**KJ2031 kompendium – Ninni**

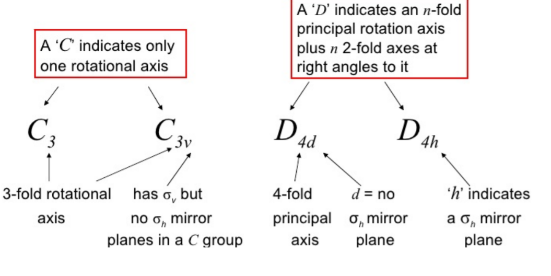
**Bond theories**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Description | Advantages | Disadvantages |
| Lewis | ▪ Covalent bonding  ▪ Octet rule  ▪ 2D structure | ▪ Bond orders  ▪ Lone pair  ▪ **Formal charge**  ▪ Bonding energy  ▪ Resonance | ▪ Molecular geometry (shape)  ▪ Bond angles |
| VSEPR | ▪ Electron density determines shape  ▪ Bonding & lone-pair regions | ▪ 3D shape  ▪ Some info on bond angles  ▪ **Best for spatial arrangement** | ▪ Difficult to predict if >1 similar energy structure  ▪ Cannot predict  actual bond angle |
| VB | ▪ Quantum mechanics  ▪ Considers orbital interaction  ▪ AO overlap 🡪 bonding  ▪ Hybridization | ▪ 3D structure  ▪ **Bond angle info**  ▪ Considers repulsion between electron density regions | ▪ Does not easily handle polyatomic molecules  ▪ Localized hybrid orbitals |
| MO | ▪ #MOs = #AOs  ▪ Probability to find in internuclear region by wavefunction for each e-  ▪ Constructive and destructive AO interference 🡪 bonding and antibonding MO’s  ▪ AOs must have the same symmetry to form MOs  ▪Aufbau, Pauli, Hund  ▪ σ, π and δ-orbitals | ▪ Good for predicting electronic spectra and ***paramagnetism***  ▪ Good for diatomic molecules | ▪ Delocalized electrons 🡪 no resonance structures  ▪ Complex for polyatomic |

|  |  |  |
| --- | --- | --- |
| Aufbau | Pauli exclusion principle | Hund’s rule |
| Electrons fill atomic orbitals of lowest available energy levels before occupying higher levels. | No two electrons in the same atom can have all 4 identical quantum numbers. Max two electrons per orbital which must have opposite spin. | * Bus seat principle.   Orbitals of equal energy are each occupied by one electron (of same spin) before any orbital is occupied by a second electron. |

|  |  |  |
| --- | --- | --- |
| σ-orbitals | π-orbitals | δ-orbitals |
| ▪ Overlapping of 2 AOs having cylindrical  symmetry around internuclear axis  ▪ 2s & 2pz | ▪ Remaining 2p orbitals having nodal plane on z-axis  ▪ 2py & 2px  ▪ Doubly degenerate pair of bonding and antibonding MOs | ▪ and dxy hav no counterparts like s and p  ▪ Match with other atoms  ▪ Doubly degenerate pairs of B and AB 𝛿 orbitals |

