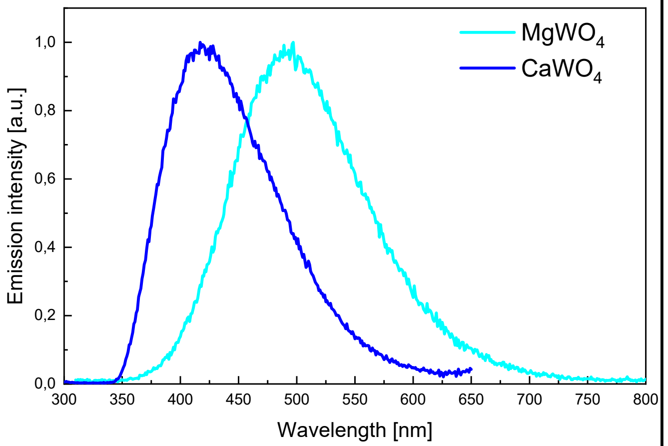
Tetrahedral anions

VO_4^{3-}, CrO_4^{2-}, MnO_4^{-}, NbO_4^{3-}, MoO_4^{2-}, TaO_4^{3-}, WO_4^{2-}, ReO_4^{-}

Octahedral anions

MoO_6^{6-}, WO_6^{6-}





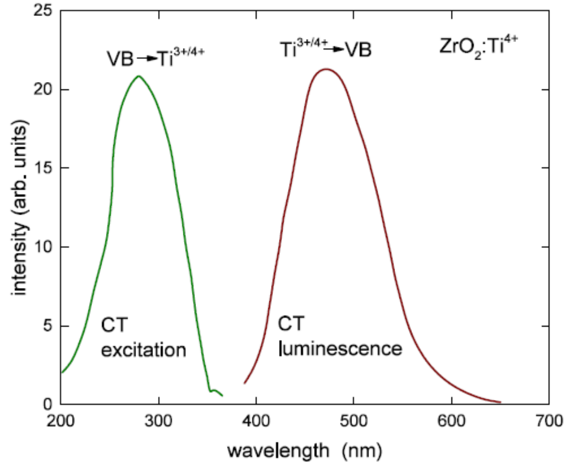
Absorption process

LMCT

$O^{2-} \rightarrow M^{n+}$

2p(non-bonding) → $d(e_g)$

VB → d^0/d^1



Emission process

MLCT

$M^{(n-1)+} \rightarrow O^{-}$

$d(e_g)$ → 2p(non-bonding)

d^0/d^1 → VB

Result: Bond strength declines ⇒ $\Delta R >> 0$ ⇒ rather large λ and broad bands

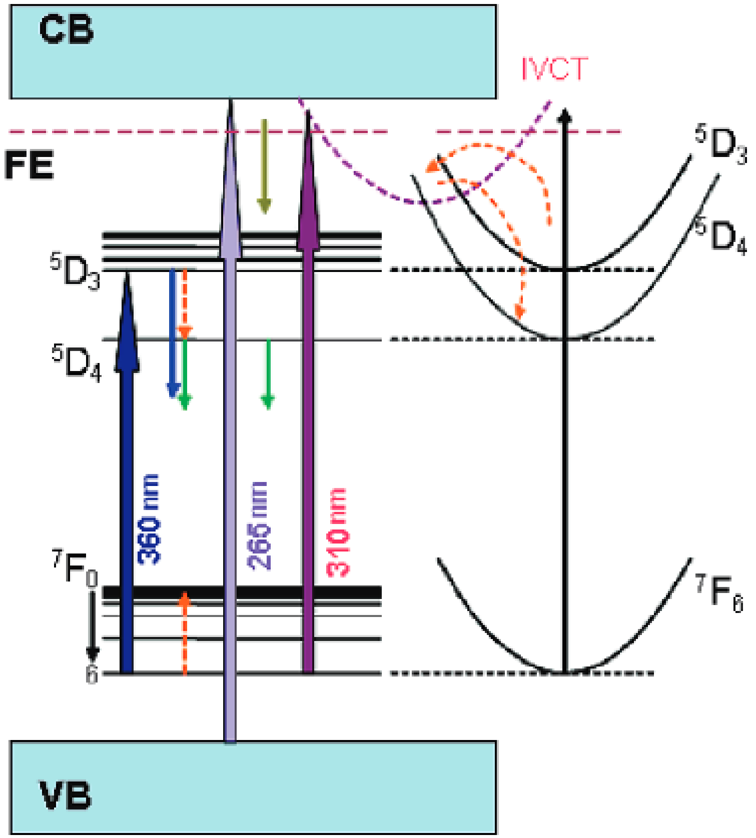
For moderate λ (tungstates): Photo-/electroluminescence

For large λ (titanates): Photocatalysis

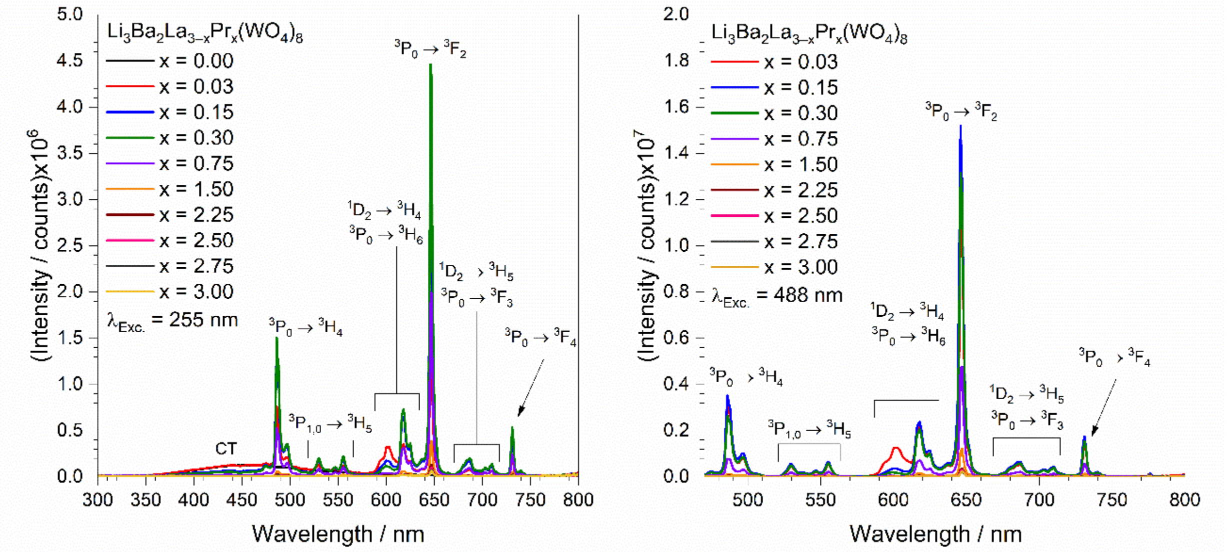
6. Intervalence Compounds

MMCT or IVCT Quenching of Higher RE Ion Energy Levels

$CaWO_4:Tb^{3+}$ ($^5D_3$ quenching)



$Li_3Ba_2La_{3-x}(WO_4)_8:Pr^{3+}_x$ ($[Xe]4f^15d^1$ quenching)



$$MMCT\left(Pr^{3+/4+} \leftrightarrow W^{6+/5+}, cm^{-1}\right) = Pr - W\ CT$$

$$= 58800 - 49800\left(\frac{\chi_{opt}(W^{6+})}{d_m(Pr^{3+} - W^{6+})}\right)$$

with $\chi_{opt} = 2$ (W^{6+}) and $d_m = 3.674$ Å

Pr-W CT level energy at 31691 cm^{-1} (316 nm)

Lit.: P. Dorenbos et al., Inog Chem. 49 (2010) 4921; T. Jüstel et al., J. Luminescence 252 (2022) 119415

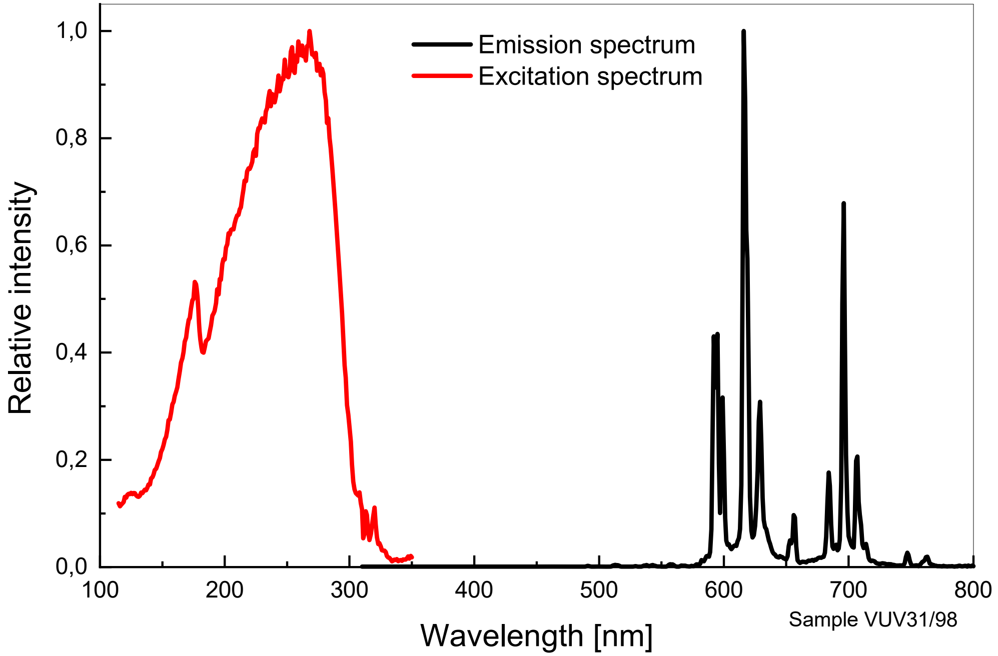
6. Intervalence Compounds

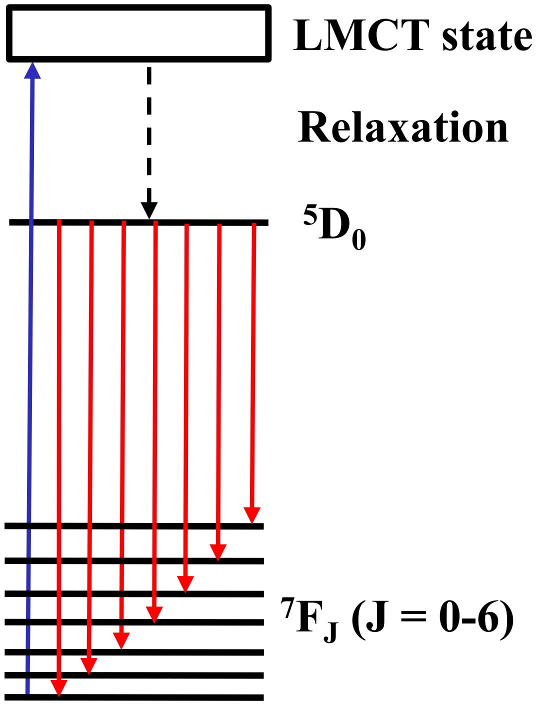
Ligand to Metal Charge Transfer (LMCT): Sensitisation of Phosphors

→ $3d^n$ - $3d^n$ and $4f^n$ - $4f^n$ transitions are forbidden and thus weak

A way to enhance absorption strength of rare earth or transition metal ion activated materials is the use of Charge Transfer (CT) states → Ce^{4+}, Eu^{3+}, Sm^{3+}, Yb^{3+}, Tm^{3+}

Example: $GdAlO_3:Eu^{3+}$ → LMCT at 250 nm (4.95 eV)





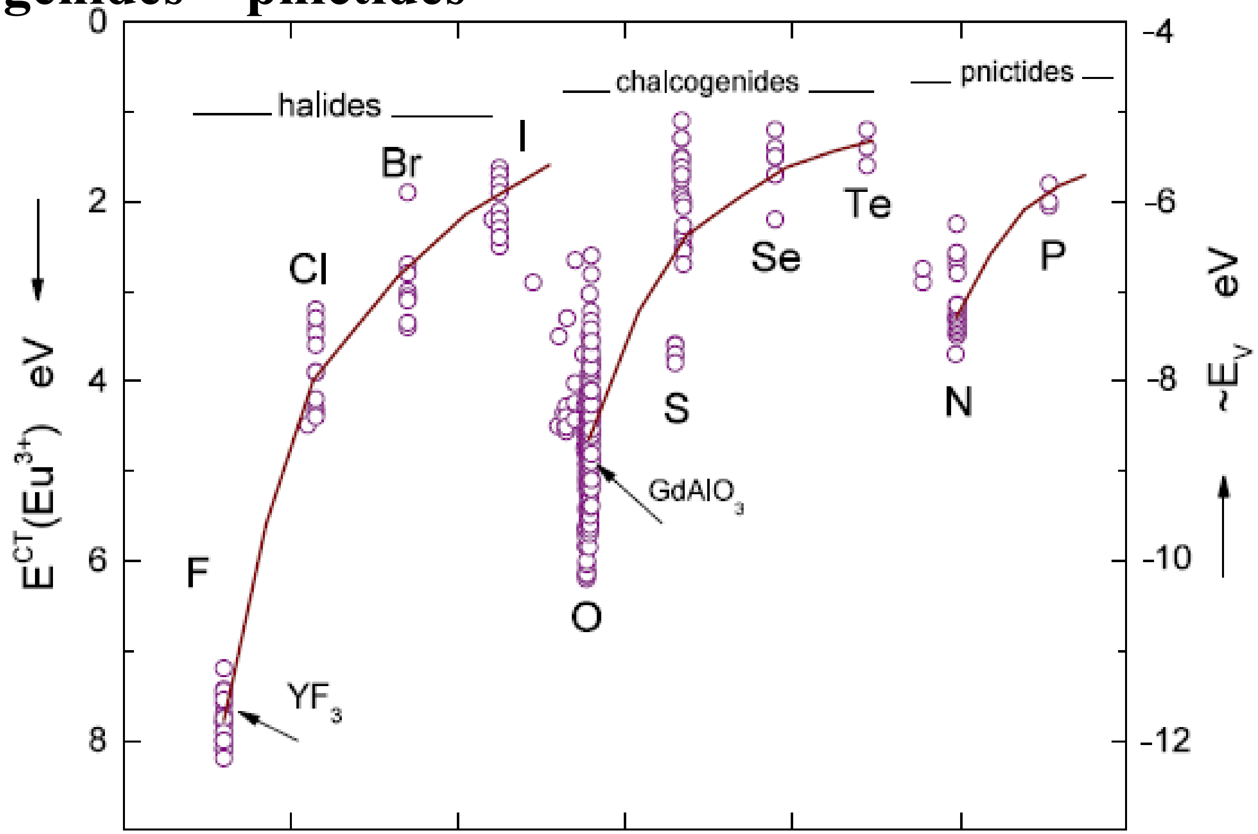
Simplified energy level diagram of Eu^{3+} [Xe]$4f^6$

6. Intervalence Compounds

Ligand to Metal Charge Transfer (LMCT): Position of the LMCT Band

Reduction in energy by enhancement of polarizability of type of inorganic anions:

Halides < chalcogenides < pnictides

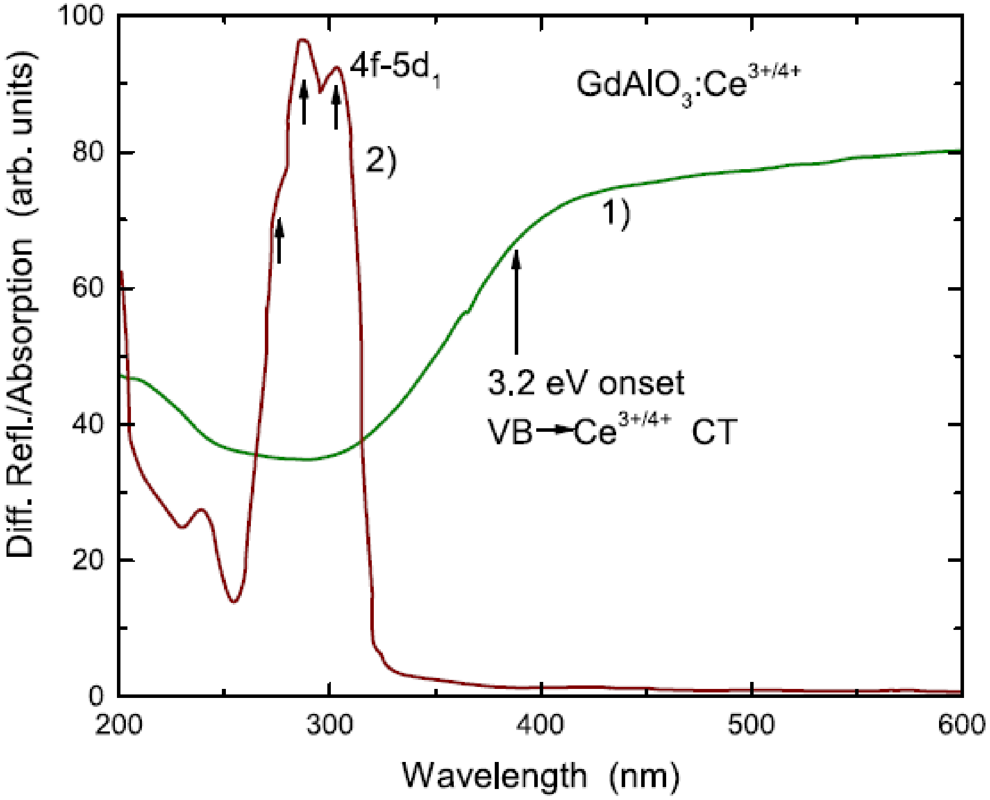


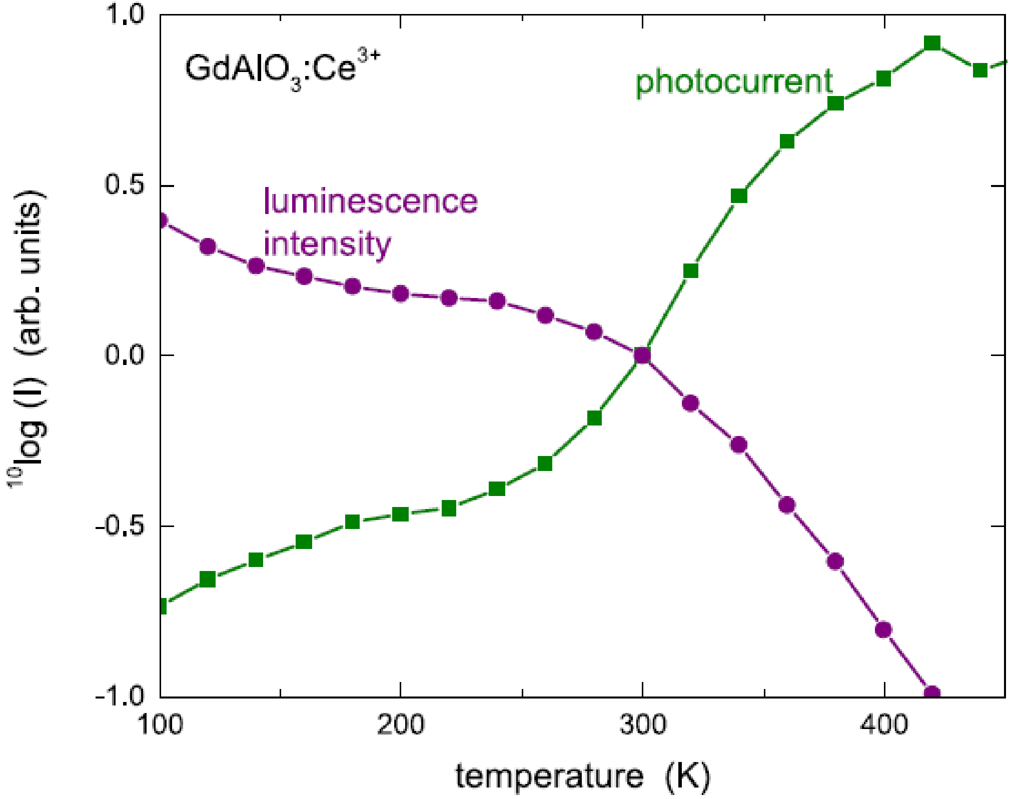
Lit.: P. Dorenbos, Optical Materials 69 (2017) 8

6. Intervalence Compounds

Ligand to Metal Charge Transfer (LMCT): Position of the LMCT Band

Position of the LMCT band relative to the CB determines: PL vs. photocurrent





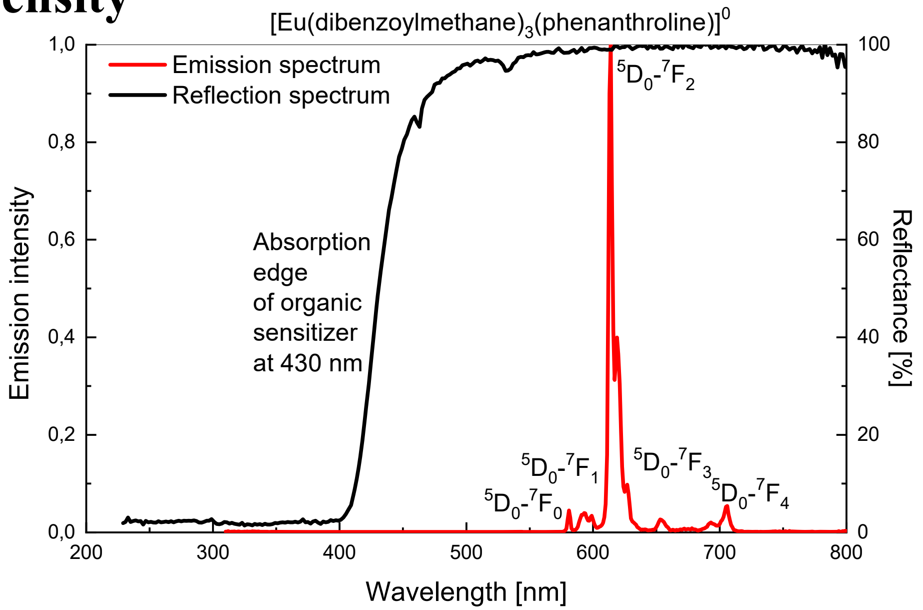
Low temp.: Photoluminescence **High temp.: Photoreductive catalysis**

Lit.: P. Dorenbos, Optical Materials 69 (2017) 8

6. Intervalence Compounds

Ligand to Metal Charge Transfer (LMCT): Position of the LMCT Band

Reduction in energy by enhancement of polarizability
i.e. by alkaline anionic moieties with high electron density



- **Organic π-donor ligands**
  → [Eu(dbm)$_3$(phen)] CN = 8
  → [Eu(ttfa)$_3$(dpphen)] CN = 8

- **Metallates**
  → VO_4^{3-}, MoO_4^{2-}, WO_4^{2-}, MoO_6^{6-}, WO_6^{6-}

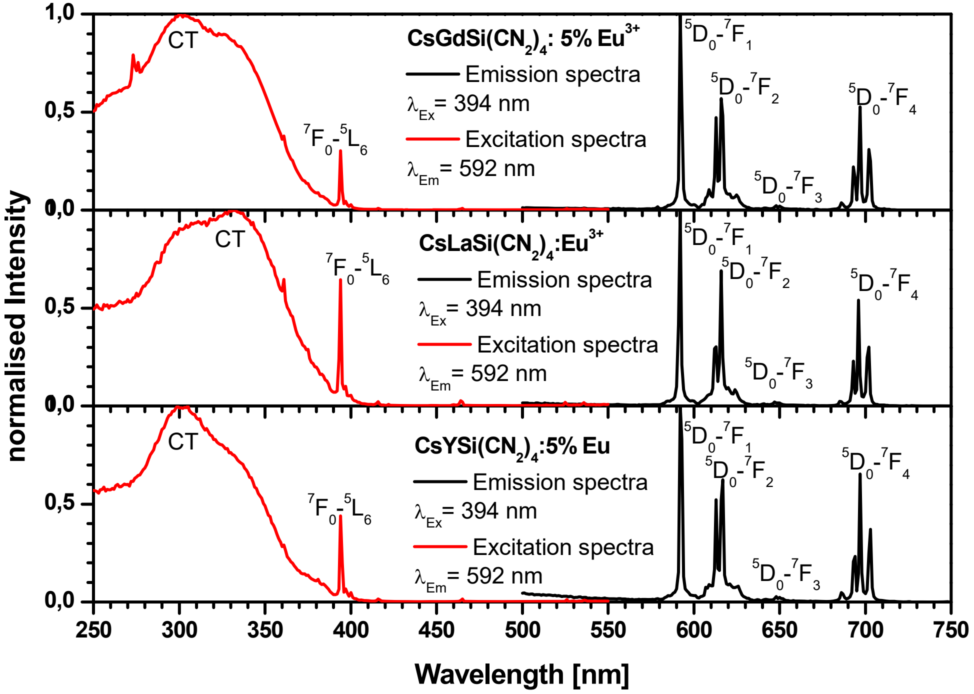
- **Other alkaline (e$^-$-rich) network formers**
  → e.g. carbodiimides
  → $M^{I}Ln^{III}(M^{IV}(CN_2)_4]:Eu^{3+}$ M^{I} = K, Rb, Cs; Ln^{III} = Y, La, Gd and M^{IV} = Si, Ge

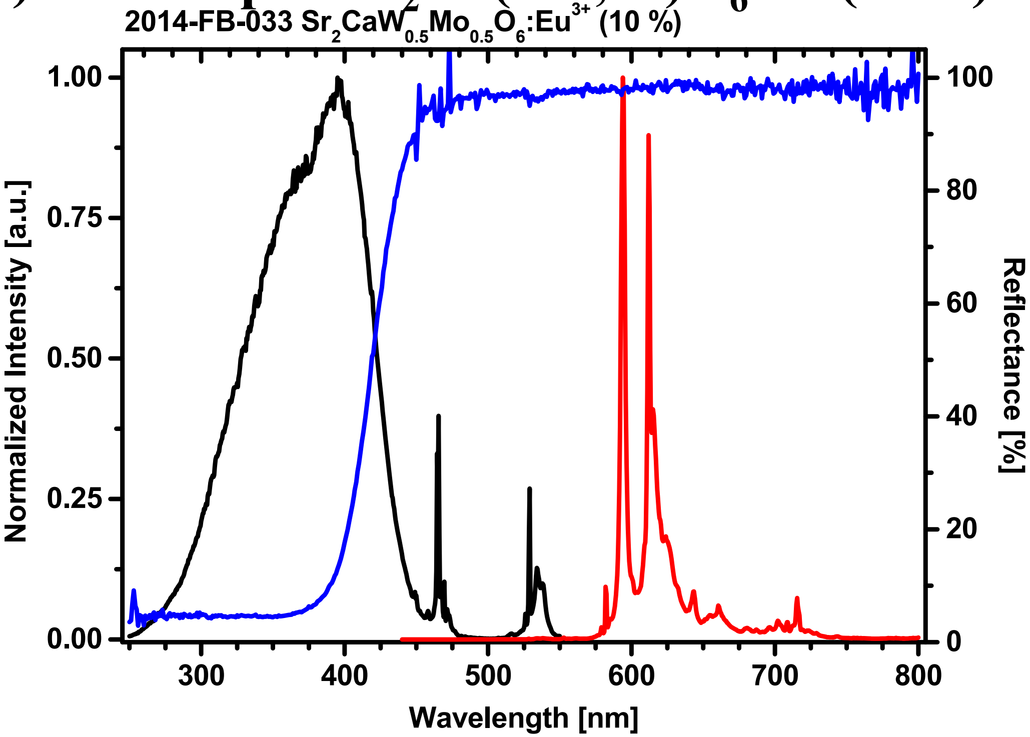
6. Intervalence Compounds

Ligand to Metal Charge Transfer (LMCT): Position of the LMCT Band

Reduction in energy by enhancement of (optical) polarizability

Eu-doped CsLn[Si(CN$_2$)$_4$] (Ln = Y, La, Gd) **Eu-doped Sr$_2$Ca(Mo,W)O$_6$:Eu(10%)**

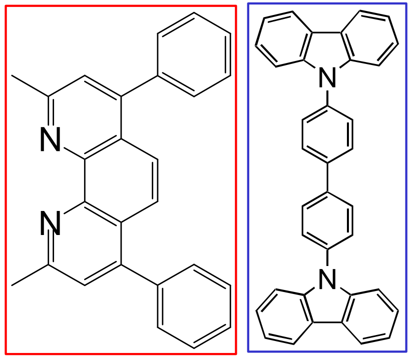


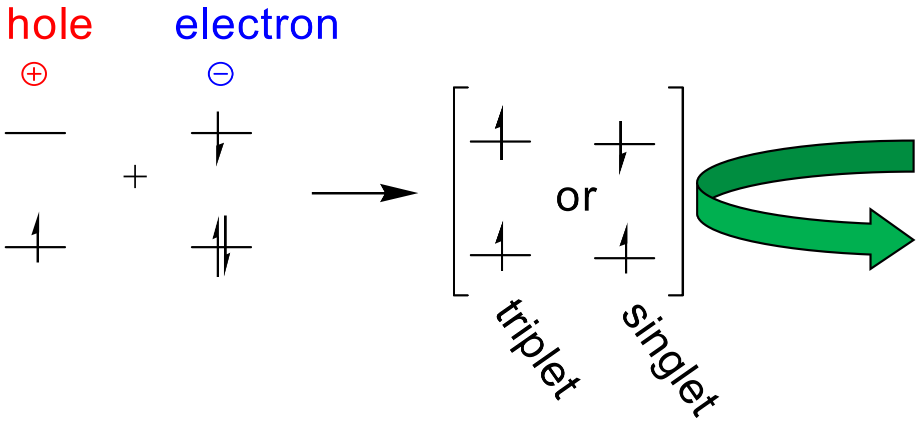


Lit.: J. Glaser, H. Bettentrup, T. Jüstel, H.-J. Meyer, Inorg. Chem. 48 (2010) 2954

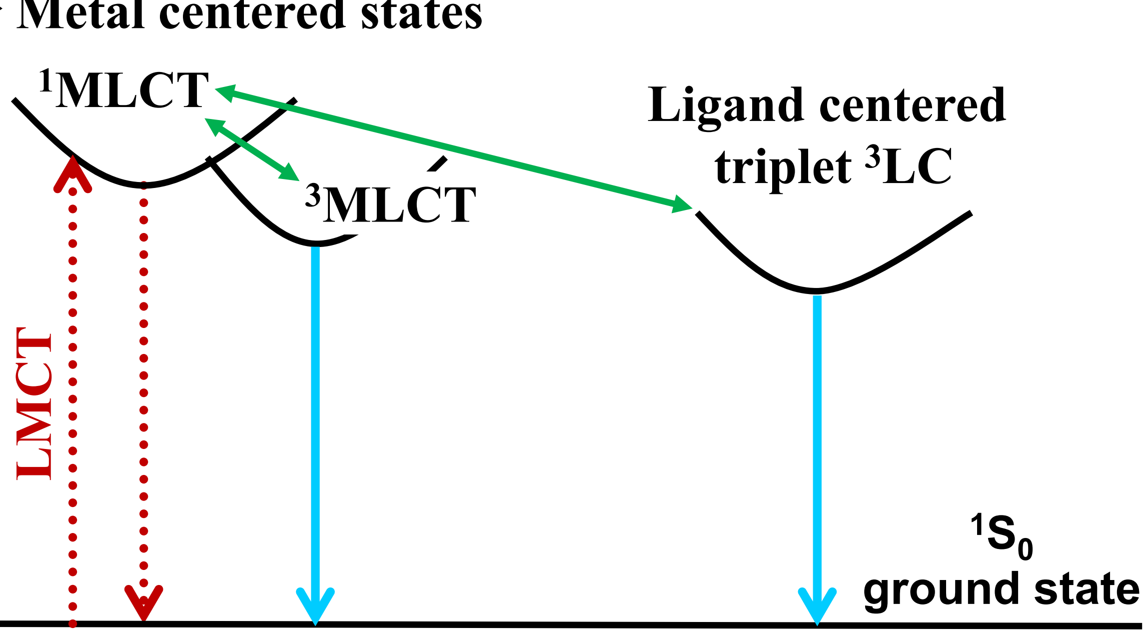
6. Intervalence Compounds

Ligand to Metal Charge Transfer (LMCT): Charge Carrier Harvesting in OLEDs: Typical hole (CBP) and electron (BCP) conductors





Metal centered states



↔ State mixing ~ to the extent of the spin-orbit-coupling of metal center

↓ Luminescence (radiative transitions)

⇣ Non-radiative transitions

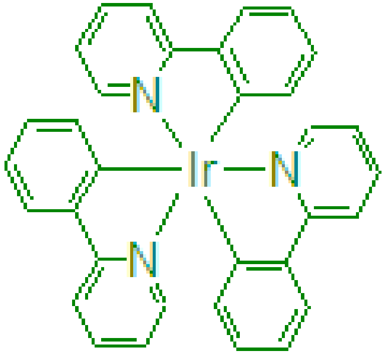
Large spin-orbit-coupling ξ for M = RE^{3+}, Re^{+}, Os^{2+}, Ir^{3+}, Pt^{4+} (with RE = Eu, Tb, Tm)

Most inert electron configuration: $[Xe]4f^{14}5d^{6}$ low-spin → -24 $Dq_{octahedral}$ ~ 40000 cm^{-1}

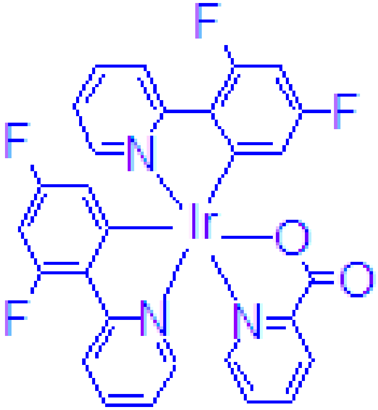
6. Intervalence Compounds

Metal to Ligand Charge Transfer (MLCT): Emission from Complexes in OLEDs

$[Ir(\mathit{ppy})_3]$ ppy = phenylpyridine

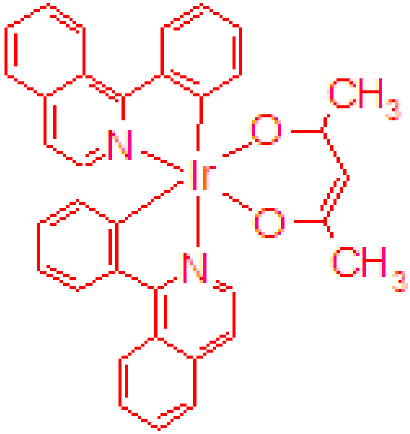


$[(4,6\text{-}F_2\mathit{ppy})_2Ir(pic)]$ pic = picolinat



$[(pch)_2Ir(acac)]$ pch = phenylquinolinate

acac = acetylacetonate



Electro- and photoluminescence of Ir^{3+} complexes

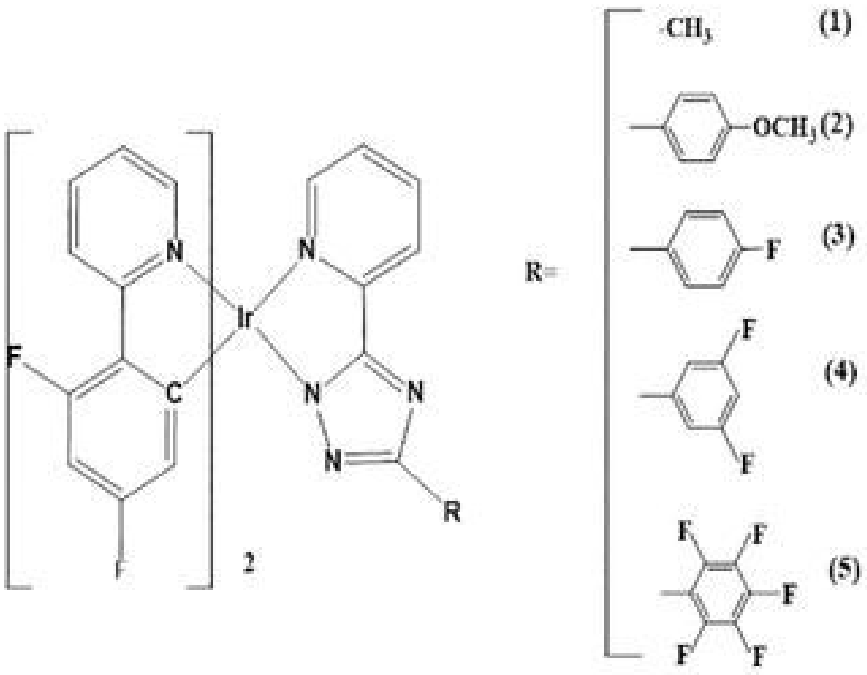
- Strong spin-orbit coupling ξ: $Ir^{3+} \sim 4000\ cm^{-1}$
- MLCT and $^3\pi$-π^* transitions
- Position of the HOMO and thus the emission bands can be determined by the ligands and controlled by substituents on the ligands

6. Intervalence Compounds

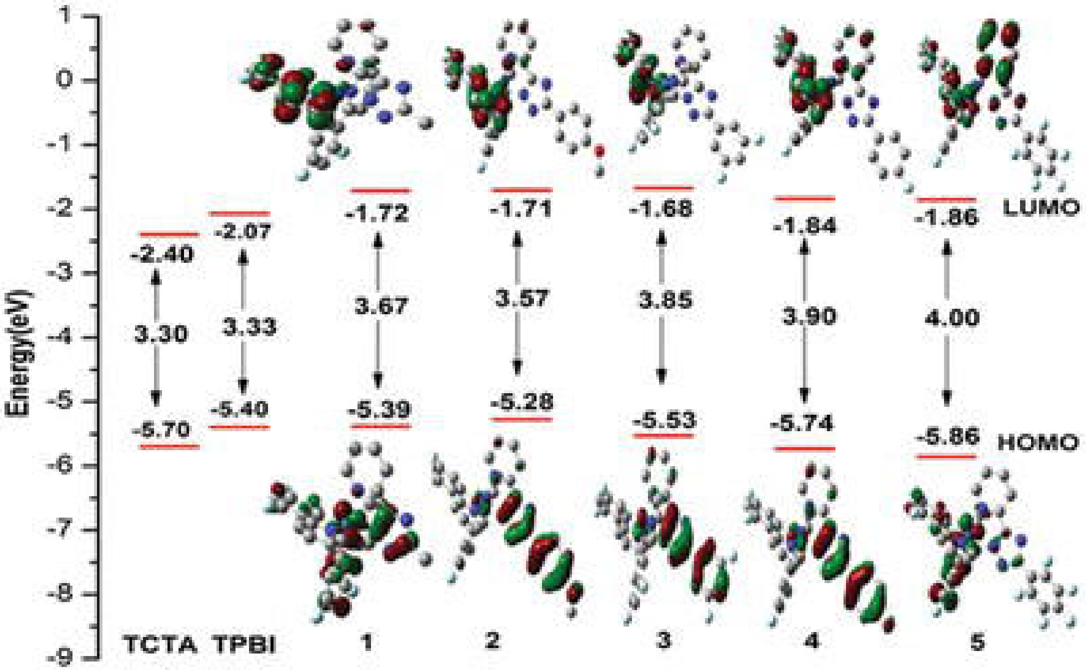
Metal to Ligand Charge Transfer (MLCT): Emission from Complexes in OLEDs

Tuning of the emission spectrum by modifying the HOMO-LUMO gap

- Electropositive substituents: Red shift
- Electronegative substituents: Blue shift



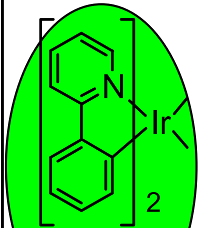
(a)



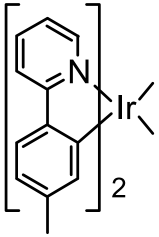
(b)

6. Intervalence Compounds

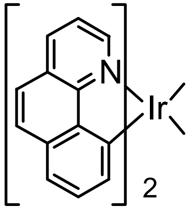
Metal to Ligand Charge Transfer (MLCT): Emission from Complexes in OLEDs



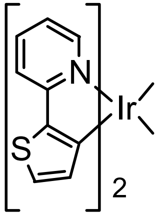
ppy



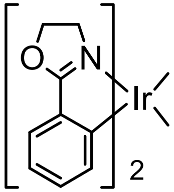
tpy



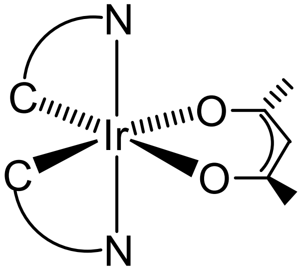
bzq



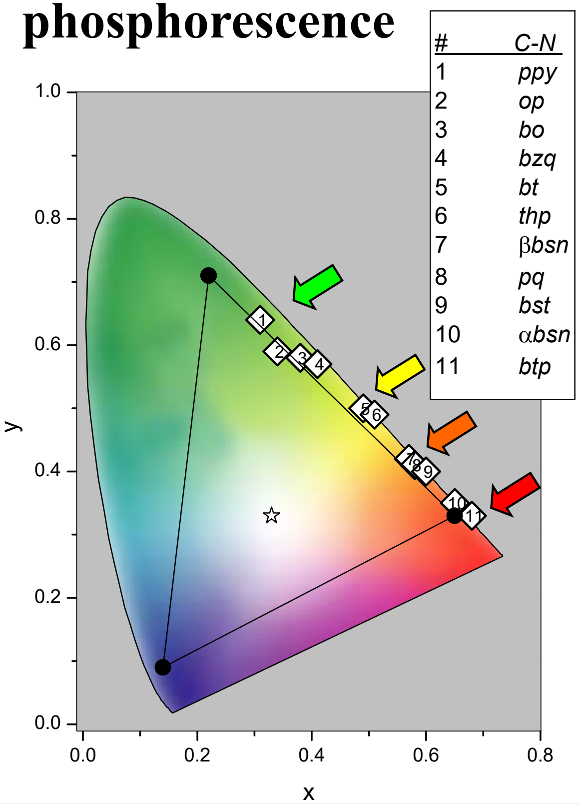
thp

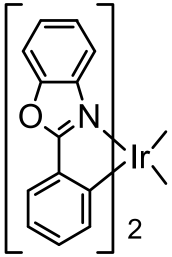


op



CIE coordinates based on phosphorescence





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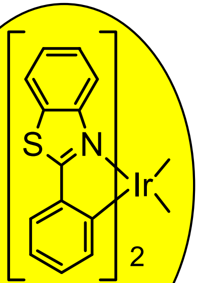

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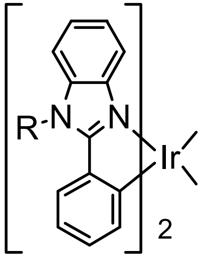
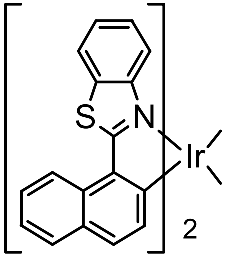
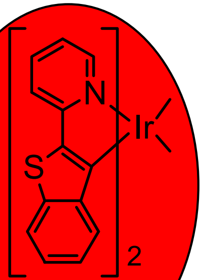


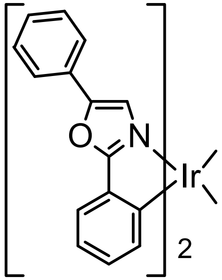
bin



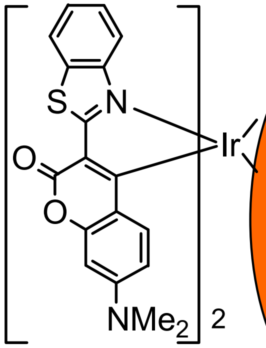
αbsn



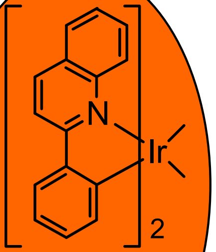
btp



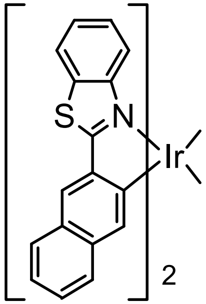
ppo



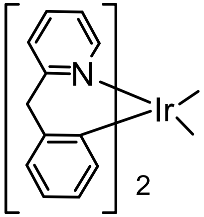
C6



pq



βbsn



pbz

6. Intervalence Compounds

Intervalence Definition and Compound Types

Compounds in which a certain metal center occurs in at least two oxidation states

Solid state compounds

- Mn_3O_4, Fe_3O_4, Fe_3S_4, Co_3O_4, Pr_6O_{11}, Tb_4O_7, Pb_3O_4, In-chalkogenides, e.g. In_3S_4

Coordination compounds

- $Fe^{2+/3+}$ complexes, e.g. Prussian blue
- $Ru^{2+/3+}$ complexes, e.g. the Creutz-Taube ion
- $[Ru_2(OAc)_4Cl]_n$ which is a coordination polymer

Bioinorganic compounds

- $[Fe^{I/II}{}_2S_2]^{0,-}$ cluster in Rieske protein
- $[Fe^{II/III}{}_4S_4(SR)_4]^{2-/3-}$ cluster in Ferredoxin
- $[Mn^{II/III/IV}{}_4Ca]^{n+}$ cluster in photosystem II
- $[Cu_2(SR)_2]$ cluster in type A copper proteins

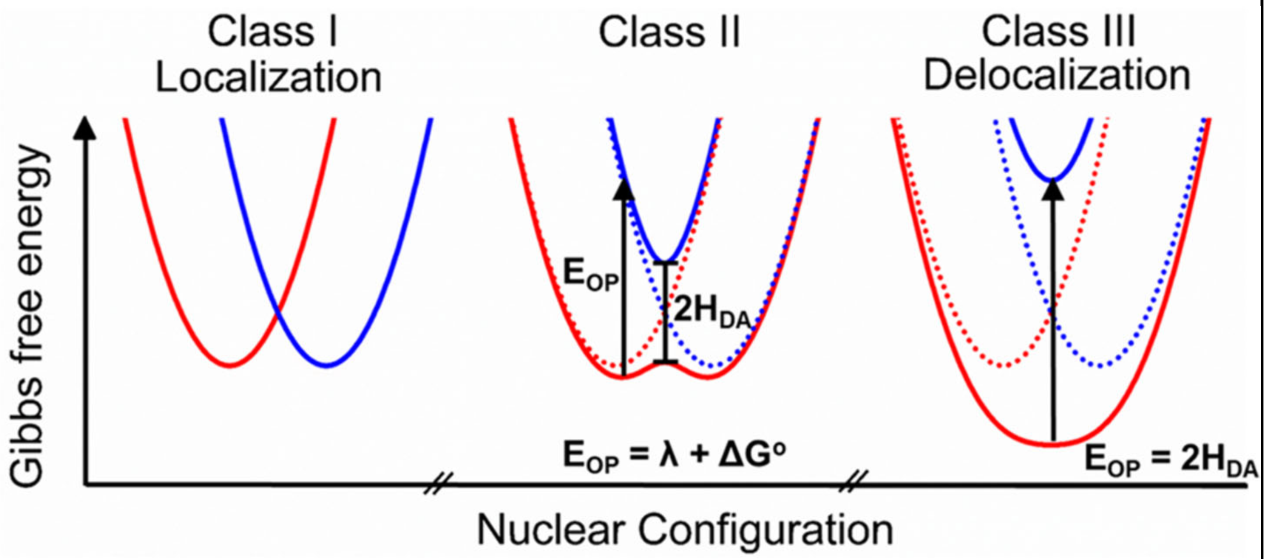
6. Intervalence Compounds

Robin and Day Classification

Class I: $H_{DA} = 0$, i.e. electron density is formally localized on the noninteracting donor or acceptor site

Class II: $0 < H_{DA} < \lambda/2$, i.e. in this case, the interaction between reactant and donor wave functions, mediated through electronic coupling, results in the generation of a new ground- and excited-state surface

Class III: $H_{DA} > \lambda/2$ electronic coupling is sufficiently large that individual molecular properties are averaged, electron density is completely delocalized between the D and A ($\rightarrow \Delta G° = 0$)



Lit.: Melvin B. Robin, Peter Day, Mixed Valence Chemistry-A Survey and Classification, Adv. Inorg. Chem. Radiochem. 10 (1968) 247-422

6. Intervalence Compounds

Robin and Day Classification

For Class I or II electron transfer that exhibits Gaussian shaped IVCT bands, the corresponding intensities (extinction coefficient, ε_{max}), transition widths (full widths at half maximum intensity, $\Delta\nu_{1/2}$), and donor-acceptor geometric distances are used to calculate the extent of coupling, H_{DA}, by the Mulliken-Hush analysis →

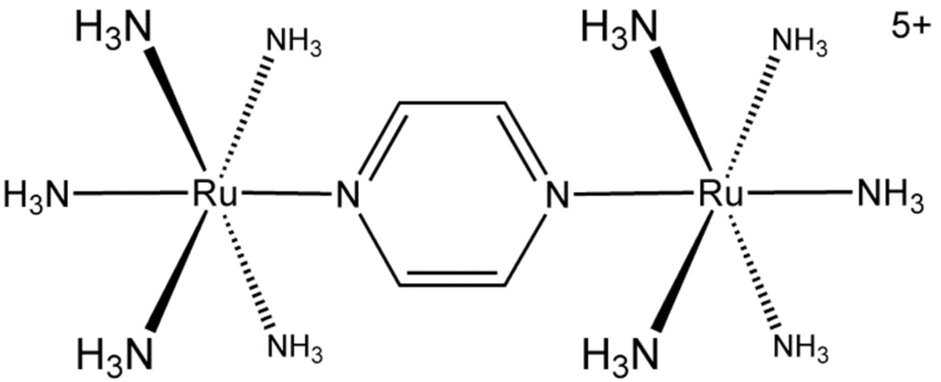
$H_{DA} = 0.0206/r\ (E_{op}\ \varepsilon_{max}\ \Delta\nu_{1/2})$ with E_{op} = Energy of optical absorption band

$\Delta\nu_{1/2} = 4\sqrt{(k_B T \lambda \ln 2)}$

Therefore, the position and shape of an intervalence absorption band can be used for the classification, but details are complicated …..

