Lesson 8

- Diffraction by an atom
- Atomic Displacement Parameters
- Low Temperature Data Collection

What Have We Done

Defined translational symmetry
Showed how translational symmetry could produce interference to magnify weak scattering
Determined where the scattered radiation would be and what the pattern would look lik
Used reciprocal space to relate the location of the scattered radiation to the unit cell
Hinted that the intensity of the scattered radiation is the Fourier transform of the electron density in the cell

A non-law Law

- Anything that perturbs the regularity of the translational lattice will cause the intensity of the scattered beam to fall off as a function of theta.
- In the extreme the lattice is destroyed and there is no scattering observed.
- So Summerfield was correct when he thought that the motion of the atoms would cause the intensity to diminish. He just overestimated the effect.

Why does the intensity of the crystal fall off with theta?

- Even if the vibration of the atoms in a lattice is ignored the intensity of the diffraction falls off with increasing theta
- A clue—the fall off is greatest for light atoms.
- Is it interference between electrons in an atom?
- Is it absorption of some sort?
- Does it have to do with the nature of the crystal?

A Thought Experiment

- Remember the intensity of the beam scattered by a free electron is independent of angle.
- Lets imagine we can construct a crystal out of hydrogen atoms.
- Furthermore lets assume there are no vibrations so each nucleus obeys exact translational symmetry.

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What is a Time Scale

- The time scale of an experiment is inversely proportional to the energy of the radiation used to illuminate it.
- Consider the time scale to be like the shutter speed on a camera. The faster the time scale the more motion can be frozen.
- X-rays have high enough energy that the motion of the electrons can be considered frozen

How Does the Diffraction Appear?

- Remember the target is a perfect hydrogen atom crystal.
- In the frozen crystal the electrons do NOT obey exactly the translational symmetry as they are moving around the nuclei and are in slightly different locations for each atom.
- By our law, the scattering should fall off as a function of theta!

A Test of this Idea.

- Neutrons are diffracted by the nuclei and not the electrons.
- Since the nuclei form a perfect crystal (ignoring vibration) their scattering should not be a function of theta.
- This is indeed what is observed.

How to determine extent of electron disorder.

- Is there a way to quantify the amount of disorder for an atom's electrons.
- Use electron density.
- If the electron density approaches the charge on an electron/volume(e/v) of an electron then the electron is essentially not moving.
- As the volume gets bigger the electrons have a bigger space to move in and are more disordered. Diffraction falls off quicker.