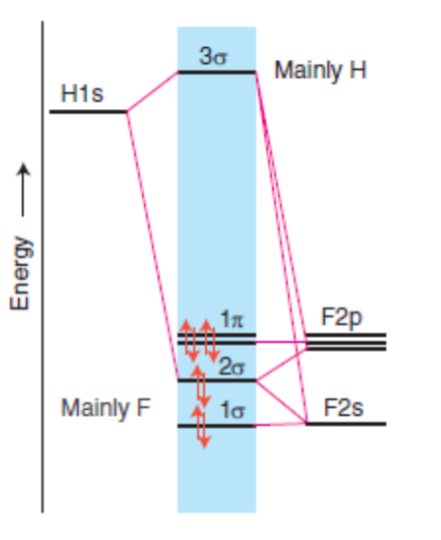
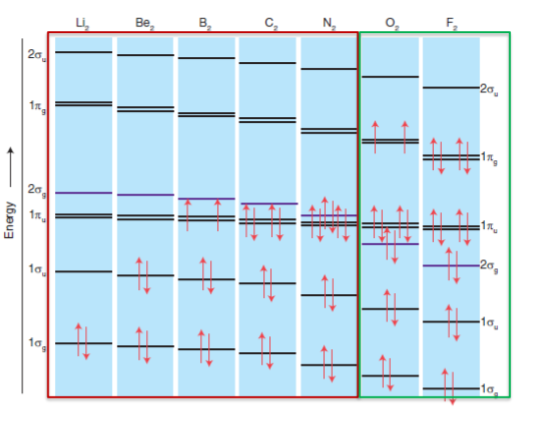
|  |  |  |
| --- | --- | --- |
| Point groups with operations | | Example |
| D∞h | Linear + i | Et bilde som inneholder sport, biljardkule  Automatisk generert beskrivelse CO2 |
| C∞v | Linear | hydrogen cyanide |
| Ih | C3 + i + C5 | Et bilde som inneholder innendørs  Automatisk generert beskrivelse buckyball |
| Oh | C3 + i + cubic | SF6 |
| Td | C3 + cubic | methane |
| Dnh | Cn + σh + nC2 Cn | Et bilde som inneholder innendørs  Automatisk generert beskrivelse D6h: benzene |
| Dnd | Cn + nσd + nC2 Cn | D3d: staggered ethane |
| Dn | Cn + nC2 Cn | Et bilde som inneholder innendørs, tilbehør  Automatisk generert beskrivelse D4: tetrathiacyclododecane |
| Cnh | Cn + σh | C3h : boric acid |
| Cnv | Cn + nσv | C4v: BrF5 & C3v: NH3 & C2v: H2O |
| Cn | Cn | Et bilde som inneholder kjede, tilbehør, veksle  Automatisk generert beskrivelse C3: triphenylphosphine |
| S2n | Cn + S2n | Et bilde som inneholder pil  Automatisk generert beskrivelseS6: posner molecule |
| Cs | σh | ethylene-BrCl |
| Ci | i | ethane-Br2Cl2 |
| C1 | E | bromochlorofluoromethane |



It has σd if it bisects two C2

|  |  |
| --- | --- |
| Symmetry operations | |
| E | Identity |
| Cn | Rotation axis |
| σ | Mirror plane: h,v,d |
| i | Inversion center |
| Sn | Rotation + reflection |

**Group orbitals and SALC’s**



N2 & O2: D∞h HF: C∞v

**Character table**

*Symmetry species / types*

* A: function is symmetric with respect to rotation character = 1
* B: function changes sign under rotation character = -1
* A1: 1 refers to symmetric with respect to reflection in principle vertical plane
* A2: 2 function changes sign under reflection

|  |
| --- |
| Point groups |
|  |

**Famous molecules**

|  |  |  |  |
| --- | --- | --- | --- |
|  | MO | Character table | Spectra |
| BeH2  Point gr.:  D∞h |  | (linear)  E + C∞, C2, i, σv  A1g: 2s + Φ+  A1u: 2pz + Φ-  E1u: (2px & 2py) |  |
| BH3  Point gr.:  D3h |  | E, C3, 3C2, σh, 3σv, 3S3  A1’: 2s + Φ1  A2’’: 2pz  E’: (2px&2py) + Φ2 + Φ3 |  |
| H2O  Point gr.:  C2v |  | E, C2, σv(xz), σv(yz)  A1: 2s, 2pz, Φ+  B1: 2px  B2: 2py + Φ- |  |
| NH3  Point gr.:  C3v |  | E, C3, σv  A1: 2s + 2pz + Φ1  E: (2px&2py) + Φ2 + Φ3 |  |
| N2  O2  Point gr.:  D∞h |  | E, C∞, C2, i, σv |  |

Which MO has higher energy?

