CRYSTALLOGRAPHY AND MINERALOGY

UNIT –2

6 Yr. Int. **M.Tech.** Geological Technology & Geoinformatics
(Paper Code: MTIGT0306)

Georgius Agricola, 'Father of Mineralogy'
German scientist '**Georg Bauer**' - named by birth
First book on Mineralogy was written by him entitled :
'Bermannus, sive de re metallica dialogus '(1530)
A description of the ore mountain(Ergebrge) – Silver mining district.

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René Just Haüy (1743 –1822)
"Father of Modern Crystallography"
French (Paris) Mineralogist
generally known as **Abbé Haüy**

MTIGT0306: THEORY – CRYSTALLOGRAPHY AND MINERALOGY 4 credits

1. **Elements of Crystallography**: Crystalline and Amorphous forms - Symmetry and Classification of Crystals - System of Crystal Notation - (Weiss and Millerian) - Forms and Habits. Crystal Systems (Isometric, Tetragonal, Hexagonal, Orthorhombic, Monoclinic, Triclinic, Twinning - Crystalline Aggregates – Columnar, Fibrous, Lamellar, Granular - Imitative shapes and Psudomorphism. **12 Hrs.**
2. **Crystal Properties:** Space Symmetry Elements- Translation – Rotation- Reflection - Inversion Screw and Glide-point groups and Crystal classes - Derivation of 32 Crystal classes based on Schoenflies notation - Bravais lattices and their Derivation - An outline of Space Groups. X-ray Crystallography. **12 Hrs.**
3. **Physical Mineralogy**: Physical Properties: (Colour – Structure – Form – Luster - Transparency – Streak – Hardness – Specific Gravity – Tenacity – Feel – Taste – Odour) - Electrical, Magnetic and Thermal properties-Determination of Specific Gravity (Jolly's spring balance, Walker's steel yard, Pycnometer methods) - Empirical and Structural formula of minerals – Isomorphism, Polymorphism and Psudomorphism - Atomic substitution and Solid solution in minerals - Non Crystalline minerals - Fluorescence in minerals - Metamict state. **16 Hrs.**
4. **Optical Mineralogy:** Optical Properties (Colour – Form – Cleavage - Refractive Index - Relief – Alteration – Inclusions – Zoning – Pleochroism – Extinction - Polarization colours – Birefringence) – Twinning - Optic sign (Uniaxial and biaxial)- Interference figures - Primary and Secondary Optic axes - Optic axial angle measurements – Optic Orientation – Dispersion in Crystals - Optic anomalies. **12 Hrs.**
5. **Mineral Groups:** Ortho and Ring Silicates (Olivine group - Garnet group). Alumino silicates (Epidote group - Zircon – Staurolite – Beryl - Cordierite and Tourmaline). Sheet Silicates (Mica group - Chlorite group and Clay minerals) - Chain Silicates (Pyroxene group - Amphibole group and Wollastonite). Frame work Silicates (Quartz -Feldspar - Feldspathoid - Zeolite and Scapolite groups) - Non-silicate (Spinel group, Carbonates and Phosphates). **12 Hrs.**

Unit-2 Crystal Properties:

2. Crystal Properties: Space Symmetry Elements- Translation – Rotation- Reflection - Inversion Screw and Glide-point groups and Crystal classes - Derivation of 32 Crystal classes based on Schoenflies notation - Bravais lattices and their Derivation - An outline of Space Groups. X-ray Crystallography.

-12 Hrs.

Space Symmetry Elements - Space Lattice

- Atoms or groups of atoms have regular arrangements throughout a crystal
- With this arrangement a three dimensional pattern is repeated many times
- The array of points at which the pattern repeats constitute a SPACE LATTICE
- i.e., the arrangement of points in space – Bravais 1848
- The unit of pattern is called ‘Unit Cell’, E.g. NaCl Cube
- There are 7 types of unit cells, crystallographic axes and Axis ratio

1. Cubic, 2. Tetragonal, 3. Hexagonal, 4. Trigonal / Rhombohedral, 5. Orthorhombic, 6. Monoclinic, & 7. Triclinic.

The 32 Point Groups

- The **crystallographic point group** or ***crystal class*** is the mathematical group comprising the symmetry operations that leave at least one point unmoved and that leave the appearance of the crystal structure unchanged. These symmetry operations include:
  - *Translation, Reflection, Rotation, Inversion, Improper Rotation*

- ***Translation,*** is the movement of face from one point to another point along a vector
- ***Reflection***, which reflects the structure across a *reflection plane*
- ***Rotation***, which rotates the structure a specified portion of a circle about a *rotation axis*
- ***Inversion*** which changes the sign of the co-ordinate of each point with respect to a *center of symmetry* or *inversion point*
- ***Improper rotation***, which consists of a rotation about an axis followed by an inversion.
- Rotation axes (proper and improper), reflection planes, and centers of symmetry are collectively called ***symmetry elements***. There are 32 possible crystal classes. Each one can be classified into one of the seven crystal systems.

