Symmetry and Structure in the Solid State
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Lecture – 61
Intermolecular Interactions

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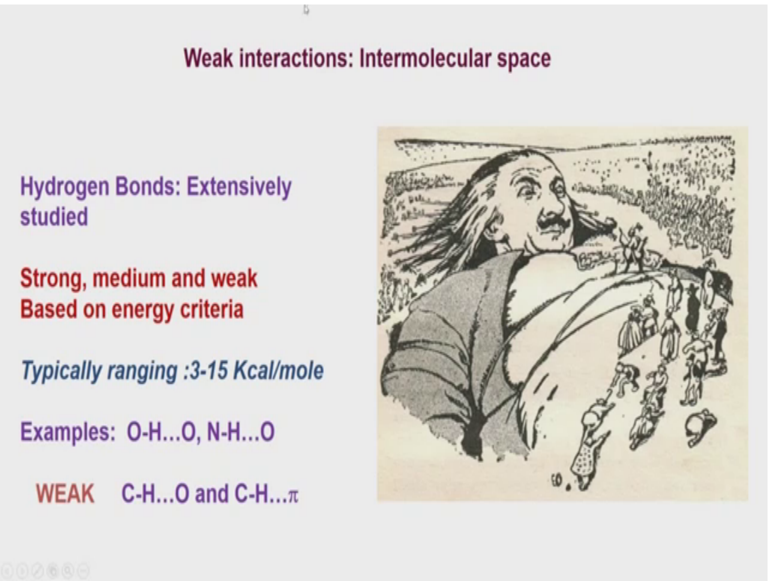

Weak interactions: Intermolecular space

Hydrogen Bonds: Extensively studied

Strong, medium and weak
Based on energy criteria

Typically ranging :3-15 Kcal/mole

Examples: O-H...O, N-H...O

WEAK C-H...O and C-H...π

Of course you all know the story of Gulliver right and this fellow was a big man compared to the small Lilliput fellows who are all here and what happened is when his boat crashed and he landed on the beach. When he really came to his senses he found that he cannot get up, he could not get up because he has been tired with so many of these his hair was tied and tied it up here so that he so many contacts were made and these people tied it up in such a way that he cannot get up.

That means, what happens to a molecule in a crystal is this is exactly what it what happens because of the crystal forces the interactions that are involved between molecules and so on the weak bonding which are essentially the way in which they are tied is hair here. For example, these are now the strong medium and weak interactions and weak interactions essentially occupy the intermolecular space.

So, since we are talking about the modeling that we can do for the molecule as a whole now in terms of multiple refinements as well as the Hirschfield atom surfaces, it should be possible therefore to look into or take a peep into the intermolecular space. If we look into the intermolecular space we will be left with a certain amount of electron density and this electron density is crucial to keep the molecule in it is position which is defined by our loss which we have formed in this course the symmetry and also keep it in that particular space group.

So, the way in which this is tied up; this fellow is tied up can be modified and you may have a different way of tying up molecules with using different interactions then the crystal structure will change and so you can get polymorphic modifications. So, essentially the weak and strong interactions, therefore based on energy criteria can actually be analyzed if we do the charge density analysis.

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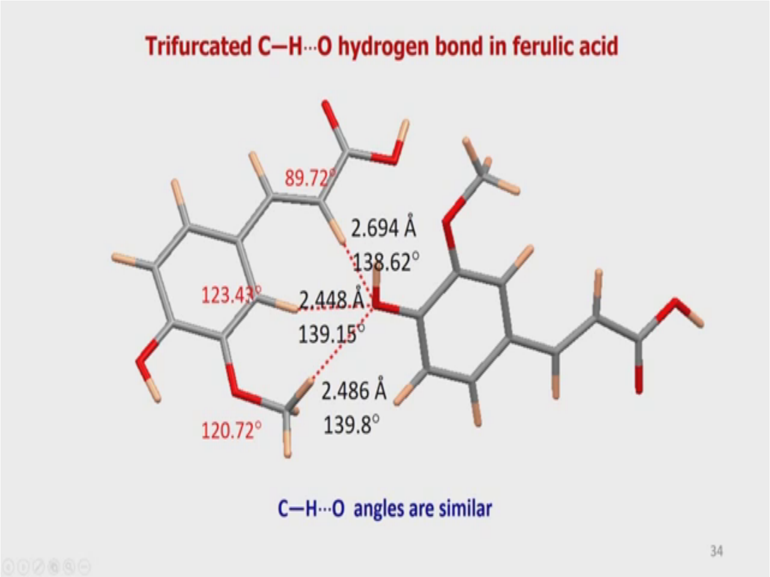

Trifurcated C—H···O hydrogen bond in ferulic acid

C—H···O angles are similar

Here is an example, a very quick example now we go through quick examples because of lack of time, we will we have to wind the wind the course and a and then I taught will stress essentially on some weak interactions which look very very critical and crucial for understanding the weak interactions and their importance.

So, here is the structure of ferulic acid it was solved long long ago and it has very strong hydrogen bonds, we are not worried about the strong hydrogen bonds because they arrest the molecules in their positions corresponding to the unit cell requirements and also the symmetry requirements. But in addition to the fact that they are located interacting this way we find some additional interactions which are essentially of the type C-H O, there is a lot of initial discussion about whether C-H O can be a hydrogen bond or not, because the polarization that is associated with the carbon atom is minimum.

So, if I said C-H O interactions exist at all was a question and if it does exist does it follow the hydrogen bonding features like directionalities, because a very strong hydrogen bond will have this angle 180 degrees and this particular angle let me show that correctly. The angle CH O will be 180 degree for a very very strong hydrogen bond and normally such bonds do exist in crystal structures where we have for example, carboxylic acid diamonds, carboxylic acid diamonds ensure very strong hydrogen bonds.

So, whether CH O will have such an interaction was discussed and finally with a lot of arguments involving crystal engineering principles it was arrived at that CH O can be called a hydrogen bond. Now our interest is that can the CH O would really hold the molecules together and what is the energy that is associated with it, if we can analyze that in terms of the charge density analysis. So, we have looked into this region there are 3 possible CH O hydrogen bonds, the lengths and the angles are given here and we wanted to see the distribution of electron density in this.

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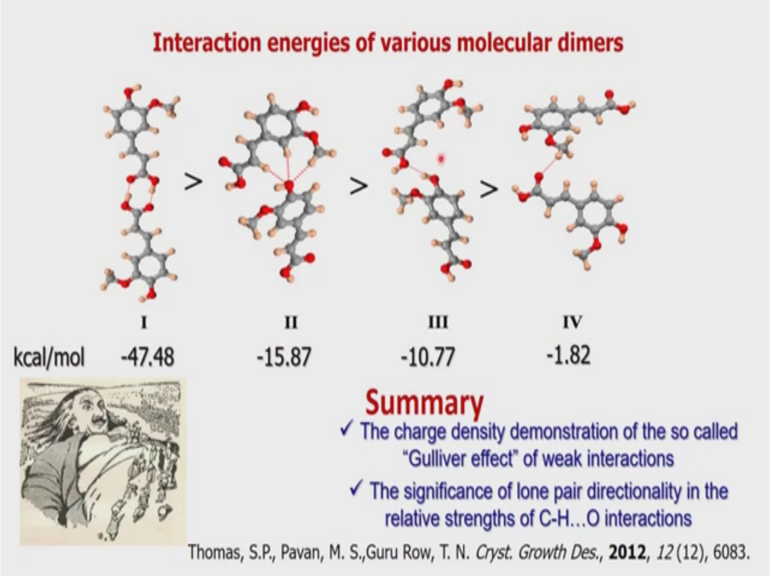

Interaction energies of various molecular dimers

	I	II	III	IV
kcal/mol	-47.48	-15.87	-10.77	-1.82

Summary

- ✓ The charge density demonstration of the so called "Gulliver effect" of weak interactions
- ✓ The significance of lone pair directionality in the relative strengths of C-H...O interactions

Thomas, S.P., Pavan, M. S.,Guru Row, T. N. *Cryst. Growth Des.*, **2012**, *12* (12), 6083.

