Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Science
Indian Institutes of Science Education and Research, Mohali

Lecture – 44
Data Reduction-Absorption Correction

Welcome back to the course of Crystallography. In previous couple of lectures, we have learned about the data collection methodologies data collection procedures. And we discussed how one can use different types of diffractometers a three circle or a four circle diffractometer to collect a data. So, you might remember that while doing a data collection, we needed to do some initial screening, which gives you the values for the a, b, c and alpha, beta, gamma.

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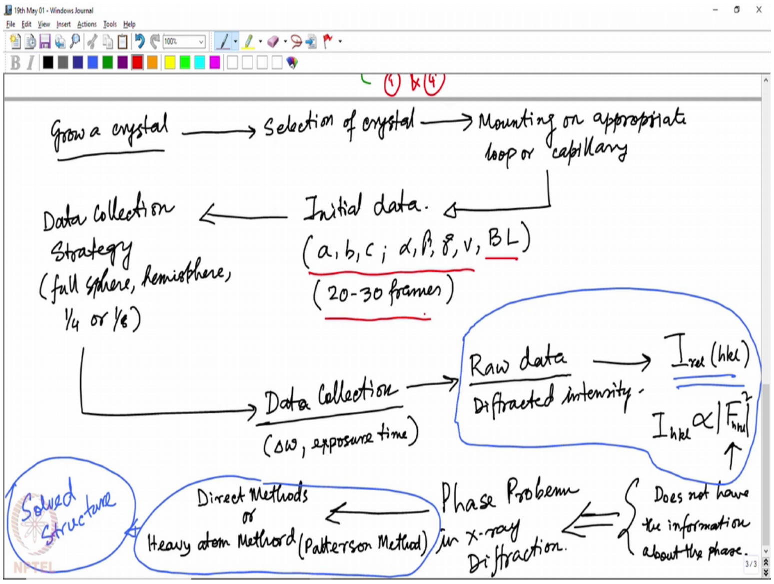

And then from there also one can calculate or one can identify the you have a lattices from about 20 to 30 frames, which are dependent on different diffractometers, their geometries and so on.

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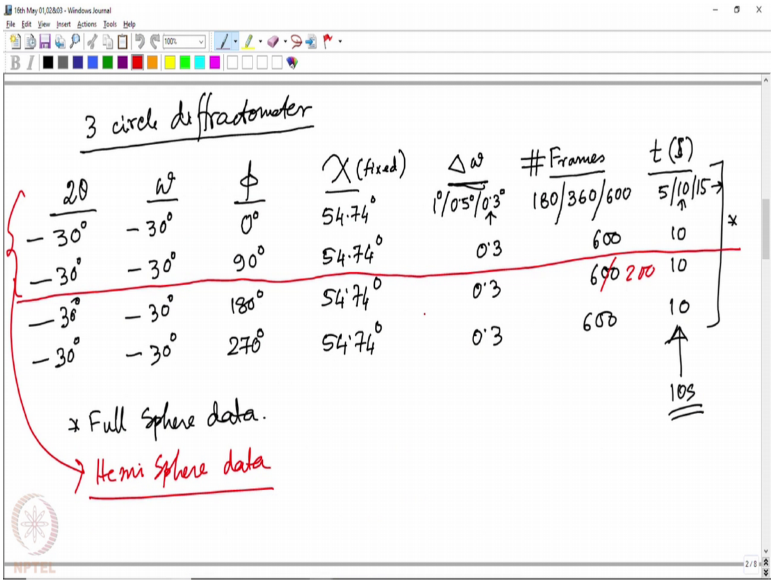

3 circle diffractometer

2θ	ω	ϕ	χ (fixed)	$\Delta\omega$	# Frames	t (s)
-30°	-30°	0°	54.74°	$1^\circ/0.5^\circ/0.3^\circ$	180/360/600	5/10/15
-30°	-30°	90°	54.74°	0.3	600	10
-30°	-30°	180°	54.74°	0.3	~~600~~ 200	10
-30°	-30°	270°	54.74°	0.3	600	10

*

10s

* Full Sphere data.

Hemi Sphere data

And from that we can use different data collection strategies incorporated by us or determined by the software. And a basic standard data collection protocol was shown on a screen like this, where you change the phi with different orientations of the crystal and record the data. So, what is this data that we are getting? These data that we are getting is a frame by frame recording of the diffracted intensity, diffracted beam intensity that appears on the screen.