The 230 Space Groups

- The **space group** of the crystal structure is composed of the translational symmetry operations in addition to the operations of the point group. These include:
- pure ***translations*** which move a point along a vector
- ***screw axes,*** which rotate a point around an axis while translating parallel to the axis
- ***glide planes***, which reflect a point through a plane while translating it parallel to the plane.

The 14 Bravais Lattices

- When the crystal systems are combined with the various possible lattice centerings, we arrive at the **Bravais lattices**.
- They describe the geometric arrangement of the lattice points, and thereby the translational symmetry of the crystal.
- In three dimensions, there are 14 unique Bravais lattices which are distinct from one another in the translational symmetry they contain.
- All crystalline materials recognized until now (not including quasicrystals) fit in one of these arrangements.
- There are fourteen three-dimensional lattices, classified by crystal system.
- The Bravais lattices are sometimes referred to as ***space lattices***.

- The crystal structure consists of the same group of atoms, the *basis*, positioned around each and every lattice point.
- This group of atoms therefore repeats indefinitely in three dimensions according to the arrangement of one of the 14 Bravais lattices.
- The characteristic rotation and mirror symmetries of the group of atoms, or unit cell, is described by its crystallographic point group.

The 14 Bravais Lattices

The 7 Crystal systems (From least to most symmetric)

Crystal systems	Symmetry elements
1. Triclinic one type	(none)
2. Monoclinic 2 types	(1 diad)
3. Orthorhombic 4 types	(3 perpendicular diads)

- 1. **Triclinic**

  one type — (none)

  1. **Simple Triclinic** – *lattice point only at the corners*

- 2. **Monoclinic**

  2 types — (1 diad)

  2. **Simple Monoclinic** – *lattice point only at the corners* (Primitive)
  3. **Base Centered**

- 3. **Orthorhombic**

  4 types — (3 perpendicular diads)

  4. **Simple Orthorhombic** – *lattice point only at the corners*
  5. **Base Centered**
  6. **Body Centered**
  7. **Face Centered**

Crystal systems Symmetry elements

- **4. Rhombohedral**

  one type (aka, trigonal)
  (1 triad)

  8. **Simple Rhombohedral** – *lattice point only at the corners*

- **5. Tetragonal**

  2 types (1 tetrad)

  9. **Simple Tetragonal** – *lattice point only at the corners*
  10. **Body Centered**

- **6. Hexagonal**

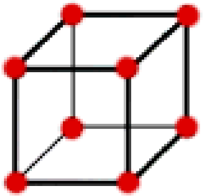
  one type (1 hexad)

  11. **Simple Hexagonal** – *lattice point only at the corners*

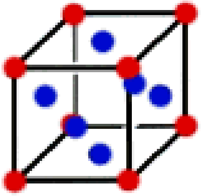
- **7. Cubic**

  3 Types (4 triads)

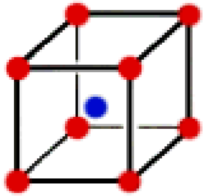
  12. **Simple Cubic** – *lattice point only at the corners*
  13. **Body Centered Cubic** - *lattice points at corners & in middle of cube*
  14. **Face Centered Cubic** - *lattice points at corners & in middle each face*