When we analyze the distribution of electron density in this as I told that Ferulic acid is held by a very strong carboxylic hydrogen bond, this decides the orientation of the molecules in the crystal essentially this is at the center of symmetry of the crystal. So, we have this very strong hydrogen bonds and the strength of it is minus 47.48 kilocalories per mole, this calculation has been done based on charge density analysis I am not going into the detail of it but essentially we will see it is a very very strong bond, the larger is the negative it is stronger it is.

Then in addition to that there is a between the 2 molecules there is a strong reasonably strong OHO hydrogen bond and then of course there is a simple CH O bond with the methyl group. So, we have calculated the energies for all these this work was done by again Thomas in our group along with power these two gentlemen graduated of out of my group recently.

See the you see that when you consider the energy that is associated with this trifurcated CH O bond there are 3 bonds do you know this is the Gulliver idea, see if the lipids can tie him down with many many such small interactions this is exactly what it does. So, these 2 molecules are now tied down with this very weak interactions they are weak individually, but collectively they generate an energy which is minus 15.87 much much higher than the energy that is involved in a typical OHO bond.

So, one would think that a typical OHO bond would be stronger when in fact it is stronger than C-H O, but the case that these 3 together the handshake between these 3 essentially holding it together will is the so called Gulliver effect of weak interaction. So, we call this as the Gulliver effect of weak interactions and this is how we could analyze the lone pair directionality is in the relative strengths of C-H O interactions.

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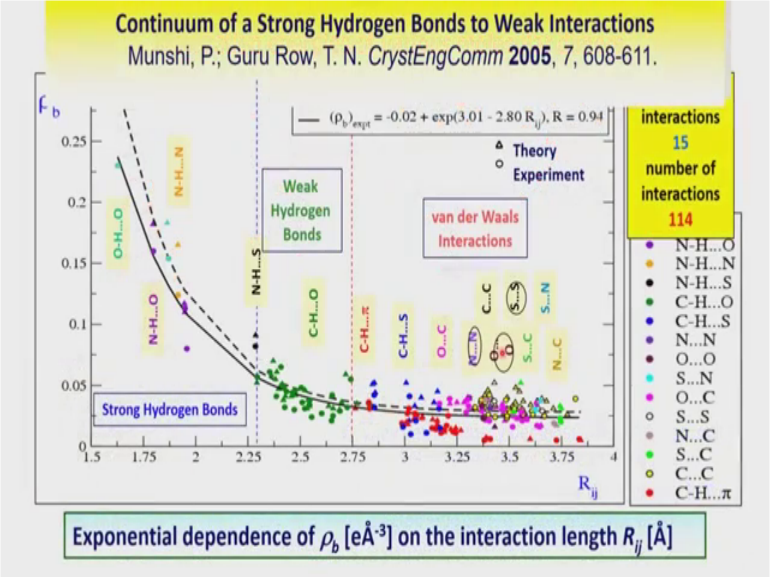

Continuum of a Strong Hydrogen Bonds to Weak Interactions

Munshi, P.; Guru Row, T. N. *CrystEngComm* **2005**, 7, 608-611.

Exponential dependence of ρ_b [eÅ^{-3}] on the interaction length R_{ij} [Å]

So, this is one example where charge density analysis can be done. In fact, at this stage we also did a little earlier on in fact, one of my students Moochie he analyzed the all possible hydrogen bonds and also all possible bonds which are in the Van der Waal interaction region, that means hardly any interactions between them and he calculated the electron density from the available data in literature and we had a very reasonably large number of such available interactions.

So, we find that we have interactions like for example N-H O, OHO and N-H O these are representing strong hydrogen bonds. So, we found that there is a universal curve between the way in which electron density occurs and this R ij now is the region between one atom center and another atom center it is not the straight line which is joining the bond, but this is known as the bond path. This is the path the electron density will take, so if the epsilon value is larger the path will be bent, if the epsilon value is very very small the path will be straight.

So, depending upon the value of the ellipticity associated with the bond we find that R ij value can be determined. So, this is a universal curve where you see that the interactions are involved in these for example, I will discuss a little bit on sulphur sulphur in a minute. But these kind of interactions also have an electron density this is the electron density plot electron density value, so they do have some electron density and they all cluster around this region.

So, much that we can now actually think of drawing a line at 2.75 angstroms for R ij which we would like to call as a limit of a hydrogen bond, so anything beyond this is not a hydrogen bond and anything before this is a hydrogen bond and it could be classified into weak and strong hydrogen bonds and this. In fact, you see the very strong hydrogen bonds go up to a distance of one point this is in oxalic acid dihydrate the hydrogen bond is the strongest.

It also tells us one other feature that is if you now keep it is this is going asymptotically towards the infinity that means it is going parallel to more or less parallel to the electron density vector. But as we keep going higher and higher, if we go through the end of this one and go further we will get the other types of normal bonds we will get the covalent bond the ionic bonds and so on.

So, any bonding therefore, in general has this continuum, so that means when 2 atoms come closer they come closer to the Van der Waals interaction region, they are happy to stay there, if they are happy to stay there they will be in this region. If there is a weak interaction it will stay in this region and if there is a strong interaction they will stay in that region and the even stronger like covalent bonds, ionic bonds and so on they go through on to the other side of this projection they will go into the room away from me.

But they will all follow this curve which is a universal curve, so we call it as the continuum of strong hydrogen bonds to weak interactions. With this we could also define the radius of the hydrogen bond I do not think I have time to go into those details.

