ELECTRON-VIBRATIONAL OPTICAL BANDS

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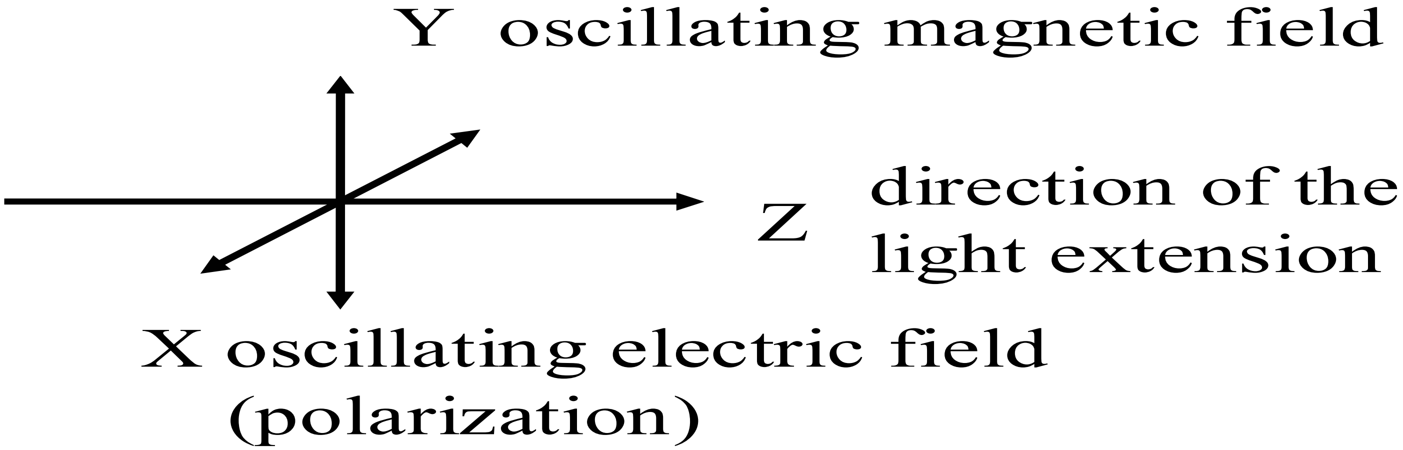
OUTLINE

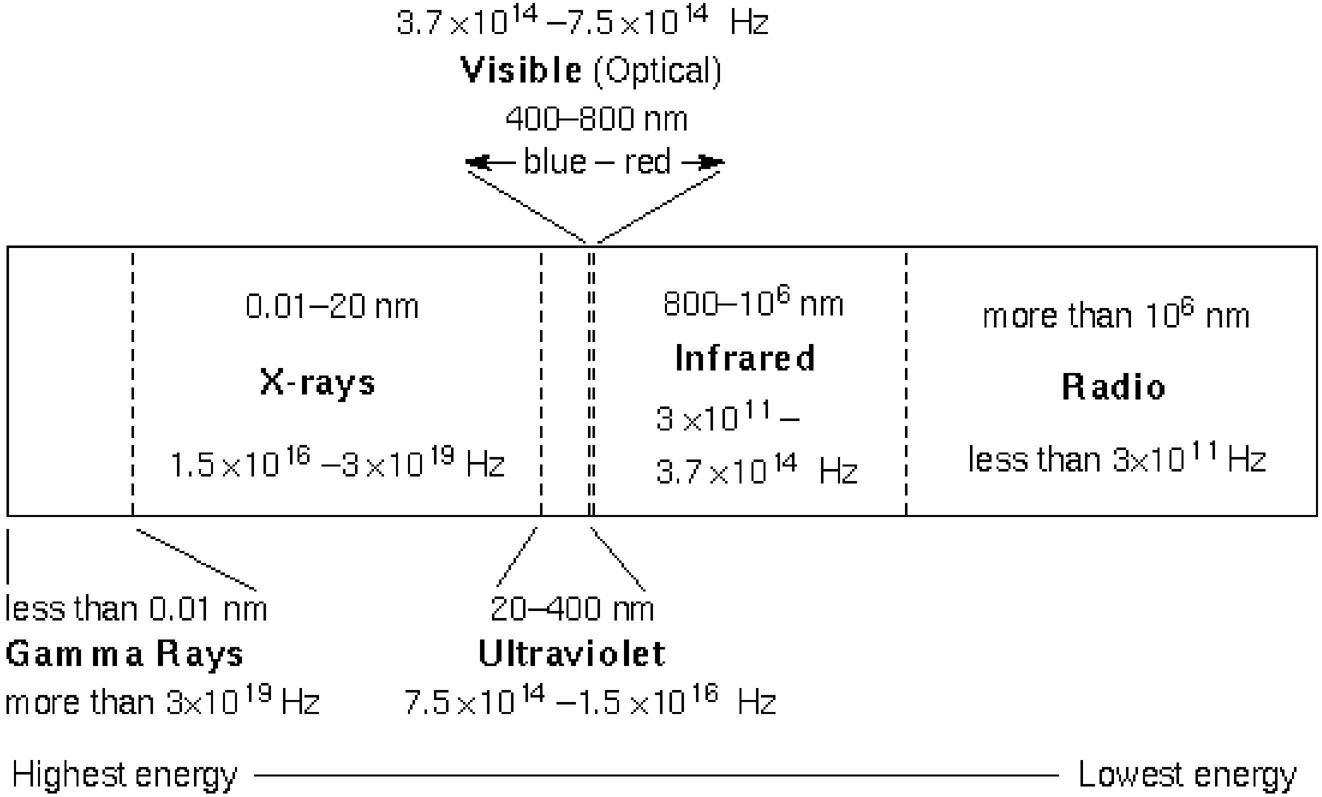
1. General introduction
2. Crystal field effects in transition metal complexes
3. Intensity of the optical line
4. Electron-vibrational interaction. Semiclassical adiabatic approximation. Franck-Condon principle-classical representation
5. Absorption optical d-d bands in the semiclassical approximation: shape and temperature dependence
6. Charge transfer bands

NATURE OF THE RADIATION

Oscillating electric and magnetic fields:
radiation, traveling in z-direction consists of electric and magnetic fields perpendicular to each other and to the z-direction. The wave travels in the z-direction with the velocity of the light $c = 3 \cdot 10^{10}$ cm sec^{-1}



Approximate wavelengths, frequencies and energies for selected regions of the electromagnetic spectrum



$3.7 \times 10^{14} - 7.5 \times 10^{14}$ Hz
Visible (Optical)
400–800 nm
← blue – red →

less than 0.01 nm
Gamma Rays
more than 3×10^{19} Hz

0.01–20 nm
X-rays
$1.5 \times 10^{16} - 3 \times 10^{19}$ Hz

20–400 nm
Ultraviolet
$7.5 \times 10^{14} - 1.5 \times 10^{16}$ Hz

800–10^6 nm
Infrared
$3 \times 10^{11} -$
3.7×10^{14} Hz

more than 10^6 nm
Radio
less than 3×10^{11} Hz

Highest energy ———————— Lowest energy

The Electromagnetic Spectrum

IMPORTANT VALUES AND SPECTROSCOPIC UNITS

Plank’s constant

$h = 6.623\times10^{-27}$ erg sec

ν - frequency of the radiation,

wavenumber $(\text{cm}^{-1}) = 1/\lambda\,(\text{cm})$,

1 cm = 10^{8} Å (angstroms)

Units for the energy

1 ev=8067 cm^{-1}

Speed of light

$c = 3\times10^{10}\ \text{cm sec}^{-1}$

$\nu\,(\text{sec}^{-1}) = c(\text{cm sec}^{-1})/\lambda\,(\text{cm})$,

λ - wavelength

E-energy of the photon : $E = h\nu = hc/\lambda$

$\hbar = h/2\pi$, $\Omega = 2\pi\nu$

Spectroscopic methods in various ranges of the energy (frequency) scale

The following sequence represents decreasing energy:

ultraviolet > visible > infrared > microwave > radiofrequency

Radiofrequency → Nuclear Magnetic Resonance (NMR)

Microwave → Electron Spin (or Paramagnetic) Resonance (ESR or EPR)

Far IR (Infrared), Near IR → IR Spectroscopy

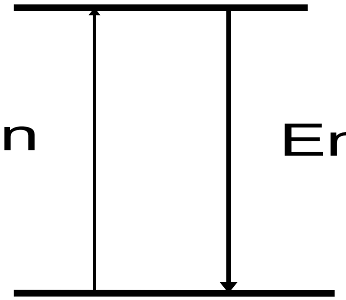
Visible, Near UV (Ultraviolet) → Electronic Spectroscopy

X ray → Photoelectron Spectroscopy

γ ray → Mössbauer Spectroscopy

MAIN FEATURES OF THE ATOMIC SPECTRA

***Narrow lines of absorption and emission*:**
Each line in the atomic spectrum corresponds to a certain transition between two atomic levels 1 and 2 :



2(excited state)

Absorption

Emission

1(ground state)

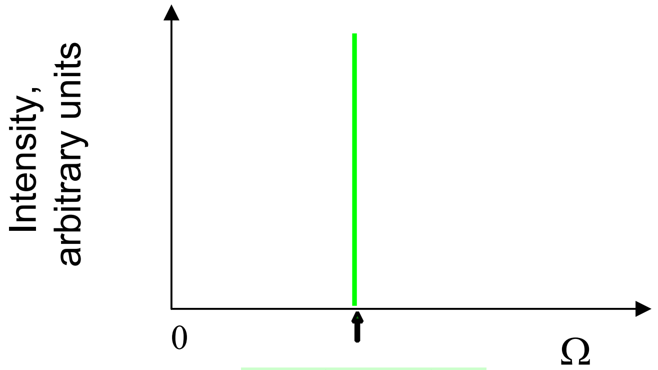
RESONACE CONDITION (ENERGY CONSERVATION):

$$E_2 - E_1 = h\nu = \hbar\Omega$$

Ω *is the frequency of the absorbed or emitted* ***photon***

$$\hbar = h / 2\pi \qquad \Omega = 2\pi\nu$$

Two- and three- level schemes

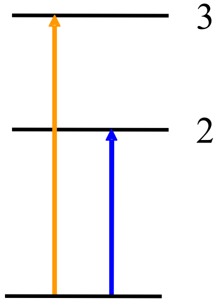


$\Omega = (E_2 - E_1)/\hbar$

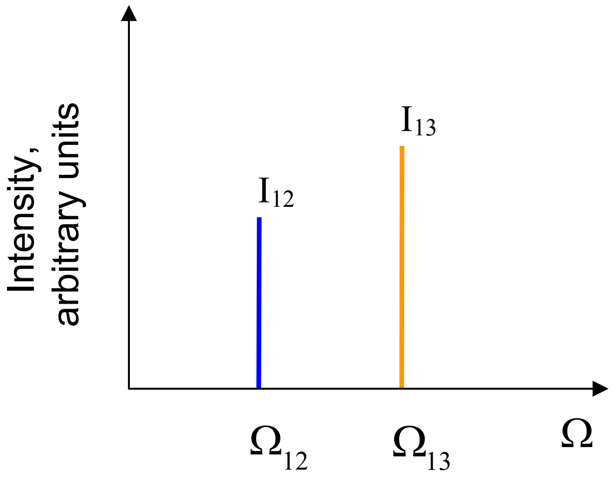
Two-level system gives rise to the only optical line, a more complicated energy pattern results in a more complicated structure of the absorption or luminescence spectrum.

Three-level scheme

two transitions

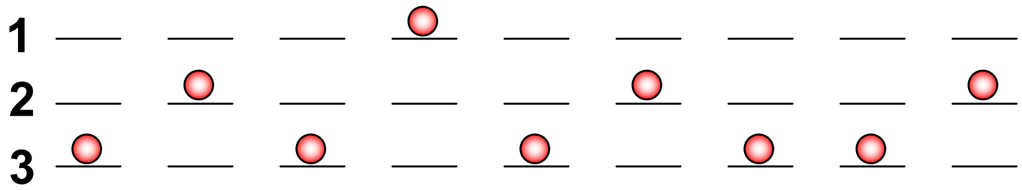


I_{12}, I_{13}-intensities of the lines



Boltzman distribution

Molecules in the medium (ensemble):
(each molecule having, let say, three levels):



Due to interaction with the medium (thermostat or bath) electrons (red balls) jump "up" (absorption of heat) and "down" (emission of heat) traveling among the levels 1, 2 and 3. These jumps are very fast, so one can speak about the distribution of the electrons over the levels in the thermodynamic equilibrium of the ensemble.

N_1 -mean number of the molecules with the energy E_1

N_2 -mean number of the molecules with the energy E_2

N_3 -mean number of the molecules with the energy E_3

$N = N_1 + N_2 + N_3$ - total number of the molecules.

$P_1 = N_1 / N$ -*probability* to find a molecule with the populated level 1 (i.e. with the energy E_1), etc…

The main question: what are these probabilities?

Boltzman distribution

Probability to find a molecule with the populated level “ i ”
(i.e. a molecule with the energy E_i)

$$p_i = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$$

k_B - Boltzman constant, T - temperature

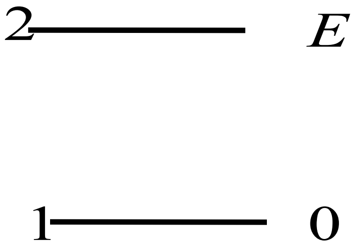
Z – partition function

$$Z = \sum_i e^{-\frac{E_i}{k_B T}}$$

(summation over all levels)

Probability p_i depends on the energy E_i and on the temperature T

BOLTZMAN DISTRUBUTION-ILLUSTRATION FOR TWO LEVELS



$$Z = 1 + e^{-\frac{E}{kT}}$$

$$E_1 = 0, \quad E_2 = E$$

$$p_1 = \frac{1}{1 + e^{-\frac{E}{kT}}}, \qquad p_2 = \frac{e^{-\frac{E}{kT}}}{1 + e^{-\frac{E}{kT}}}$$

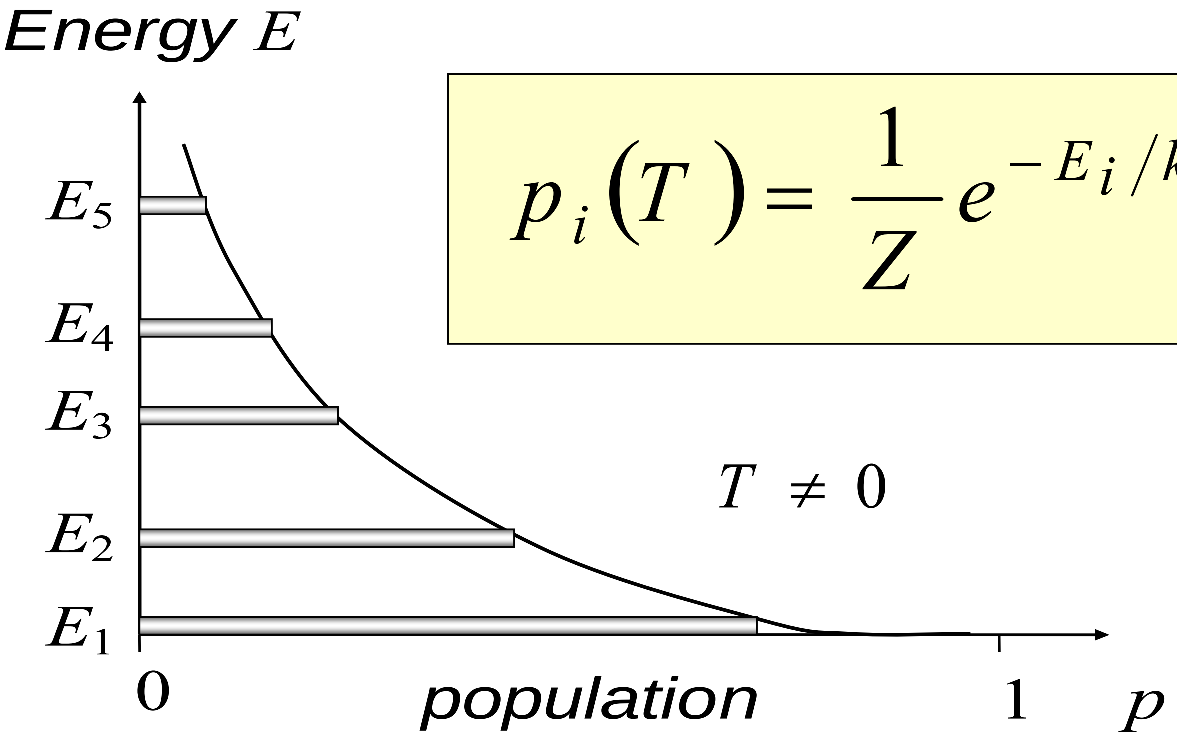
$$T \Rightarrow 0, \quad p_1 = 1, \quad p_2 = 0$$

(only level "1" is populated)

$$T \to \infty, \quad p_1 = p_2 = \frac{1}{2}$$

(levels "1" and "2" are equally populated)

POPULATION OF THE ENERGY LEVELS IN THE THERMODYNAMIC EQUILIBTIUM



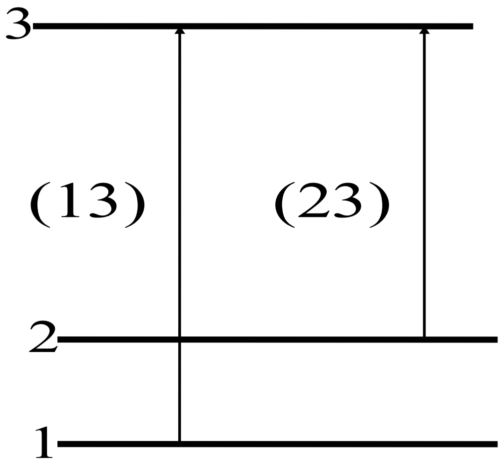
$$p_i(T) = \frac{1}{Z} e^{-E_i/kT}$$

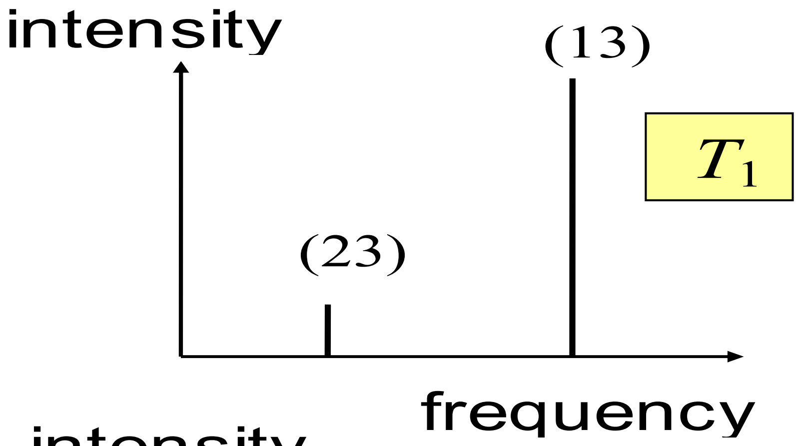
1)Population exponentially decreases with the increase of the energy; level "i" is populated significantly if $kT \geq E_i$;

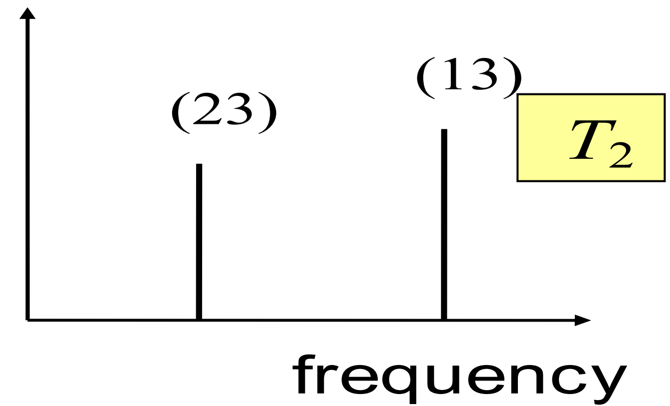
2)The ground level is always (at any T) the most populated level .