6. Intervalence Compounds

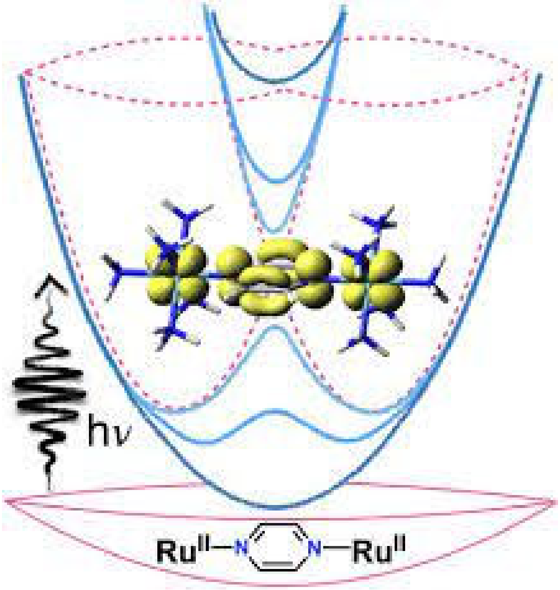
Class III (or Class II?): The Creutz-Taube Ion

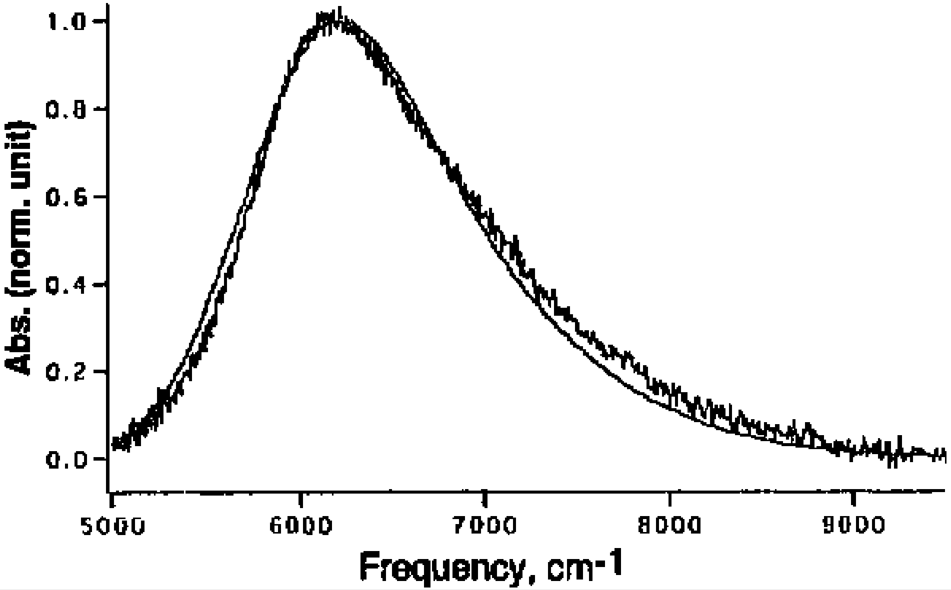


E_{op} = 1560 nm (6410 cm^{-1}) in D_2O at RT
ε_{max} = 5000 $M^{-1}cm^{-1}$
$\Delta\nu_{1/2}$ = 1480 cm^{-1} (i.e. it is narrow)

$\Rightarrow H_{DA} = 3300\ cm^{-1}$

The odd electron is located along the the Ru-p_z-Ru axis

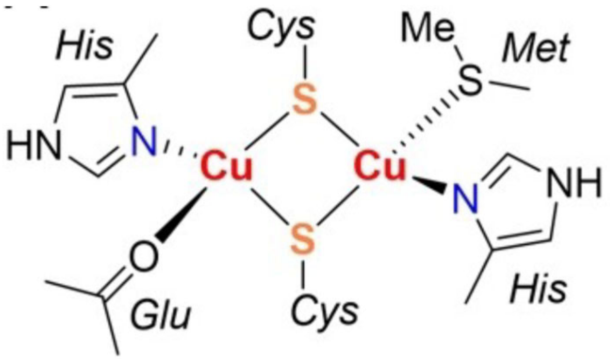




6. Intervalence Compounds

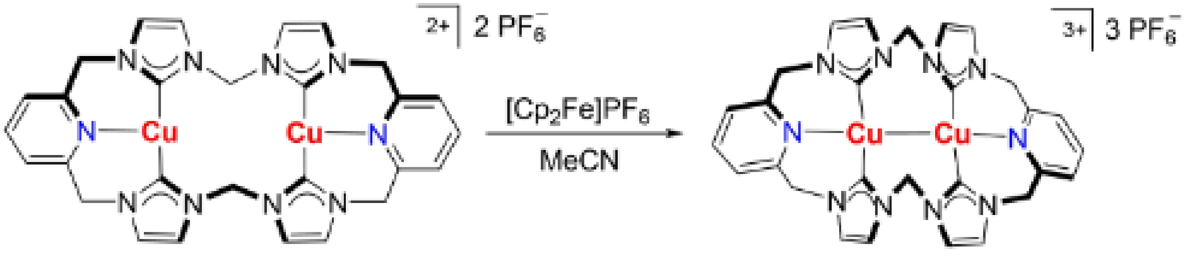
Class III: Dimeric Copper Complexes

Type A copper proteins

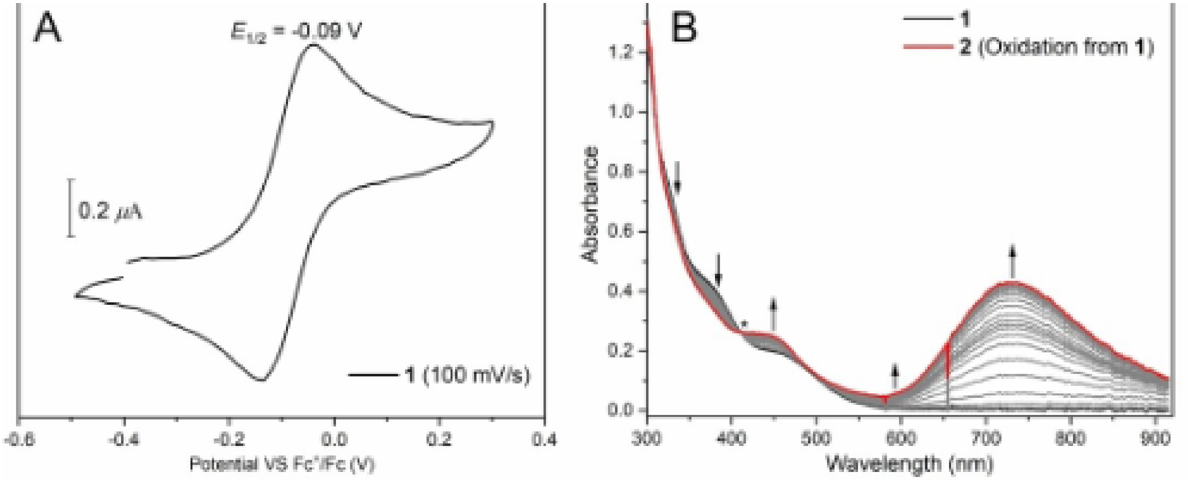


$Cu^{1.5}Cu^{1.5}$: ~2.5 Å

Cu^{I}-Cu^{I} and $Cu^{1.5}$-$Cu^{1.5}$ model complexes



$[LCu_2](PF_6)_2$ (**1**) $[LCu_2](PF_6)_3$ (**2**)



Absorption spectrum and CV

- E_{op} = 740 nm (13500 cm^{-1})
- ε_{max} = 7000 $M^{-1}cm^{-1}$
- $\Delta\nu_{1/2}$ = 3200 cm^{-1}
- $E_{1/2}$ = -0.09 V vs. Fc^+/Fc

Observed delocalization by direct Cu-Cu 3d orbital overlap

Lit.: F. Meyer et al., Angew. Chem. Int. Ed. 2023, 62, e202215840

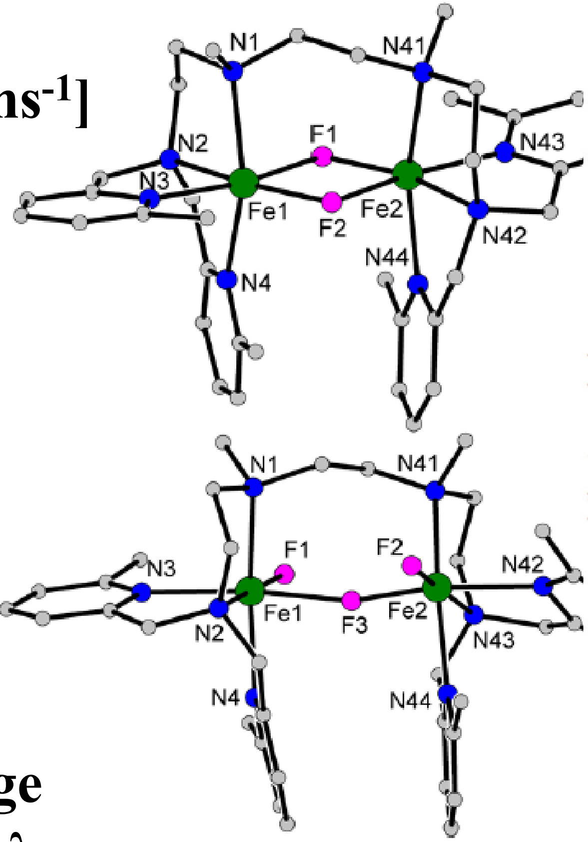
6. Intervalence Compounds

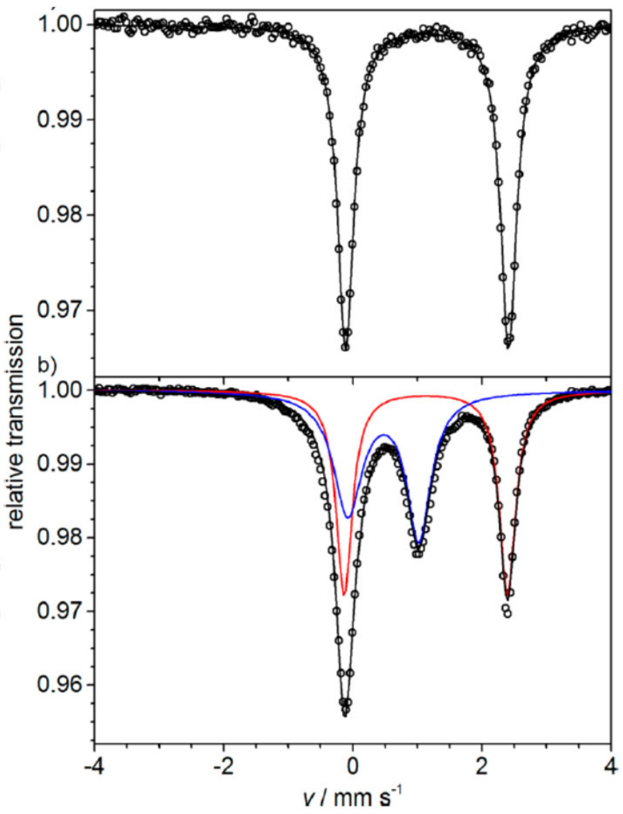
Class II: Fluoro Bridged Dinuclear Fe complex [(susan 6-Me){$Fe^{II}F(\mu\text{-}F)Fe^{III}F$}]$^{2+}$

Crystal structure and Mößbauer spectra of the Fe^{II}-Fe^{II} and Fe^{II}-Fe^{III} complexes

Mößbauer spectra at 77 K

	I.S. [mms^{-1}]	Q.S. [mms^{-1}]
$Fe^{II/II}$	1.15	2.52
$Fe^{II/III}$	1.13	2.53
	0.47	1.10





Absorption spectrum

- E_{op} = 1000 nm (10000 cm^{-1})
- ε_{max} = 80 $M^{-1}cm^{-1}$
- $\Delta\nu_{1/2}$ ~ 9000 cm^{-1}

Observed highly asymmetric bridge yields large reorganisation energy λ

Lit.: T. Glaser et al., Inorg Chem. 56 (2017) 1779

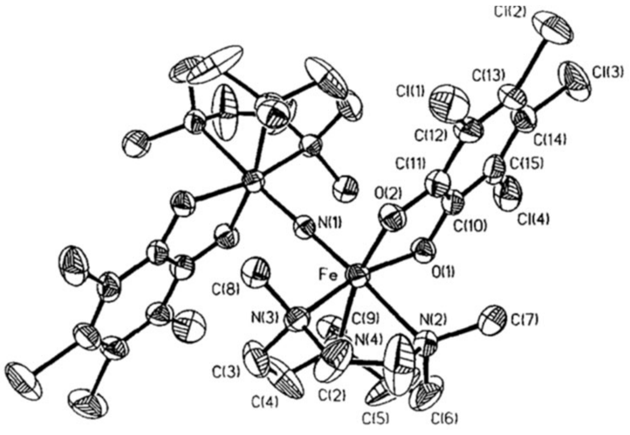
6. Intervalence Compounds

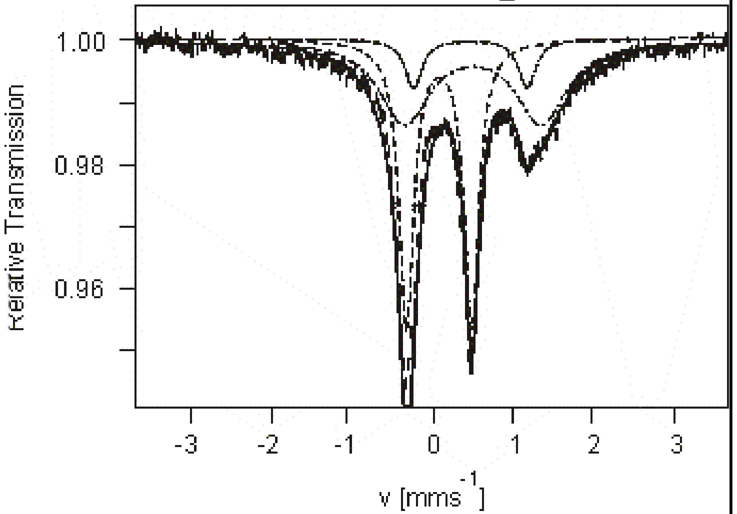
Class II: Nitrido Bridged Dinuclear Fe complex [L(tccat)Fe^{III}(μ-N)Fe^{IV}(tccat)L]

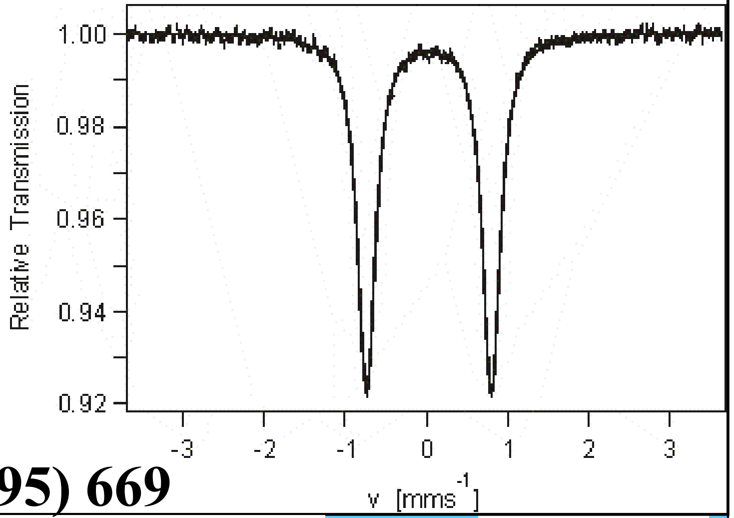
Crystal structure and Mößbauer spectra of the Fe^{III}-Fe^{IV} and Fe^{IV}-Fe^{IV} complexes

Mößbauer spectra at 77 K

	I.S. [mms^{-1}]	Q.S. [mms^{-1}]
$Fe^{III/IV}$	0.52	0.81
	0.09	1.67
$Fe^{IV/IV}$	0.04	1.55







Absorption spectrum

- E_{op} = 876 nm (11400 cm^{-1})
- $\varepsilon_{max} = 300\ M^{-1}cm^{-1}$
- $\Delta\nu_{1/2} \sim 5000\ cm^{-1}$

Observed highly asymmetric bridge yields very large reorganisation energy λ

Lit.: T. Jüstel et al., Angew. Chem. Int. Ed. Engl. 34 (1995) 669

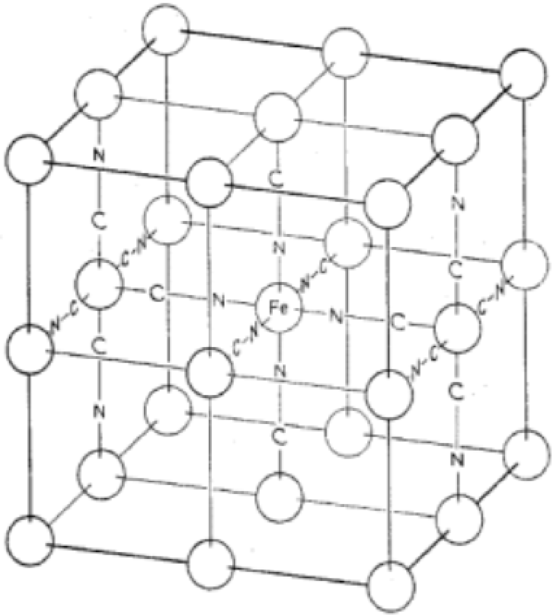
6. Intervalence Compounds

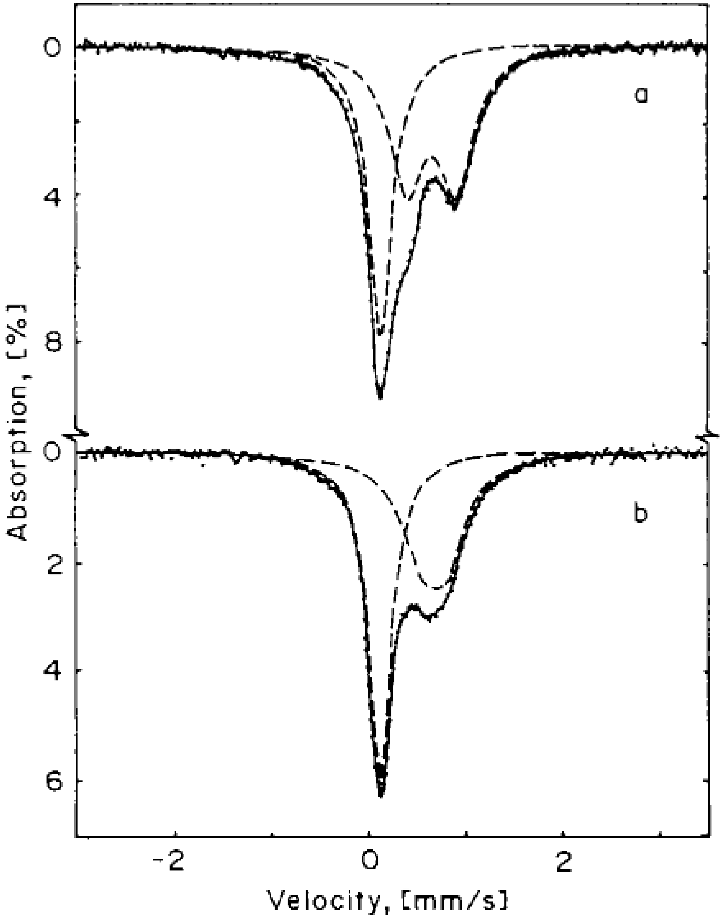
Class II: Prussian Blue Solid State Pigment $Fe_4[Fe(CN)_6]_3 \cdot xD_2O$ (x = 14-16)

Structure: Cubic Face-Centered Fe^{III}-N-C-Fe^{II} framework with space group Fm3m

Mößbauer spectra at 77 K

	I.S. $[mms^{-1}]$	Q.S. $[mms^{-1}]$
$Fe^{II/III}$	0.645	0.584
	0.104	~ 0.0





Absorption spectrum

- E_{op} = 710 nm (14100 cm^{-1})
- ε_{max} = 9800 $M^{-1}cm^{-1}$
- $\Delta\nu_{1/2}$ ~ 6000 cm^{-1}

Observed asymmetric bridge yields moderate reorganisation energy λ

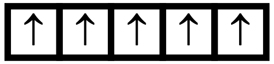
Lit.: M.B. Robin, Inorg. Chem. 1 (1962) 337

7. Spectroscopy of Inorganic Compounds

Description of Electronic States in Multiple-Electron-Atoms

Weak field approach: LS-coupling is notably stronger than the crystal field splitting ⇒ valid from element #30 onwards, thus for the elements of the 4d- and 5d-series as well as the lanthanides (→ Dieke-diagram) and the actinides

Electron configuration ⟶ **orbital and spin momentum L and S**



ml -2 -1 0 1 2

$L = |\Sigma l_i|$ and $S = \Sigma s_i$

↓ **Coulomb-interactions**

↓ **Spin-orbit coupling ξ**

Crystal field splitting

Crystal field energy terms ⟵ **Total angular momentum J**

⇒ A, B, E, T

$J = |L - S|, |L - S + 1|, \ldots. |L + S|$

7. Spectroscopy of Inorganic Compounds

Quantum Mechanical Microstates

$$\boxed{\text{Number } \# = \frac{n!}{e!h!}}$$

with

n = maximal number of electrons in sub-shell (sum of e + h)

e = number of electrons of corresponding configuration

h = number of holes of corresponding configuration

d-shell ⇒ n = 10

e^-	1	2	3	4	5	6	7	8	9
#	10	45	120	210	252	210	120	45	10

<u>Further discussion for TM (+, 2+, …. , 8+) and RE (2+, 3+, 4+) ions</u>

1. Transition metal ion configurations $[Ar]3d^n$, $[Kr]4d^n$, $[Xe]4f^{14}5d^n$
2. Lanthanide ion configurations $[Xe]4f^n$

RS Ground Terms for the d^n-Configurations

$$\boxed{^{2S+1}L_J}$$

d^n/m_l	-2	-1	0	1	2	L	S	Ground term h.s. (l. s.)
d^1	↑					2	1/2	$^2D_{3/2}$
d^2	↑	↑				3	1	$^3F_2$
d^3	↑	↑	↑			3	3/2	$^4F_{3/2}$
d^4	↑	↑	↑	↑		2	2	$^5D_0$ (^3H)
d^5	↑	↑	↑	↑	↑	0	5/2	$^6S_{5/2}$ (^2I)
d^6	↑↓	↑	↑	↑	↑	2	2	$^5D_4$ (^1I)
d^7	↑↓	↑↓	↑	↑	↑	3	3/2	$^4F_{9/2}$ (^2H)
d^8	↑↓	↑↓	↑↓	↑	↑	3	1	$^3F_4$
d^9	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	$^2D_{5/2}$
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	$^1S_0$

7. Spectroscopy of Inorganic Compounds

RS Terms for the d^n-Configurations

All Russell Saunders terms for 3d^n free ion configurations

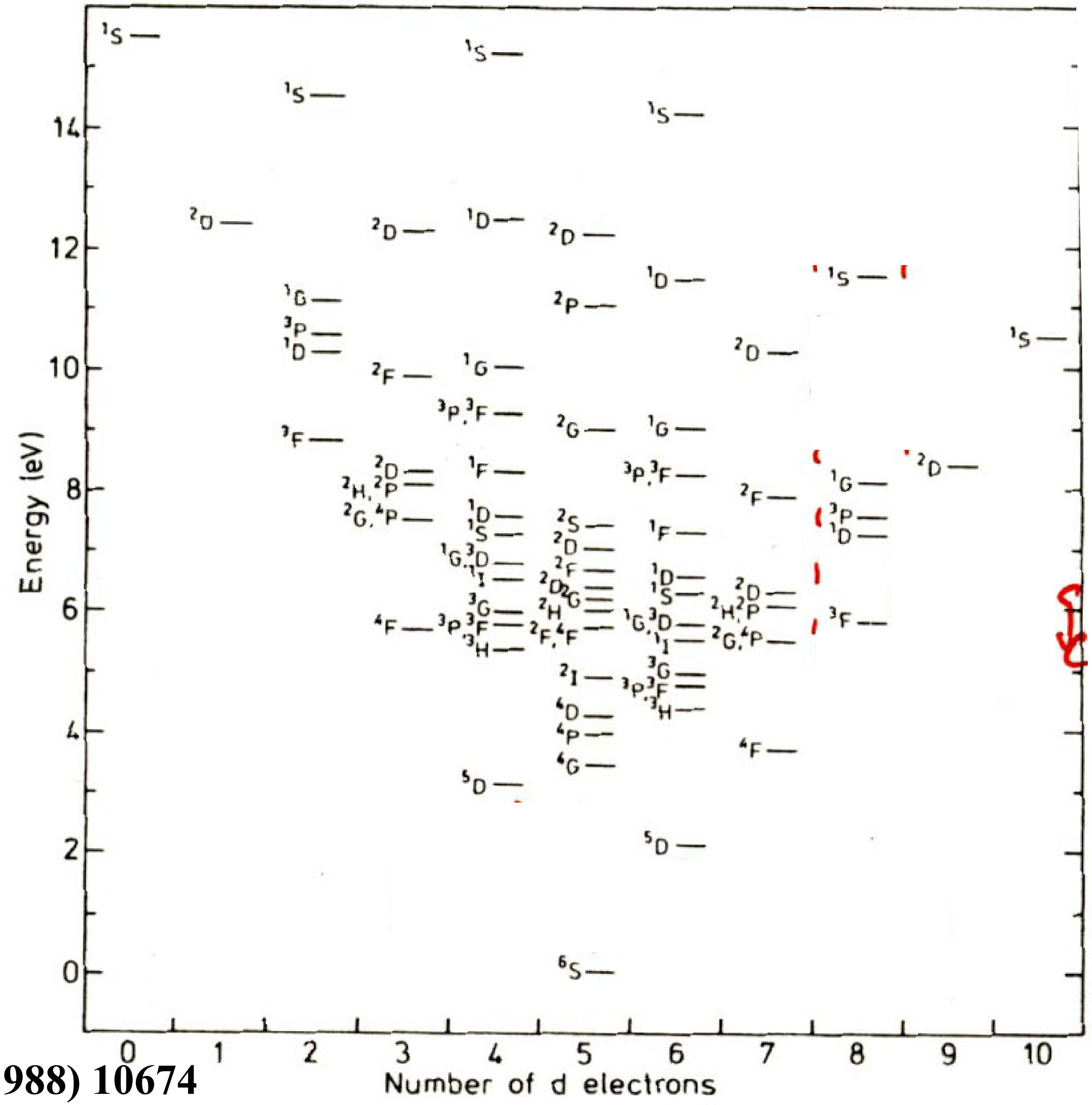
Configuration	# Micro-states	# Energy levels	Ground state terms	Excited state terms
d^1, d^9	10	1	^2D	-
d^2, d^8	45	5	^3F	^3P, ^1G, ^1D, ^1S
d^3, d^7	120	8	^4F	^4P, ^2H, ^2G, ^2F, 2x ^2D, ^2P
d^4, d^6	210	16	^5D	^3H, ^3G, 2x ^3F, ^3D, 2x ^3P, ^1I, 2x ^1G, ^1F, 2x ^1D, 2x ^1S
d^5	252	16	$^6S_{5/2}$	^4G, ^4F, ^4D, ^4P, ^2I, ^2H, 2x ^2G, 2x ^2F, 3x ^2D, ^2P, ^2S
d^{10}	1	1	$^1S_0$	-

7. Spectroscopy of Inorganic Compounds

RS Terms for the d^n-Configurations

Multiplet structure of all free 3d transition metal atoms

Note: The ground state can be found by the three Hund rules



Lit.: D. van der Marel et al., Phys Rev B 37 (1988) 10674

7. Spectroscopy of Inorganic Compounds

RS Ground Terms for the $4f^n$-Configurations

Configuration	# Microstates (SLJM)	# Energy Levels (SLJ)	Ground term
$4f^0$	1	1	$^1S_0$
$4f^1$	14	2	$^2F_{5/2}$
$4f^2$	91	13	$^3H_4$
$4f^3$	364	41	$^4I_{9/2}$
$4f^4$	1001	107	$^5I_4$
$4f^5$	2002	198	$^6H_{5/2}$
$4f^6$	3003	295	$^7F_0$
$4f^7$	3432	327	$^8S_{7/2}$
$4f^8$	3003	295	$^7F_6$
$4f^9$	2002	198	$^6H_{15/2}$
$4f^{10}$	1001	107	$^5I_8$
$4f^{11}$	364	41	$^4I_{15/2}$
$4f^{12}$	91	13	$^3H_6$
$4f^{13}$	14	2	$^2F_{7/2}$
$4f^{14}$	1	1	$^1S_0$

Mirror symmetry?

7. Spectroscopy of Inorganic Compounds

Splitting of RS Terms S, P, D, F, G and symmetry of the s, p, d wavefunctions

Atom-Term (L)	O_h	T_d	D_{4h}
S (0)	A_{1g}	A_1	A_{1g}
P (1)	T_{1g}	T_1	$A_{2g} + E_g$
D (2)	E_g	E	$A_{1g} + B_{1g}$
	T_{2g}	T_2	$B_{2g} + E_g$
F (3)	A_{2g}	A_2	B_{1g}
	T_{1g}	T_1	$A_{2g} + E_g$
	T_{2g}	T_2	$B_{2g} + E_g$
G (4)	A_{1g}	A_1	A_{1g}
	E_g	E	$A_{1g} + B_{1g}$
	T_{1g}	T_1	$A_{2g} + E_g$
	T_{2g}	T_2	$B_{2g} + E_g$

ψ_i G	R_3	O_h	T_d	D_{4h}	C_{4v}	C_{2v}	D_{3v}
s	s_g	A_{1g}	A_1	A_{1g}	A_1	A_1	A_{1g}
p_x	p_u	T_{1u}	T_1	E_u	E	B_1	E_u
p_y						B_2	
p_z				A_{2u}	A_1	A_1	A_{2u}
d_{z2}	d_g	E_g	E	A_{1g}	A_1	A_1	E_g
d_{x2-y2}				B_{1g}	B_1	A_1	
d_{xy}		T_{2g}	T_2	B_{2g}	B_2	A_2	A_{1g}
d_{xz}				E_g	E	B_1	E_g
d_{yz}						B_2	

spherical octahedral tetrahedral square-pl. square-pyr.

- **Non-capital letters assign orbitals**
- **Capital letters assign terms**
- **Note: Symmetry of orbitals and terms is identical**
- **Assignment of CF terms by degeneracy, i.e. 1: A, B; 2: E; 3: T, and by symmetry**

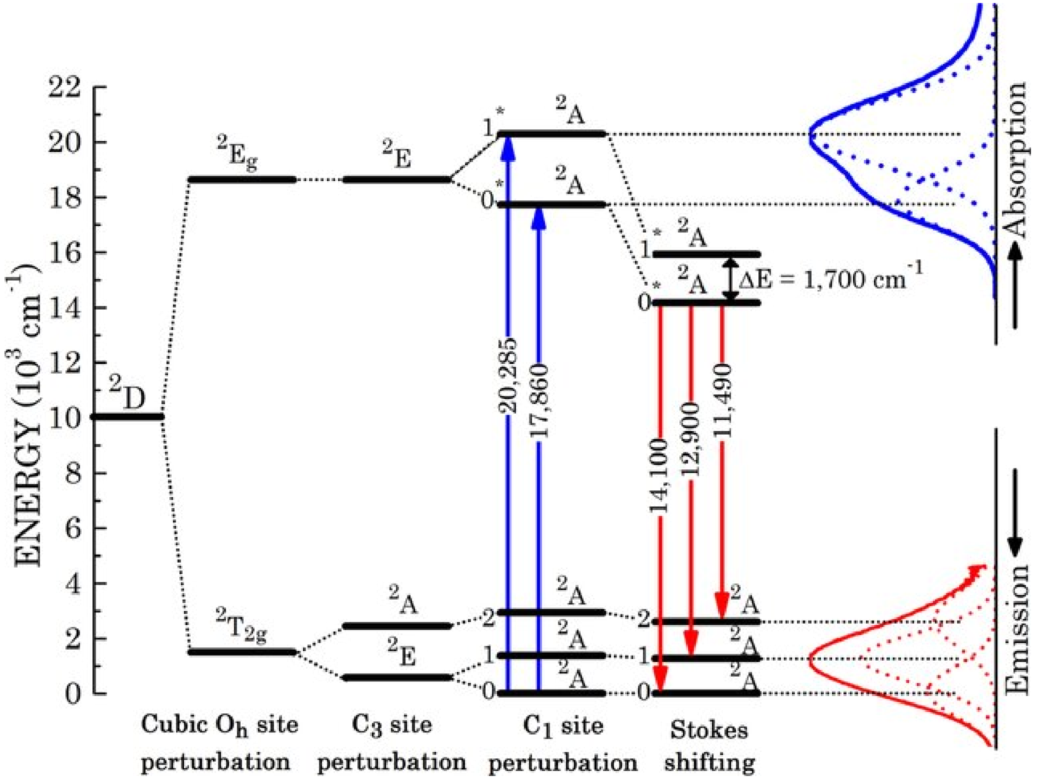
by symmetry:	Principal rotation axis (C_n)	Center of inversion (i)	plane || to princip. axis (σ_v)	plane ⊥ to princip. axis (σ_h)
symmetric	A	g	1	'
antisymmetric	B	u	2	''

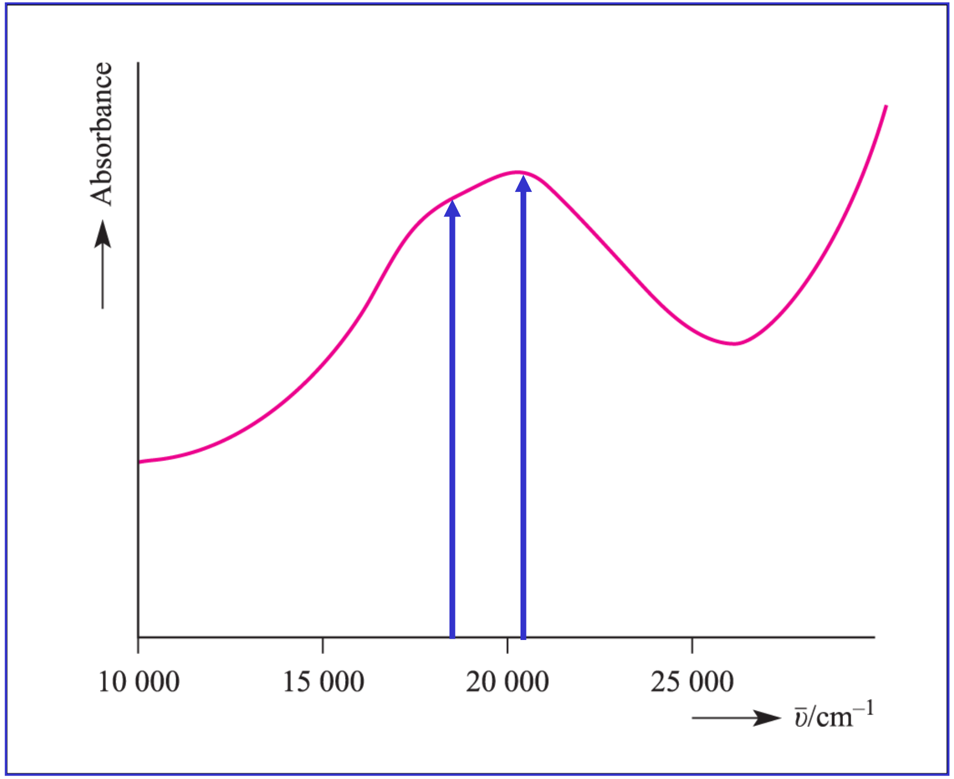
7. Spectroscopy of Inorganic Compounds

Ions with Separated Outer Electron/Hole: d^1/d^9 Configuration

Example: $[Ti(H_2O)_6]^{3+}$ Ti^{3+}: [Ar]$3d^1$ Jahn-Teller distorted (like V^{4+}, Cr^{5+}, Mn^{6+})

Russel-Saunders (RS) ground state term: S = ½, L = 2, J = 3/2 $\Rightarrow$ $^2D_{3/2}$
CF Split terms in octahedral fields: $^2T_{2g}$ and ^2E_g



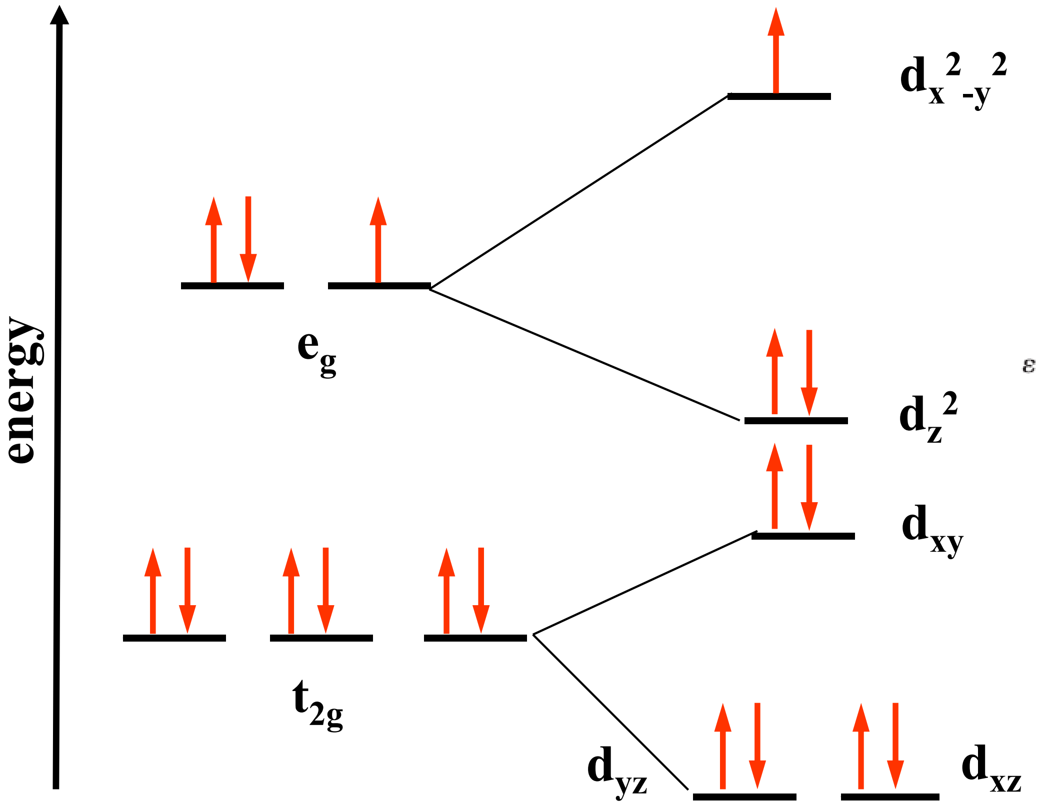


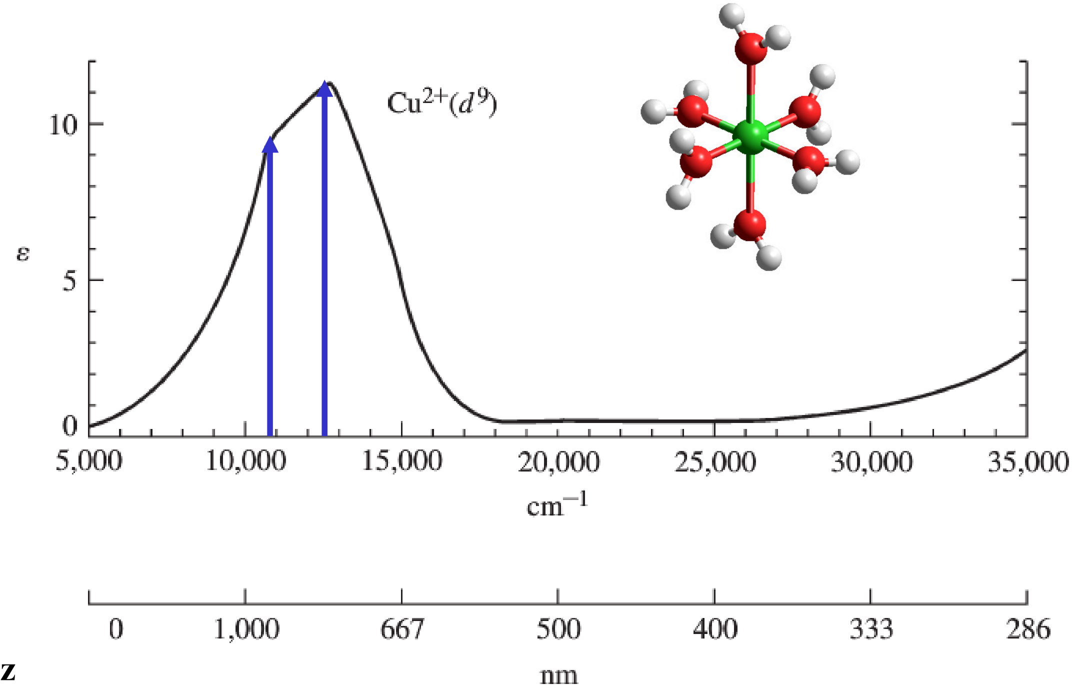
7. Spectroscopy of Inorganic Compounds

Ions with Separated Outer Electron/Hole: d^1/d^9 Configuration

Example: $[Cu(H_2O)_6]^{2+}$ Cu^{2+}: $[Ar]3d^9$ Jahn-Teller distorted (Cu-O: 200 vs. 245 pm)

Russel-Saunders (RS) ground state term: $S = ½, L = 2, J = 5/2 \Rightarrow {}^2D_{5/2}$
CF Split terms in octahedral fields: ${}^2T_{2g}$ and ${}^2E_g$