A Point to Remember

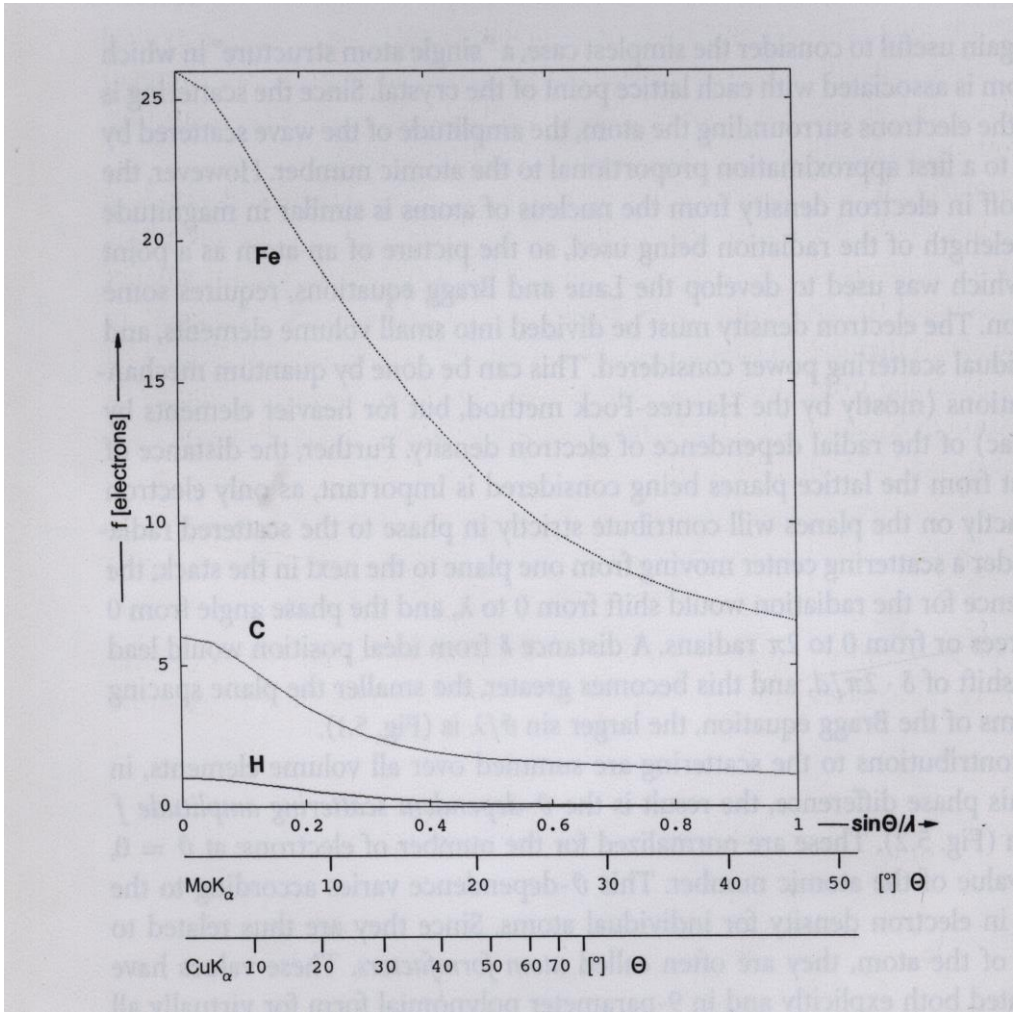
- When we speak of electrons we mean all the electrons not just the valence electrons.
- In general valence electrons are more diffuse than the other electrons so adding or subtracting them makes little difference.
- The one strange case is hydrogen—in this case even acidic hydrogen atoms can be observed and for hydride ions the diffraction may need to be reconsidered.

How to calculate the Scattering Power of an atom.

- There is a Fourier Transform(FT) that transforms the scattered intensity to electron density space.
- There must be an inverse FT that can change electron density into scattering space.
- The electron density of an isolated atom can be calculated using quantum mechanical means such as Hartree-Fock or Dirac methods.
- The transformed values are called atomic scattering factors and given the symbol f.

Scattering Factors

- At zero degrees in theta each atom scatters proportional to its atomic number.
- Note the use of sin(Θ)/λ which avoids the different Θ values for different wavelengths.