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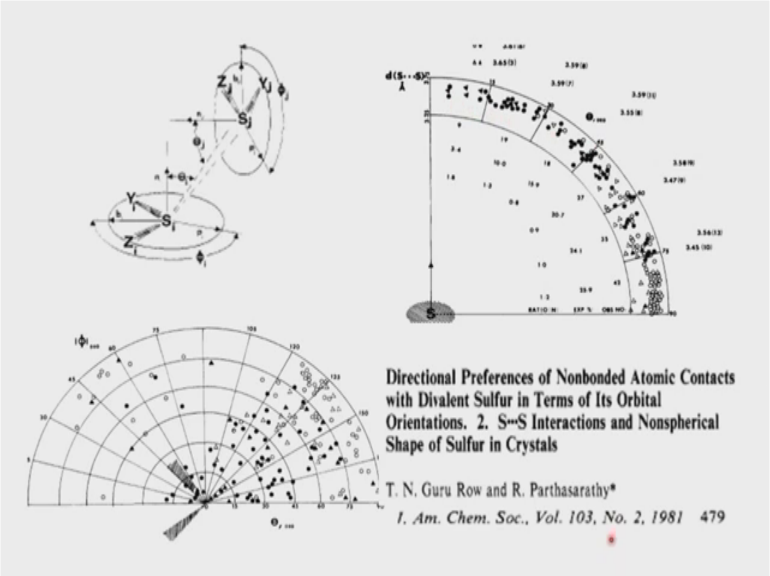

Directional Preferences of Nonbonded Atomic Contacts with Divalent Sulfur in Terms of Its Orbital Orientations. 2. S···S Interactions and Nonspherical Shape of Sulfur in Crystals

T. N. Guru Row and R. Parthasarathy*

J. Am. Chem. Soc., Vol. 103, No. 2, 1981 479

Except to go to the next one where I talked about Sulphur Sulphur bond, this is something which by chance was done by me in 1981. So, what I will do in the next 15 20 minutes having made you sit through this entire course over the last so many days I think I will highlight the work which has been done in our group on charge densities.

This is something of a propaganda for our group as well as something which has been done in India for the first time and also there are not many groups in India who are doing this kind of work. And this is the some kind of a basis for the futuristic outlook of quantum crystallography. So, I thought I will generally discuss the work which has come out from our group and probably it will take another 10 minutes at the most.

So, what I will do is here is what is done here is the we have looked into all crystal structures you have seen this is 1981 there were not too many structures, but whatever structures were available in the Cambridge structural database. We looked at that and found elected it and found out that shorter distances between sulphur and sulphur. So, there is there are molecules which have sulphur atoms on them and these sulphur now come due to the crystallography interactions the symmetry and so on, they come closer.

But when they come closer what kind of interaction develops between them? This is purely Van der Waal in nature, but does it give any indication of what is the nature of sulphur atom. Say I mentioned a couple of days ago about a couple of day classes ago the importance of this year which is the year of periodic table. So, sulphur is a very crucial element in the periodic table, now we assume that the radius of sulphur is so much.

But it shows in this particular way of analyzing, we see that the radius of sulphur is no longer spherical it has got a non spherical shape, the reason is that whenever there is an atom which is approaching in this direction which is in fact a nucleophile approaching sulphur. If the other sulphur is a part of a molecule which makes it look like a nucleophile, so the approach of the nucleophile to this sulphur atom is concentrated in the open circles. And the concentration of the closed circles will tell us that it is approaching from a direction which is about 20 degrees to the normal, this is the approach of the electrophiles and this is the approach of the nucleophiles.

So, effectively when you take at sulfur atom it is not a hard sphere sulfur atom is now ready to accept electrons and give out electrons as well and so now like it is more likely you know you put a you have a pomegranate and you put a hole through the pomegranate.

So, pomegranate hole and you press the pomegranate it compresses in that direction ok, when it compresses in the direction the overall shape of pomegranate is going to change and that is what happens to every atom, not just the sulfur atom and therefore there are interaction regions which develop. And these interaction regions have been theoretically calculated and those interaction regions are the so called sigma holes and pi pi holes.

We do not have time to go into the detail of it, but those can be characterized from the quantum mechanical calculations as well as from charge density measurements of very highly accurate datasets. At this particular time there were not many accurate data sets available, but we could predict that the sulfur into sulfur interactions will generate non spherical shape of sulfur in crystals, this is something which is just out of the hat kind of explanation in those days, but then this defined they so called bonding in groups all groups of atoms of 14 to 17.

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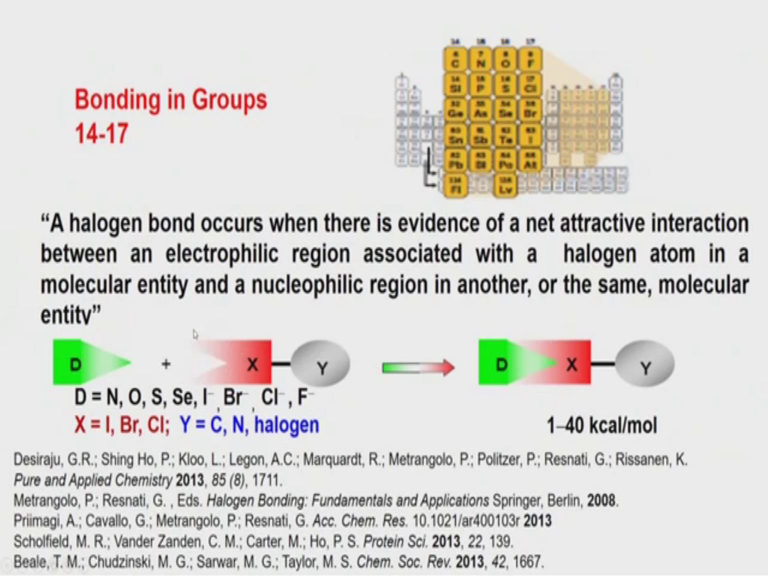

Bonding in Groups 14-17

"A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entitv"

D = N, O, S, Se, I^-, Br^-, Cl^-, F^-

X = I, Br, Cl; Y = C, N, halogen

1–40 kcal/mol

Desiraju, G.R.; Shing Ho, P.; Kloo, L.; Legon, A.C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. *Pure and Applied Chemistry* **2013**, *85 (8)*, 1711.
Metrangolo, P.; Resnati, G. , Eds. *Halogen Bonding: Fundamentals and Applications* Springer, Berlin, **2008**.
Priimagi, A.; Cavallo, G.; Metrangolo, P.; Resnati, G. *Acc. Chem. Res.* 10.1021/ar400103r **2013**
Scholfield, M. R.; Vander Zanden, C. M.; Carter, M.; Ho, P. S. *Protein Sci.* **2013**, *22*, 139.
Beale, T. M.; Chudzinski, M. G.; Sarwar, M. G.; Taylor, M. S. *Chem. Soc. Rev.* **2013**, *42*, 1667.

So, they add the groups 14 to 17 are shown here we have therefore, the carbon atom, we have the nitrogen atom, we have the oxygen atom and the fluorine. This now belongs to the halogen group. This belongs to the sulfur group that is the chalcogen group this belongs to the pnictogen group and this belongs to the carbon group. So, the all these atoms now will have therefore a behavior which is like what we described in case of the sulfur. So, the non spherical shape is associated it with every one of these elements in the periodic table and therefore they can have these kind of directed interactions and these directed interactions come as a consequence of what we have defined here.

For example, a halogen bond it is the definition which has been accepted by all these crystal engineering community as well as charge density community, that is the definition, a halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity. And a nucleophilic region in another or the same molecular entity I think this part is cut I will just try to see.

So, you see this is the definition, halogen bond of I moved this one away specifically it is it happens when you give let us make it smaller right. So, yeah this is the definition a halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with the halogen bond.

So, we are now concentrating on halogen bonds and this diagram clearly shows you that there is a donor and then there is an acceptor donor can be any of these atoms acceptors or halogens and the value of the Y atom could be again carbon, nitrogen, halogen so it could be anything. So, the halogen bonding occurs between these which is now shown as a something which is ready to open mouth and a gulp this part and then this association takes place.