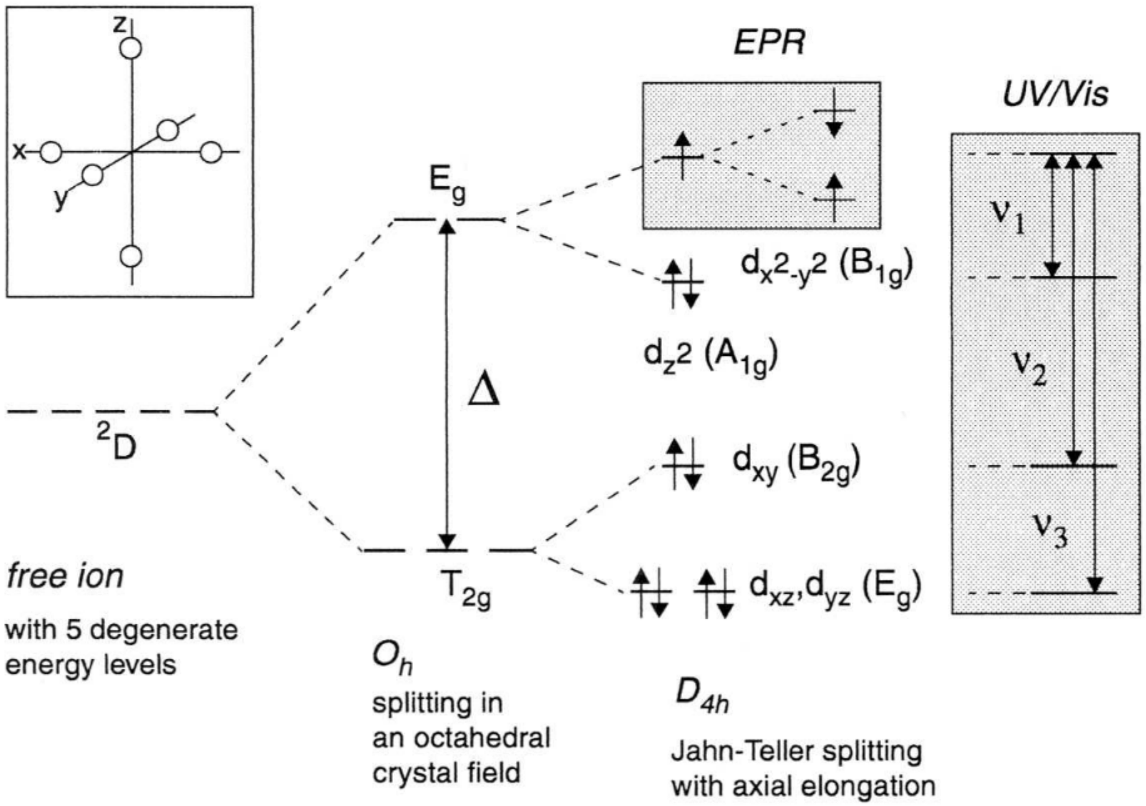


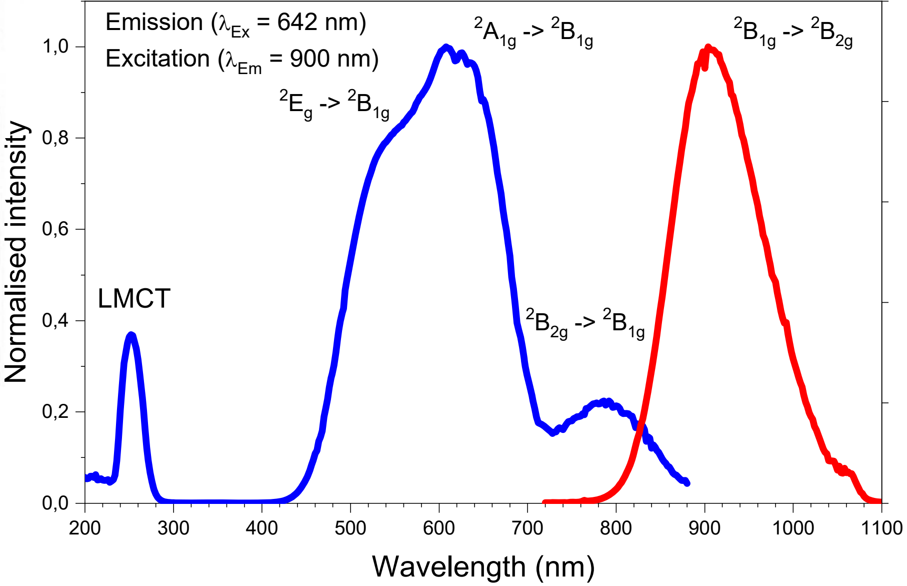
7. Spectroscopy of Inorganic Compounds

Ions with Separated Outer Electron/Hole: d^1/d^9 Configuration

Example: $CaCuSi_4O_{10}$ **Cu^{2+}: [Ar]$3d^9$ square-planar coordinated (D_{4h})**

$\rightarrow$ $^2B_{2g}$ moves up and $^2B_{1g}$ shifts down to change position

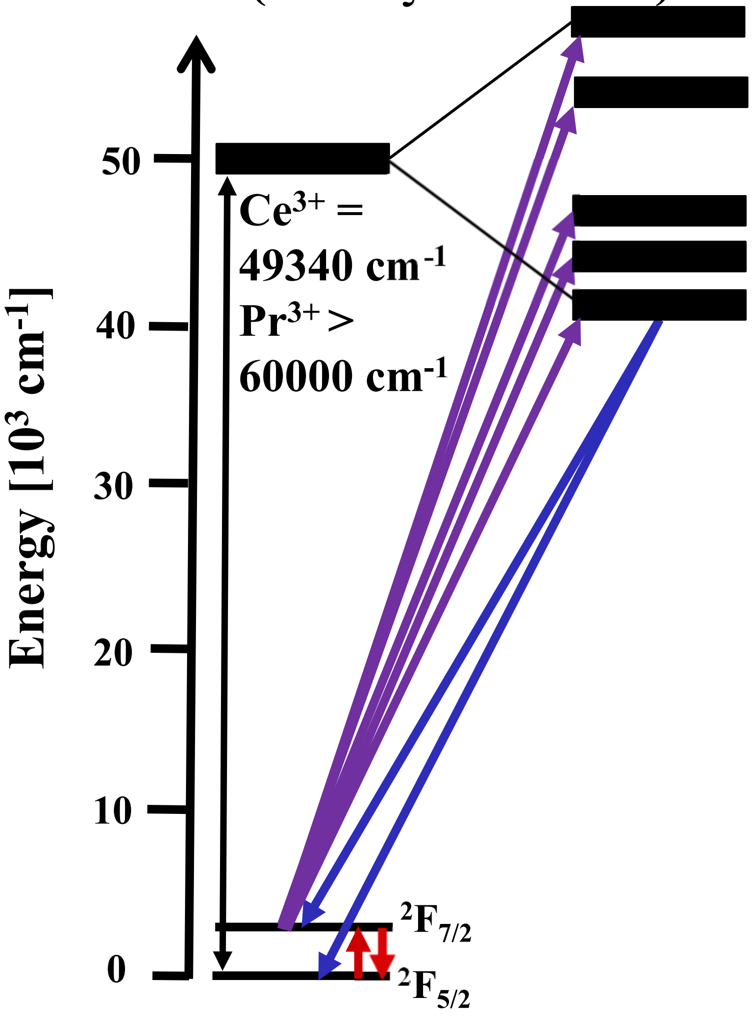


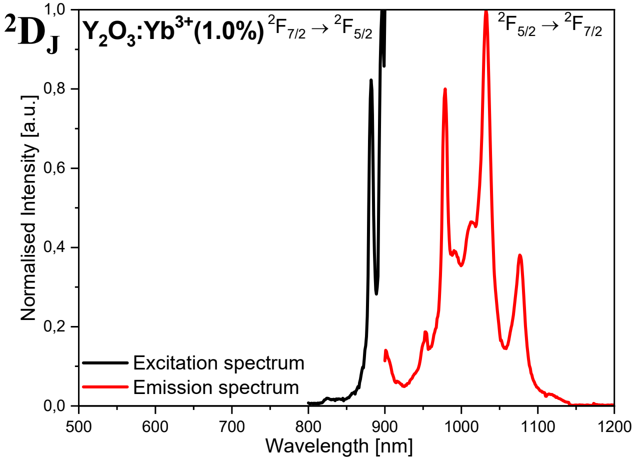


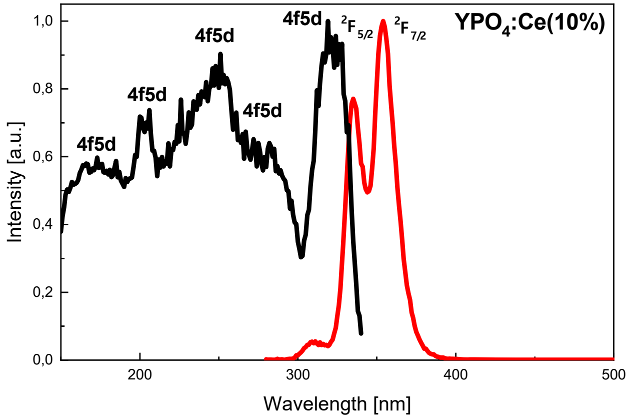
7. Spectroscopy of Inorganic Compounds

Ions with Separated Outer Electron/Hole: $4f^1$/$4f^{13}$ Config. → Ce^{3+}, Pr^{4+}, Tm^{2+}, Yb^{3+}

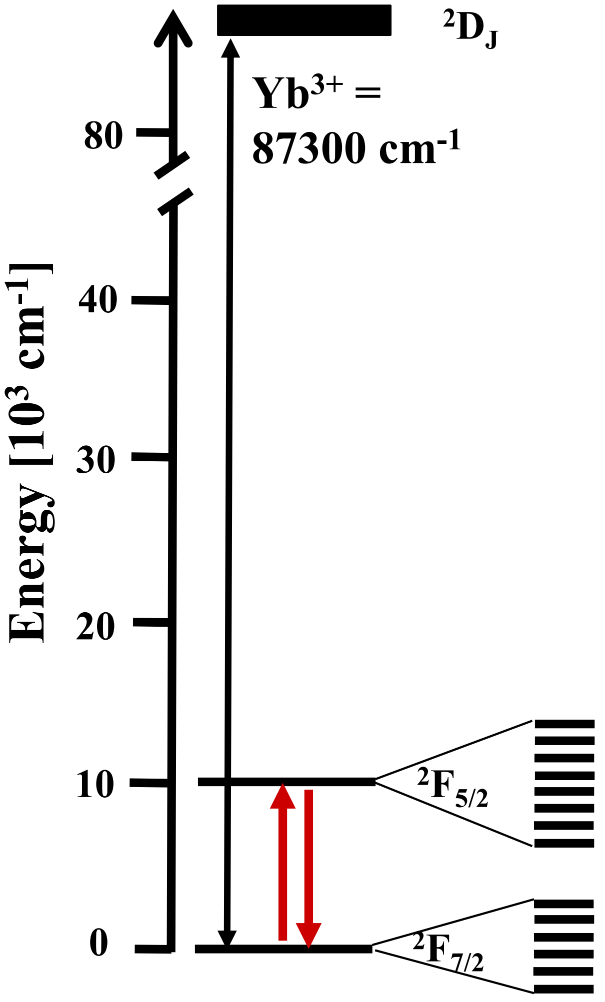
free ion (Ce^{3+}: $\zeta = 625\ cm^{-1}$)







free ion (Yb^{3+}: $\zeta = 2870\ cm^{-1}$)



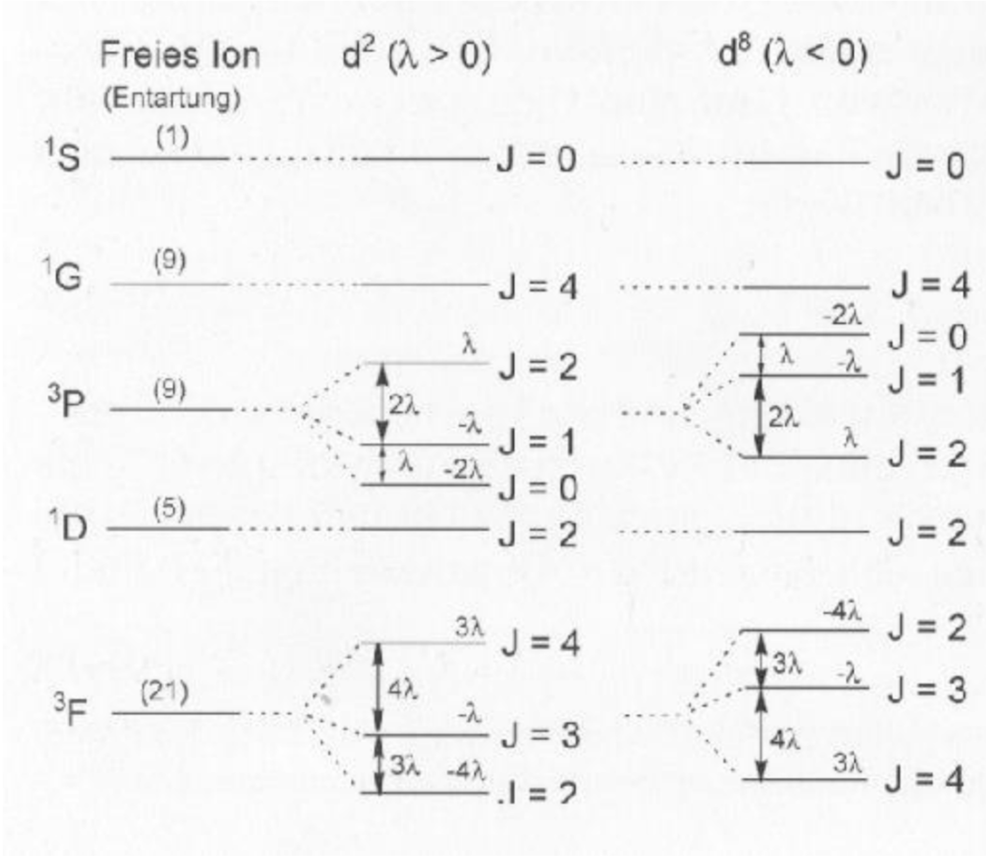
Ce^{3+}, Pr^{4+} [Xe]$4f^1$ **14 Microstates & 2 energy levels** Tm^{2+}, Yb^{3+} [Xe]$4f^{13}$

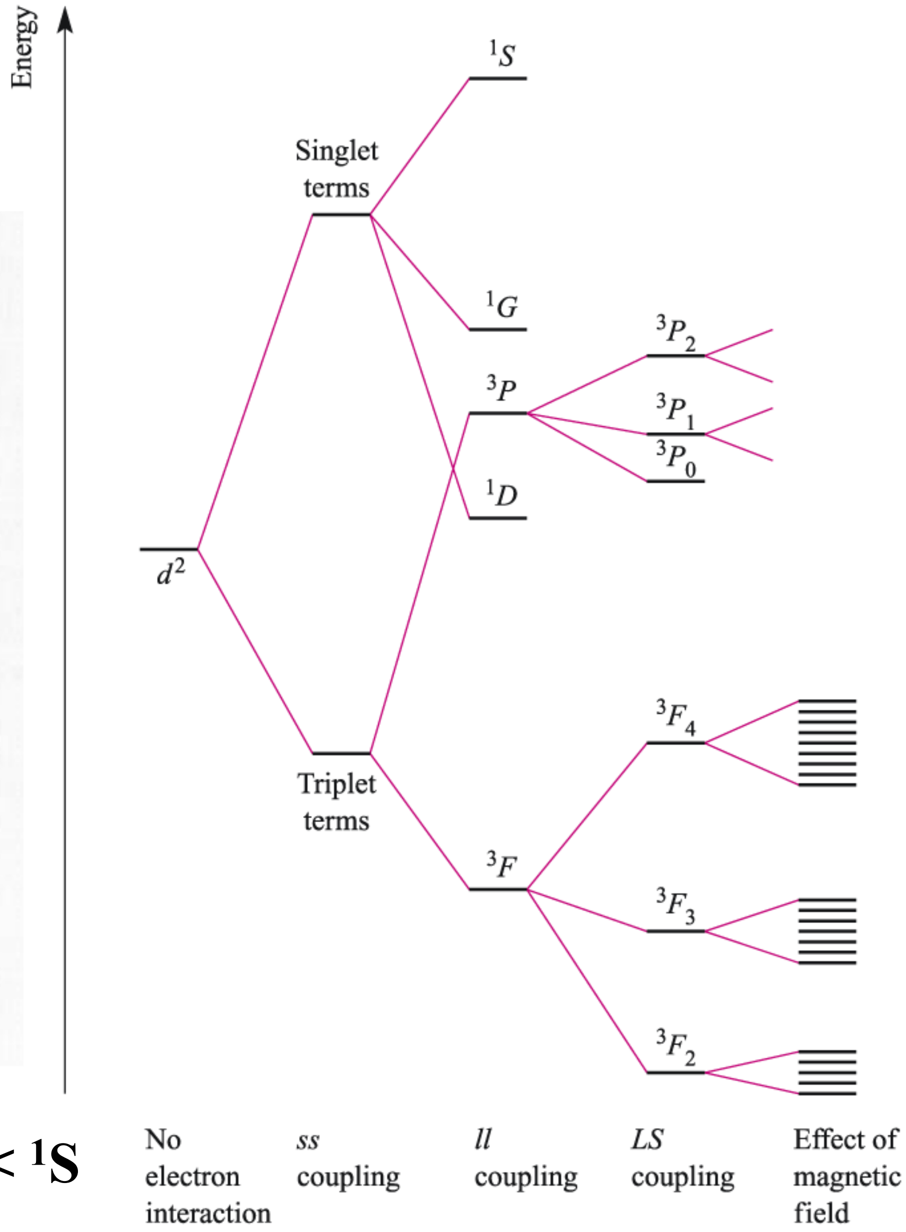
7. Spectroscopy of Inorganic Compounds

Ions with d^2 Configuration

Examples for ions with $[Ar]3d^2$ configuration

Ti^{2+}
V^{3+}
Cr^{4+}
Mn^{5+}
Fe^{6+}
Co^{7+}





RS terms: ^3F, ^3P, ^1G, ^1D, ^1S

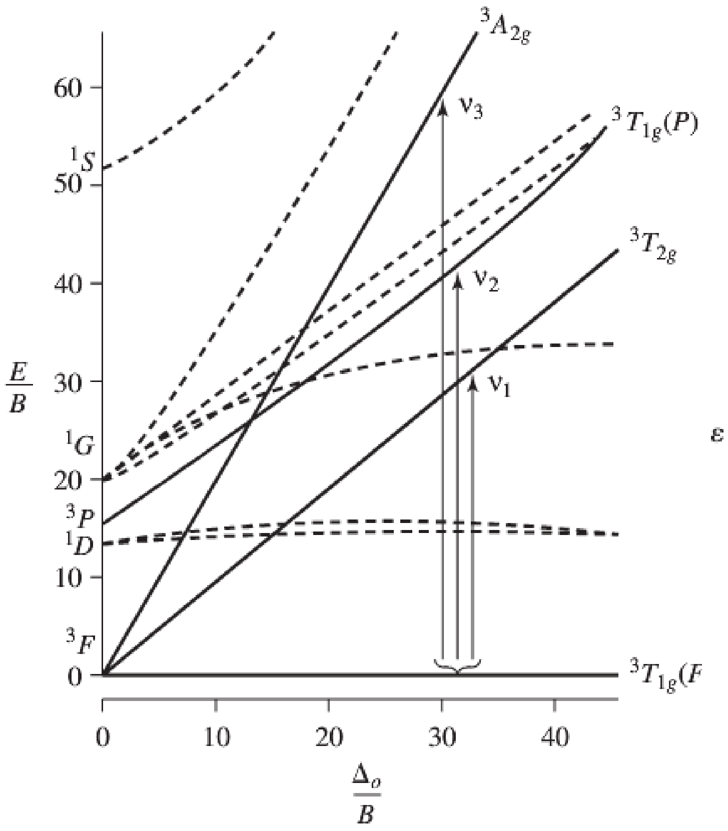
Energy series by Hund rules: $^3F < {}^1D < {}^3P < {}^1G < {}^1S$

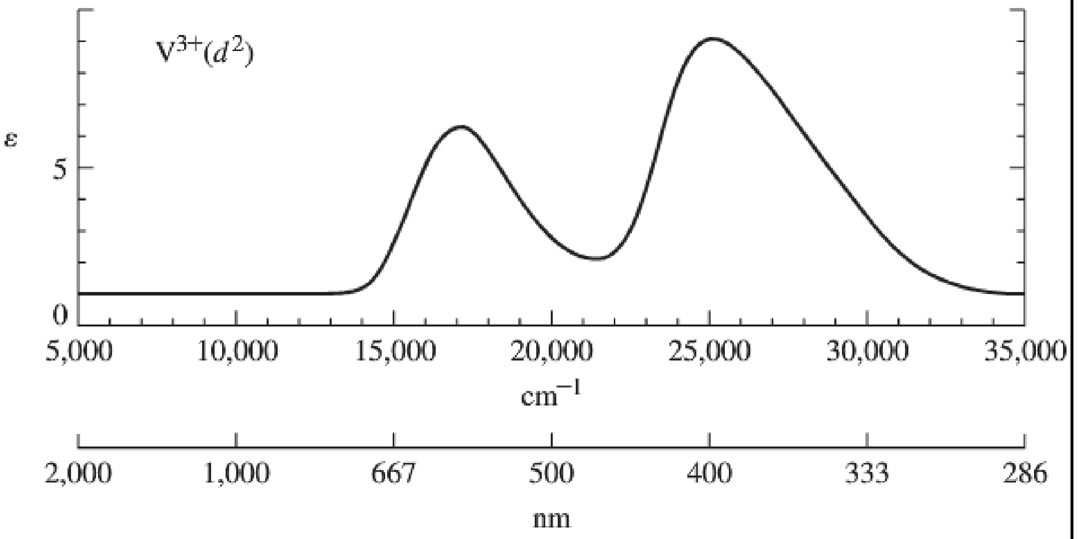
7. Spectroscopy of Inorganic Compounds

Ions with d^2 Configuration

Example: 0.0472 M $V(ClO_4)_3$ in $HClO_4$ ⇒ [$V(H_2O)_6]^{3+}$ V^{3+}: [Ar]$3d^2$ J.T. distorted
Russel-Saunders (RS) ground state term: S = 1, L = 3, J = 2 ⇒ $^3F_2$
Related crystal field terms (see above): $^3T_{1g}$, $^3T_{2g}$, $^3A_{2g}$

ν_1: $^3T_{1g}(F) \rightarrow {}^3T_{2g}$
ν_2: $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$
ν_3: $^3T_{1g}(F) \rightarrow {}^3A_{2g}$





7. Spectroscopy of Inorganic Compounds

Ions with d^2 Configuration

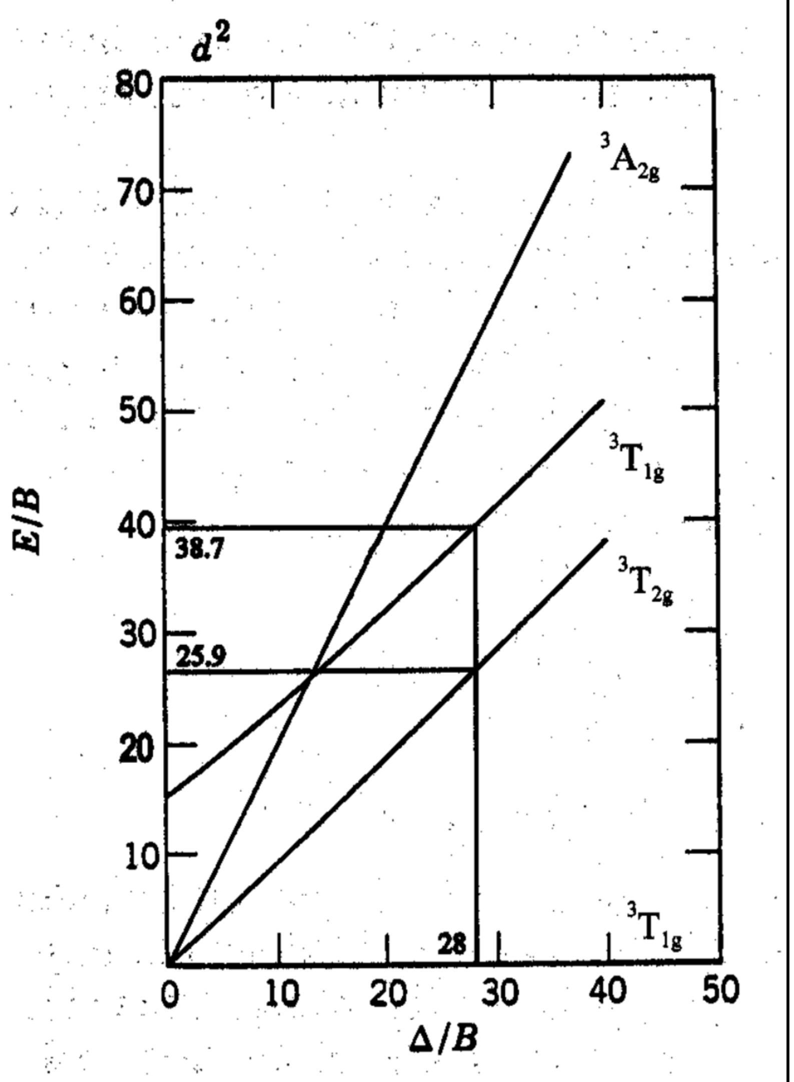
Example: $[V(H_2O)_6]^{3+}$ V^{3+}: $[Ar]3d^2$ J.T. distorted

E_1	17,200 cm^{-1}	${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$
E_2	25,600 cm^{-1}	${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$

$(E_2/B)/(E_1B) = E_2/E_1 = 1.49$

$\Delta_o/B = 28$ $\Delta_o = 28B = 10$ Dq for $E_2/E_1 = 1.49$

Find this ratio in the Tanabe-Sugano diagram



$E_2/B = 38.7$ $\Rightarrow B = 662\ cm^{-1}$

$E_1/B = 25.9$ $\Rightarrow B = 664\ cm^{-1}$

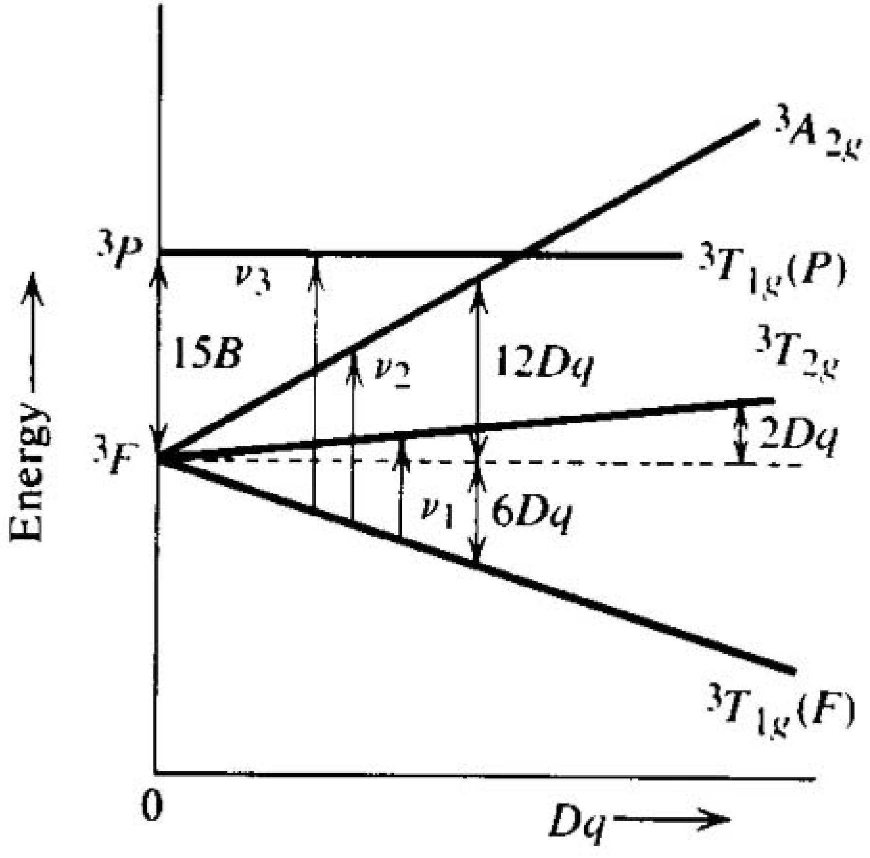
(free ion $B_0 = 860\ cm^{-1}$)

$\Delta_o = 18,600\ cm^{-1}$

7. Spectroscopy of Inorganic Compounds

Ions with d^2 Configuration

- To determine Δ_o one need to approximate the value of the Racah parameter B
- B accounts for electron-electron repulsions
- It is a measure of the energy splitting of the initial atomic RS states



d^2 octahedral
without bending

Observed bands

- $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $\nu_1 = 8\ Dq$
- $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ $\nu_2 = 18\ Dq$
- $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $\nu_3 = 15B + 6\ Dq$

$10\ Dq = \nu_2 - \nu_1$

B can be derived from optical spectra or can be calculated from Slater-Condon parameter

7. Spectroscopy of Inorganic Compounds

Interelectronic Repulsion: Racah-Parameter A, B, and C (Giulio Racah 1909-1965)

Means to describe the interelectronic repulsion or Coulomb-repulsion between the terms, with B being the most important Racah-parameter, because it directly describes the energetic splitting between the RS-terms!

Free M^{n+}-ion $B_0 \sim$ 500 - 1100 cm^{-1}

$C_0 \sim 4 B_0$ (approximation)

Coordinated M^{n+}-ion B is about 30% smaller due to the nephelauxetic effect, i.e. the delocalisation of metal-centred electrons to the ligands

Nephelauxetic ratio $ß = B/B_0$

with B_0: free ion

B: coordinated ion

⇒ B is a measure for the covalent interaction around the metal ion

Configuration	Ion	B_0 [cm^{-1}]	C_0 [cm^{-1}]
$3d^2$	V^{3+}	860	
$3d^3$	Cr^{3+}	918	3850
	Mn^{4+}	1064	
$3d^4$	Cr^{2+}	830	3430
	Mn^{3+}	1140	3675
$3d^5$	Mn^{2+}	960	3325
$3d^6$	Fe^{2+}	1058	3901
	Co^{3+}	1100	

7. Spectroscopy of Inorganic Compounds

Interelectronic Repulsion: Racah-Parameter A, B, and C (Giulio Racah 1909 - 1965)

The Racah Parameter A, B, and C can be traced back to the Slater-Condon parameters:

$A = F_0 - 49\ F_4$
$B = F_2 - 5\ F_4$
$C = 35\ F_4$

F_0	monopole like integral = Coulomb integral determine the average Coulomb interaction between d electrons. It is basically described by the Hubbard model, i.e. the related Hamiltonian (energy operator) and strongly reduced in polarizing environments: Reduction of interaction of 2 charges in matter
F_2	dipole like integral
F_4	quadropole like integral

The latter two parameters contribute to the multiplet energy structure, which is dependent on exactly which orbitals and spin states are occupied, thus complicated

The B and C Racah parameters are rather close to the free ion values and can be carried over from tabulated gas phase spectroscopy data B_0 and C_0 of “free ions”

7. Spectroscopy of Inorganic Compounds

Interelectronic Repulsion: Racah-Parameter A, B, and C (Giulio Racah 1909 - 1965)

The energy of the RS states E(L,S) is generally expressed by

$E(L,S) = aA + bB + cC$ with $a + b + c = 1$

e.g. d^2 (or d^8) with five RS terms:

$E(^3F) = 2\,I_{dd} + F_0 - 8F_2 + 9F_4 = A - 8B$

$E(^3P) = 2\,I_{dd} + F_0 + 7F_2 + 84F_4 = A + 7B$ $\rightarrow \Delta E(^3P\text{-}^3F) = 15B$

$E(^1G) = 2\,I_{dd} + F_0 + 4F_2 + F_4 = A + 4B + 2C$ $\rightarrow \Delta E(^1G\text{-}^3F) = 12B + 2C$

$E(^1D) = 2\,I_{dd} + F_0 - 3F_2 + 36F_4 = A - 3B + 2C$ $\rightarrow \Delta E(^1D\text{-}^3F) = 5B + 2C$

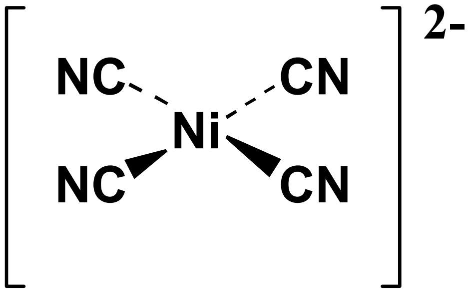
$E(^1S) = 2\,I_{dd} + F_0 + 14F_2 + 126F_4 = A + 14B + 7C$ $\rightarrow \Delta E(^1S\text{-}^3F) = 22B + 7C$

- with I_{dd} = Integral of single electron operator (for H-type atoms)
- Racah-Parameter B and C are adapted to fit observed absorption spectra
- Racah-Param. A is removed by calculating energy differences between RS states

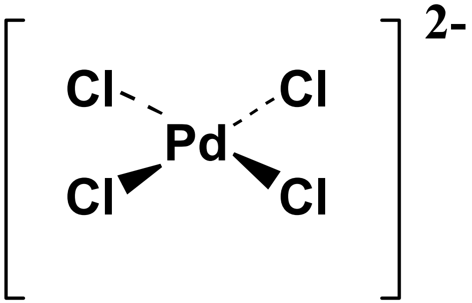
7. Spectroscopy of Inorganic Compounds

Ions with d^8 Configuration

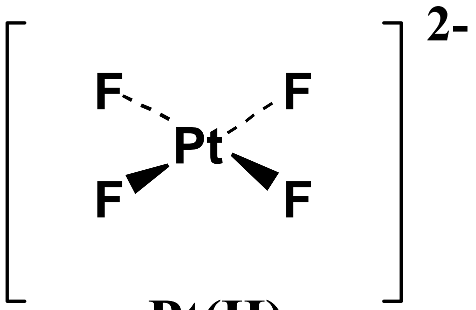
Metal ions with d^8 configuration: Co^+, Rh^+, Ir^+, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{3+}, Ag^{3+}, Au^{3+}
Russel-Saunders (RS) ground state term: $S = 1, L = 3, J = 2 \Rightarrow {}^3F_4$



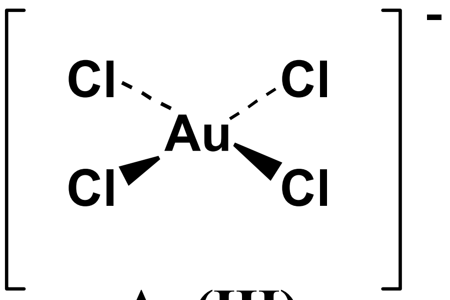
Ni(II)



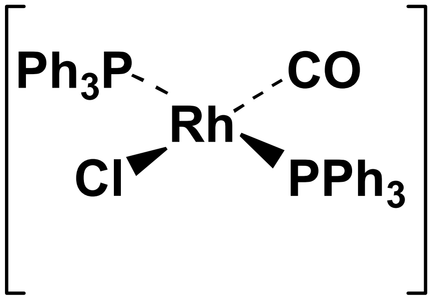
Pd(II)



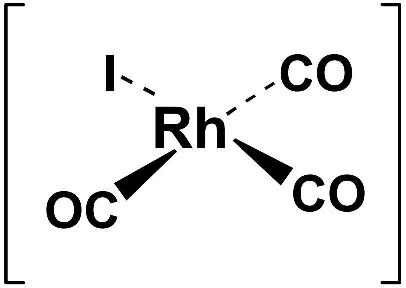
Pt(II)



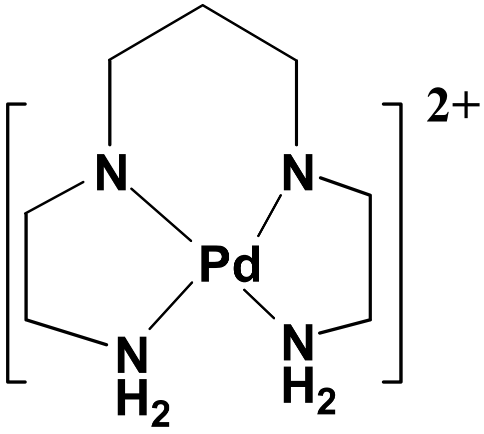
Au(III)



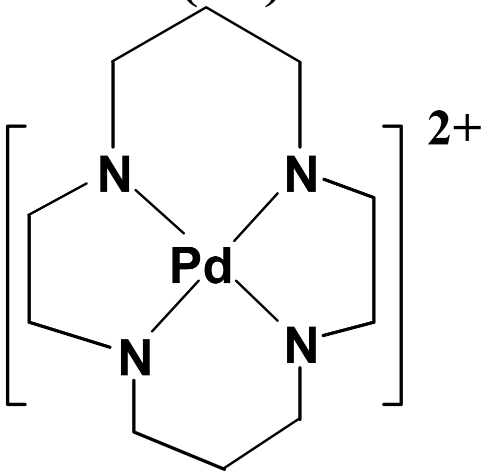
Rh(I)



Rh(I)



Pd(II)



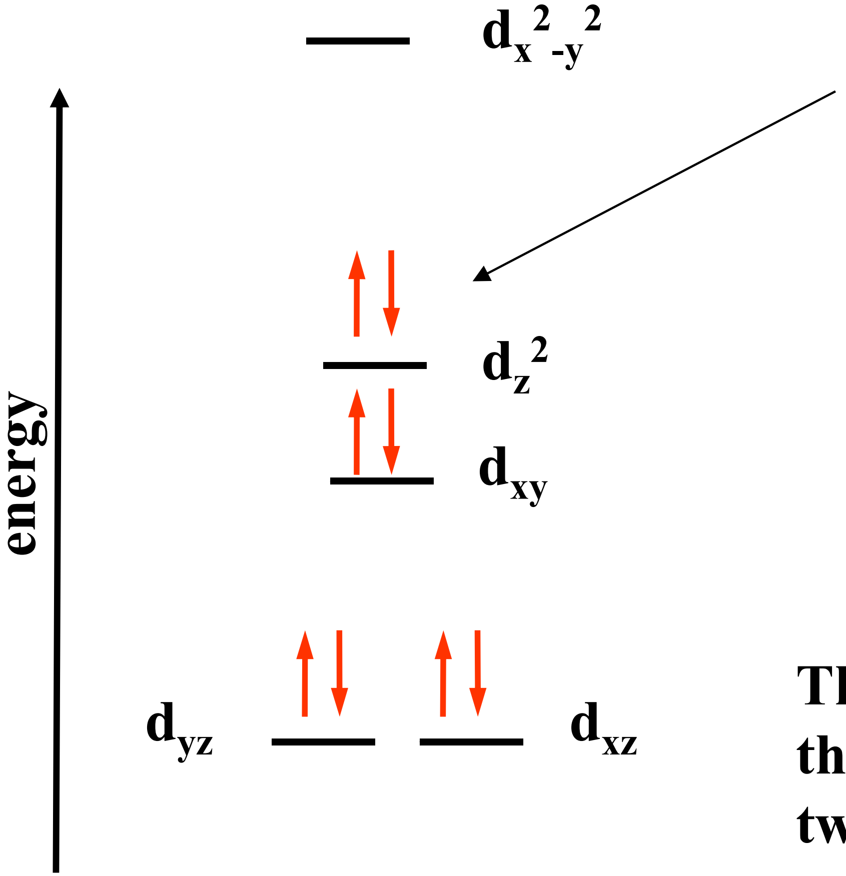
Pd(II)

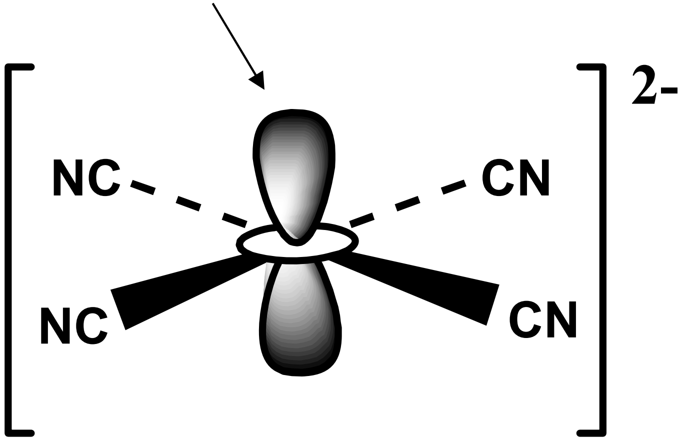
7. Spectroscopy of Inorganic Compounds

Ions with d^8 Configuration

Example: $[Ni(CN)_4]^{2-}$

The filled d_{z^2} orbital occupies two coordination sites in the VSEPR view, and so the four donor atoms occupy the plane:



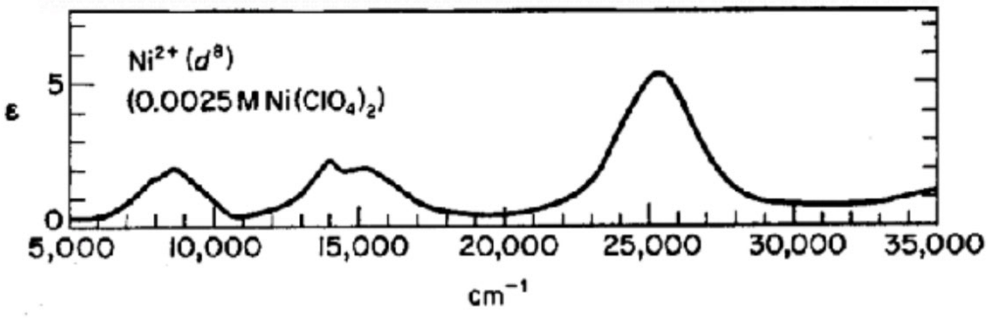


The structure of $[Ni(CN)_4]^{2-}$ can be compared to that of square planar $[IF_4]^-$, where from VSEPR two lone pairs occupy the axial sites.

