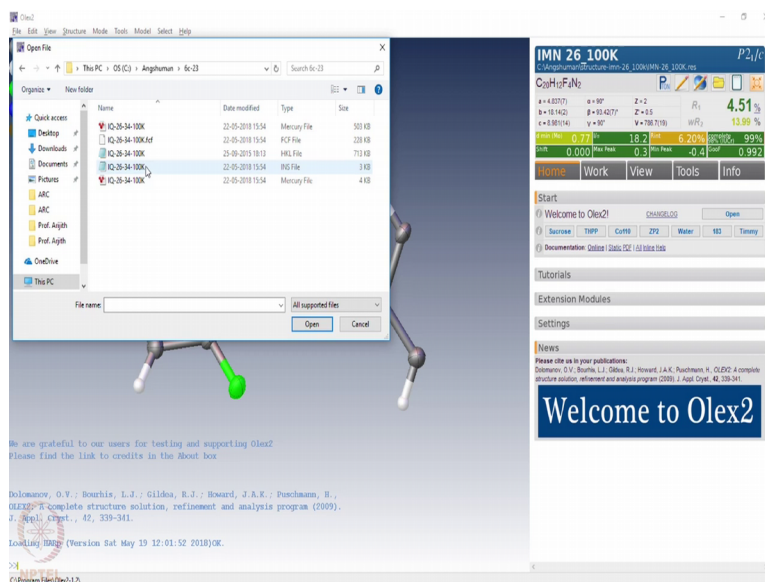


Chemical Crystallography
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Lecture - 42
Disorder Treatment using Olex2

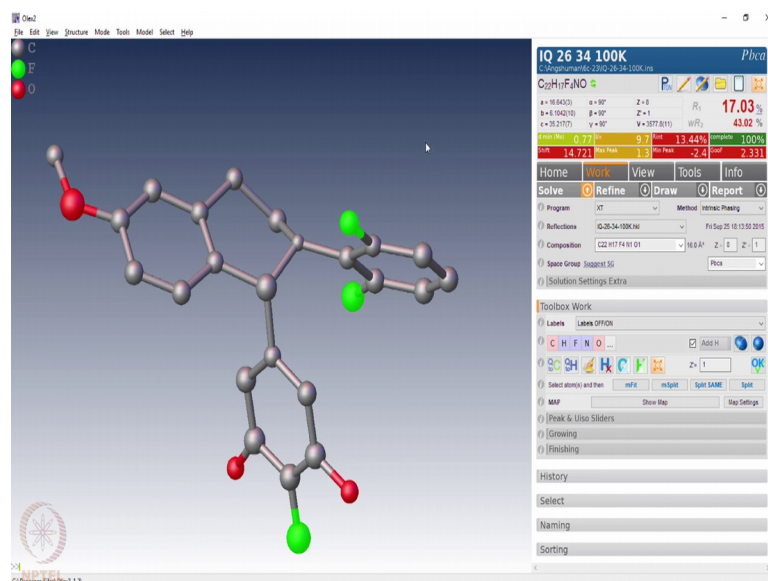
Welcome back to the course of Crystallography. In the previous lecture, we were discussing about the disordered structures, and we had discussed about how to treat a disorder structure using part comments. So, now, we will see how we really do it using one particular data.

(Refer Slide Time: 00:39)



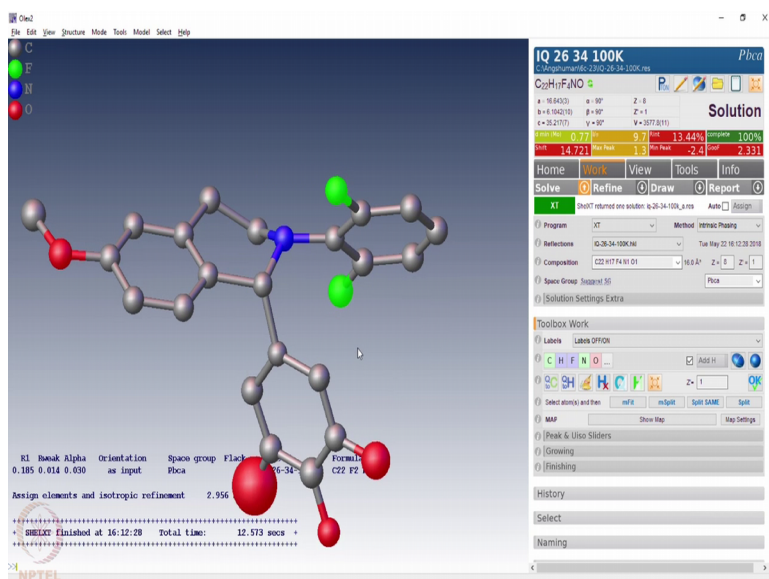
In this particular data you will see a molecule which I am going to solve from scratch, and then I will show you how the disorder is visible in that particular molecule.

