# Chemical Crystallography
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## Lecture – 28
## Diffractometers

Welcome back to the lectures on data collection theory and experimental details in this course of Chemical Crystallography. In the previous lecture, we discussed about the how much of data is required for different systems like triclinic, monoclinic and orthorhombic systems. And in that we understand that depending on the lattice symmetry that is the (Refer Time: 00:39) symmetry one only needs half one-fourth or one-eighth of data in case of triclinic, monoclinic and orthorhombic systems to correspond the actual data that is required to be collected.

This was extremely important even about 20 years ago, because in those days even when I started my Ph.D. in 99, we used to have a diffractometer equipped with a detector which is a point detector. So, what a point detector does is that it records one reflection at a time and that detector would take a large amount of time to record and center one particular reflection and record its intensity.

So, suppose for a triclinic system if there are 10000 reflections possible with all h, k, l and h bar, k bar, l bar measured then if we want to record those 10,000 reflections, one would spend days about 6 to 8 days for one data collection. Because what used to happen is if you mount a crystal on the tip of a loop or a glass fiber, and then if you rotate the crystal by 360 degree about its axis which we identified as phi, the diffraction comes in all directions, but unfortunately the detector is in one particular plane on the diffractometer it can rotate like this. And the detector is a tip is a point detector it can only record reflections which are coming in this particular plane out of that crystal.

So, what it used to do is that the detector would move very, very slowly and find one reflection at some point. Then it will try to maximize the signal by moving it about that spot and stop at one place where the intensity is maximum. Then it would move the crystal by this crystal axis phi slowly once again to maximize the intensity. And there are other axis which I am going to talk about now the crystal would be moved in other axis also to maximize the diffracted intensity and would record that intensity for one reflection.

So, to measure one reflection it used to take 5 to 7 minutes. If there is intensity is weak if the diffracted intensity is weak, it may have taken about 15 minutes to record that intensity very accurately. So, as a result if we did not apply Friedle's law we would have collected 10,000 reflections costing us about a week or maybe 10 days to record the entire data. So, when we now know that we can apply Friedle's law we only need half of the data not the full sphere only the half of the data immediately the data collection time is reduced to about 5 to 6 days.

Then if we know that the system is monoclinic, we need only one-fourth. We again restrict our diffractometer to collect data only in certain regions which we indicated here that h or k, h or l would run from one of them will run from minus 2 plus, other one from 0 to plus, and k are running from 0 to plus indicating that we collect only one-fourth of data. And in case of orthorhombic, we only need one x of data that we have discussed in the previous class. So, the data collection time drastically reduces the same is also applied in today's diffractometer systems, well we are collecting data using an area detector which we will discuss in a few minutes.

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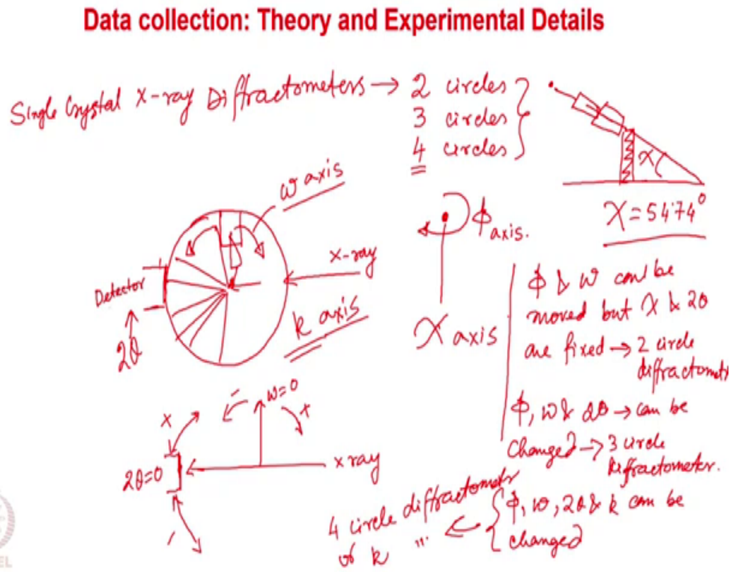

Data collection: Theory and Experimental Details

In today's date, we have diffractometers of three different types and this single crystal diffractometers are categorized using the number of circles about which the crystal can be rotated or the number of cycles about which the data can be collected. So, the single crystal X-ray diffractometers can be divided into 2 cycle, 3 cycle and 3 cycle.