7. Spectroscopy of Inorganic Compounds

Ions with d^8 Configuration

Example: $[Ni(H_2O)_6]^{2+}$



Band	E [cm^{-1}]	Ext. ε [$M^{-1}cm^{-1}$]	opt. transition
E_1	8700	1.6	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$
E_2	14500	2.0	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
E_3	25300	4.6	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$

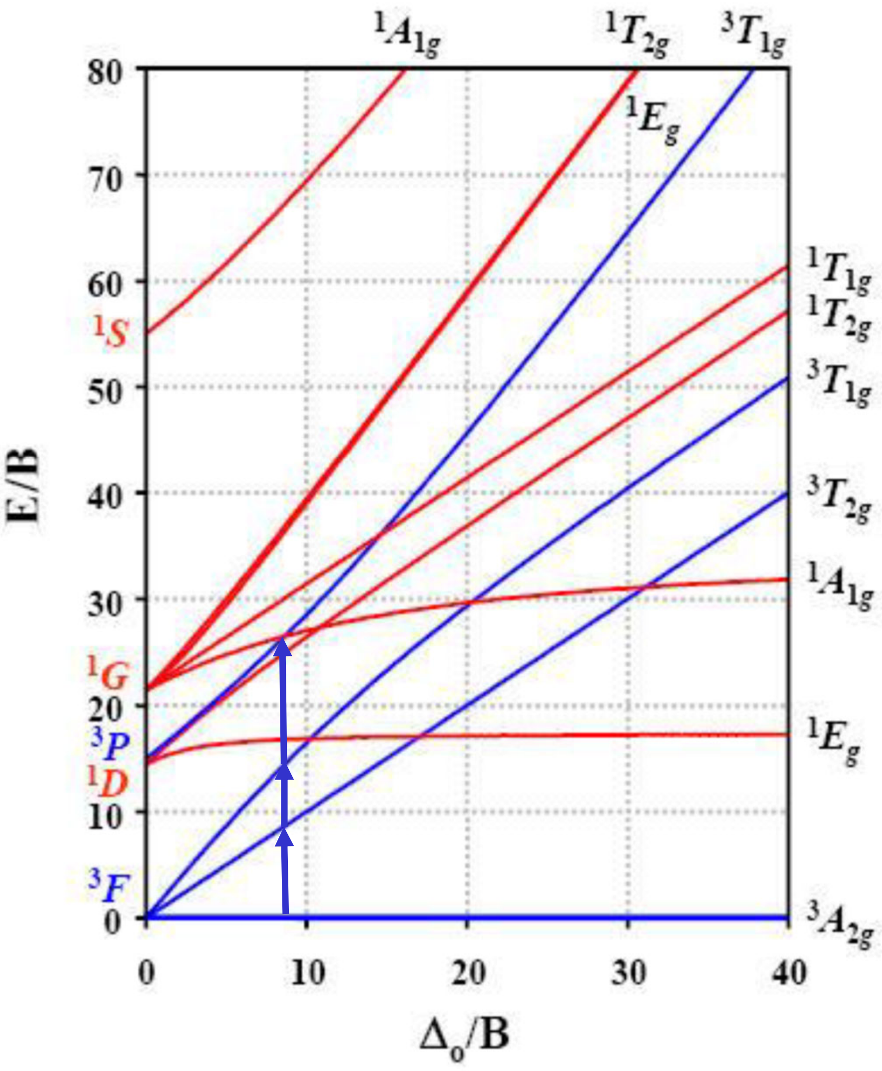
$(E_3/B)/(E_2B) = E_3/E_2 = 1.74$

→ Find this ratio in the Tanabe-Sugano diagram

$E_2/B = 16 \Rightarrow B = E_2/16 = 905\ cm^{-1}$

$\Delta_o/B = 9.8$ $\quad\quad$ $\Delta_o = 9.8B = 8900\ cm^{-1} = 10Dq$

d^8 Tanabe-Sugano Diagram



7. Spectroscopy of Inorganic Compounds

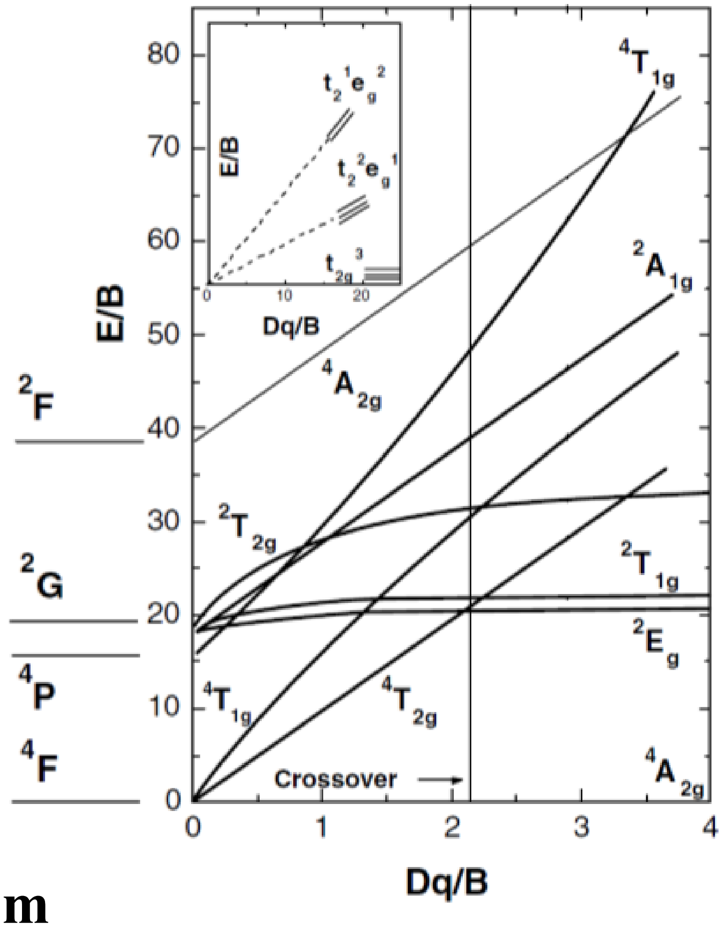
Ions with d^3 Configuration

Example: V^{2+}, Cr^{3+}, Mn^{4+}, Fe^{5+} in α-Al_2O_3

Crystal field splitting Δ_o in sapphire

V^{2+}	15240 cm^{-1}
Cr^{3+}	18145 cm^{-1}
Mn^{4+}	21290 cm^{-1}
Fe^{5+}	(> 22000 cm^{-1})

Lit.: J. Phys. Soc. Jpn. 81 (2012) 104709



→ Mn^{4+} show solely line emission (^2E-$^4A_2$): 620 – 750 nm

→ Band emission ($^4T_2$-$^4A_2$) only expected for Cr^{3+} and V^{2+}

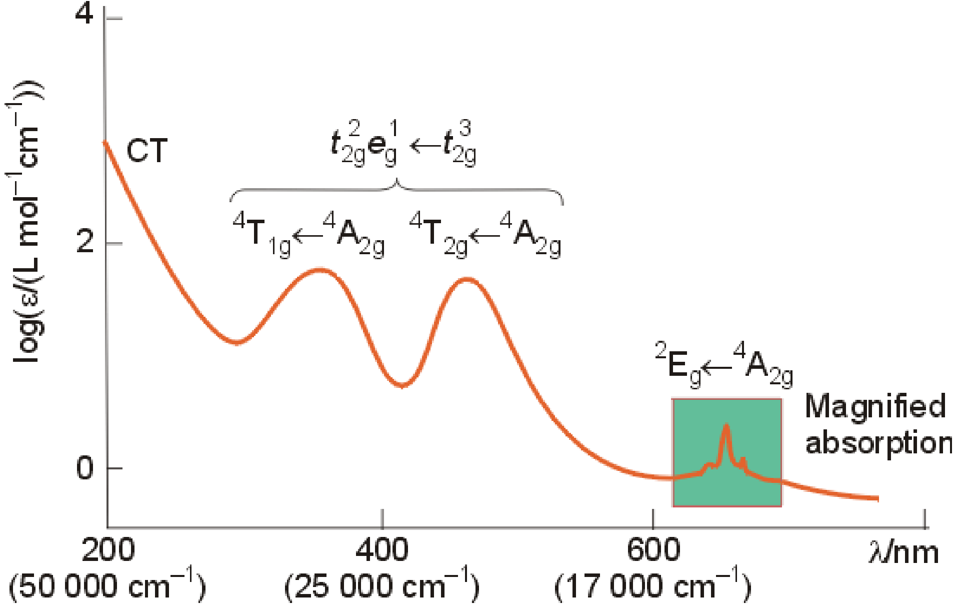
Tanabe-Sugano diagram for d^3-ions

→ V^{2+} and Fe^{5+} stabilization in solids is difficult

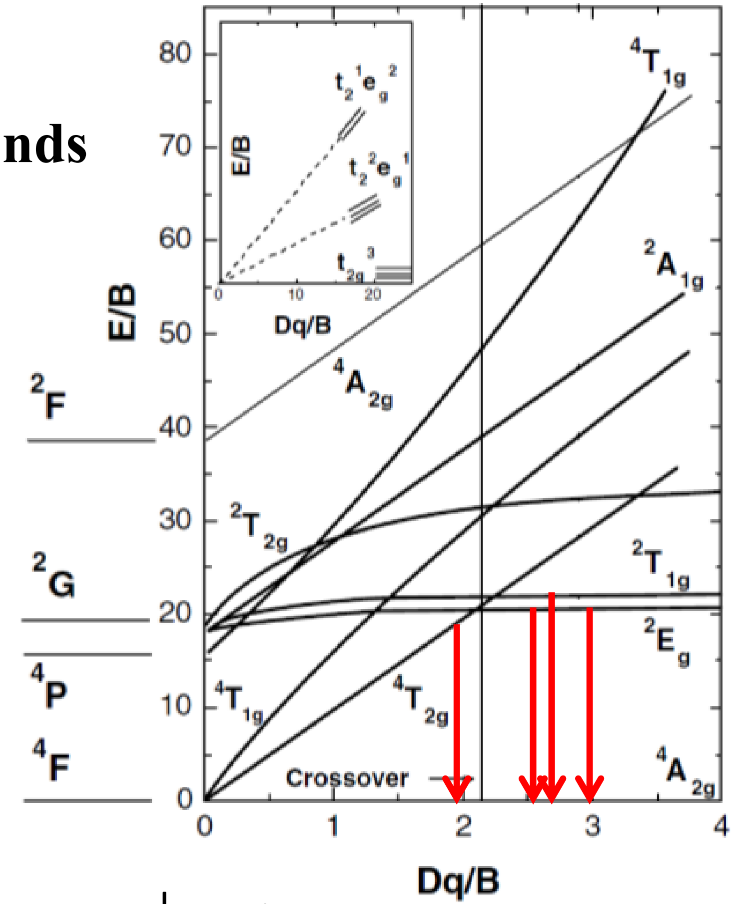
7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Cr^{3+}

Example: Cr^{3+} in $[Cr^{III}(NH_3)_6]^{3+}$ or solid-state compounds



Host	Dq/cm^{-1}	B/cm^{-1}	$E(^2E)/cm^{-1}$	Dq/B
α-Al_2O_3	1795	630	14399	2,85
$SrAl_{12}O_{19}$	1707	636	14575	2,68
$GdAl_3(BO_3)_4$	1672	677	14633	2,47
$Sr_8MgLa(PO_4)_7$	1421	686	-	2,07



B ↓ increased covalency of Cr-O bonds

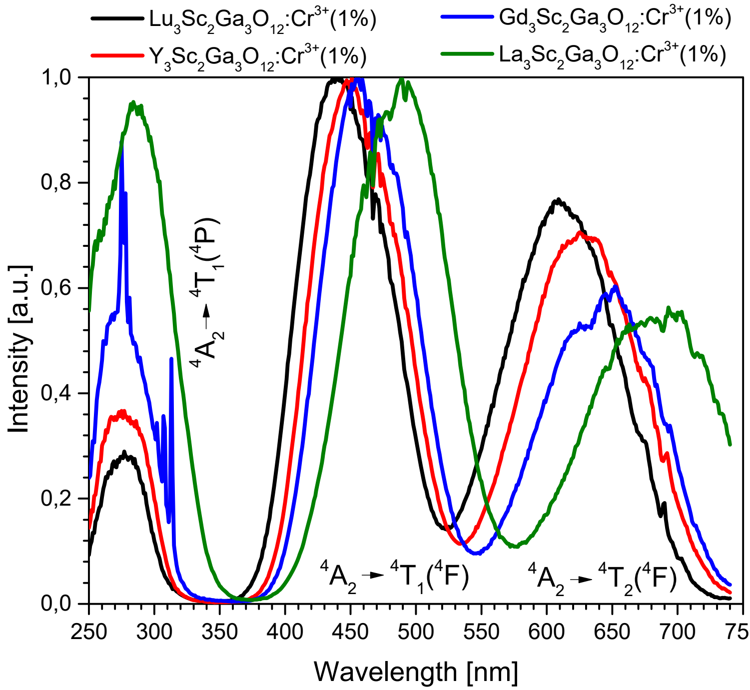
B ↑ decreased covalency of Cr-O bonds

7. Spectroscopy of Inorganic Compounds

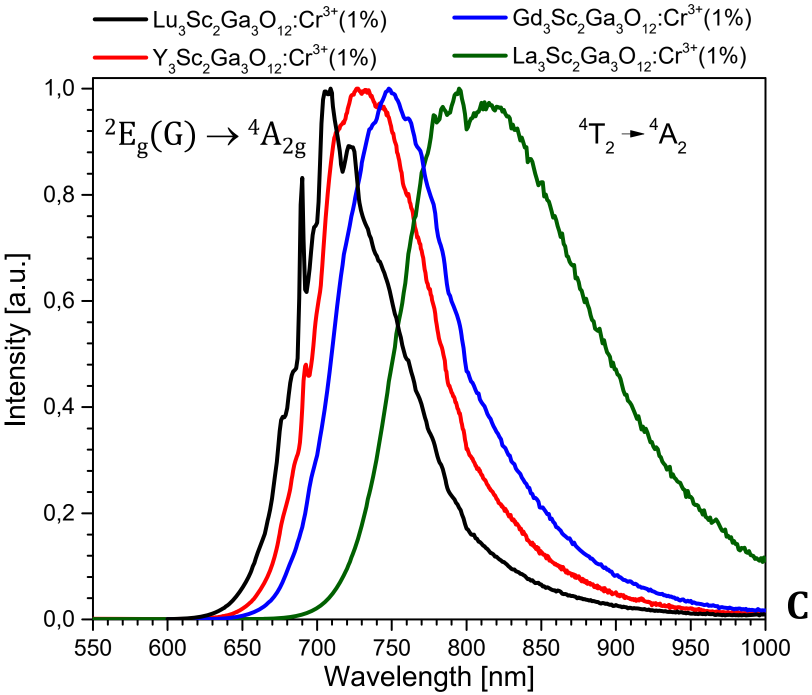
Ions with d^3 Configuration: Cr^{3+}

Example: Cr^{3+} in garnets $X_3Sc_2Ga_3O_{12}:Cr^{3+}$ (X = Lu, Y, Gd, La)

Excitation spectra



Emission spectra



$$\mathbf{Dq} = \frac{\mathbf{E}(\,^4\mathbf{A}_{2g} \rightarrow \,^4\mathbf{T}_{2g})}{\mathbf{10}}$$

$$\mathbf{\Delta E} = \mathbf{E}(\,^4\mathbf{A}_{2g} \rightarrow \,^4\mathbf{T}_{1g}) - \mathbf{E}(\,^4\mathbf{A}_{2g} \rightarrow \,^4\mathbf{T}_{2g})$$

$$\mathbf{B} = \frac{\frac{(\mathbf{\Delta E})^2}{\mathbf{Dq}} - \mathbf{10} \cdot \mathbf{\Delta E}}{\mathbf{15} \cdot \left(\frac{\mathbf{\Delta E}}{\mathbf{Dq}} - \mathbf{8}\right)}$$

$$\mathbf{C} = \frac{\mathbf{E}(^2\mathbf{E}) - \mathbf{7.90B} - \mathbf{1.80}\,\frac{\mathbf{B}^2}{\mathbf{Dq}}}{\mathbf{3.05}}$$

Host	Ionic radius X^{3+} /Å	Sc-O distance /Å	X-O distance /Å
LuSGG	1.12	1.993	2.490
YSGG	1.16	2.018	2.522
GSGG	1.19	2.041	2.550
LaSGG	1.30	2.086	2.607

Host	Dq [cm^{-1}]	Em. max	FWHM	Stokes Shift
LuSGG	1626	722 nm	73 nm	2585 cm^{-1}
YSGG	1587	740 nm	90 nm	2445 cm^{-1}
GSGG	1563	754 nm	90 nm	2354 cm^{-1}
LaSGG	1458	818 nm	145 nm	2392 cm^{-1}

7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Cr^{3+}

Example: Cr^{3+} in garnets $X_3Sc_2Ga_3O_{12}:Cr^{3+}$ (X = Lu, Y, Gd, La)

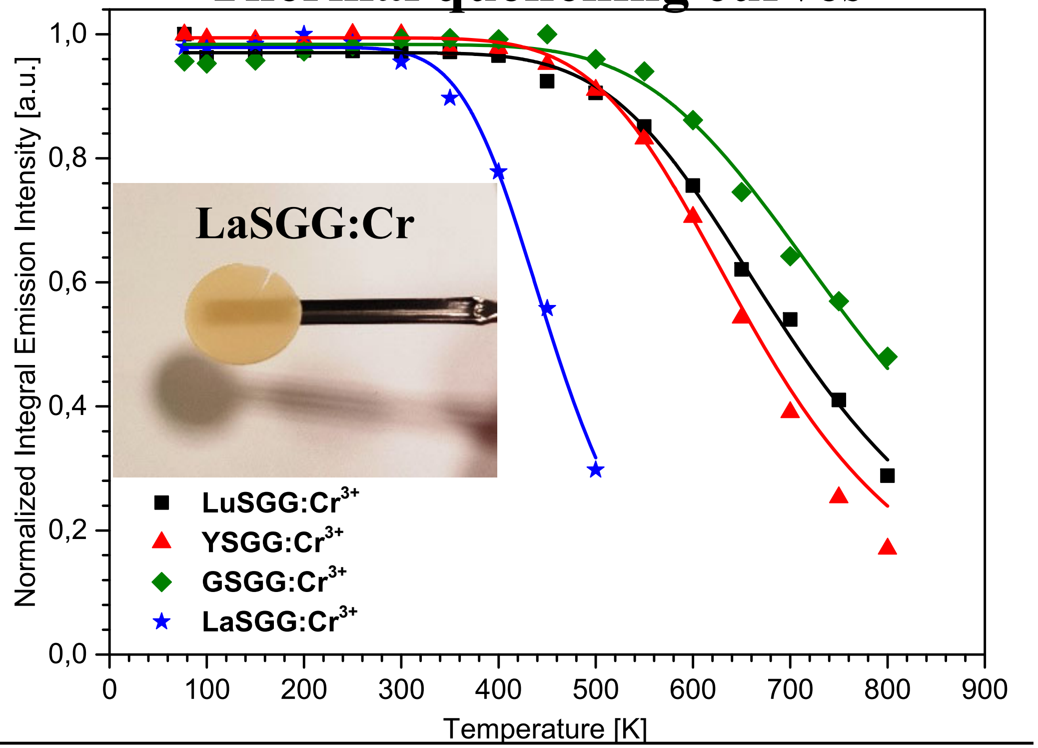
X = Y, Gd, and Lu

- **$T_{1/2}$ > 600 K**

X = La

- **$T_{1/2}$ ~ 450 K**
- **Rather strong thermal quenching**
- **Small Dq, i.e. low energy position of $^4T_2$ level**
- **Large Stoke'sche Shift**
- **Large FWHM of $^4T_2$ band**

Thermal quenching curves

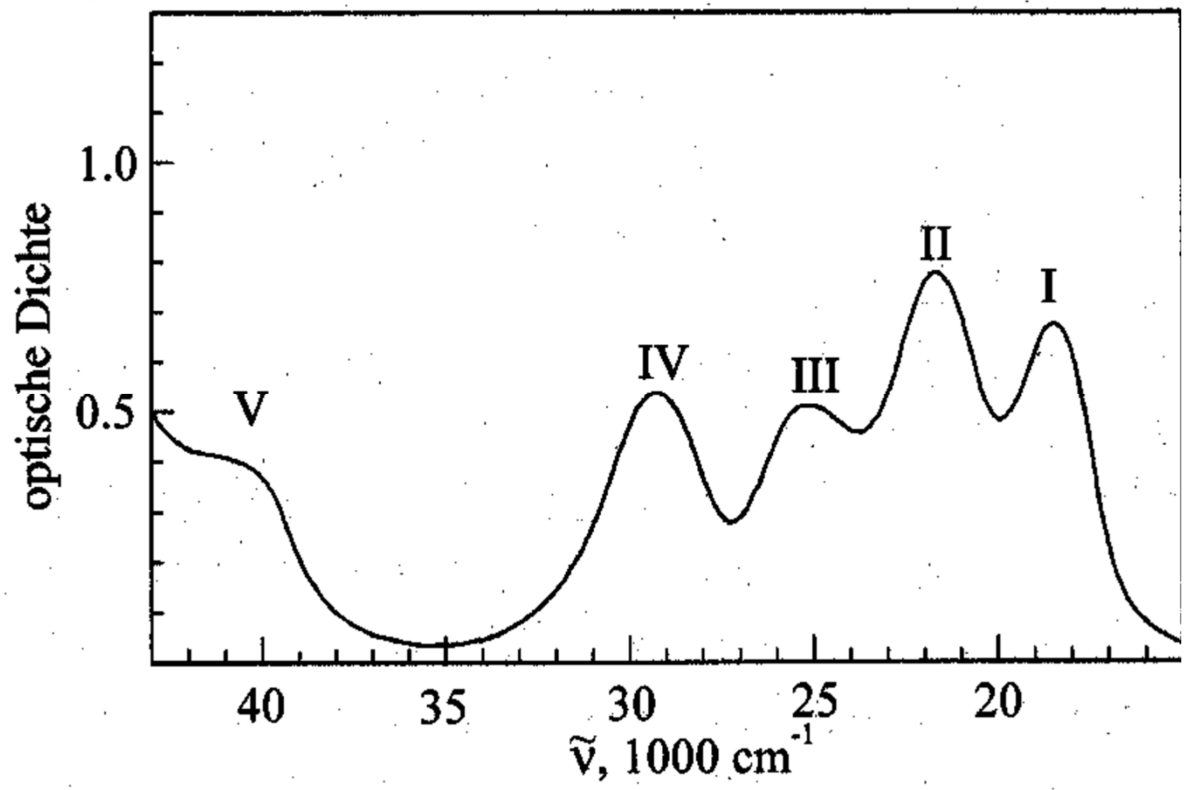


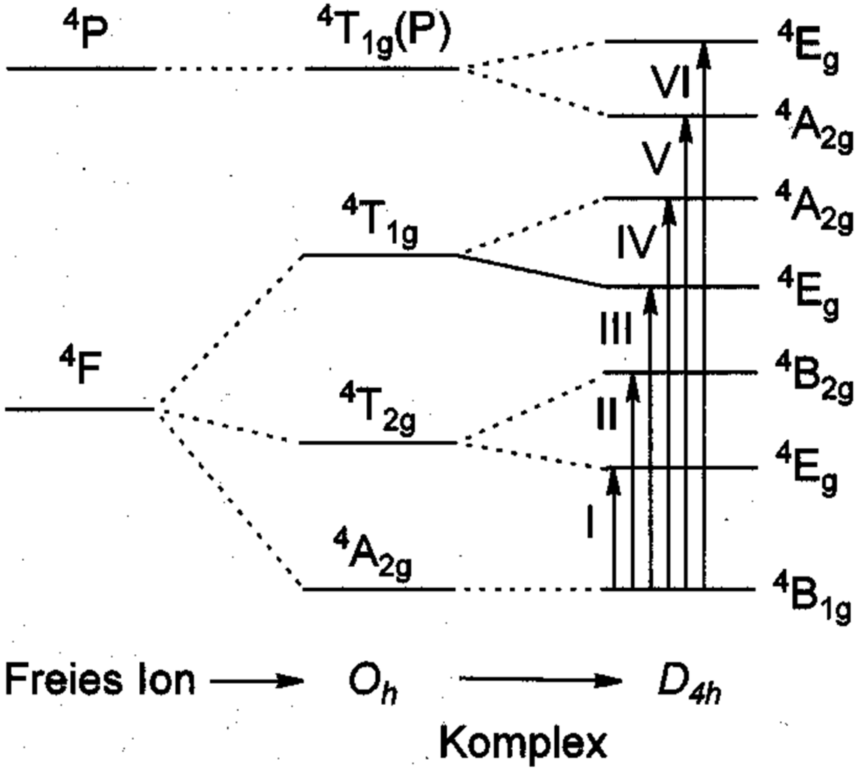
Host	Dq [cm^{-1}]	Em. max	FWHM	Stokes Shift	$T_{1/2}$
LuSGG	1626	722 nm	73 nm	2585 cm^{-1}	714 K
YSGG	1587	740 nm	90 nm	2445 cm^{-1}	660 K
GSGG	1563	754 nm	90 nm	2354 cm^{-1}	780 K
LaSGG	1458	818 nm	145 nm	2392 cm^{-1}	450 K

7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Cr^{3+}

Example: Cr^{3+} in the low symmetric complex trans-$[Cr^{III}F_2(en)_2]^+$





ν(I) = 18500 cm^{-1} **ν(II) = 21700 cm^{-1}**

ν(III) = 25300 cm^{-1} **ν(IV) = 29300 cm^{-1}**

ν(V) = 41000 cm^{-1} (shoulder) **ν(VI) = 43650 cm^{-1} (calculated)**

7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+}

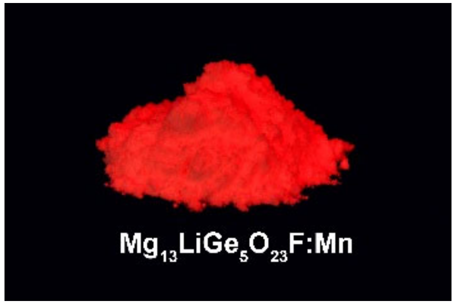
Example: $[MnF_6]^{2-}$

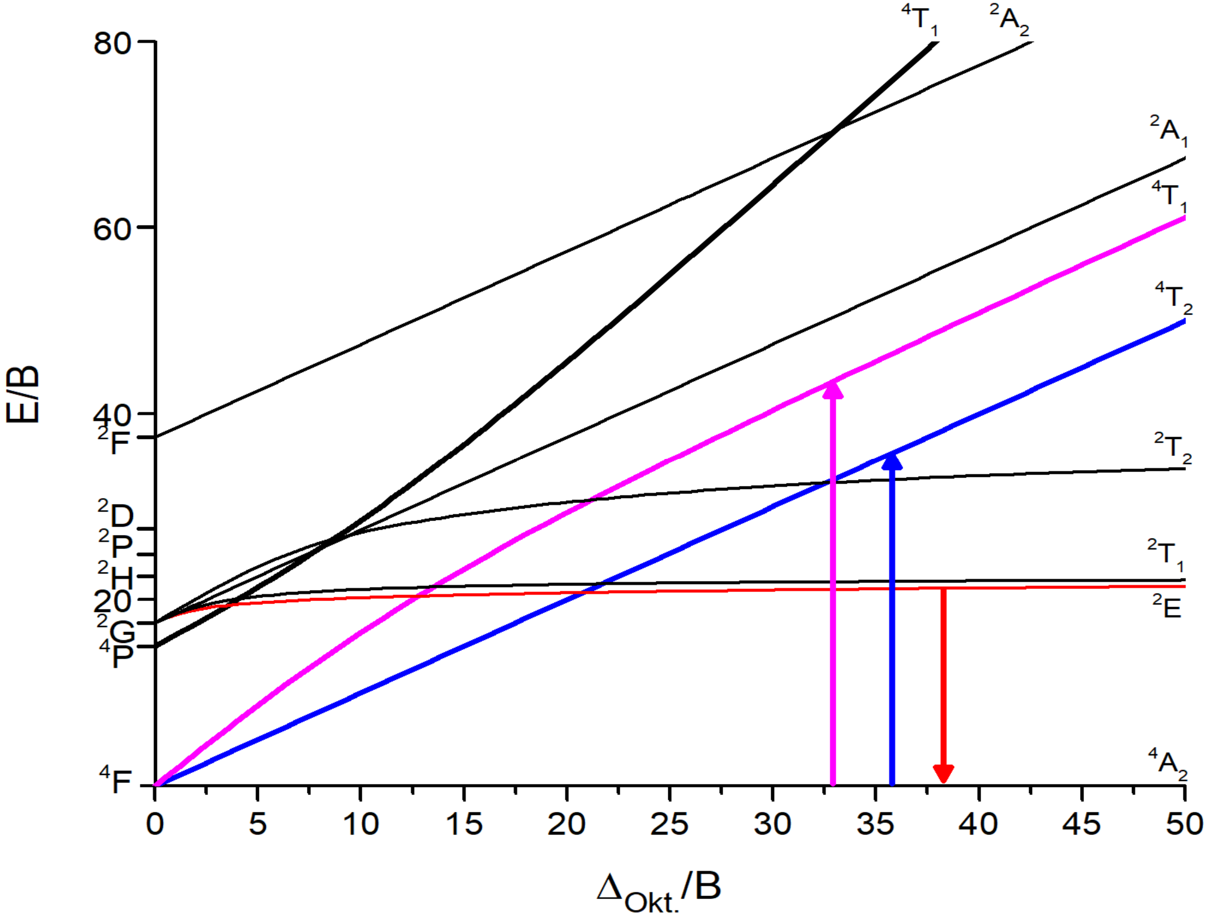
$\Delta_o = 21800\ cm^{-1}$

$B < 1000\ cm^{-1}$

$\zeta = 408\ cm^{-1}$

- Coordination compounds: MPR & photooxidation of itself: Release of O_2 or F_2↑
- Solid state compounds: Red PL





In general:

$\Delta_o \approx 20{,}000\ cm^{-1}$

Absorption bands due to $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ and $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$

Line emission due to $^2E(^2G) \rightarrow {}^4A_2(^4F)$ ~ 620 – 730 nm = f(CFS, nephelauxetic effect)

7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+} Line Emission due to spin-forbidden $^2E(^2G) \rightarrow {}^4A_2(^4F)$ transitions

Optical properties of Mn^{4+} activated luminescent materials are governed by

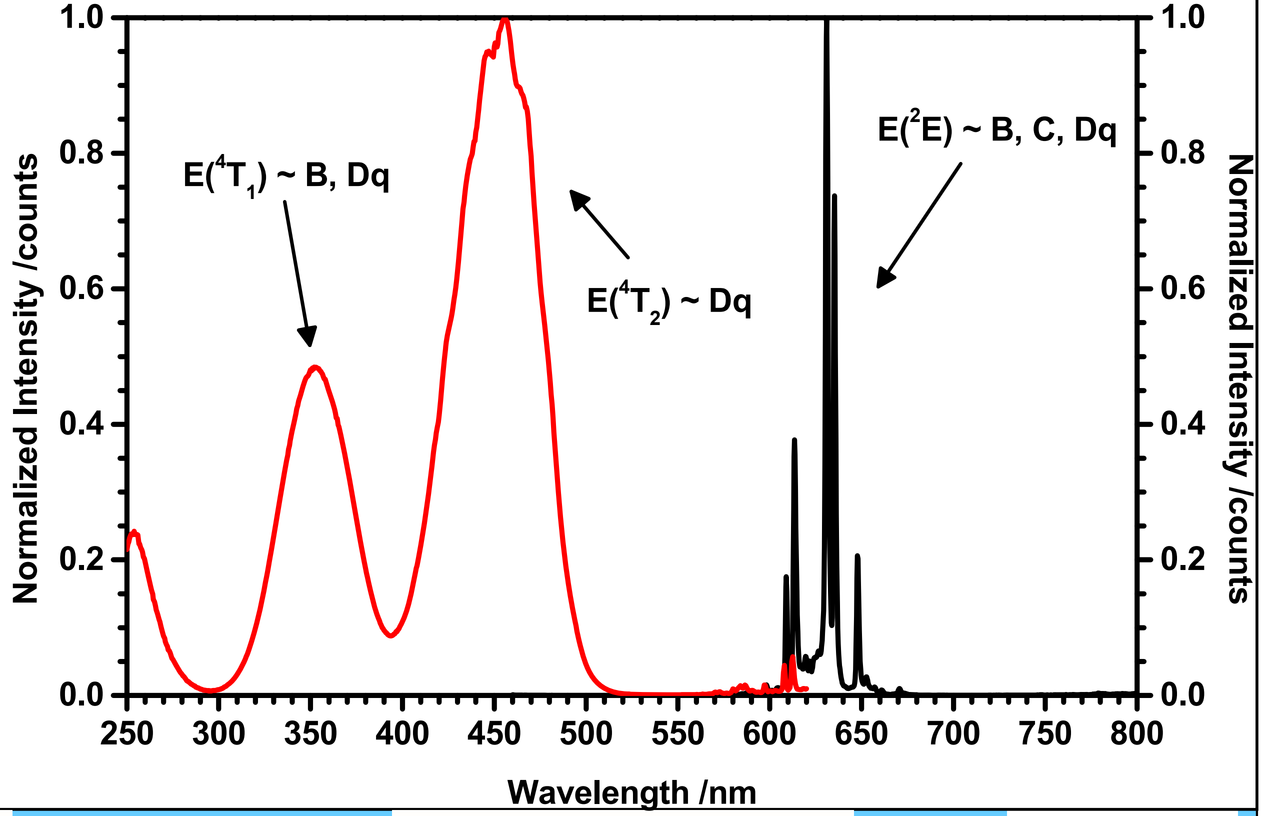
- **Crystal field splitting 10Dq, usually in the rance $1.9 - 2.3 \cdot 10^4$ cm^{-1}**
- **Covalency can be parametrised**

B: Usually 600 – 800 cm^{-1}
C: Usually 2800 – 3300 cm^{-1}

Determination of B and C →

$$B = \frac{\frac{(\Delta E)^2}{Dq} - 10 \cdot \Delta E}{15 \cdot \left(\frac{\Delta E}{Dq} - 8\right)}$$

$$C = \frac{E(^2E) - 7.90B - 1.80\frac{B^2}{Dq}}{3.05}$$

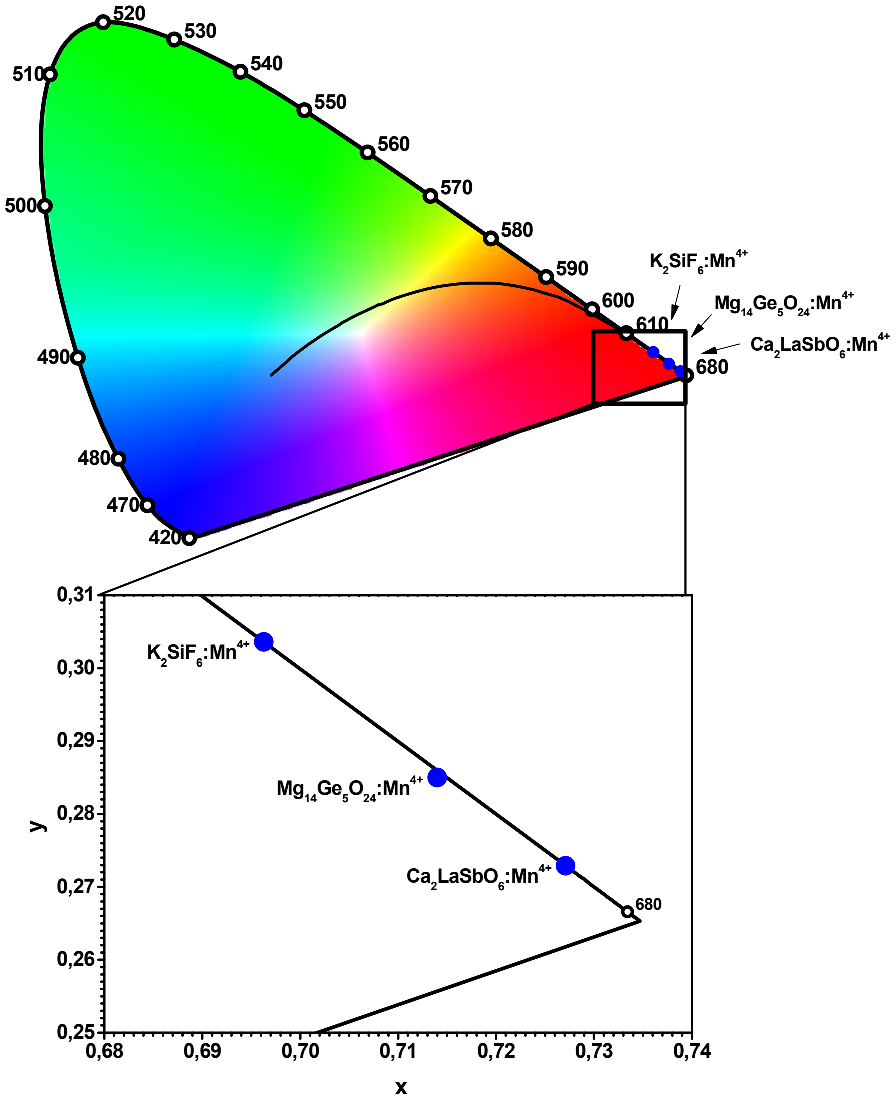


7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+} Shows solely Line Emission due to Spin-forbidden $^2E(^2G) \rightarrow {}^4A_2(^4F)$ Transitions

Compound	LE [lm W^{-1}]	Peak λ_{em} [nm]
$K_2SiF_6:Mn^{4+}$ (PSF)	196	631
$K_2TiF_6:Mn^{4+}$	192	632
$K_2GeF_6:Mn^{4+}$	191	632
$Mg_{14}Ge_5O_{24}:Mn^{4+}$	80	658
$K_2Ge_4O_9:Mn^{4+}$	46	663
$Rb_2Ge_4O_9:Mn^{4+}$	38	667
$Ca_2YNbO_6:Mn^{4+}$	15	680
$Ca_2LaSbO_6:Mn^{4+}$	7	699
$LaScO_3:Mn^{4+}$	7	703

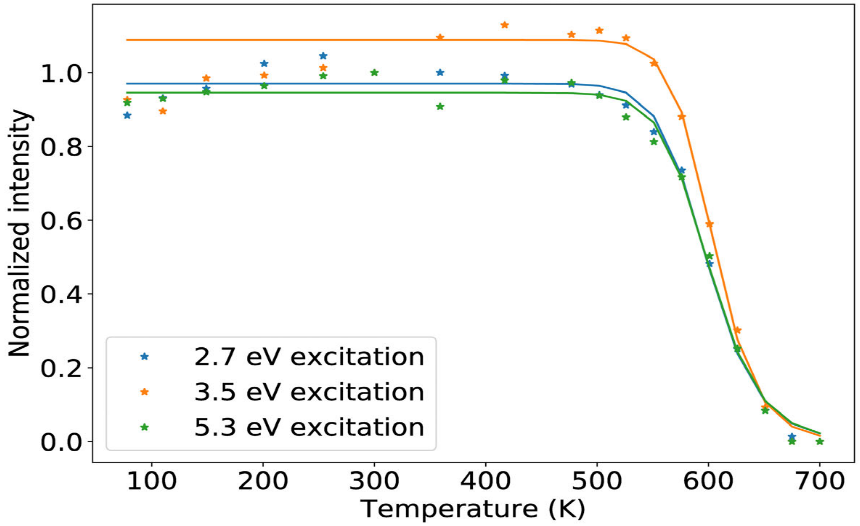
Fluorides	**red emission**
Oxides	**deep red emission**
Perovskites	**NIR emission**



7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+} Thermal Quenching of the PL

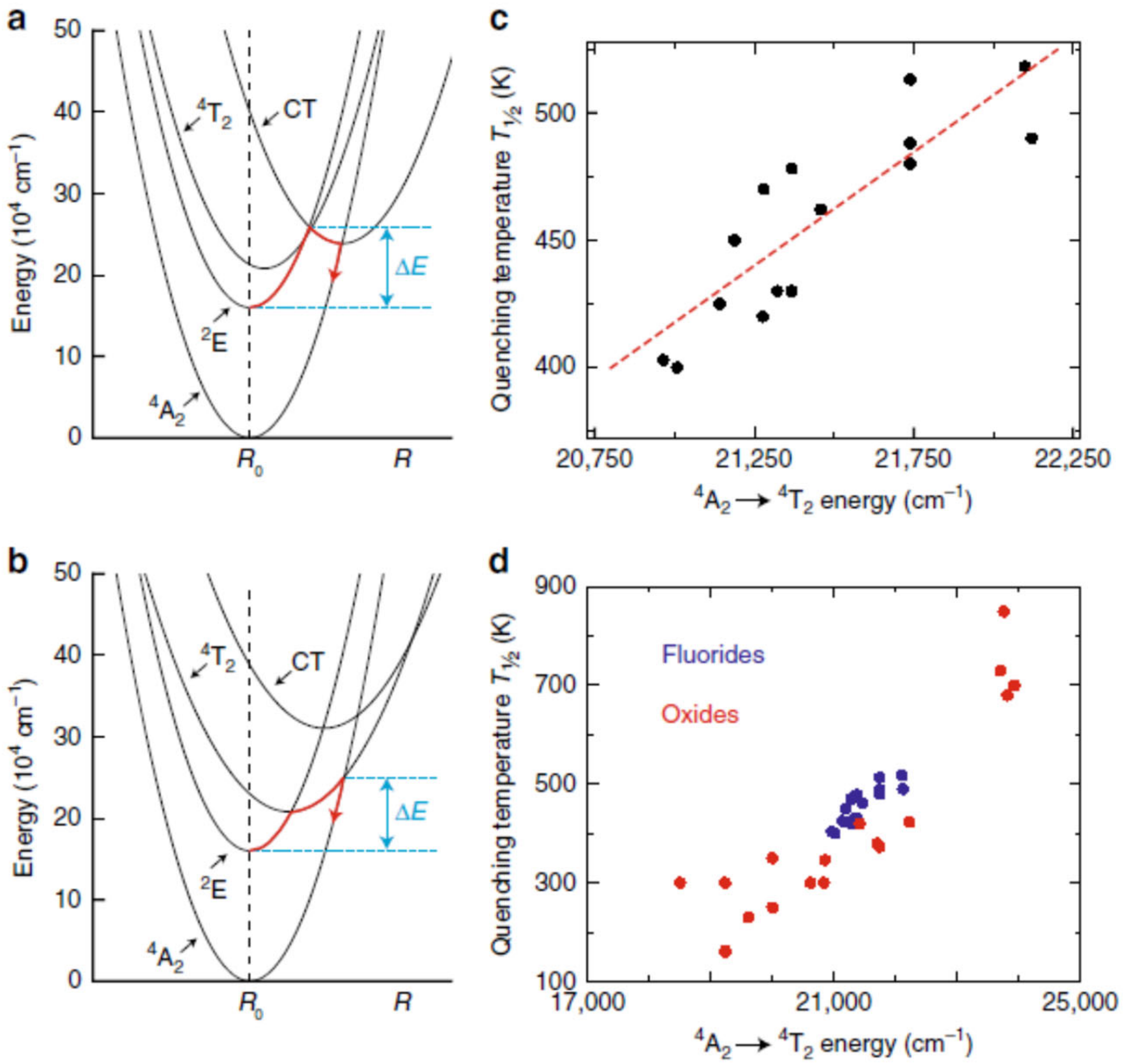
Example: $K_2SiF_6:Mn^{4+}$



Fit by the Struck-Fonger model:

$$I_{PL}(T) = I(0)/(1 + A\cdot\exp(-\Delta E/k_BT))$$

Fit results: $T_{1/2}$ = 600 K, ΔE = 1.35 eV

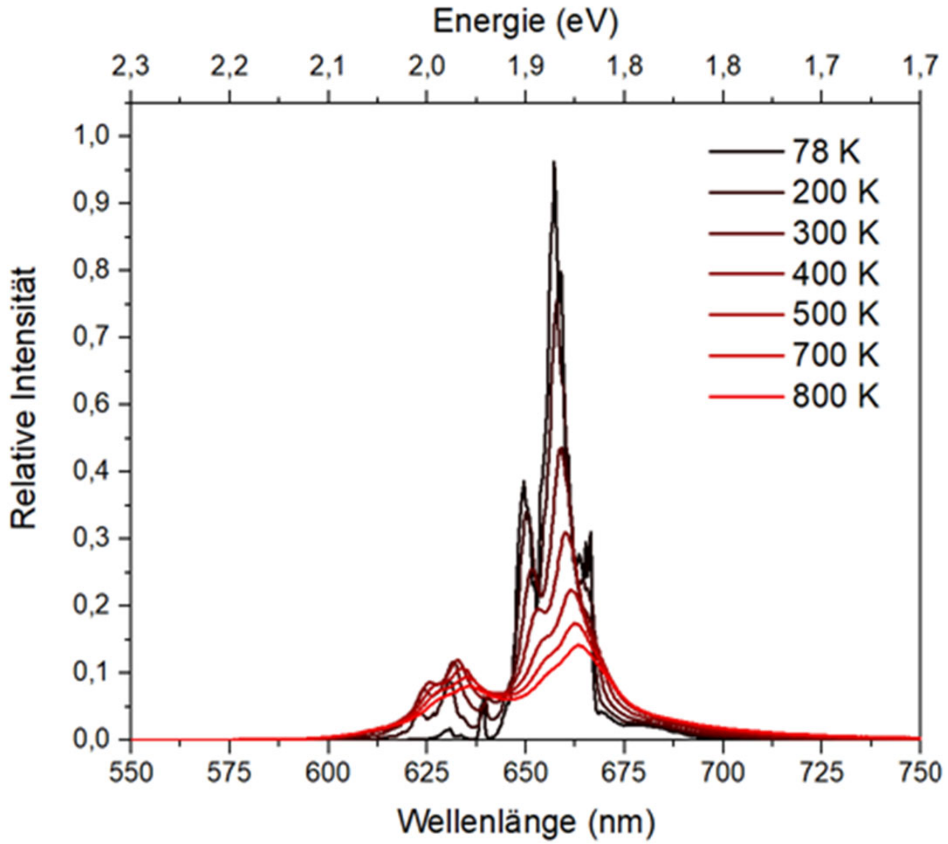


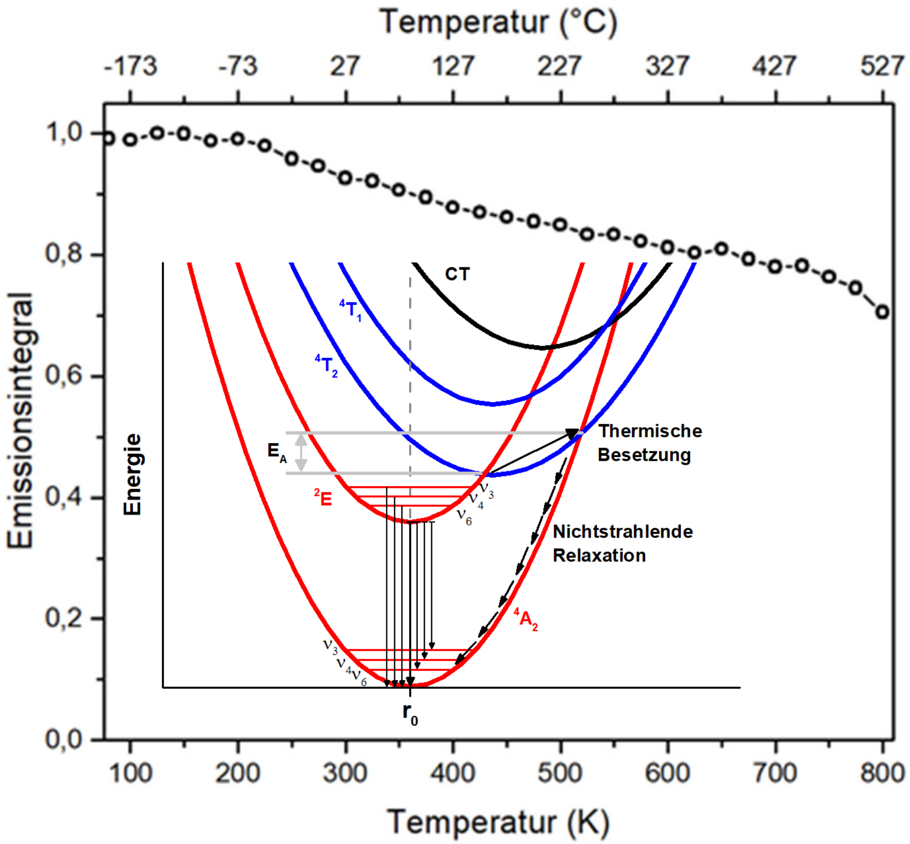
Lit.: T. Senden, R.J.A. van Diek-Moes, A. Meijerink, J. Luminescence 192 (2017) 644

7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+} Thermal Quenching of the PL

Example: $Y_2Mg_3Ge_3O_{12}:Mn^{4+}$





- $Y_2Mg_3Ge_3O_{12}:Mn^{4+}$ has very high $T_{1/2}$ value
- This is most likely related to the high energy of the $^4T_2$ band and thus large E_A

7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+} Doped Materials: Impact of Alkalinity

Mn^{4+} in fluorides (acidic environment)

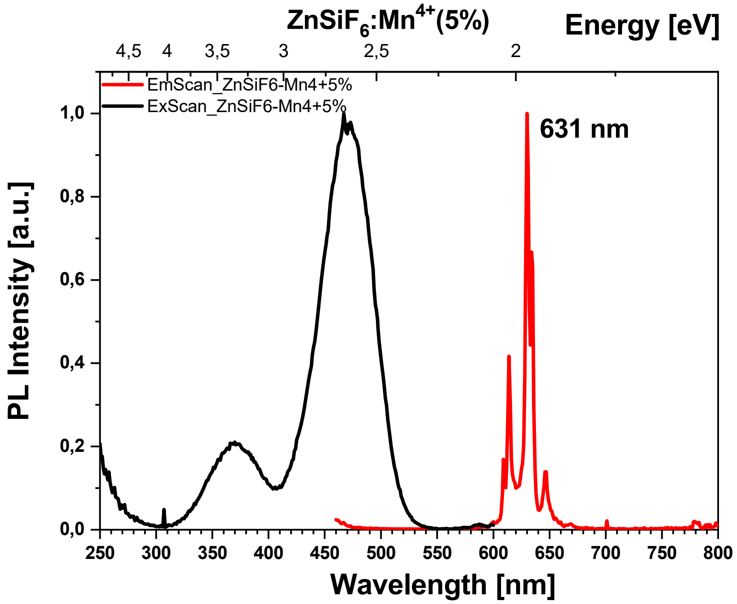
PL in the red range

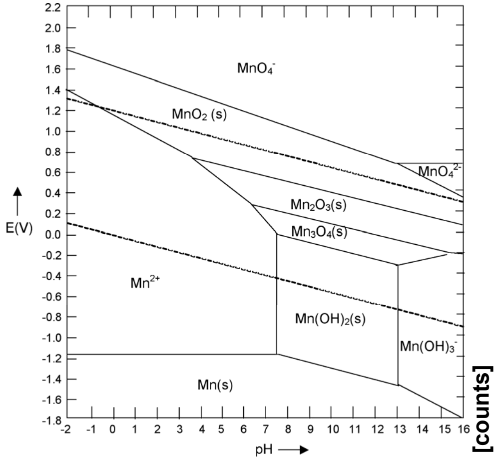
Strong oxidiser (even F^- and O^{2-})

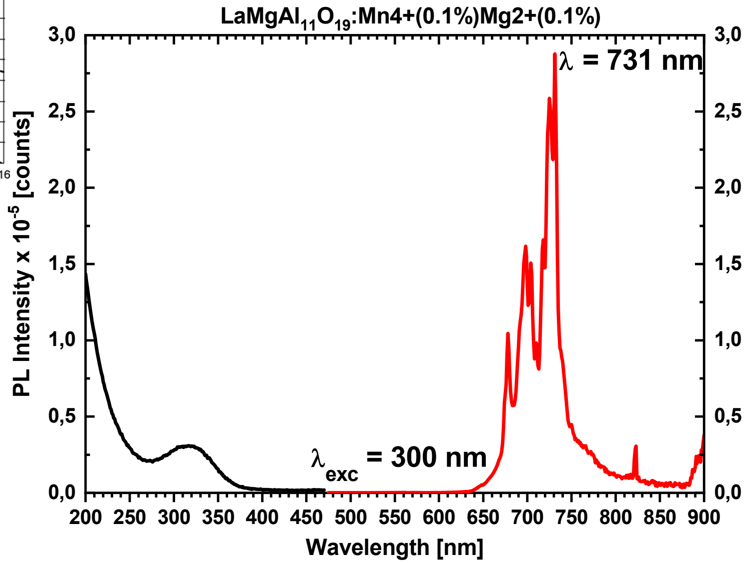
Mn^{4+} in oxides (alk. environment)