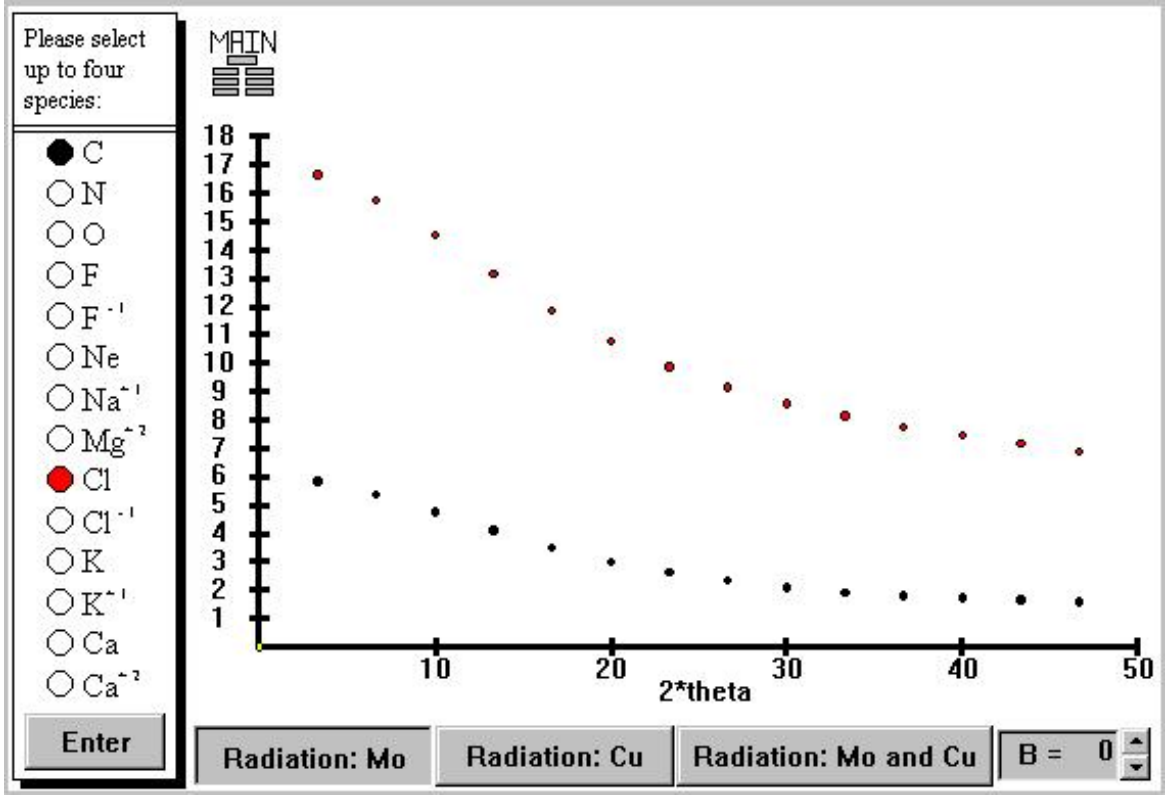


At high theta

- The overall scattering of a crystal is the sum of the scattering factors of the composite atoms.
- Since the atomic factors fall off as a function of theta so does the x-ray diffraction of the crystal.
- At high angles the scattering by the heavier elements predominate.