And we convert that diffractive beam intensity, which is number of photons that is falling on that particular pixel in case of CCD or CMOS detectors, we convert that intensity into the signal in terms of voltage and then we record it. So, now from this recorded data how can we extract our required information on the intensity.

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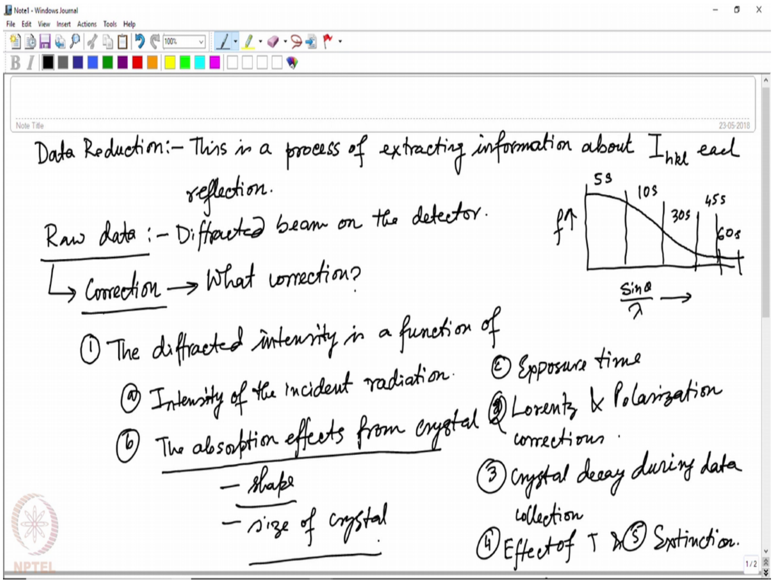

Data Reduction:– This is a process of extracting information about I_{hkl} each reflection.

Raw data :– Diffracted beam on the detector.

↳ Correction → What correction?

① The diffracted intensity is a function of

ⓐ Intensity of the incident radiation.

ⓑ The absorption effects from crystal

– shape

– size of crystal

ⓒ Exposure time

② Lorentz & Polarization corrections.

③ Crystal decay during data collection

④ Effect of T & ⑤ Sxtinction.

So, the process of extracting the data from the raw data is called the data reduction. This is a process of extracting information about the intensity I hkl for each reflection. What we have for that is just the raw data that means, just the diffracted beam on the detector. So, the diffracted beam intensity is then corrected for various aspects, because these diffracted intensities are affected by different physical properties related to the diffractometer related to the crystal and so on.

So, the raw data needs correction, what corrections, the corrections are different types. Number 1 the diffracted intensity is a function of a number of points things; a, the intensity of the incident radiation; b, the absorption effects from crystal, due to the shape or and size of crystal. This is also function of exposure time for which the crystal was exposed in each and every frame.

And mind you it is possible to collect data on one crystal with different exposure time for different to theta position of the detector. Because, if you want to record any high resolution X-ray data, you will have to move the detector to a very high angle maybe 40, 50, 70, 80, 90 degree into theta to record data up to 110, 112 degree in 2 theta.

And as you know the atomic scattering factor f of every atom falls drastically by sine with respect to sine theta y lambda to a large extant and becomes very small and very high value of sine theta by lambda. So, if you want to collect a data where the scattering factor falls in this region, you may have to spent 60 seconds for every frame. Whereas, collecting data for this region, you may be spending 5 seconds per frame. The middle region you may be spending 10 seconds per frame, This portion you may be spending 30 seconds per frame and this region, which is here maybe 45 seconds per frame.

So, that means, the exposure time is changing. As a result the beam intensity diffracted beam intensity is also changing, but diffracted beam intensity is related to this scattering factor f. So, the same atom that is scattering very significantly at low angle will scattered less at high angle. But while recording the high angle reflection, we are increasing the exposure time to about 5 to 6 times maybe sometimes even 10 times. So, the intensity becomes larger so, we need a correction for such change in exposure time as well.

There are other corrections which I am just writing here we will talk about it is soon they are like d are Lorentz and polarization corrections. This I probably should number as point number two, number 3 is crystal decay during data collection and 4 - effect of temperature and 5 - extension so, we will discuss all these points one by one when we come.

