Fundamentals and Applications of Supramolecular Chemistry

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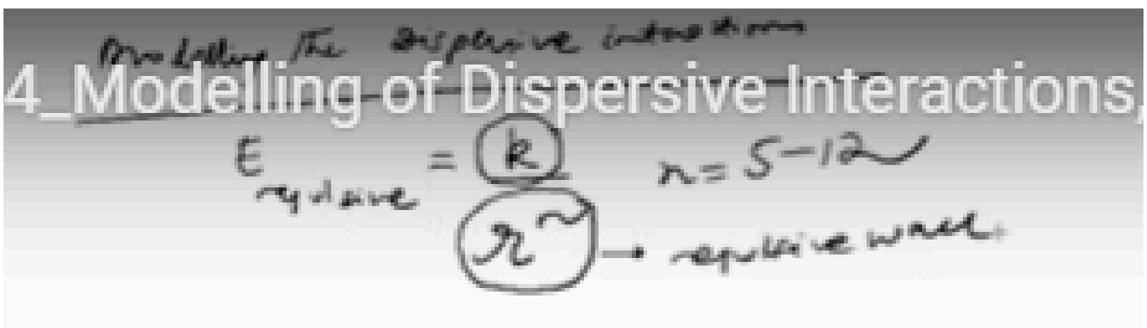
Week 01
Lecture 04

W1L4_Modelling of Dispersive Interactions, Introduction to H-bonds

So, hello everybody. Now, let us continue our discussion further with respect to the van der Waals interactions and the role of van der Waals radii. Now, the most important thing now we would like to look at is modeling the dispersive interactions.



Now what was essentially proposed here is that to start with the E repulsive component. It was written as equal to a proportionality constant k and r to the power n where the value of n can vary from 5 to 12. This can be attributed to the repulsive wall.

This is also referred to as the repulsive wall. And in this regard, there is one particular potential which is very popular, and which is also a part of different ab initio simulation packages which we will refer to as the Lennard Jones potential.

Lennard Jones potential (LJ- potential)

6-12

$$\boxed{V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}}$$

This is also called the 6-12 potential where the V(r), that is a potential energy as a function of distance r is expressed in the following form where we have the attractive part of the potential and we also have the repulsive part of the potential. It is attractive as 1 by r to the power of 6, this is something we realized when we discussed about instantaneous dipole-induced dipole interactions, and this is the repulsive part of the potential.

$$= 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

σ = equilibrium separation between the atoms

So, to start with we can write a more generalized expression for the potential energy as a function of distance where we have the attractive term and the repulsive term. And, the actual expression for the Lennard Jones potential is as follows, it is written as 4 epsilon sigma by rij to the power of 12 minus sigma by rij to the power of 6, where sigma is actually the separation between the atoms.

We can call this the equilibrium separation. So, we have got these two atoms, this is the inner electron cloud, and this is the outer valence electrons, and we say that the two atoms essentially are touching each other, and so this is sigma by 2, this is sigma by 2. So, the total separation is sigma and this is the repulsive part and this is the attractive part and if you were to actually see how this looks.

This is a function of r, this is a function of the potential energy and this is the 0, this is essentially minus epsilon, this is rmin which actually corresponds to the equilibrium inter nuclear separation. And this is actually sigma, when at the distance sigma, the attractive and the repulsive forces now essentially balance each other, and it lies essentially at this particular value of sigma, the value of E is equal to 0, or the value of the potential is equal to 0. V is equal to 0. So, we can now determine the value of rmin by taking the first derivative of dV with respect to r and putting it equal to 0. So, the first derivative of V with r is also a measure of the force, the force acting on the system.

$$\frac{dV}{dr} = 0$$

Force acting on the system

$$\boxed{r_{min} = 2^{1/6}\sigma \sim \underline{1.12\sigma}} \quad V = -\epsilon$$

And when you equate this to be equal to 0, you can get the rmin as 2 1 by 6 sigma which is approximately 1.12. This is approximately 1.12 sigma. So, this is the limiting distance and when you put this value of rmin in the expression for V(r), then V becomes equal to minus epsilon, and this is referred to as the depth of the well.

