INDIAN INSTITUTE OF TECHNOLOGY PATNA
DEPARTMENT OF CHEMISTRY

CH 103

Instructor: Dr. Neeladri Das
Email: neeladri@iitp.ac.in

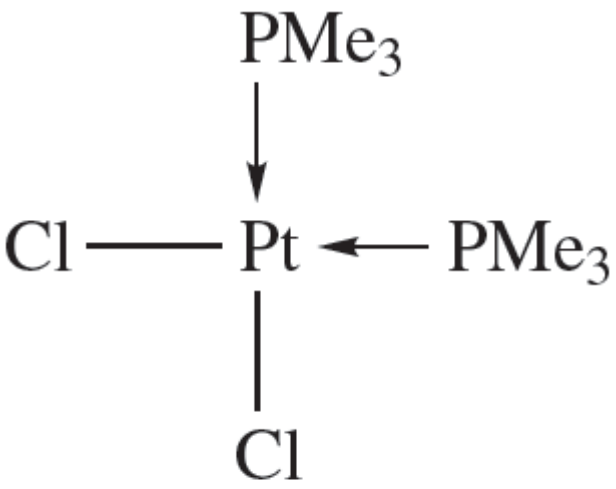
Associate Professor, Chemistry Dept., IIT Patna
Rm-215, Block-IV
Chemistry department
IIT Patna

geometrical isomerism

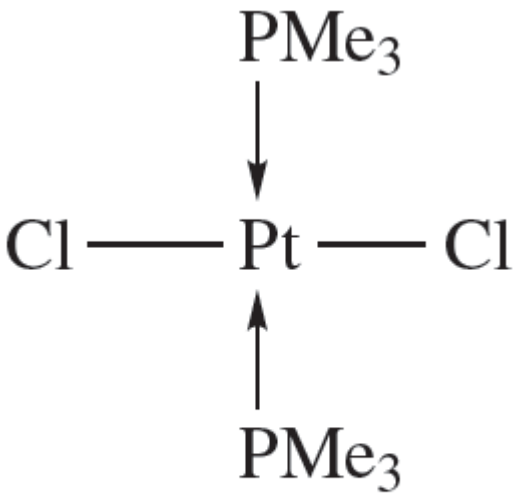
- Two species have the
  - same molecular formulae and
  - same structural framework,
  - but differ in the spatial arrangement of different atoms or groups about a **central atom** or a double bond, then the compounds are geometrical isomers.
- Where do we find such examples?
- Square planar species
- Octahedral species
- Trigonal bipyramidal species

Square planar species

- Square planar species of the general form **EX_2Y_2** or **EX_2YZ** may possess cis- and trans-isomers.