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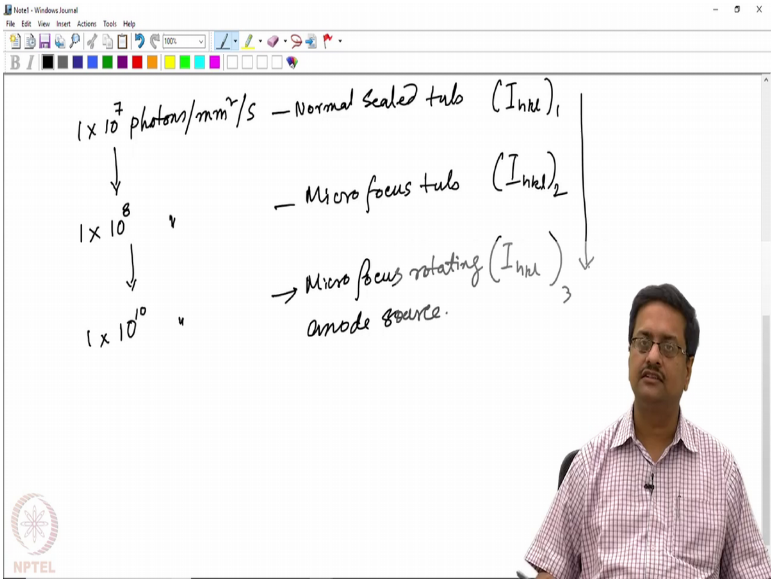

1×10^{7} photons/mm^2/s – Normal sealed tube $(I_{hkl})_1$

1×10^{8} " – Micro focus tube $(I_{hkl})_2$

1×10^{10} " → Micro focus rotating anode source. $(I_{hkl})_3$

So, what happens is when we use different various sources, the beam intensity that is the incident beam intensity varies significantly, when you have a source of which is a sealed tube x-ray resource normal sealed tube source, which may have an intensity corresponding to about 1 into 10 to the power 7 photons per square millimetre per second for sealed tube or routine normal sealed tube. Compared to that a micro focus sealed tube might give you about 10 to the power 8 photons per square millimetre for a micro focus tube. And if you are using a rotating anode, you may end up getting the intensity of 10 to the power even 10 using a micro focus rotating anode source.

So, if you take the same crystal and collect the data in different diffractometers having different sources, the diffracted intensities will be enormously different, because the source intensity itself is different. And what we are recording is the diffracted intensity, source intensity being much larger, the diffracted intensity will be much larger. So, it should not happen that I hkl recorded here, I hk l recorded using the second type and I hkl recorded by third type should be continuously increasing.

If that happens then what will happen is that, the structure solution program will not be able to identify the atoms correctly, because for the structure solution program to identify atoms is the basis is the intensity of diffracted beam. See, if I have a large diffracted beam coming from 100 reflection and that 100 reflection having a lower intensity with a micro focus source much lower with a sealed tube source. The atom that may be responsible for that particular intensity may become different.

So, you will have a problem in structure solution and you will not be actually able to solve this structure correctly. So, one has to then apply a suitable correction for beam intensity in this data reduction procedure. Then I indicated about the absorption effects from crystal, the absorption is very important why? You may have noticed in, if we visible spectrophotometry, if the path length of the a cube weight is increased, the absorption of radiation increases.

If the concentration of the material is increased, then the absorption of light is also increased. So, in extend that crystallography also the sample that we are counting the crystal that we are mounting on a diffractometer is highly related to the corresponding absorption coefficient of the elements present and also the thickness or size of the crystal.

