Chemical Crystallography
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Lecture - 46
Data Reduction – Scale and Temperature Factor

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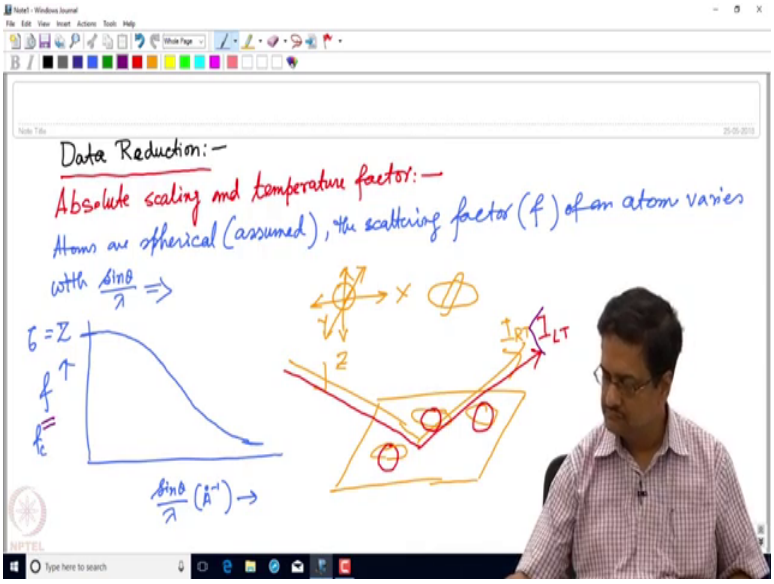

Data Reduction:–

Absolute scaling and temperature factor:–

Atoms are spherical (assumed), the scattering factor (f) of an atom varies with $\frac{\sin\theta}{\lambda} \Rightarrow$

Welcome back to the course of Chemical Crystallography. In last few lectures, we were discussing about the theoretical aspects behind the data reduction. As you already are aware that a raw data which is nothing but a set of images which was recorded using some two-dimensional area detectors. And those images contain the X-ray intensity from the diffracted beams coming out of a given crystal. So, whenever a diffracted beam meets the detector, it creates a signal there, and that signal is just the raw intensity which has to be corrected for various factors as you have already learned that we need to do a correction for the incident beam intensity, depending on beam intensity the diffracted beam intensity will vary.

Then we have learned about the exposure time and then its affect, then we have discussed about the Lorentz and polarization corrections in the previous class. And in the previous class, we have seen that Lorentz and polarization corrections are must for data collections using a refractometer, and use if you are using a crystal monochromator. So, now we should concentrate on a different aspect on data reduction, which we call as the absolute scaling and the effect of temperature factor. If we assume the atoms are spherical in nature, so with the assumption that the atoms are spherical, the scattering factor of an atom that is f of an atom varies with sin theta by lambda in the following fashion as we already know; f verses sin theta by lambda when it is plotted in terms of Armstrong inverse unit, this corresponds to the value Z of the atom in concerned.

So, if it is carbon, so if we are plotting atomic scattering factor of carbon, then this point is 6. So, as we know that if we have an atom in the crystal, and it is considered to be spherical at any given temperature the atom has thermal vibration along X along Y and along Z, so because of this thermal vibration the electron density is no longer spherical is rather diffused over a three-dimensional space. So, when this diffractted when this electron density is diffused, then the diffraction from a given plane having several diffused electron densities at different places will have a certain intensity of diffraction.

When the X-ray hits the plane and gets diffracted, it will have a certain intensity of diffraction. And which temperature by reducing the temperature, when the atoms are more confined towards its nuclei, the electron density on this plane is more tightly bound. As a result the intensity of the diffracted beam at low temperature I L T will be greater than I R T. So, this effect has to be incorporated in the expression for the actual scattering factor f of any atom.