(Refer Slide Time: 00:49)



This is a model structure, but we can redo the structure solution part for all of you. So, I use the XT to solve the structure you can see it is orthorhombic with space group $Pbca$ with cell dimensions 16, 6, 35 and volume 3577.

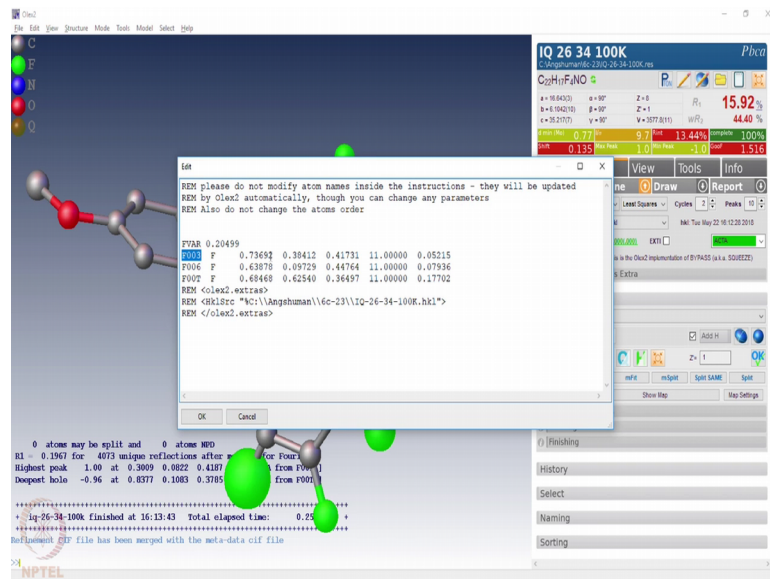
(Refer Slide Time: 01:20)



So, I am trying to solve it using the direct methods. It will quickly give you a structure which is the starting model for this solution, where you will see that the molecule is coming with one very large ellipsoid; another small ellipsoid and a very small ellipsoid here. And with my chemical knowledge because we know what molecule we made. We

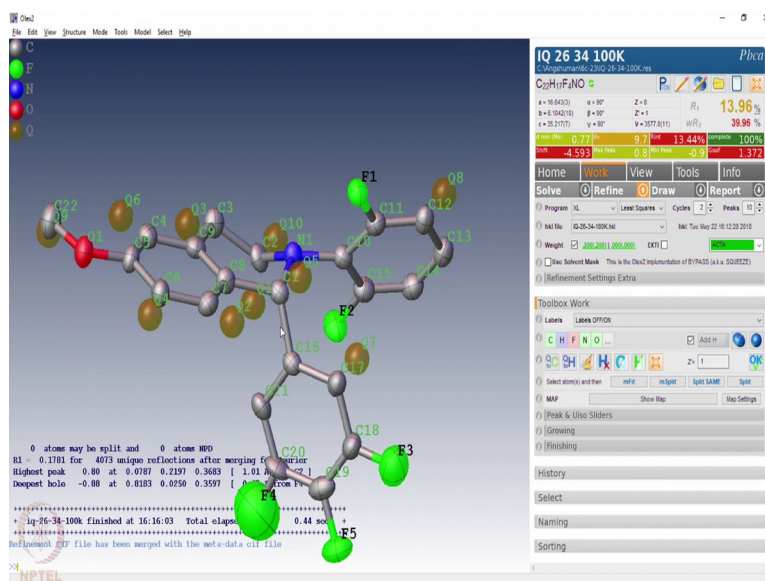
now know that there are two fluorine atoms, one here and one there; only these two should have been the fluorine atoms. But here also one large density is appearing and the software is thinking that it may be oxygen, but now since we know that there is no oxygen here. What can happen is this particular fluorine because of a rotation about this particular CC bond here, the when you rotate a CC bond there by 180 degree, this fluorine can appear here. So, we write that also as fluorine and carry out this structure refinement as usual.

