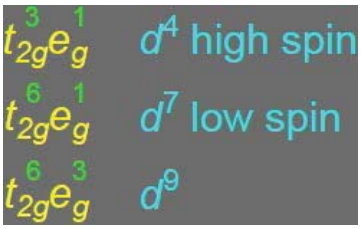
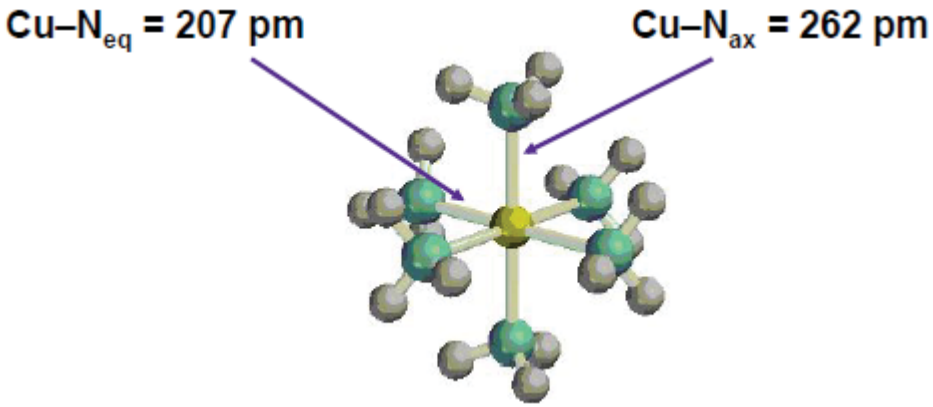
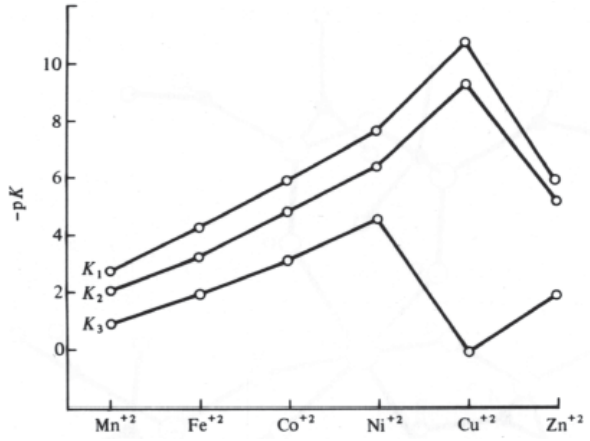
- Configurations with the greatest Jahn-Teller distortion is:
  - → Greatest when asymmetry is in the $e_g$ since these point to the ligands.
  - → Common example of something that is JT distorted is Cu(II) complexes.




- The Jahn-Teller effect can cause problems in chelating ligands.
  - → $K_1$ refers to the first ethylenediamine (en) binding to the metal ion - similarly to $K_2$ and $K_3$.
  - → For Cu(II), the third ethylenediamine molecule, it's not stable because it would result in a lot of ring strain.

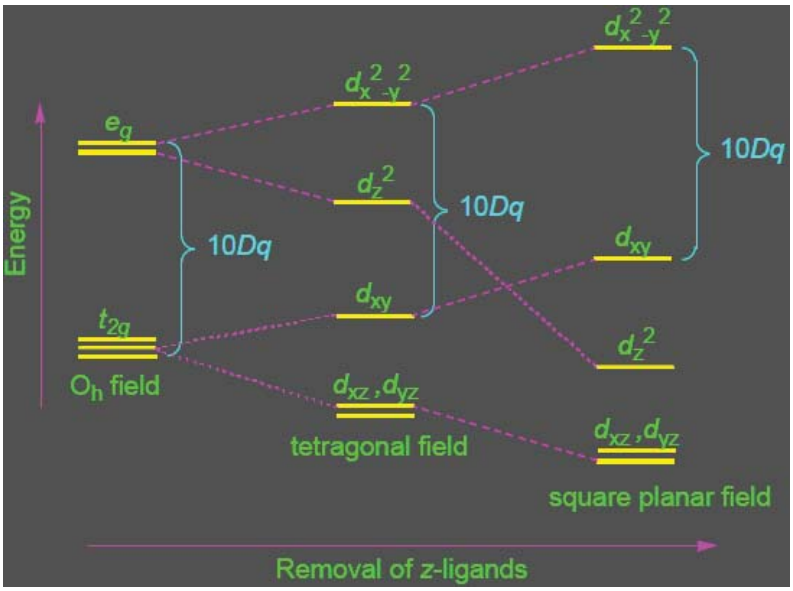



## Lecture 20: Jahn-Teller Effect II

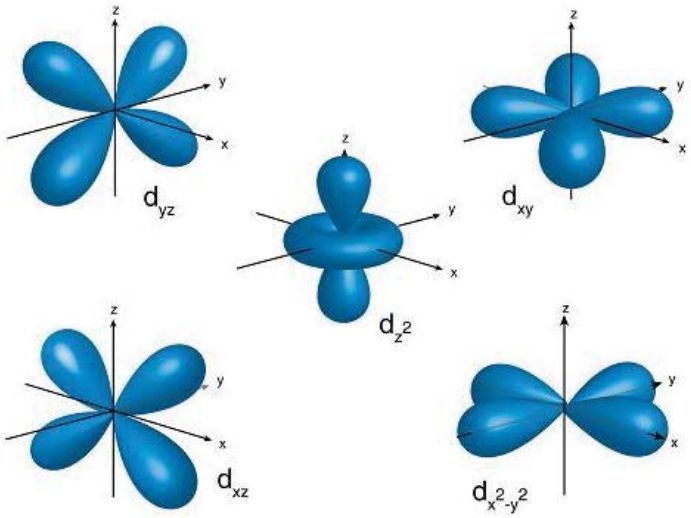
- Many reasons why $K_1>K_2>K_3$ - one is for statistical reasons, more sites where ethylenediamine can bind for $K_1$ but for Cu(II), tetragonal distortion from the JT effect makes it too strained if there are three (en) ligands.
- $[Cu(en)_3]^{2+}$ does not display a detectable distortion because the distortions are constantly changing - this is called *Dynamic Jahn-Teller effect*.
  - → If measured at an instant, you will see the Jahn-Teller effect but if measured over time and averaged, you won't see any distortion.