PL in the NIR range

weak oxidiser (Pourbaix diagram)





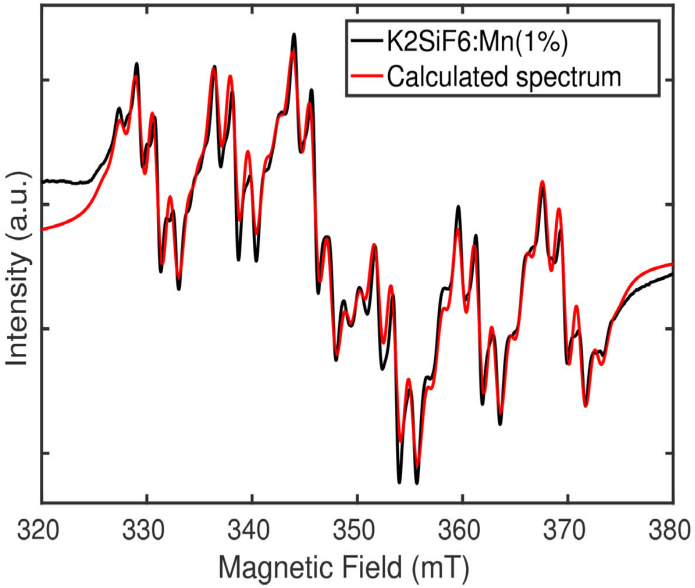


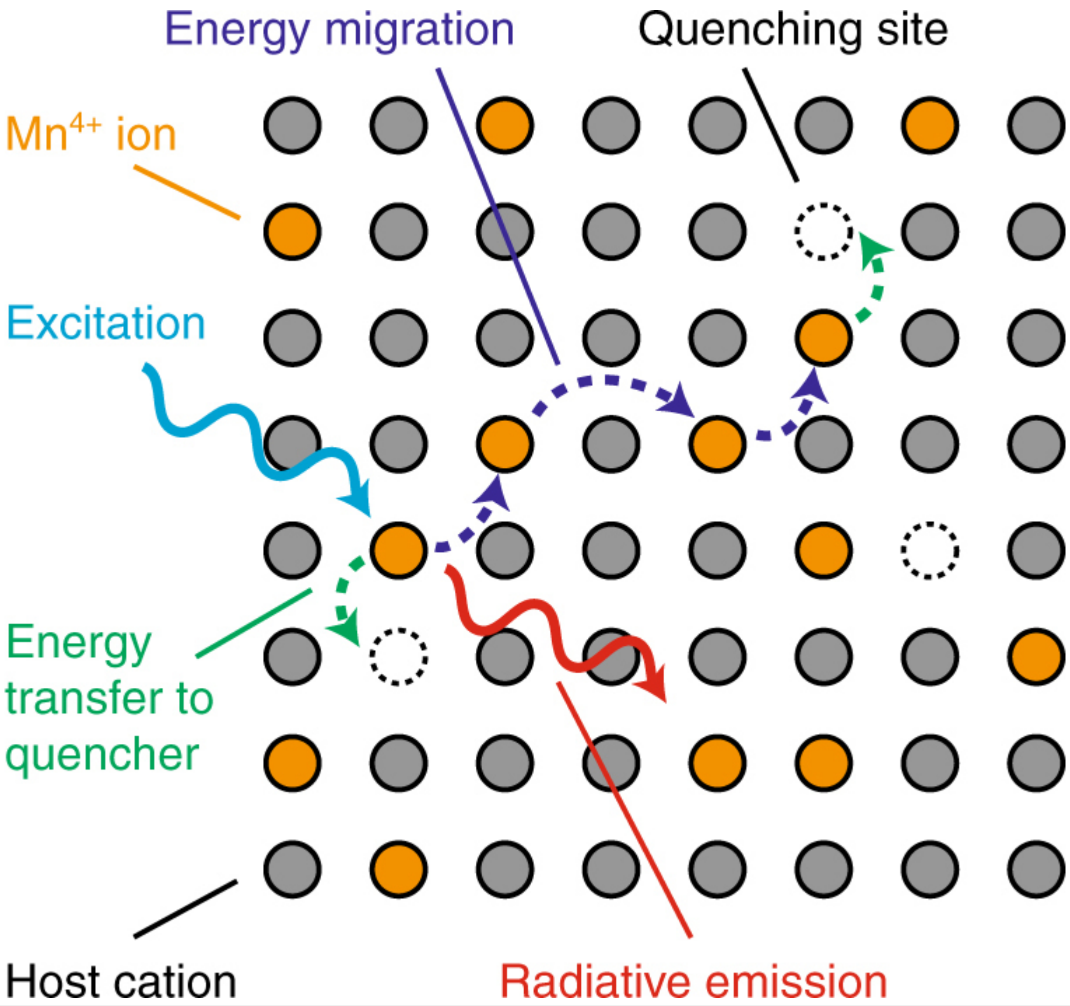
7. Spectroscopy of Inorganic Compounds

Ions with d^3 Configuration: Mn^{4+} Concentration Quenching of the PL

Mn^{4+} shows strong concentration quenching in oxides (it sets already in for c > 0.5 atom-% Mn^{4+})

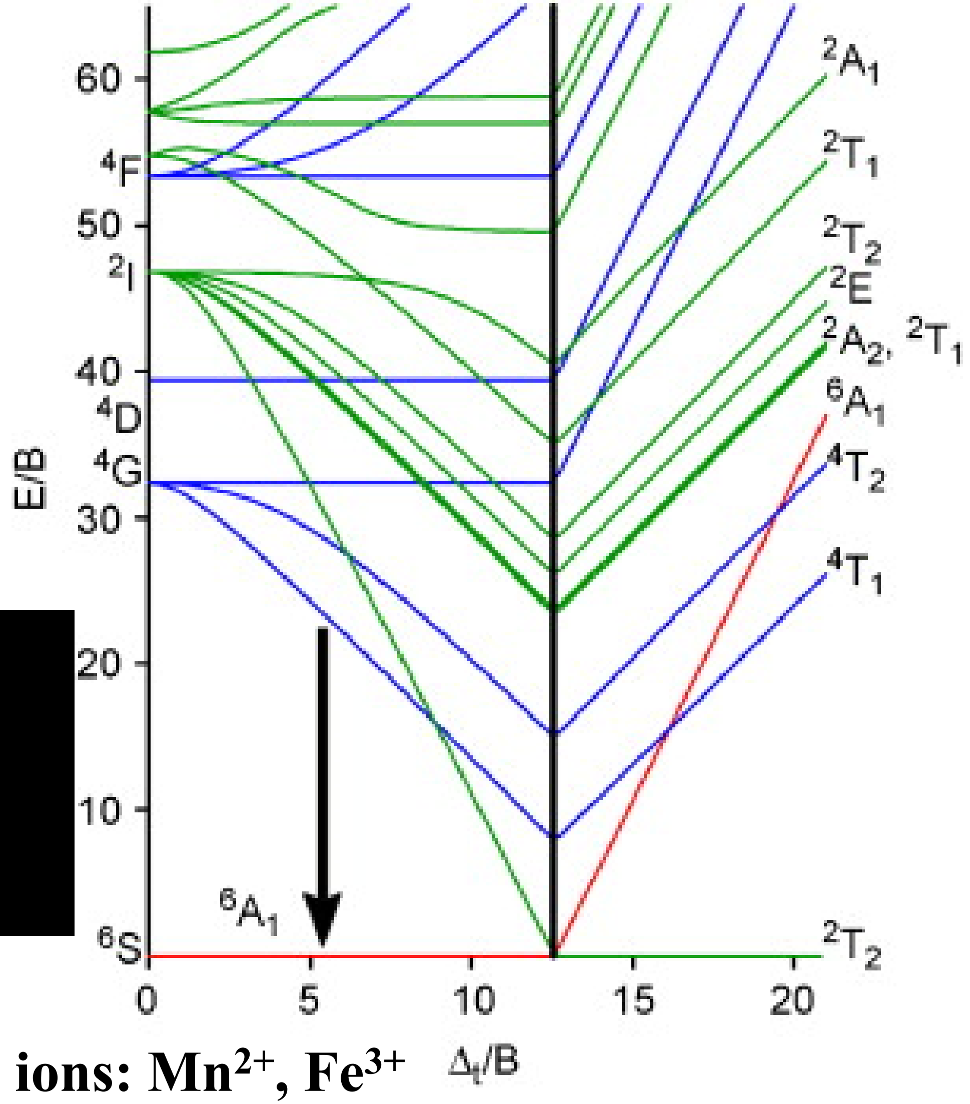
Role of superexchange
→ Mn^{4+} clustering due to ferromagnetic interaction?





7. Spectroscopy of Inorganic Compounds

Ions with d^5 Configuration: Mn^{2+}



Example: $[Mn(H_2O)_6]^{2+}$

$\Delta_o = 8500\ cm^{-1}$

$B = 960\ cm^{-1}$

$\zeta = 315\ cm^{-1}$

- Coordination compounds: MPR and redoxstable ground state

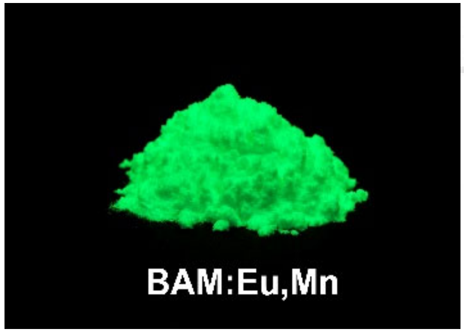
a) Solid state compounds: Green to red PL

Zn_2SiO_4:Mn^{2+}

$BaMgAl_{10}O_{17}$:$Eu^{2+}Mn^{2+}$

ZnS:Mn^{2+}

$Ca_5(PO_4)_3(F,Cl)$:$Sb^{3+}Mn^{2+}$


BAM:Eu,Mn

In general:

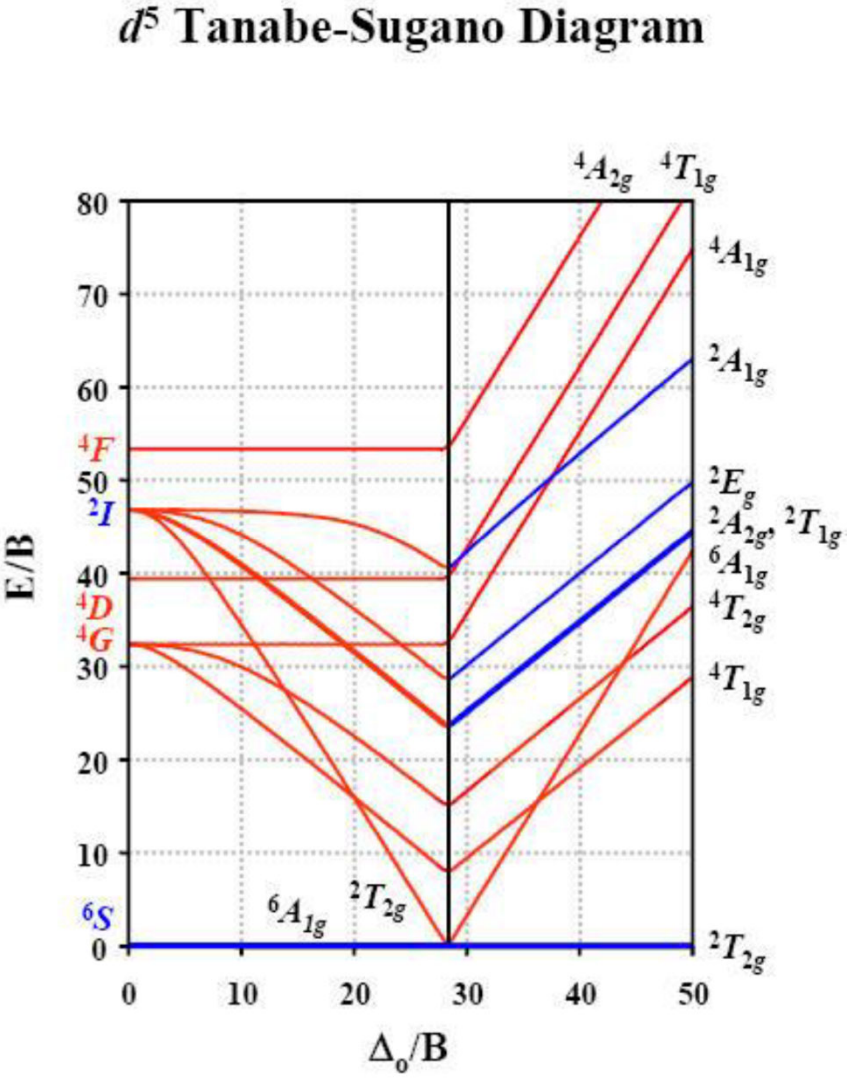
$\Delta_o < 10,000\ cm^{-1}$

Many weak absorption bands for [Ar]$3d^5$ h.s. ions: Mn^{2+}, Fe^{3+}

Band emission due to $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ ~ 500 – 750 nm = f(symmetry)

7. Spectroscopy of Inorganic Compounds

Ions with d^5 Configuration: Mn^{2+}



High spin **low-spin**

Weak field (high spin): $[Mn(H_2O)_6]^{2+}$

- $^6A_{1g}$ is the ground state
- No spin-allowed transitions
- Weak absorption

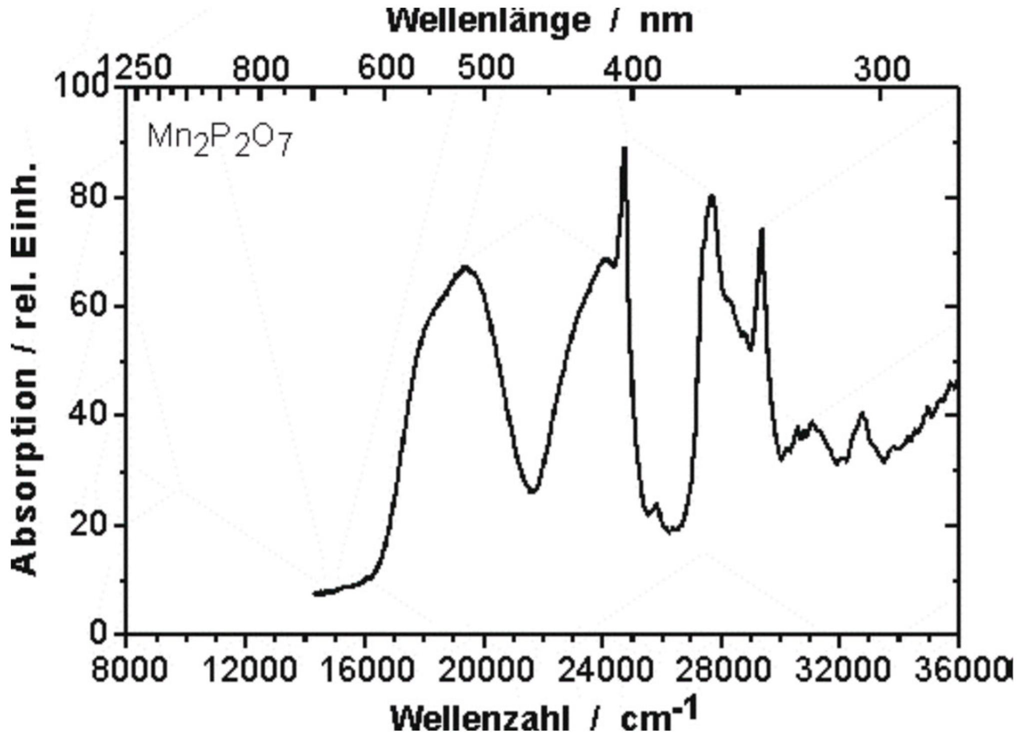
Strong field (low spin): $[Mn(CN)_6]^{4-}$

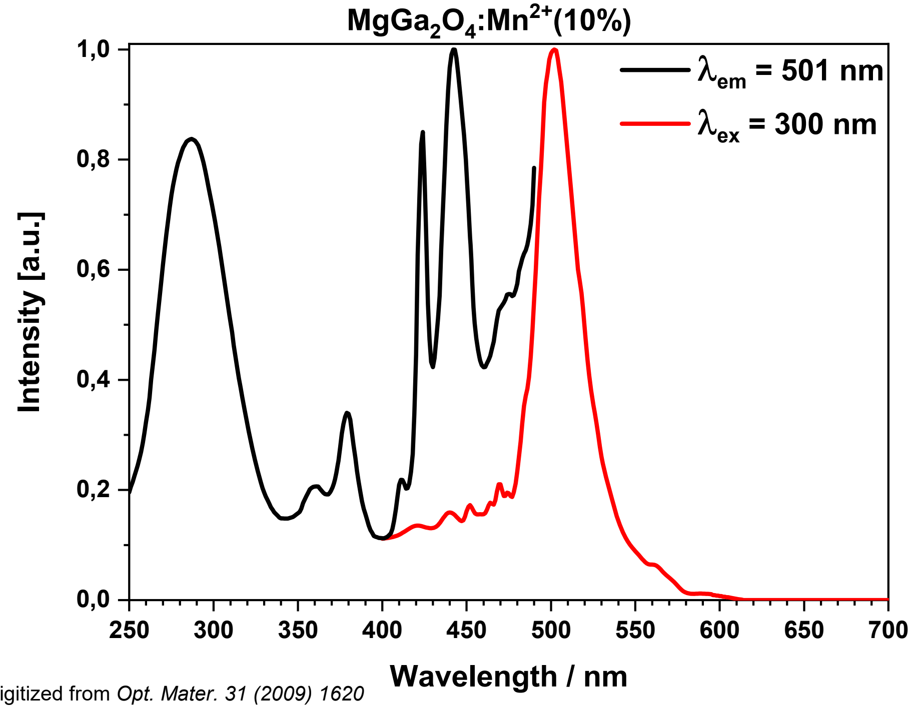
- $^2T_{2g}$ is the ground state
- Four allowed transitions
  - $^2T_{2g}$ to $^2A_{2g}$ or $^2T_{2g}$ to $^2T_{1g}$
  - $^2T_{2g}$ to ^2E_g
  - $^2T_{2g}$ to $^2T_{2g}$ (^2I)
  - $^2T_{2g}$ to $^2A_{1g}$
- Four absorption bands but due to low resolution one may not observe them all

7. Spectroscopy of Inorganic Compounds

Ions with d^5 Configuration: Mn^{2+}

Octahedral chromophore $[Mn^{II}O_6]^{10-}$: Weak absorption and $^4T_1$ - $^6A_1$ emission





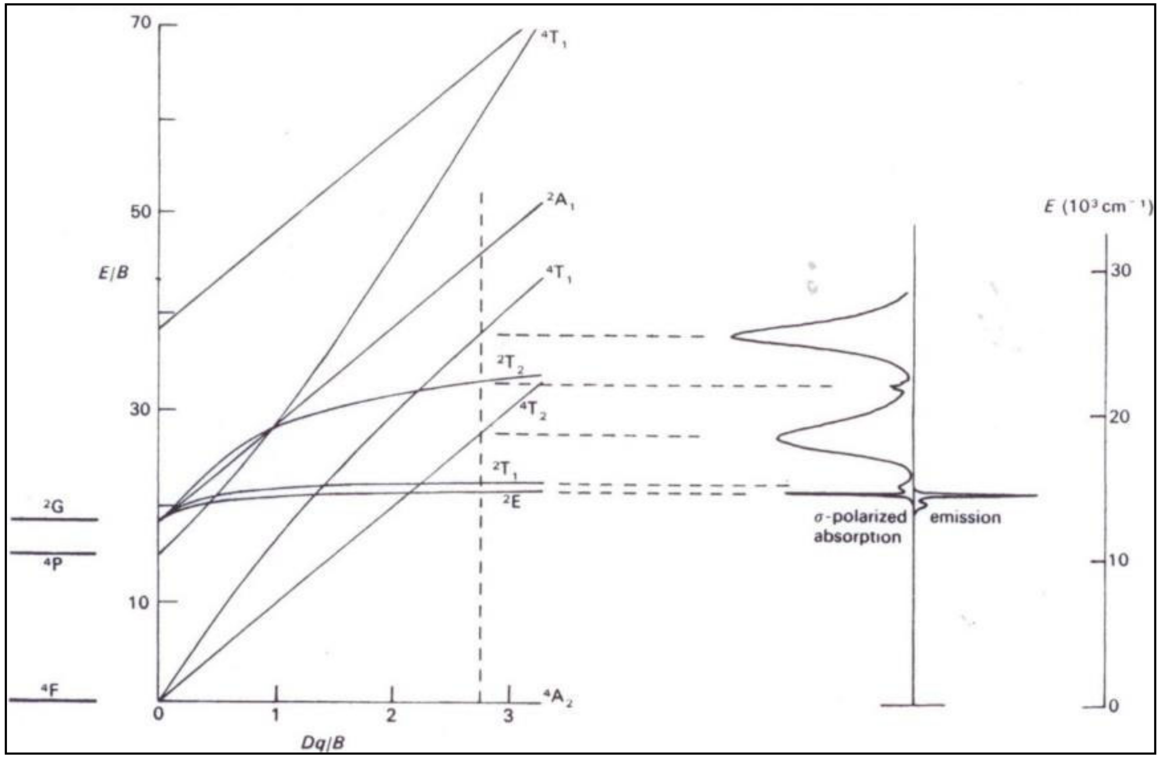
Digitized from *Opt. Mater. 31 (2009) 1620*

$Mn^{II}{}_2P_2O_7$

$MgGa_2O_4:Mn^{2+}$

7. Spectroscopy of Inorganic Compounds

Optical Spectra of 3d-Ions



Energetic positions of terms

- Coulomb-interaction ~ 10000 cm^{-1}
- Spin-orbit-coupling ~ 100 cm^{-1}
- Crystal field splitting ~ 1000 cm^{-1}

Shape of optical transitions

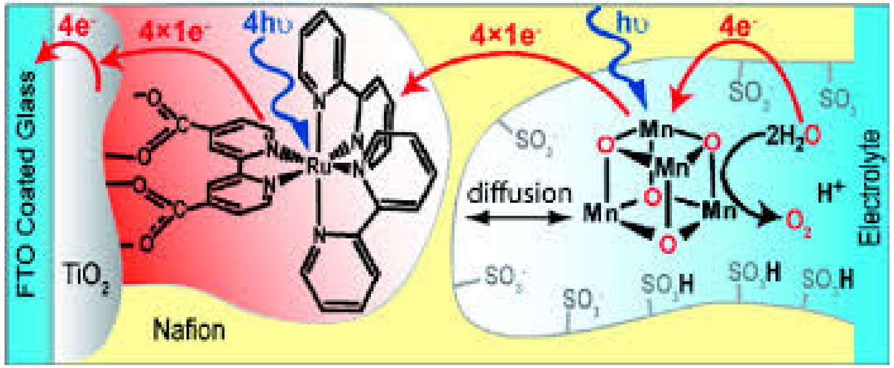
- Parallel terms:
  Sharp lines
- Terms with different slopes:
  Broad bands

Selection rules

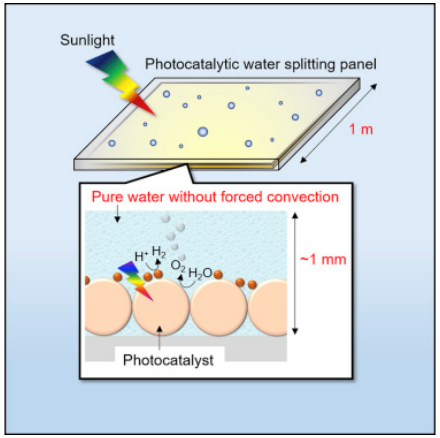
- All $d^n \rightarrow d^n$ transitions are parity-forbidden (g ↔ g)
- Transitions between states with different spins are also spin-forbidden
- Specific symmetric selection rules according to group theory (Lit.: F. Albert Cotton, Chemical Applications of Group Theory, 3rd Edition, 1990)

8. Catalysis in Inorganic Chemistry

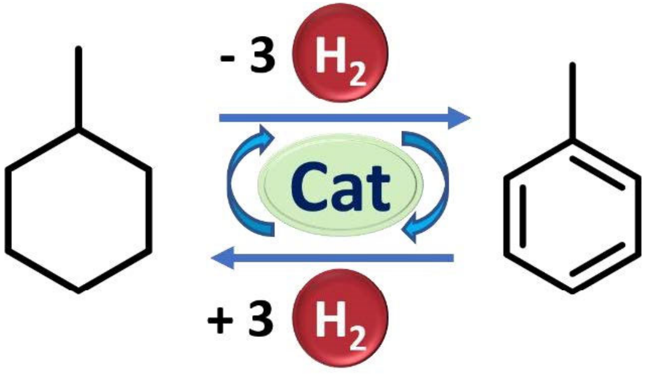
Selected Topics in Heterogeneous Catalysis



- Water splitting to generate H_2
- CO_2 conversion to organic molecules



- NH_3 formation from N_2 and water or H_2
- Liquid Organic Hydrogen Carrier (LOHC) formation e.g. Toluene, Triphenyltoluene (TPT) or Dibenzoyltoluene (DBT)



- Oxidation of SO_2 to SO_3 for sulfuric acid production
- Lignin decomposition to organic molecules

8. Catalysis in Inorganic Chemistry

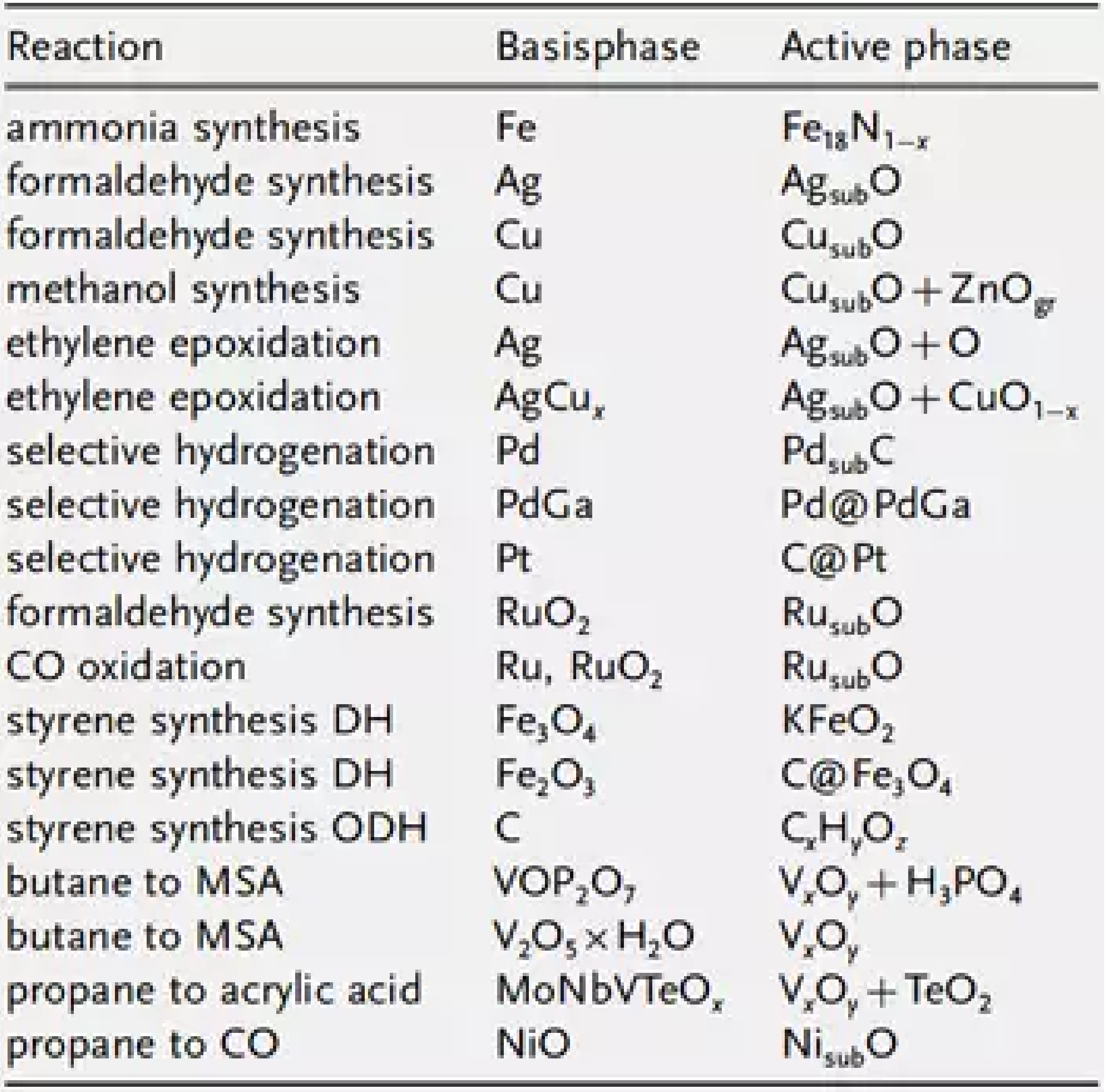
Selected Metals in Heterogeneous Catalysis

- **p-Block metals**
  Al, Si, Ga, Ge, In, Sn, Pb

- **Transition metals**
  Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn,
  Zr, Nb, Mo, Ru, Rh, Pd, Ag,
  Ta, W, Re, Os, Ir, Pt, Au

- **Lanthanide metals**
  La, Ce, Pr, Nd,
  Sm, Eu, Gd, Tb, Dy
  Ho, Er, Tm, Yb, Lu

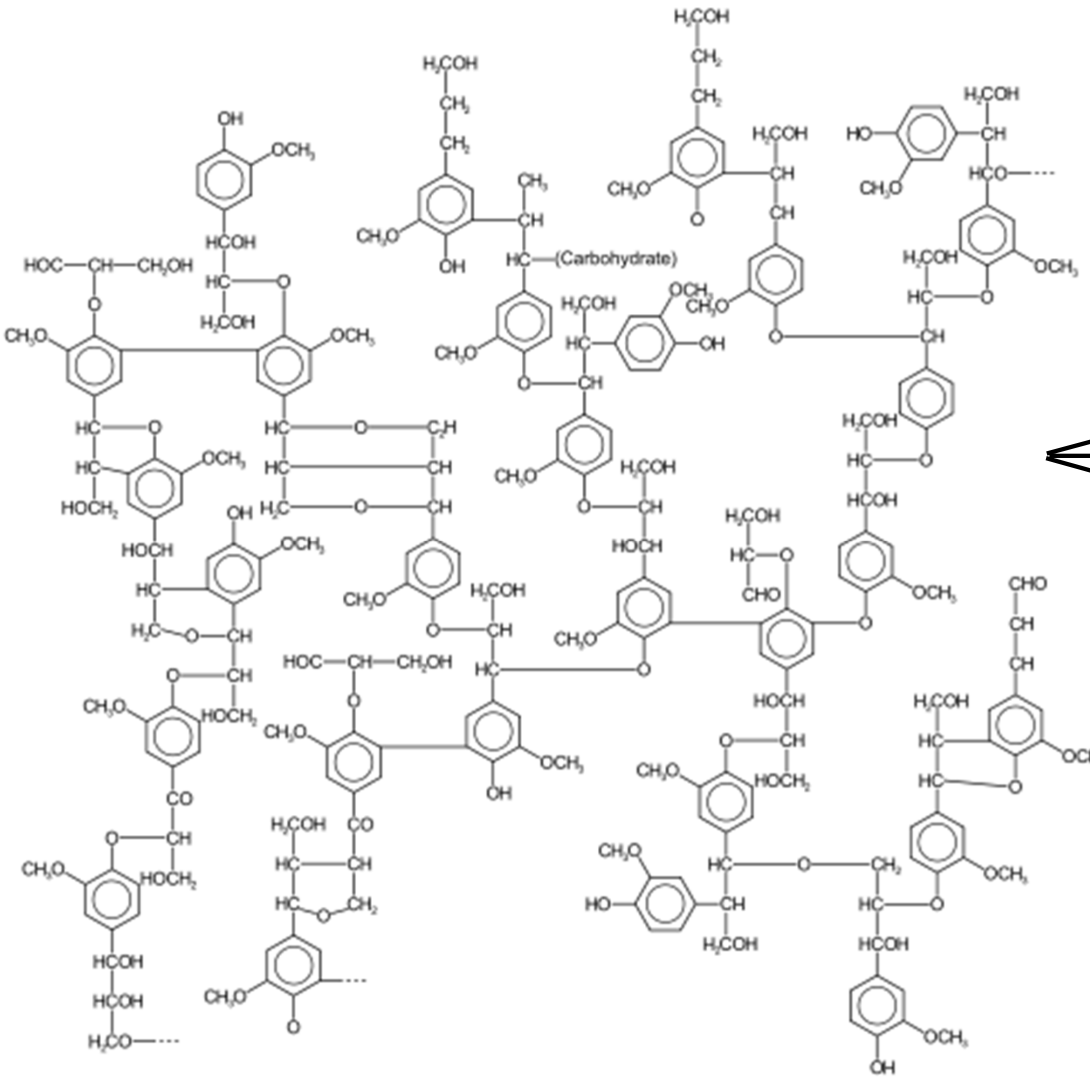
- **Actinide metals**
  Th, U

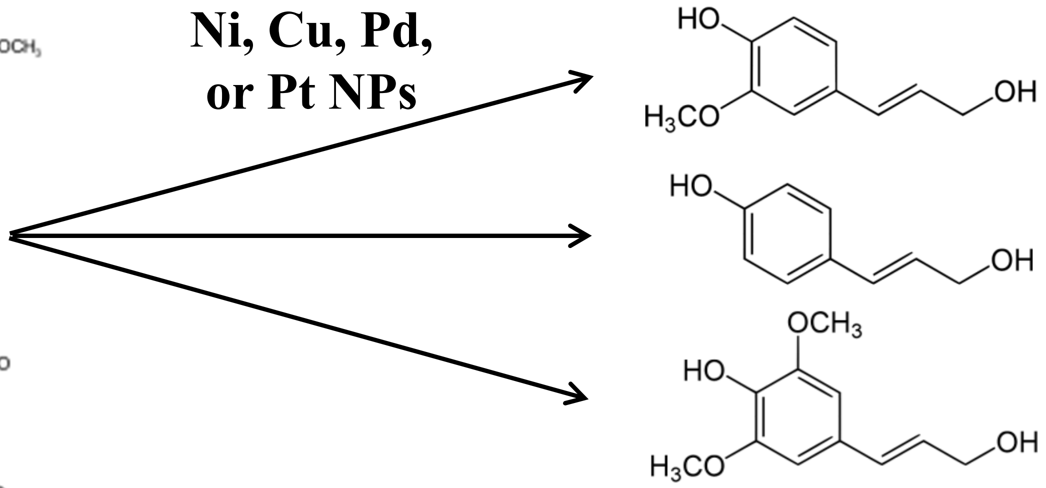


Reaction	Basisphase	Active phase
ammonia synthesis	Fe	$Fe_{18}N_{1-x}$
formaldehyde synthesis	Ag	$Ag_{sub}O$
formaldehyde synthesis	Cu	$Cu_{sub}O$
methanol synthesis	Cu	$Cu_{sub}O + ZnO_{gr}$
ethylene epoxidation	Ag	$Ag_{sub}O + O$
ethylene epoxidation	$AgCu_x$	$Ag_{sub}O + CuO_{1-x}$
selective hydrogenation	Pd	$Pd_{sub}C$
selective hydrogenation	PdGa	Pd@PdGa
selective hydrogenation	Pt	C@Pt
formaldehyde synthesis	RuO_2	$Ru_{sub}O$
CO oxidation	Ru, RuO_2	$Ru_{sub}O$
styrene synthesis DH	Fe_3O_4	$KFeO_2$
styrene synthesis DH	Fe_2O_3	$C@Fe_3O_4$
styrene synthesis ODH	C	$C_xH_yO_z$
butane to MSA	VOP_2O_7	$V_xO_y + H_3PO_4$
butane to MSA	$V_2O_5 \times H_2O$	V_xO_y
propane to acrylic acid	$MoNbVTeO_x$	$V_xO_y + TeO_2$
propane to CO	NiO	$Ni_{sub}O$

8. Catalysis in Inorganic Chemistry

Lignin Decomposition Catalyzed in a UV Reactor





Ni, Cu, Pd,
or Pt NPs

Typical breakdown products are
Cumaryl alcohol, coniferyl alcohol,
and sinapyl alcohol, which are …

… highly interesting as raw materials for
synthesis of specialty chemicals

8. Catalysis in Inorganic Chemistry

Ways towards NH_3 Production

- **Haber-Bosch (α-Fe)** $N_2 + 3\ H_2 \leftrightarrows 2\ NH_3$ **400 – 500 °C**
- **V-nitrogenase (Fe^{n+})** $2\ N_2 + 14\ H^+ + 12\ e^- \leftrightarrows 2\ NH_4^+ + 3\ H_2$ **RT**
- **Mo-nitrogenase (Fe^{n+})** $2\ N_2 + 10\ H^+ + 8\ e^- \leftrightarrows 2\ NH_4^+ + H_2$ **RT**

- **Heterogenous photocatalysis by up-conversion induced photoionisation via a doped wide band gap semiconductors (SC):**

$SC + \text{blue (In,Ga)N laser} \longrightarrow$

$SC^* \longrightarrow SC^{**}\ (e^-_{CB} + h^+_{VB})$

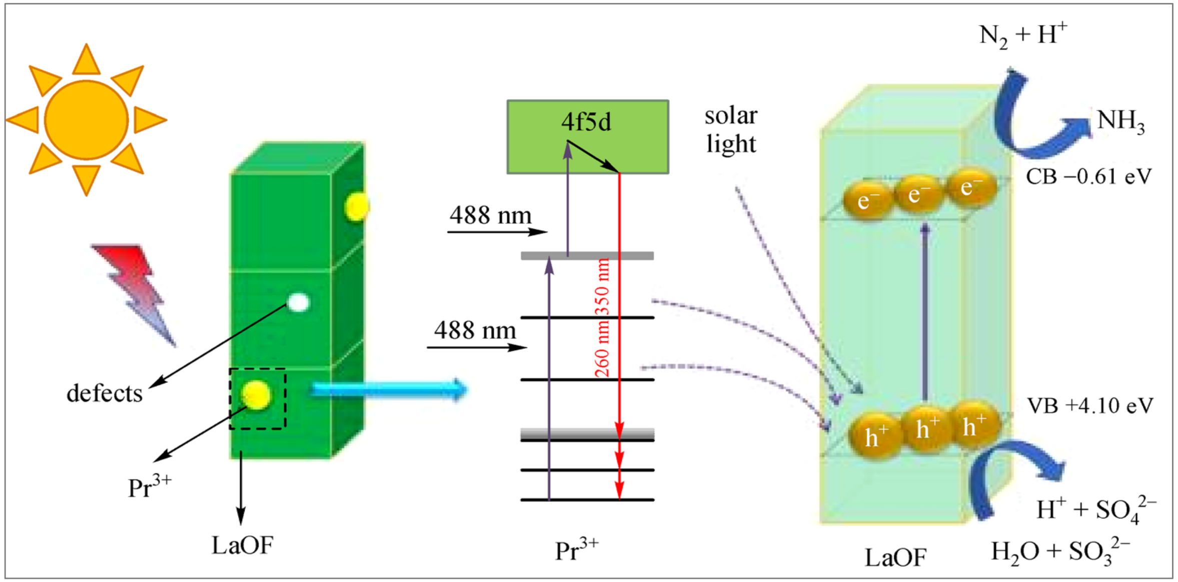
$e^-(CB) + N_2 \longrightarrow (N_2)^-$

$(N_2)^- + H_2O \longrightarrow OH^- + N_2H$

$2\ N_2H \longrightarrow N_2H_2 + N_2$

$2\ N_2H_2 \longrightarrow N_2H_4 + N_2$

$3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2$



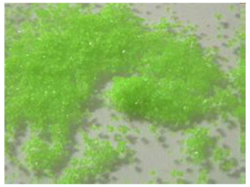
Lit.: LaOF-Pr MW hydrothermal synthesis for photocatalytic N fixation, Front Mater. Sci. 14 (2020) 43

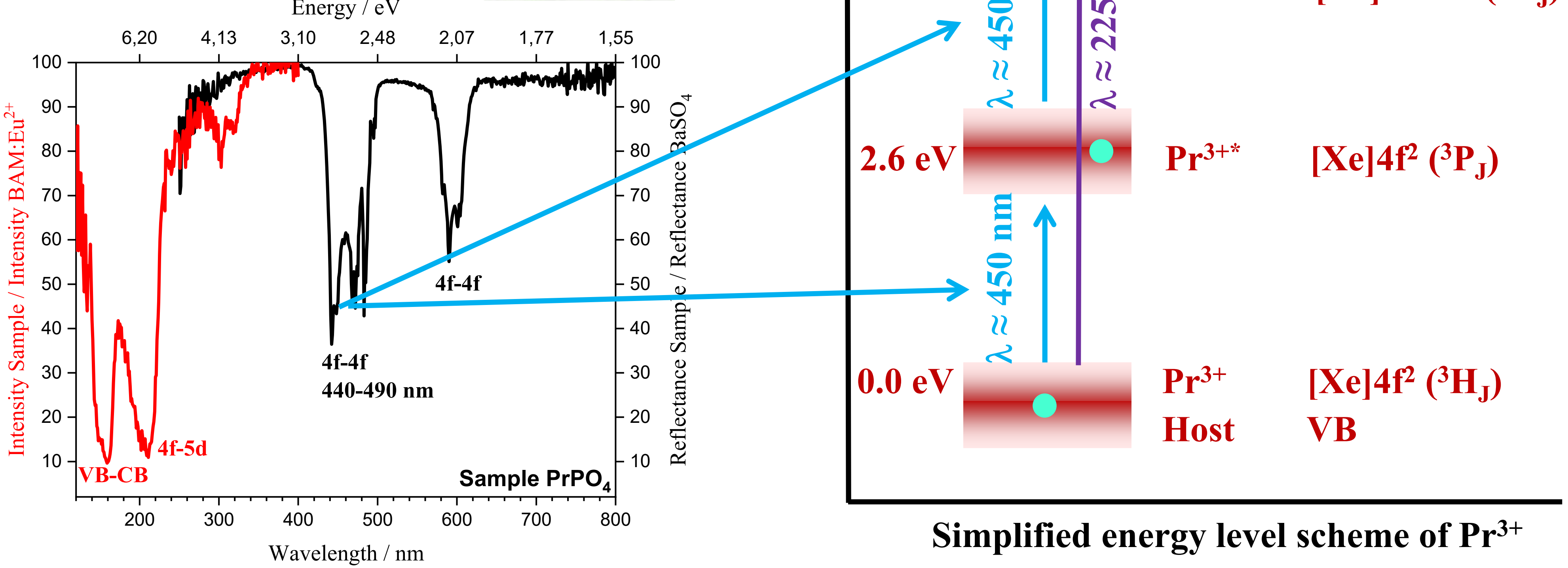
8. Catalysis in Inorganic Chemistry

Ways towards NH_3 Production

Pr^{3+} doped water stable photocatalysts: $E^0(Pr^{3+/4+}) = 3.2$ V in $[Pr(H_2O)_9]^{3+}(aq)$

Examples: $PrPO_4$ $Pr_2(SO_4)_3$





Simplified energy level scheme of Pr^{3+}

8. Catalysis in Inorganic Chemistry

Ways towards NH_3 Production

Via hydrolysis of metal nitrides

- **Titania route** $TiO_2 \rightarrow Ti + O_2$ Tm:YAG SS laser
  $2\ Ti + N_2 \rightarrow 2\ TiN$
  $2\ TiN + 2\ H_2O + H_2O_2 \rightarrow 2\ NH_3 + TiO_2$

- **Magnesia route** $2\ MgO \rightarrow 2\ Mg + O_2$ KrF* excimer laser
  $3\ Mg + N_2 \rightarrow Mg_3N_2$
  $Mg_3N_2 + 6\ H_2O \rightarrow 2\ NH_3 + 3\ Mg(OH)_2$

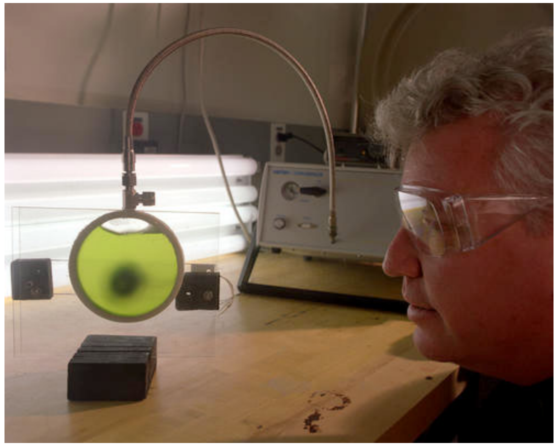
Note: Both ways require the reduction of oxides from very electropositive metals, which is only economically viable, if the energy for the reduction is easily accessible and show a reasonable cost price

Lit.: Mg-Production Laser-induced, J. Appl. Phys. 109 (2011) 013103

8. Catalysis in Inorganic Chemistry

Ways towards Water Cleavage: Overview

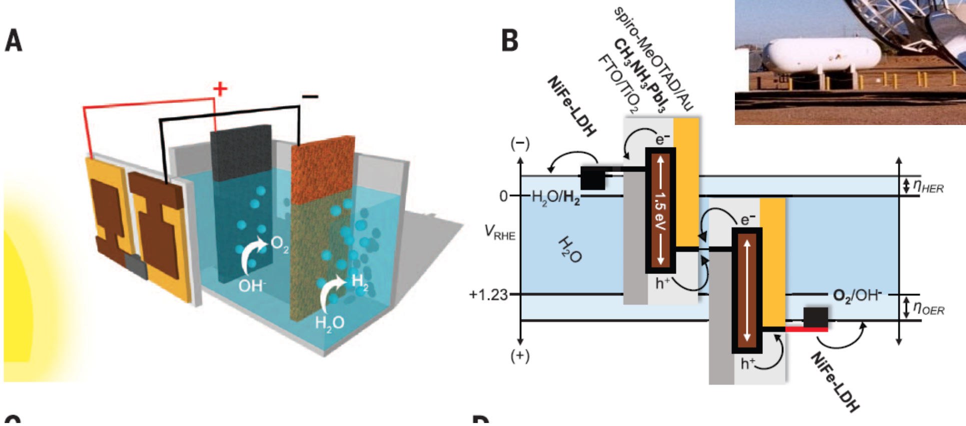
$$2\ H_2O(g\ \text{or}\ l) \rightarrow O_2(g) + 2\ H_2(g)$$