The effects of vibration

- Obviously the atoms in a crystal are not stationary. They vibrate.
- This will cause the lattice to be less regular and the diffraction should fall off even faster.
- The effect can be lessened by lowering the temperature. This increases the intensity of the higher angle reflections.
- Since atoms vibrate even at 0 K this effect cannot be eliminated. Zero point energy! ($E=(n+1/2)h\nu$)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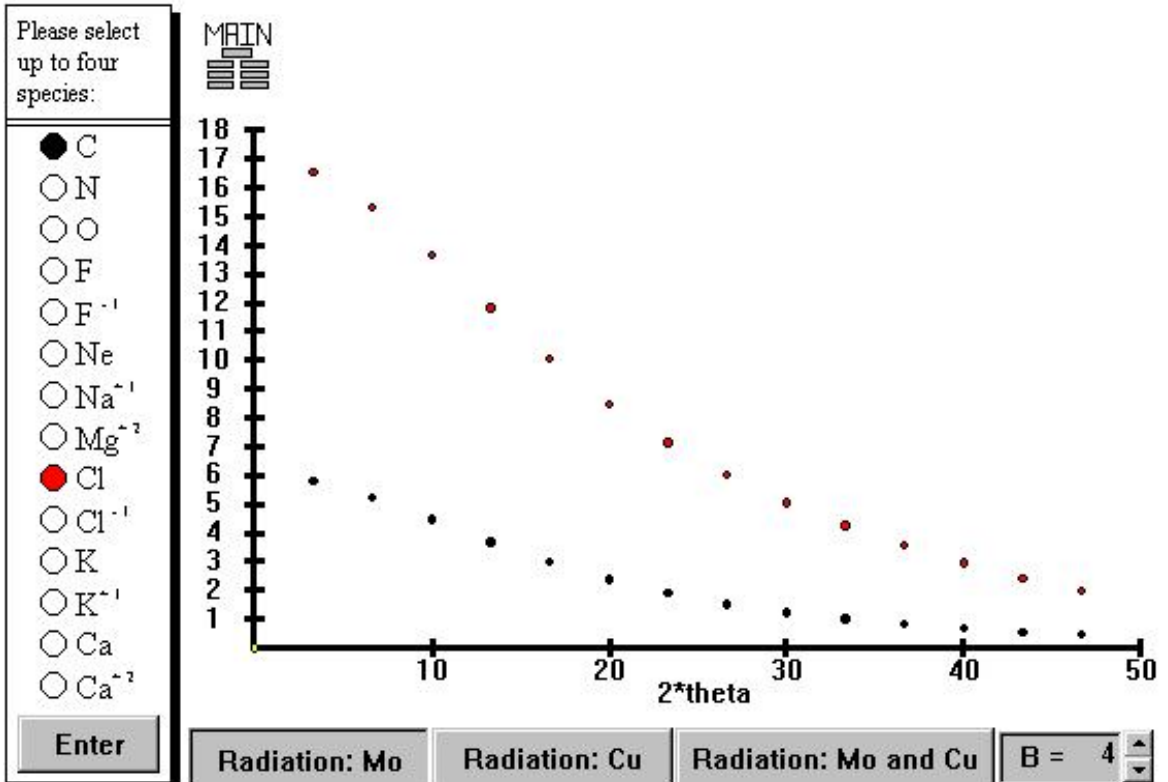
2*theta
Radiation: Mo
Radiation: Cu
Radiation: Mo and Cu
B = 0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MAIN
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
10 20 30 40 50
2*theta
Radiation: Mo
Radiation: Cu
Radiation: Mo and Cu
B = 4

Isotropic Adjustment

- The correction for vibration can be made either assuming the vibrational motion is defined by a a sphere or an ellipsoid.
- If a sphere is assumed the adjustment is isotropic because it has no directional component.
- These corrections are referred to as the atomic displacement parameters (adp's)
- They used to be called the Temperature Factors

Isotropic ADP's

- Unfortunately there are two systems used. Both have units of length^2 usually Å^2
- One is called U it is the root mean square of the average vibrational amplitude. That is $\sqrt{U}$ is the average radius of vibration.
- The other comes from studies of vibration by Peter Debye and is called B.
- $B=8\pi^2U$ or B is about 80 times U. The use of B is disappearing.

What are typical values.