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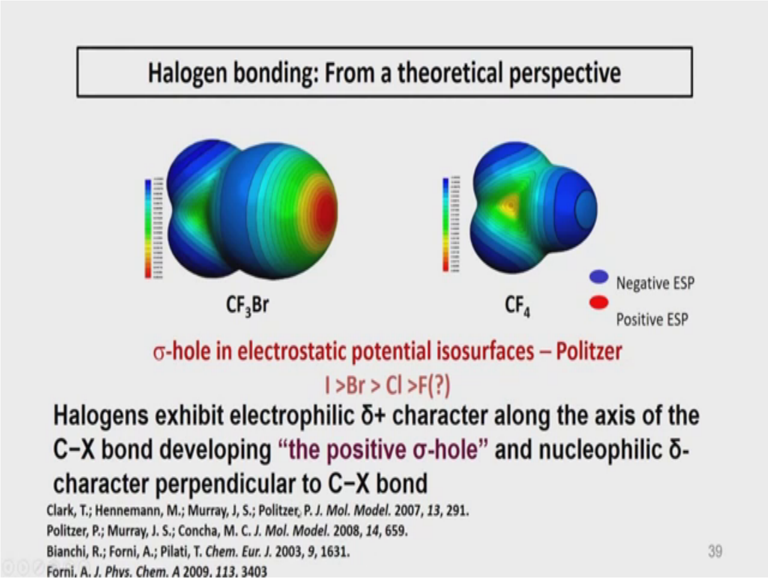

Halogen bonding: From a theoretical perspective

σ-hole in electrostatic potential isosurfaces – Politzer

I >Br > Cl >F(?)

Halogens exhibit electrophilic δ+ character along the axis of the C–X bond developing "the positive σ-hole" and nucleophilic δ- character perpendicular to C–X bond

Clark, T.; Hennemann, M.; Murray, J, S.; Politzer, P. *J. Mol. Model.* 2007, *13*, 291.
Politzer, P.; Murray, J. S.; Concha, M. C. *J. Mol. Model.* 2008, *14*, 659.
Bianchi, R.; Forni, A.; Pilati, T. *Chem. Eur. J.* 2003, *9*, 1631.
Forni, A. *J. Phys. Chem. A* 2009, *113*, 3403

And this was further characterized theoretically by remarkable work of Politzer who actually found out these kind of regions where now bromine in a CF 3 Br situation is now exhibiting what is known as a sigma hole. And this sigma hole is something which now tells us that this bromine is ready to have this sigma hole behavior and ready to accept interactions. So, the interactions will develop in that region so they become a highly directional, so halogen bonding is highly directional, chalcogen bonding is highly directional. In fact, we have also demonstrated the pnictogen bonding involving nitrogen is also a highly directional interaction. All these carry this issue of a sigma hole and things like that.

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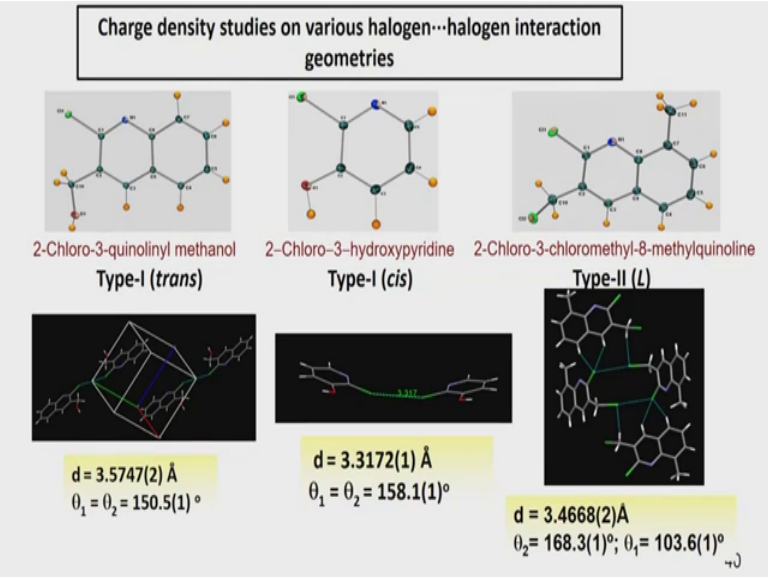

Charge density studies on various halogen···halogen interaction geometries

2-Chloro-3-quinolinyl methanol
Type-I (*trans*)

2-Chloro-3-hydroxypyridine
Type-I (*cis*)

2-Chloro-3-chloromethyl-8-methylquinoline
Type-II (*L*)

d = 3.5747(2) Å
$\theta_1 = \theta_2 = 150.5(1)°$

d = 3.3172(1) Å
$\theta_1 = \theta_2 = 158.1(1)°$

d = 3.4668(2)Å
$\theta_2 = 168.3(1)°$; $\theta_1 = 103.6(1)°$

This was extended in the case of halogen bonding.

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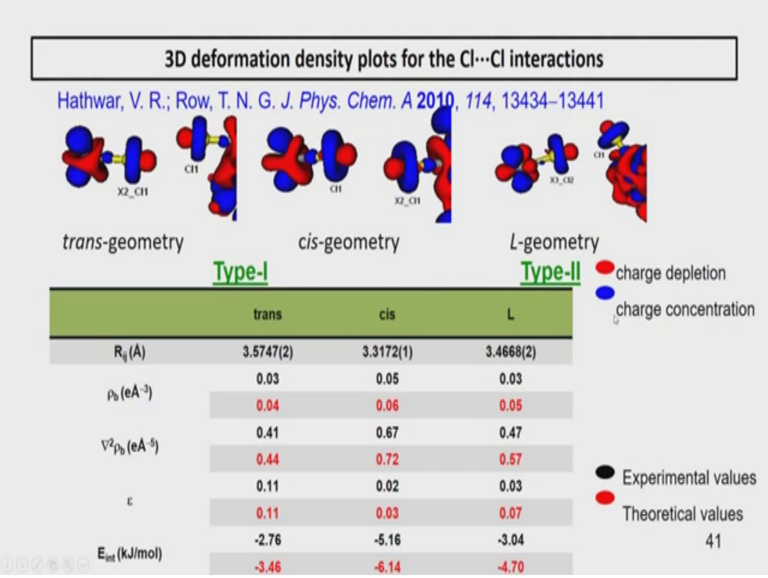

3D deformation density plots for the Cl···Cl interactions

Hathwar, V. R.; Row, T. N. G. *J. Phys. Chem. A* **2010**, *114*, 13434–13441

trans-geometry

cis-geometry

L-geometry

Type-I

Type-II

● charge depletion
● charge concentration

	trans	cis	L
R_{ij} (Å)	3.5747(2)	3.3172(1)	3.4668(2)
ρ_b (eÅ^{-3})	0.03	0.05	0.03
	0.04	0.06	0.05
$\nabla^2\rho_b$ (eÅ^{-5})	0.41	0.67	0.47
	0.44	0.72	0.57
ε	0.11	0.02	0.03
	0.11	0.03	0.07
E_{int} (kJ/mol)	-2.76	-5.16	-3.04
	-3.46	-6.14	-4.70

● Experimental values
● Theoretical values

This was the work of Venkatesha who did this work and calculated the energies that are involved and showed that in different kinds of geometrical situations we can show that sigma hole.