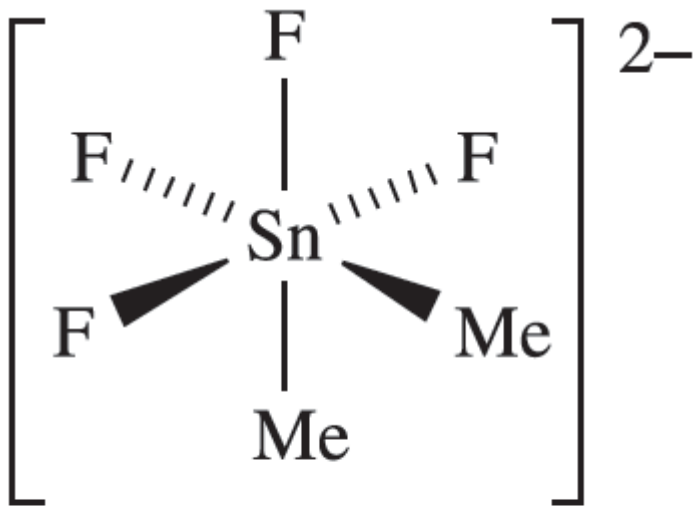
cis-isomer



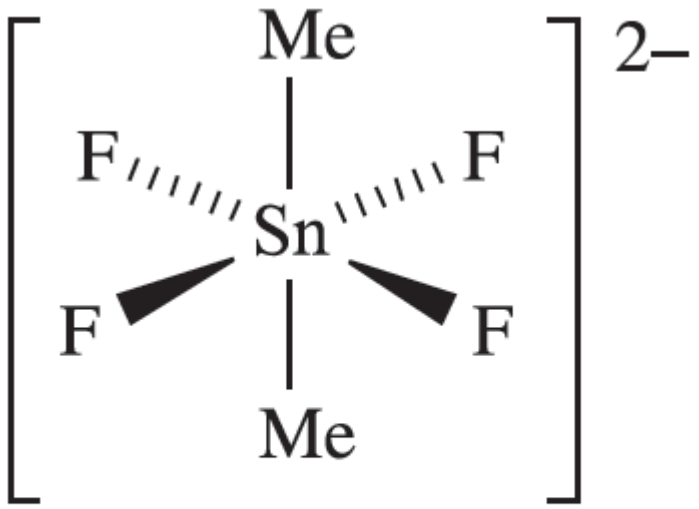
trans-isomer

Octahedral species: EX_2Y_4

- two types of geometrical isomerism associated with octahedral species.
- In EX_2Y_4, the X groups may be mutually cis or trans



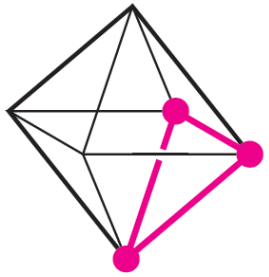
cis-isomer



trans-isomer

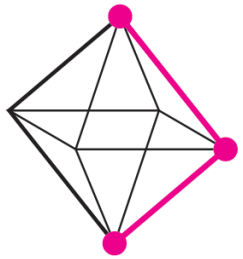
Octahedral species : EX_3Y_3

- If an octahedral species has the general formula EX_3Y_3, then the X groups (and also the Y groups) may be arranged so as to define one face of the octahedron or may lie in a plane that also contains the central atom E.
- These geometrical isomers are labelled fac (facial) and mer (meridional) respectively.



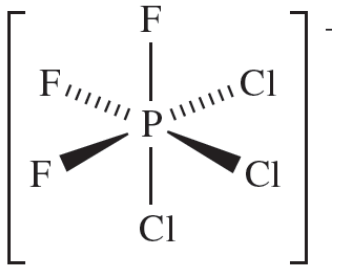
Facial arrangement

fac-isomer

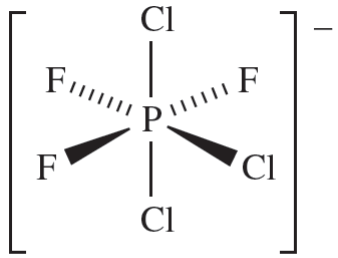


Meridional arrangement

mer-isomer



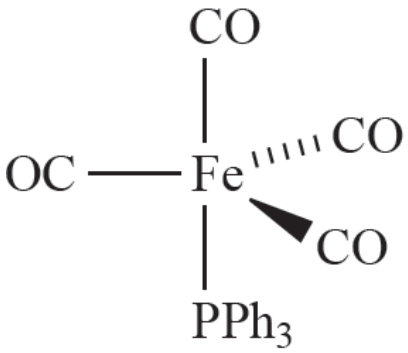
fac-isomer

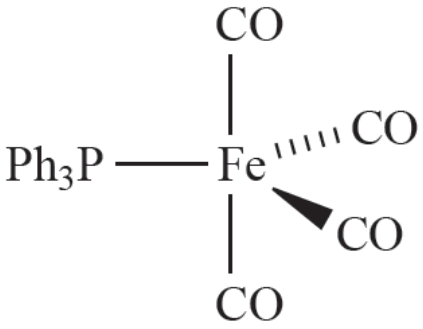


mer-isomer

Trigonal bipyramidal species: EXY_4 type

- In trigonal bipyramidal EX_5, there are two types of X atom: axial and equatorial.
- This leads to the possibility of geometrical isomerism **when more than one type of substituent** is attached to the central atom.

