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ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES.

Spectroscopy is one of the most powerful tool available for the study of atomic and molecular structure. The study in which the transition metal complex ions absorb electromagnetic radiation is called the electron absorption spectroscopy. The absorbed radiation promotes electrons from d-orbitals of lower energy to d-orbital of higher energy. Due to promotion of electrons there occurs a change in the overall arrangement of electrons in d-orbitals. The change in the overall arrangement of electrons in d-orbitals give rise to electron absorption spectrum. The study of electron absorption spectrum of transition metal complex ion gives important information about the colour of complexes, the magnitude

of energy gaps between ground state and excited state energy level of metal ions in their complexes, the extent of covalent character in metal-ligand bonds, geometry of complexes, the position of metal ions and ligands in the spectrochemical and nephelauxetic series etc.

Spectra arise because electrons may be promoted from one energy level to another. Such electronic transitions are of high energy and in addition much lower energy vibrational and rotational transitions always occur. The vibrational and rotational ~~vele~~ levels are too close in energy to be resolved into separate absorption bands, but they result in considerable broadening of the electronic absorption bands in d-d spectra. Band width are commonly found to be of the order of 1000 – 3000 cm^{-1}.

The spectrum of a coloured solution may be measured quite easily using a spectrophotometer. A beam of monochromatic light obtained using a prism and a narrow slit is passed through the solution and on to a photoelectric cell. The amount

of light absorbed at any particular frequency can be read read off or a whole frequency range can be scanned, and the absorbance A plotted as a graph on a paper chart recorder. The absorbance was formerly called the optical density. If I_0 is the intensity of the original beam of light, and I the intensity after passing through the solution, then

$$\log\left(\frac{I_0}{I}\right) = A$$

The molar of absorption coefficient ε is usually calculated from the absorbance

$$\varepsilon = \frac{A}{cl}$$

where c is the concentration of the solution in mol l^{-1}, and l is the path length in centimetres.

Not all of the theoritically possible electronic transitions are actually observed. The position is formalised into a set of selection rules which distinguish between allowed and forbidden transitions. Allowed transitions occur commonly. Forbidden transitions do occur, but much less frequently, and They are consequently of much lower intensity.