This by the way these are not orbital’s as one they look like, but they are not orbital’s these are 3D deformation density maps. So in fact, one cannot see the electron insane one cannot see the orbital’s because orbital is a quantum mechanical phenomena. So, at one time people thought that they are looking at orbital's, but they are not realistically orbital's there are orbital their deformation density has 3 dimensional deformation density map. So, you can see that there is a sigma hole here which is now facing the electron dense annulus region which is blue. So, the red blue portion interacts with the blue portion and that is how you get an interaction between Cl 1 and Cl 2 in this particular case.

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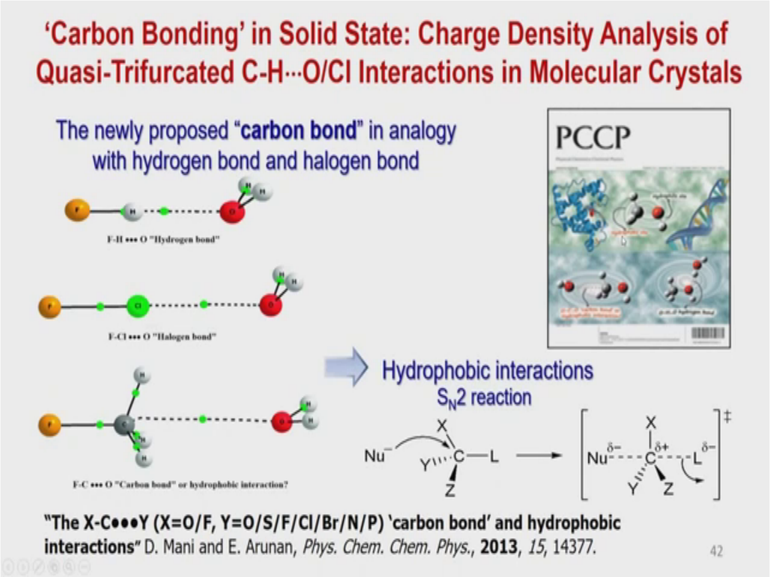

'Carbon Bonding' in Solid State: Charge Density Analysis of Quasi-Trifurcated C-H···O/Cl Interactions in Molecular Crystals

The newly proposed "**carbon bond**" in analogy with hydrogen bond and halogen bond

Hydrophobic interactions
S_N2 reaction

"The X-C•••Y (X=O/F, Y=O/S/F/Cl/Br/N/P) 'carbon bond' and hydrophobic interactions" D. Mani and E. Arunan, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 14377.

So, there are other examples which have been worked out as far as then came the realistic understanding of this sigma hole. And then the bonding features when the work is purely from IASC this theoretical prediction was made by Professor Arunan of IPC in organic physical chemistry department. See there is always this hydrophobic interactions which occur and how do they occur because, we already have a tetrahedrally satisfied 4 bonds with carbon. So that means it is a very stable atom still the nucleophile can attack on this one and we can form this so called SN 2 reactions.

So, the basis of incentive reactions tells us that we can have interactions where we can have a whole of the carbon exposed for possible interaction profile. So, what was predicted by Arunan was the fact that he proposed what is known as a carbon bond, it is an analogy with hydrogen bond, an halogen bond and he said that for example, in these 3 cases which were theoretically calculated, they theoretically found find the presence of finds, the presence of the critical point which is shown as a green dot here.

So, the green dots are critical points and if since you find a critical point by definition we gave it defines a bond. And therefore there is a shortage interaction in this particular case it is a FH O hydrogen bond in this case it is a F Cl O halogen bond and in this particular case you have a carbon and you see that the oxygen atom now has a bond path which is shown like that.

So, it is not going to be an interaction associated with these hydrogen atoms and then coming in which would be a CH O bond it is essentially a direct interaction, that means the carbon atom now has opened out its a sigma hole and this interaction is now accepted and that is the reason why you get a fifth bond with carbon. Because there are already 4 bonds the fifth bond with carbon now becomes reactive and so you proceed with the reaction.

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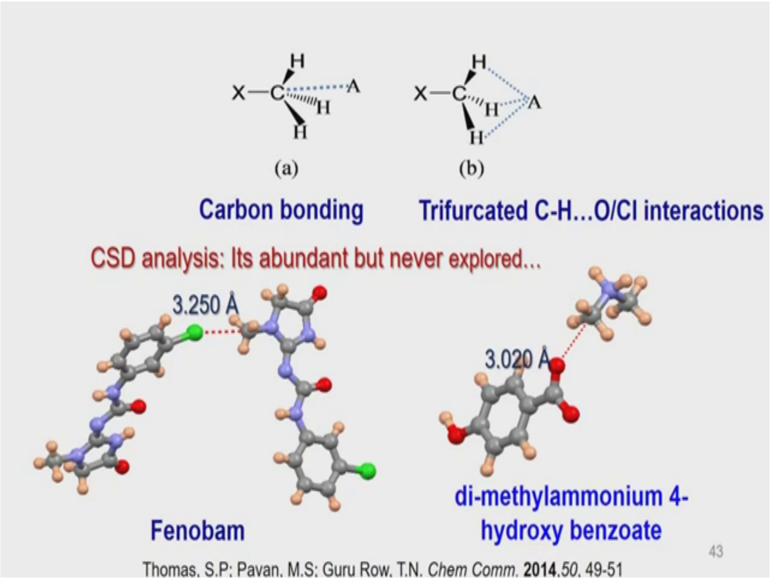

(a) Carbon bonding

(b) Trifurcated C-H...O/Cl interactions

CSD analysis: Its abundant but never explored...

Fenobam

di-methylammonium 4-hydroxy benzoate

Thomas, S.P; Pavan, M.S; Guru Row, T.N. *Chem Comm.* **2014**,*50*, 49-51

So, this was the prediction which was made and then we wanted to verify it experimentally. So, we made 2 compounds, 1 compound which was we had already studied at this short interaction between chlorine and carbon which is 3.25 and there was another case which we designed so that we have this carbon oxygen distance of 3.02 this again is the work of Thomas and S. P: Pavan. So, there are 2 possibilities, one possibility is the definition of carbon bonding which is given by Arunan, the other possibility is the trifurcated hydrogen bond C-H O right. So, A is being the acceptor atom in this particular one case it is chlorine, the other case it is oxygen; agreed.

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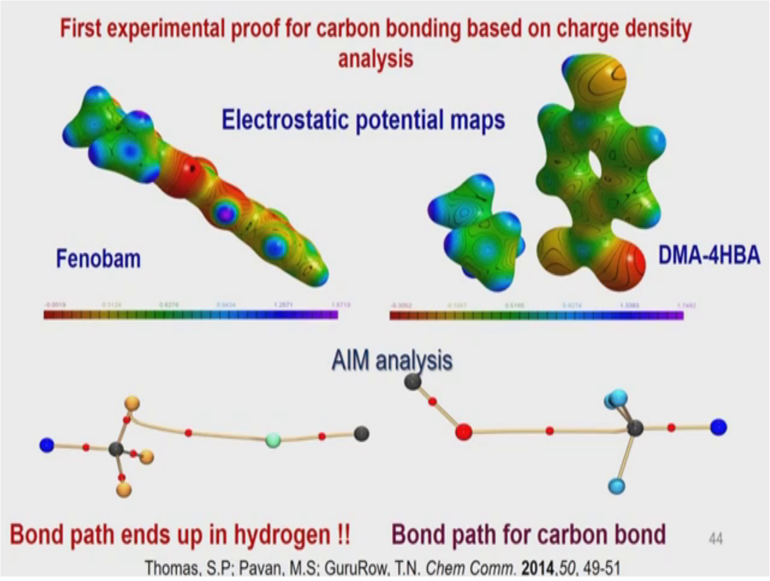

First experimental proof for carbon bonding based on charge density analysis

Electrostatic potential maps

Fenobam

DMA-4HBA

AIM analysis

Bond path ends up in hydrogen !!

