X-Ray Crystallography

I. History: (Source: Hardinger's Lecture Supplement: X-ray Crystallography)

- 1895: Roentgen discovered x-rays
- 1912: von Laue, Friedrich, and Knipping passed x-rays through crystal of ZnS and concluded that:
  a) Crystals are composed of periodic arrays of atoms
  b) Crystals cause distinct x-ray diffraction patterns due to atoms
- 1914: Bragg and Lawrence showed that diffraction pattern can be used to determine relative positions of atoms within a single crystal (i.e., molecular structure)
- Rosalind Franklin: collected X-ray diffraction data on Na salt of DNA → Guides Watson and Crick to determine that DNA is a double helix.

II. X-ray Diffraction: (Atkins, Jones; Chemical Principle; 3rd edition; pg 196-197)

- Used to determine the arrangement of atoms in a solid compounds and to measure bond lengths and structures.
- Diffraction: interference between scattered waves, which arises when there is an object in their path. *Note: For diffraction to be observed, the wavelength of radiation must be about equal to the distances between the atoms. X-rays are used because they have short wavelengths, which correspond to the bond length.*
  a) Constructive interference: troughs and crests overlap in phase → amplitudes add
  b) Destructive interference: troughs and crests overlap out of phase; occur when the peaks of one wave coincide with the troughs of the other wave → amplitudes cancel out
  c) Partial interference: complex wave patterns result. (A collection of atoms produces complex interference depending upon bond lengths and angles.)

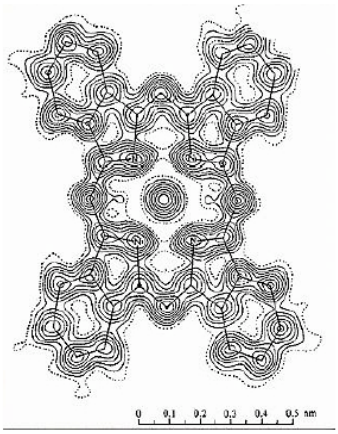
II. Procedure and Instrumentation: (Source: Hardinger's Lecture Supplement: X-ray Crystallography)

1) Grow Crystal: a challenging process.
Must be perfect – no twinning, or inclusions; small (0.1-0.5mm)

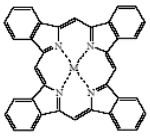
2) Place crystal in **Four-circle Diffractometer**: a device for rotating the crystal and the detector so that the entire diffraction pattern can be recorded under the control of a computer.

- X-rays are beamed at the crystals, electrons diffract the x-rays, producing diffraction patterns.
- Because of the crystals' highly ordered and repetitive structure, many X-rays diffracting off many electron clouds in approximately the same relative position and orientation throughout the crystal will result in constructive interference and give a detectable signal (http://en.wikipedia.org/wiki/Crystallography).

3) **Fourier Synthesis** is used to analyze the intensities of the x-rays at all the settings of the angles in the diffractometer, and convert these measurements into the locations of the atoms.
4) From these informations, the **Electron Density Map** is created. It shows the contour lines of electron density, and therefore, provides location of atoms relative to each other.
   - Smaller circle = higher electron density
   - Center of circles = atom
   - Bond angles and bond lengths may be determined to get the position of atoms in space.
   - Hydrogen atoms often cannot be located because they contain only 1 electron and has large thermal motion.



Electron density map


Molecular structure

(Source: Hardinger's Lecture Supplement: X-ray Crystallography)

X-ray Crystallography is the most precise method of structure determination; it however requires the challenging process of growing crystals.