TRANSITIONS FROM THE EXCITED STATES

Three-level scheme: energies $E_1=0$, E_2, E_3 we assume also that $kT << E_3$, so that only the levels 1 and 2 are populated







Intensities:

$p_1(T)\ \mathrm{I}_{13}$ and

$p_2(T)\ \mathrm{I}_{23}$

$T_2 > T_1$

QUANTUM NUMBERS FOR AN ELECTRON IN A SPHERICHAL POTENTIAL (HYDROGEN ATOM, ONE-ELECTRON ION)

n – the main quantum number

($n = 1, 2, 3\ldots$)

l – quantum number of the orbital angular momentum

($l = 0, 1, 2, \ldots, n-1$)

m_l – magnetic quantum number

($m_l = -l, -l+1, \ldots, l-1, l$)

m_s – spin projection quantum number

(spin $s = 1/2$, $m_s = \pm 1/2$)

p – parity of the quantum state,

$p = (-1)^l$

spectroscopic notations:

$l = 0,\ 1,\ 2,\ 3,\ 4,\ 5, \ldots$

s, p, d, f, g, h, …

“even” and “odd” states:

s – even ($l=0$), p – odd ($l=1$), d –even ($l=2$), etc.

ELECTRONIC CONFIGURATIONS OF 3d ELEMENTS

The closed d-shell contains 10 electrons

The filling up of the 3d shell takes place in the iron group

$[(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6]$ –closed electronic shell

Instead of a regular sequence of configurations of the type $3d^n (4s)^2$ with increasing n, configurations of the type of $3d^{n+2} 4s$ are found

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$

Ions of transition metals of iron group have unfilled d-shells: n=3, l=2

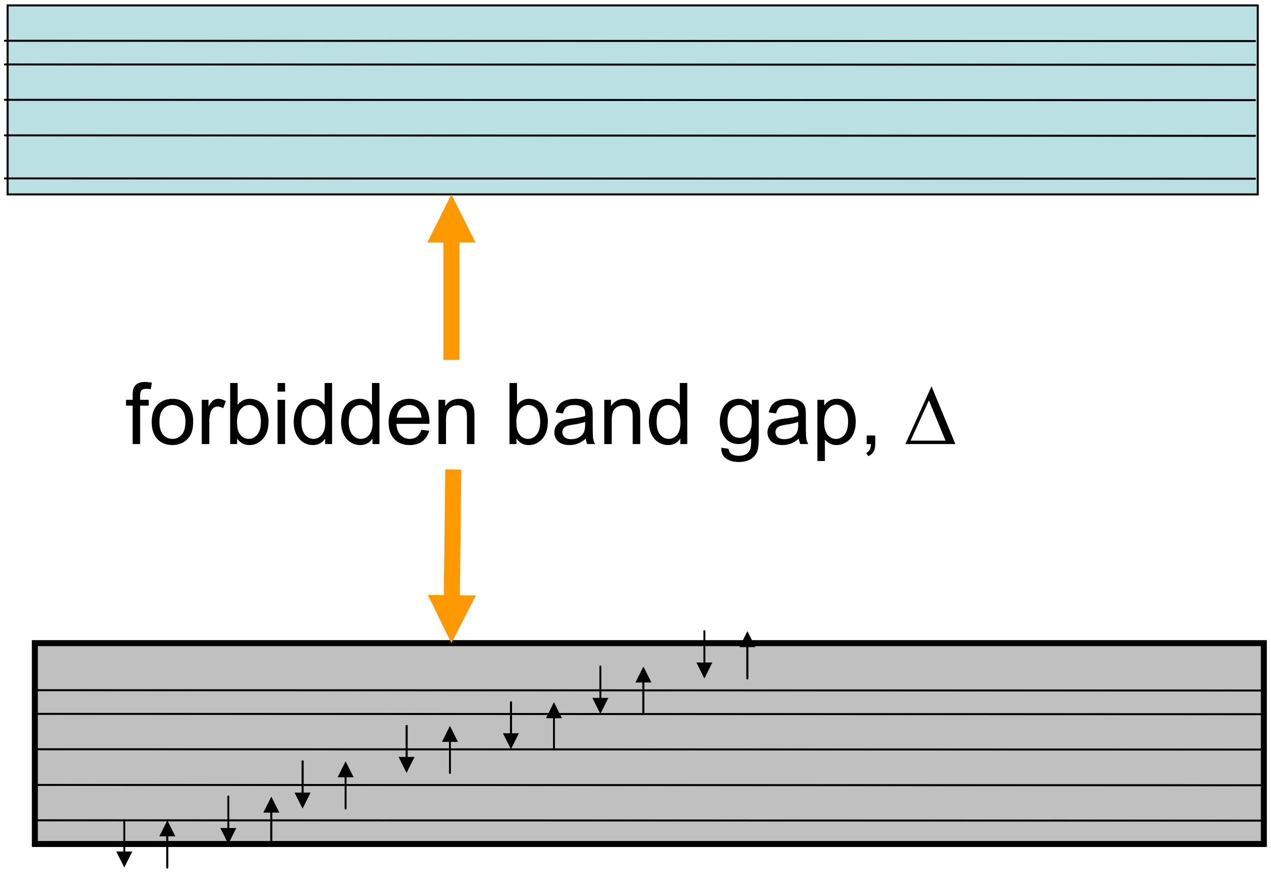
TYPICAL OXIDATION DEGREES AND d^n CONFIGURATIONS

$d^1(Ti^{3+})$, $d^2 (V^{3+})$, $d^3 (Cr^{3+},V^{2+})$, $d^4(Mn^{3+},Cr^{2+})$, $d^5(Fe^{3+},Mn^{2+})$,

$d^7(Co^{2+})$, $d^8(Ni^{2+})$, $d^9(Cu^{2+})$

BAND STRUCTURE OF SOLIDS:
dielectrics, semiconductors

Atomic levels are split into bands when atoms form a crystal

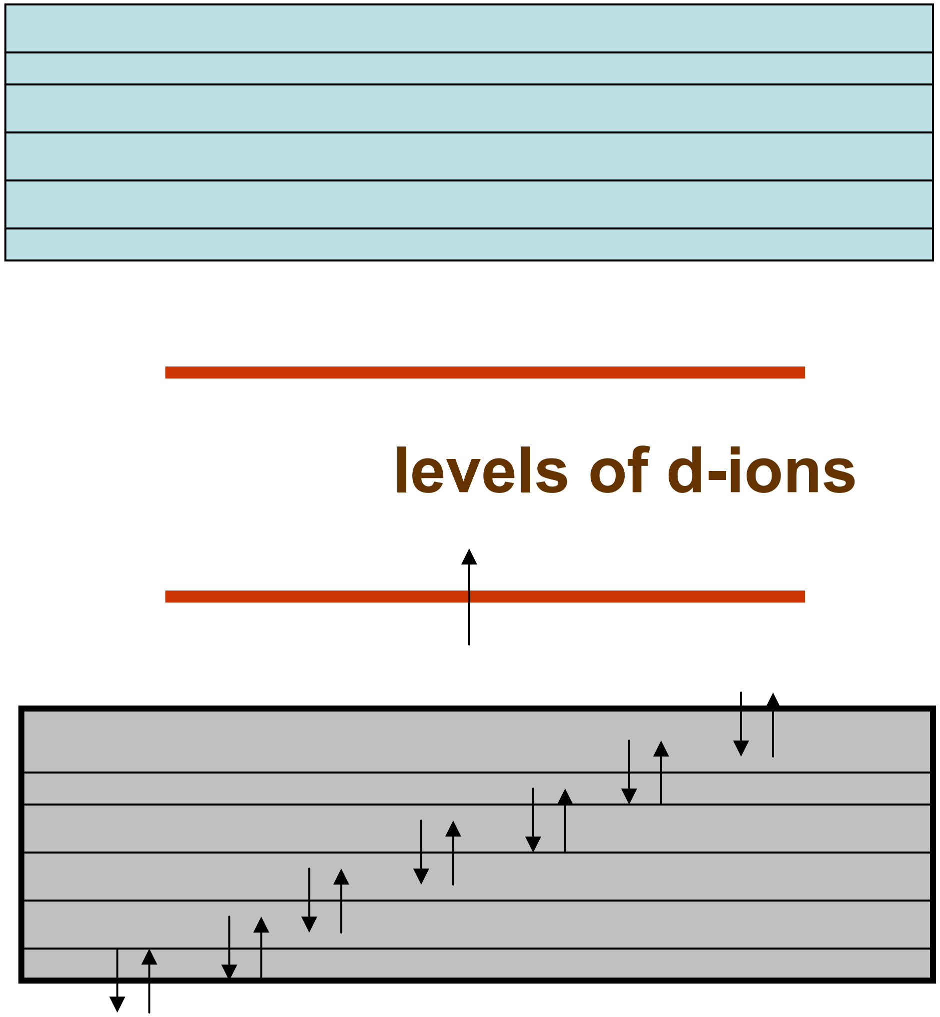


Conduction band is empty

forbidden band gap, Δ

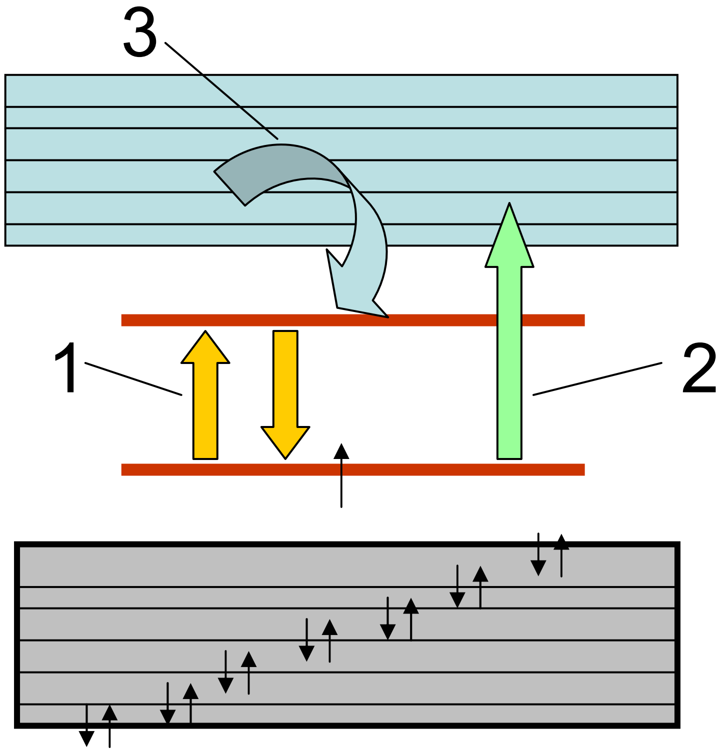
Valent band is filled, each level is occupied by a pair of electrons at T=0

BAND STRUCTURE OF SOLIDS -
levels of transition metal ions



- Levels of of transition metal ions fall into the forbidden band gap
- These levels are populated by d-electrons

THE MAIN CONSEQUENCES: levels of transition metal ions



1. Additional bands of light absorption and emission related to the transitions between the levels of the d-ions

2. Photoconductivity-conductivity induced by light absorption – transitions from d-levels to the conduction band. Electron jumps from the d-level to the conduction band

3. Caption of the electrons from the conduction band-decrease of conductivity

CRYSTAL FIELD

Crystal field theory treats a complex as if it consists of a positive metal ion surrounded by negatively charged ions (ligands)

PHYSICAL PICTURE

Shapes of the electronic clouds:

$\Psi(r)$ – wave-function

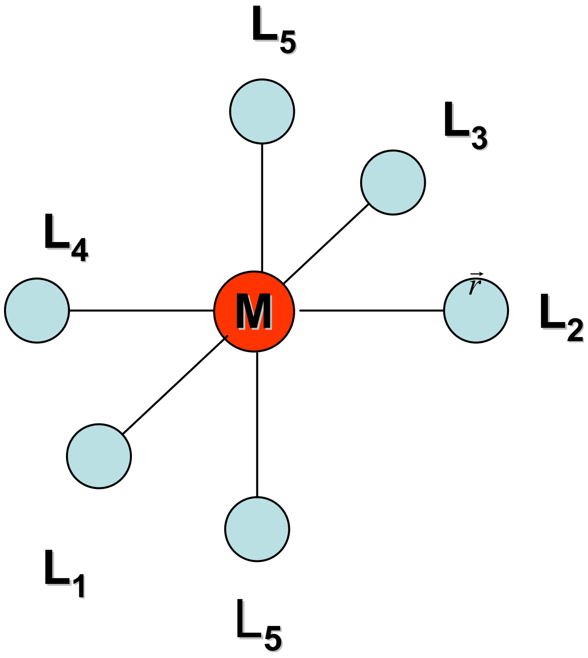
$|\Psi(r)|^2$ – spatial distribution of the electronic density

(shape of the electronic “cloud”)

Energy in the crystal field =Interaction of the electronic cloud with the charges of the ligands

CRYSTAL FIELD

The crystal field theory assumes that the ligands are point charges or point dipoles and the d-orbitals are entirely non-bonding



The energy of interaction *V* of an electron of the metal ion M with the negatively charged ligands L_i

$$V = \sum_{i=1}^{6} \frac{Ze^2}{\left|\vec{r} - \vec{R}_i\right|}$$

Ze - ligand charge, **e - the electron charge,**

$\vec{r}$ **- the electron coordinate**

$\vec{R}_i$ - the position –vector of the ligand L_i

M – transition metal ion

L_i –ligand

Schrödinger Equation for the stationary states

$$\boxed{\hat{H}\Psi = E\Psi}$$

$\hat{H}$ -the Hamiltonian of the system
(operator of the energy
including kinetic and potential energy of
the system of electrons)

$\Psi(\boldsymbol{r})$ -the wave function

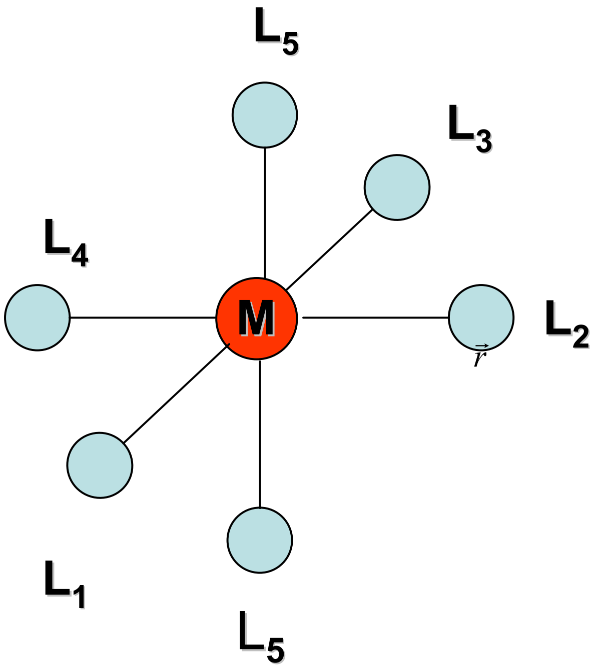
By solving Schrödinger Equation one can
find the energy levels E_n and the wave-functions
corresponding to these energy levels

$\left|\Psi(\boldsymbol{r})\right|^2$ -spatial distribution
of the probability (electronic density)

SPLITTING OF THE d-LEVEL INTO A TRIPLET AND A DOUBLET IN THE CUBIC CRYSTAL FIELD

Octahedral transition metal complex

Point symmetry group : cubic,O_h



M – transition metal ion
L_i –ligand

Transition metal ions –d orbitals

$l=2 \rightarrow m=-2\ -1,0,\ 1,2$

___ ___ ___ ___ ___

Five orbitals with the same energy

The d-level is 5-fold degenerate !!!