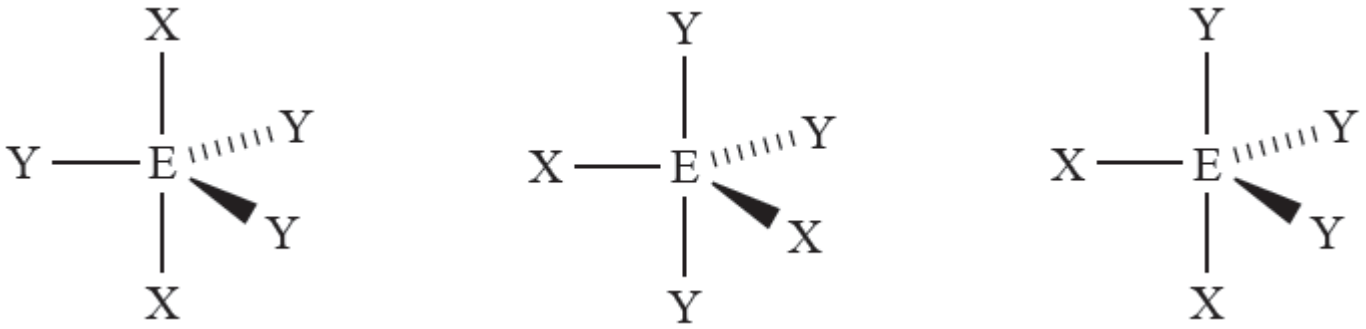




- two geometrical isomers are possible depending on **whether the PPh_3 ligand is axial or equatorial**.

Trigonal bipyramidal species: EX_2Y_3 type

- **How many geometrical isomers are possible ?**
- depending on the relative positions of the X atoms, **three** geometrical isomers are possible.

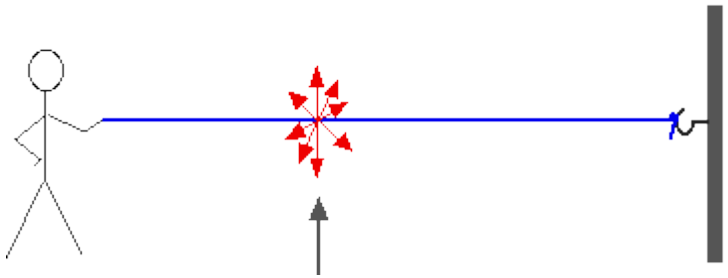


- Which isomer is preferred given a set of ligands?
- Steric factors may dictate which isomer is preferred for a given species

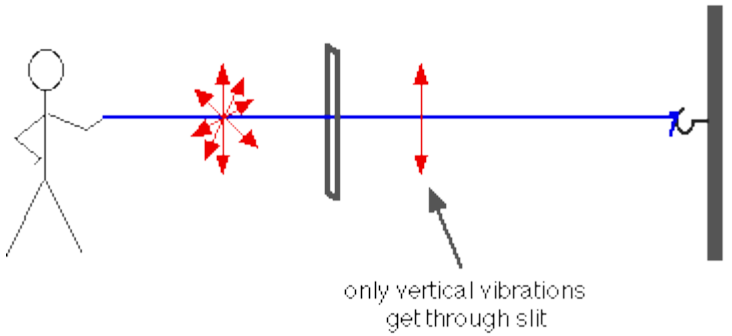
Other forms of geometrical isomers

- The existence of ions or molecules in different structures is just a special case of geometrical isomerism.
- e.g. $[Ni(CN)_5]^{3-}$.
- trigonal bipyramidal and square-based pyramidal
- $[NiBr_2(PBzPh_2)_2]$ (Bz = benzyl)
- tetrahedral and square planar forms
- These can be distinguished by the fact that they exhibit different magnetic properties
- To complicate matters, square planar $[NiBr_2(PBzPh_2)_2]$ may exist as either trans- or cis-isomers.