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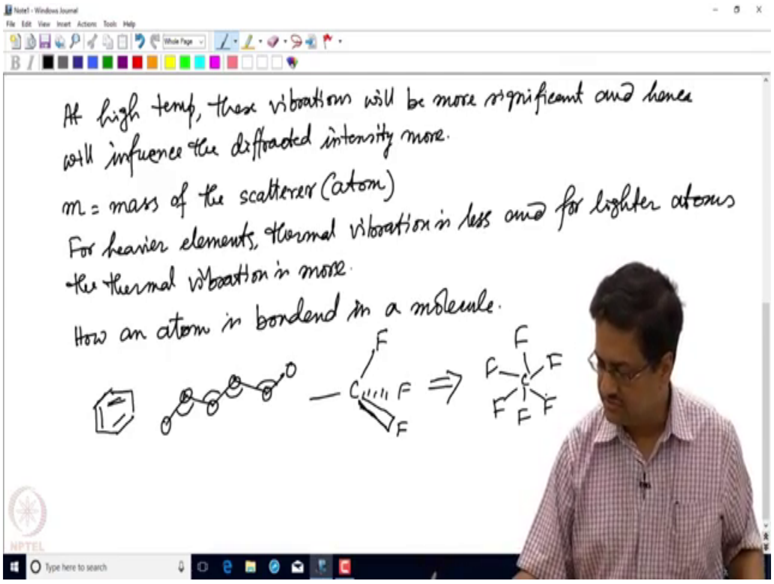

At high temp, these vibrations will be more significant and hence will infuence the diffracted intensity more.

m = mass of the scatterer (atom)

For heavier elements, thermal vibration is less and for lighter atoms the thermal vibration is more.

How an atom is bondend in a molecule.

It is very clear that at high temperature. These vibrations will be more significant and hence will influence the diffracted intensity more. And also this thermal vibration depends on the mass m mass of the scatterer atom, because the heavier the mass lower is the vibration, so for heavier elements thermal vibration is less, and for lighter atoms the thermal vibration is more. And then also depends the thermal vibration depends on how an atom is bonded in a molecule.

Suppose, if we have an aromatic ring with six carbon atoms with alternate single, and double bonds, they are more tightly bound to each other, they have constraints in their bond length and bond angles. As a result the thermal vibration for every individual carbon ion aromatic ring is restricted. While if you have a an hexane chain having six carbon atoms, they all have a fixed bond length, but they have a flexible bond angle which can change and you can rotate the bond without breaking or making a new bond. So, these bonds are more flexible as a result it is possible that these atoms can vibrate mode freely compared to the other one.

And then in case of some groups like this which is a trifluoromethyl group. When you have three large highly electronegative elements bonded to a carbon, these three electronegative elements repel each other that is electrostatic repulsion. Associated with a thermal motion of this fluorines the electrostatic repulsion in between these fluorines will result into a situation where it will look like there are multiple fluorines, connected to the central carbon atom, because this group is vibrating in such a way that it is as if doing is like a rotation. So, this thermal vibration makes the scattering from this type of compounds very week very feeble. And hence we need to take care of that kind of thermal vibrations.

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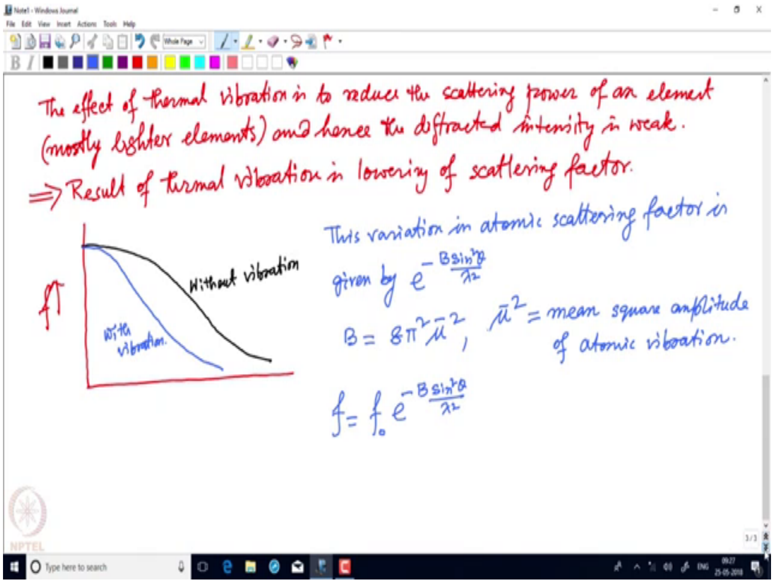

The effect of thermal vibration is to reduce the scattering power of an element (mostly lighter elements) and hence the diffracted intensity is weak.

$\Rightarrow$ Result of thermal vibration is lowering of scattering factor.

This variation in atomic scattering factor is given by $e^{-\frac{B\sin^2\theta}{\lambda^2}}$

$B = 8\pi^2\bar{\mu}^2$, $\bar{\mu}^2$ = mean square amplitude of atomic vibration.