What do we mean by that? If we have mounted the crystal at the tip of this pen, and then if we are rotating the crystal about its axis, this axis is called phi. So, in a in an X-ray diffractometer, if this is a base of the diffractometer on which all these axis are mounted, and X-ray beam comes from the right side and the source is fixed. You have a crystal in the middle and a detector sitting behind that is a standard geometry of a diffractometer.

So, when x-ray falls on the sample, it diffracts in all possible angles. So, if a crystal is mounted here on a loop or a glass fiber. And if it is rotated about its own axis that axis is called the phi axis. In previous class, as I have shown you a photography picture of a goniometer head. So, this crystal is mounted on the goniometer head like that. And this goniometer head is mounted on the base of the diffractometer called a goniometer. So, the base of the diffractometer can rotate like this, it can rotate like that so that the crystal rotates like this the base rotates. So, the crystal rotates like this in a vertical axis.

So, if we have that base somewhere here holding the goniometer head and the crystal here, this base can rotate in either direction and rotate the crystal. So, if the crystal is like this, the base can be rotated here; if the base is rotated this base is called the omega axis. And then this goniometer head which is here suppose and the tip of the goniometer head you have the crystal, it makes an angle with the horizontal plane that particular angle is called the chi axis that is if this is the base, this is these goniometer holder. And on this you have a goniometer placed and the crystal is mounted here. So, this particular attachment makes an angle phi with the omega base. And this chi is fixed in case of a 2 circle or 3 circle diffractometer to a magic angle of 54.74 degree.

The fourth axis sorry, the third axis is kappa, which is like if you have the sample like this, and then the crystal can be rotated in this vertical axis is kappa. So, when chi is not fixed, it becomes kappa. So, that in case of kappa axis diffractometer, if you have the crystal like this it can be kept like that it can be made vertical like this it can be rotated like that. So, the fourth axis that we can think third axis that we know is a kappa axis which makes the crystal rotate about instead of this vertical axis which is like this, it rotates the crystal in horizontal axis like that.

So, the crystal is rotated like this in the axis in the horizontal direction and it is called the kappa axis. The fourth one that we can change is the position of the detector and we call it as a 2 theta axis. So, with respect to the direct beam, this position is 2 theta equal to 0 a perpendicular position with respect to the direct beam is omega equal to 0. And kappa 0 is this one, so that is exactly vertical from the goniometer base, and kappa can be then rotated to plus 90 to the other side minus 90. And phi is something which is rotated by 360 degree.

So, by having my a detector located at 2 theta 0, one can rotate the position of the detector in either direction in plus and minus with respect to 2 theta, and simultaneously this omega can be rotated in either side plus and minus simultaneously along with 2 theta. So, now, in this particular setup, there are three different possibilities a diffractometer in which you can rotate both phi and omega can be moved, but chi and 2 theta are fixed that is called a 2 circle diffractometer. The diffractometer in which one can change phi, omega and 2 theta can be changed that is called a 3 cycle diffractometer.

The third type, where we talk about four circles in that all phi, omega, 2 theta and kappa can be changed. This is called a 4 circle diffractometer or kappa diffractometer or kappa access diffractometer. What are the technical differences between these? When we have a 2 circle refractometer, we are restricted in two angles; we cannot change the detector 2 theta, we cannot change the kappa or chi. So, in that what happens is we cannot record any diffraction data beyond the fixed to theta value.