Bond path for carbon bond

Thomas, S.P; Pavan, M.S; GuruRow, T.N. *Chem Comm.* **2014**,*50*, 49-51

So, what we did was to do the charge density analysis and plot the deformation densities. What is found is that in the case of the first compound which is Fenobam we find that it is actually going to the hydrogen atom, the bond path when we calculate the critical point is up here and the bond path goes to the hydrogen atom nothing exciting. So, this is essentially a C-H O on the other hand in this compound DMA 4 HBA we see that this now goes to the carbon atom directly, avoiding the 3 hydrogen atoms which are readily looking for it. You know it is like in cricket there are 3 slips on the galley and somebody pushes the ball between the 2 slips.

So, which one is, which fellow is going to catch it and of course, nowadays Indian team has improved their performance otherwise what will happen is if the ball goes between the second slip and the third slip both of them dive on each other and the balls escapes. But it may so happen that one of them make a slip on it.

So, in this particular case this fellow caught the ball which is nothing exciting which is a allowed interaction, but this is an interaction which we were looking for. So, effectively if you see this carbon now it has 1 2 3 4 and 5 bonds and therefore it is an intermediate to a possible reaction site.

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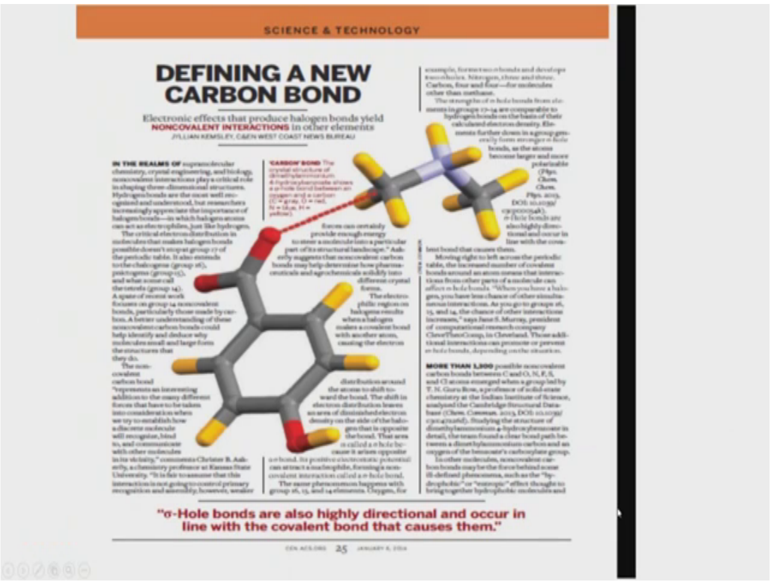

SCIENCE & TECHNOLOGY

DEFINING A NEW CARBON BOND

Electronic effects that produce halogen bonds yield **NONCOVALENT INTERACTIONS** in other elements

JYLLIAN KEMSLEY, C&EN WEST COAST NEWS BUREAU

"σ-Hole bonds are also highly directional and occur in line with the covalent bond that causes them."

So, we found for the first time the bond path which represents the carbon atom and we almost forgot it, but then it became very famous it came in CND News. So, the last part of the course I thought we will give some publicity to my group. So, this came in CND News it became very famous, people said we defined a new carbon bond and electronic effects that produce halogen bonds. We did non covalent interactions in other elements and so on and so forth.

And there is a big paragraph written about what we have done in this case, sigma hole bonds are also highly directional and occur in line with the covalent bond that causes them. So, again the universal plot which we did in 2003 is verified even in this particular case, so this was a quite an excitement at that time.

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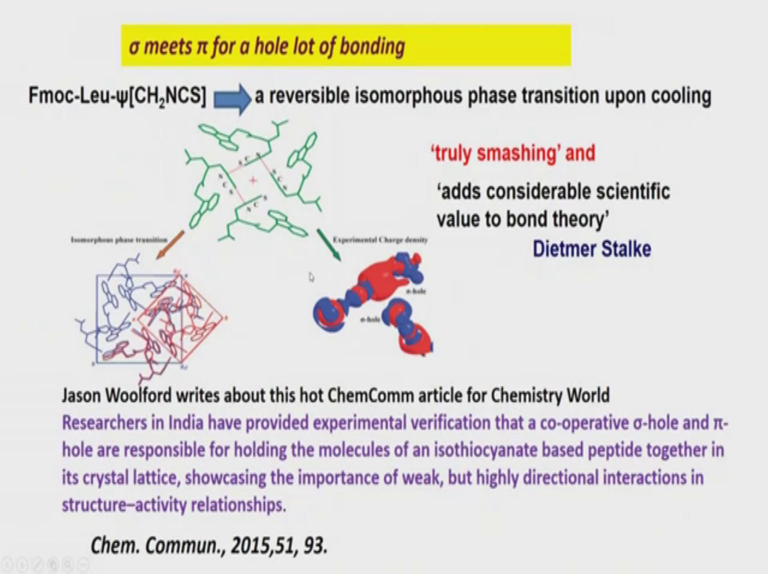
σ meets π for a hole lot of bonding

Fmoc-Leu-ψ[CH_2NCS] → a reversible isomorphous phase transition upon cooling

'truly smashing' and

'adds considerable scientific value to bond theory'

Dietmer Stalke

Jason Woolford writes about this hot ChemComm article for Chemistry World

Researchers in India have provided experimental verification that a co-operative σ-hole and π-hole are responsible for holding the molecules of an isothiocyanate based peptide together in its crystal lattice, showcasing the importance of weak, but highly directional interactions in structure–activity relationships.

Chem. Commun., 2015,51, 93.

The next excitement came with a title which we see here sigma meets pi for a hole lot of bonding and this was the work done by Rumpa in our group with me and then we find that in this particular case it is a compound which is biologically important and there is a S CN a bond it is just linear bond and then there is an interaction between the sulfur and the center of this NHC bond N CS bond and also there is a center interaction.

So, it is its space group is p 4 1 and so it is quite an interesting organic molecule and when we analyze this structure we had some interesting phase transitions. So, I do not want to touch upon that but what we found is that in one direction it has the sigma hole interaction dominates and in the other direction the pi hole interaction dominates.

So, one goes this way forward direction sigma hole and the other goes from the perpendicular direction which is the pi hole and then of course Jason who is a editor of chemistry world he wrote that we found the co operative sigma hole and pi hole responsible for rolling molecules in a isothiocyanate based peptide. So, this compound of course we got from Professor Balaramas group. So this work was praised again truly smashing and acts considerable scientific value to bond theory this was written by one of the pioneers in charge density analysis Dietmer Stalke.