- Photosynthesis
  - Plants
  - Algae
  - Phytobacteria
- Photolysis

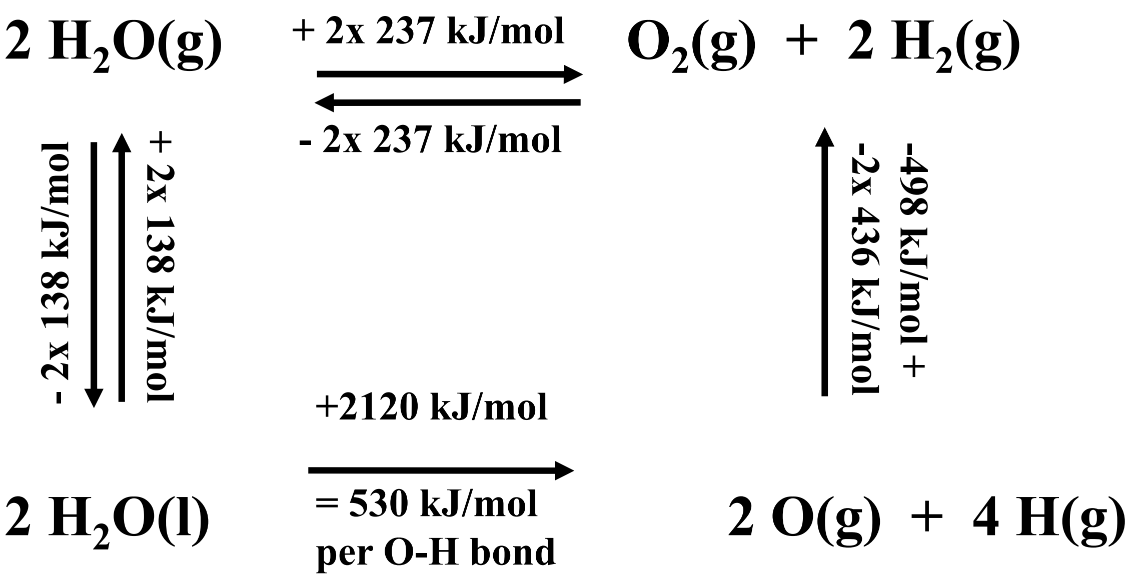
- Thermolysis
- Electrolysis

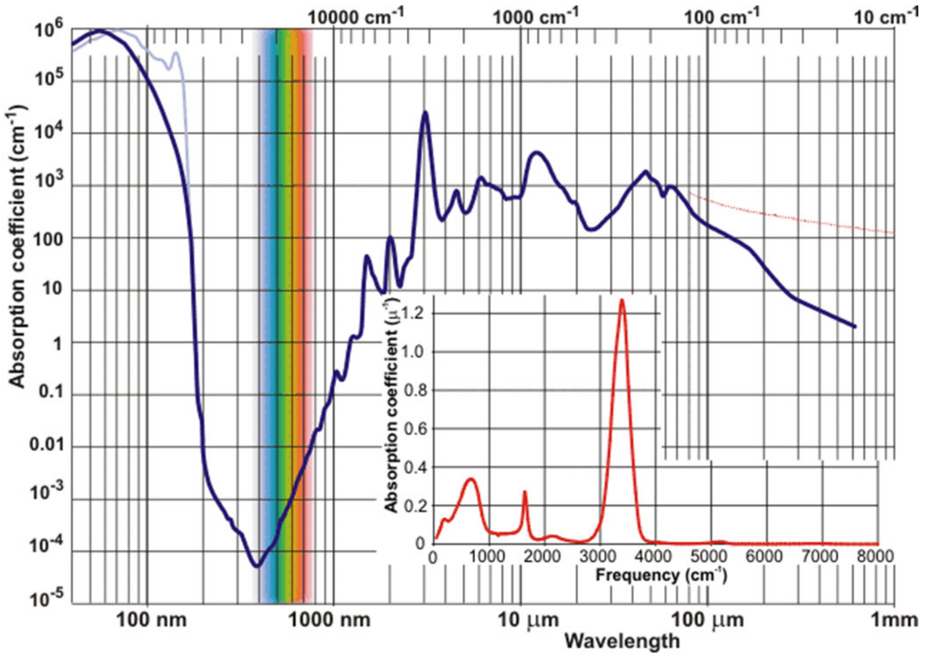
- Photocatalysis
- Chemistry (e.g. via Mg)

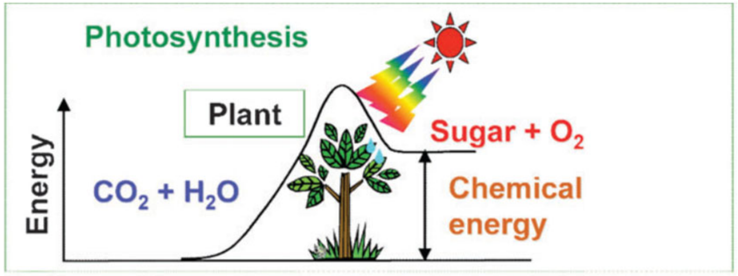


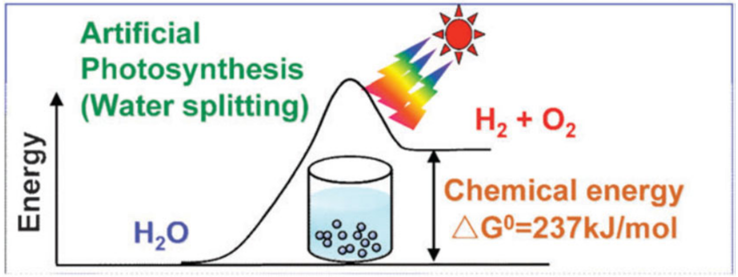
8. Catalysis in Inorganic Chemistry

Energy Balance









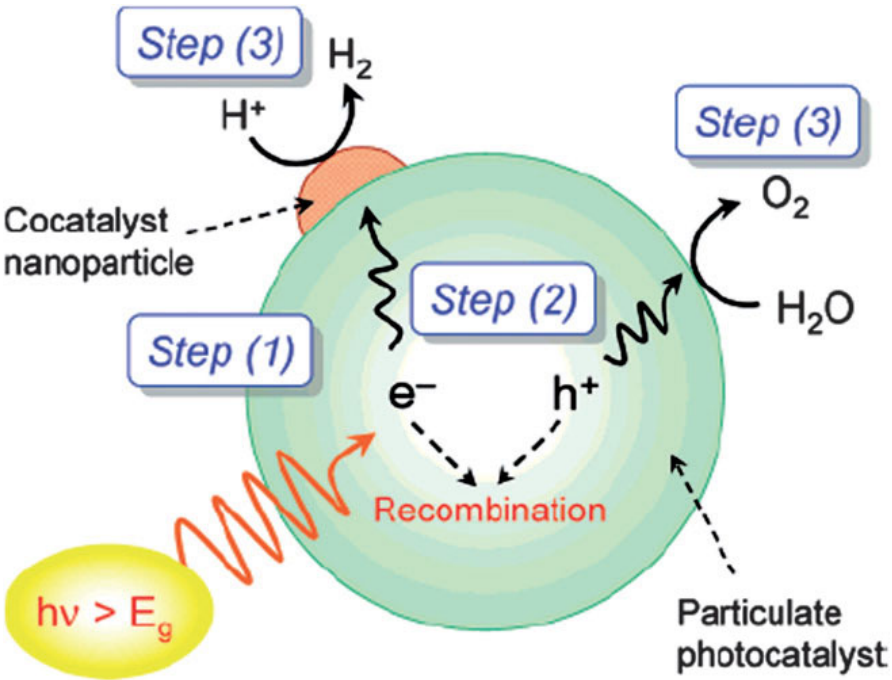
Photolysis of water without any photocatalyst requires VUV or EUV Radiation, i.e. 10 – 200 nm

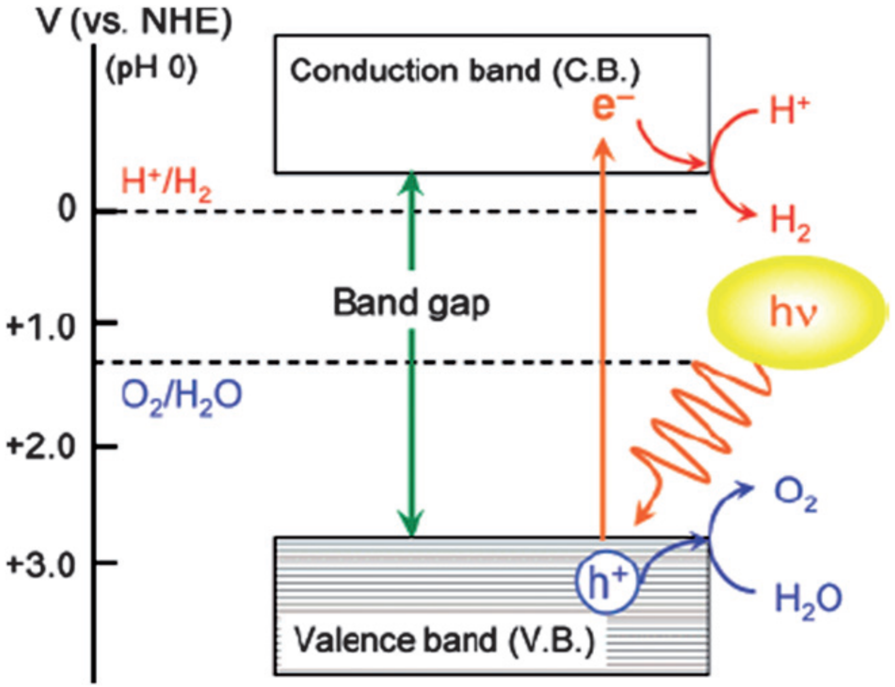
→ Radiolysis loss of water in stratosphere and mesosphere: $2\ H_2O(g) \rightarrow O_2(g) + 2\ H_2(g)\uparrow$

8. Catalysis in Inorganic Chemistry

Photocatalytic Process by Using Semiconductors

- First system explored in 1971
- Lit.: A. Fujishima, K. Honda, Nature 238 (1972) 38 → TiO_2 with Pt as a co-catalyst
- In general water splitting is possible at around 1000 nm (1.23 eV), in real systems voltage is higher ~1.8 V (due to overvoltage)

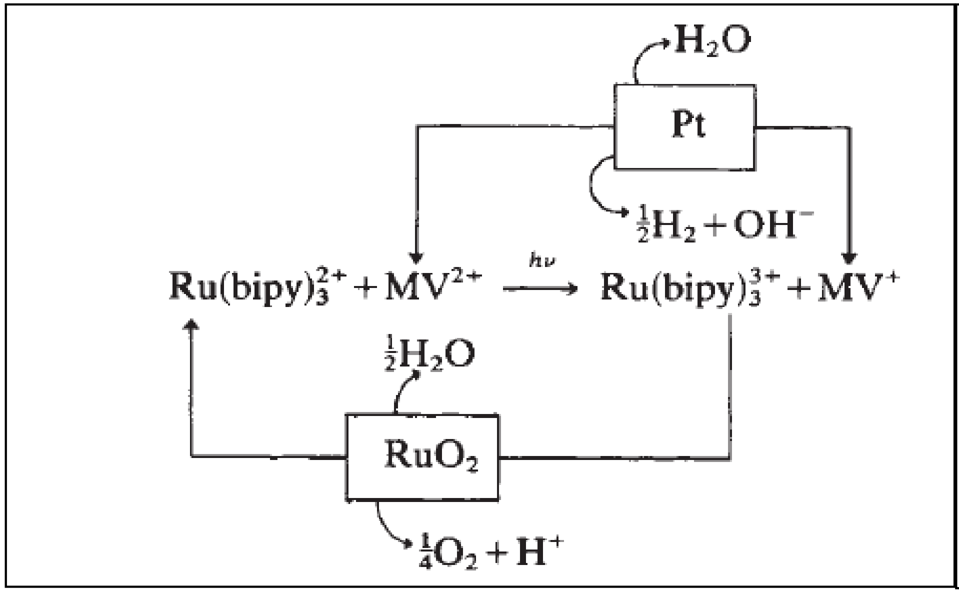


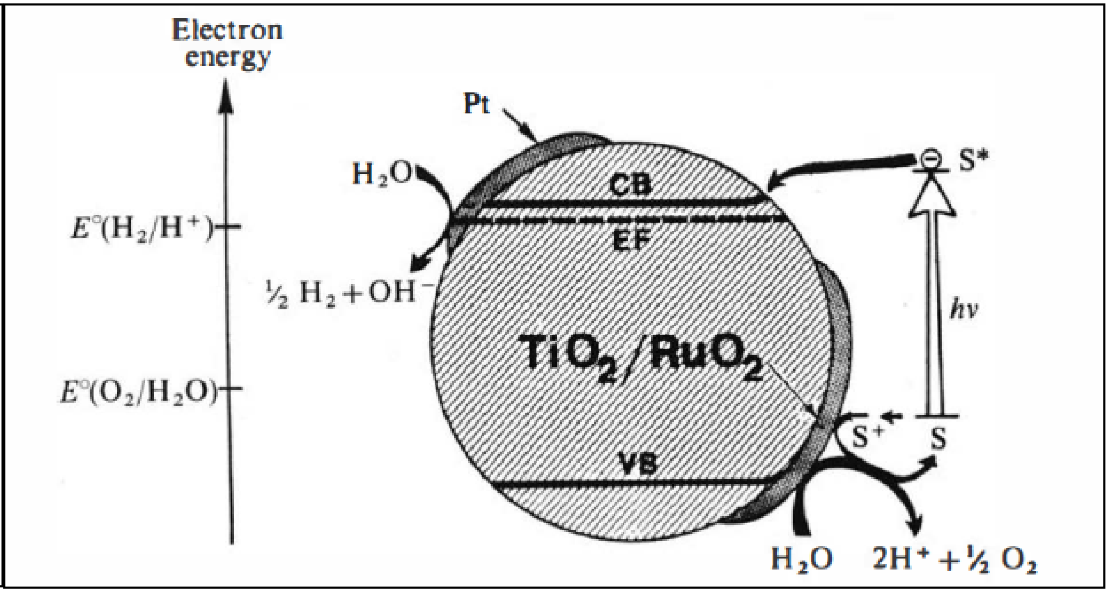


8. Catalysis in Inorganic Chemistry

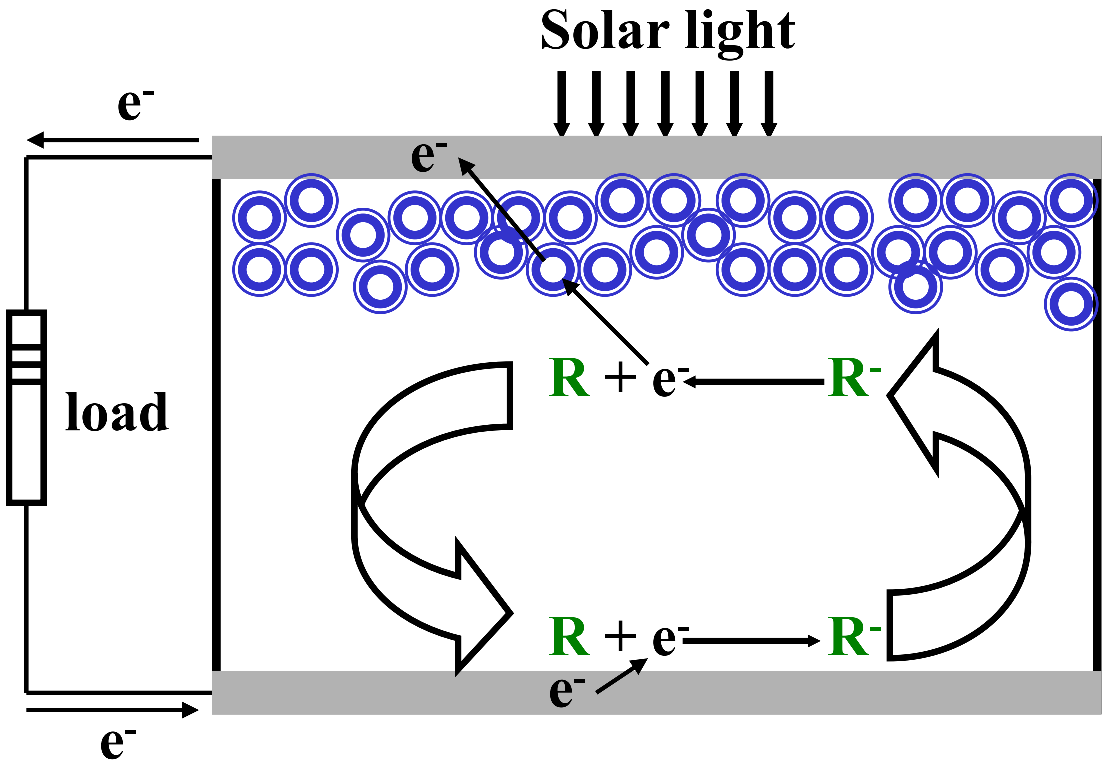
Photocatalytic Process by Using Semiconductors and a Sensitizer

- First system using a sensitizer in 1981 by Michael Graetzel
- Lit:: Nature 289 (1981) 158
- → TiO_2 with Pt and RuO_2 as co-catalysts and $[Ru(bpy)_3]^{2+}$ and methylviologen as sensitizers (antennae)
- Coating of TiO_2 by Pt nanoparticles precipiated from H_2PtCl_6 and citrate





Lab Work: Dye Sensitised Solar Cells (DSSC or Graetzel cells)



Glass substrate with SnO_2:F (0.5 µm)

Dye sensitised TiO_2 nanoparticle membrane (5-10 µm)

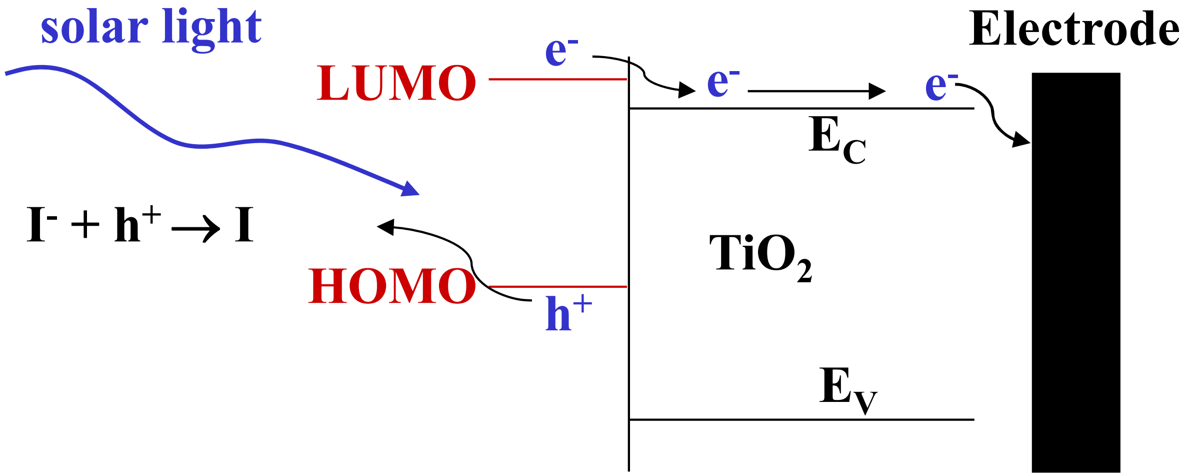
Electrolyte solution with redox mediator

Glass substrate with SnO_2:F (0.5 µm), Pt coated (2 µm) → counter electrode

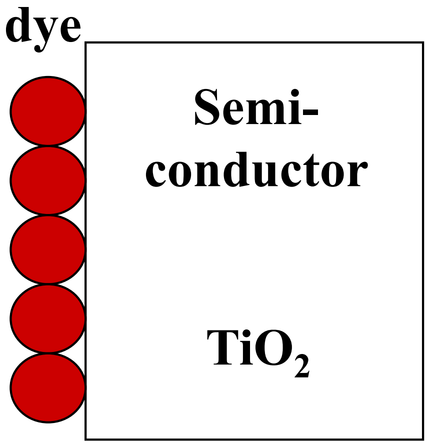
Solar cell type	Light absorption by	Charge separation by
Graetzel	dye molecules	TiO_2 + redox mediator
pn-semiconductors	band absorption in the semiconductor	electrostatic field at the pn-junction

8. Catalysis in Inorganic Chemistry

Lab Work: Dye Sensitised Solar Cells (DSSC Graetzel cells)



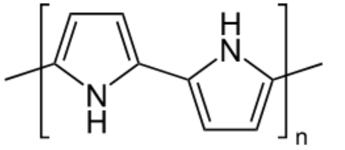
$I^- + h^+ \rightarrow I$



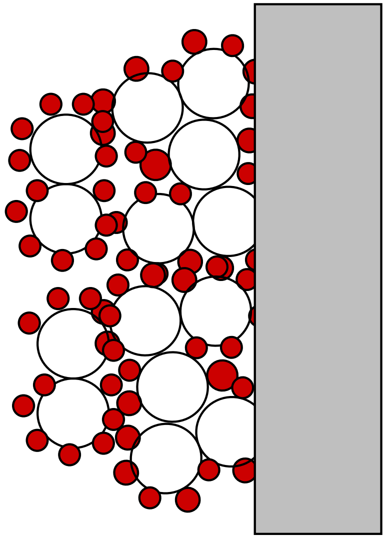
$I_2 + I^- \rightarrow I_3^-$ (I_2 is soluble in presence of I^-)

single monolayer dye on TiO_2 → low absorption

Solvent: Water or conductive polymers, e.g. polypyrrole

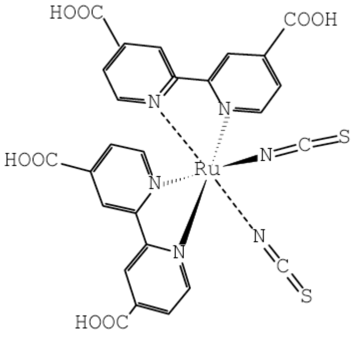


At counter electrode, I is reduced back to I^-



Glass substrate

Most common dyes are Ru^{2+} complexes



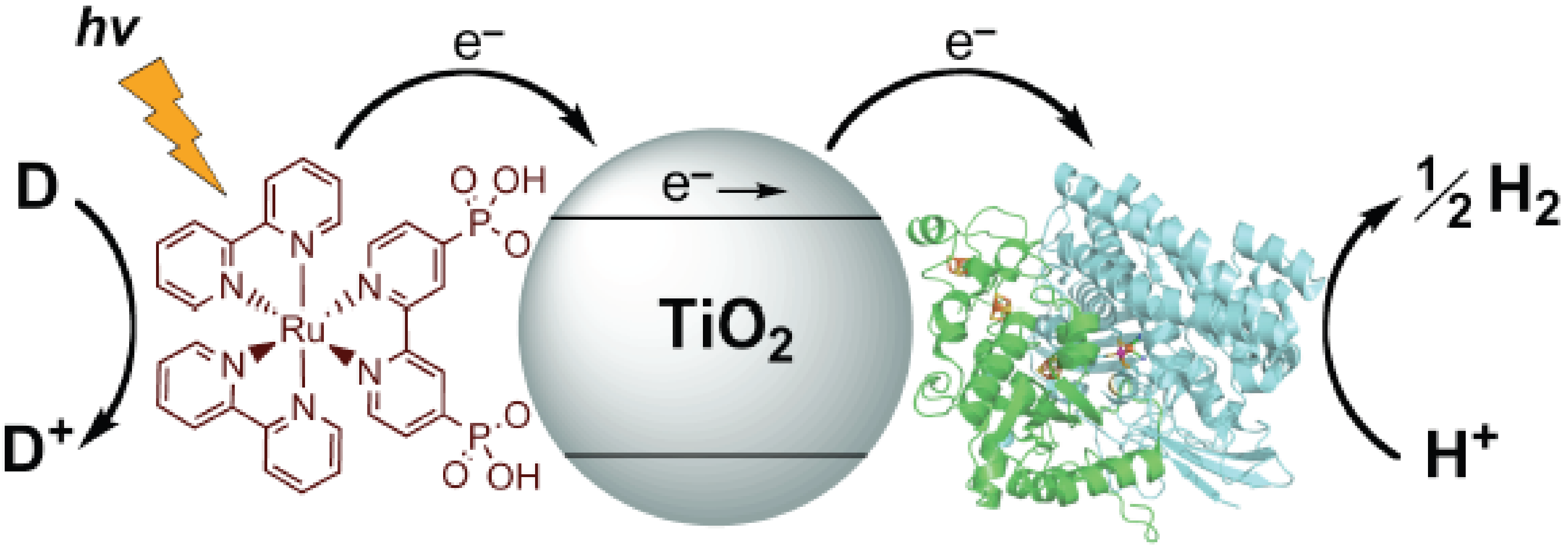
Breakthrough: Use of porous, nanocrystalline TiO_2

Made by sintering a colloid or suspension of TiO_2

Lit.: B. O'Regan, M. Grätzel, Nature 353 (1991) 737

8. Catalysis in Inorganic Chemistry

Photocatalytic Process by Using Semiconductors and a Sensitizer



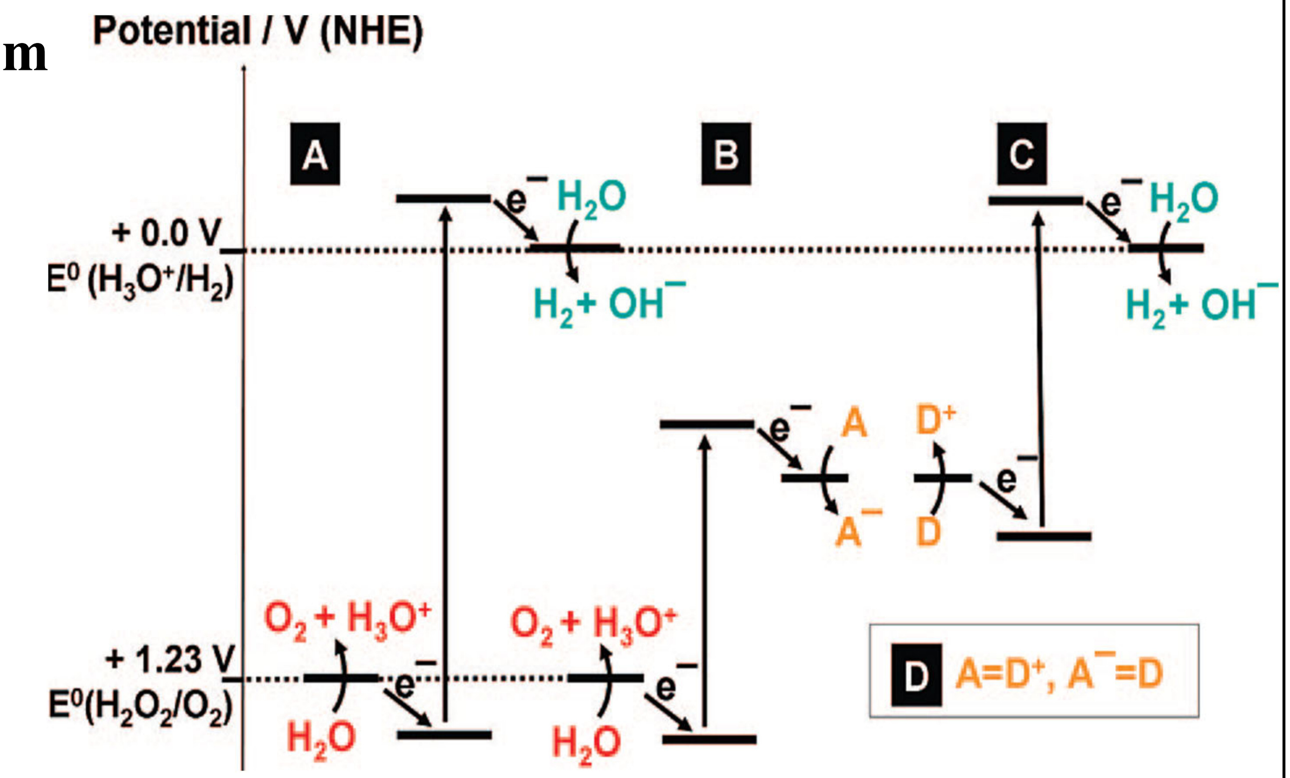
Schematic representation of visible light-driven H_2 production with D [NiFeSe]-H attached on ruthenium-dye sensitized TiO_2 nanoparticles, in the presence of a sacrificial electron donor D.

Visible light irradiation ($\lambda > 420$ nm) excites the Ru(bipy)$_3$ photo-sensitizer, which injects electrons into the conduction band of TiO_2 and on to the hydrogenase, resulting in H^+ reduction.

Lit.: F. A. Armstrong, E. Reisner et al., Chemical Society Reviews, 2008

8. Catalysis in Inorganic Chemistry

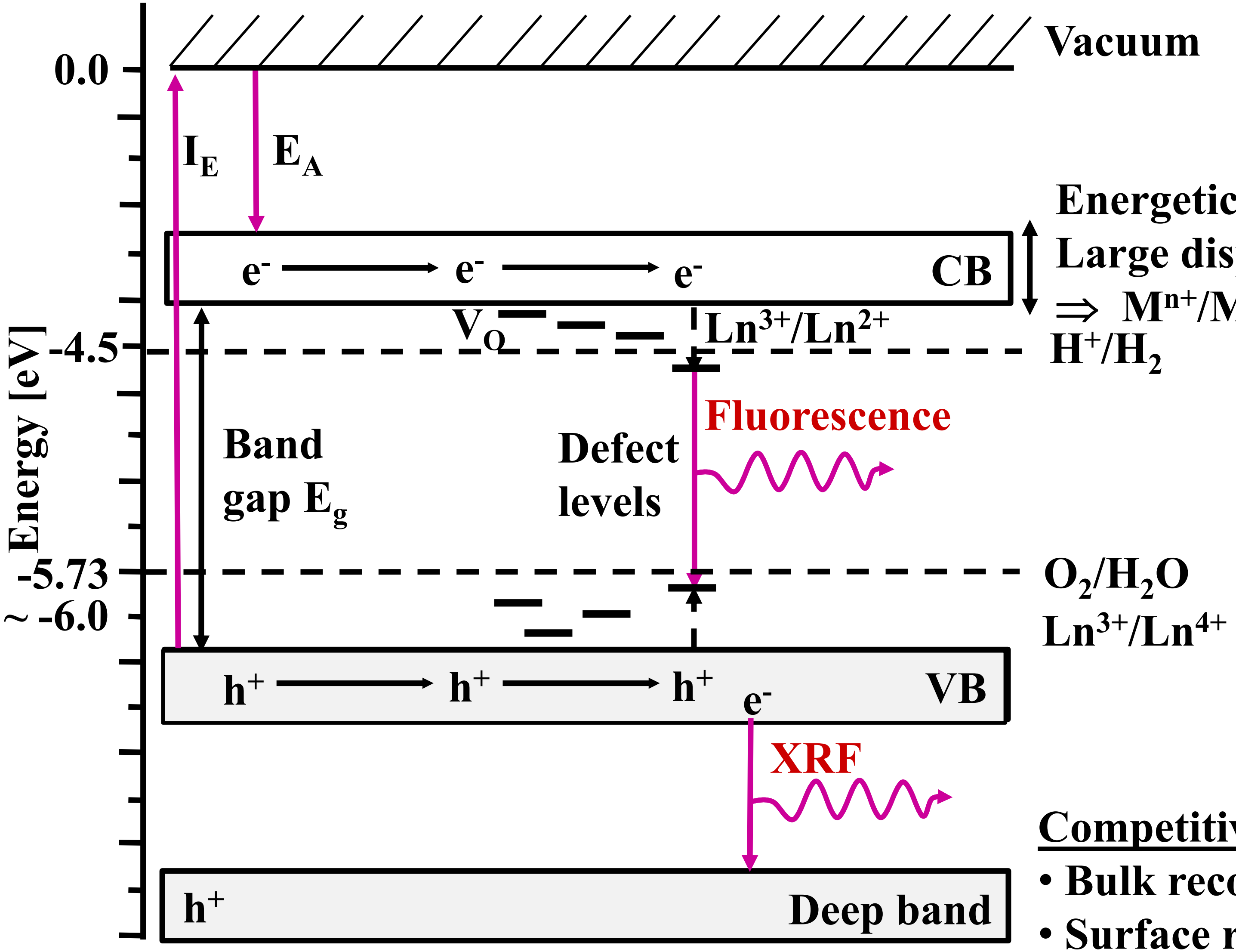
Photocatalytic Process by Using Semiconductors - Approaches



- A: single semiconductor system
- B: single semiconductor system with electron acceptor → O_2
- C: single semiconductor system with electron donor → H_2
- D: combination of B and C → tandem system → Z-Scheme (photosynthesis)

8. Catalysis in Inorganic Chemistry

Required Electrochemical Potentials for a Single Semiconductor System



Energetic pos. compliable for H^+ red.
Large dispersion for high e^- mobility
⇒ M^{n+}/M^{n+}

Material aimed at

- $E_A \sim -3.5 - -4.5$ eV
- $E_g \sim 3.0 - -4.0$ eV
- $\Delta E(E_{Ln3+/4+}$ - CB) ~ 2.0 eV
- ΔE(CB - $E_{Ln2+/3+}$) < 1.0 eV

⇒ Ln = Pr, Nd, Ho, Er

Competitive Processes to Photolysis

- Bulk recombination ⇒ Fluorescence
- Surface recombination ⇒ Heat

8. Catalysis in Inorganic Chemistry

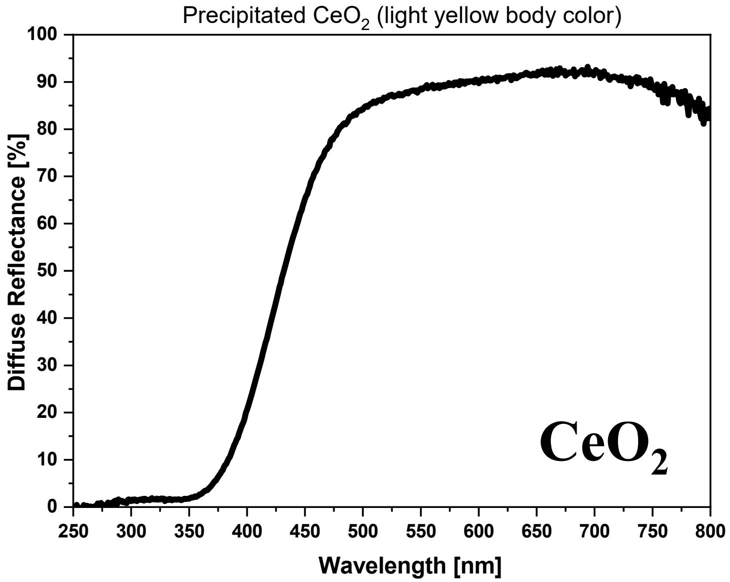
Requirements on Inorganic Photocatalysts

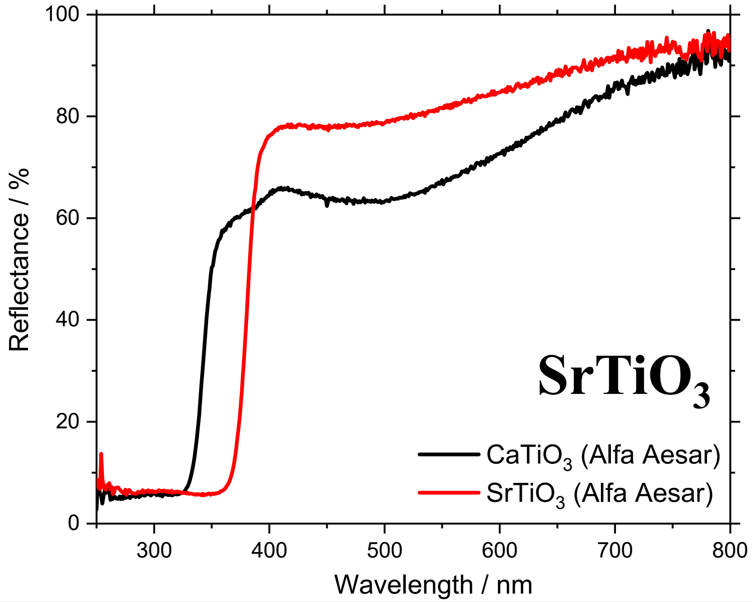
- Stability in water
  The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3.0 eV), or their semiconductor characteristics are poor.
- Efficiency (band gap)
  For reasonable solar efficiencies, the band gap must be less than 2.2 eV, unfortunately, most useful semiconductors with band gaps in this range are photochemically unstable in water.
- Energetics
  In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energy levels where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.

8. Catalysis in Inorganic Chemistry

Stability

Oxide	Band gap [eV]	Body colour
$ZrSiO_4$	6.5	white
ZrO_2	5.0	white
$CaWO_4$	4.1	white
ZnS	3.8	white
$CaTiO_3$	3.5	white
$KTaO_3$	3.4	white
ZnO	3.3	white
$SrTiO_3$	3.2	white
TiO_2	3.0	white
CeO_2	2.8	yellow
WO_3	2.7	yellow
$BiVO_4$	2.4 - 2.5	yellow
CdS	2.3	orange
Fe_2O_3	2.0	red
InN	1.9	red

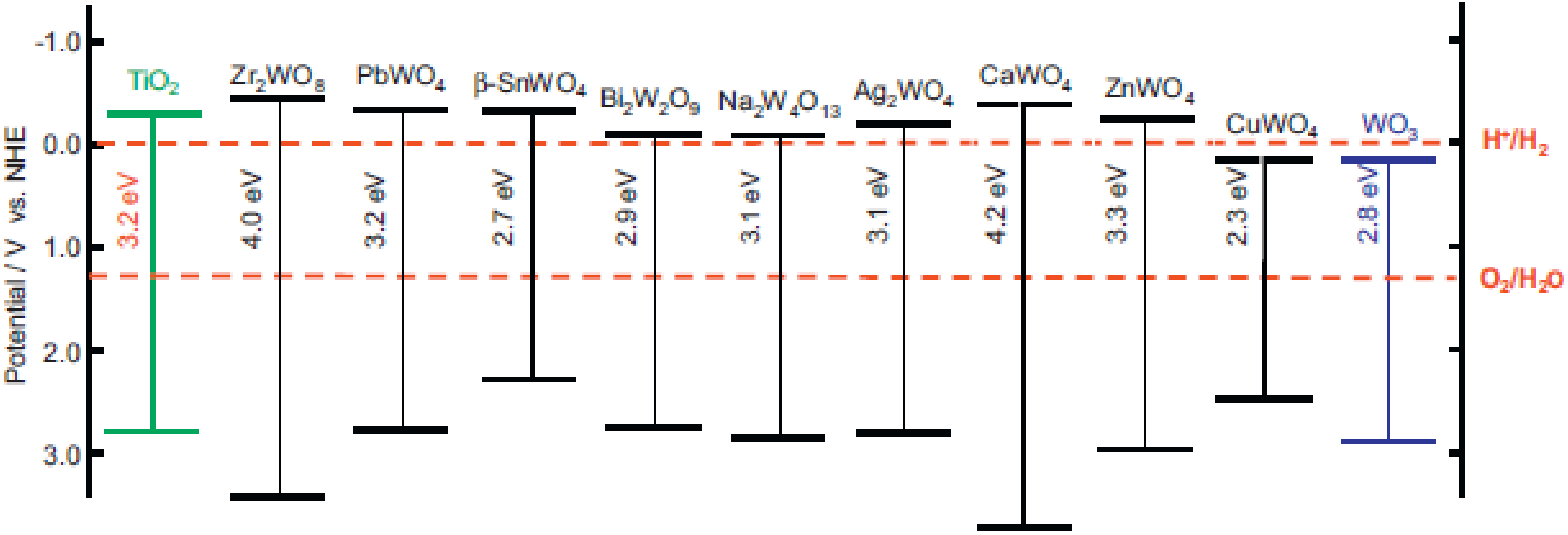




8. Catalysis in Inorganic Chemistry

Efficiency and Energetics

Band gap	**2.0 – 3.0 eV**
Valence band	**~ -6.0 V below vacuum level**
Conduction band	**above -4.0 V below vacuum level**



8. Catalysis in Inorganic Chemistry

Efficiency and Energetics

Band gap	**2.0 – 3.0 eV**
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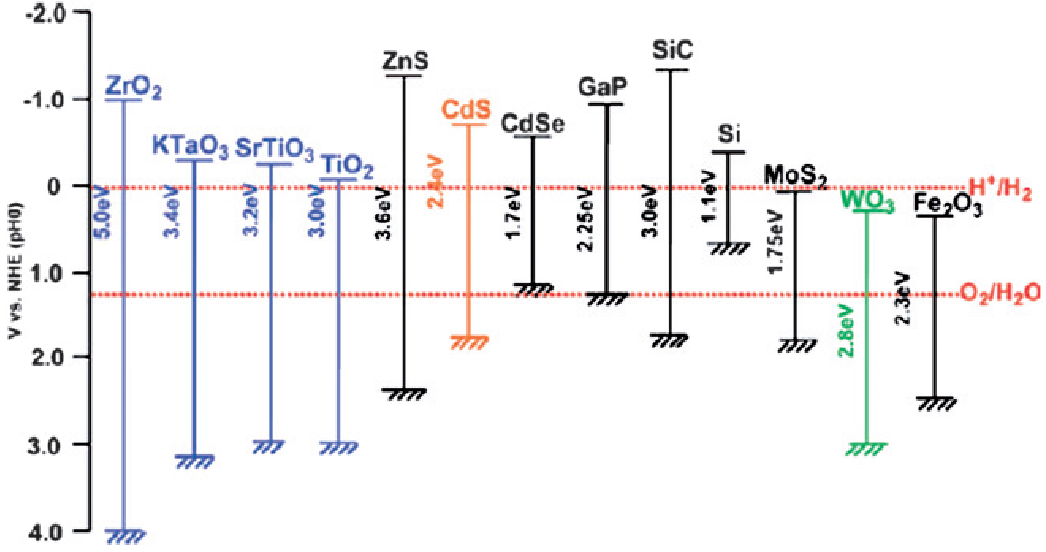
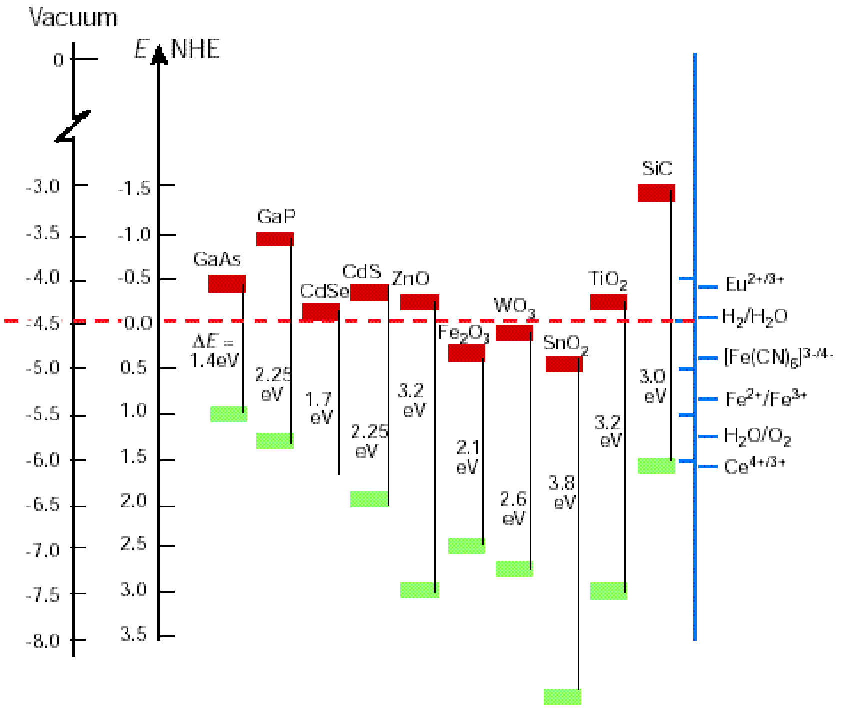




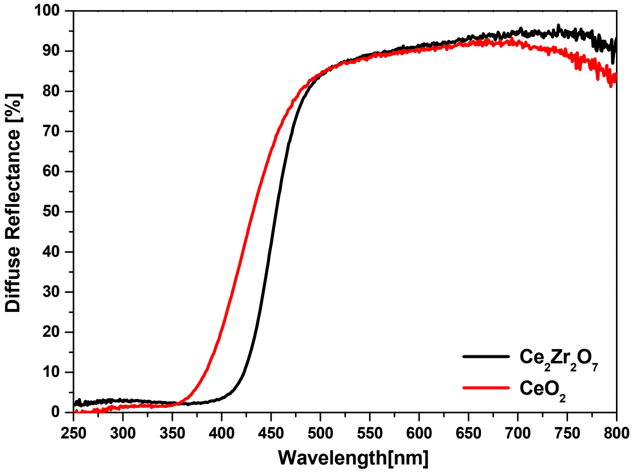
8. Catalysis in Inorganic Chemistry

Photocatalysts with Cubic Structures

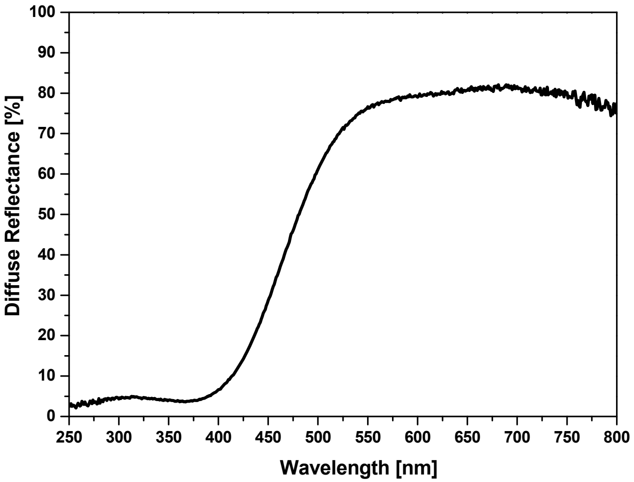
Absorption edge between 2.0 and 3.0 eV

Material class	Band gap [eV]
$MeTi_xO_y$	3.2 - 3.8
$Ce_xW_yO_z$	2.5 - 2.8
$Ln_xZr_yO_z$	2.5 - 3.5
$Bi_xW_yO_z$	3.1 - 3.5
$Ln_2W_2O_9$	3.4 - 3.7
$Me_xW_yO_z$	4.4 - 6.8
$Me_xTa_yO_z$	4.6
$Me_xNb_yO_z$	2.4 - 3.8
$BiVO_4$	2.4
$NaBiMo_2O_8$	3.1

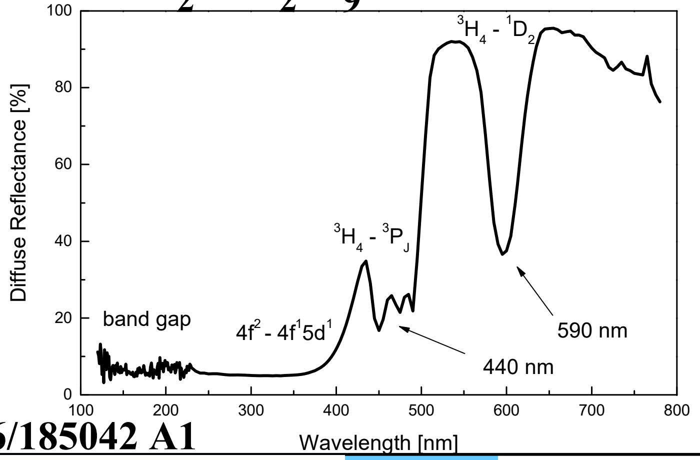
$Ce_2Zr_2O_7$



Ba_2CeTaO_6



$Pr_2Mo_2O_9$



Note: Doping as an option to modify absorption edge and stability, e.g. $Pr_2Mo_2O_9$:Ce, $Ce_2Zr_2O_7$:Pr

Lit.: WO Patent: J. Werner, N. Kratz, T. Jüstel, et al., Photocatalyst, WO2016/185042 A1

8. Catalysis in Inorganic Chemistry

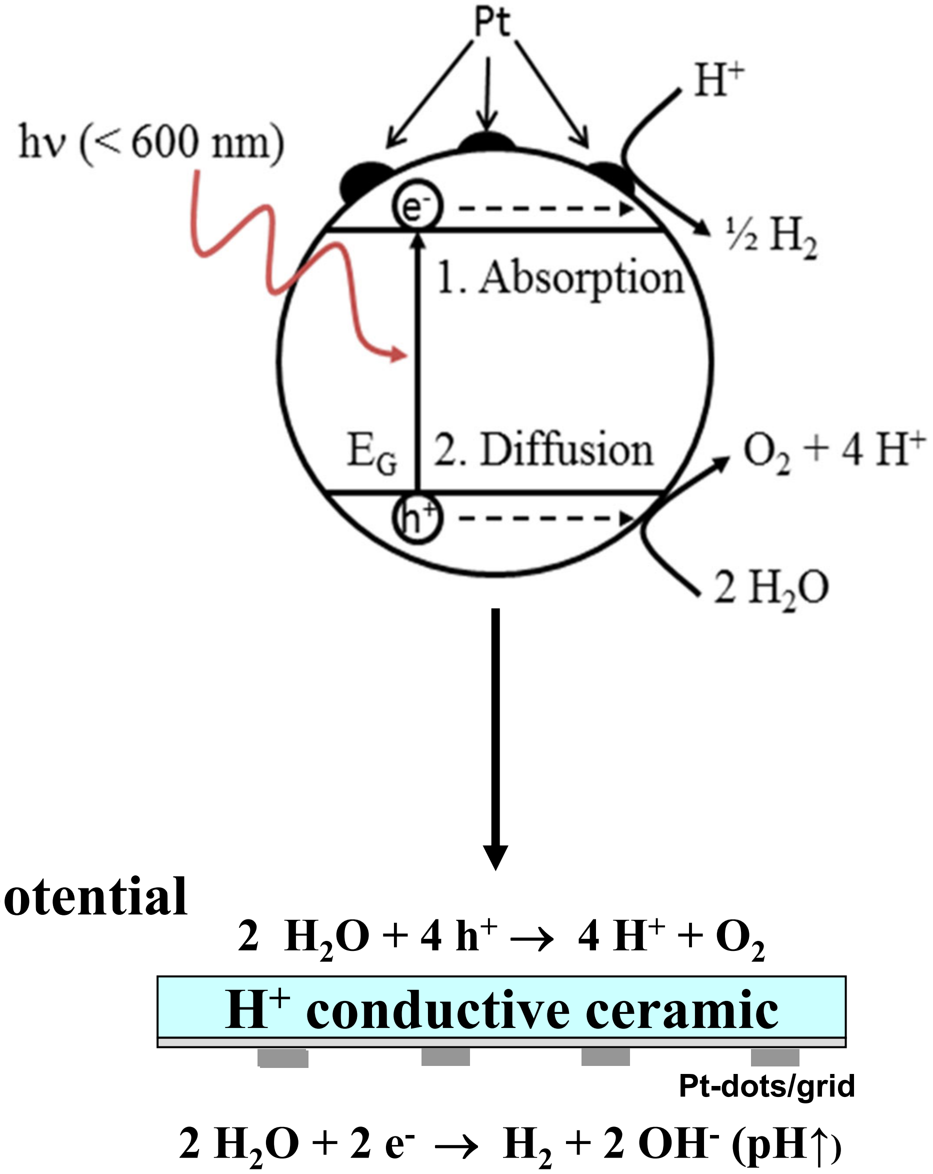
Photocatalysts: From Powder to Ceramics

Problem of powders in water:
Production of detonating gas due to the lack of OER and HER separation

Solution:
Application of a H^+ conductive ceramic to avoid build-up of pH gradient

OER: **Oxidic material with high oxidation potential**
MnO_2, CoO_2, RuO_2, IrO_2, ….