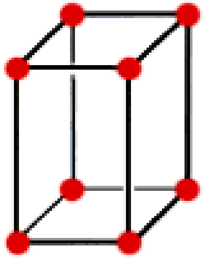
Simple cubic



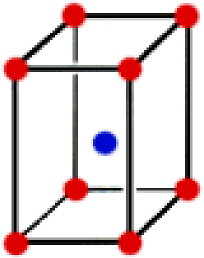
Face-centered cubic



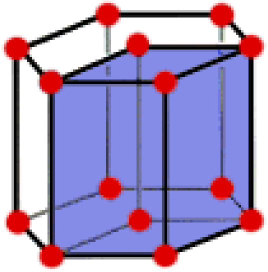
Body-centered cubic



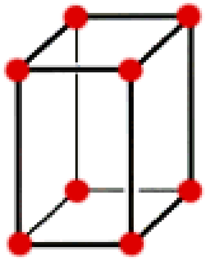
Simple tetragonal



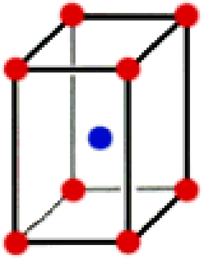
Body-centered tetragonal



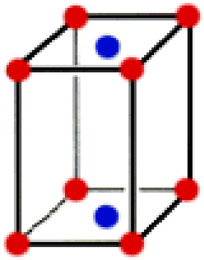
Hexagonal



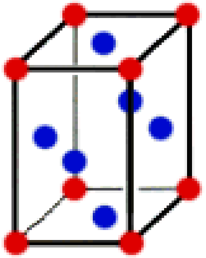
Simple orthorhombic



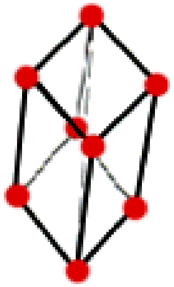
Body-centered orthorhombic



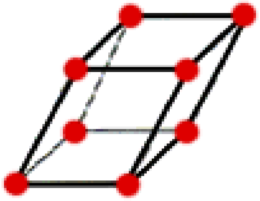
Base-centered orthorhombic



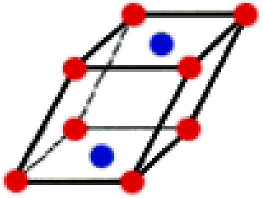
Face-centered orthorhombic



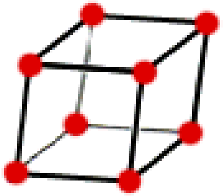
Rhombohedral



Simple Monoclinic



Base-centered monoclinic



Triclinic

X-ray Crystallography

A study of crystals, esp. the atomic structure, bonds, disorders, etc., using the x-ray which has scattered after striking the crystal is known as X-ray Crystallography.

X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and causes the beam of light to spread into many specific directions.

Importance of X-ray Crystallography

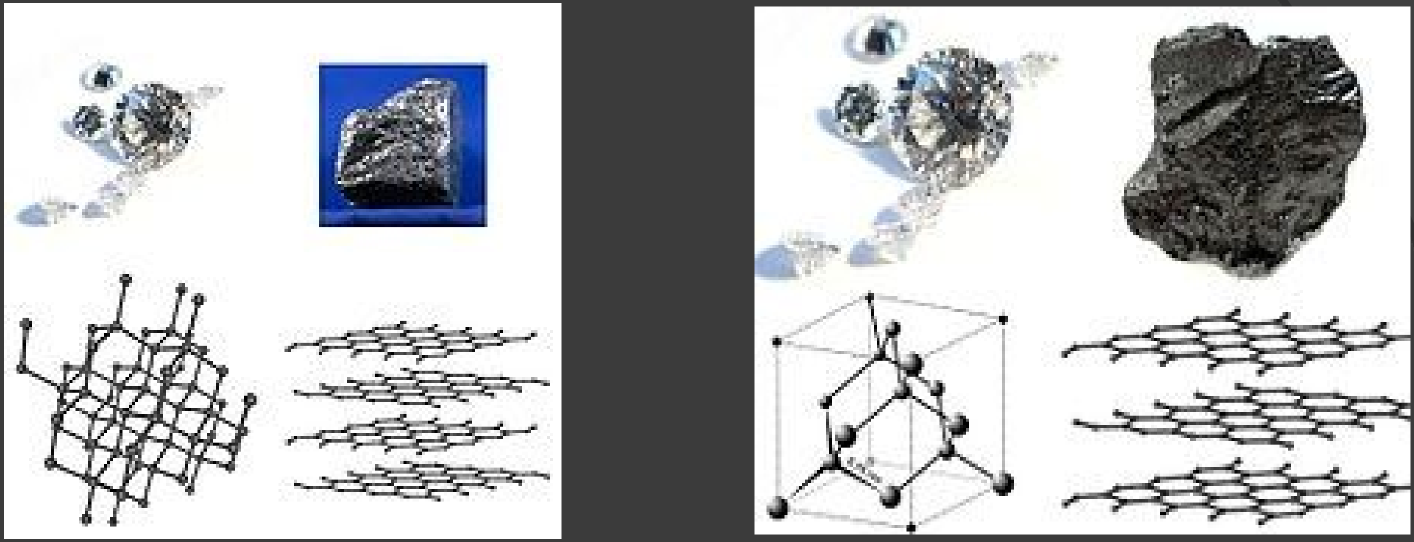
- From the angles and intensities of these scattered beams, a crystallographer can produce
- a three-dimensional picture of the density of electrons within the crystal.

- From this electron density, the mean positions of the atoms in the crystal can be determined, as well as

- their chemical bonds,
- their disorder and
- various other information.