(Refer Slide Time: 02:40)



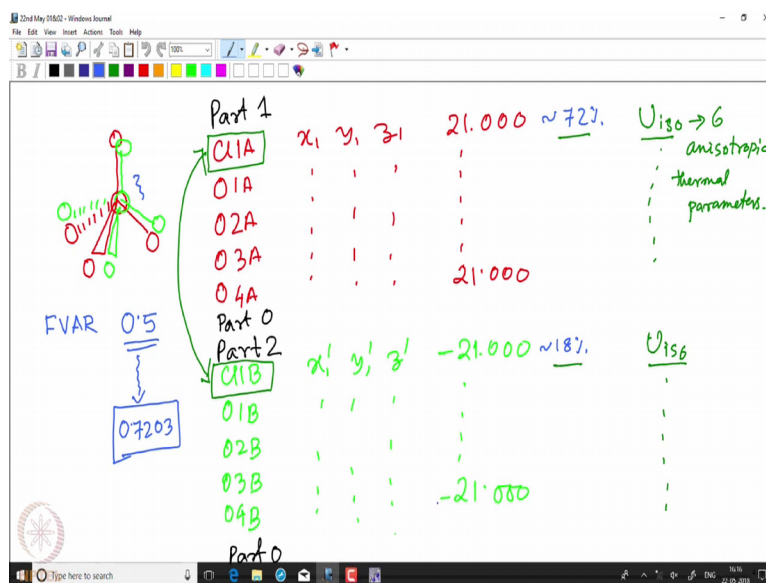
And try to reach a convergence on that. You see here what is happening is the thermal parameter of this fluorine and that fluorine are different compared to that. So, if we try to see the isotropic thermal parameters, this fluorine 3 has 0.05, fluorine 6 has 0.79 and fluorine T has this you see these are not numbered properly. So, better be number them appropriately. And if we put the labels on, then we know which is what.

(Refer Slide Time: 03:23)

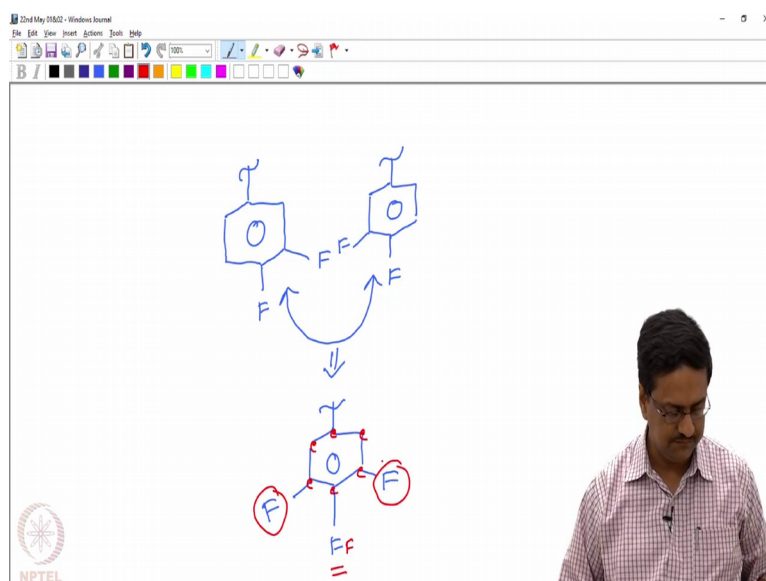


So, first thing first we should name the atoms. And refine it once again until it is easy if we try to see this thermal parameters which is higher, which is lower. So, the thermal parameter of 4 is much higher; 5 is probably the correct; 6 sorry 3 is also high this indicates that there is some disorder there. If we compare with other two fluorines on the other ring, we can see that the other two fluorines F 1 and F 2 have 0 3 and 0 4; the third fluorine on the second ring has 0 5 which is sort of ok. And 4 and 5 have higher thermal parameters. So, at the moment, we do nothing; at the moment we just try to continue the refinement as usual we do it with an isotropic refinement. And we recognise that these fluorines are disordered because they are now rotated by 180 degree.

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(Refer Slide Time: 05:02)



So, what is happening is in this particular case we have a phenyl ring with 2 fluorines at these two positions with respect to the attachment that is position 3 and 4. And this ring being rotated by 180 degree in two different locations, the fluorines are appearing on either side. The asymmetry unit represents an overall average of these two structures are these two confirmations like this. So, what we need to now understand that there are 6 carbon atoms in the ring which are falling at same place; and 1 fluorine atom which is falling at same place on rotation. So, these carbon atoms should be splitted, but then converted to $e x y z$ and $e a d p$, so that they fall on that at the same place along with the

fluorine and the other two fluorines will have two independent positions with different occupancies.