Five d –functions :

$\varphi_{3dlm}(r, \theta,\varphi)=R_{3d}(r)Y_{lm}(\theta,\varphi)$

$R_{3d}(r)$ – radial wave function,

$Y_{lm}(\theta,\varphi)$ –spherical harmonic

Angular parts of d-functions

$Y_{2,-2},\ Y_{2,-1,}Y_{2,0},\ Y_{2,1},Y_{2,2}$

$D^{(2)}=T_2+E$ - crystal field

(triplet + doublet)

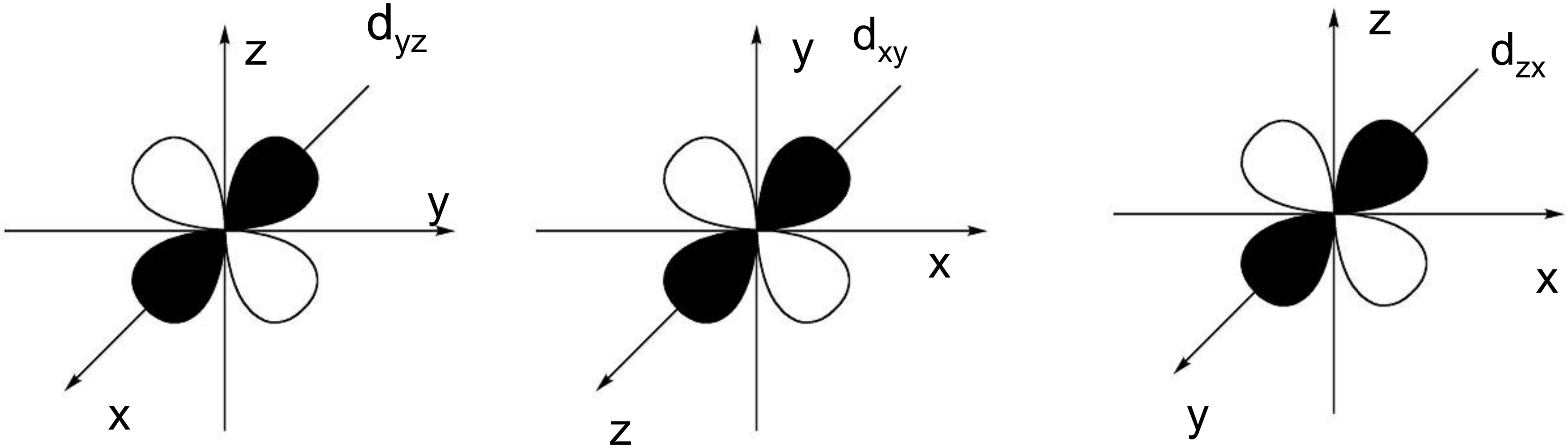
Wavefunctions for the T_2 state

$$\varphi_{yz} = (i/\sqrt{2})(Y_{2,1}(\vartheta,\varphi) + Y_{2,-1}(\vartheta,\varphi))R_{3d}(r) = (15/4\pi)^{1/2}(yz/r^2)R_{3d}(r) \equiv \varphi_{\xi}$$

$$\varphi_{xy} = -(i/\sqrt{2})(Y_{2,2}(\vartheta,\varphi) - Y_{2,-2}(\vartheta,\varphi))R_{3d}(r) = (15/4\pi)^{1/2}(xy/r^2)R_{3d}(r) \equiv \varphi_{\varsigma}$$

$$\varphi_{zx} = -(1/\sqrt{2})(Y_{2,1}(\vartheta,\varphi) - Y_{2,-1}(\vartheta,\varphi))R_{3d}(r) = (15/4\pi)^{1/2}(zx/r^2)R_{3d}(r) \equiv \varphi_{\eta}$$

In a regular octahedral complex(point group O_h) ,where there is no distinction between the x,y,z coordinates, the zx , yz and xy orbitals lying between these coordinates are undistinguishable and of equal energy: the T_2 -state is triply degenerate



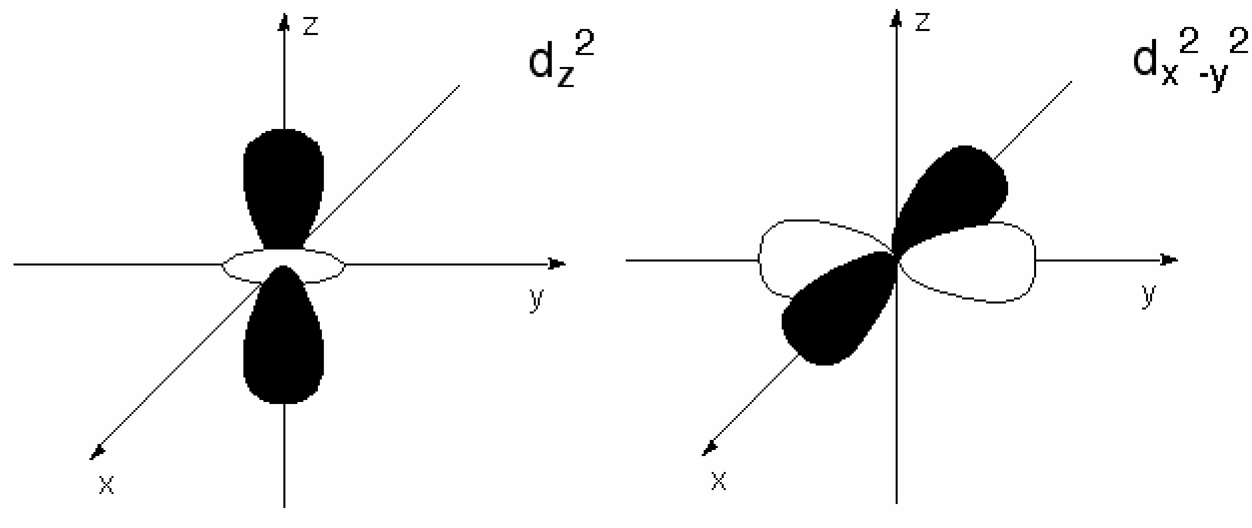
Shapes of three d-orbitals of t_2 type

Wavefunctions for the E state

$$\varphi_{3z^2-r^2} = Y_{2,0}(\vartheta,\varphi)R_{3d}(r) = (15/4\pi)^{1/2}((3z^2-r^2)/r^2)R_{3d}(r) \equiv \varphi_u$$

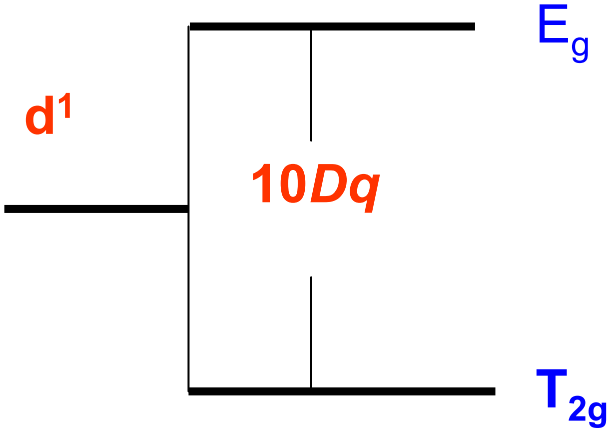
$$\varphi_{x^2-y^2} = (1/\sqrt{2})(Y_{2,2}(\vartheta,\varphi)+Y_{2,-2}(\vartheta,\varphi))R_{3d}(r) = (15/6\pi)^{1/2}(x^2-y^2/r^2)R_{3d}(r) \equiv \varphi_v$$

The z^2 and x^2-y^2 orbitals lie along the x,y,z axes. Since these axes are indistinguishable, it follows that these two orbitals are also indistinguishable, have equal energy and therefore form the basis for the two dimensional representation E



Shapes of two orbitals of e-type

SPLITTING OF THE d-LEVEL INTO A TRIPLET AND A DOUBLET IN THE OCTAHEDRAL CRYSTAL FIELD



Cubic crystal field parameter *Dq*

$$Dq = \frac{Ze^2\langle r^4\rangle}{6R_0^5}$$

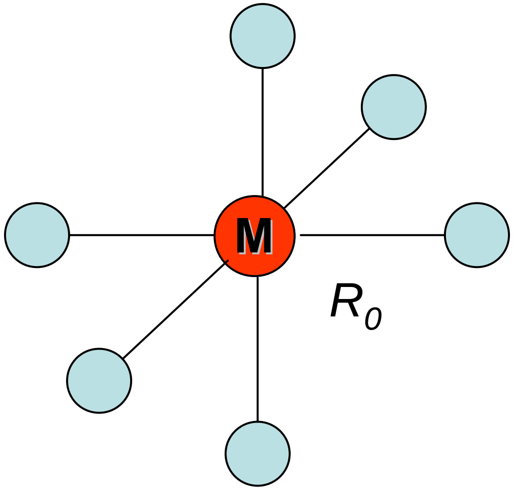
Ze – *charge of the ligands*

R_0 – *metal-ligand distance in the octahedral surrounding*

10 Dq – *crystal field splitting of the one-electron d-level*

$\langle r^4\rangle$ – *mean value of r^4 for the d-electron*

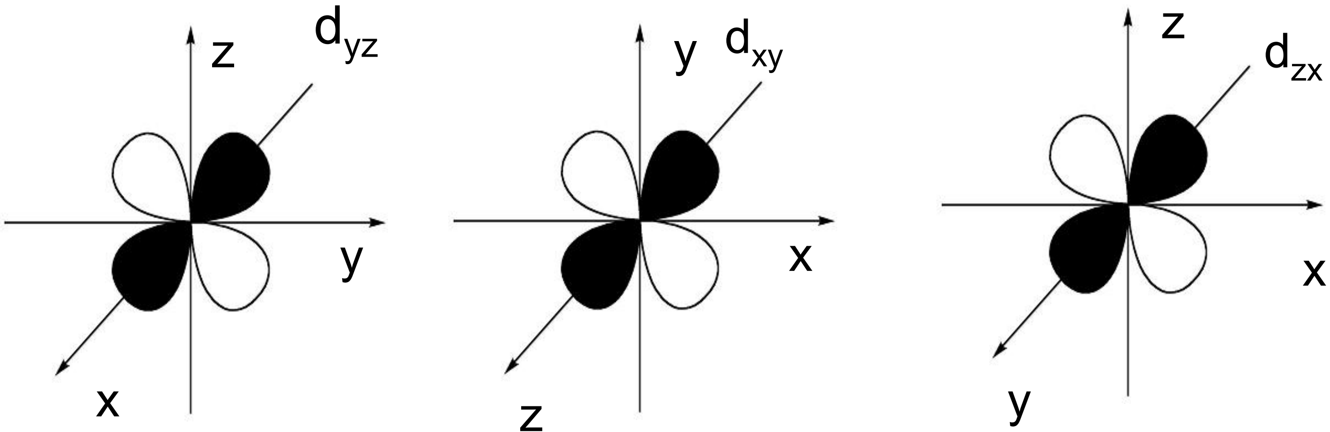
Octahedral surrounding



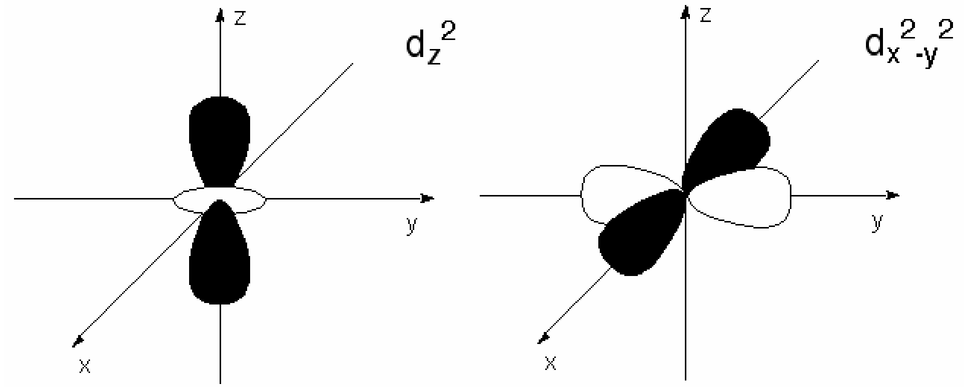
d^1-electron → Ti^{3+}, V^{4+}, Mo^{5+}, Zr^{3+}

Qualitative interpretation of the obtained result

d-orbitals of t_2 type



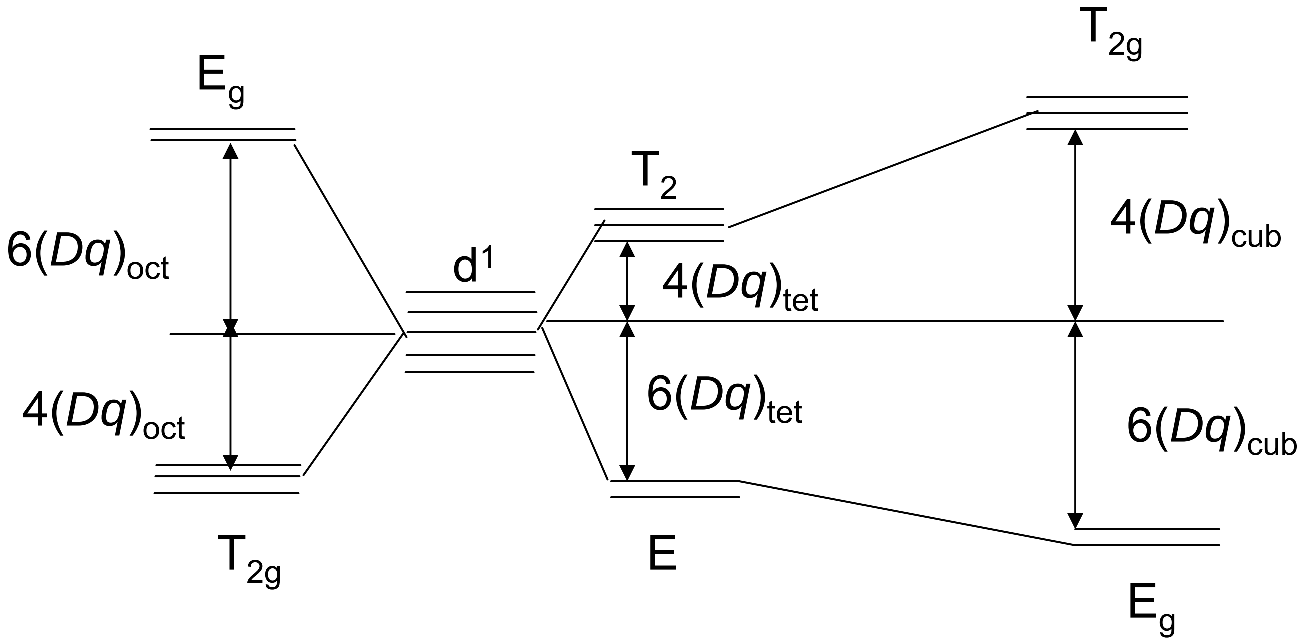
d- orbitals of e-type

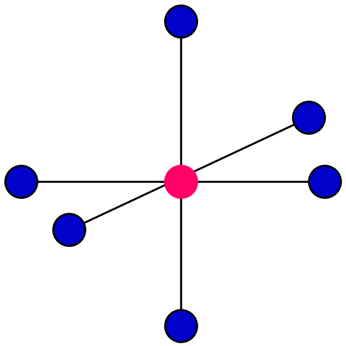


- The two sets of orbitals are distinguishable because the orbitals d_{yz},d_{xy}, d_{zx} lie between the axes, and the orbitals $d_{x^2-y^2}$, d_{z^2} along them

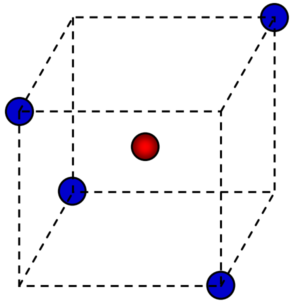
- An electron in the *e* set points directly towards the charge of the ligand and therefore suffers greater destabilization than an electron in the t_2 set which points between the ligands

d-level splitting in a crystal field

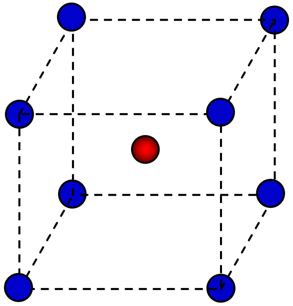




Octahedral ligand surrounding



Tetrahedral ligand surrounding



Cubic ligand surrounding

$$(Dq)_{oct} = \frac{Ze^2\left\langle r^4\right\rangle}{6\ R_0^5}$$

$$(Dq)_{tet} = -\frac{2\,Ze^2\left\langle r^4\right\rangle}{27\ R_0^5}$$

$$(Dq)_{cub} = -\frac{4\,Ze^2\left\langle r^4\right\rangle}{27\ R_0^5}$$

$$(Dq)_{oct} = -(9/4)(Dq)_{tet}$$

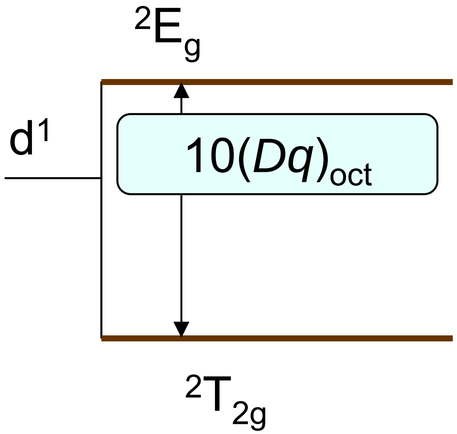
$$= -(9/8)(Dq)_{cub}$$

ABSORPTION SPECTRA OF d¹ IONS

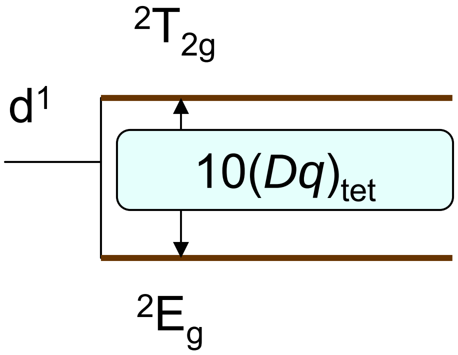
$^{2S+1}\Gamma$

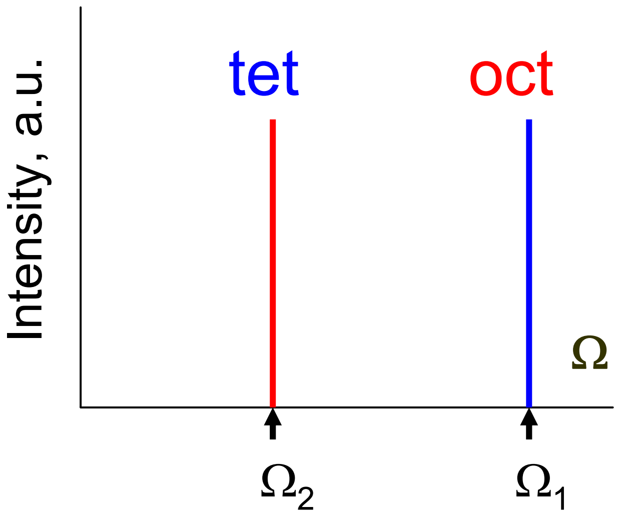
2S+1-spin multiplicity, Γ -irreducible representation