$f = f_0 e^{-\frac{B\sin^2\theta}{\lambda^2}}$

So, the effect of thermal vibration is to reduce the scattering power of an element mostly lighter elements. And hence the diffracted intensity is weak. The result of thermal vibration is lowering of scattering factor which means, if this is the scattering factor curve for an element without the thermal vibration, the same atom would have a scattering factor varying like this with thermal vibration. This variation in atomic scattering factor this change or variation in atomic scattering factor is given by e to the power minus B sin square theta by lambda square, where B is the B is equal to 8 pi square mu bar square, where mu bar square is equal to the mean square amplitude of atomic vibration. So, the actual f is equal to f observed multiplied by e to the power minus B sin square theta by lambda square.

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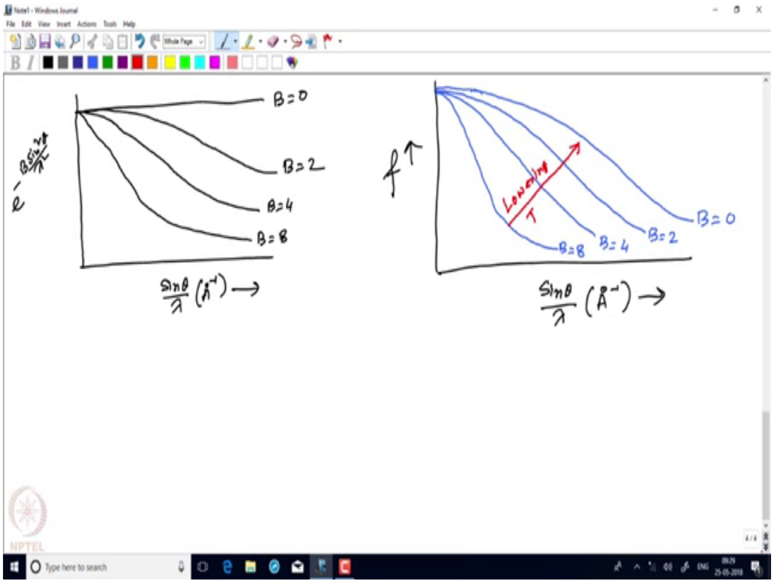

So, if we try to plot E to the power minus B sin square theta by lambda square verses sin theta by lambda in Armstrong inverse unit, we would get a straight line, when B is equal to 0, when B is 2, we get a line like that. When B is 4 it is more severe. And when b is 8, this decreases significantly. As a result the corresponding plot for atomic scattering factor f with sin theta by lambda plotted in Armstrong inverse unit should look like this.

This top plot is without the thermal vibration that is when B is equal to 0, but then with a increase in the value of B this curve reduces quickly that means, the atomic scattering factor of the element reduces significantly with larger and larger value of B and so, so that means on reducing the temperature we approach from higher value of B to lower value of B. This is the direction of lowering the temperature T. So, when you lower the temperature the mean square displacement of every atom decreases, as a result the atomic scattering factor reaches its actual value when there is no thermal vibration. So, this correction has to be incorporated for each and every reflection in a particular data, when we are collecting at a given temperature. So, we need an estimate of this thermal parameter B from the measurement.

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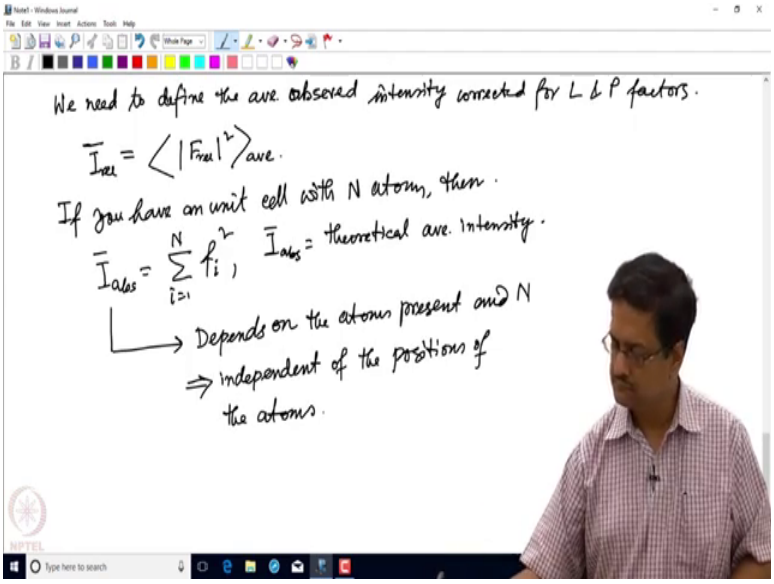

We need to define the ave. observed intensity corrected for L & P factors.