Plane polarized light

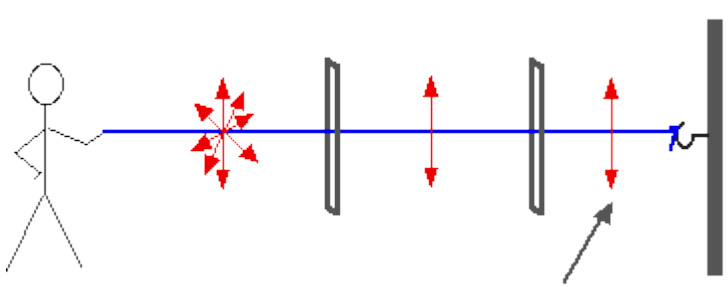


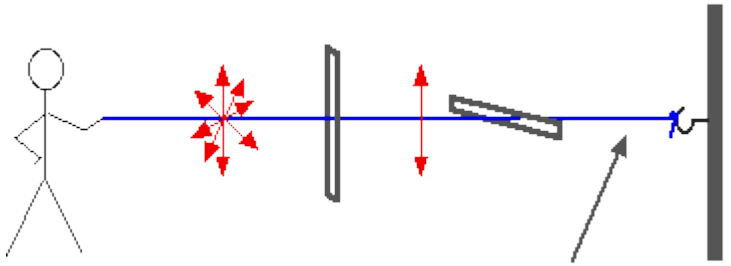
The string will be vibrating in all possible directions - up-and-down, side-to-side, and all the directions in-between - giving it a really complex overall motion



suppose you passed the string through a vertical slit. The only vibrations still happening the other side of the slit will be vertical ones. All the others will be prevented by the slit.

Plane polarized light





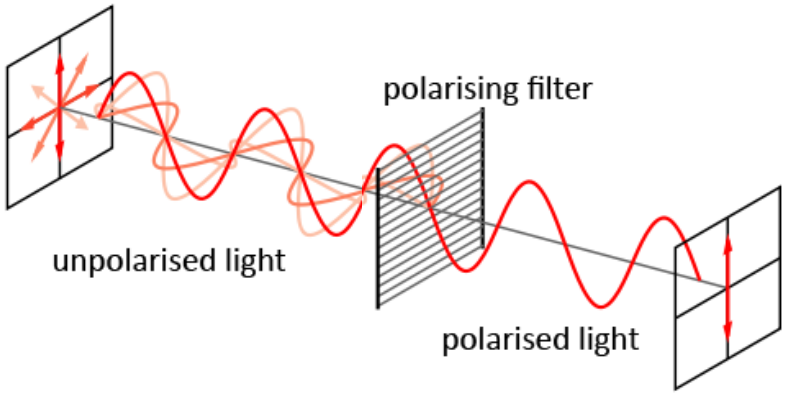
put a second slit on the string. If it is aligned the same way as the first one, the vibrations will still get through.

if the second slit is at 90° to the first one, the string will stop vibrating entirely to the right of the second slit.

The second slit will only let through horizontal vibrations - and there aren't any

Plane polarized light

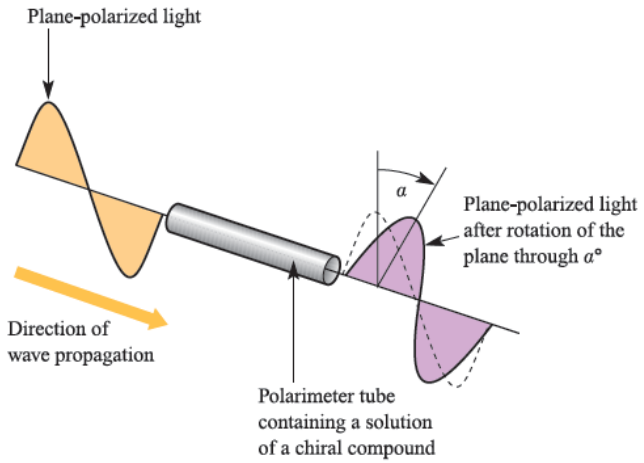
- Light is also made up of vibrations - this time, electromagnetic ones.
- Some materials have the ability to screen out all the vibrations apart from those in one plane and so produce **plane polarised light**.