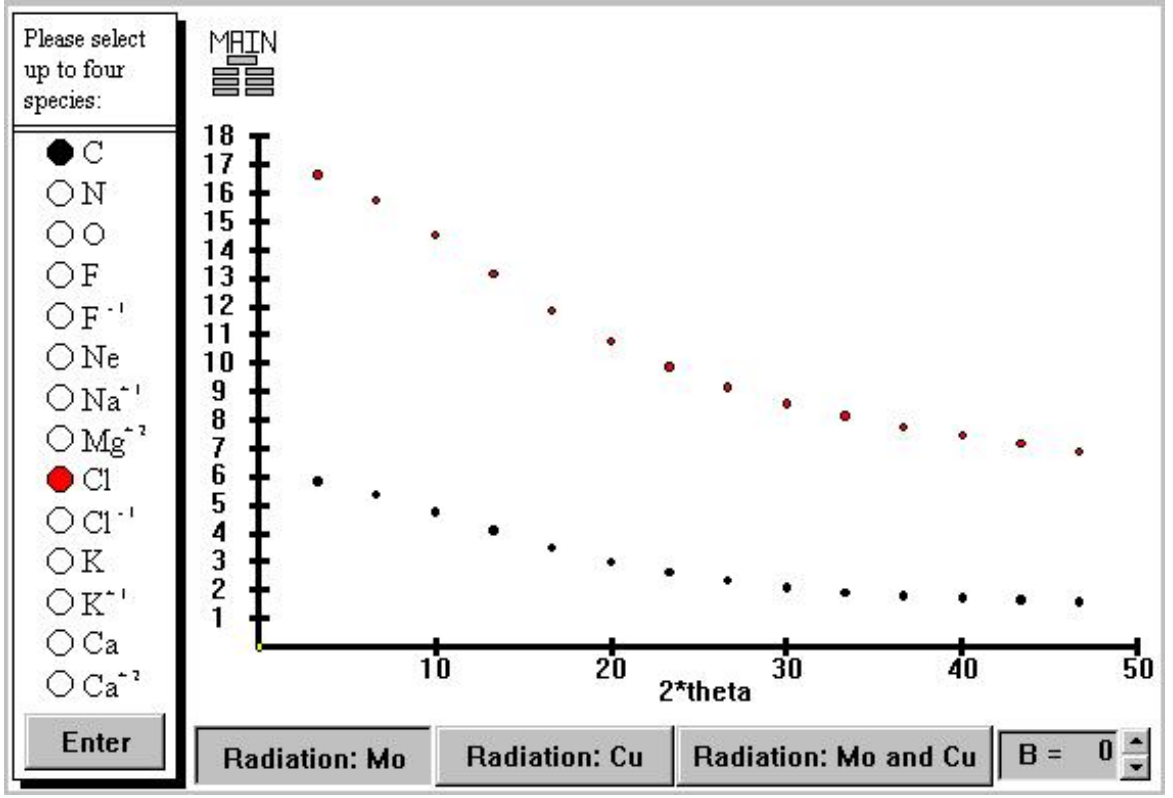
- A carbon atom in a typical room temperature structure has a U of 0.05 or a B of 4.
- Note a U of 0.05 means the average vibration is 0.22Å
- Heavier atoms will have smaller values as their amplitude of vibration is smaller
- The SHELX program package we will be using works totally in U.

Anisotropic Vibration

- The vibration can be better described by an ellipsoid. This is a football with a non-circular cross section.
- It takes 6 parameters to define the ellipsoid—3 represent the principal axes and 3 orient it
- In this case $U=(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}hla^*c^*+2U_{12}hka^*b^*)$
- Atoms should vibrate $\perp$ to bonds not $\parallel$
- The U parameters form a tensor of rank 2