Through this method the

- size of atoms,
- lengths and types of chemical bonds, and
- atomic-scale differences among various materials, especially minerals and alloys.



- Although diamonds (top left) and graphite (top right) are identical in chemical composition — being both pure carbon — X-ray crystallography revealed the arrangement of their atoms (bottom), which accounts for their different properties.

- In Diamond, the carbon atoms are arranged **tetrahedrally** and held together by **single covalent bonds**, making it strong in all directions. By contrast, **Graphite** is composed of stacked sheets, in which the carbon atoms are bonded **hexagonally** by **delocalized bonds** of average order 4/3; there are no covalent bonds between sheets, making graphite easy to cleave into flakes.

Single-crystal X-ray diffraction

•The oldest and most precise method of X-ray crystallography is single-crystal X-ray diffraction, in which a beam of monochromatic and collimated X-rays strikes a single crystal, producing scattered beams.

•When they land on a piece of film or other detector, these beams make a diffraction pattern of spots; the strengths and angles of these beams are recorded as the crystal is gradually rotated.

•Each spot is called a reflection, since it corresponds to the reflection of the X-rays from one set of evenly spaced planes within the crystal.

•For single crystals of sufficient purity and regularity, X-ray diffraction data can determine the mean chemical bond lengths and angles to within a few thousandths of an Ångström and to within a few tenths of a degree, respectively.

•The atoms in a crystal are also not static, but oscillate about their mean positions, usually by less than a few tenths of an Ångström. X-ray crystallography allows the size of these oscillations to be measured quantitatively. (1 Ångström = 0.1 nm or 10^{-10} m = one ten-billionth of a meter)

- In an X-ray diffraction measurement, a crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections.
- The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample.
- Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup.
- X-ray crystallography is related to several other methods for determining atomic structures. Similar diffraction patterns can be produced by scattering electrons or neutrons, which are likewise interpreted as a Fourier transform.
- If single crystals of sufficient size cannot be obtained, various other X-ray methods can be applied to obtain less detailed information; such methods include **fiber diffraction, powder diffraction and small-angle X-ray scattering (SAXS).**
- If the material under investigation is only available in the form of nanocrystalline powders or **suffers from poor crystallinity**, the methods of electron crystallography can be applied for determining the atomic structure.

Procedure

Three basic steps:

1. Sufficiently large (typically larger than 100 micrometres generally smaller than a millimeter across, in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning.

2. The crystal is placed in an intense beam of X-rays, usually of a single wavelength (monochromatic X-rays) and collimated to a single direction, producing the regular pattern of reflections.

As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflection intensities.

3. These data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal.

The final, refined model of the atomic arrangement — now called a **crystal structure** — is usually stored in a public database.

Data analysis – Crystal symmetry, unit cell, and image scaling

Having recorded a series of diffraction patterns from the crystal, each corresponding to a different crystal orientation, the crystallographer must now convert these two-dimensional images into a three-dimensional model of the density of electrons throughout the crystal using the mathematical technique of Fourier transforms.

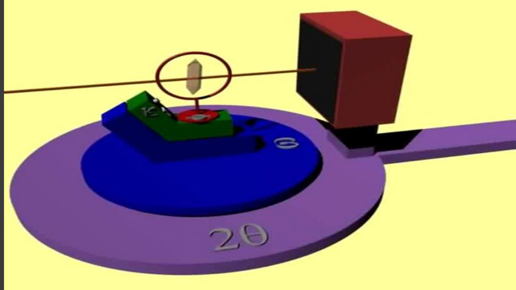
Roughly speaking, each spot corresponds to a different type of variation in the electron density.