HER: **Structured Noble metal, e.g. Pt**

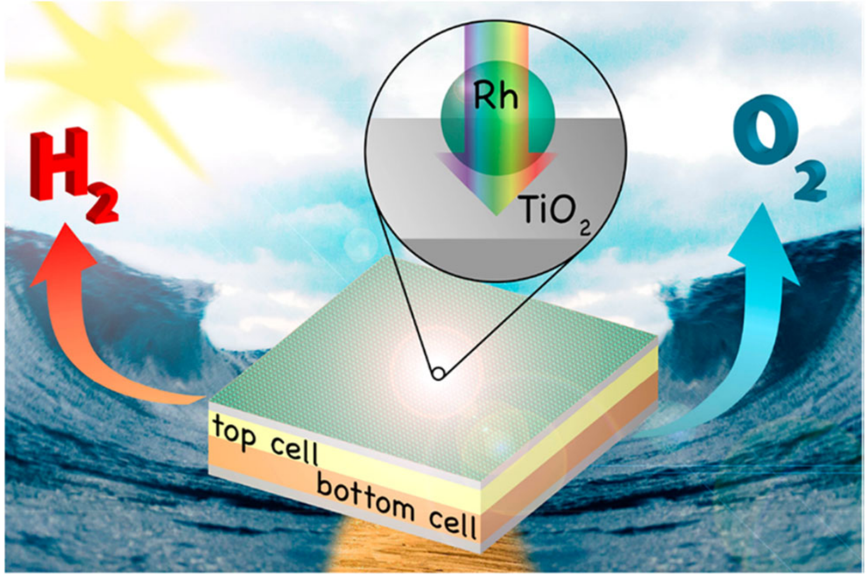


$2\ H_2O + 4\ h^+ \rightarrow 4\ H^+ + O_2$

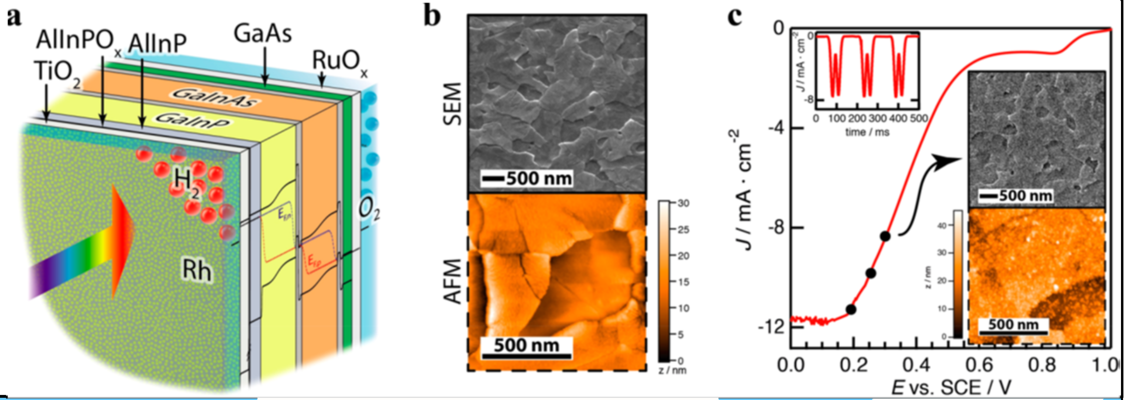
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ (pH↑)

8. Catalysis in Inorganic Chemistry

Photocatalysts: From Powder to Ceramics



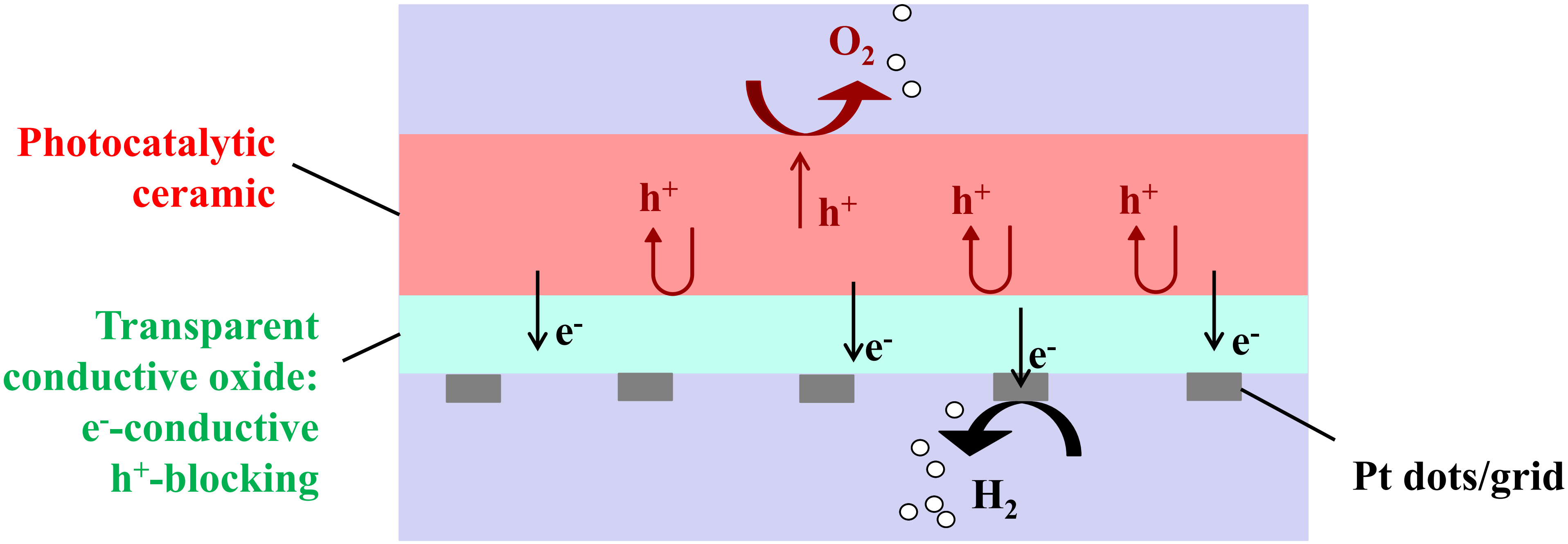
- Water stable charge carrier separating and e^-/h^+ conductive by a layered ceramic
- Goal: Relief of evolving pH gradient
- OER: RuO_x
- Potential role of $Mn^{3+}/Mn^{4+}/Mn^{5+}$ for oxidation of OH^- as in $[Mn_4Ca]^{n+}$-Cluster of PSII:
  $[Mn^{3+}]_{octahedral} + 2\ h^+ \rightarrow [Mn^{5+}]_{tetrahedral}$
  $[Mn^{5+}]_{tetrahedral} + 2\ OH^- \rightarrow [Mn^{3+}]_{octahedral} + 2\ OH^{\cdot} \rightarrow H_2O_2 \rightarrow H_2O + ½\ O_2$
- HER: Ni, Pd, Pt, Co, Rh, or Ir
- 19% direct conversion efficiency



Lit.: ACS Energy Lett. 2018, 3, 1795−1800

8. Catalysis in Inorganic Chemistry

Photocatalysts: From Powder to Ceramics

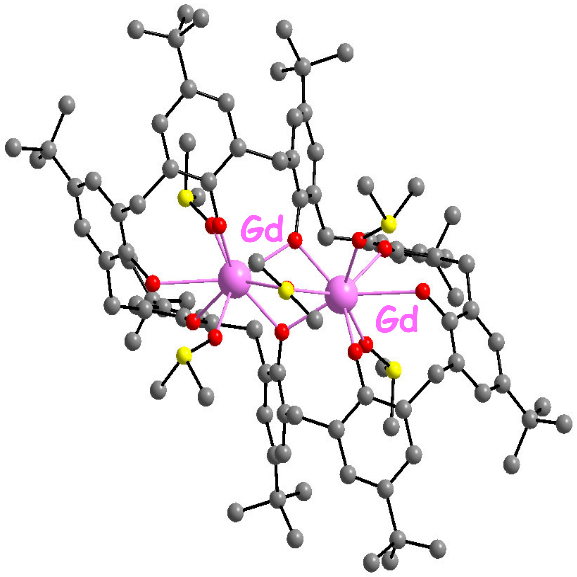


Photochemical water splitting → The "Holy Grail of Chemistry"

9. Lanthanides and Actinides

Atoms and ions with f-electrons

Definitions



Lanthanides:	**58-71**	**Ln**
Actinides:	**90-103**	**An**

Parent elements La and Ac are often included in Ln and An

Rare earths: Sc, Y, La + Ce-Lu

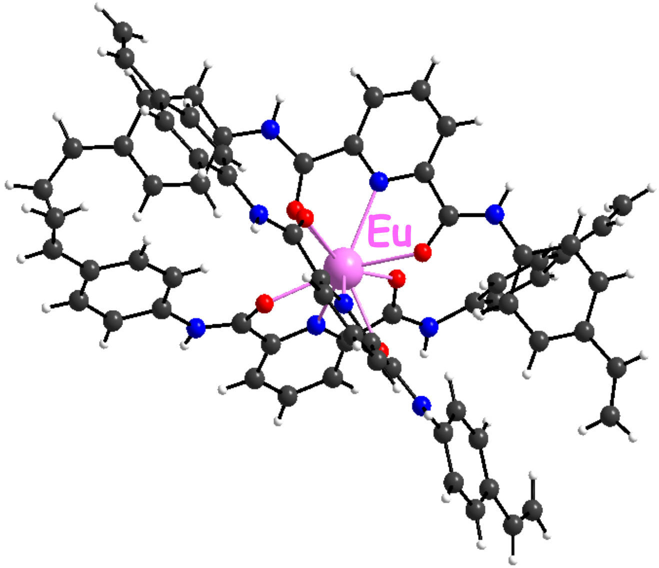
Discovery of rare earths

1794 (Y) – 1947 (Pm)

Discovery of actinides

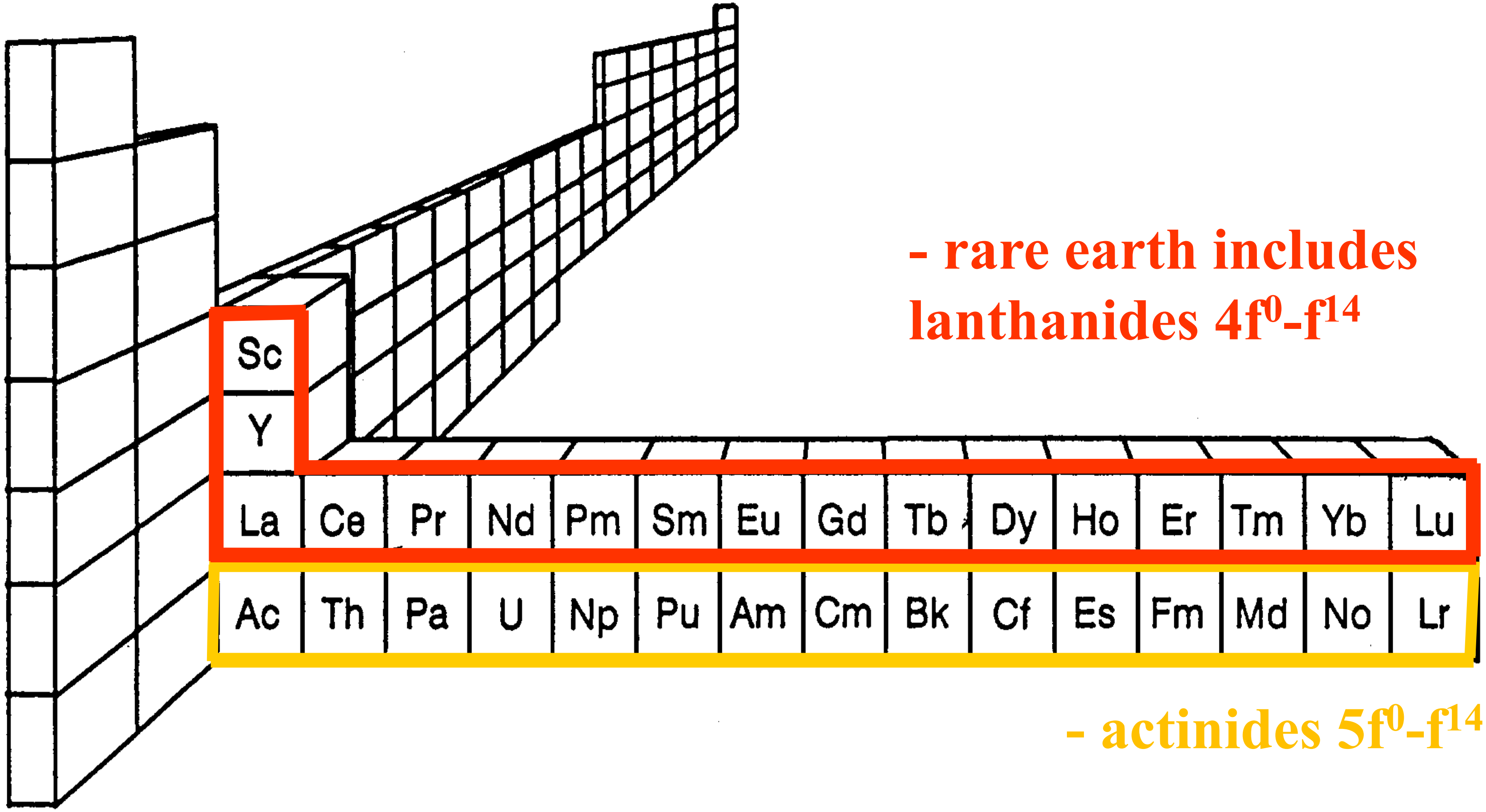
1789 (U) – 1971 (Lr)

Naturally occurring: Ac, Th, Pa, U, (Np, Pu)



9. Lanthanides and Actinides

Atoms and ions with f-orbitals



- rare earth includes lanthanides $4f^0$-f^{14}

- actinides $5f^0$-f^{14}

Yttrium was discovered in 1794 by Johan Gadolin, in Åbo (Turku)

9. Lanthanides and Actinides

Discovery of Yttrium (1794)

1787 Carl Axel Arrhenius, an artillery lieutenant and amateur geologist, found a black mineral in a quarry near Ytterby, 30 km away from Stockholm

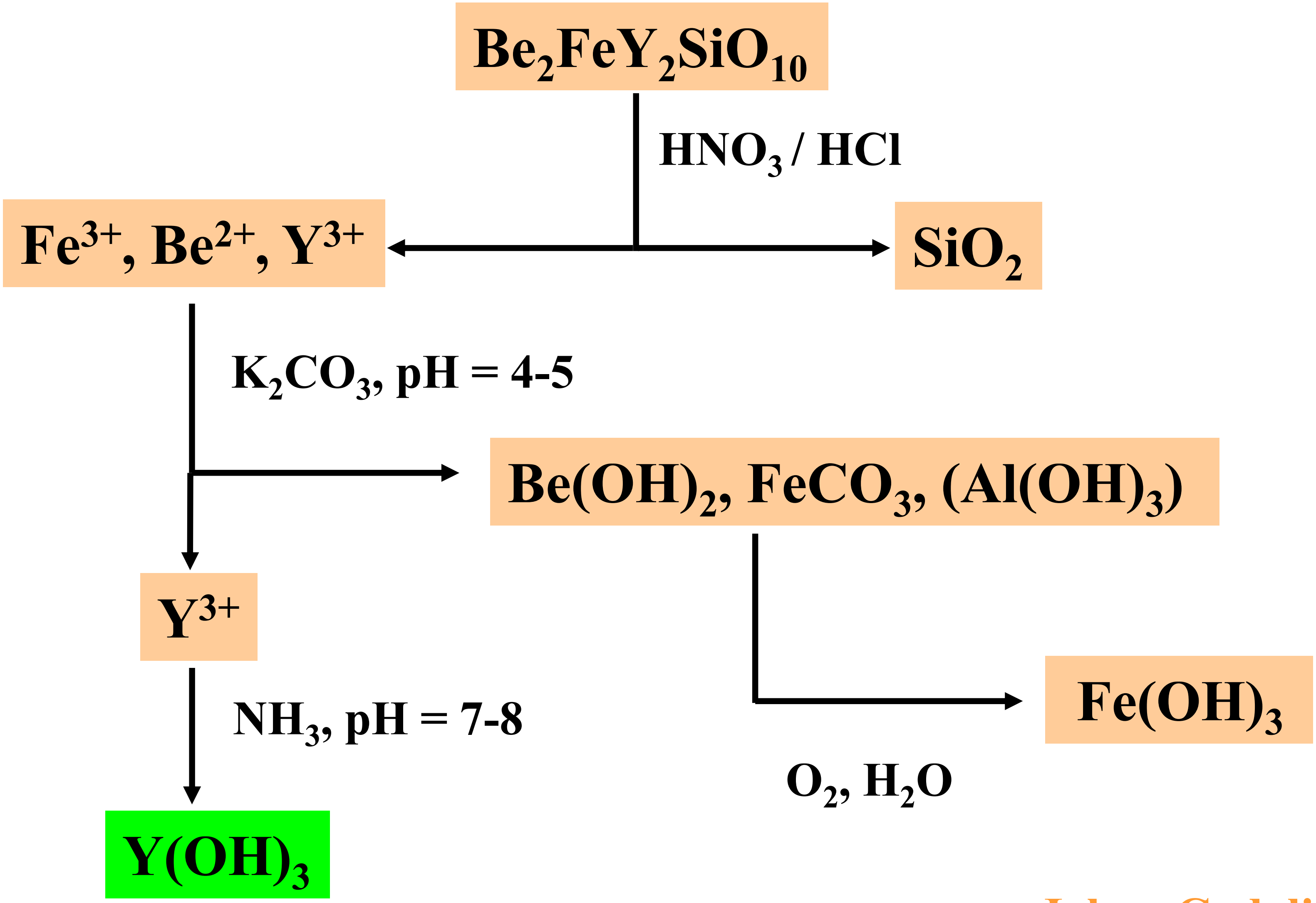
1788 B.R. Geijer (Stockholm) described the mineral (density = 4.25) and named it ytterbite, presently known as gadolinite, with the formula $Be_2FeY_2SiO_{10}$ (Gadolinite)

1792 Johan Gadolin (1760-1852) studied the mineral and published a 19-page report in 1794 in the Proceedings of the Royal Swedish Academy of Sciences, concluding to the presence of a new "earth", which he named Yttrium

Subsequent work revealed that yttrium contained the oxides of 10 other elements

9. Lanthanides and Actinides

Chemical Separation of Yttrium



$Be_2FeY_2SiO_{10}$

HNO_3 / HCl

Fe^{3+}, Be^{2+}, Y^{3+}

SiO_2

K_2CO_3, pH = 4-5

$Be(OH)_2$, $FeCO_3$, $(Al(OH)_3)$

Y^{3+}

NH_3, pH = 7-8

$Fe(OH)_3$

O_2, H_2O

$Y(OH)_3$

Johan Gadolin, 1794

9. Lanthanides and Actinides

Discovery of Cerium (1804)

1751 The mineralogist Cronstedt found a peculiar heavy stone near Bastnäs

1803 W. Hisinger and J.J. Berzelius analysed this stone and found that it contains an unknown "earth", which they named ceria after the recently discovered planet Ceres. Their findings were published in 1804 in a 24-page report and confirmed by the German chemist Klaproth

The silicate type material has a variable composition close to $(Ce,La)_3M^{II}H_3Si_3O_{13}$ and is presently named cerite (M = Ca, Fe)

9. Lanthanides and Actinides

Discovery of other rare Earth Elements (1839-1947)

- Most of the other rare earths were discovered by further analysing the two initial minerals, viz. gadolinite and cerite

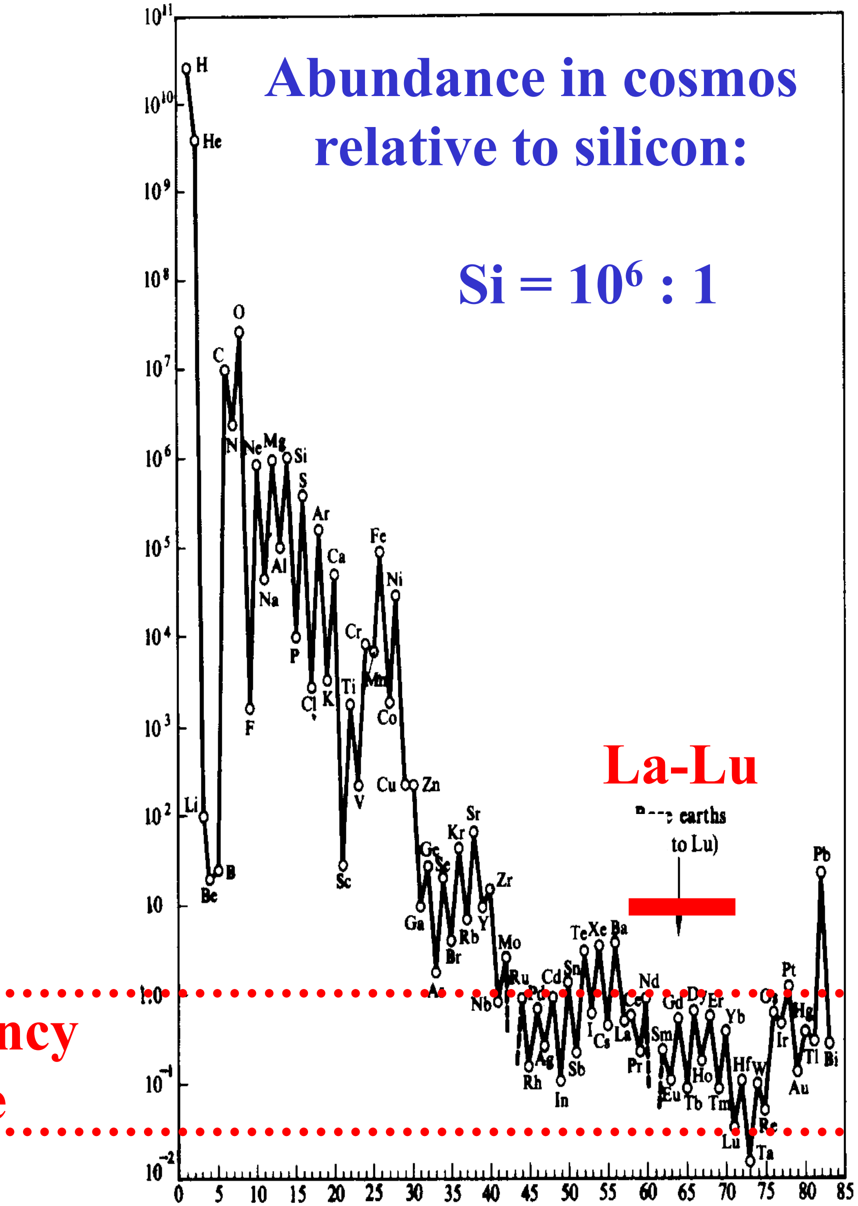
- The main techniques were fractional precipitation and crystallisation, as well as flame spectroscopy (absorption and emission)

- These operations were tedious: for instance, 20 tons were needed to produce 82 mg of element # 61 by ion-exchange separation techniques (61 = radioactive promethium), that is a fraction equal to $4x10^{-12}$!)

9. Lanthanides and Actinides

Occurrence of 4f Elements

The elements are “rare” but not rarer than many other metals, such as Au, Pt, Pd, or Rh



Abundance in cosmos relative to silicon:

Si = 10^6 : 1

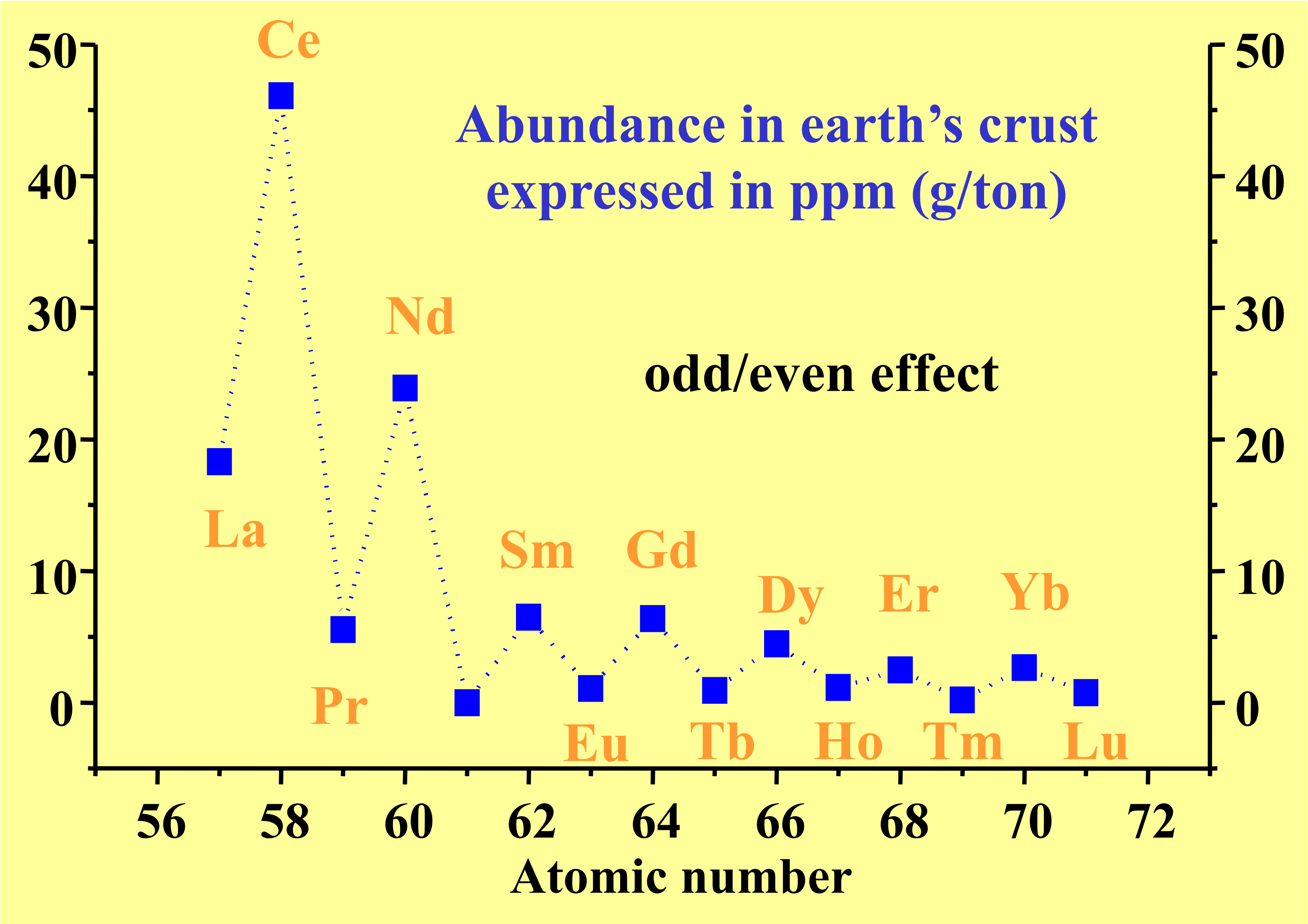
La-Lu

Abundancy range

9. Lanthanides and Actinides

Occurrence of 4f Elements

Oddo-Harkins rule = odd/even effect



9. Lanthanides and Actinides

Main Minerals/Ores of 4f Elements

Cerium group (lighter elements)

Bastnasite	$Ln(CO_3)F$	65-70%
Monazite	$LnPO_4$	50-75%
Cerite	$(Ce,La)_3M^{II}H_3Si_3O_{13}$	50-70%

Yttrium group (heavier elements)

Xenotime	$LnPO_4$	55-65%
Gadolinite	$Ln_2M_3Si_2O_{10}$	35-50%
Euxenite	$Ln(Nb,Ta)TiO_6xH_2O$	15-35%

9. Lanthanides and Actinides

Ressources of 4f Elements

World reserves (2018) are estimated to 116.1 million metric tons for a present usage of about 160,000 metric tons a year

China	44 mill. tons
Vietnam	22 mill. tons
Brazil	22 mill. tons
Russia	12 mill. tons
India	6.9 mill. tons
Australia	3.4 mill. tons
USA	1.4 mill. tons
Other	4.4 mill. tons

Bayan Obo mine (Inner Monolia)

Baotou (Inner Mongolia)

Lit.: R. Pöttgen, T. Jüstel, C. Strassert, Rare Earth Chemistry, De Gruyter 2020

9. Lanthanides and Actinides

Application Areas of 4f Elements

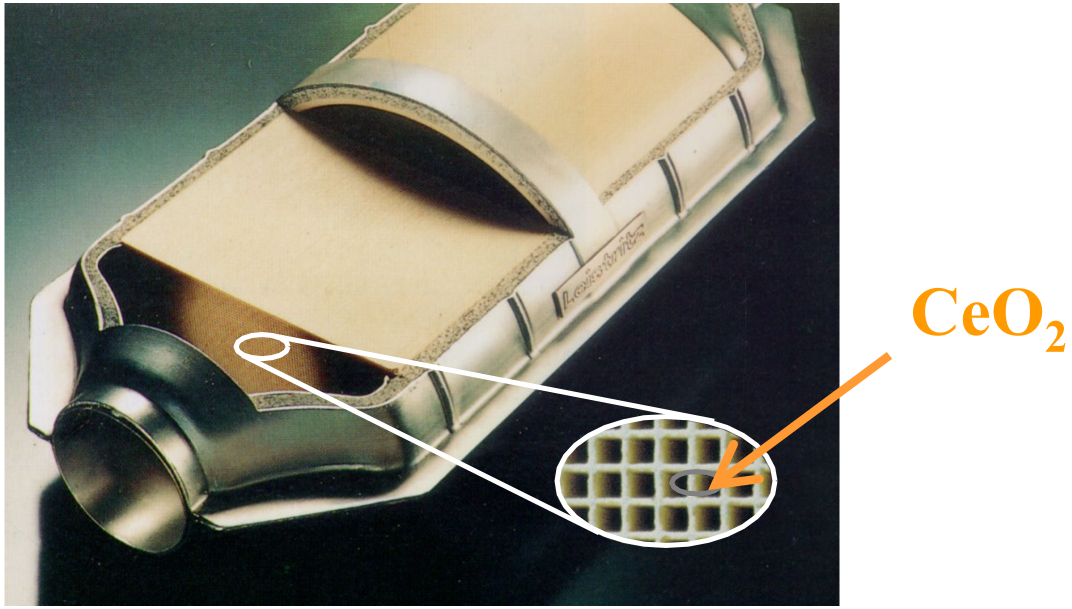
- **Catalysts**
  - cracking of hydrocarbons
  - conversion of exhaust gases (gasoline and diesel)

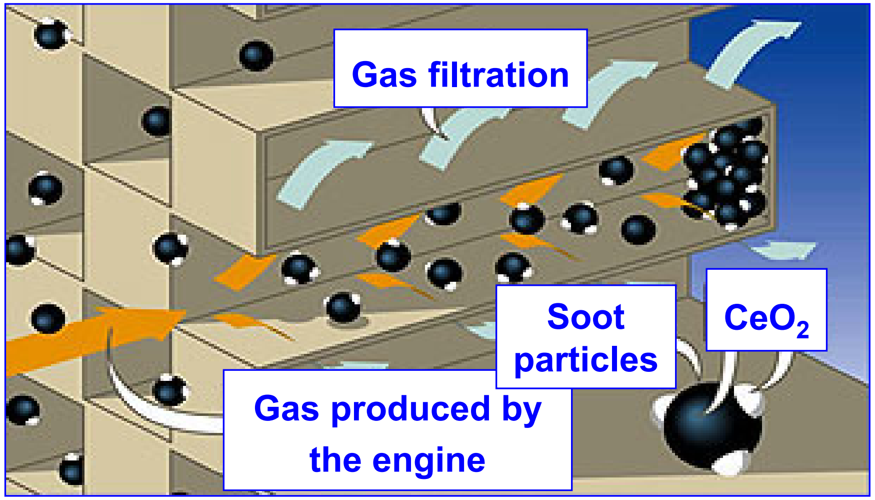
- **Metallurgy**
  - Steel production (removal of O, S)
  - Nodular graphite
  - Hardener (*e.g.* in magnesium)

- **Materials**
  - High temperature superconducting ceramics
  - Electronic devices (capacitors, O_2-sensors)
  - Magnets (Sm_5Co, Nd_5Fe)
  - Neutron moderators in nuclear reactors
  - Hydrogen storage with metal hydrides

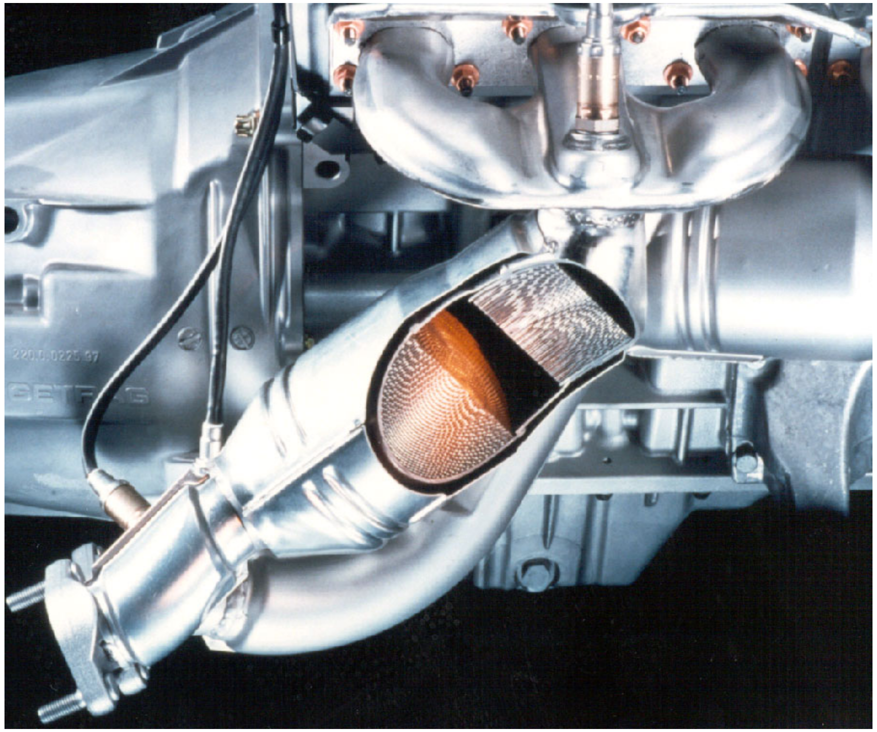
9. Lanthanides and Actinides

Application Areas of 4f Elements





Eolys Powerflex® (Rhodia)
Soot emission of Diesel engines reduced by about 99.9%

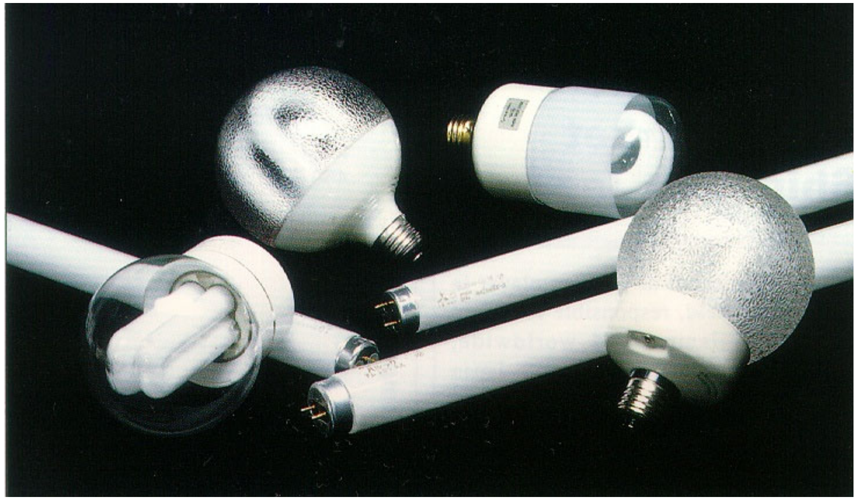


Application Areas of 4f Elements

- **Imaging, lighting, and optics**
  - Polishing powders
  - Protection against sun (sunglasses)
  - Laser gain media, e.g. YAG:Nd, YAG:Yb, KY_3F_{10}:Pr, KYW_2O_8:Eu
  - Amplifiers (YAG:Er)
  - Phosphors for displays (CRTs, PDPs, and electroluminescent screens)
  - Fluorescent lamps (CFLs, TLs, PLs, QLs, SLs, LEDs)
- **Medicine**
  - Seasickness (Ce oxalate), thromboses (Nd oxalate)
  - Renal insufficiency ($La_2(CO_3)_3 \cdot 4H_2O$)
  - X-ray intensifying screens
  - NMR imaging
  - Cancer treatment by radio- and phototherapy
  - Laser surgery (YAG:Nd laser)
  - Luminescent immunoassays
- **Science**
  - NMR shift reagents, luminescent and magnetic probes
  - Catalysts for organic chemistry