Octahedral complex

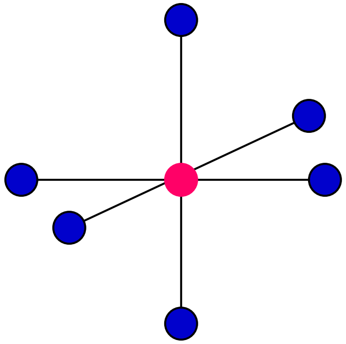


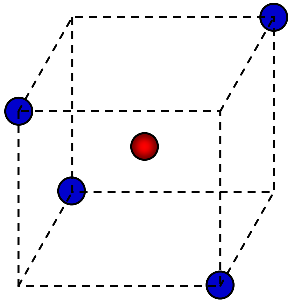
Tetrahedral complex





peak positions of the absorption bands



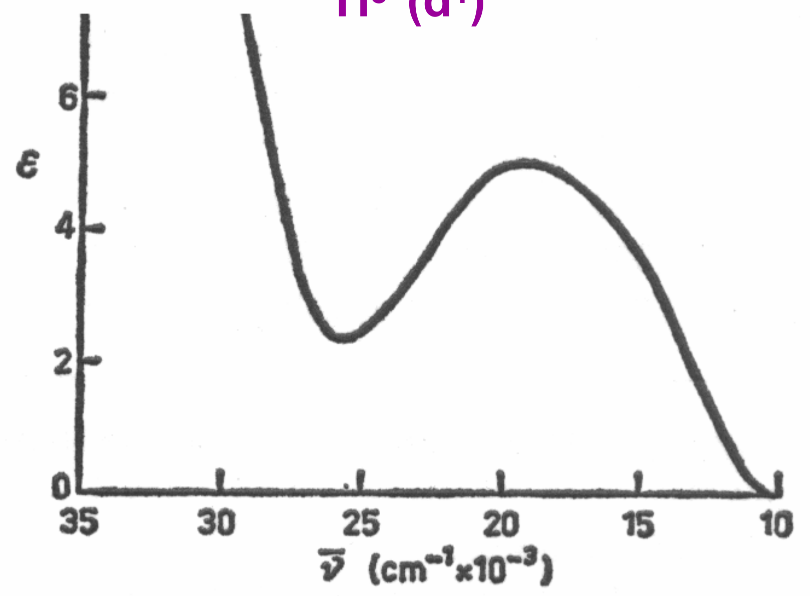


$(Dq)_{oct} > (Dq)_{tet} \longrightarrow \Omega_1 > \Omega_2$

● → transition metal ion

● → ligand

OCTAHEDRAL $Ti(H_2O)_6^{3+}$ COMPLEX $Ti^{3+}(d^1)$

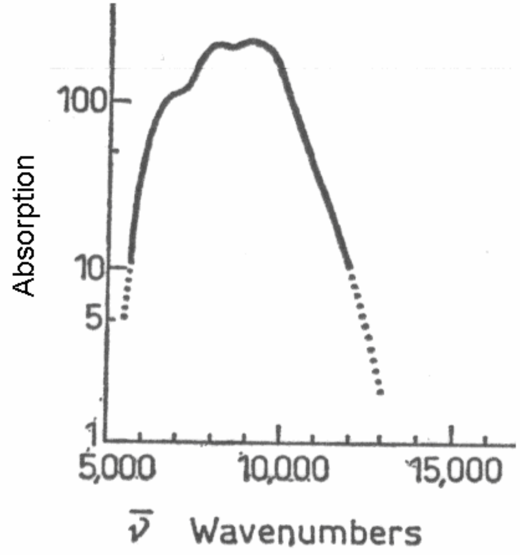


The spectrum of the $Ti(H_2O)_6^{3+}$ ion.

The band at 20100 cm^{-1} is a crystal field transition $^2T_{2g} \rightarrow {}^2E_g$

- **The tetrahedral $TiCl_6^{3-}$ complex has an absorption band at 13000 cm^{-1}**
- **Few tetrahedral complexes of Ti^{3+} are known**

TETRAHEDRAL VCl_4 COMPLEX $V^{4+}(d^1)$



The absorption spectra of VCl_4

The band at 9000 cm^{-1} is assigned to the $^2E \rightarrow {}^2T_2$ transition

Octahedral V^{4+} complexes have bands in the range of 14000-18000 cm^{-1}

The absorption d-d bands of tetrahedral complexes are red shifted in comparison with those arising from octahedral ones

Typical (experimental) values of *Dq* in transition metal complexes with H_2O ligands

Ion	Ti^{3+} (d^1)	V^{3+} (d^2)	Cr^{3+} (d^3)	Mn^{3+} (d^4)	Fe^{3+} (d^5)	Co^{3+} (d^6)
Dq, cm^{-1}	2030	1860	1720	2100	1350	1920
Ion	Cr^{2+} (d^4)	Mn^{2+} (d^5)	Fe^{2+} (d^6)	Co^{2+} (d^7)	Ni^{2+} (d^8)	Cu^{2+} (d^9)
Dq, cm^{-1}	1390	1230	1030	840	820	1220

- Crystal field splitting 10*Dq* in octahedral complexes is of the order of 10,000-20,000 cm^{-1}
- Empirical rule: irrespective of the ligand and metal ions, 10*Dq* in the systems with divalent metal ions is around 10,000 cm^{-1} and in those with trivalent metal ions around 20,000 cm^{-1} (1 eV =8066 cm^{-1})

SPECTROCHEMICAL SERIES

✓ **The change of the ligand elements gives the variation of 10*Dq* which is of the order of 1000 cm^{-1}**

✓**When the metal element is fixed and the ligand is varried, the magnitudes of 10*Dq* may be arranged in the following order:**

I<Br<Cl<S<F<O<N<C,

where the elements are those in ligands attached directly to the metal ion

(Tsuchida's spectrochemical series)

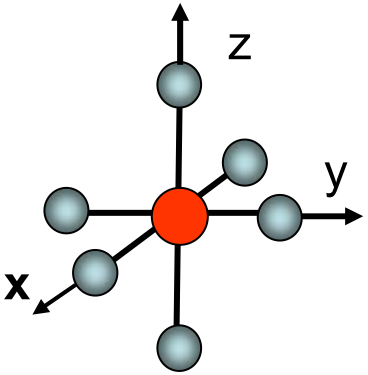
✓**When the ligand is fixed and the metal ion is varied, the magnitudes of 10*Dq* may be arranged in the following order:**

$\mathbf{Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}}$

$\mathbf{< Mn^{4+} < Mo^{3+} < Rh^{3+} < Pd^{3+} < Ir^{3+} < Re^{4+} < Pt^{4+}}$

(Joergensen's rule)

Low-symmetry crystal field -a qualitative consideration



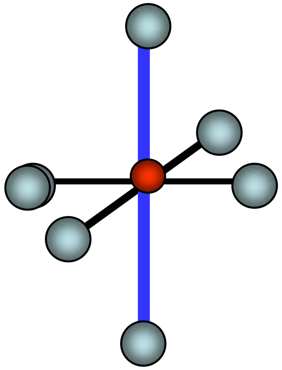
Point symmetry group O_h-cubic

● -metal ion

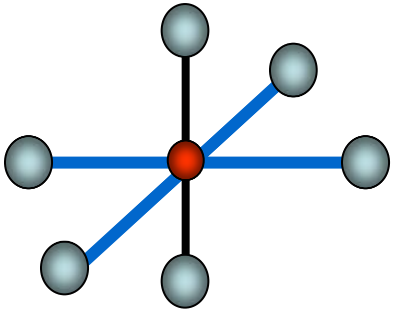
● -ligand

Tetragonally distorted octahedral complexes

point symmetry group D_{4h}: metal-ligand distances are equal in the equatorial plane (x,y), but different from those for axial ligands (z-axis)

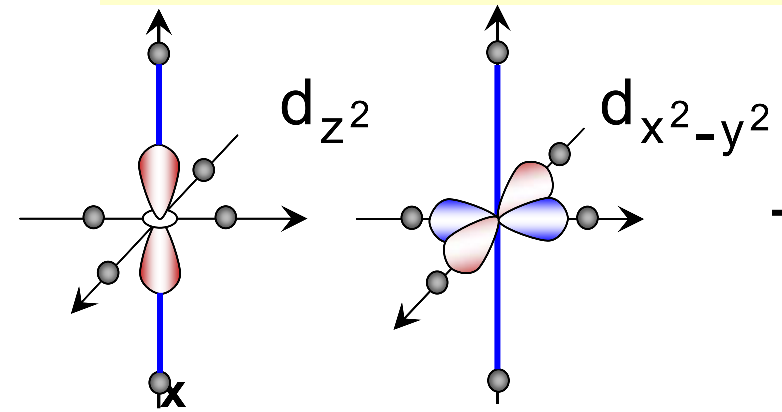


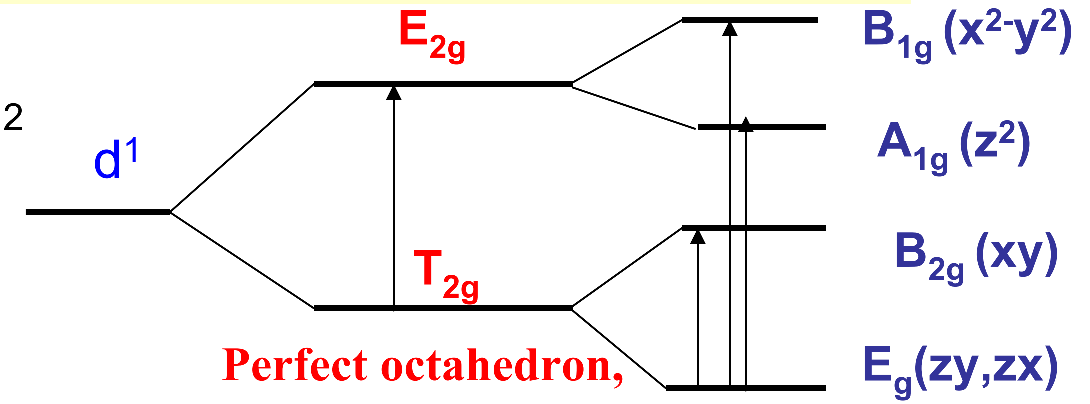
Elongated along the C_4 axis



Compressed along the C_4 axis

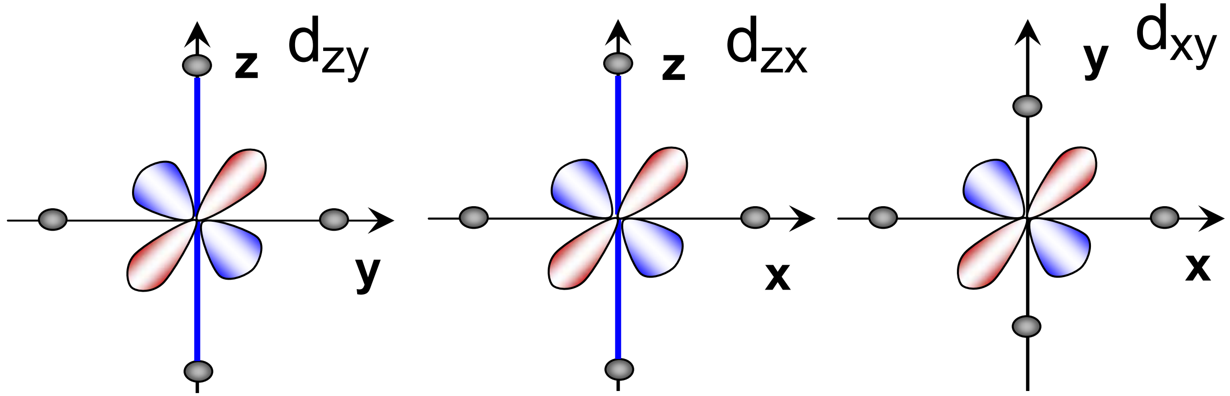
Octahedral complex elongated along the C_4 axis





Perfect octahedron, O_h point group

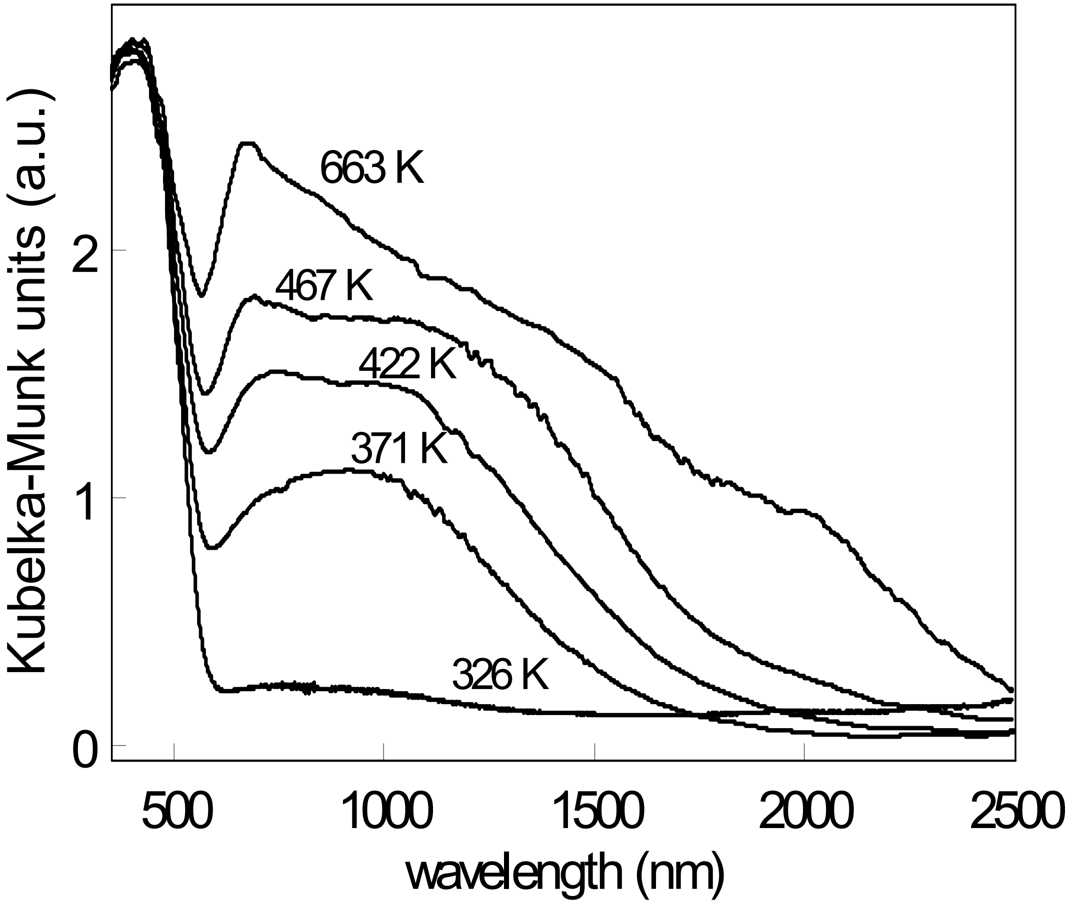
Elongated along the C_4 axis, D_{4h} point group



The optical band splits into three bands

- The z-axis is distinquishable from the x and y axes
- Due to the elongation of the octahedron along the z-axis the z^2 orbital suffers less repulsion from the ligands than the x^2-y^2 orbital and its energy becomes lower than that of the x^2-y^2 orbital
- The energy of the xy orbital is higher than that of the zy and zx orbitals because it suffers more repulsion from the ligands

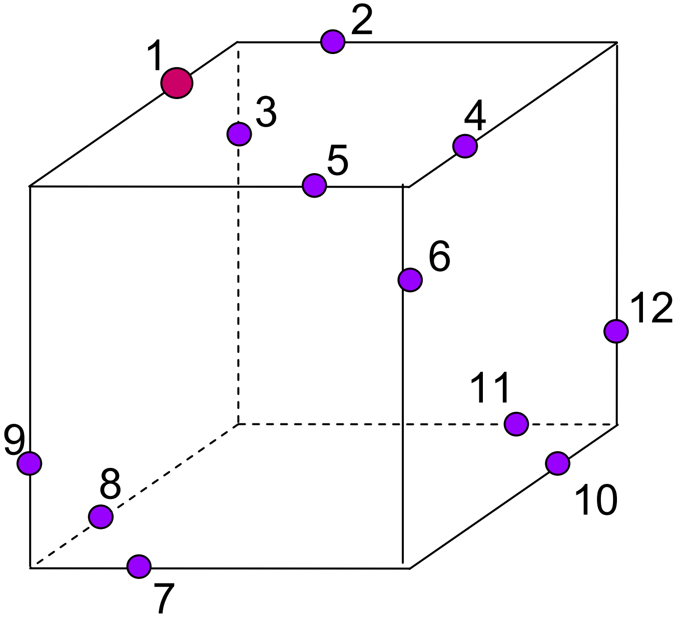
UV/Vis/NIR spectra of vanado-molybdophosphate heteropoly acid $H_4PVMo_{11}O_{40} \bullet y\ H_2O$ treated in He

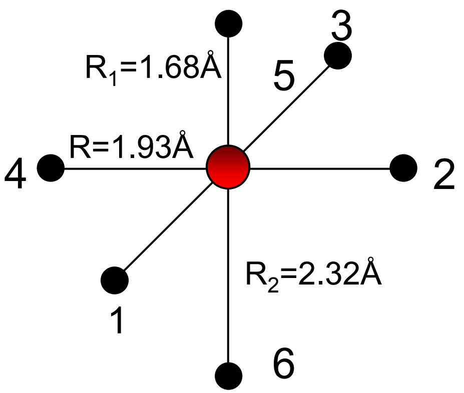


❑Treatment in He from RT to 663 K leads to the strong increase of the apparent absorption

❑ The NIR absorption bands of the crystal water disappear completely

❑At higher temperatures a Vis broad absorption band, and additionally a NIR absorption band can be clearly detected