So, what we need to do is we need to split the atoms which are this at two different sites. So, we will split these carbons 16, 17, 18, 19, 20, 21 and fluorine as set of 2, and then select all these fragments along with the fluorines and rewrite the atom table.

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The screenshot displays the Olex2 software interface. The main window shows the atom table with columns for atom name, element, and coordinates. The table is divided into several parts (PART 0, PART 1, PART 2). The refinement statistics on the right show a weight of 200.2001, an R1 of 13.96%, and an R2 of 39.96%.

| Atom | Element | x | y | z | Occupancy |
|--------|---------|---------|---------|---------|-----------|
| FVAR | F | 0.20821 | 0.5 | | |
| PART 2 | | | | | |
| F5b | F | 0.73852 | 0.39470 | 0.41396 | -21.00000 |
| F3 | F | 0.63905 | 0.09592 | 0.44747 | 11.00000 |
| PART 0 | | | | | |
| F4 | F | 0.69419 | 0.62325 | 0.36496 | 11.00000 |
| PART 1 | | | | | |
| C16a | C | 0.51111 | 0.29744 | 0.37702 | 21.00000 |
| C17a | C | 0.53843 | 0.18492 | 0.40437 | 21.00000 |
| C18a | C | 0.61438 | 0.21908 | 0.41844 | 21.00000 |
| C19a | C | 0.66015 | 0.24304 | 0.40559 | 21.00000 |
| C20a | C | 0.63707 | 0.48115 | 0.37707 | 21.00000 |
| C21a | C | 0.56296 | 0.45895 | 0.36124 | 21.00000 |
| F5a | F | 0.73485 | 0.37379 | 0.42090 | 21.00000 |

So, this is part one which has 16 a to 21a F 1a. And along with F 1 a we should have the atom F 3 as well which is this one. So, you bring that F 3 here and write this a as 21 and make it isotropic. Similarly, this atom we make it bring it here is already isotropic F 4 goes to the other part, and we make it isotropic and make it minus 21. And here it is FVAR 0.5, FVAR variable this 0.5, which means these two fractions are 50-50 populated. So, we should conclude this with part 0 and this also with part 0. Let us define once, so now, we can see two separate parts.

(Refer Slide Time: 09:24)

```
File Edit Format View Help
IQ-26-34-100K - Notepad
C5 1 0.32827 -0.00129 0.00390 0.00304
0.03826 0.00004 0.00228 -0.00354
C6 1 0.428470 0.166268 0.257306 11.00000 0.03843 0.03591
0.03039 -0.00070 -0.00223 0.00160
C4 1 0.347966 0.452250 0.268851 11.00000 0.03479 0.03025
0.03320 -0.00092 0.00266 -0.00404
C15 1 0.404366 0.549588 0.450847 11.00000 0.03447 0.03270
0.03078 0.00070 0.00031 -0.00565
C3 1 0.322990 0.649292 0.331780 11.00000 0.04628 0.02532
0.03378 -0.00212 -0.00077 0.00270
C2 1 0.365350 0.656970 0.260004 11.00000 0.04245 0.02372
0.03221 0.00294 0.00670 -0.00027
C14 1 0.400213 0.524325 0.485487 11.00000 0.03448 0.03700
0.04020 -0.00033 -0.00204 0.00232
C12 1 0.320392 0.185166 0.479554 11.00000 0.04300 0.03263
0.03101 -0.00011 -0.00036 0.00000
C13 1 0.361363 0.343872 0.506610 11.00000 0.04417 0.04146
0.03330 -0.00249 -0.00530 0.00054
C22 1 0.330657 0.520912 0.187526 11.00000 0.06384 0.04480
0.04097 0.00771 -0.01073 0.00551
PART 1
C16A 1 0.509522 0.204372 0.376456 21.00000 0.01927
C17A 1 0.537321 0.182334 0.404627 21.00000 0.02955
C18A 1 0.614764 0.216488 0.418242 21.00000 0.03224
C19A 1 0.659911 0.342537 0.406132 21.00000 0.02735
C20A 1 0.637040 0.463734 0.376647 21.00000 0.03132
C21A 1 0.562186 0.450854 0.361352 21.00000 0.02659
F3A 3 0.734743 0.373580 0.420716 21.00000 0.04400
F3 3 0.638010 0.094730 0.447423 21.00000 0.04222
PART 2
F4 3 0.700212 0.401222 0.411103 -21.00000 0.03177
F16B 1 0.508421 0.325810 0.377081 -21.00000 0.02900
C17B 1 0.531246 0.155057 0.409854 -21.00000 0.03177
C18B 1 0.607166 0.170463 0.420212 -21.00000 0.03407
C19B 1 0.652420 0.300915 0.397027 -21.00000 0.03266
C20B 1 0.620900 0.493111 0.369020 -21.00000 0.03410
C21B 1 0.550582 0.462201 0.355343 -21.00000 0.02905
F4 3 0.680572 0.629176 0.361167 -21.00000 0.03007
PART 3
```