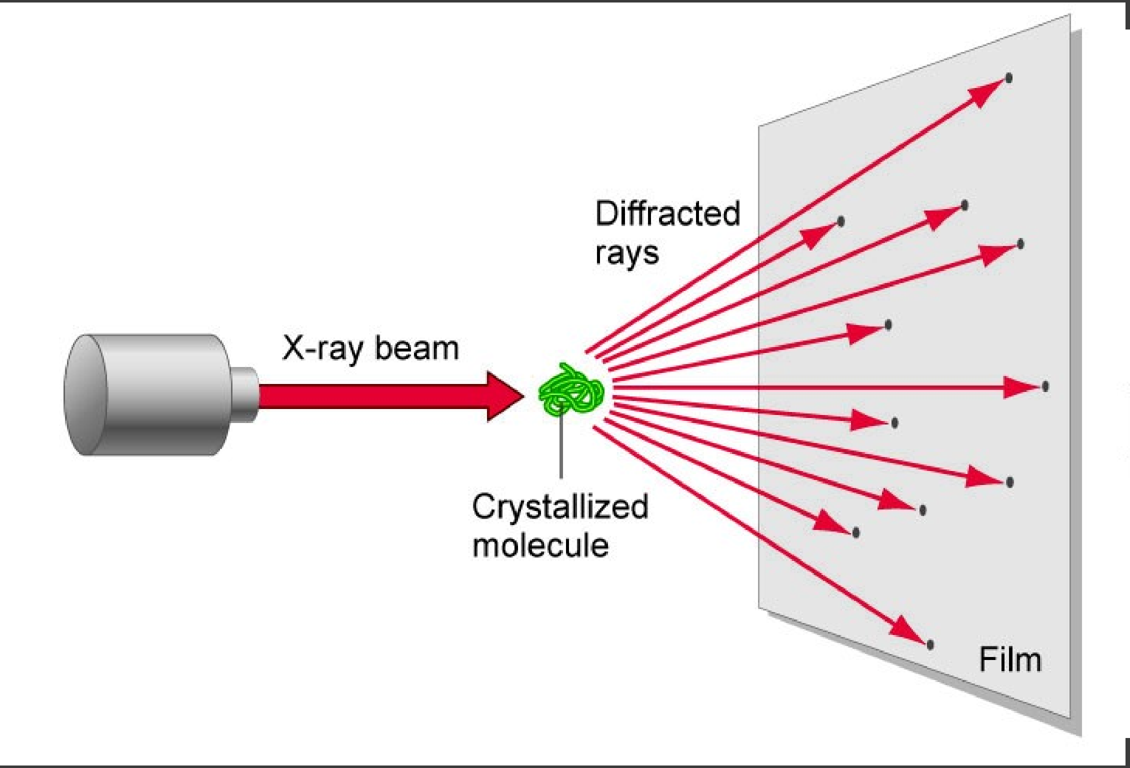
This is to determine,

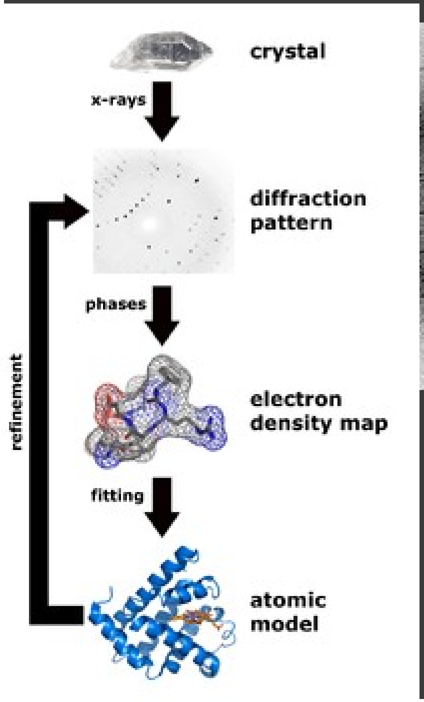
- which variation corresponds to which spot (indexing),
- the relative strengths of the spots in different images (merging and scaling) and
- how the variations should be combined to yield the total electron density (phasing).

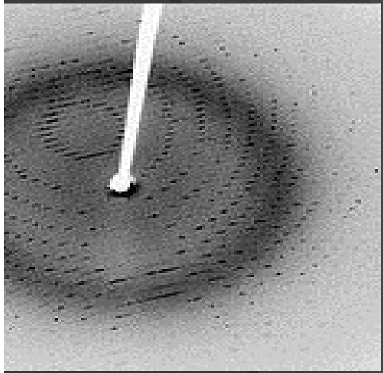
A diffractometer

Mounting the crystal

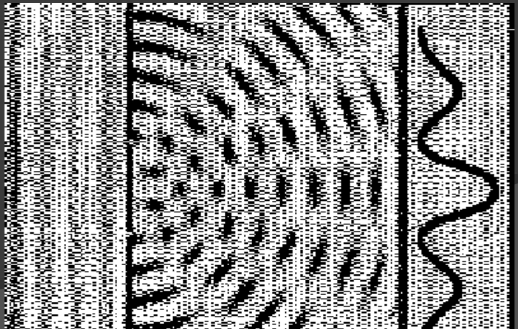


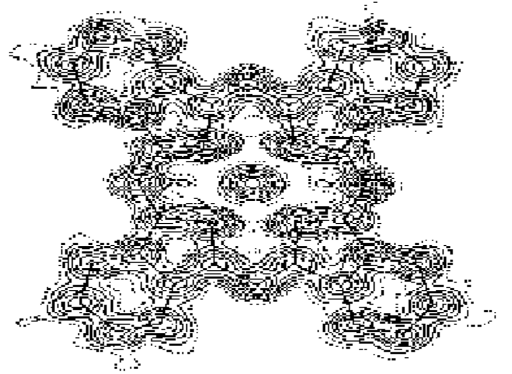






Recording the reflections





Similar Types of Crystal studies using Spectroscopic methods

- NMR spectroscopy
- Electron spin resonance (ESR)
- Raman Spectroscopy
- IR spectroscopy
- Mössbauer spectroscopy
- Atomic absorption spectroscopy (AAS)
- Mass spectrometry

1. NMR - Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is the name given to a technique which exploits the magnetic properties of certain nuclei.