- It is important not to take the string analogy too far. **The polaroid material doesn't consist of "slits"** in any sense of the word. The way it actually polarises the light is quite different.

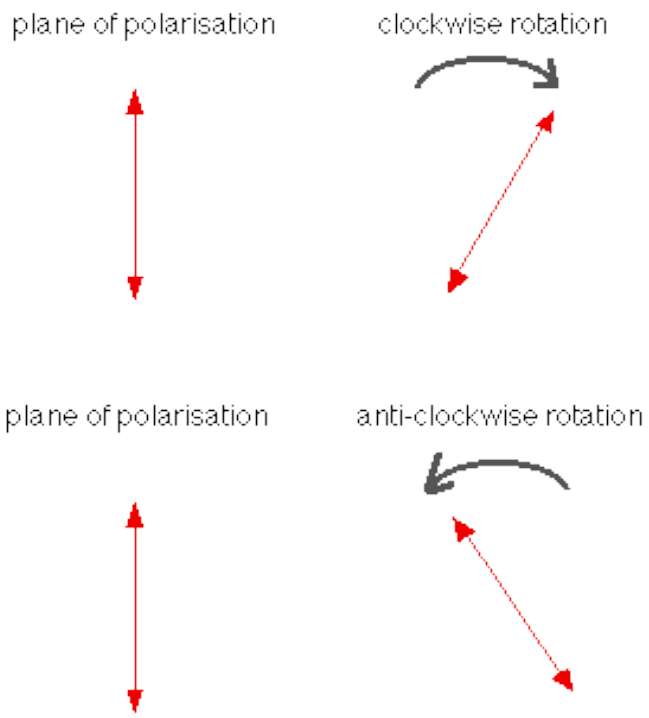
Optically active substances

- An optically active substance is one which can rotate the plane of polarisation of plane polarised light.
- if you shine a beam of polarised monochromatic light through a solution of an optically active substance, when the light emerges, its plane of polarisation is found to have rotated.

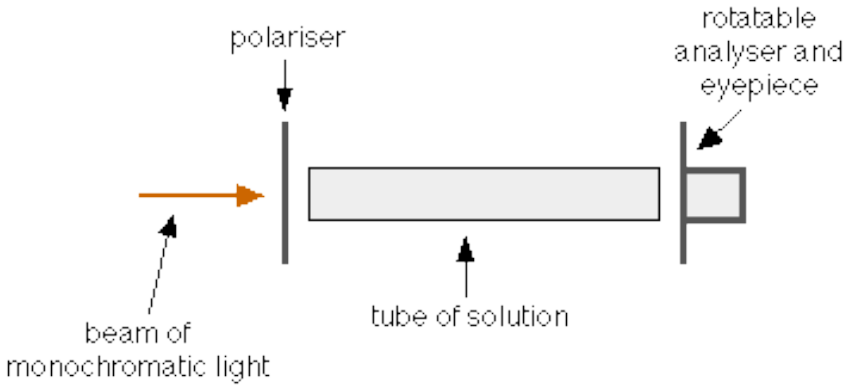


Optically active substances

- The rotation may be either clockwise or anti-clockwise.
- Assuming the original plane of polarisation was vertical, you might get either of these results.



- **How can you tell that the plane of polarisation has been rotated?**
- **Use a polarimeter**



- The polariser and analyser are both made of polaroid material.