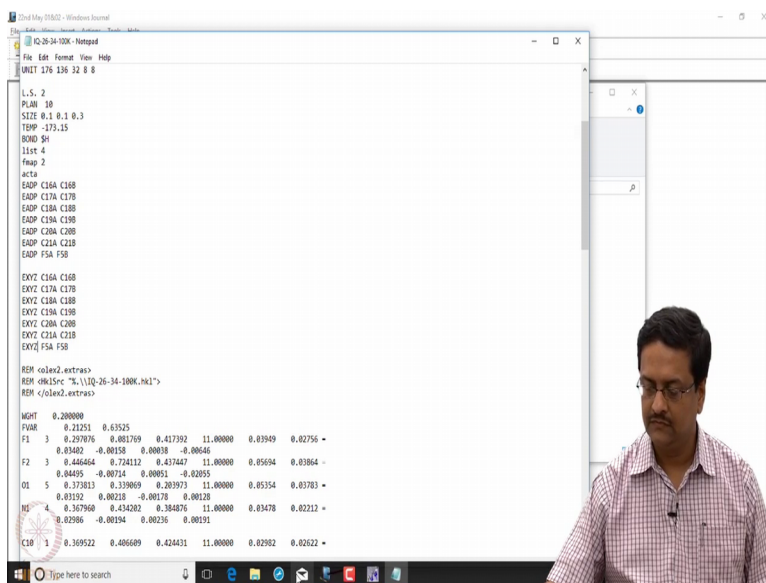
We try to modify this atom table. So, now, here we have arranged the two parts in the less file as part 1 and part 2. And you can see now all of them have isotropic thermal parameters and 16 AB 16 BC 16B, 17B to 21B is here and 16A to 21A is there. F 3 is one component which is only present in part 1. F 4 is a component which is only present in part 2, whereas all others are present in their same location

(Refer Slide Time: 10:01)

```
File Edit Format View Help
IQ-26-34-100K.res created by SHELXL-2014/7
TITL IQ-26-34-100K_a.res In Poca
REM O16 TITL IQ-26-34-100K In Poca #01
REM SHELXT solution In Poca
REM R1 0.105, Rweak 0.014, Alpha 0.010, Orientation as input
REM Formula found by SHELXT: C22 F2 H 04
CELL 0.71073 16.6432 6.1042 35.2168 90 90 90
ZERR 0 0.0029 0.001 0.0066 0 0 0
LATT 2
SWMR 0.5-X,-Y,0.5+Z
SWMR -X,0.5+Y,0.5-Z
SWMR 0.5+X,0.5-Y,-Z
SEAC C = F : H 0
UNIT 176 136 32 8 0
L.S. 2
PLAN 10
SIZE 0.1 0.1 0.3
TEMP -175.15
BOUND 0#
list 4
fnop 2
acta
EADP C16A C16B
EADP C17A C17B
EADP C18A C18B
EADP C19A C19B
EADP C20A C20B
EADP C21A C21B
EADP F3A F3B
REM colex2.extras
REM cmlsfc "k:\IQ-26-34-100K.hkl">
REM c:\olex2.extras
MIGHT 0.200000
PWRK 0.21251 0.63525
F4 3 0.27070 0.001769 0.417392 11.00000 0.03949 0.02756
0.03482 -0.00150 0.00038 -0.00646
F2 3 0.446464 0.724112 0.437447 11.00000 0.05604 0.03864
```