Including Vibration

- The scattering factor f needs to be modified for the adp.
- Define a new factor f' where
  - $f'=f*\exp(-8\pi^2 U\sin^2(\theta)/\lambda^2)$
- In this case U can either be the single isotropic value or the anisotropic form.
- The negative in the exponential means that as U increases the scattering power falls off.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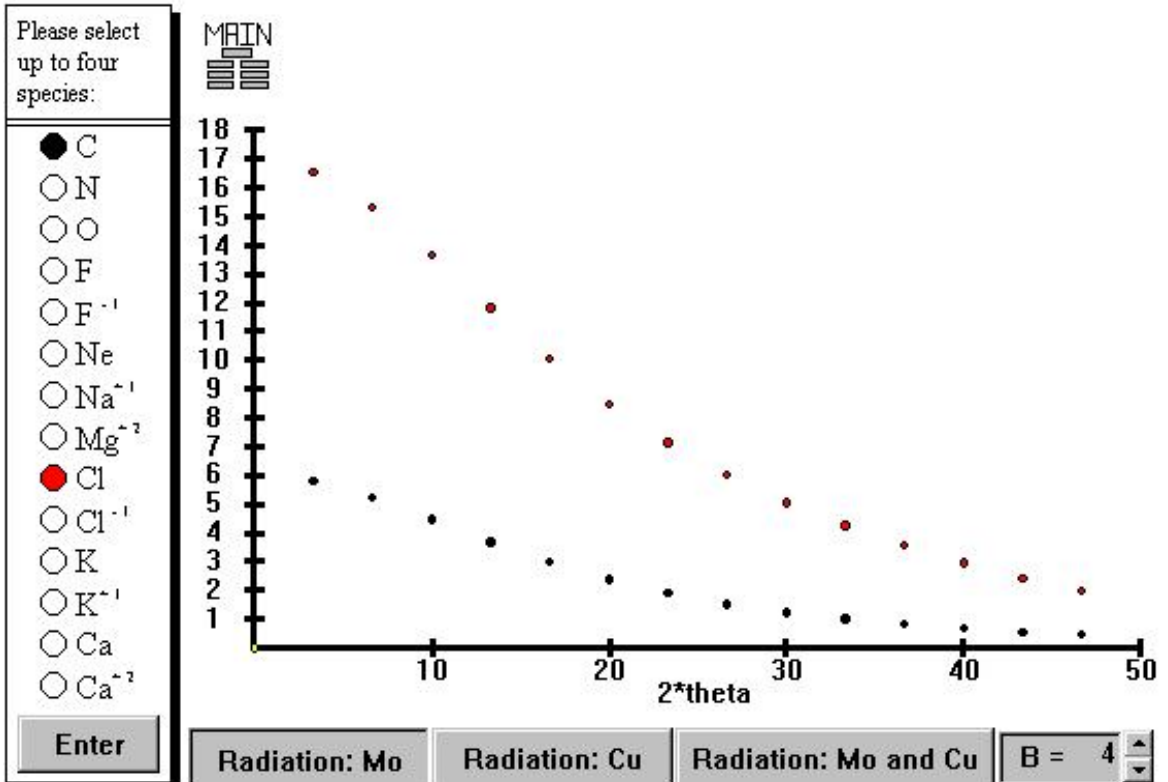
Ca
Ca+2
Enter
MAIN
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
10 20 30 40 50
2*theta
Radiation: Mo
Radiation: Cu
Radiation: Mo and Cu
B = 0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18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
10 20 30 40 50
2*theta
Radiation: Mo
Radiation: Cu
Radiation: Mo and Cu
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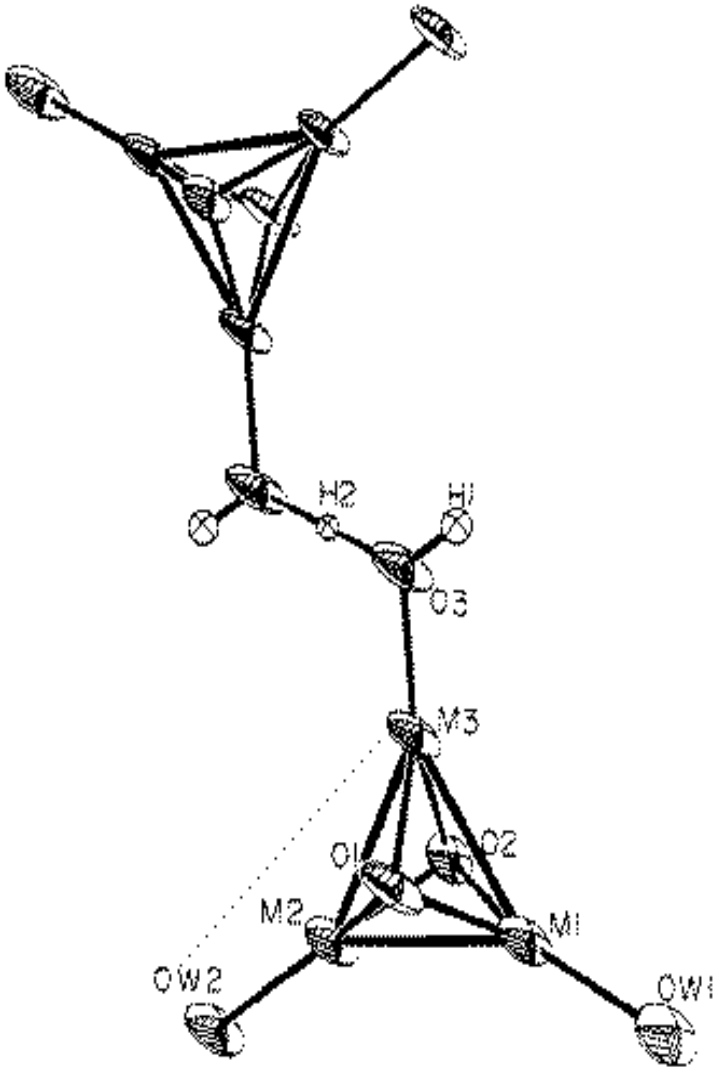
A Note About adp's