* Number of nodes
* Amount destructive interference

|  |  |
| --- | --- |
| Walsh diagrams | |
| AH2 | **AH3** |

|  |  |  |
| --- | --- | --- |
| XPS (PES) | UPS (PES) | XAS |
| ▪ Source: often Mg or Al-anode  ▪ bombardment of high energy electron beam 🡪 radiations 🡪 ionization from core orbitals of elements in the sample  ▪ Characteristic of elements  ▪ Oxidation states  ▪ Line width of radiation is 1-2 eV  ▪ Not suitable to study the fine detail of valence orbitals  ▪ To study the band structure of orbitals  ▪ For surface elemental analysis of solids  ▪ Due to mean free path of electron in solid being 1 nm | ▪Source: He discharge lamp  ▪ Line width is much smaller than XPS (0.01)   * valence energy levels * vibrational fine structure * Bonding or antibonding character of orbitals from which electrons are ejected   ▪ Koopman’s theorem:   * ionization energy is equal to the negative of orbital energy   ▪ The KE of photoelectron can be used to determine orbital energy | ▪ Find local geometry and electronic structure  ▪ EMR from charged particles (e-) in a magnetic field  ▪ Intensity from ionization of core-electrons in transition metals  ▪ XANES (near edge)   * Find oxidation state (higher state = higher ionization energy) * Symmetry (shoulder and pre-edge) * Fingerprint (compare)   ▪ EXAFS   * #neighbors & type * Bond length * # of shells and distance * Fourier transformation   ▪ Limitations   * Cannot differentiate oxidation states if mix * Cannot differentiate very similar atoms * Short-range technique   GOOD: Precise atomic distance and bond length |

**Fotoelektronspektroskopi (PES)** er en teknikk hvor man sender inn monokromatisk elektromagnetisk stråling på en prøve som fører til utsendelse av elektroner. Ved å måle den kinetiske energien til utsendte elektroner kan man finne ioniseringsenergien/bindingsenergien til AO/MO nivået elektronet kom fra ved hjelp av Koopmanns likning: Ek = hv – Ei. Ved innsendelse av røntgen slår man løs kjerneelektroner og kan brukes til bestemmelse av båndstruktur til faste stoffer og bestemmelse av sammensetning i et materiale (overflatebestemmelse). Ved innsendelse av UV får vi ionisering av valenselektroner og kan benyttes til verifisering av rekkefølge på MO-diagram.

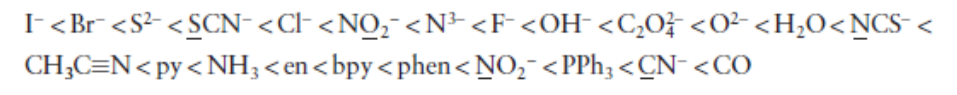
**Røntgenabsorbsjonsspektroskopi (XAS)** er en teknikk som baserer seg på ionisering av elektroner ved hjelp av røntgenfotoner. Her måles den transmitterte intensiteten av fotonstrålen som igjen forteller oss energien som kreves for å ionisere et 1s elektron. Energien vil være sensitiv til valenstilstand på grunn av endring i effektiv kjerneladning og dette fører til at absorpsjonskanten vil flytte seg mot økende energi ved økning av oksidasjonstilstand. XAS kan benyttes til bestemmelse av hvordan et metall foreligger i et materiale (gjennomsnittsteknikk) ved sammenlikning av kjente standarder.

**UV-vis spektroskopi** sendes monokromatisk stråling i området synlig lys og UV. Her ser man på eksitasjoner, og da særlig på d-d overganger i synlig lys området samt CT i UV området. Her får man karakteristiske topper avhengig av d-konfigurasjon, geometri og antall/type ligand, men er mindre egnet til identifisering av oksidasjonstilstand på metall. Referanser er nødvendig for å anslå ukjent materiale.