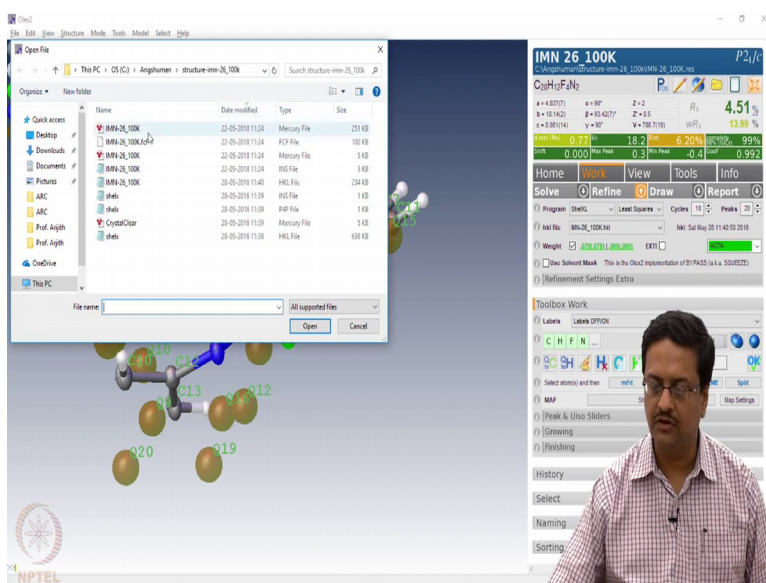
So, to incorporate that what we need here in this instructions that we should have a certain number of EADP and E XYZ comments. So, we should also right EADP C 16A is equal to C 16B. EADP C17A is equal to C17B, C18A equal to C 18B.

(Refer Slide Time: 11:20)



And simultaneously we should write the corresponding E XYZ for all of these set of atoms, group of atoms. So, copy and paste it here and change the ADP to XYZ and save this arias file and now we go back to our structure solution.

(Refer Slide Time: 12:05)



And select the arias file that we have just now modified. And then refine it a couple of times. What do we see now is that the atoms which are having near the EADP and EXYZ comments are having those symbols embedded in those atoms. And the atoms which are refine general they are not having any information of EADP or EXYZ. And at the moment these are all in an isotropic format. The top part of the molecule and the bottom part of the molecule has only isotropic thermal parameters.

So, to make everything anisotropic then we can click on the anisotropic option. So, now, it is defined anisotropically you can see the ones which were initially spheres has now become ellipsoids. The R factored has slightly fallen and now we should do this refinement a few cycle of tens each till it gets converged and the shift is coming down to green. If it is not coming, do not worry we just add hydrogens because that is not done here.

So, until and unless we add hydrogens, the structure is not complete. So, now, when we added hydrogens and we try to refine it a few more cycles you can see that the shift is coming close to 0. And R factor has come down to about 9 percent which is showing here. Now, look at the atom you can look at the part of the molecule here which is now disorder treated. We have part one which looks like that 0 and 2 which looks like this. So, all the parts if you show it looks like that which means this particular fluorine is on right hand side and has occupancy of 64 percent and this has occupancy of about 35 percent.

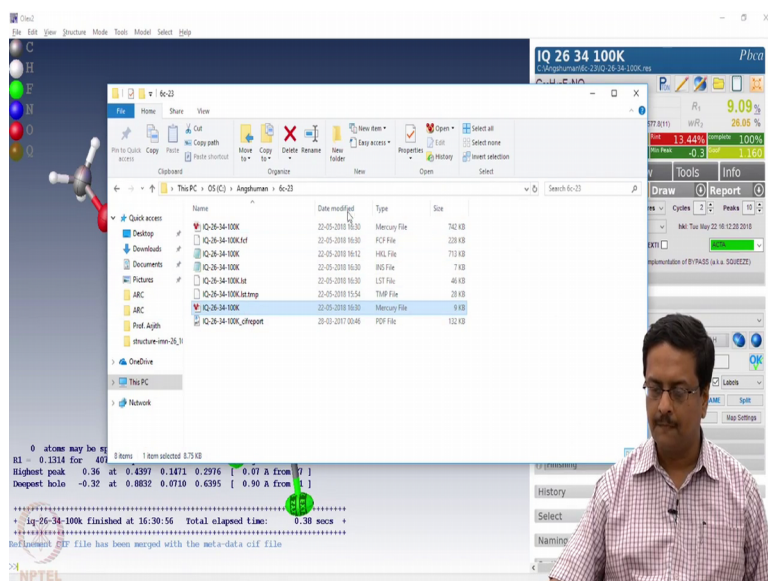
(Refer Slide Time: 14:51)

The screenshot displays the Olex2 software interface. A dialog box titled 'Info' is open, showing instructions for using EXYZ and EADP commands. The dialog text includes: 'REM please do not modify atom names inside the instructions - they will be updated', 'REM by Olex2 automatically, though you can change any parameters', and 'REM Also do not change the atoms order'. Below this, it lists EXYZ instructions for atoms C16A-C19B and F3A-F3B. The dialog also shows the FVAR value (0.21992) and the coordinates for PART 1 and PART 2. A 3D ball-and-stick model of the molecule is visible in the background, showing two disordered positions for the F3 atom. The main Olex2 window shows the title 'IQ 26 34 100K', the chemical formula 'C₉H₉FNO', and various refinement statistics including R1 (9.09%), wR2 (26.05%), and a list of peaks. A man is overlaid on the right side of the screenshot, appearing to be presenting the software.