→ Tetragonal distortion alternates very rapidly in the x, y, and z axes.

- Bond lengths to ligands can be different even if it's not Jahn-Teller distorted.
  → For trans-$[CoCl_2(NH_3)_4]^+$ is a low spin $d^6$ complex so it should not show JT effects but is tetragonal in geometry.
  → This is due to $Cl^-$ being a weaker field ligand than $NH_3$ so there's a less powerful effect along the z-axis.
- For $d^8$, it is usually square planar if there are strong field ligands and it seems to be always true for Pt(II).
  → For 4d and 5d, even weak field ligands can cause square planar geometry.
  → All of them have low spin - no high-spin square planar complexes are known.
  → It is a result of extreme tetragonal distortion.
  → In 3d metals, you need a strong field (eg $CN^-$ ligands) to distort the configuration enough for the square planar arrangement to be seen (eg $[Ni(CN)_4]^{2-}$].




- The stronger the field that is applied to the $d_{x2-y2}$ orbital, the bigger the splitting.
  → Other orbital will be lowered in energy, resulting in stabilisation.




- The transition between $d_{xy}$ and $d_{x2-y2}$ corresponds to 10Dq.

- d-orbital splitting for gold is much larger than for copper - for $d^9$ gold(II), an electron is forced to occupy the very high energy $d_{d2-y2}$ orbital which is unfavourable and so there is a tendency for it to lose the electron to make gold(III).
  - → This is why 3+ is the most common oxidation state for gold.
  - → It can also gain an electron to fill all of the orbitals but losing an electron is more common.

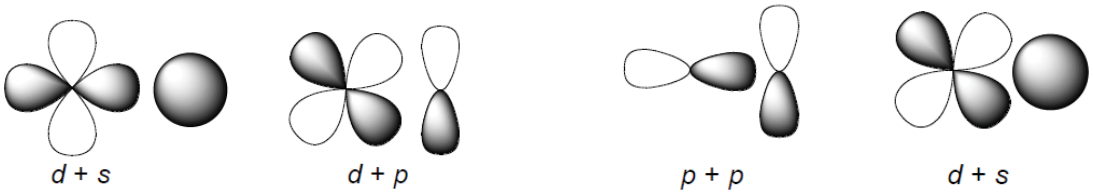
**The energy levels of *d*-orbitals in crystal fields of different symmetries (in *Dq* units)**

| CN | Geometry | $d_z^2$ | $d_{x^2-y^2}$ | $d_{xy}$ | $d_{xz}$ | $d_{yz}$ |
|---|---|---|---|---|---|---|
| 1 | linear[a] | 5.14 | –3.14 | –3.14 | 0.57 | 0.57 |
| 2 | linear[a] | 10.28 | –6.28 | –6.28 | 1.14 | 1.14 |
| 3 | trigonal[b] | –3.21 | 5.46 | 5.36 | –3.86 | –3.86 |
| 4 | tetrahedral | –2.67 | –2.67 | 1.78 | 1.78 | 1.78 |
| 4 | square planar[b] | –4.28 | 12.28 | 2.28 | –5.14 | –5.14 |
| 5 | trigonal bipyramid[c] | 7.07 | –0.82 | –0.82 | –2.72 | –2.72 |
| 5 | square pyramid[c] | 0.86 | 9.14 | –0.86 | –4.57 | –4.57 |
| 6 | octahedron | 6.00 | 6.00 | –4.00 | –4.00 | –4.00 |
| 6 | trigonal prism | 0.96 | –5.84 | –5.84 | 5.36 | 5.36 |
| 7 | pentagonal bipyramid | 4.93 | 2.82 | 2.82 | –5.28 | –5.28 |
| 8 | cube | –5.34 | –5.34 | 3.56 | 3.56 | 3.56 |
| 8 | square antiprism | –5.34 | –0.89 | –0.89 | 3.56 | 3.56 |
| 9 | $ReH_9$ structure | –2.25 | –0.38 | –0.38 | 1.51 | 1.51 |

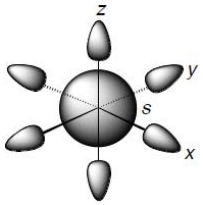
[a] Ligands lie along z-axis. [b] Ligands lie in *xy* plane. [c] Pyramid base in *xy* plane.

## Lecture 21: Orbital Overlapping

- Ligand field theory is similar to CFT except it takes into account the covalency of ligands.
- In a transition metal, you have many valence orbitals (eg 4s, 4p, 3d) making a total of 9 orbitals.
- Only some orbital overlaps are allowed (d+s, d+p, left), some are not allowed (p+p, d+s, right).
  - → If overlap integral is 0, it is not allowed.




- The 4s orbital overlaps with all six ligands of an octahedral complex.
  - → Produces the $a_{1g}$ orbital.




  - → When the ligands aren't in phase, it's the $a_{1g}^*$ orbital.