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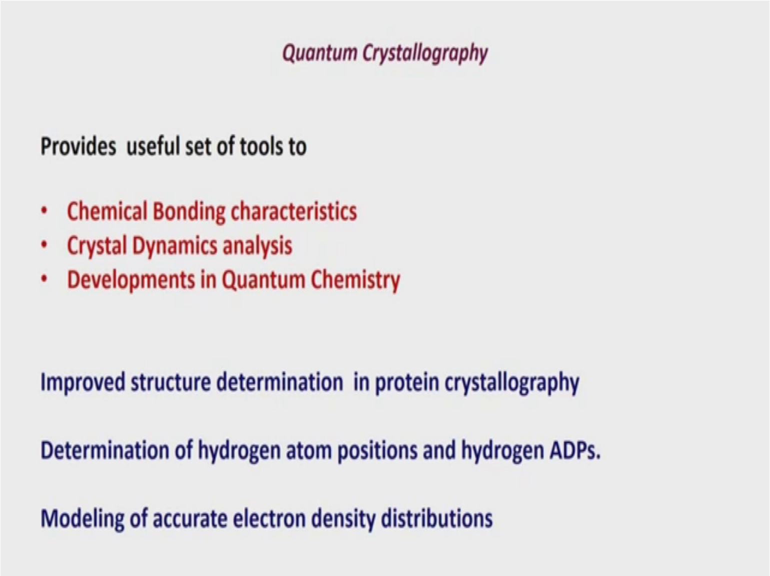

Quantum Crystallography

Provides useful set of tools to

- Chemical Bonding characteristics
- Crystal Dynamics analysis
- Developments in Quantum Chemistry

Improved structure determination in protein crystallography

Determination of hydrogen atom positions and hydrogen ADPs.

Modeling of accurate electron density distributions

And thereby we essentially see that a typical X-ray diffraction experiment with of course, a little more analysis using quantum crystallography providing chemical bonding, characteristics crystal dynamics etcetera and it gives various ideas about how to go further is emerging.

So, again the rules of symmetry play a major role, the way in which the sigma hole orientation takes place depends upon where the symmetry element is located in the atomic arrangement. It also depends upon where how many molecules are there in the unit cell and in what way the molecules direct themselves with involving these very very weak interactions, these are all very very small in terms of electron densities unless you do a very high resolution X ray diffraction data you cannot see them experimentally. And then of course theoretical modeling is also equally difficult.

But once the modeling is done there is a nice handshake, this is the only area where there is for once the theoreticians and the experimentalists shake hands and agree with each other. Normally theoreticians are always thinking they are somewhere above space and they are doing wonderful work, experimentalists are very humble and they say well we have found this. But this is the first time an experimentalists are dictating the theoreticians and vice versa. So, this is therefore an area of future and you see that improved structure determination in protein crystallography we are looking for that.

Determination of hydrogen atom positions hydrogen ADPs is already possible and modeling of accurate. So this part which is which we should have discussed a little more when you had time is essentially it depends upon the way in which the atoms are and the way in which the atoms are interacting with each other and the way in which molecules are put inside the crystal. So, again the symmetry probably will add on to the contributions of modeling electron density distributions, we do not know the issues associated with symmetry if they are brought along with the concept of modeling that will definitely help. In fact, the multi pole model also when we do the expansion about Monopole, Dipole Quadrupole and so on.

Depending upon the symmetry of the system some of the values associated with these polar components will either appear or disappear effectively like systematic absences. So, there will not be any contribution coming in certain directions because of the fact that there is symmetry that is associated with the crystal structure.

So, that way the study of symmetry at the basic level which we have done in the entire course and then the way in which we have carried out the understanding of the development of point groups, the space group, the systematic absences through experiments and the type of experiments we perform using X-ray diffraction. And at the later stage when we have looked at the accuracies with which we can analyze the results and then the risk based refinement, the powder diffraction. All these in a nutshell are a part and parcel of the basic understanding of symmetry and structure in the solid state. And I think in this particular course we have been able to cover that aspect to a reasonable extent.

We have expanded this into the recent areas we have seen many a potential applications that are possible, but since it is a short course of this kind we cannot go into the detail of that. So, maybe there is an advanced course which we will now use the ideas which we have learnt from this short course. And then go to the advanced course where you will learn more details of all these methodologies which again require the basic understanding of symmetry and structure, so symmetry and structure is different foundation for any of these discussions we have had until now.

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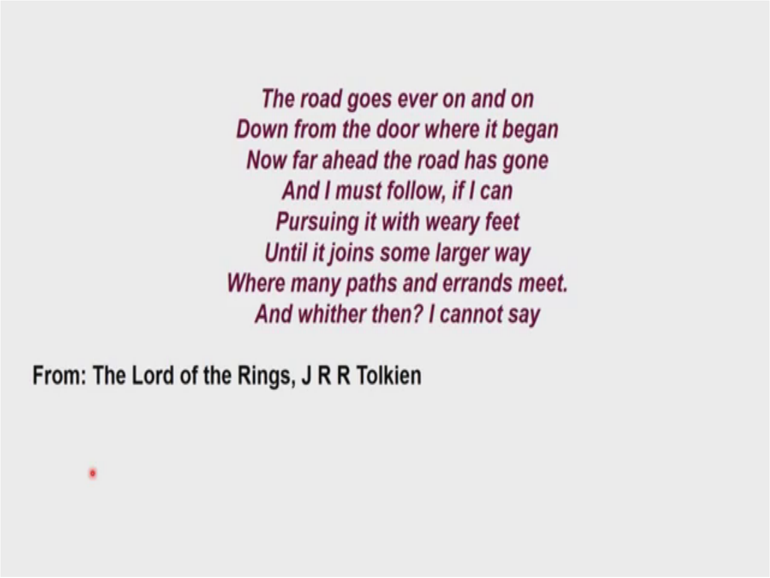

The road goes ever on and on
Down from the door where it began
Now far ahead the road has gone
And I must follow, if I can
Pursuing it with weary feet
Until it joins some larger way
Where many paths and errands meet.
And whither then? I cannot say

From: The Lord of the Rings, J R R Tolkien

So, I say this I always like to say something at the end of a lecture in this like this series of talks, this series of classes never ends, because it has to go on and on and on this is a statement from Tolkien in the Lord of the Rings, he says that the road goes ever on and on is what we came from structure and symmetry we went to various directions.

Down from the door where it began, it began at a point it began with what it began with the definition of point groups and it began at a point center of symmetry it then went to 2 fold symmetry it went to the plains and so on. Now, far ahead the road has gone so we have gone far away in those directions we have understood all the symmetry principles and so on and I must follow if I can this is the problem I must follow these whatever I have understood I must follow pursuing it weary feet obviously because we have learned. So, many things I have talked for so long in fact I have coughed many times some of it may be recorded also.