- Ideally the adp only reflects the motion of the atom in the crystal.
- Unfortunately, the way atoms are refined during crystallographic calculations the adp actually contains many systematic and other errors.
- When looking at a drawing showing adp's (ORTEP) always look at the atom shapes. This is where the real problems in any structure are observed.

Bad Values for ADP's

- For an isotropic refinement U can never be negative. This implies a negative radius of vibration.
- For anisotropic refinement the diagonal elements of the orthogonalized U tensor cannot be negative. The refinement program reports these values.
- An atom is said to be non-positive definite when it has impossible values. Causes: bad data or mis-assigned elements.

Absorption

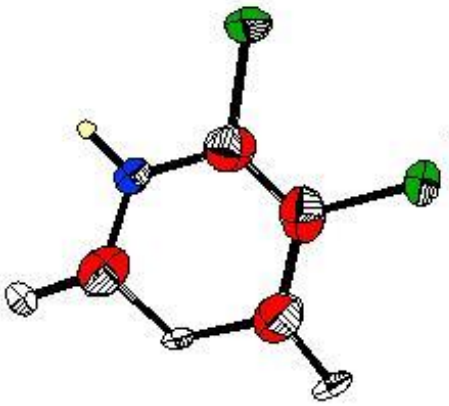


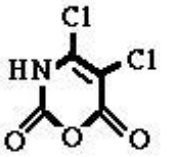
Incorrect Atoms

Thermal Ellipsoids

The Ugly (misassignment of atomic type).

The relatively large size of the atoms assigned as oxygens, relative to those assigned as carbons, suggests a major blunder!