● –Mo, V ● –O

O_1, O_2, O_3, O_4 –bridging oxygens (**O_b**)

O_5 –terminal oxygen (**O_t**)

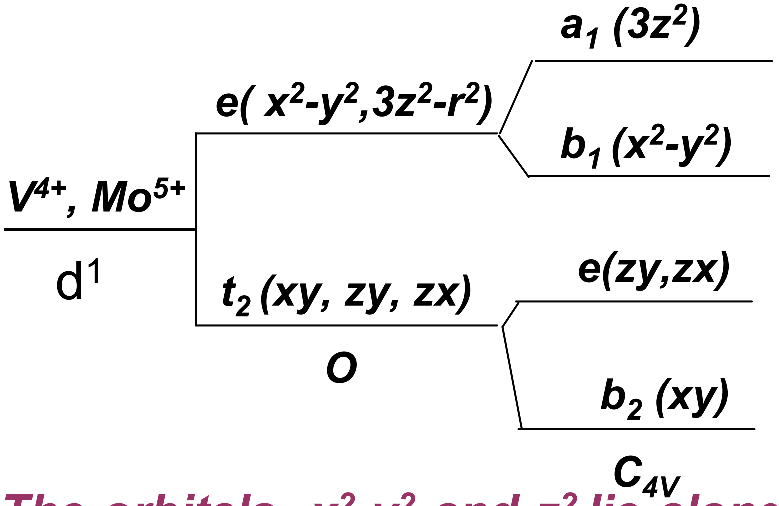
O_6 –oxygen in the phosphorus environment (**O_p**)

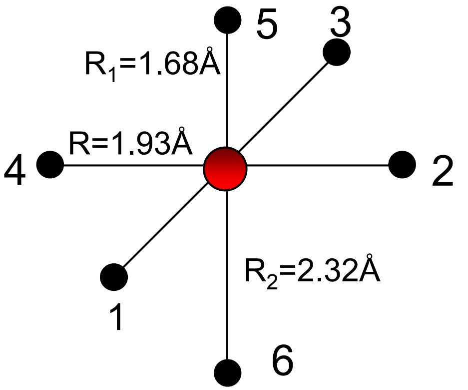
Idealized structure of a Keggin molecule
1. V , 2-12– Mo

According to structural data in heteropoly compounds of Keggin type the site symmetry of Mo and V ions is close to C_{4v}

At 300K the loss of crystal water begins after a certain time of gas flux. At this initial stage there is no reduction, the HPA is partially hydrated, the protons are not localized and reside on the bridging water moieties $H_5O_2^+$. Thus, initially the spectra should originate from d-d transitions in the unimpaired $Mo^{5+}(O)_6$ and $V^{4+}(O)_6$ units

d-d transitions in the unimpaired MoO_6 and VO_6 units





$R_1<R<R_2$

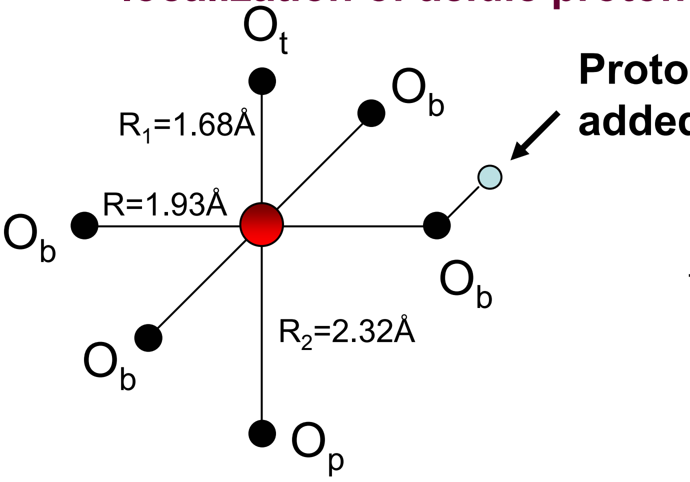
- The orbitals x^2-y^2 and z^2 lie along the x-,y- and z-axes, respectively, whereas the orbitals xy,zy,zx lie between the axes, therefore, the interaction between the orbitals x^2-y^2 and z^2 and the ligands is stronger, and they are higher in energy
- The **z^2 orbital** has the highest energy because it overlaps with the orbital of the ligand **5** having the shortest distance **R_1** from the metal ion. Under the condition **$R_1<R$** the orbital **xy** is the ground one

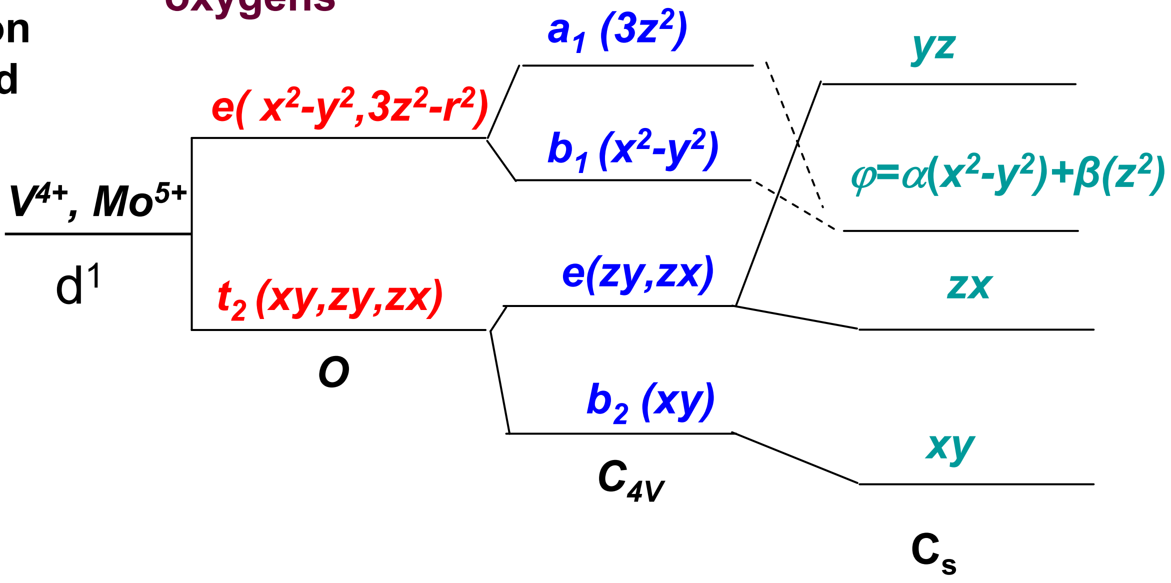
Peak positions (in nm) of the d-d transitions in intact species MoO_6 and VO_6

V^{4+}		Mo^{5+}	
$b_2 \rightarrow e$	$b_2 \rightarrow b_1$	$b_2 \rightarrow e$	$b_2 \rightarrow b_1$
770	625	710	440

d-d transitions in protonated units

At temperatures from 326 to 422 K the crystal water loss is accompanied by the localization of acidic protons the most preferable sites of which are the bridging oxygens





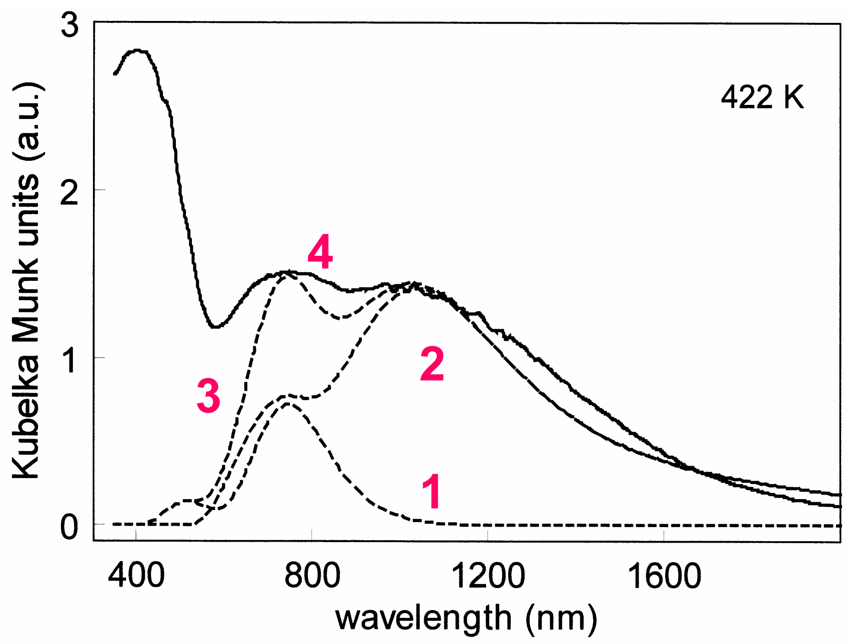
- ❖ If a proton resides on the bridging oxygen the charge of this ligand becomes less negative, the repulsion between the xy orbital and the ligand is weaker, and the energy of this orbital diminishes
- ❖ The energy of the xz orbital also decreases ,but it is higher than that of xy, because the orbital xz lies in the xz-plane , and R_1<R

Peak positions (in nm) of the d-d transitions

	V^{4+}			Mo^{5+}		
Intact species	$b_2\to e$	$b_2\to b_1$		$b_2\to e$	$b_2\to b_1$	
	770	625		710	440	
Protonated species	$xy\to zx$	$xy\to\varphi$	$xy\to zy$	$xy\to zx$	$xy\to zy$	$xy\to\varphi$
	743	720	520	700	505	495

Protonated reduced species give rise to new d-d transitons blue shifted in comparison with those arising from intact ones

Absorption band of the $H_4PVMo_{11}O_{40}$ compound at 422 K



- - - - – calculated

1 – contribution from the d-d transitions

2 – contribution from the charge transfer band

3 – total calculated spectrum

4 – experimental data

✓ At 422 K the crystal water is completely lost

✓ The total spectra arises from intact and protonated species

✓ The calculations make it possible to separate the contributions of the d-d –transitions and the charge transfer band to the total spectrum intensity

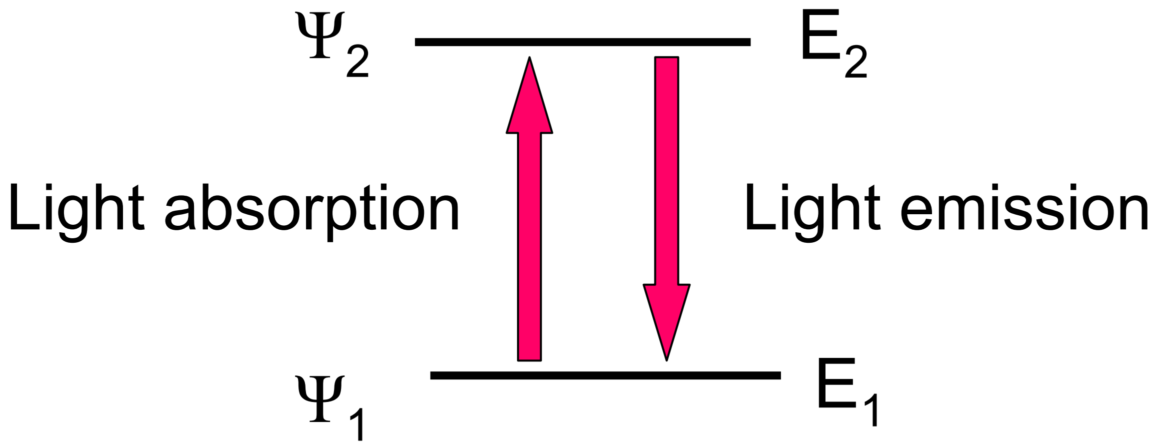
Questions to be discussed

1. Which d-d transitions are allowed ?
2. What interaction is responsible for the shape of the d-d bands ?
3. What is the origin of charge transfer bands?

Which d-d transitions are allowed ?

Probabilities of transitions in quantum mechanics

Two d- levels with energies E_1 and E_2 ,
corresponding wave functions Ψ_1 and Ψ_2



The intensity of the optical line – probability of the transition 1↔2 . The transition 1↔2 is caused by the interaction of the quantum system with light. This interaction is mainly the interaction of the dipole moment of the quantum system with the electric component of the radiation (electric dipole transitions)

Probabilities of transitions

Operator of the dipole moment for an electron

$$\boldsymbol{d} = e\boldsymbol{r}$$

r is the coordinate of the electron

Intensity of the spectral line is proportional to the squared matrix element of the dipole moment :

$$\boldsymbol{d}_{21} = \int \Psi_2^*(\boldsymbol{r})\boldsymbol{d}\,\Psi_1(\boldsymbol{r})\,d\tau$$

Dirac's notation for the matrix element

$$\langle 2|\boldsymbol{d}|1\rangle$$

Intensity of the optical line 1↔2

$$\left|\langle 2|\boldsymbol{d}|1\rangle\right|^2$$

The electronic transition is assumed to be allowed if the matrix element of the transition <2|***d***|1> is non-zero

What interaction is responsible for the shape of the d-d bands ?

Main observations

- The optical d-d bands are very broad

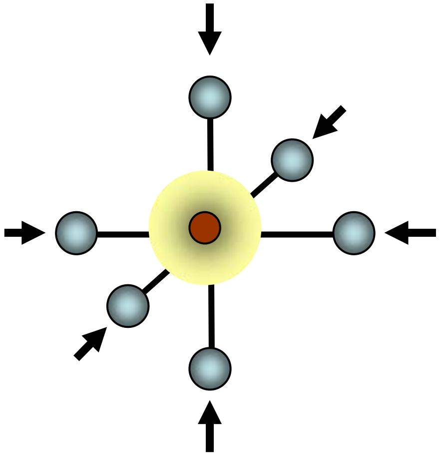
- The widths of the d-d bands are of the order of 10^3-$6\bullet10^3$ cm^{-1}

- The d-d bands in crystals are considerably broader than the lines in the atomic spectra

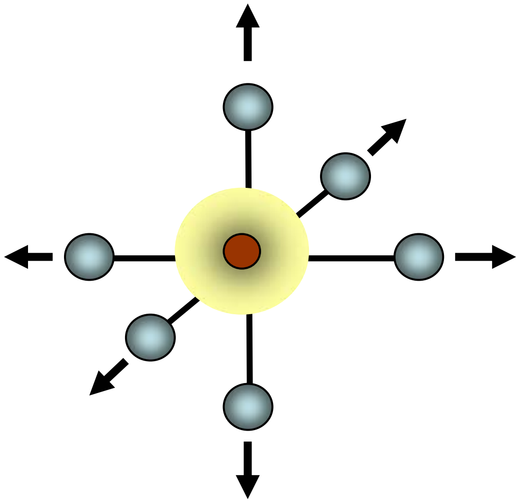
- The interaction of d-electrons with the crystal or molecular vibrations is responsible for the width of the d-d bands

Electron-vibrational interaction

- **The transiton metal center is considered as a complex formed by the central ion and the adjacent ions of the lattice (ligands)**
- **The displacements of the ligands appear due to the modulation of the crystal field by lattice vibrations**
- **The interaction of the d-ion electrons with the ligand displacements represents the electron -vibrational interaction . Actually, the electron-vibrational interaction is the change in the energy of the cluster due to the displacements of the ligands**

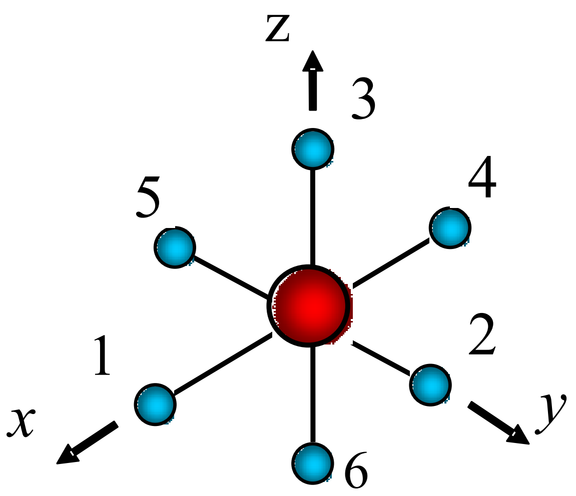


Increase in energy



Decrease in energy

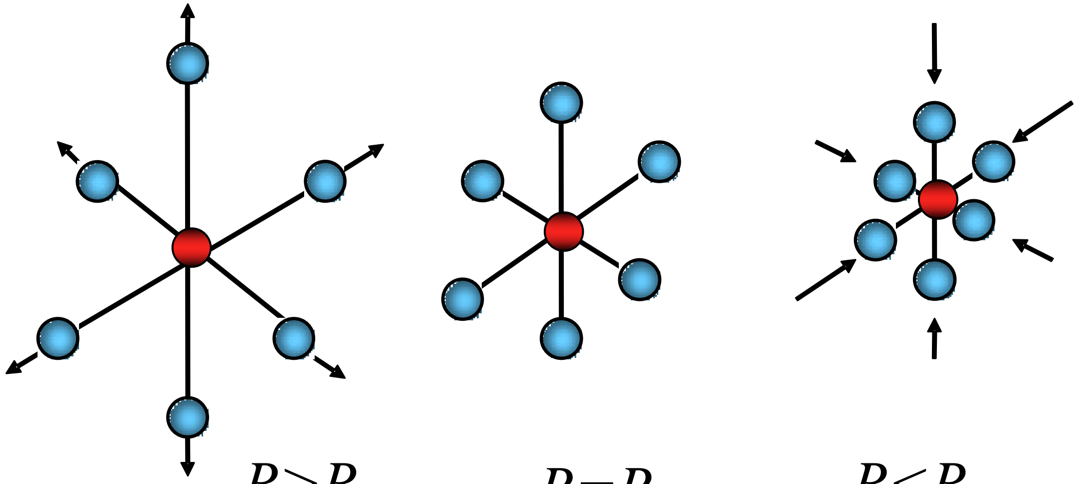
Full –symmetric vibration of the octahedral metal complex