$\bar{I}_{rel} = \langle |F_{rel}|^2 \rangle_{ave}$.

If you have an unit cell with N atoms, then.

$\bar{I}_{abs} = \sum_{i=1}^{N} f_i^2$, $\bar{I}_{abs}$ = theoretical ave. intensity.

→ Depends on the atoms present and N

⇒ independent of the positions of the atoms.

Now, we need to define we need to define. The average observed intensity corrected for Lorentz and polarization factors that I rel is equal to the average of f relative square. So, if you have an unit cell with N atoms then we can show that I absolute is equal to sum over i equal to 1 to N f i square where is the theoretical average intensity. And this I abs depends on the atoms present and number of such atoms present. It is independent of the positions of the atoms.

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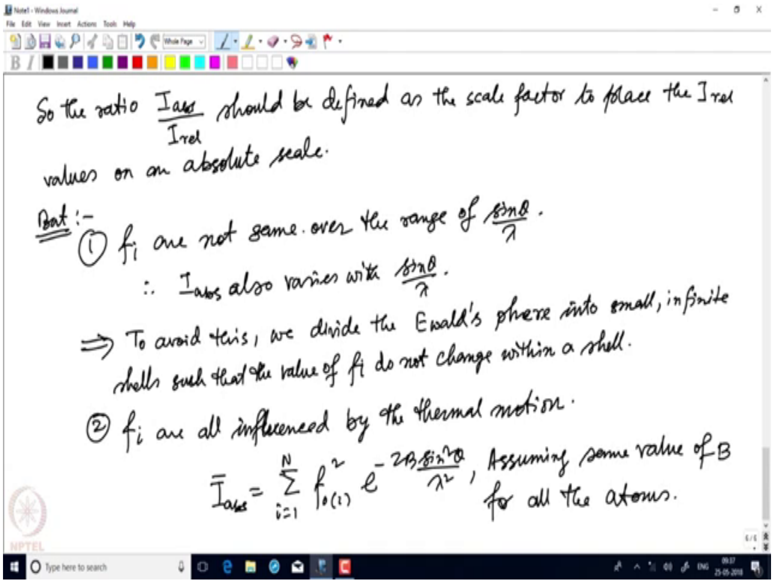

So the ratio $\frac{I_{abs}}{I_{rel}}$ should be defined as the scale factor to place the I_{rel} values on an absolute scale.

But :-

① f_i are not same over the range of $\frac{\sin\theta}{\lambda}$.

$\therefore$ I_{abs} also varies with $\frac{\sin\theta}{\lambda}$.

⇒ To avoid this, we divide the Ewald's phere into small, infinite shells such that the value of f_i do not change within a shell.

② f_i are all influenced by the thermal motion.

$\bar{I}_{abs} = \sum_{i=1}^{N} f_{0(i)}^2 e^{-2B\frac{\sin^2\theta}{\lambda^2}}$, Assuming same value of B for all the atoms.

So, the ratio I abs by I rel should be defined as the scale factor to place the I relative values on an absolute scale. But, we have few problems number 1 f i are not same. And by means same that is not same over the range of sin theta by lambda it is dependent on sin theta by lambda. So, I abs also varies with sin theta by lambda. This f i which is coming here, because of the value of f being not constant over the entire range of sin theta by lambda; it being changing with sin theta by lambda I abs also varies with sin theta by lambda

So, to avoid this to avoid this we divide the Ewald's sphere into small infinite shells such that the value of f I do not change within a shell. And the second problem that we encounter is that as we already discussed f i are all influenced by the thermal motion. So, actually what we should write for I abs average as the sum over i equal to 1 to N f o i square e to the power minus 2 B sin square theta by lambda square, assuming same value for B of B for all the atoms.