So, this is the depth of the potential energy well, which is minus epsilon, and the rmin is equal to 2 to power 1 by 6 sigma. So, that tells you that the equilibrium internuclear separation is actually slightly greater than the value of sigma because at this particular distance the attractive and the repulsive forces perfectly balance each other.

That means there is little bit of separation. This is the state when it is sigma when they absolutely touch either each other and if you little bit separate this distance, you create little bit of separation, then this is the equilibrium situation where the attractive forces about which we discussed, and repulsive forces balance each other. So, the limiting situation is sigma when they completely touch each other and beyond which they compress each other.

Now, when they compress each other, you see that the repulsive potential comes into picture and the V(r) shoots up. Whereas, when you increase the distance further, again you see that we know that these are short range forces. So, if you increase the distance further then again, the stabilization decreases, and the potential energy tends towards 0. So, there is a maximum stabilization value for the potential energy at this particular rmin value, beyond this the stabilization decreases and lower than this it becomes highly repulsive in nature. So, and we know that so, here we say that the force acting on the system is the less than 0, it is an attractive force and here the force is greater than 0, it is a repulsive force because here the first derivative of the potential energy with distance is negative the slope falls.

So, overall F becomes greater than 0, because F is nothing, but minus this particular value. So, when the slope falls the force becomes repulsive and when the slope increases that is dV by dr is positive then the force is negative. That means the force is less than 0 that means these are the attractive forces and greater than 0 means these are the repulsive forces. So, this is one way the Lennard Jones potential which is very important to understand. Now, how we model the dispersion interactions and essentially this depends upon the number of electrons which are present in the atom, more is the number of electrons, more is going to be the attraction and consequently more is also going to be the repulsion.

Because more is the electrons means then the attraction of the nucleus for the electrons increases, but at the same time the electron-electron repulsion also increases. So, this concept of van der Waals radius and Lennard Jones potential are very, very important. So, with this background, let us now go into a bit more deeply into one special classification of dipole-dipole interactions, which we call as hydrogen bonds.

Because we are going to look at supramolecular chemistry and we are going to understand hydrogen bonds, let us try to understand what are hydrogen bonds. So, in case of hydrogen bonds what happens is that you have a general classification like this.

This is the system which represents a hydrogen bond, where you have hydrogen which is essentially devoid of a core electron. There is no core electron present in hydrogen atom, it only has a valence electron. It is covalently bonded to X which is more electronegative than hydrogen and then it interacts to start with electrostatically with another electronegative atom Y.

And more importantly there is evidence of bond formation between the hydrogen atom and the acceptor atom Y, then this situation represents a hydrogen bond. Now, because these are of electrostatic origin and this electronegativity difference, this is delta minus this is delta plus and associated incipient positive charge and this is also more electronegative than hydrogen you see that there is an attraction for the hydrogen atom by the Y atom.

And this hydrogen bond has got macroscopic manifestations because it affects the melting and boiling points of substances.

For example, water, hydrofluoric acid, H2S, H2Se. You can actually see that the boiling points of different substances are different on account of the variations in the strength of the hydrogen bond in the associated entities.

The next thing to keep in mind is that the hydrogen atom is very small in size, compared to X and Y. And because it is having a positive character associated with it, the hydrogen atom is able to penetrate into the region of the acceptor.

In other words, it is able to go very close to the electron density associated with the Y atom. It is able to actually deform the electron density cloud of this Y atom because of the positive charge associated with it. So, there is some kind of polarization of the electron density at the acceptor end and the hydrogen atom is able to penetrate into the region of the acceptor such that the hydrogen acceptor distance is much smaller than the sum of the van der Waals radius of hydrogen plus the van der Waals radius of the acceptor.