Octahedral ML_6 complex: coordinate system and enumeration of ligands

R_0-equilibrium metal-ligand (M-L) distance

$X_i,\ Y_i, Z_i$ – *ligand displacements*



$R>R_0$ $R=R_0$ $R<R_0$

Q –full symmetric (“breathing”) collective coordinate of the ML_6 complex

$$Q=\frac{1}{\sqrt{6}}\left(X_1-X_4+Y_2-Y_5+Z_3-Z_6\right)$$

Electron-vibrational interaction

$$H_{ev} = v(\vec{r})Q$$

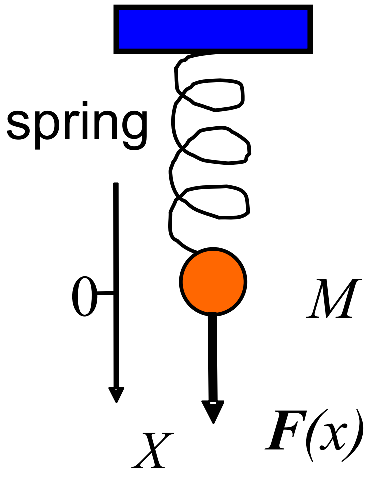
$$v(\vec{r}) = \left(\frac{\partial V(\vec{r}, \vec{R})}{\partial R} \right)_{R=R_0}$$

$$Q = \frac{1}{\sqrt{6}}\left(X_1 - X_4 + Y_2 - Y_5 + Z_3 - Z_6\right)$$

$$V = \sum_{i=1}^{6} \frac{Ze^2}{\left|\vec{r} - \vec{R}_i\right|}$$

Q –full symmetric collective coordinate of the metal-ligand complex

Analogy derived from the classical mechanics



Potential energy

$$U(x) = \frac{kx^2}{2}$$

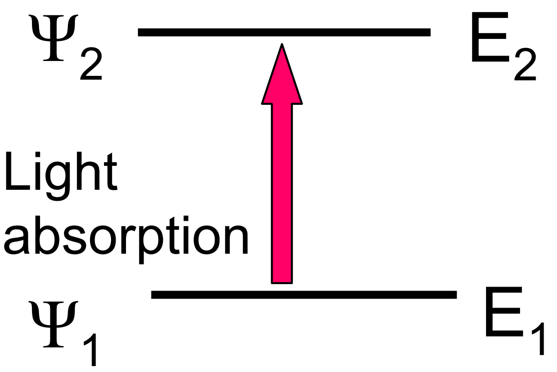
$k = M\omega^2$ –force constant, *M* –mass, ω- frequency of vibration

Force acting on the mass M

$$F(x) = -\frac{\partial U(x)}{\partial x} = -\frac{\partial}{\partial x}\frac{kx^2}{2}, \quad F(x) = -kx$$

Vibronic parameters

Two d- levels with energies E_1 and E_2 and wave functions Ψ_1 and Ψ_2



Electron-vibrational interaction

$$H_{ev} = v(\vec{r})Q$$

❑**The value** $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$ **is the probability to find the electron in the proximity of the point with the coordinate r**

❑ $e\rho(\mathbf{r})$ is the density of the electronic charge**(“cloud”)** in the point **r** (e –charge of electron)

❑ electronic densities are different in the states ψ_1 and ψ_2

$$\rho_1(\mathbf{r}) = |\psi_1(\mathbf{r})|^2$$

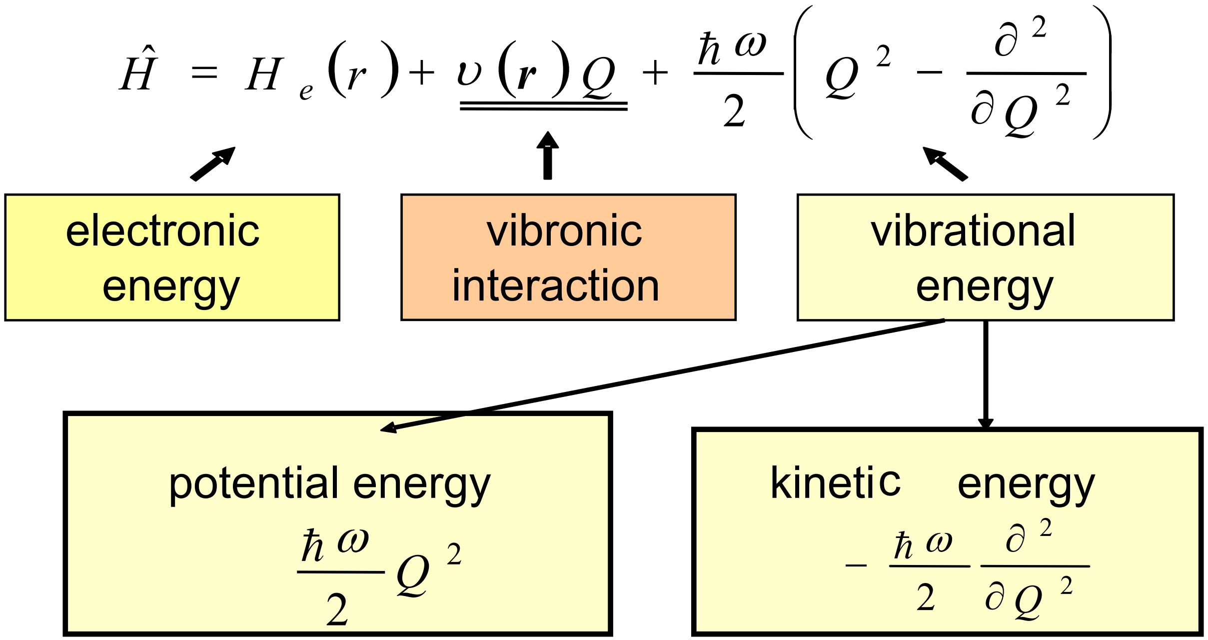
$$\rho_2(\mathbf{r}) = |\psi_2(\mathbf{r})|^2$$

❖**Vibronic parameters v_1 and v_2 represent the mean values of the operator $v(r)$ in the states Ψ_1 and Ψ_2**

$$v_1 = \int dr\, v(r)|\psi_1(r)|^2, \quad v_2 = \int dr\, v(r)|\psi_2(r)|^2$$

❖**Vibronic parameters <u>do depend on the electronic state</u> and are different for states 1 and 2**

HAMILTONIAN OF THE COUPLED ELECTRON-VIBRATIONAL SYSTEM



$$\hat{H} = H_e(r) + \underline{\underline{\upsilon(\mathbf{r})Q}} + \frac{\hbar\omega}{2}\left(Q^2 - \frac{\partial^2}{\partial Q^2}\right)$$

electronic energy

vibronic interaction

vibrational energy

potential energy $\frac{\hbar\omega}{2}Q^2$

kinetic energy $-\frac{\hbar\omega}{2}\frac{\partial^2}{\partial Q^2}$

electrons ⇨ move fast

ligands ⇨ move slowly

$$M_{ion} >> m_{electron}$$

At the first step one can neglect the kinetic energy of ligands (heavy ions)

TWO STEPS OF THE ADIABATIC APPROXIMATION

1) **Neglect of the kinetic energy of ligands (heavy ions)**

Initial (exact) Hamiltonian

$$H = \underbrace{H_e(\vec{r})}_{\text{Electronic energy}} + \underbrace{v(\vec{r})Q}_{\text{Vibronic interaction}} + \frac{\hbar\omega}{2}(\underbrace{Q^2}_{\text{Potential energy of ligands}} - \underbrace{\frac{\partial^2}{\partial Q^2}}_{\text{Kinetic energy of ligands}})$$

New (approximate) Hamiltonian

$$H = H_e(\vec{r}) + v(\vec{r})Q + \frac{\hbar\omega}{2}Q^2$$

2) **Averaging of the vibronic interaction over all possible positions of the electron**

New concept : Adiabatic potential

What does it mean ?

ADIABATIC POTENTIALS $U_1(Q)$ AND $U_2(Q)$ FOR A TWO LEVEL SCHEME

$$U_1(Q) = E_1 + \upsilon_1 Q + \frac{\hbar\omega}{2} Q^2 \Rightarrow state \ \text{"1"}$$

$$U_2(Q) = E_2 + \upsilon_2 Q + \frac{\hbar\omega}{2} Q^2 \Rightarrow state \ \text{"2"}$$

E_1,E_2–*energies of an electron in a static crystal field (full energy of an electron)*

υ_2 , υ_1 –*vibronic parameters for states 1 and 2*

$\upsilon_1 Q$, $\upsilon_2 Q$ –*averaged energies of the interaction of the electron with the vibration* Q

$\frac{\hbar\omega}{2} Q^2$ –*potential energy of vibrations*

ADIABATIC POTENTIAL CAN BE ASSOCIATED WITH THE FULL ENERGY OF THE SYSTEM , WHEN THE KINETIC ENERGY OF LIGANDS IS NEGLECTED

ADIABATIC POTENTIALS $U_1(Q)$ AND $U_2(Q)$ FOR A TWO LEVEL SCHEME

$$U_1(Q) = E_1 + \upsilon_1 Q + \frac{\hbar\omega}{2} Q^2 \Rightarrow state \ \ "1"$$

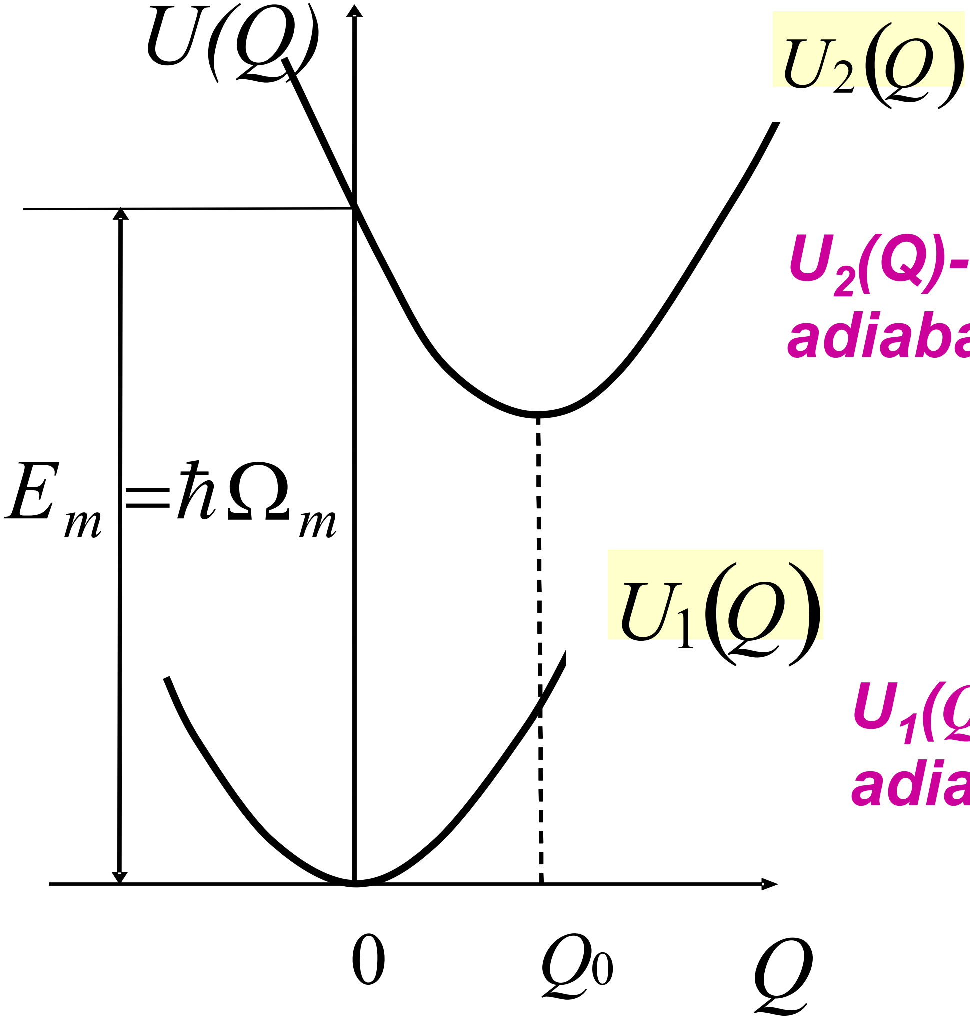
$$U_2(Q) = E_2 + \upsilon_2 Q + \frac{\hbar\omega}{2} Q^2 \Rightarrow state \ \ "2"$$

- Adiabatic potential=Full energy of the system (electron+vibration) in the adiabatic approximation

- The full energy of the system = the energy of the electron in the crystal field (E_1, E_2) + the potential energy of the vibration($\hbar\omega Q^2/2$) + the energy of the interaction between the electron and ligands ($\upsilon_1 Q$, $\upsilon_2 Q$) averaged over all instant positions of the electron

- The full energy of the system depends on the vibrational coordinate Q

ADIABATIC POTENTIALS $U_1(Q)$ AND $U_2(Q)$ FOR A TWO LEVEL SCHEME



$U_2(Q)$-excited state adiabatic potential

$U_1(Q)$-ground state adiabatic potential

ELECTRON-VIBRATIONAL TRANSITIONS-
FRANCK-CONDON PRINCIPLE

- ☐ **This principle represents the main tool for understanding the optical absorption and emission in electron vibrational systems and the basis for calculation of the shape of the optical bands**

REMINDER

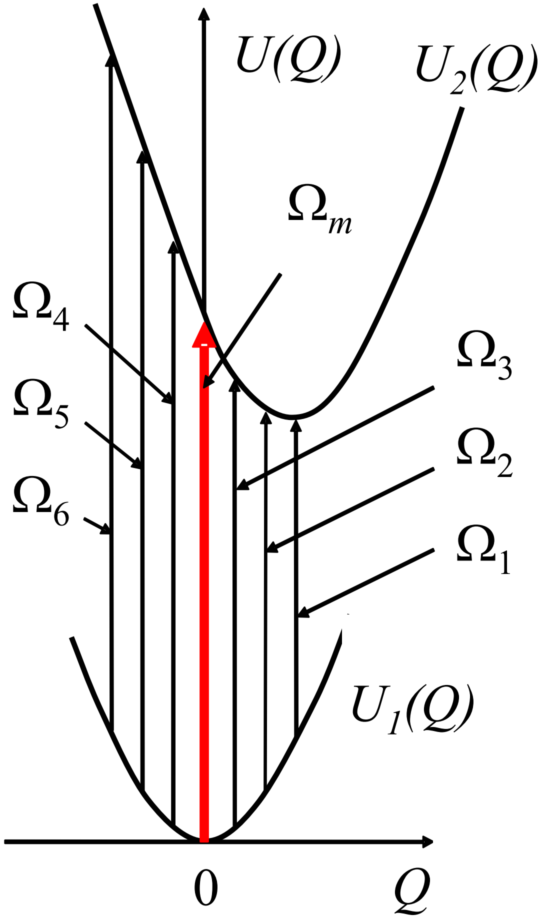
ELECTRONS ⇒ "fast" subsystem, LIGANDS ⇒"slow" subsystem

"CLASSICAL" FRANCK-CONDON PRINCIPLE

- ☐ **In the event of light absorption the electronic state ("fast" subsystem) changes so rapidly, that during the time of electronic transition in course of the photon absorption the ligands ("slow" subsystem) have no time to move (to change their positions)**

- ☐ **The condition implied by the adiabatic approximation should be fulfilled: the kinetic energy of the ligands is zero**

ORIGIN OF THE OPTICAL d-d BAND



$\Omega_6>\Omega_5>\Omega_4>\Omega_m>\Omega_3>\Omega_2>\Omega_1$

frequencies

- **Instead of one transition we see a series of transitions at different *Q* that form the absorption d-d band**
- **Each transition from the lower adiabatic sheet to the upper one corresponds to a certain frequency**
- **In correspondence with the Franck-Condon principle only vertical transitions are allowed**
- **Non-vertical transitions are forbidden because in this case the ligands change their positions during the event of the light absorption**

Adiabatic potentials (already found):

$$U_1(Q) = E_1 + \upsilon_1 \, Q + \frac{\hbar\omega}{2} Q^2 \Rightarrow \mathit{state} \;\; "1"$$

$$U_2(Q) = E_2 + \upsilon_2 \, Q + \frac{\hbar\omega}{2} Q^2 \Rightarrow \mathit{state} \;\; "2"$$

SHAPE-FUNCTION OF THE ABSORPTION BAND

$$\boldsymbol{F}(\Omega) = \boldsymbol{d}_{21}^{2} \sqrt{\frac{\hbar^3 \omega}{2\pi \boldsymbol{k}_{\boldsymbol{B}} \boldsymbol{T} (\boldsymbol{v}_2 - \boldsymbol{v}_1)^2}} \exp\left(- \frac{\hbar^3 \omega (\Omega - \Omega_{\boldsymbol{m}})^2}{2\pi \boldsymbol{k}_{\boldsymbol{B}} \boldsymbol{T} (\boldsymbol{v}_2 - \boldsymbol{v}_1)^2} \right)$$

$$\hbar\Omega_m = E_2 - E_1 + \frac{\nu_1 (\nu_1 - \nu_2)}{\hbar\omega} \qquad \boldsymbol{d}_{21} = \int \psi_2^{*}(\boldsymbol{r}) \boldsymbol{d} \psi_1(\boldsymbol{r}) d\tau$$

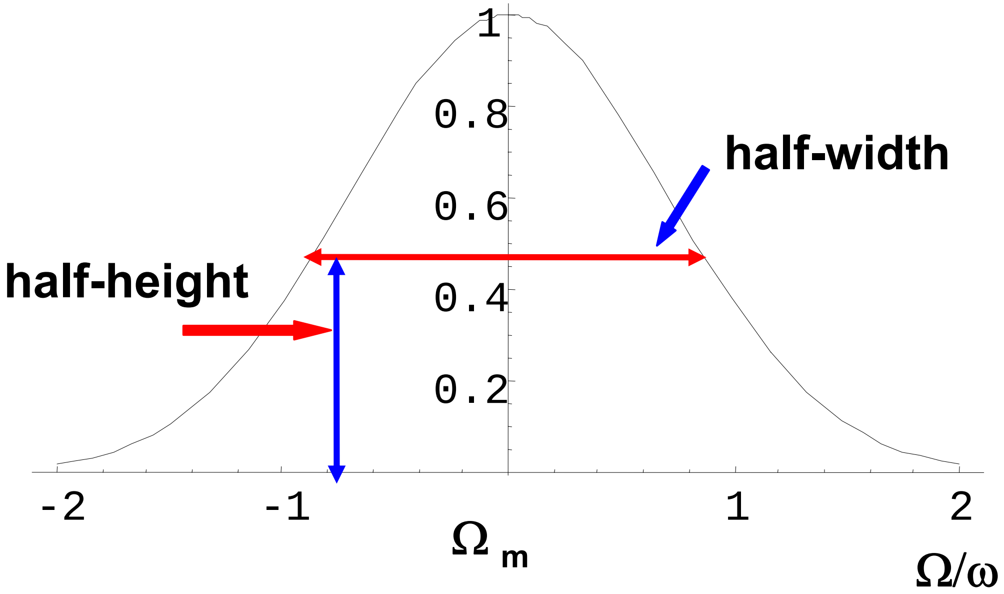
❖ The absorption band is described by a “GAUSSIAN “ curve