So, it went on and on it is quite vary to go through this until it is joined some larger way finally we have put them all together we are looking at very finer aspects of the small molecule, structure determination bring in quantum chemistry into the picture. Of course, we have not seen the other aspect of large molecules that is also very fascinating. So, there are 2 major developments in the last decade or so one is understanding small molecules to the best possible extent leave, for the first time we are seeing holes in atoms in the periodic table in a loose sense. We have identified the sigma holes and the pi holes associated with atoms and how they provide electrophilic and nucleophilic interactions. So, pursuing it with weary feet until it joins is larger way there are many paths and errands meet. So, all these things sigma all meets pi hole something we wrote that fellow wrote I did not write and without them I cannot say so we are reached the main road now.

Now, after reaching the main road what we will do whether we will take a taxi, we will take a bus, we will take a bullock cart I do not know this petrol is getting over in this world. So, we may even end up with a bullock cart, but whatever we cannot say right now and that is the statement of lord of the rings which I will end this course. And I must acknowledge because I have just left and right copied the beautiful equations and diagrams which are there in these text books.

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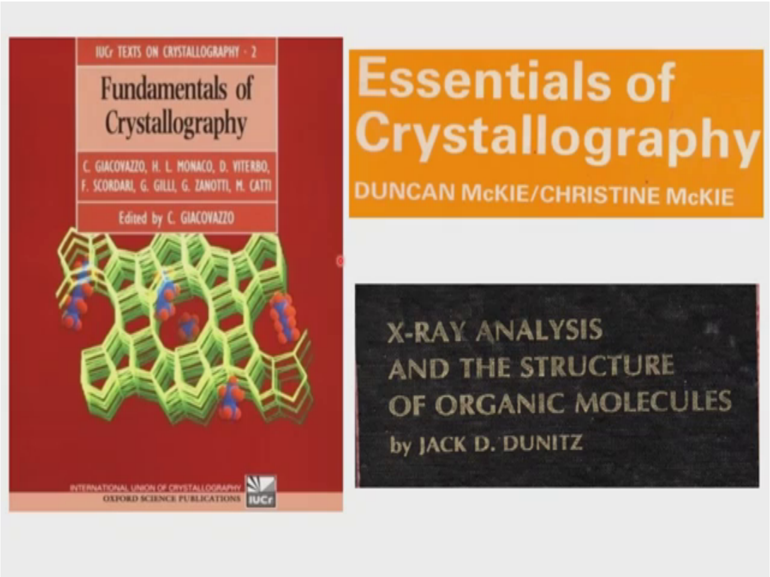

I do not know how to thank these guys because, unless I had these books at my disposal and of course you know copyright issues being violated left and right these days. So I could get the scanning done and get the diagrams out. So, many of the diagrams are taken directly from these books and so I thought I should acknowledge all the people who wrote those books there are wonderful books, for example this one the Fundamentals of Crystallography which is edited by Giacovazzo. But you see there are. So, many high quality authors who have contributed to this; this is a more recent book published by IUCR the Oxford University press we have brought it out that is what science publications.

So, you can see that all the modern methods of structure determination are covered here. So, this is the most recent book, one of the older books is the essentials of crystallography Duncan Mckie and Christine Mckie these 2 have written a wonderful book this probably the best book to understand symmetry. If anyone wants to get a complete understanding of how symmetry develops. What are the various symmetry elements in terms of both physics as well as chemistry? I have not gone into the detail of how mathematically we can come to these understanding of point groups and space group, but that is an issue which is not for our course.

So, but we could have one could study the group theory associated with it and still arrive at all the details, but this is a book I must acknowledge this is by far the most referred book in our course. The other is the Gurus book this is Jack Dunitz I consider him my Guruji because, he is the one who explained all the scattering phenomena in such a way that a very simple person like me can understand the entire structure the entire scattering theory. So, whatever scattering theory we did and how we arrived at the Bragg condition and the Laue conditions and so on were all taken from this textbook of Jack Dunitz.

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And then we have got the other 3 books the next book of course is the X-ray structure determination practical guide Stout and Jensen as the title says it is a practical guide. So, most of the tables which we have in the presentation are from the textbook, which tells you how to get the equivalent points how together it the equivalent diagrams how to get the symmetry points and then the equivalent points and so on. Then of course, the book of the crystal structure analysis which is now one of the current books which are in which are available in many bookshops and this is for the modern day crystallographers who used the machines.

We do not have to learn too much of crystallography but depending on the machines, but having depended on the machines what are the principles and practice one has to go through for crystal structure analysis is beautifully compiled in this, it is again this is edited by William Clegg. So, this has articles by many of the top crystallographers currently in the world, so this is another textbook which we have referred to it is also an IUCR textbook. And then of course the bible or the Bhagavath Gita or the Quran whatever it is that is our international tables for crystallography.

Now, without this the course could not have been done at all and the contents of this book the tables have been displayed many many times and we have discussed every point with respect to the international tables of crystallography. And so I think I am very grateful to the availability of these 6 textbooks and the tables without which the course could not have been completed. I come to the end of the course now with a last slide.

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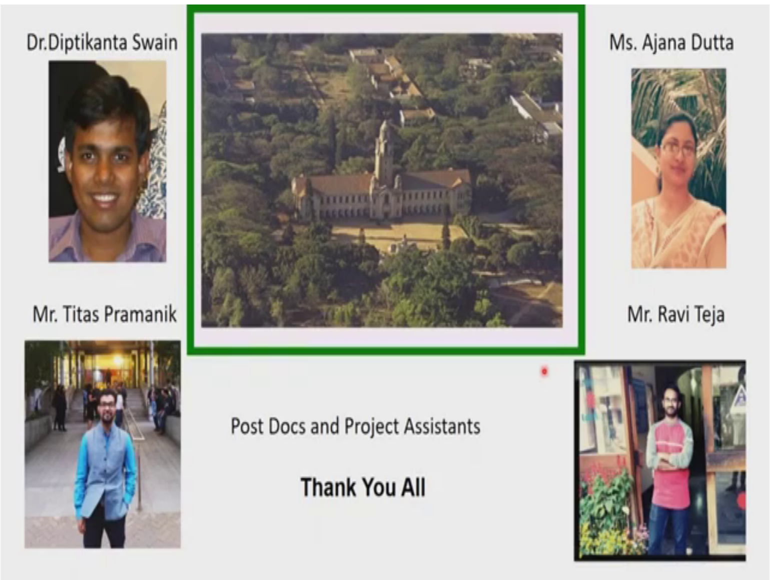

Dr.Diptikanta Swain

Ms. Ajana Dutta

Mr. Titas Pramanik

Mr. Ravi Teja

Post Docs and Project Assistants

Thank You All

The last slide is very crucial because if you want to do something like this you need the help of people right and I have got some 4 mug shots or 4 guys 4 people who are in my group Diptikanta Swain is a post doc, Titas Ajana and Ravi. In fact, these 4 fellows will continue to be with you during the TA programs and also the monthly discussion programs and so on throughout the course. And of course, IASC without which we cannot do this NPTEL is also situated they have an office in ISAC and if any time you are there you can see that this is a very beautiful symmetric building surrounded by of course a lot of nature around it.

But if you look at it carefully you can see the symmetry that is associated with the main building, I as a challenge I want you to find the symmetry associated with this at the end of the course. I also thank all my other postdocs and project assistants who now participated very actively in this course program and also helped me out to make some correction here and there particularly English corrections and at the end I would like to Thank you all for participating in the course.