Since the nucleus is surrounded by electrons that's why this energy - the strength of the electromagnetic field (pulse) - needed for excitation is changing depending on (first of all) the structure of the electron shell of that atom.

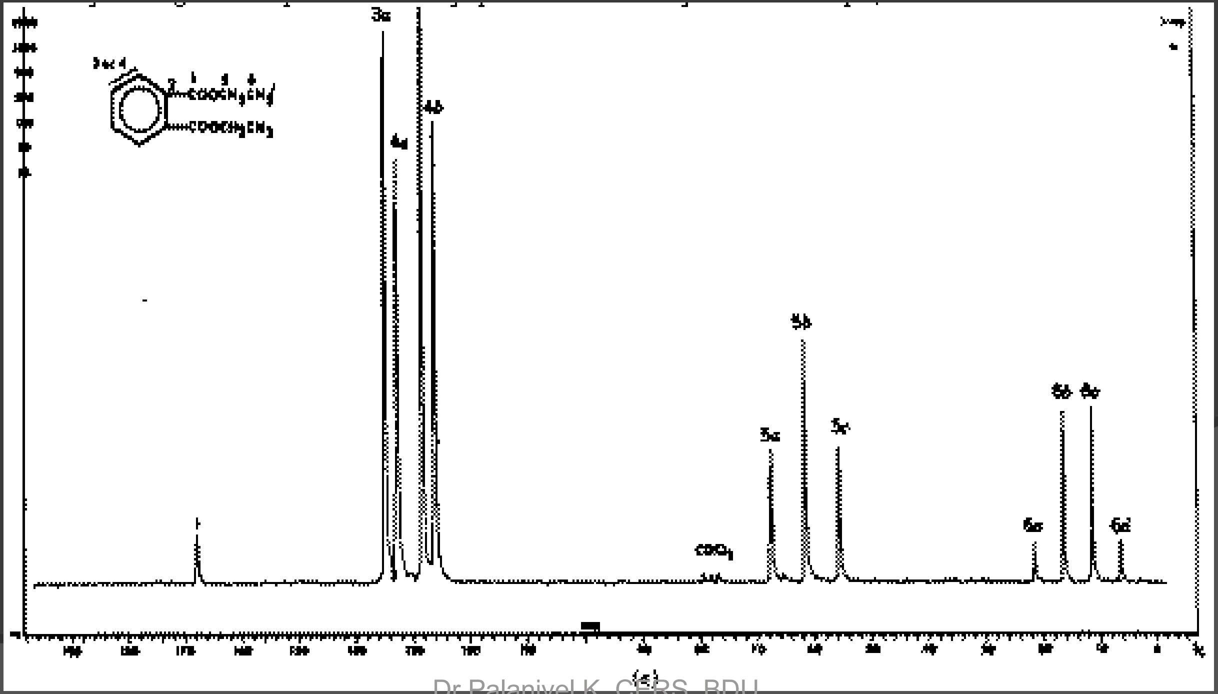
If the atoms are in connection with different atoms in a chemically bonded molecule by their outer valence electrons this new electron distribution also changes the electromagnetic field around the nucleus. In this way the transition energy may change again since it is the function of the strength of the electromagnetic field around the given nucleus.

That's why if we go through a range of wavelengths around the average transition energy we can get the absorptions as a function of the wavelength. This is the NMR spectrum.

From the extent of the shift and the efficiency of transmission we can conclude which type of and how many atoms or particles are connected directly to that atom or in which type of environment this is.
This way the chemical surrounding or environment can be solved.