❖ The band has a maximum at $\Omega = \Omega_m$, the band can be observed if $d_{21} \neq 0$

❖ The shape of the band and the position of the maximum depend on the vibronic parameters υ_1, υ_2 , temperature T and the energy gap $E_2 - E_1$ between the electronic levels in the crystal field

Optical absorption band ⇒symmetric “bell-shaped” curve with the maximum at $\Omega = \Omega_m$

Intensity of absorption, $F(\Omega)/d_{21}^2$



Frequency of the absorbed light

$$F(\Omega) = d_{21}^2 \sqrt{\frac{\hbar^3 \omega}{2\pi k_B T (\nu_2 - \nu_1)^2}} \exp\left(- \frac{\hbar^3 \omega (\Omega - \Omega_m)^2}{2\pi k_B T (\nu_2 - \nu_1)^2} \right)$$

$F(\Omega_m)$ –height of the band in the maximum

$$F(\Omega_m) = d_{21}^2 \sqrt{\frac{\hbar^3 \omega}{2\pi k_B T (\nu_2 - \nu_1)^2}}$$

Half-height

$$\frac{F(\Omega_m)}{2} = \frac{d_{21}^2}{2} \sqrt{\frac{\hbar^3 \omega}{2\pi k_B T (\nu_2 - \nu_1)^2}}$$

Half-width

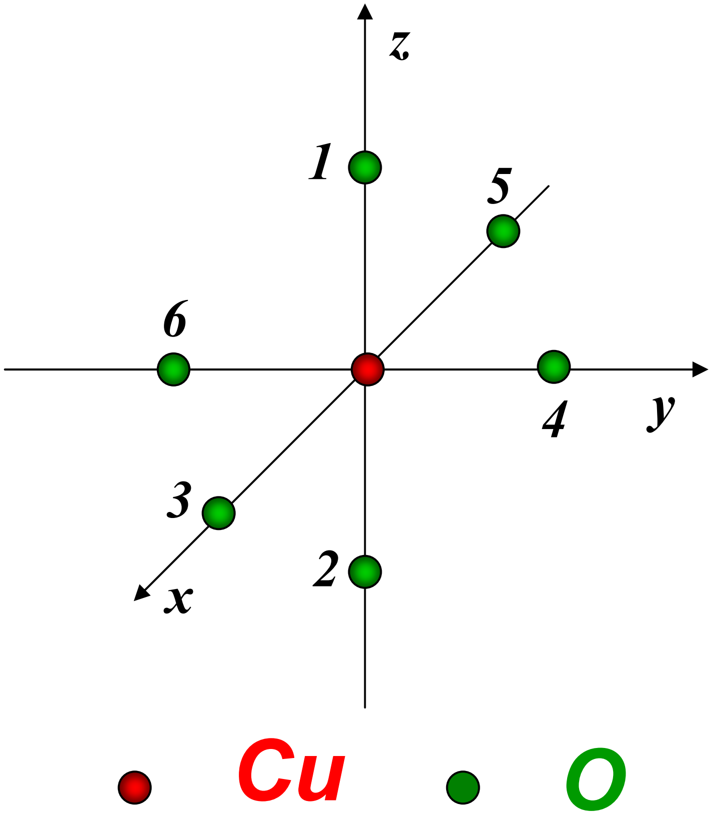
$$\delta\,\Omega = 2\sqrt{2 \ln 2 \frac{(\nu_2 - \nu_1)^2 kT}{\hbar^3 \omega}}$$

$$\delta\,\Omega \sim \sqrt{T}$$

$$F(\Omega_m) \sim 1/\sqrt{T}$$

EXAMPLE

Structural data: Malachite contains two types of Cu species



Malachite Cu1

R_1=2.51 Ǻ, R_2=2.64 Ǻ,

R_3=R_5=1.91 Ǻ, R_4=R_6=2.02 Ǻ

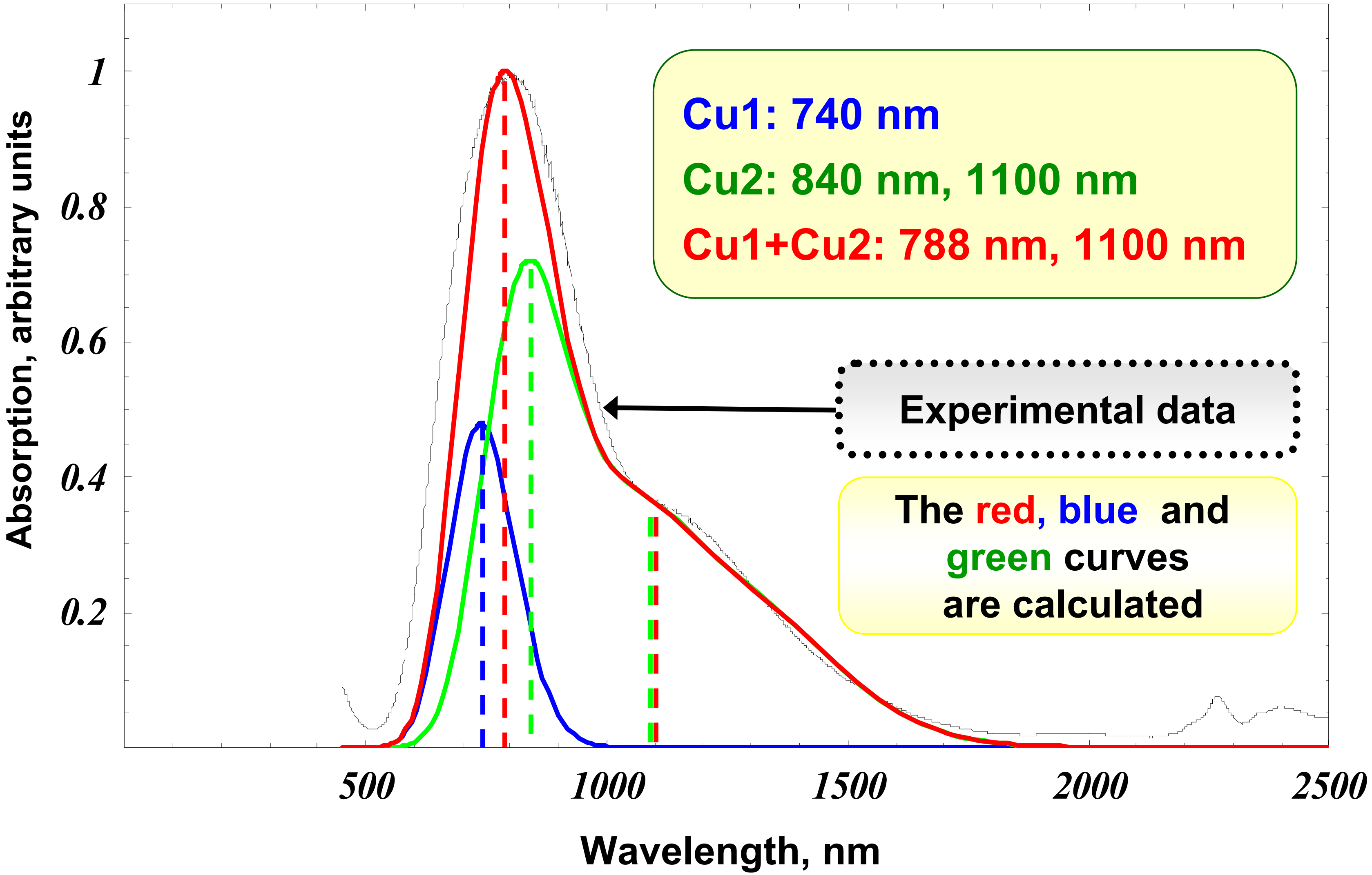
Malachite Cu2

R_1=2.28 Ǻ, R_2=1.92 Ǻ,

R_3=R_5=2.08 Ǻ, R_4=R_6=2.37 Ǻ

d-d bands of malachite

Malachite $Cu_2(CO_3)(OH)_2$ (Germany, FHI, Nov. 2006)



Cu1: 740 nm

Cu2: 840 nm, 1100 nm

Cu1+Cu2: 788 nm, 1100 nm

Experimental data

The red, blue and green curves are calculated

What is the origin of charge transfer bands?

CHARGE TRANSFER BANDS

- Charge transfer bands arise as a consequence of the absorption of light which occurs when an electron is transferred from an orbital primarily on the ligand to one primarily on the metal, or *vice versa*

- Charge transfer or electron transfer processes are termed “ligand to metal charge transfer” (LMCT) and “metal to ligand” (inverse) charge transfer (MLCT), respectively . Such a transfer occurs frequently in transition metal complexes, but only if this absorption occurs in the visible range it will give rise to a color visible to the human eye

- Charge transfer transitions are commonly of higher energies than the crystal field transitions and generally lie at the blue end of the visible region, or in the ultraviolet region

- If the metal is easily oxidisable and the ligand readily reducible ,or *vise versa* , then charge transfer transitions may occur at quite low energies

EXAMPLE : METAL HEXAHALIDES

Three main regions are observed in the charge transfer electronic spectra of these species:

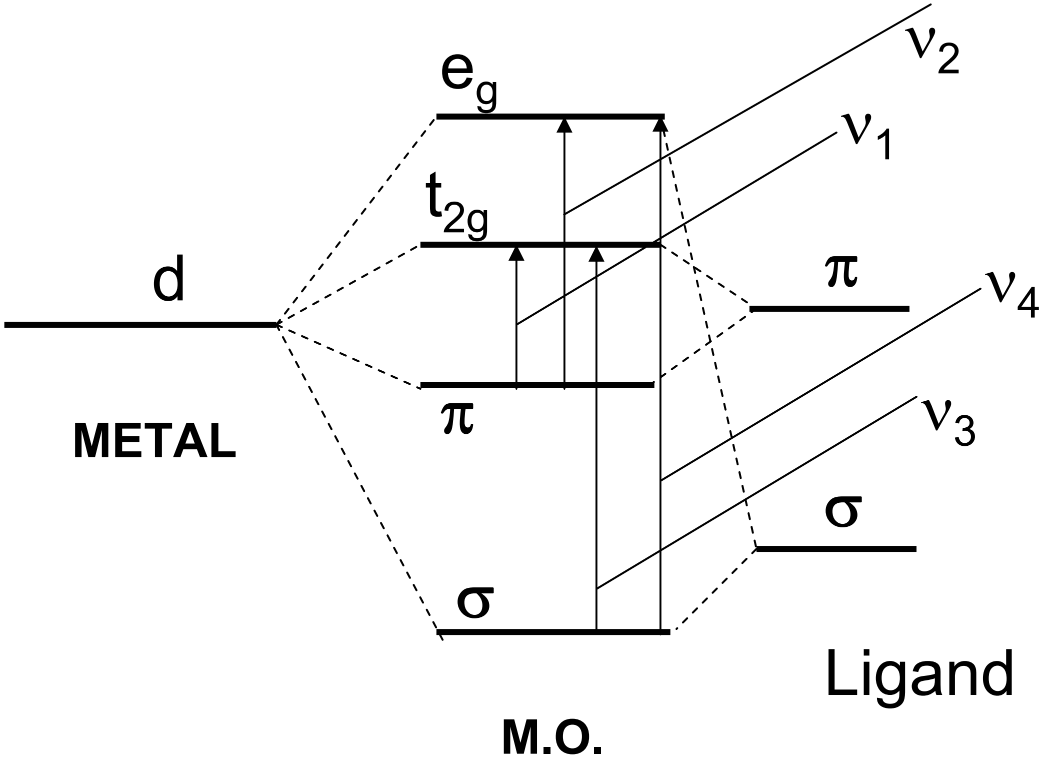
- **nd^3,nd^4,nd^5 complexes exhibit narrow LMCT bands between 15,000 and 30,000 cm^{-1}**

- **All hexahaloanions of the 4d and 5d elements exhibit broad strong absorption in the region 25,000-45,000 cm^{-1}**

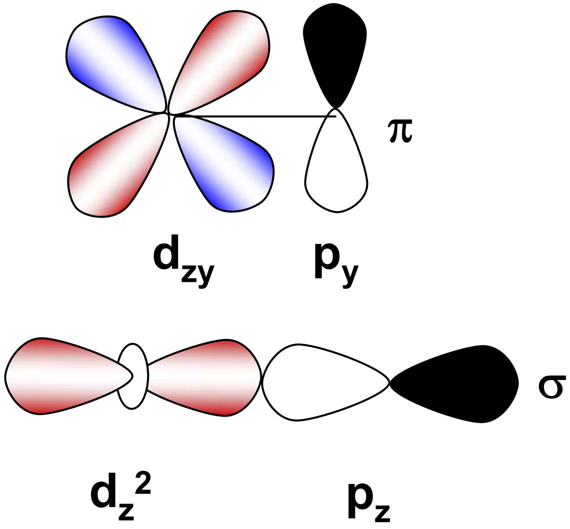
- **In certain cases it is possible to observe a very strong band lying above 44,000 cm^{-1}**

Simplified approach to the explanation of charge transfer spectra in hexahalides

- A single metal-halogen bond is considered
- The lone pairs of the halogen form the basis for the σ and π bonds to the d-ion



A molecular orbital diagram illustrating the potential ligand to metal charge transfer transitions



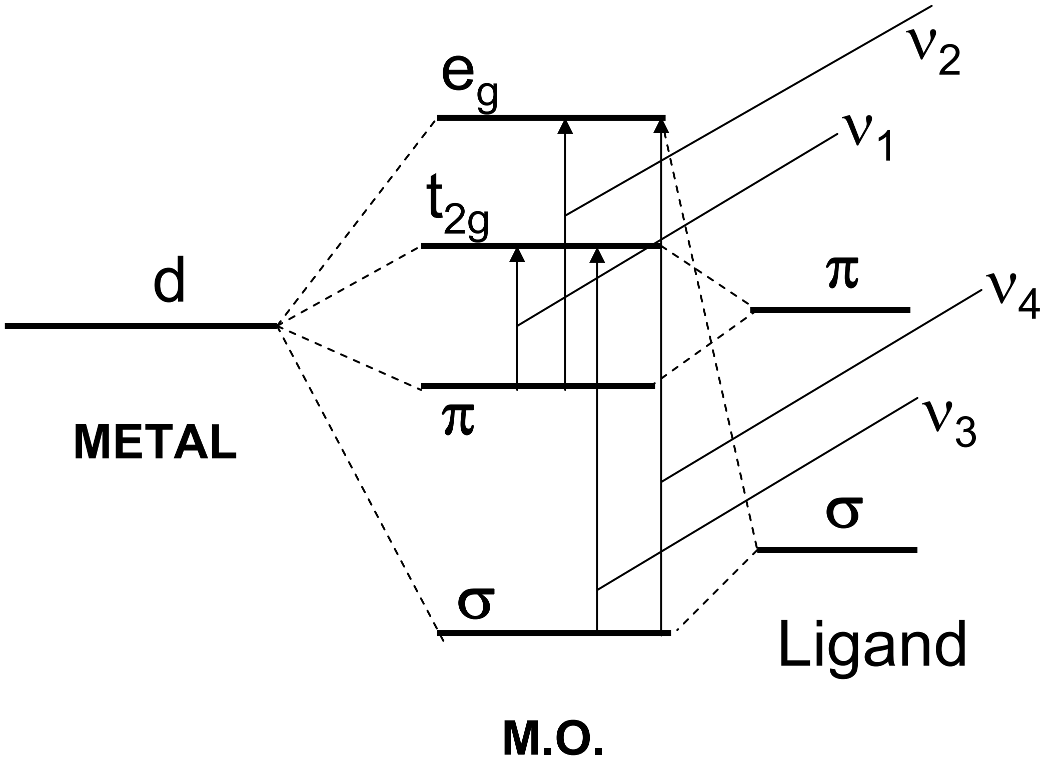
ν_1 πL---Mt_{2g}

ν_2 πL---Me_g

ν_3 σL ---Mt_{2g}

ν_4 σL ---Me_g

ASSIGNMENT OF THE LMCT TRANSITIONS IN HEXAHALIDES



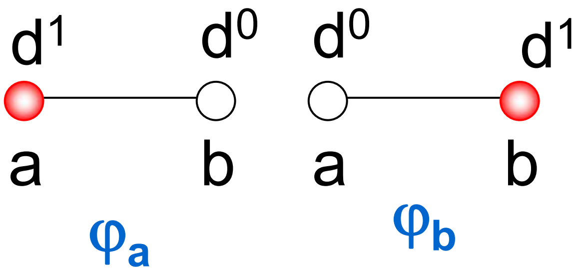
- The first set of comparatively low energy bands observed in the hexahalides may be ascribed to the ν_1 transitions. They are narrow because they involve the transitions between orbitals almost non-bonding

- The ν_2 transitions are expected to be broad because the upper level is antibonding

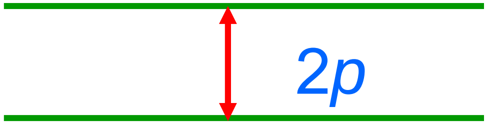
- The very high energy, and very intense, bands are assigned to ν_4

INTERVALENCE OPTICAL ABSORPTION

Let us consider a cluster containing a single d-electron over the filled ion shells ⇒d^0-d^1 (Mo^{5+}- Mo^{6+}cluster)