If we just take those two atoms and try to see what we see is 0.64. So, 0.64 is for class 21 which is F 3; and the other one is minus 21, so that is 1 minus 0.64 is about 0.36. This is not reducing. So, we may try to see the bad reflections. Here we do not see much of bad reflections. So, we cannot do much here. And we should leave it with it and try to complete the refinement if at all to a very small shift.

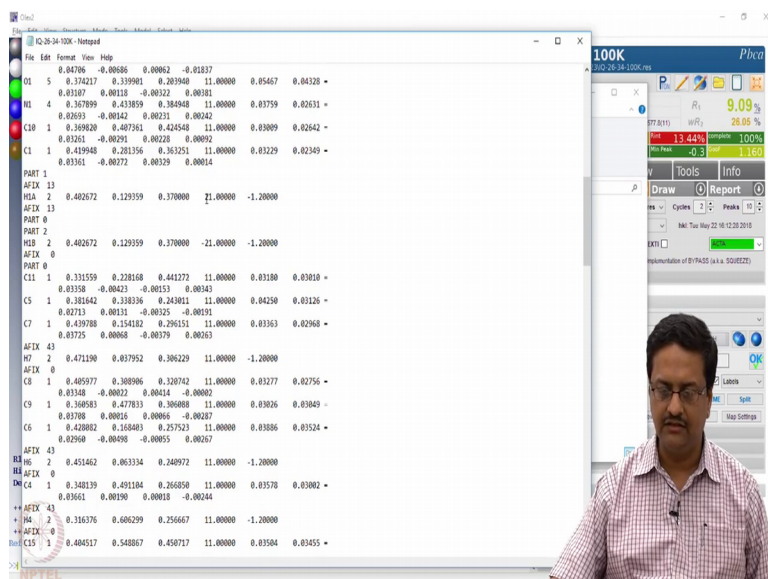
So, this is how one can do a disorder treatment using the EADP and EXYZ comments. See this is how the EADPs are written, this is how the EXYZs are written. And then we have two parts which are disordered.

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So, now, if I tried to open the res file which now will have the disordered sections.

(Refer Slide Time: 16:05)



Again got segregated, but now are with the corresponding hydrogens.

(Refer Slide Time: 16:15)

IQ-26-34-100K - Notepad

```
AFIX 0
C22 1 0.331475 0.528571 0.187786 11.00000 0.86235 0.04495 -
0.04069 0.00983 -0.00416 0.00183
AFIX 137
H2JA 2 0.338864 0.511562 0.168025 11.00000 -1.50000
H2JB 2 0.355999 0.458152 0.196214 11.00000 -1.50000
H2JC 2 0.275277 0.515742 0.156851 11.00000 -1.50000
AFIX 0
PART 1
C16A 1 0.587491 0.383760 0.375318 21.00000 0.83271 0.02483 -
0.83075 -0.00655 0.00287 -0.00168
C17A 1 0.535420 0.174072 0.404017 21.00000 0.83599 0.03790 -
0.02951 -0.00025 0.00095 -0.00009
AFIX 43
H2A 2 0.501634 0.064918 0.415530 21.00000 -1.20000
AFIX 0
C18A 1 0.612331 0.203452 0.418640 21.00000 0.83737 0.04018 -
0.33445 -0.00700 0.00309 -0.00027
C19A 1 0.640960 0.356930 0.403326 21.00000 0.82787 0.04937 -
0.85220 -0.01783 -0.00356 0.00236
C20A 1 0.635829 0.427043 0.373983 21.00000 0.83528 0.03615 -
0.85370 -0.00605 0.00755 -0.00727
AFIX 43
H2BA 2 0.649610 0.595207 0.363537 21.00000 -1.20000
AFIX 0
C21A 1 0.558080 0.459633 0.359690 21.00000 0.83318 0.03230 -
0.83554 0.00163 0.00086 0.00055
AFIX 43
H2IA 2 0.548046 0.547833 0.339164 21.00000 -1.20000
AFIX 0
F3A 3 0.737119 0.384204 0.417202 21.00000 0.83886 0.06166 -
0.87719 -0.01381 -0.01336 -0.00155
F3B 3 0.639580 0.895170 0.447785 21.00000 0.84513 0.05460 -
0.83887 0.00739 -0.00427 0.01222
PART 0
PART 2
H2FA 2 0.737119 0.384204 0.417202 21.00000 0.83886 0.06166 -
0.87719 -0.01381 -0.01336 -0.00155
H2FB 2 0.587491 0.383760 0.375318 21.00000 0.83271 0.02483 -
0.83075 -0.00655 0.00287 -0.00168
C17B 1 0.535420 0.174072 0.404017 21.00000 0.83599 0.03790 -
0.02951 -0.00025 0.00095 -0.00009
```