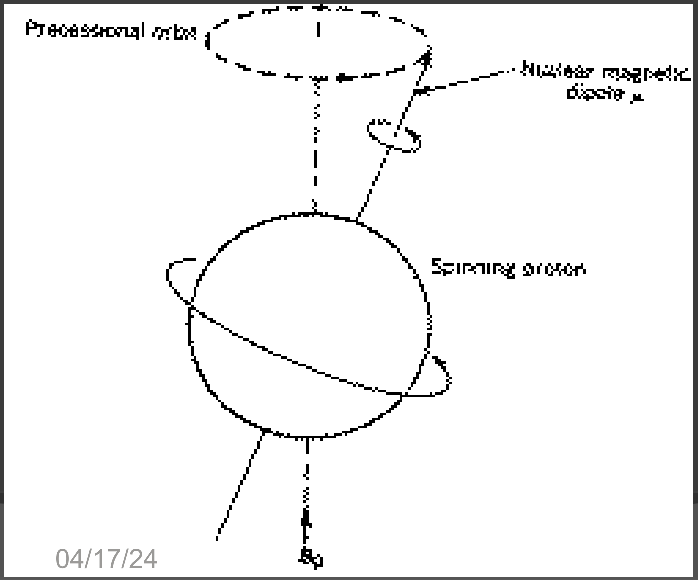
With a suitable computer apparatus we can calculate the whole 3D structure. But we have lots of atoms and a lot of extracted data from a system. This is good for the more accurate determination of the structure, but not for the availability of higher molecular masses. That's why, the resolving power of NMR is less than some other type of experiments (e.g.: X-ray crystallography) since the information got from the same material is much more complex. The cost of the experimental implementation is increasing with the higher strength and the complexity of the determination.

Here is a tipical ^{13}C NMR spectrum (but not for a protein, since it would be very confused and complex (so, it is just for illustration):



Since the only one factor which makes difference in the spectrum is the difference in the strength of the electromagnetic field around the nucleus that's why in this method (the name of which is NMR - Nuclear Magnetic Resonance) there could be (and are) several methods which play with this principle to get several types of information from lots of types of experiments (with programmed impulses of the magnetic field).

In this way they obtain angles, distances, coupling constants, chemical shifts, rate constants etc.



A 900MHz NMR instrument with a 21.2 T magnet at HWB-NMR, Birmingham, UK, being loaded with a sample.

Raman spectroscopy (Roman Spectroscopy)

Raman spectroscopy (pronounced: [rə.mən] , named after C. V. Raman) is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary, information.

Note: A phonon is a quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency.

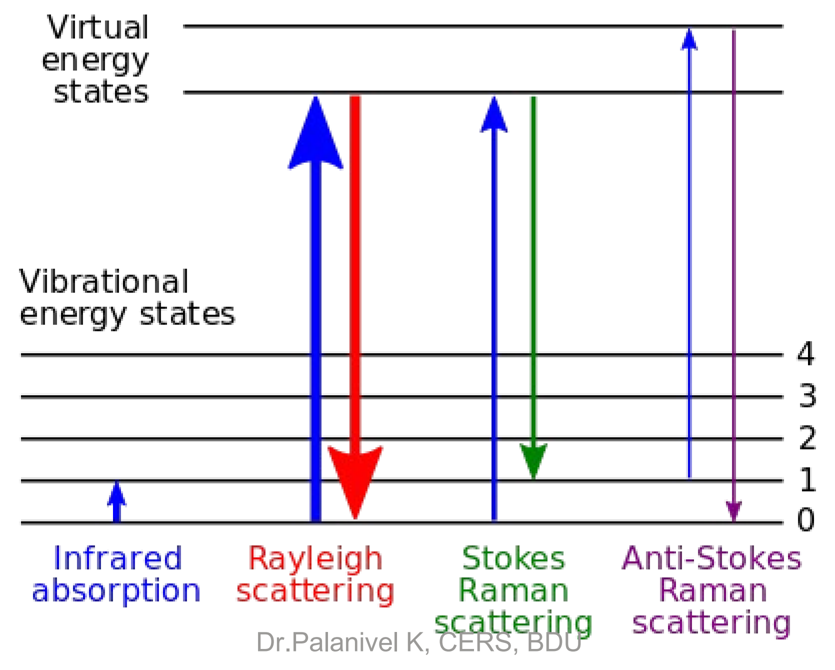
Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Historically, Raman spectrometers used holographic diffraction gratings and multiple dispersion stages to achieve a high degree of laser rejection.

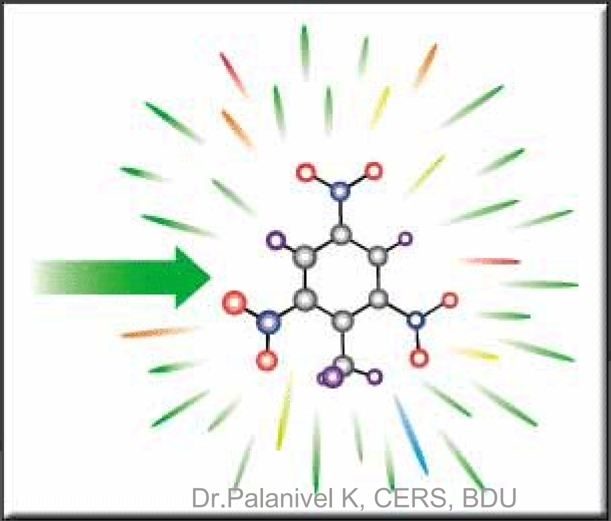
In the past, PMTs were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either Czerny-Turner, echelle or FT based) and CCD detectors.