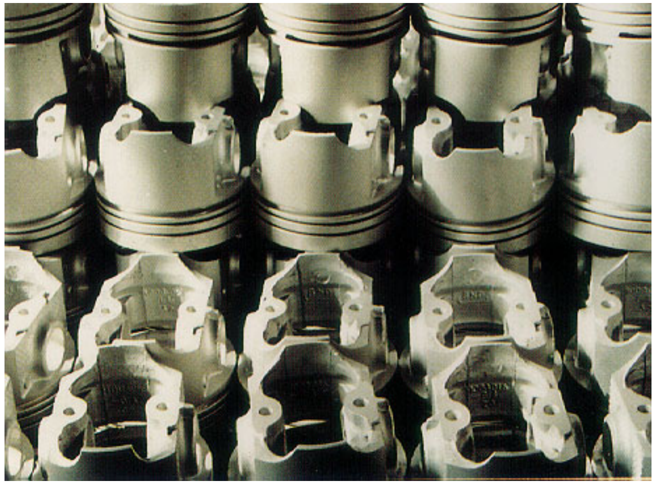
9. Lanthanides and Actinides

Application Areas of 4f Elements

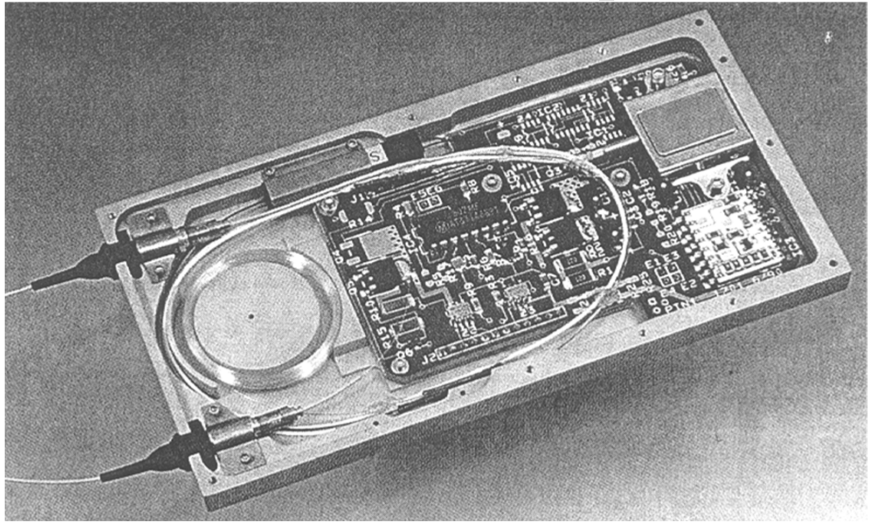


Fluorescent lamps

Pigments

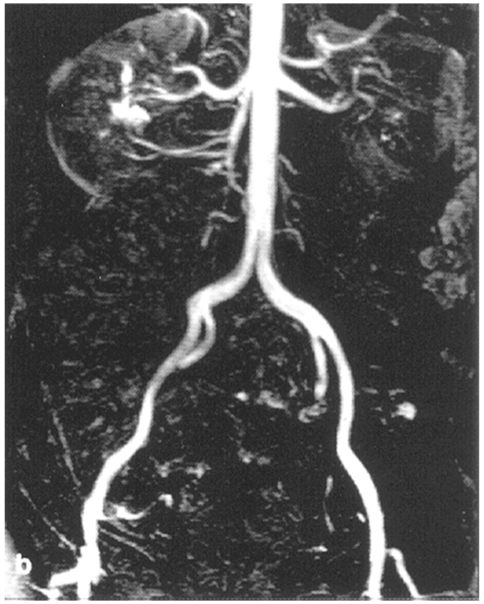


Re-inforced cast Al pistons



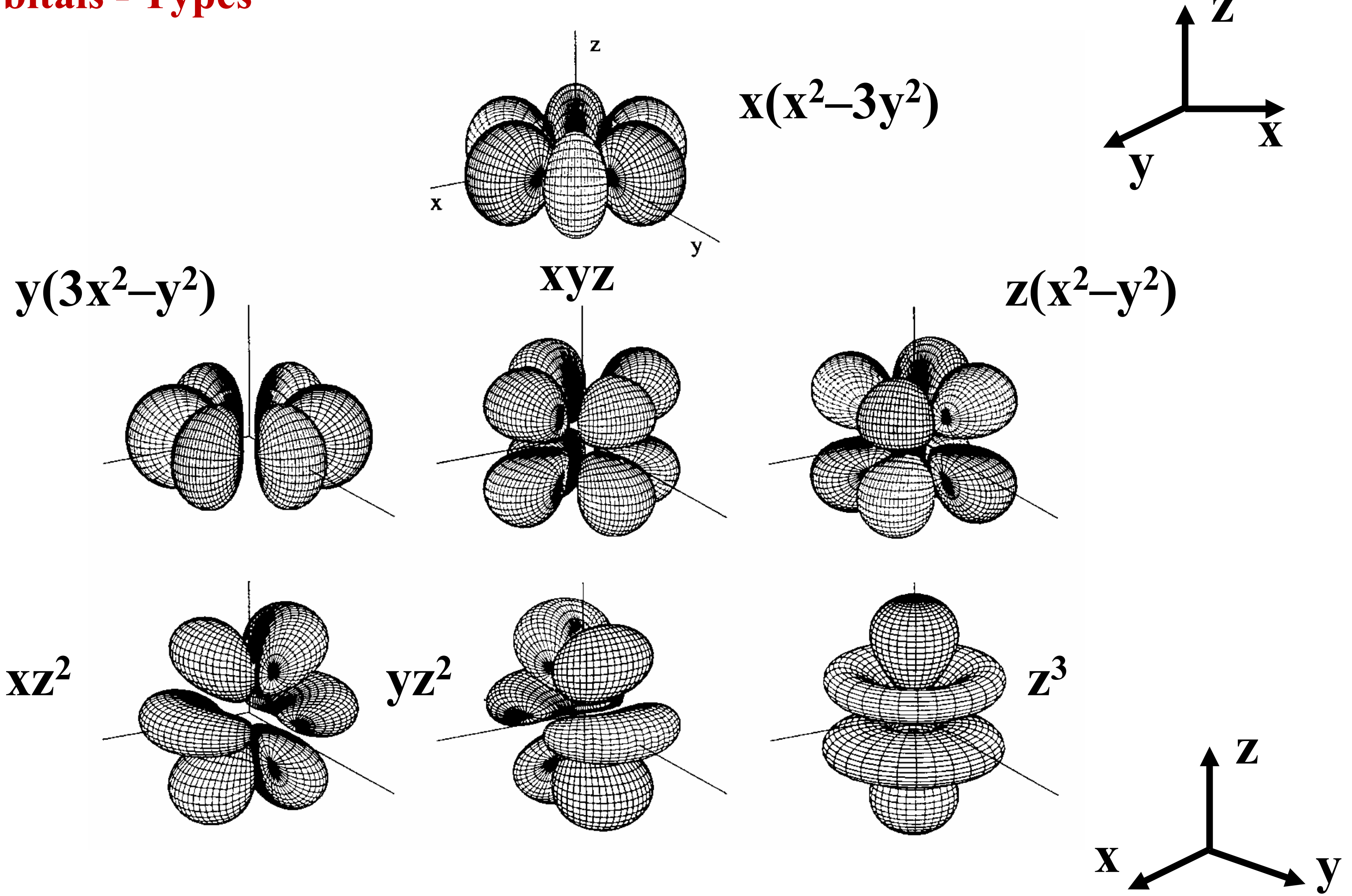
Er amplifier for optical fibers

Rechargeable batteries



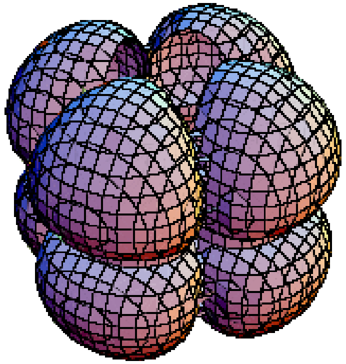
MRI images

4f and 5f Orbitals - Types

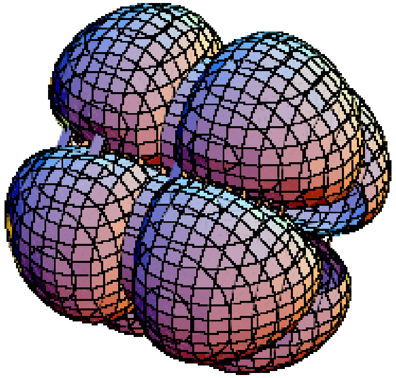


9. Lanthanides and Actinides

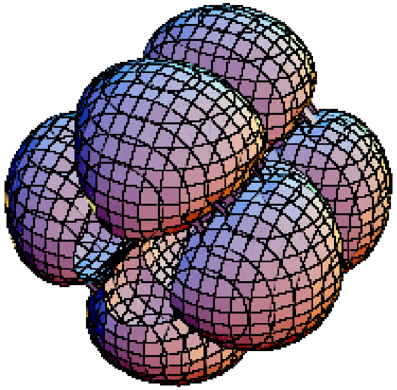
4f and 5f Orbitals - Symmetry



$z(x^2-y^2)$



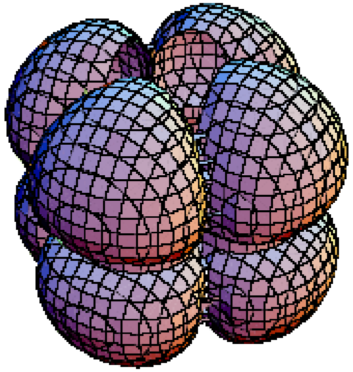
$y(z^2-x^2)$



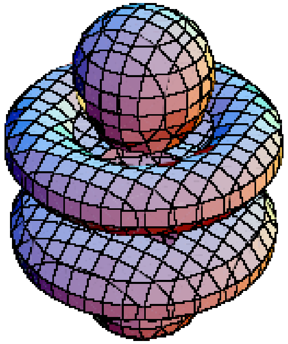
$x(z^2-y^2)$

T_{2u}

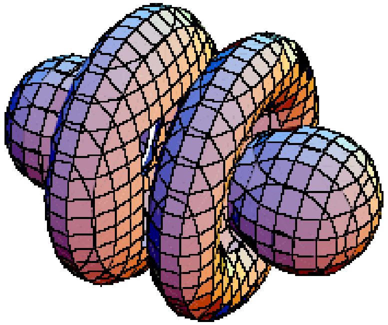
A_{2u}



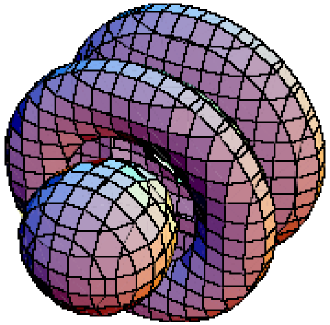
xyz



z^3

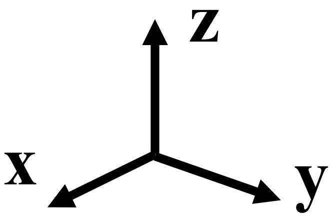


y^3



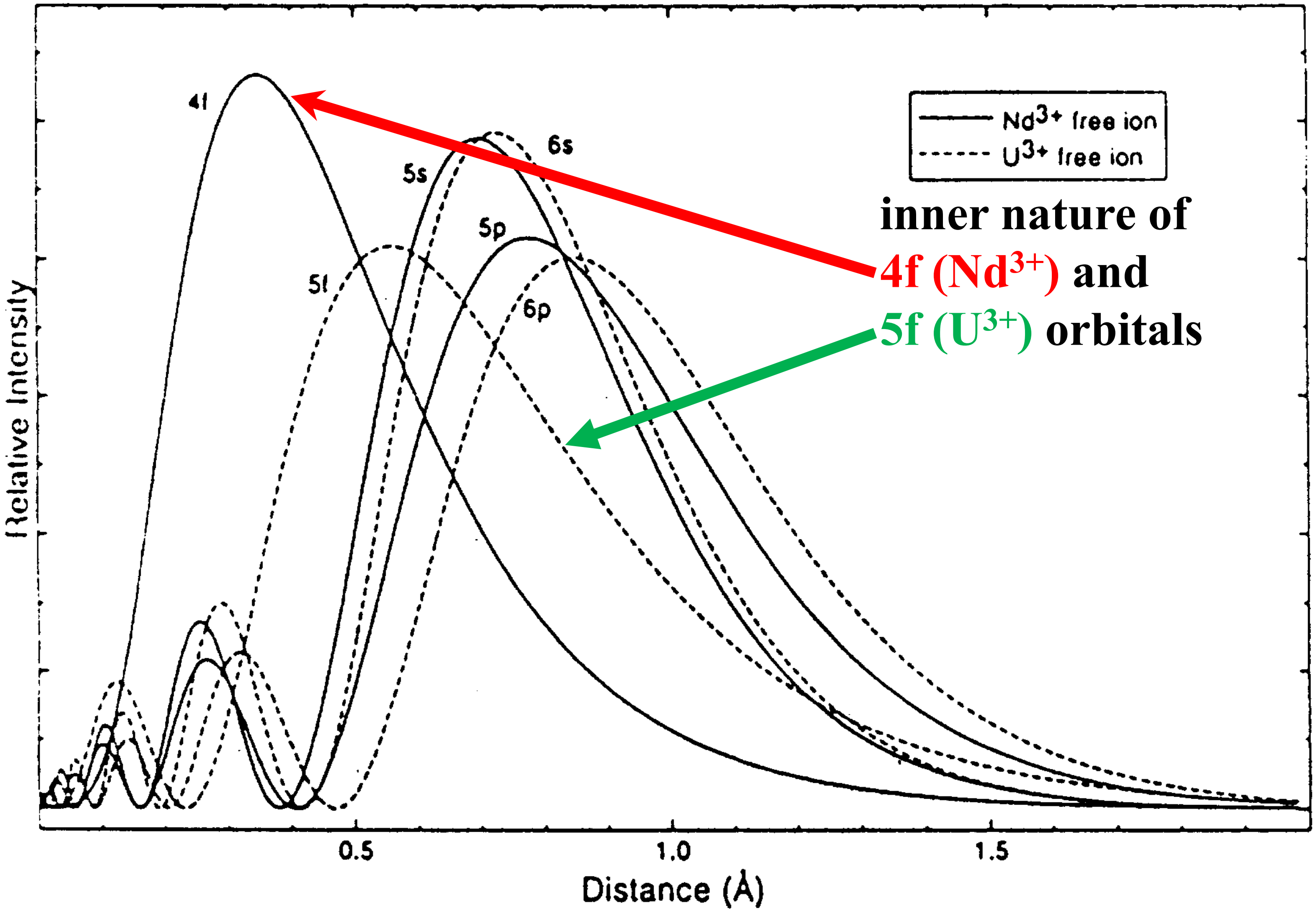
x^3

T_{1u}



9. Lanthanides and Actinides

4f and 5f Orbitals - Shielding

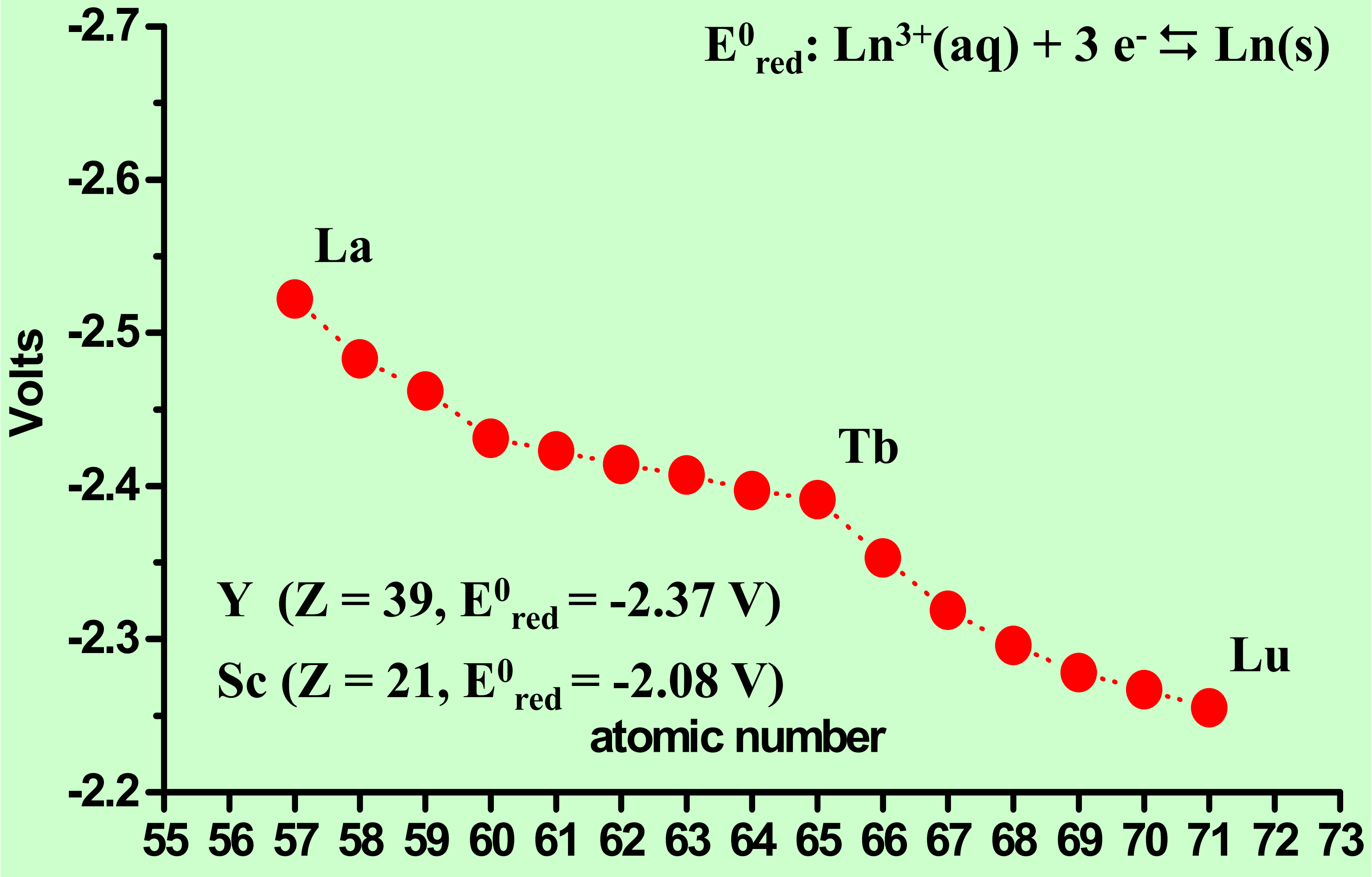


inner nature of **4f** (Nd^{3+}) and **5f** (U^{3+}) orbitals

9. Lanthanides and Actinides

4f Elements – Oxidation States

The most stable oxidation state of alle Ln elements is +III

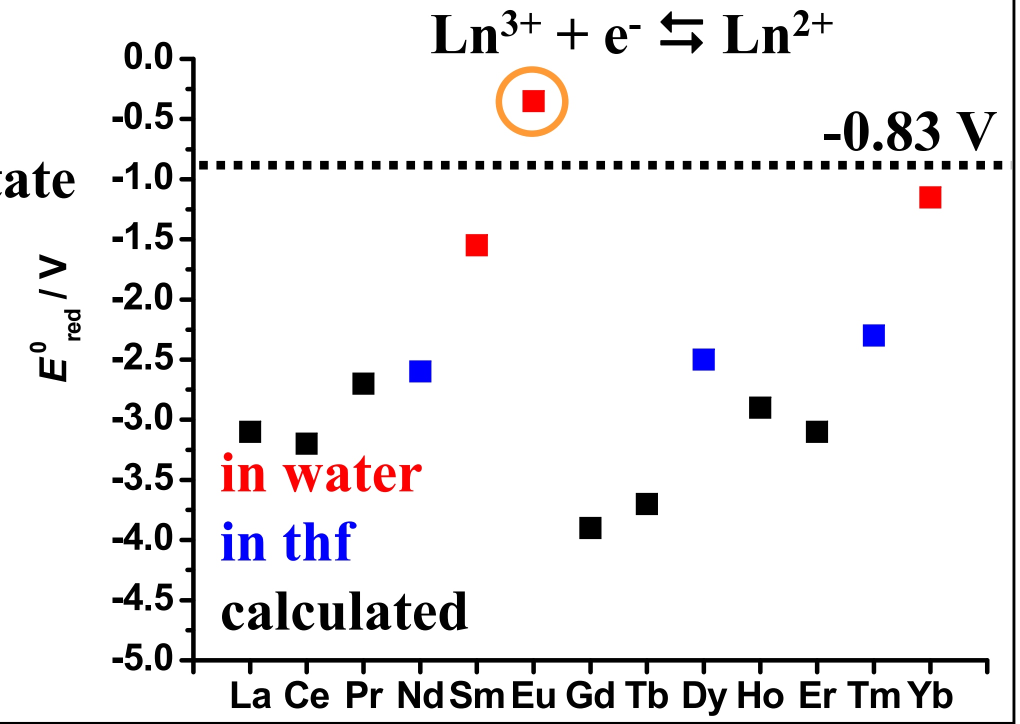


9. Lanthanides and Actinides

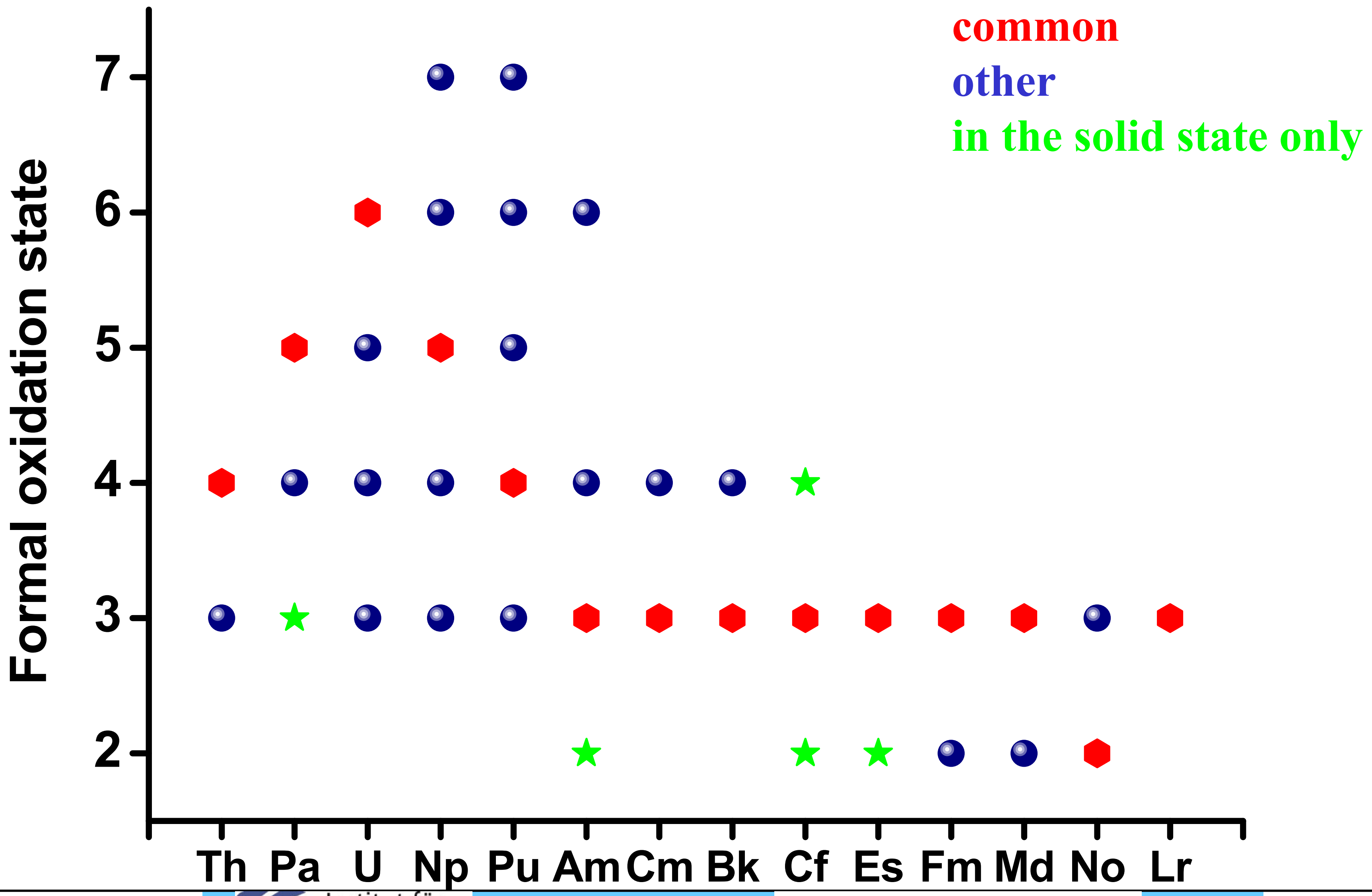
4f Elements – Oxidation States

- **Ce, Pr, Nd, and Tb can have +IV oxidation state**
  E^0_{red} for $Ln^{4+}(aq) + e^- \leftrightarrows Ln^{3+}(aq)$ in acidic solutions:
  +1.72 V for Ce^{4+}, stable in water
  +3.20 V for Pr^{4+}, oxidizes water
  +3.10 V for Tb^{4+}, oxidizes water

- **Sm, Eu, and Yb have rather stable +II state**
  E^0_{red} for $Ln^{3+}(aq) + e^- \leftrightarrows Ln^{2+}(aq)$ in acidic solutions:
  -0.35 V for Eu^{2+}, stable in water
  -1.15 V for Yb^{2+}, reduces water
  -1.56 V for Sm^{2+}, reduces water

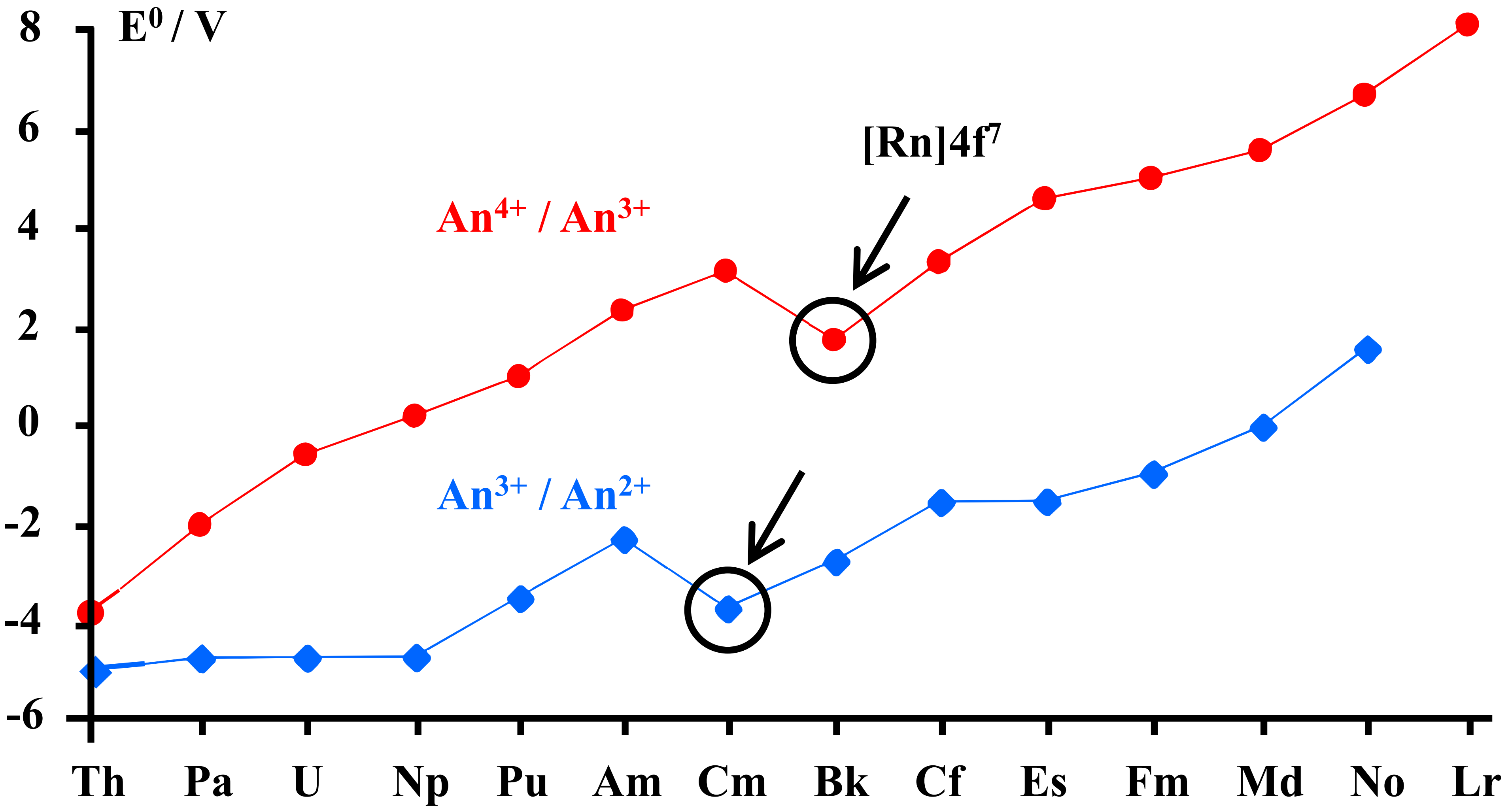


5f Elements – Oxidation States



9. Lanthanides and Actinides

5f Elements – Reduction Potentials



9. Lanthanides and Actinides

Electron Configuration of the Lanthanides and their Cations

Metals

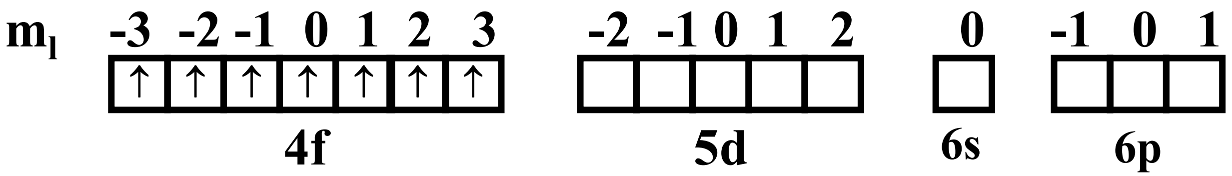
[Xe]	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14

Cations

[Xe]	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
	Ce^{4+}	Pr^{4+}	Nd^{4+}				Sm^{2+}	Eu^{2+}	Dy^{4+}					Tm^{2+}	Yb^{2+}
								Tb^{4+}							
4f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Examples

$Gd^{3+}/Eu^{2+}/Tb^{4+}$



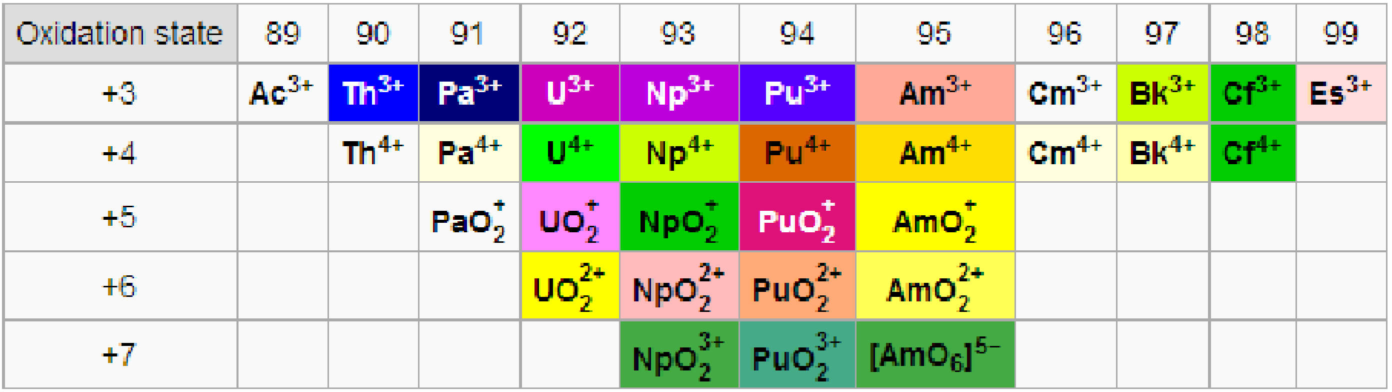
Total spin $S = \Sigma s = 7/2$ → $2S+1 = 8$ → highly paramagnetic cations

Electron Configuration of the Actinides and their Cations

Metals

[Rn]	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
7s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
6d	1	1	1	1	1	0	0	1	0	0	0	0	0	0	1
5f	0	1	2	3	4	6	7	7	9	10	11	12	13	14	14

Cations and their colours in aqueous solution



Oxidation state	89	90	91	92	93	94	95	96	97	98	99
+3	Ac^{3+}	Th^{3+}	Pa^{3+}	U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}
+4		Th^{4+}	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}	Bk^{4+}	Cf^{4+}	
+5			PaO_2^+	UO_2^+	NpO_2^+	PuO_2^+	AmO_2^+				
+6				UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}				
+7					NpO_2^{3+}	PuO_2^{3+}	$[AmO_6]^{5-}$				

9. Lanthanides and Actinides

Lanthanide and Actinide Contraction

Ln^{3+} ions: **116 pm → 100 pm (Lu^{3+})**

An^{3+} ions: **126 pm → 109 pm (Cf^{3+})**

An^{4+} ions: **123 pm → 107 pm (Pu^{4+})**

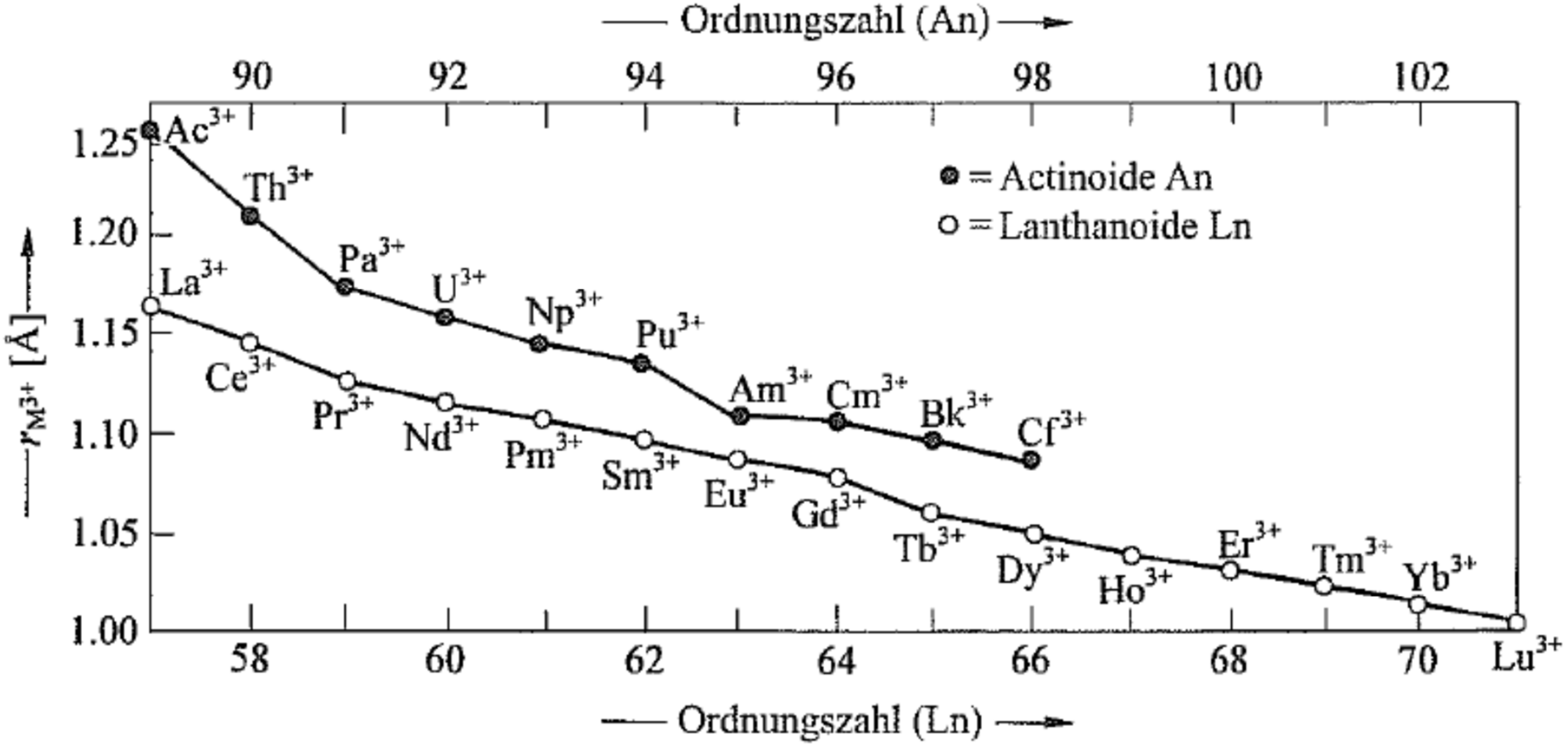


Fig. 394 Lanthanoid- und Actinoid-Kontraktion dreiwertiger Ionen $M^{3+} = Ln^{3+}$, An^{3+} (eine analoge Kontraktion beobachtet man bei den vierwertigen Ionen M^{4+}; vgl. Anhang IV).

9. Lanthanides and Actinides

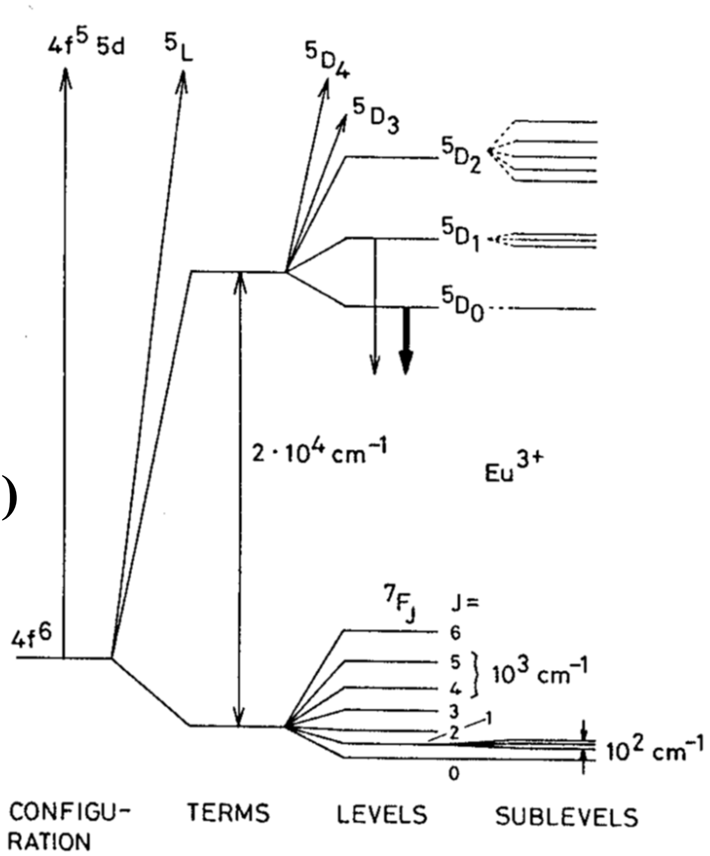
Energy Level Structure of Trivalent Lanthanide Ions

- Partly filled 4f shell, e.g. for Eu^{3+} [Xe]$4f^6$, i.e. 6 electrons in 7 4f-orbitals with two possible spin orientations: 14!/(6!(14-6)!) = 3003 different arrangements

- 4f shell well shielded from the outer and closed $5s^2$ and $5p^6$ shells

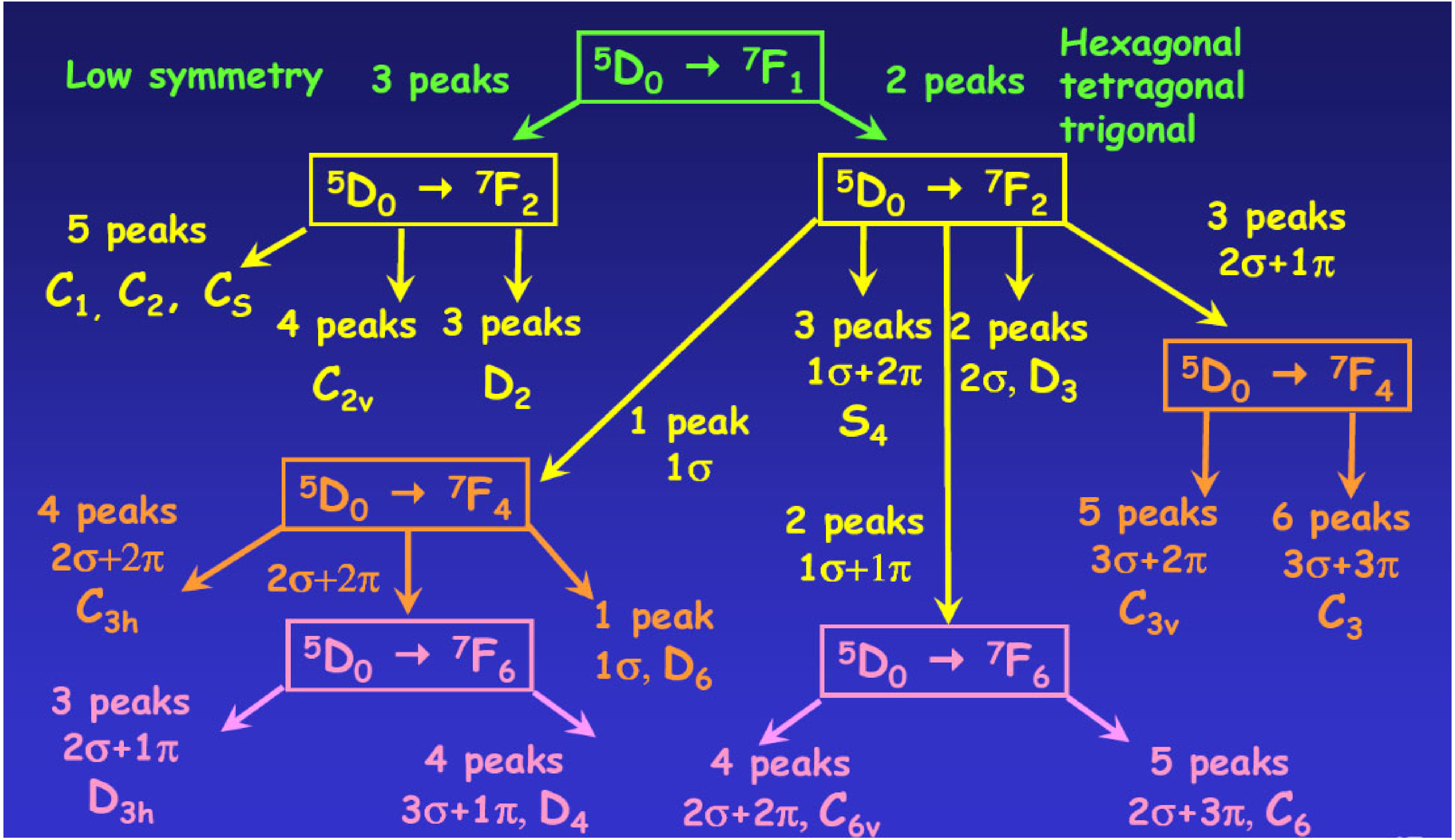
- Energy level by splitting of configuration due to

– Electron repulsion	terms
– Spin-orbit (SO) coupling	SO components (levels)
– Crystal-field (CF) splitting	CF components
– Magnetic field	sublevels



9. Lanthanides and Actinides

Eu^{3+} Luminescence as a Symmetry Probe



$^5D_0 \rightarrow {}^7F_1$

Low symmetry 3 peaks

2 peaks Hexagonal tetragonal trigonal

$^5D_0 \rightarrow {}^7F_2$

5 peaks C_1, C_2, C_s

4 peaks C_{2v}

3 peaks D_2

$^5D_0 \rightarrow {}^7F_2$

1 peak 1σ

3 peaks $1\sigma+2\pi$ S_4

2 peaks 2σ, D_3

2 peaks $1\sigma+1\pi$

3 peaks $2\sigma+1\pi$

$^5D_0 \rightarrow {}^7F_4$

4 peaks $2\sigma+2\pi$ C_{3h}

$2\sigma+2\pi$

1 peak 1σ, D_6

$^5D_0 \rightarrow {}^7F_6$

3 peaks $2\sigma+1\pi$ D_{3h}

4 peaks $3\sigma+1\pi$, D_4

$^5D_0 \rightarrow {}^7F_4$

5 peaks $3\sigma+2\pi$ C_{3v}

6 peaks $3\sigma+3\pi$ C_3

$^5D_0 \rightarrow {}^7F_6$

4 peaks $2\sigma+2\pi$, C_{6v}

5 peaks $2\sigma+3\pi$, C_6

Ref.: J.C.G. Bünzli, Lausanne, CH

10. Selected Applications Areas

Cancer Therapy

- **Drug Delivery**: Nanoparticles can be engineered to carry chemotherapy drugs, targeted therapies, or other therapeutic agents directly to cancer cells. This can improve drug efficacy while reducing side effects on healthy tissues. The nanoparticles can be designed to release their cargo in response to specific stimuli, such as changes in pH or temperature, which are characteristic of the tumor microenvironment.
- **Photothermal Therapy**: Some nanomaterials, like gold nanoparticles, can absorb light and convert it into heat. This property is being exploited in photothermal therapy, where nanoparticles are delivered to tumors and then exposed to near-infrared light. This localized heat generation can selectively destroy cancer cells while sparing healthy tissue.
- **Photodynamic Therapy**: Nanoparticles can also be used in conjunction with light to activate photosensitizers, which produce reactive oxygen species when exposed to light. These reactive species can cause cell death in cancer cells. This approach, known as photodynamic therapy, can be targeted using nanoparticles to enhance its effectiveness.
- **Hyperthermia Treatment**: Nanoparticles can be heated using external magnetic fields to induce hyperthermia, which is the elevation of tissue temperature. Hyperthermia treatment can damage cancer cells and enhance the effects of traditional therapies like radiation and chemotherapy.
- **Targeted Therapy and Imaging**: Nanoparticles can be functionalized with molecules that specifically bind to cancer cells, allowing for targeted drug delivery and imaging. This helps in accurately locating tumors and delivering therapies directly to them.
- **Gene Therapy**: Nanoparticles can also be used to deliver genetic material, such as small interfering RNA (siRNA) or gene-editing tools like CRISPR-Cas9, to cancer cells. This approach can modulate gene expression in cancer cells to halt their growth or trigger cell death.
- **Immune System Modulation**: Certain nanomaterials can interact with the immune system, either by enhancing immune responses against cancer cells or suppressing immunosuppressive mechanisms that tumors often employ.

10. Selected Applications Areas

Recycling of Dyes, Metals, and Pigments

- **Chemical and Solvent-Based Methods:** Chemical processes involve using specific solvents or chemicals to dissolve or strip away pigments and dyes from plastics. These methods can be effective but must be carefully managed to ensure environmental safety and regulatory compliance.
- **Mechanical Separation:** Mechanical processes involve physically separating colored plastics from non-colored plastics. This can include techniques such as air classification, flotation, and screening based on size and density differences.
- **Heat Treatment:** Some plastic recycling processes utilize heat treatment to remove colorants. This can involve exposing the plastic scrap to high temperatures, which can cause the colorants to degrade or evaporate, leaving behind colorless plastic.
- **Additives and Chemical Treatments:** Certain additives and chemical treatments can be incorporated into the recycling process to facilitate the removal of colors. These additives can interact with pigments and dyes to make them easier to separate from the plastic matrix.
- **Hydrogen Peroxide Treatment:** Hydrogen peroxide is sometimes used to bleach colored plastics. It can break down color molecules and remove pigments and dyes, leaving the plastic with a lighter or colorless appearance.
- **Activated Carbon Adsorption:** Activated carbon can be used as an adsorbent to remove colorants from plastic solutions or melts. The colorants can adsorb onto the surface of the activated carbon, leaving the plastic colorless.
- **Biological and Enzymatic Processes:** Researchers are exploring biological and enzymatic methods to break down colorants in plastics. Microorganisms or enzymes can target and degrade color molecules.
- **Advanced Recycling Technologies:** Advanced recycling technologies, such as depolymerization and chemical recycling, can break down plastics into their original monomers, effectively removing all colorants. The resulting monomers can be used to create new, colorless plastic products.

10. Selected Applications Areas

Why is mercury a liquid and a bad conductor?

Comparison of the properties of Hg with Au

Melting point m.p.

Au	1064 °C
Hg	-39 °C

Conductivity

Au	426 kSm^{-1}
Hg	10.64 kSm^{-1}

Density

Au	19.3 gcm^{-3}
Hg	13.5 gcm^{-3}

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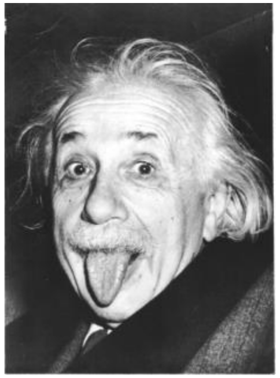
These and many other properties of heavy elements can not be explained by the Lanthanide contraction, etc.

10. Selected Applications Areas

Relativistic Effects: In 1905 Einstein Published Special Relativity



It states that the mass of any moving massive object increases with its speed

$$m_{rel} = \frac{m_{rest}}{\sqrt{\left(1-\left(v/c\right)^2\right)}}$$

Neils Bohr calculated the speed of a 1s electron in a H atom in the ground state to be 1/137 = α (fine structure constant) of the speed of light. This speed is so low that the relativistic mass is only 1.00003 times the rest mass of the atom

But,

once one consider heavy elements like ^{79}Au or ^{80}Hg, things change:
The expected radial velocity of a 1s electron in atoms, which is much heavier than Hydrogen is:

Hg: (80/137) • c = 0.58 c or 58% of the speed of light in vacuum

$$\langle v_r \rangle \approx \left(Z/137\right) \cdot c$$

This in turn shrinks the 1s orbital radius by 23%, thus the 1s orbitals dramatically shrinks. All other orbitals must do the same, to remain orthogonal

10. Selected Applications Areas

Relativistic Effects

Hg(I) only exists as Hg_2^{2+} which is isoelectronic with Au_2

Hg(0) does not form strong covalent bonds with itself like gold.

The shrinking of the orbitals decreases so much that the 6s electrons are not available to form bonds, thus Hg is atomic not molecular in the gas phase

Hg(0)-Hg(0) does not exist: Relevant for Hg low and high-pressure discharge lamps!

In the gas phase, Hg is the only metal that exists as a monomer, gold forms stable Au_2(g) molecules

Analogous to H_2(g) vs. He(g)

This property also explains why the conductivity is so low:
The 4s electrons are very localized and can not populate the conductance band very well