So, if you actually take the sum of the van der Waals radius of hydrogen plus that of the acceptor Y, this distance d is much smaller than this particular sum. In most of the cases, we will see that when you have non-hydrogen atoms, then for example, if you were to take carbon interacting with another carbon atom, the separation is almost close to twice the van der Waals radius of carbon.

We looked at it in case of fluorine also, that it is approximately twice the van der Waals radius of the fluorine atom. Chlorine same, bromine, there is not much difference, there might be some contraction or expansion there might be some changes in the distance, the separation between the two atoms will be in the vicinity of twice the sum of the van der Waals radius.

But when you have a hydrogen bond it is a very special case of dipole-dipole interactions because here you have, say, a Z. So, you have a Y-Z dipole and a X-H dipole. Hydrogen bonds are a special case of dipole-dipole interactions, where the distance between the donor, so the species which donates the hydrogen atom is called the donor and the one which accepts the hydrogen atom is called the acceptor.

This is electron deficient hydrogen, this is electron rich. So, in other words, we can also call this electron acceptor, that is hydrogen and Y we can call an electron donor, but so there are two different ways of looking at the definition, but commonly we refer to as a donor and an acceptor being a more popular concept. So, these non-hydrogen atoms by and large they are close to the sum of the van der Waals radii, but for hydrogen the equilibrium inter nucleus separation can be very, very short depending upon the electronegativity at the acceptor side.

So, the H....Y bond is associated with quite a bit of covalent component also. In fact, there is a phenomenon, where you can actually take the hydrogen atom which is covalently bonded with one oxygen and move this electron density of the covalent bond to the other oxygen atom and now this becomes a covalent bond, and this becomes a hydrogen bond.

So, this phenomenon is referred to as resonance assisted hydrogen bond, where you can see that this kind of resonance like situation where the proton essentially covalently bonds with the acceptor atom in the resonance canonical. And this is more facilitated by the presence of negative charges. If you have got negative charges on this oxygen, then this happens in a more facile way.

The negative charge will get delocalized from one oxygen atom to the other oxygen atom. So, this is referred to as resonance assisted hydrogen bond and this also is a very important concept, and the stabilization energy of such strong hydrogen bonds is also very high. We will come to the magnitudes later.

So, now we can see that normally traditionally when you have AH plus a base B interacting with a donor, you have a hydrogen bond and normally the enthalpy change for this process is around 50 kilojoule per mole. For a strong hydrogen bond, it is roughly around 50 kiloJoule per mole.

Obviously, you can have even more stronger hydrogen bonds. For example, resonance assisted hydrogen bonds, the values can go up to 100 to 120 kilo Joule per mole as well. And you can also have weaker hydrogen bonds depending upon the donor strength of AH. So, now, if A is equal to oxygen, nitrogen, you have the stronger donors and B is equal to oxygen or nitrogen, then you are going to have strong hydrogen bonds. But if A is equal to carbon and B is equal to oxygen and nitrogen then you are going to have weaker hydrogen bonds.

And if you have going to have B is equal to carbon then you will have essentially C H...C which are the weakest of hydrogen bonds. So, the spectrum of hydrogen bonds can be tuned depending upon the donor and the acceptor strength.

Now, it is also important to realize that what are the distances which are observed in case of strong hydrogen bonds. So, let us go to the next page. So, here I like to give you a chart where we look at these distances more carefully and appreciate the distances involved in hydrogen bond recognition.

So, for example, let us take fluorine FH...F. So, this involves a hydrogen bonding interaction between the most electronegative atoms that is the fluorine atoms and here we see, where I will say AHB as the nomenclature, we take the distance AB observed, we take the HB calculated and the HB observed.

So, for example, in the case of FH...F, this is around 240pm. This becomes 260pm, the hydrogen...fluorine distance is 260pm and this is around 120pm.

And when we go to OH...O, this is 270pm, this is 260pm and this is around 170 pm. When we go to OH...F, this is 270pm, 260pm, this is 170 pm.

When you go to NH...S, this is 330pm, and this is around 240 pm, CH...O 300pm, 260pm, 230 pm.