**CFT vs LFT** *d-orbitals*

|  |  |  |
| --- | --- | --- |
|  | Crystal Field Theory | Ligand Field Theory |
| For? | Metal ions essentially |  |
| From? | Analysis of spectra | CFT + Application of MO  - SALCs |
|  | Essence of electronic structure of complexes | More complete description of electronic structure of complexes |
|  | - Lewis’s acid / base concept  - Ligand = negative point charge  - Splitting of d-orbitals | Sprectrochemical series:  - Order partly from effective M-L σ bonding  - Significant π-bonding🡪 strong influence on Δo  π-donor decrease Δo (WFL)  π-acceptor increase Δo (SFL)  Overall order “dominated” by π effects |
| Splitting parameter determined by | - Oxidation state of metal ion  - Nature of metal ion  - **Spectro**chemical series (nature of ligand)  - Ligand = point charge  - Only σ-bonding | MO theory  ▪ A good σ donor ligand (strong ML overlap)  ▪ π bonding  Ligand π-orbitals can interact with metal t2g orbitals ▪ Energy up or down 🡪 Δo will decrease or increase |

**Spectrochemical series**

Et bilde som inneholder tekst

Automatisk generert beskrivelse

**LFSE/CFSE (without PE)**

|  |  |
| --- | --- |
| Octahedral |  |
| Tetrahedral   * Fewer ligands * no direct overlap * most HS due to Δt < PE |  |
| Square planar complexes | Mostly d8 and SFL |

**High spin vs low spin for d4 to d7**

CFSE larger for LS complexes (maximum for low spin d6)

* explains stability of LS complexes and why octahedral coordination is preferred
* explains why HS complexes are more reactive

**Jahn-Teller distortion** (z-elongation)

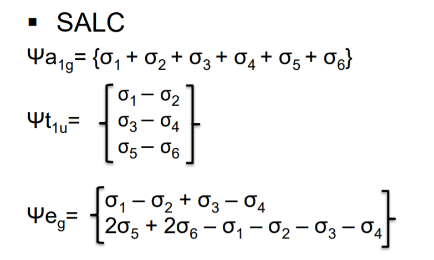
|  |  |
| --- | --- |
| Significantly | HS d4, LS d7 and d9 |
| Weakly | d1, d2, LS d4, LS d5, HS d6 and HS d7 |

NB: T2g in Oh and all d-orbitals in Th do not point directly at ligands.

**π-donor and π-acceptor effect**

|  |  |  |
| --- | --- | --- |
|  | π-donor | π-acceptor |
| MO |  |  |
| Description | Filled (bonding) π-orbitals  Typically π-bases  Decraeses ΔO  With filled electrons in π symmetry orbitals ▪ π bases such as Cl- , Br- , OH- , O2- , H2O ▪ Lower in energy than partially filled d orbitals ▪ π orbitals of ligand and t2g of metal form bonding and antibonding MOs ▪ Electron from ligand π orbitals occupy bonding MOs ▪ Metal electron occupy | vacant (antibonding) π orbitals (LUMO)  Typically π-acids  Increases ΔO  ▪ Bondig t2g MOs are largely of d character ▪ Lower in energy than previously t2g ▪ Large Δo ▪ π-acceptor ligands increase Δo |
| Examples | Cl-, Br- , OH- , O2- , H2O | CO, PR3 , N2 |

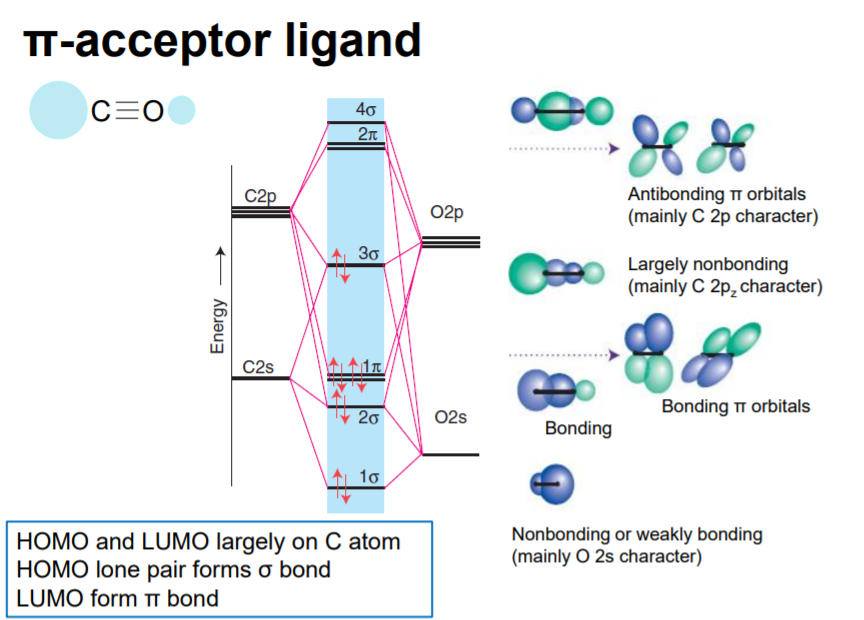
|  |  |
| --- | --- |
| SALC orbitals for metal complexes | |
| Metal ion | s 🡪 A1g  p 🡪 T1u  d 🡪 T2g (no sigma) + Eg |
| Ligands | Varies a lot |