There are a number of advanced types of Raman spectroscopy, including surface-enhanced Raman, tip-enhanced Raman, polarised Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially-offset Raman, and hyper Raman.

Energy level diagram given here shows the states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.



Raman spectroscopy provides information about molecular vibrations that can be used for sample identification and quantitation. The technique involves shining a monochromatic light source (i.e. laser) on a sample and detecting the scattered light. The majority of the scattered light is of the same frequency as the excitation source; this is known as Rayleigh or elastic scattering. A very small amount of the scattered light (ca. 10-5% of the incident light intensity) is shifted in energy from the laser frequency due to interactions between the incident electromagnetic waves and the vibrational energy levels of the molecules in the sample. Plotting the intensity of this "shifted" light versus frequency results in a Raman spectrum of the sample. Generally, Raman spectra are plotted with respect to the laser frequency such that the Rayleigh band lies at 0 cm-1. On this scale, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations. The Raman spectrum can thus be interpreted similar to the infrared absorption spectrum.



Raman scattering is a spectroscopic technique that is complementary to infrared absorption spectroscopy. Raman offers several advantages over mid-IR and near-IR spectroscopy, including:

- Little or no sample preparation is required
- Water is a weak scatterer - no special accessories are needed for measuring aqueous solutions
- Water and CO_2 vapors are very weak scatterers - purging is unnecessary
- Inexpensive glass sample holders are ideal in most cases
- Fiber optics (up to 100's of meters in length) can be used for remote analyses
- Since fundamental modes are measured, Raman bands can be easily related to chemical structure
- Raman spectra are "cleaner" than mid-IR spectra - Raman bands are narrower, and overtone and combination bands are generally weak
- The standard spectral range reaches well below 400 cm^{-1}, making the technique ideal for both organic and inorganic species
- Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum (e.g. -S-S-, -C-S-, -C=C-).
- Raman spectroscopy can be used for both qualitative and quantitative applications. The spectra are very specific, and chemical identifications can be performed by using search algorithms against digital databases. As in infrared spectroscopy, band areas are proportional to concentration, making Raman amenable to quantitative analysis. In fact, because Raman bands are inherently sharper than their infrared counterparts, isolated bands are often present in the spectrum for more straightforward quantitative analysis.

IR spectroscopy

- Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light.
- It covers a range of techniques, mostly based on absorption spectroscopy.
- As with all spectroscopic techniques, it can be used to identify and study chemicals.
- A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

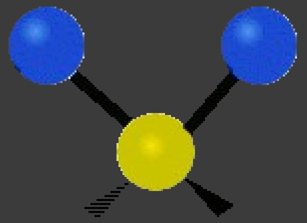
- Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes).

- These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling.

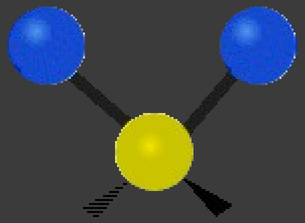
- Simple diatomic molecules have only one bond, which may stretch. More complex molecules have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups.

- For example, the atoms in a CH2 group, commonly found in organic compounds can vibrate in six different ways: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting:

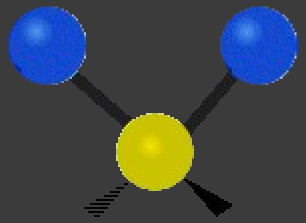
Symmetrical stretching



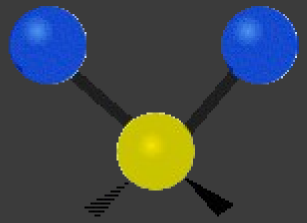
Antisymmetrical stretching



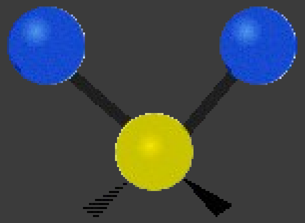
Scissoring



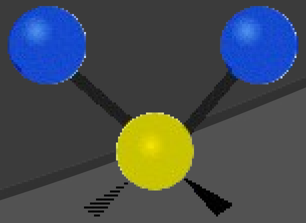
Rocking



Wagging



Twisting



Thank you

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