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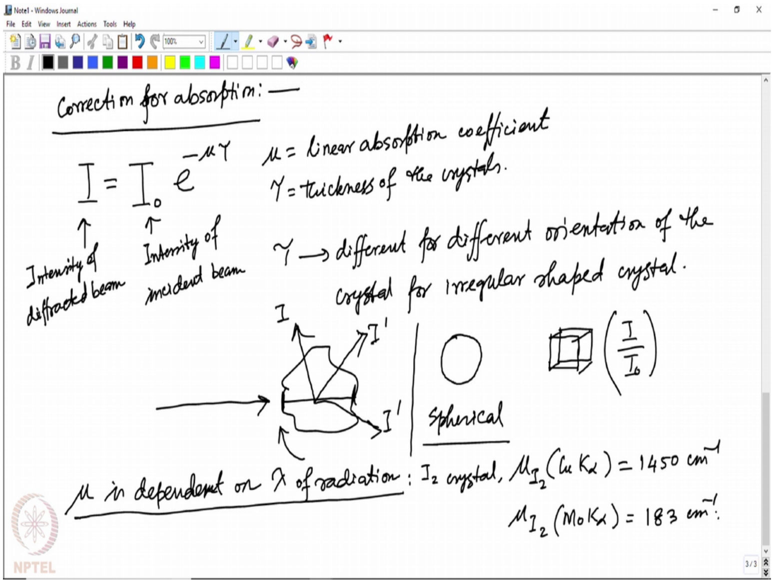

Correction for absorption: —

$I = I_0 e^{-\mu \tau}$

μ = linear absorption coefficient

τ = thickness of the crystals.

↑ Intensity of diffracted beam

↑ Intensity of incident beam

$\tau \rightarrow$ different for different orientation of the crystal for irregular shaped crystal.

μ is dependent on λ of radiation : I_2 crystal, $\mu_{I_2}(\text{Cu } K_\alpha) = 1450 \text{ cm}^{-1}$

$\mu_{I_2}(\text{Mo} K_\alpha) = 183 \text{ cm}^{-1}$.

So, correction for absorption is a difficult task correction for absorption is the difficult task. And it is most often done at the later stage, when it we it is found to be extremely necessary. So, why it is very difficult, because as we know the intensity of the diffracted beam is related to the intensity of the incident beam by this formula I equal to I 0 e to the power minus mu tau. Where, I is the intensity of diffracted beam, I 0 is the intensity of incident beam, mu is the linear absorption coefficient and tau is the thickness of the crystals.

So, if we have a crystal of irregular shape, this quantity tau is different for different orientation of the crystal, for irregular shaped crystal. What does it mean? Suppose, if we have a crystal of some irregular shape and at some point the x-ray meets the crystal like this, the path length inside the crystal is this one. But, on that when it gets diffracted, if it gets diffracted in this direction, if it gets diffracted in that direction, if it gets diffracted in this direction, the path lengths are not same. As a result the corresponding I the diffracted beam intensity suffers different absorption in different direction.

And then during the data collection the crystal is moved about it is axis. So, about 5 it is moved, as a result the shape with respect to which the beam is passing through is different. So, at some point it maybe longer, some point it may be shorter and so on as a result the value of tau will keep on changing during the data collection from one frame to another one set to another set and so on. So, tau changing continuously for irregular crystal makes it even more difficult for any crystal any absorption correction program to apply.

So, to reduce this what one should do is to choose a crystal of some regular shape ideally it is spherical. If a crystal can be ground to a spherical shape that is the best crystal for any x-ray diffraction experiment where the absorption effect is minimised in all the directions and we do not need to do any correction for absorption. If not possible one should try to make the crystal as a cubic shape, which is also very, very symmetric and is very close to a spherical shape. So, the absorption in all directions will be uniform and one can neglect the influence of absorption and collect the data and use the data as such without doing any observation correction.

So, what will happen is in this when you use the spherical or cubic shape crystals the I by I 0 for all the reflections, we will have the same or similar relationship. So, one do not have to do any further absorption correction this absorption is also dependant on wavelength of radiation. So, the absorption coefficient mu is dependent on the wavelength lambda of radiation, the shorter the wavelength more penetrating the wave is, so lower is the value of mu.

So, one the example for I 2 crystal this mu for I 2 using copper k alpha radiation is found to be about 1450 centimetre inverse. Whereas, the same mu for I 2 using Mo K alpha radiation is reduced to just 183 centimetre inverse; that means, to avoid any significant influence of absorption, one should use a shorter wavelength like molybdenum, and that is why, when we collect data on our routine crystals using molybdenum as a source, this effects of absorption is minimised. And most of the time, we do not worry about absorption correction and we are the find with it.