**Metal complexes and π-effects**

|  |  |  |
| --- | --- | --- |
| Octahedral – ML6 | Tetrahedral – ML4 | Square planar - ML4 |
| For π-effects:  See last page | Similar effect of π-donor  NB: e-orbital participates |  |

**CO as a ligand = π-acceptor**



* SFL
* Poor sigma-donor
* Good pi-acceptor (pi from CO and t2g of M has same symmetry)
* In UV-Vis we get d-d transitions at higher energy / lower wavelength

**CO in metal complex (metal carbonyl)**

* M donates electron density to pi\* orbitals of CO via pi-backbonding
  + Bond order lowers (not pure triple bond any more)
  + The more backbonding, the lower frequency in FTIR

**Microstates**

are the different ways in which the electrons can occupy the orbitals specified.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | |  |
| +1 | 0 | -1 | |

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | |  |
| +1 | 0 | -1 | |

(1+,1-) = (1+,-1+) = for 2p2

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | |  |
| +1 | 0 | -1 | |

**Calculate number of microstates**

Et bilde som inneholder tekst, klokke

Automatisk generert beskrivelse

**Terms**

=groups of microstates of same energy when electron-electron repulsion are taken into account.

Russel-Saunders coupling:where S=possible values of ms and L=possible values of ml.

*(PS: L-S coupling is for lighter atoms, and J-J coupling for heavier atoms i.e., Z>30).*

Term energies determined by:

1. Highest multiplicity gives lowest energy
2. Highest permitted value of L gives lowest energy

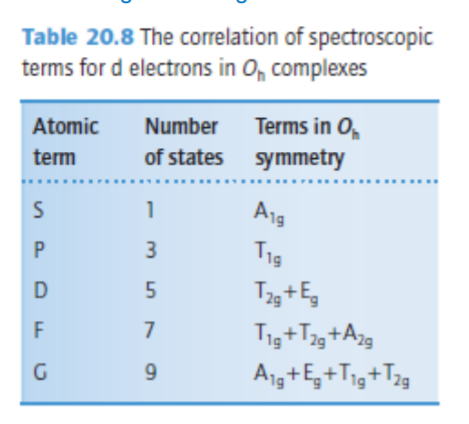
|  |  |
| --- | --- |
| All possible atomic terms | The ground term |
| How to find the atomic terms?   * Combine all values of L and S | The atomic term of lowest energy.  **The direct method for finding ground term?**   1. Find microstate of highest value of S/MS 2. Find the highest permitted value of L/ML for that multiplicity |