And you can see this 21 and minus 21, they have the anisotropic thermal parameters also associated with it and this structure is complete.

(Refer Slide Time: 16:25)

IQ-26-34-100K - Notepad

```
H18B 2 0.631189 0.115266 0.439019 -21.00000 -1.20000
AFIX 0
C18B 1 0.640960 0.356930 0.403326 21.00000 0.82787 0.04937 -
0.85220 -0.01783 -0.00356 0.00236
C19B 1 0.635829 0.427043 0.373983 21.00000 0.83528 0.03615 -
0.85370 -0.00605 0.00755 -0.00727
C21B 1 0.558080 0.459633 0.359690 21.00000 0.83318 0.03230 -
0.83554 0.00163 0.00086 0.00055
AFIX 43
H2IB 2 0.548046 0.547833 0.339164 21.00000 -1.20000
AFIX 0
F4 3 0.687624 0.632831 0.365176 21.00000 0.84044 0.05214 -
0.85167 -0.00049 0.00422 -0.01616
H2LF 4
REM IQ-26-34-100K_a.res In PbcA
REM R1 = 0.0089 for 2671 Fo > 4|sig(Fo)| and 0.1315 for all 4073 data
REM 264 parameters refined using 0 restraints
END
WGHT 0.1279 0.0000
REM Highest difference peak 0.358, deepest hole -0.322, 1-sigma level 0.075
O1 1 0.3653 0.1493 0.4230 11.00000 0.85 0.23
O2 1 0.2614 0.0881 0.3993 11.00000 0.85 0.26
O3 1 0.5222 0.1980 0.4437 11.00000 0.85 0.26
O4 1 0.3956 0.0880 0.3189 11.00000 0.85 0.26
O5 1 0.4658 0.3140 0.3690 11.00000 0.85 0.26
O6 1 0.5574 0.1448 0.3094 11.00000 0.85 0.26
O7 1 0.4613 0.0000 0.2360 11.00000 0.85 0.23
O8 1 0.7219 0.4919 0.3556 11.00000 0.85 0.23
O9 1 0.7728 0.5426 0.4189 11.00000 0.85 0.23
O10 1 0.5197 0.8168 0.3994 11.00000 0.85 0.23
RE
REM The information below was added by Olex2.
END
REM
REM R1 = 0.0089 for 2671 Fo > 4|sig(Fo)| and 0.1315 for all 24325 data
REM n/a parameters refined using n/a restraints
REM Highest difference peak 0.36, deepest hole -0.32
REM Mean Shift 0.002, Max Shift -0.024.
```

The residual electron dense it is that are coming here are extremely small, these are all very small values for a slight atom structure. And hence we do not need to do anything further this indicates the structure is fully solved and refines the well and we have the all factor of about 9 percent.

So, with this we conclude this section of our discussion on structure solution and refinement using a standard data using different crystals data sets which we have learned now. We have done data analysis using the Rigaku and Bruker software, those who are users of these packages if you have any doubt or query you can write back to me, I can help you out in solving those structures. And if you have any problem in using Olex 2 or Shell x or any such things you are free to write to me, we can discuss all these over emails.

So, with this we conclude this section of our discussion, I mean the next lecture we will now move to another part where we would discuss about the Cambridge structural database which is very useful tool for all of us in doing this search on X-ray crystallography data which we is already reported in literature, how to do the databases, how to do the analysis using database these are all parts of our day to day life due in extra crystallography laboratory. So, those who are interested in joining X-ray diffraction laboratory in future will, they should have a knowledge of usage of Cambridge structural database.