The problem appears in cases where you have heavy elements which are strong absorbers. Suppose compounds containing led, bismuth, mercury you things like that bromine, iodine are very strong absorbers, in those cases one has to apply some kind of theoretical are calculated or computed absorption correction. One can think of doing the empirical observation collection based on the shape.

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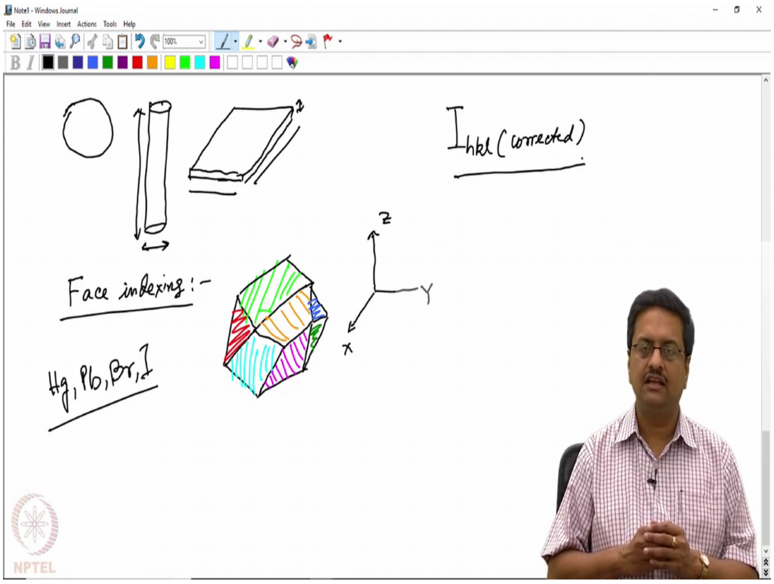

So, based on the actual shape of the crystal which could be nearest here, which could be like a cylinder, which we call as a middle shape crystal or one may end up getting a thin plate like crystal. And one has to then determined this exact size of the crystal using a microscope and is vernier scale associated with the microscope one should be able to find out the actual length of the crystal, actual thickness of the crystal here the length width and the thickness of the crystal. And then with that information, one should be able to apply some theoretical or calculated absorption corrections in the data that is collected.

In some cases, we also do an absorption correction based on phase indexing. What does it mean? Suppose, we have a crystal which has several exposed phases and that those expose phases represent the irregular shaped crystal like this. So, this irregular shaped crystal in mounted on the diffractometer you have collected the data. And then one can find out the actual orientation of the crystal with respect to the beam and identify which is x, y and z direction.

And then eventually can identify each and every exposed phase by the corresponding miller indices. So, every phase that I am marking with different colours can then be identified using different h, k, l and then one can apply appropriate corrections using this indexed phases.

So, this type of corrections are done very rarely as if we encountered a situation where we have irregular shape crystals having heavy elements like mercury, led, bromine and so on, bromine, iodine etcetera and then also heavy large size crystals. So, the absorption correction is important, but it is minimised by using a lower wavelength source like molybdenum source by choosing a crystal of appropriate shape and size, one can reduce the effects of absorption.

In case of doing these data collections on crystals which are and needle shaped or plate shaped by default it is not possible to convert them to a spherical crystal, then one can apply cylindrical or a plate shape crystal correction theoretically using computational results.

And then proceed with the corrected data or in some cases as I just indicated the phase indexing also can be done to do an appropriate absorption correction. So, this will finally, lead to a set of corrected hkl s, the I hkl will be then corrected for absorption and it will be then used for the structure solution program for solving the crystal structure.

So, in today’s lecture, we just learned about some basics of data reduction. We want we have understood that the data that we are recording is highly dependent on some parameters on which the diffractometer is built. One point I want to mention here also is that the sample to detected distance becomes an important aspect, because with the sample to detect at distance increasing the a diffracted beam in tensed in decreases drastically.

So, a correction for sample to detect a distance is also necessary. In case the detail data was collected with more than one detector distances during the data collection process, in general the detected sample detected distance is fixed during a data collection and hence the correction for that detector distance is not incorporated in the calculation.

So, in the next class, we will continue to discuss about these data collection methodologies, we will discuss about the scaling and temperature factor. We will talk about the Lawrence and polarization corrections. And we will see how a data that is recorded using a two-dimensional area detector can be reduced to an useful set of h, k, l versus intensity for structure solution.