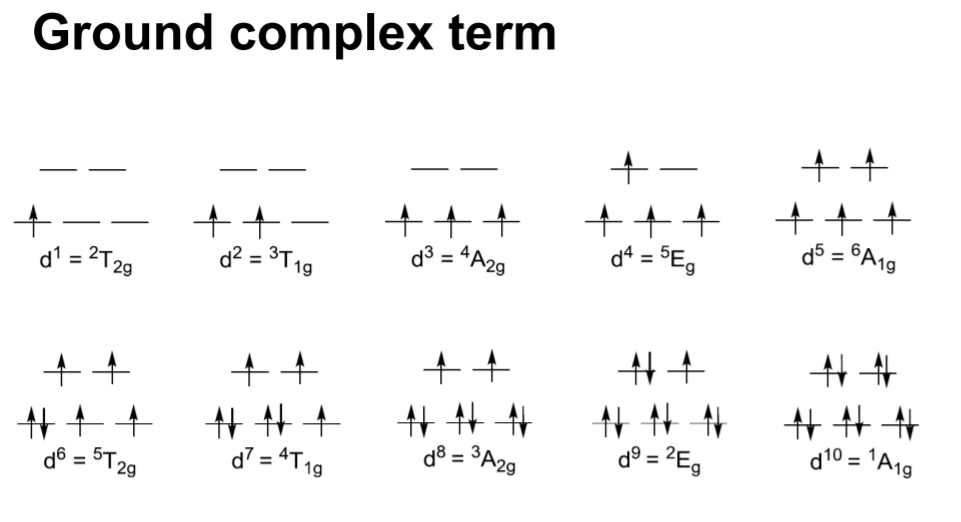
**Overview of terms for different configurations**

Et bilde som inneholder bord

Automatisk generert beskrivelse

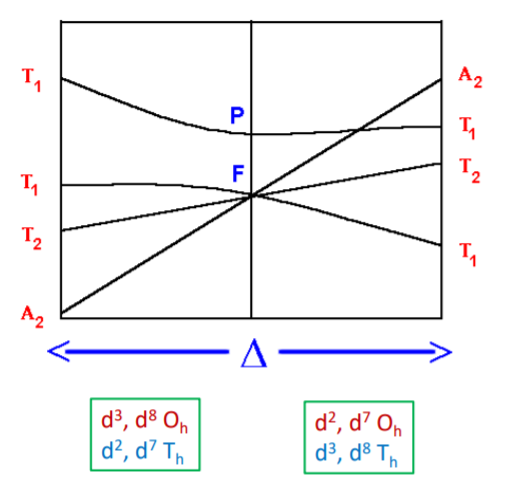
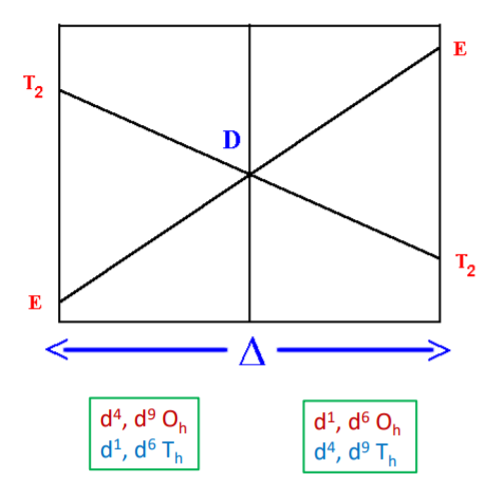
**Complex terms**





**Orgel diagrams**

* For discussion of simple electronic spectra
* Only spin allowed transitions
* Oversimplified and qualitative (doesn’t show all possible terms and transitions)
* Mostly for high spin complexes



**Tanabe-Sugano diagram**

* To predict the UV-Vis spectra
* Shows the correlation of all terms
  + Energies expressed as E/B
  + E/B plotted against Δo /B
  + B is Racah parameter
  + Energy of ground term is set to zero ▪ Energies of other terms are plotted with respect to ground term
* Abrupt change in slope 🡪 change in the identity of ground term
* High spin to low spin by increasing ligand field strength
* Non-crossing rule: Two terms of same symmetry type approaching each other by increasing ligand field will not cross but bend apart from each other

PS: Til eksamen – Sammenlign orgel med tanabe-sugano!

|  |  |
| --- | --- |
| d2 configuration | d3 configuration |
|  |  |

Regn ut B (Racah) fra kombo av UV-VIS og tilhørende Tanabe-Sugano diagram:

**Width of absorption bands**

* Some changes with (if then even broader)
* Spin forbidden = sharp but weak

**Selection rules**

1. **Spin selection rule**

Electronic transitions with change in spin multiplicity are forbidden.

Same spin = allowed.

1. **The Laporte selection rule**

All transitions in a centrosymmetric must be accompanied by a change in parity.