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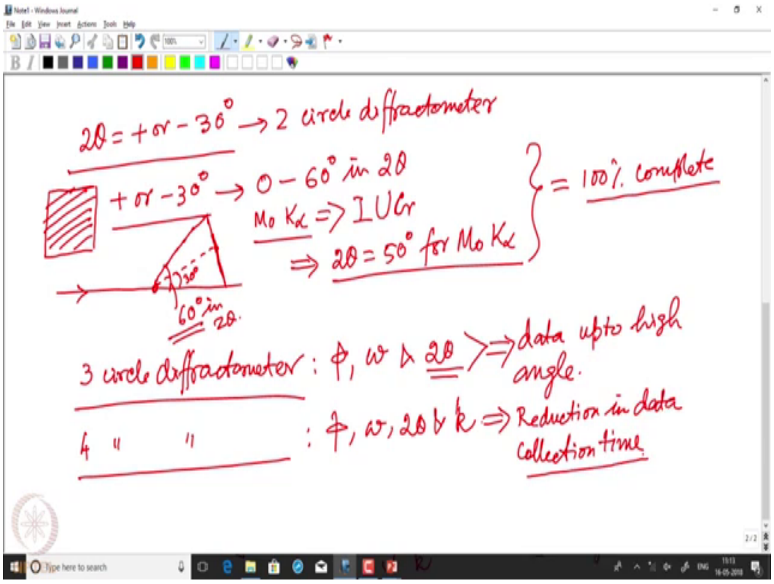

$2\theta = +\text{ or } -30^\circ \rightarrow$ 2 circle diffractometer

$+\text{ or } -30^\circ \rightarrow 0-60^\circ$ in $2\theta$

Mo $K_\alpha \Rightarrow$ IUCr

$\Rightarrow 2\theta = 50^\circ$ for Mo $K_\alpha$

= 100% complete

3 circle diffractometer : $\phi$, $\omega$ & $2\theta$ $\Rightarrow$ data upto high angle.

4 " " : $\phi$, $\omega$, $2\theta$ & $k$ $\Rightarrow$ Reduction in data collection time

In case of any two circle diffractometer, in case of a two circle diffractometer, the 2 theta value is generally fixed at plus or minus 30 degree in case of a two circle diffractometer. Why so, the size of the detector the coverage area of the detector is such that if it sits at plus or minus 30 degree, it can cover from 0 to about 60 degree in 2 theta that is if we have the x-ray beam coming like that and we have a crystal in middle and the detector is located somewhere here. Which is at about 30 degree with respect to the direct beam it records data in the range of total 60 degree in 2 theta.

And what is the limit for IUCR using molybdenum data, mind you for routine single crystal x-ray diffraction, everyone uses molybdenum because it has much higher penetrating power and it gives much less absorption and it can then collect the required data with less amount of 2 theta span. So, we collect this data using 6 molybdenum radiation Mo K alpha radiation, and we collect 60 degree because the IUCR limit - International Union of Crystallography limits minimum of 2 theta equal to 50 degree for Mo K alpha radiation.

So, by keeping the detector at about minus 30 degree, one gets that up to 60 degree in 2 theta. So, whatever data we collect is about 100 percent complete; is about 100 percent complete with respect to the IUCR limit, what are the disadvantages. Since we cannot change the detector position, we cannot record any high angle x-ray diffraction data. So, only routine analysis can be done using this two circle diffractometer.

In case of a 3 circle diffractometer where we can rotate phi, omega and 2 theta. Now, we can rotate the crystal about its own axis, we can rotate the crystal in omega, and we also can change the detector position. So, this allows us to record data up to high angle. So, this type of diffractometers can be used for doing any advanced applications which requires high resolution data that is high angle x-ray diffraction data.