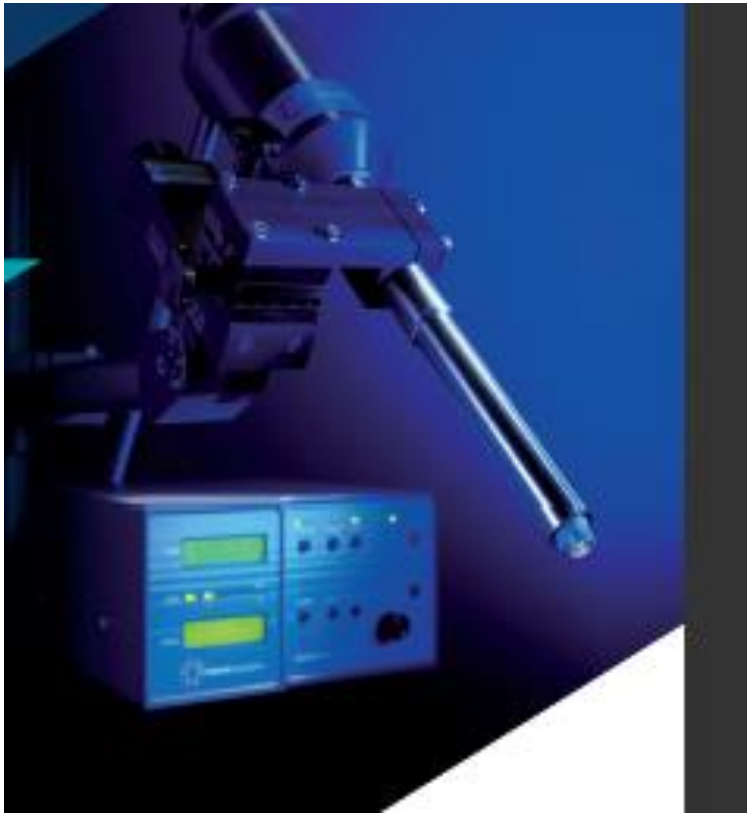


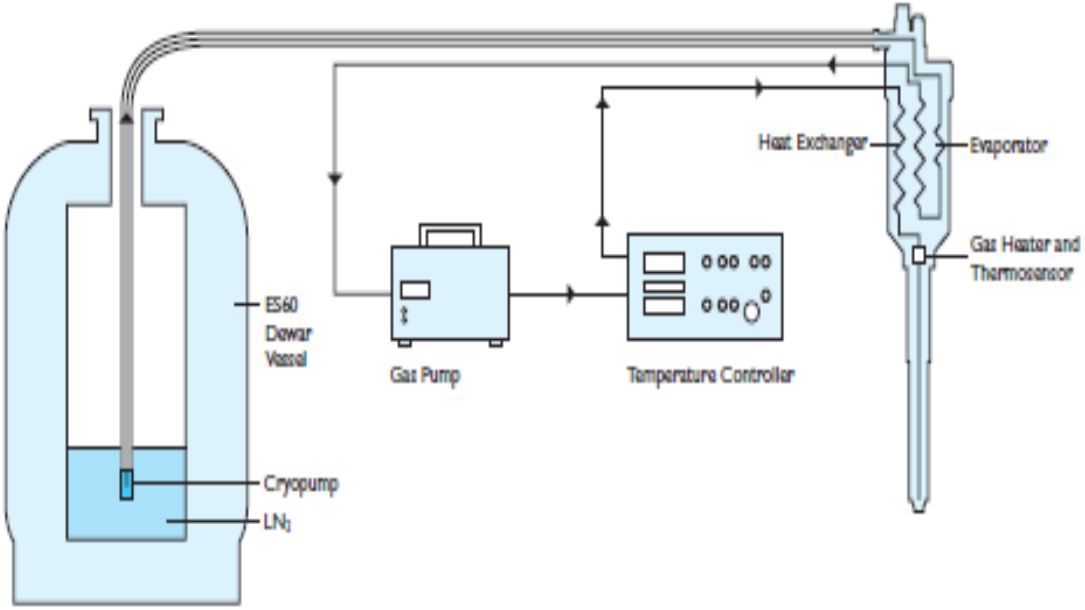
Actual Molecule

Low Temperature Data Collection

- The less the atoms vibrate the stronger the high angle data will be because the less the data will fall off with theta.
- However, at some point all the vibrations will reach the ground state and the cooling will be less effective.
- In the Purdue Lab I typically work at 150K.

Oxfordcryosystems 700




Heat Exchanger
Evaporator
Gas Heater and
Thermosensor
ES60
Dewar
Vessel
Gas Pump
Temperature Controller
Cryopump
LN_2

De-Icing

Advantages of Low Temp

- Better data and more high angle data
- Easier to mount crystals—use grease instead of glue
- Prevents air sensitive crystals from reacting
- Prevents solvent loss
- Can coat with cryo protectant to handle in air before mounting

Problems with low temp

- Must keep crystals at a steady temperature for hours or days
- Crystals may fracture or blow up when exposed to low temperature beam.
- Cracking because of large quantities of water in the crystal
- Phase change may produce result different from room temperature
- If in phase change region get multiple peaks or even no peaks