Allowed:

Forbidden:

i.e. all d-d-transitions in Oh complexes are forbidden

**Different types of transitions**

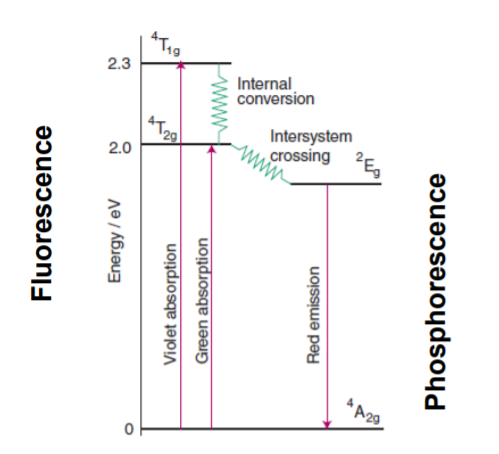
* Charge transfer
  + LMCT or MLCT
  + Excitation of electrons from MO of predominately M or predominately L character
  + very high intensity (spin allowed, Laporte allowed)
* d-d transitions
  + Laporte forbidden (in Oh complex)
  + Spin…
    - … allowed: excitation of electrons from t2g to eg, intermediate intensity
    - … forbidden: Very weak intensity due to both spin and Laporte forbidden. Can be seen due to LS coupling.

**More on UV-VIS and spectroscopy**

Et bilde som inneholder bord

Automatisk generert beskrivelse

**Fluorescence and phosphorescence**



**Techniques to determine oxidation state:**

* UV-Vis: Yes
  + Cu+ is d10 – no dd transition & Cu2+ is d9 – dd transitions
  + Needs references
* XPS: Yes
  + Kinetic E of core electrons measured, Bond E of electrons calculated
  + Bond E depends on effective nuclear charge (which depends on oxidation state)
* XAS: Yes
  + E0 is measured in the XANES region
  + Same principle as XPS
  + Needs references, Average technique

**Techniques to determine geometry (octahedral/tetrahedral)**

* XPS: No (ikke info om naboer)
* UV-Vis: Yes. Oh complex larger splitting than Th Higher energy / lower wavelength for Oh complex in UV Vis Needs references Due to Laporte: Th will be more intense than Oh
* XAS: Yes XANES Pre-edge (1s to 3d): Due to Laporte, higher intensity for Th EXAFS: Number of neighbors, average technique Needs references

**True/false:**

* 6-koordinerte ML-komplekser er mer stabile fordi de oppfyller 18-elektronregelen.
* Topper for d-d-overganger har lavere energi for tetraedriske enn oktaedriske.
* Absorbansen i et UV-vis-spekter avhenger av Beer-Lamberts lov (A = ε\*c\*l)
  + type overgang, konsentrasjon og lengde av lysvei
* XPS er overflatesensitiv (kort mean free path of e-), XAS er ikke det.
* Overgangen 1s 🡪 3d vil si noe om geometrien (Laporte, ses i pre-edge XAS).
  + Sentrosymmetrisk 🡪 lav
* XPS kan skille mellom ulike oksidasjonstilstander. Bindingsenergi fra Koopmans ligning:
  + Ulike topper for ulik kjerneladning og ergo ulike oksidasjonstilstander
* UPS gir informasjon om energien til molekylorbitaler og i hvilken grad molekylorbitalene er viktige for strukturen på molekylet
  + Vi finner bindingsenergien til MO’ene via Koopman’s likning og dersom vi får finstruktur i spekteret har MO stor betydning for strukturen.

Jahn Teller vil gi multiple topper og ytterligere energifordeling av d-orbitalene. I utgangspunktet kan man skille mellom geometri for forbindelser som det kjøres UVvis på, men det krever veldig mange forskjellige referanseprøver dersom vi innehar forskjellige metall/ligand-komplekser da enhver absorpsjonstopp ikke nødvendigvis tilsvarer én geometri. Vi har derfor måttet sammenlikne med kjente miljøer og kjente komplekser for å kunne si noe om forskjellig geometri så det er ikke sikkert prosessen hadde vært så lett totalt sett.