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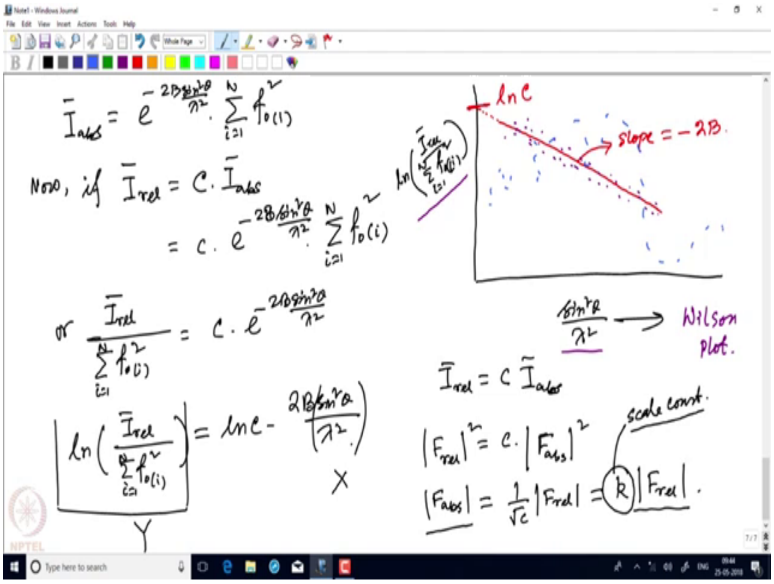

$$\bar{I}_{abs} = e^{-2B\frac{\sin^2\theta}{\lambda^2}} \cdot \sum_{i=1}^{N} f_{0(i)}^2$$

Now, if $\bar{I}_{rel} = C \cdot \bar{I}_{abs}$

$$= c \cdot e^{-2B\frac{\sin^2\theta}{\lambda^2}} \cdot \sum_{i=1}^{N} f_{0(i)}^2$$

or $$\frac{\bar{I}_{rel}}{\sum_{i=1}^{N} f_{0(i)}^2} = c \cdot e^{-2B\frac{\sin^2\theta}{\lambda^2}}$$

$$\underbrace{\ln\left(\frac{\bar{I}_{rel}}{\sum_{i=1}^{N} f_{0(i)}^2}\right)}_{Y} = \ln c - 2B\underbrace{\left(\frac{\sin^2\theta}{\lambda^2}\right)}_{X}$$

$$\bar{I}_{rel} = c\,\bar{I}_{abs}$$

$$|F_{rel}|^2 = c \cdot |F_{abs}|^2$$

$$|F_{abs}| = \frac{1}{\sqrt{c}}|F_{rel}| = \boxed{k}\,|F_{rel}|.$$

scale const.

So, we can rewrite this expression as e to the power minus 2 B sin square theta by lambda square into sum over i equal to 1 to N f o i square. So, now, if I relative is equal to this scale factor C multiplied by I abs average, then we can write it as c into e to the power minus 2 B sin square theta by lambda square into sum over i equal to 1 to N f o of i square. So, we can rearrange this equation like this. I relative divided by sum over i equal to 1 to N f o i square is equal to c into e to the power minus 2 B sin square theta by lambda square. By taking natural level in on both sides, we can write l n I relative by sum over i equal to 1 to N f o i square equal to l n c minus 2 B sin square theta by lambda square.

So, now, if we try to plot, the left hand side as Y, and this as X what do we get, on y axis we are plotting l n I relative by sum over i equal to 1 to n f o i square verses sin square theta by lambda square like this. So, what would we get? Would we get, we would get a straight line with negative slope. If we extrapolate that straight line to sin theta by sin theta by lambda whole square equal to 0 that is at 0 degree angle of diffraction this intercept would give us the value of l n c.

And the slope here will be equal to minus 2B. So, we can then calculate both the scale factor and the temperature factor from this measurement. So, if you write this in this manner, now I relative is equal to c I abs. So, I relative is nothing but mod of F relative square is equal to constant c mod of F abs square, which means amplitude F abs equal to 1 by root over c F relative, which we can rewrite as k into F relative. So, we can establish a relationship between the absolute stretcher factor amplitude with the relative stretcher factor amplitude with a constant quantity k which is written as the scale constant.

So, this is how we can get the value of the absolute structure factor amplitude from the relative values using scale constant for a given data. So, this method of scaling is applied in a data reduction program and then we generate this plot which is called the Wilson plot. So, the feature of an Wilson plot is supposed to be a straight line with negative slope. If we are plotting these two quantities, and this straight line with negative intensity should have all the reflections falling very close by this straight line like that.

So, this reflection should represent a linear distribution with a negative slope. If in case we encounter with a data set where the intensities are scattered like this, and a best fit straight line cannot be drawn that means, there must be something wrong in the data. Probably you have not determine the unit cell correctly, and you are not considering this required number of atoms inside the unit cell and so on. So, those corrections then need to be checked those parameters need to be checked at the time of data reduction. So, this is how we can handle a raw data. And try to process it for the next step which will be the determination of symmetry whether it is having a centrosymmetric distribution or a non-centrosymmetric structure or whether it has a two-fold or a mirror plane.

So, these things we will discuss in the next class.