The fourth circle diffractometer is the latest introduction where you can change all four - phi, omega, 2 theta and also kappa allowing you to reduction in the data collection time. Because when you are able to rotate the crystal about this horizontal axis as well, you are able to bring all the reflections which are falling at various places in the reciprocal sphere much of the detector can be now made to fall on the detector by rotating the kappa from 0 to plus 90 and minus 90 and recording the data.

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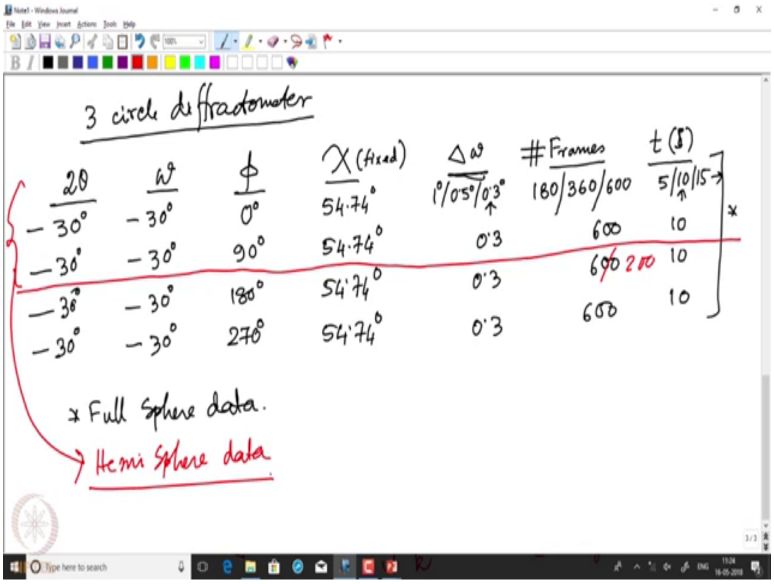

3 circle diffractometer

| $2\theta$ | $\omega$ | $\phi$ | $\chi$ (fixed) | $\Delta\omega$ | # Frames | t (S) |
|---|---|---|---|---|---|---|
| | | | | 1°/0.5°/0.3° | 180/360/600 | 5/10/15 |
| −30° | −30° | 0° | 54.74° | | 600 | 10 |
| −30° | −30° | 90° | 54.74° | 0.3 | ~~600~~ 200 | 10 |
| −30° | −30° | 180° | 54.74° | 0.3 | 600 | 10 |
| −30° | −30° | 270° | 54.74° | 0.3 | | |

* Full Sphere data.

Hemi Sphere data

So, using suppose a 3 circle diffractometer how much data one has to record, how you decide that the total number of images that one has to record, what should be the exposure time and so on. What is exposure time? Exposure time is a time in seconds for which the crystal is exposed to -ray for recording one image. This exposure time can vary from some fraction of seconds to several seconds to minutes depending on the quality of diffraction from your crystal. And that exposure time one has to determine while recording the standard x-ray diffraction while recording the initial frames for unit cell determination, what is that we will now do this in a while.

So, in case of a 3 circle diffractometer, a following table that I am going to write is generally used for a data collection limiting to either hemisphere or quadrant or a full sphere data. So, what are the variables? We can change 2 theta that is the detector position; we can have a change of omega; we can change phi. In case of 3 cycle diffractometer, this is fixed and then we record the data with the change or with the moving omega. So, we need a width in delta omega.

And what we need is to move omega from one point to another by total 180 degree, so depending on the width that I am using the number of frames is determined. And the exposure time in seconds is also indicated here. As I indicated already in case of two circle diffractometer, if we place the detector at about minus 30 degree or a plus 30 degree, it records data up to plus 60 degree or minus 60 degree. So, with detector at minus 30 degree we start omega also at suppose minus 30 degree. We start phi at 0, degree chi is fixed at 54.74 degree.