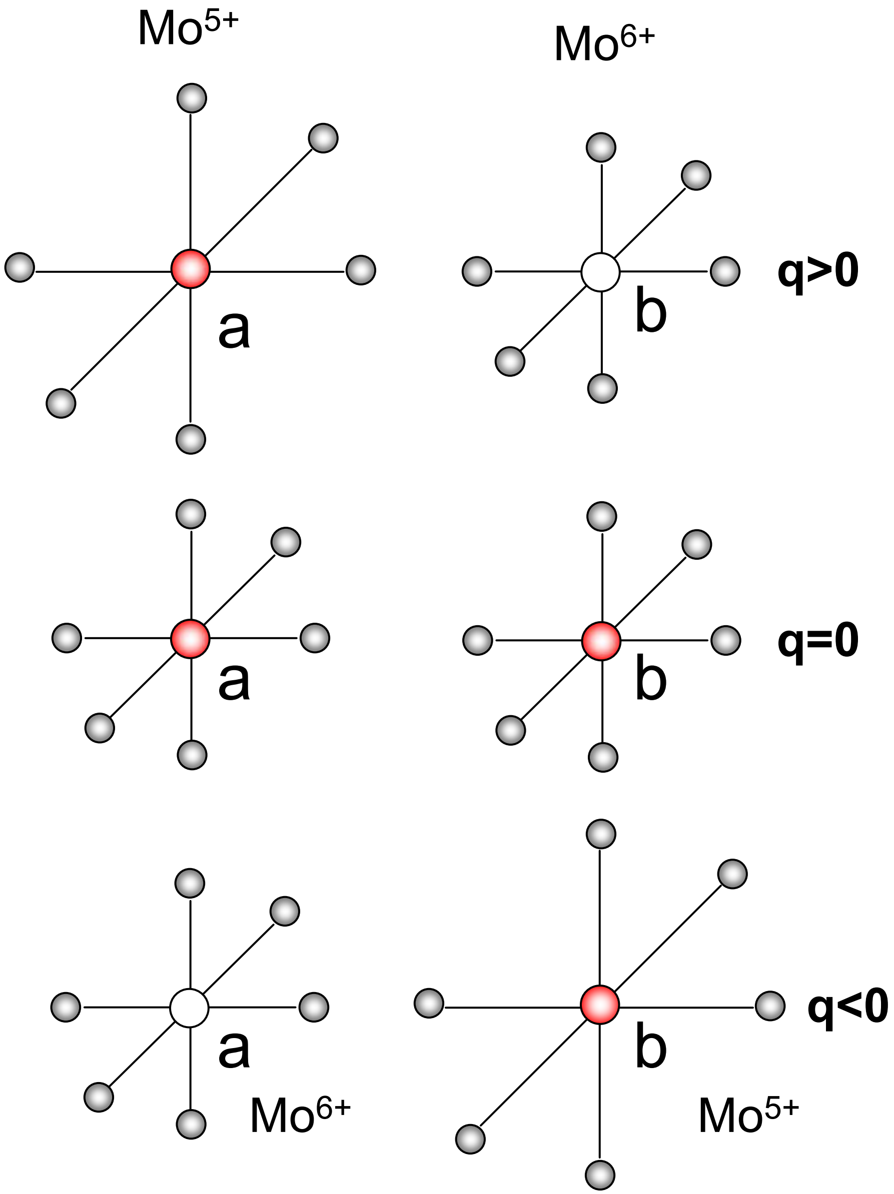
- The moving electron can be with equal probability on each of the cluster ions
- the wave functions φ_a and φ_b corresponding to the states of the electron localized on ions a and b are not the stationary states of the system



$$\psi_+ = \frac{1}{\sqrt{2}}(\varphi_a + \varphi_b)$$

$$\psi_- = \frac{1}{\sqrt{2}}(\varphi_a - \varphi_b)$$

The energy spectrum of such a system consists of two tunnel electronic levels with energies ±p and wavefunctions $\psi_\pm = \frac{1}{\sqrt{2}}(\varphi_a \pm \varphi_b)$



$q=(Q_a-Q_b)/(2)^{1/2}$

Mo^{5+}-Mo^{6+} -cluster

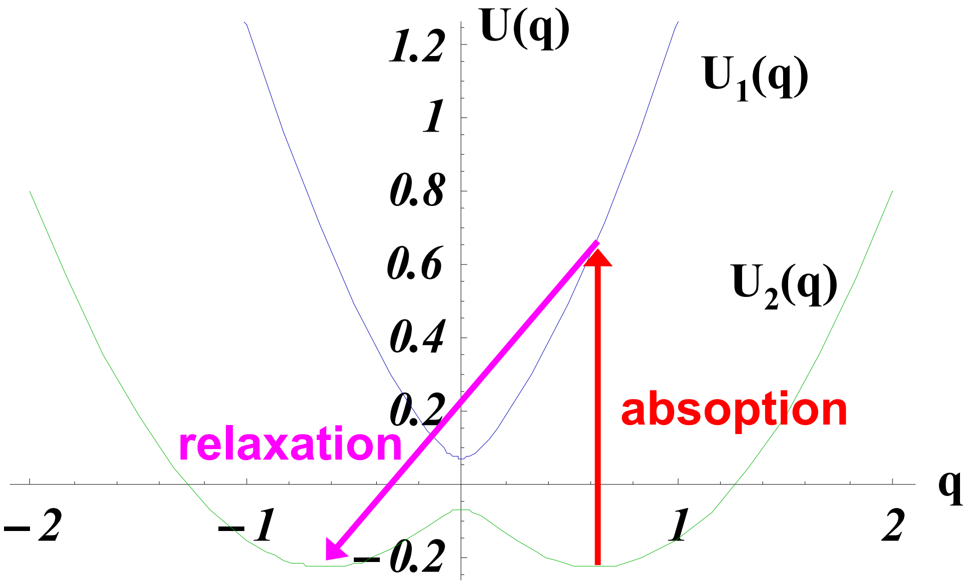
Q_a, Q_b are the totally symmetric (breathing) modes of the two cluster moieties

The breathing mode best of all “pushes” out or “draws” in the excess electron when the nearest surrounding of the metal ion contracts or expands

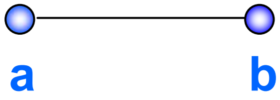
$q=(Q_a- Q_b)/(2)^{1/2}$ is the antisymmetric mode of the whole cluster consisting of two coupled octahedral metal centers

INTERVALENCE OPTICAL BANDS

(light induced electron transfer)

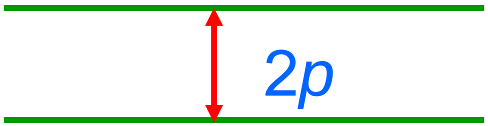


a(Mo^{6+})b(Mo^{5+}) a(Mo^{5+})b(Mo^{6+})



Dimeric cluster $Mo^{5+} – Mo^{6+}$

a, b- Mo ions



the transition

a(Mo^{6+}) b(Mo^{5+}) ⟹ a(Mo^{5+}) b(Mo^{6+})

Is induced by light

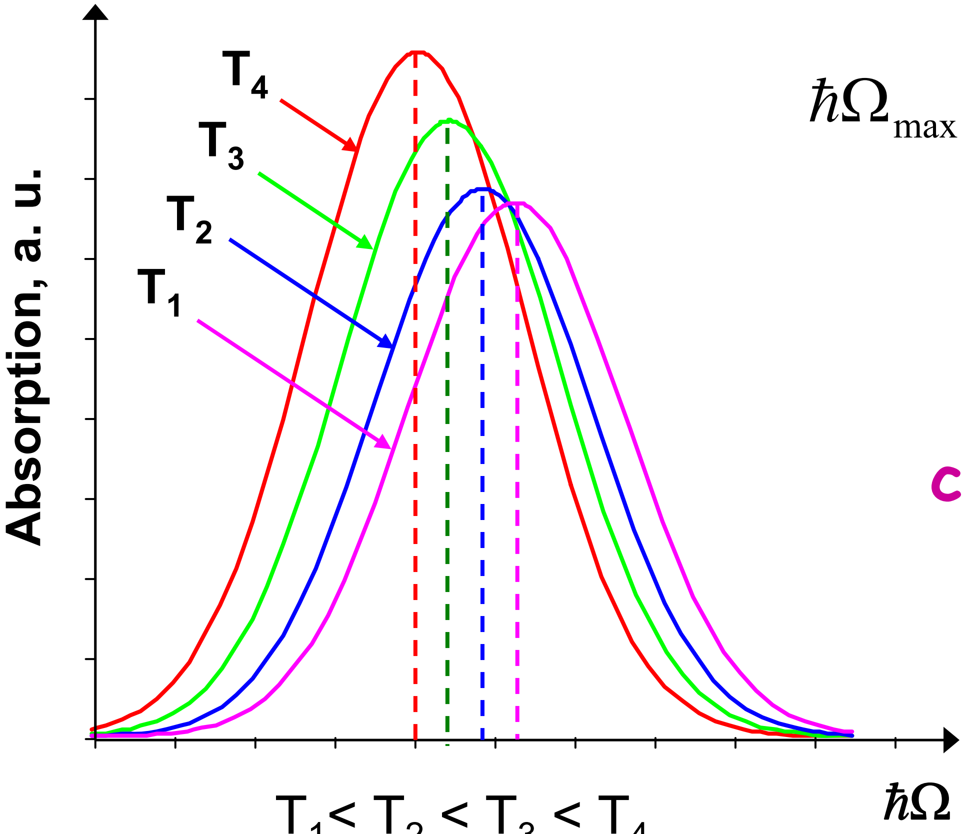
ADIABATIC POTENTIALS

$$U_{1,2}(q) = \frac{\hbar\omega}{2} q^2 \pm \sqrt{p^2 + \upsilon^2 q^2}$$

$$q = \frac{1}{\sqrt{2}} (Q_a - Q_b)$$

p – transfer parameter, ω – vibrational frequency, υ – vibronic constant, Q_c - full symmetric breathing mode of the local surrounding of ion c (c=a,b)

INTERVALENCE OPTICAL BANDS



$T_1 < T_2 < T_3 < T_4$

$\hbar\Omega_{max1} > \hbar\Omega_{max2} > \hbar\Omega_{max3} > \hbar\Omega_{max4}$

$\lambda_{max1} < \lambda_{max2} < \lambda_{max3} < \lambda_{max4}$

$$\hbar\Omega_{\max} = \frac{\upsilon^2}{2\hbar\omega} + \sqrt{\left(\frac{\upsilon}{2\hbar\omega}\right)^2 - \frac{4k_B T\upsilon^2}{\hbar\omega}}$$

The energy of the maximum of the charge transfer band decreases with temperature

RED SHIFT

CHARGE TRANSFER BAND IN THE HETEROPOLY ACID $H_4PVMo_{11}O_{40} \cdot y\ H_2O$ AT 422 K

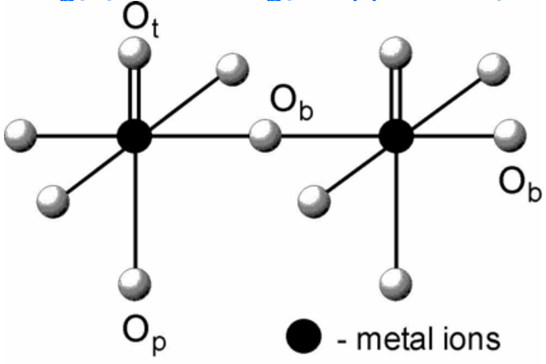
- ☐ The TG experiments evidence complete crystal water loss at 422K
- ☐ After crystal water loss all four acidic protons are attached to the polyanion
- ☐ EPR data show that in the untreated HPA the Keggin unit represents a one electron-reduced structure. The electron can be delocalized over twelve metal sites (11Mo and V) of the Keggin molecule

CHARGE TRANSFER BAND IN THE HETEROPOLY ACID $H4PVMo_{11}O_{40}$ .y H_2O AT 422 K

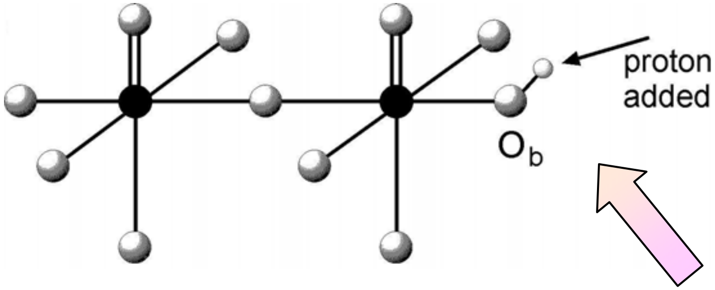
- The charge transfer band was shown to be formed by intervalent optical transitions in intact and protonated species $(Mo^{5+}H_b)(Mo^{6+}H_b)O_{11}$, $(Mo^{5+}H_b)(Mo^{6+})O_{11}$,

$(Mo^{5+}H_b)(V^{5+})O_{11}$, $Mo^{5+}Mo^{6+}O_{11}$

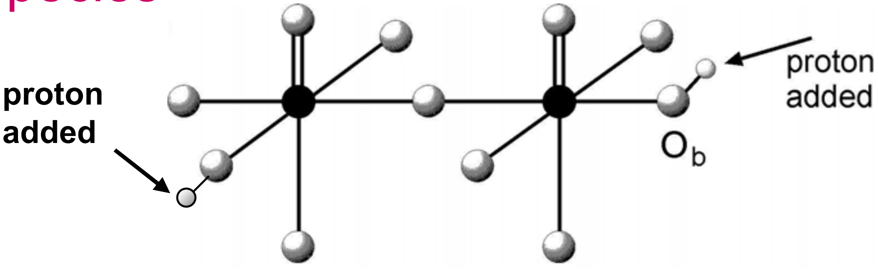
$(V^{4+}H_b)(Mo^{6+}H_b)O_{11}$, $(V^{4+}H_b)(Mo^{6+})O_{11}$, V^{4+} $Mo^{6+}O_{11}$



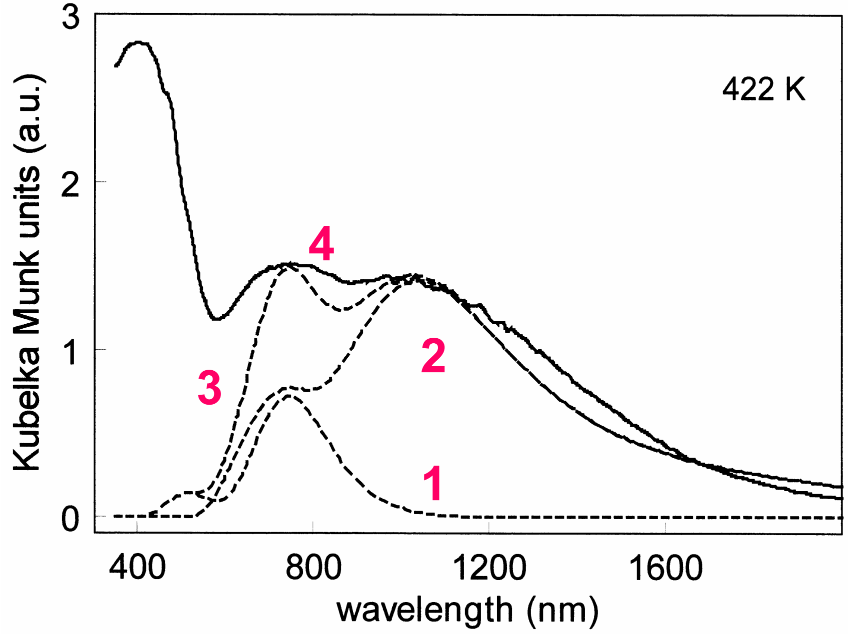
intact species

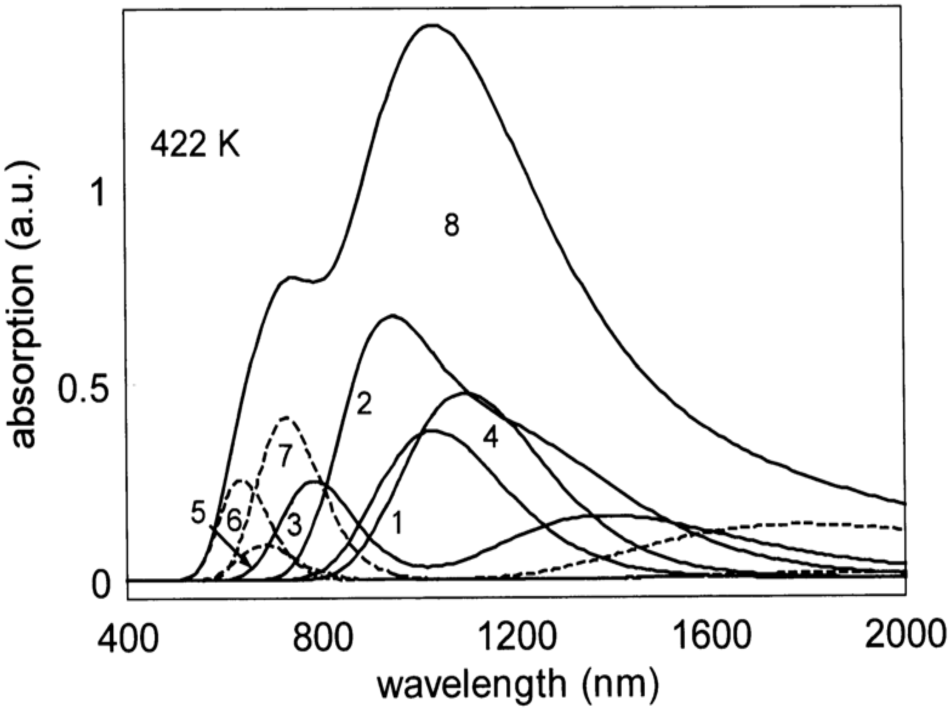


protonated species



Absorption band of the $H_4PVMo_{11}O_{40}$ compound at 422 K





- - - - – calculated

1 – contribution from the d-d transitions

2 – contribution from the charge transfer band

3 – total calculated spectrum

4 – experimental data

Contributions from different intervalent transitions in binuclear species to the charge transfer band

1.$(MoH_b)(MoH_b)O_{11}$-13.2%;

2. $(MoH_b)MoO_{11}$-33%;

3. $(MoH_b)VO_{11}$-15%;4.Mo_2O_{11}-18.2%;

5. $(VH_b)(MoH_b)$O11-1.6%;

6. $(VH_b)MoO_{11}$-4%; 7.$VMoO_{11}$-15%;

8-total charge transfer band

THANK YOU FOR ATTENTION