And now this is the width what is the width, width is when the crystal is being exposed to X-ray, we do not keep the crystal static rather we move the crystal about a certain amount in omega that certain amount is the width in omega. This delta omega can be 1 degree, can be 0.5 degree, can be 0.3 degree or even smaller. So, if we move omega by 1 degree for every image to be recorded, and if we want to have a 180 degree rotation of omega with steps of 1 degree width, then I would need to record 180 frames if it is 1 degree width. If it is 0.5 degree width, then I would need 360 such frames. So, the number of frames get increased. If I use 0.3 degree width, I would need 600 such frames that means, much more number of frames. And this time in second can be 5 or 10 or 15 or more depending on the quality of the crystal the way in diffracts. So, this is one set of data.

The second set should be collected as minus 30, again we start at minus 30 now I change the phi to 90 degree keep the chi fixed this cannot be changed. And follow the same width, suppose I follow the width of 0.3 degree and I record 600 for the same amount of times suppose say 10 seconds. Do it again. Remember now I have rotated the crystal by 180 degree, I have the same width of 0.3, 600 such frames with 10 second exposure. And do it a fourth time we 30 degree starting at 30 degree in omega, and doing it at 270 degree of phi with same kind, and same width same number of frames and 10.

So, what are we doing we are doing the data collection with phi equal to 0, phi equal to 90, phi equal to 180 and phi equal to 270 which means technically we have rotated the entire sphere of reflection about phi and recorded the data with the width of omega by moving omega also from minus 30 to another plus 180 degree so that goes to plus 150 degree. So, in this process all the reciprocal lattice points which come under a sphere is going to be recorded. And whatever strategy I have drawn written here corresponds to a full sphere data. This all these four sets represent a full sphere data that means we have collected much much excess of data if we have done these four sets.

In some cases we really need this full sphere data we will come to that when we discuss about the non centrosymmetric structures and anomala scattering. If we had stopped after recording the first two sets of data, this represents nearly the hemisphere data, but in some diffractometers it may not be doing this as hemisphere data, we may have to record about another 200 frames here to correspond to the hemisphere data depending on the size of the detector that we have on that particular diffractometer.

Nowadays, diffractometers are coming with a very very large detector, so that if you just do first two sets of data collections that is 600 frames in each of those two sets using a three cycle diffractometer, it gives you the coverage of hemisphere data. And if you just do the first line, it corresponds to almost about one-fourth of the data and corresponds to a sufficient data for orthorhombic unit cell.

This strategy is sort of fixed if we are trying to do a data collection using 3 circle diffractometer. There are some variations of these angles you may choose to collect with plus 30 degree of 2 theta plus 30 degree of omega, you may choose to do the data collection with phi from 40, 135, 215 and so on, but the general strategy is like this.

What applies when you try to choose delta omega. If you choose a large width, then actually you are moving the omega by a large angle. So, you are actually slicing the reciprocal lattice in a much wider region and recording the data. So, if you want to have use a larger slice of 1 degree, it is preferred that you use a longer exposure time, so that the exposure time part degree in omega is fixed. If you change from 1 degree width to 0.5 degree width, and then to 0.3 degree width, what one can see is that the quality of data improves with the finer and finer and finer slicing of the reciprocal lattice and that is why we try to collect data using 0.3 degree width in most of the crystals that we do. But for routine extra data for any reasonable publication, one can use a 0.5 degree width and collect the data much quicker.

So, if we have access now to a 4 circle diffractometer, what with happens is that the fixed value of time is no longer fixed, chi can be changed. And because of chi being changed, the crystal can be aligned from vertical to corresponding exact horizontal. In case of fixed chi the crystal stays at a particular angle of 54 degree with respect to the base. So, by rotating the crystal about this axis like this, one can make the data collection faster, one can bring the reciprocal lattice points which are much higher than the detector to the to fall on the detector easily. So, the data collection time reduces significantly. So, in today's lecture we have learned a few basic things about data collection strategies and procedures. And we will continue from here in the next lecture.