So, you can see that in all the cases, this is calculated based on the sum of the van der Waals radii of hydrogen plus the B. So, say you have got fluorine for example, the van der Waals radius of fluorine is around 1.47 angstrom plus hydrogen is around 1.2 angstrom.

So, this comes out to be around 2.67 angstrom that is around 267 pm, ok. There can be some variations, but essentially this is what it is, but the actual distance you see is much shorter to 120 picometer.

And that is because I told you that fluorine is a highly electronegative atom, hydrogen is having strong positive charge, it is able to penetrate into the electron density region of fluorine atom and therefore decrease the separation between the hydrogen and fluorine.

So, whenever you have got strong hydrogen bonds you will see that the distance between the donor and the acceptor is very small compared to the sum of the van der Waals radii. In all these cases, you will see that the observed distance is smaller than the sum of the van der Waals radii.

Now, the difference is more, but then the difference decreases when you actually decrease the electronegativity of the donor atom. So, as you decrease the electronegativity of the donor atom, for example, if you have a C-H or you decrease the electronegativity at the acceptor side, for example, you have got sulfur, then you will see that the difference also decreases.

It is around 60 picometer here, it was around 90 picometer here, and here it is only 30 picometer. So, the difference between the calculated and observed decreases if you change either the donor strength or the acceptor strength because that influences the extent to which the hydrogen can interact with the acceptor and also the magnitude of electrostatics in deciding the role of dipole-dipole interactions in these hydrogen bonded systems.

So, particularly in case of fluorine, this is a situation which is like more intrinsic for example, we can look at HF2-.

We know that the next thing to be concerned about is the directionality. The directionality of the hydrogen bond, this is a very important feature. So, the first geometrical feature for a hydrogen bond is that what is the separation between the hydrogen bond donor and the acceptor and then what is the directionality at the hydrogen bonding region. This angle ideally should be 180 degree for a truly hydrogen bonded system.

Now, why is it that you would like to have this directionality? This is because when you have two highly electronegative species coming close to each other then you know that there is going to be repulsive forces which are operational.

And to minimize this repulsive forces what I put is I put in a positive charge which will effectively screen the negative charges from the two approaching electronegative atoms and create a more stabilizing situation and that is the reason why you put in a proton which actually screens the negative charges most effectively because now the proton is put in the center and therefore, it now minimizes the electron-electron repulsions and maximizes the attraction of the hydrogen nucleus with either of the fluorine atoms.

And because this situation is overall stabilizing the directionality of hydrogen bonds approach towards 170 to 180 degree. Now this situation is a rare situation mostly it is prevalent in gases or in liquids, but when you go to solids then things change because in solids because of the presence of other interactions also the hydrogen bond directionality gets reduced.

Nevertheless, it tries to maintain the hydrogen bonding nature in the associated solids. But particularly for HF2-, this is a very interesting picture where you have the highly directional hydrogen bonds.

Same thing is for OH...O, NH...O, OH...N, these kinds of hydrogen bonds tend to retain very high directionality. And hydrogen bonds can be present within the molecule also.

They can influence the properties of the molecule, and they are also present between the molecules. So, we can look at examples in this regard. For example, we can consider the phthalate ion which comes from phthalic acid.

So, in this case we have got O minus, and we have got this OH which hydrogen bonds electrostatically with O minus. So, there is an intramolecular hydrogen bond. There is an intramolecular hydrogen bond which actually forms a cyclic structure, a loop in which the proton is effectively captured within the cyclic loop forming the strong intramolecular hydrogen bond.

We can also have a very classical example of benzoic acid. This we have studied in high school as well that benzoic acid or acetic acid exists as a dimer and this is a centrosymmetric dimer because it exists across the center of inversion and there are strong OH...O hydrogen bonds and these are also directional hydrogen bonds. Directionality is almost 180 degree and also the separation between the hydrogen and the oxygen is smaller than the sum of the van der Waals radius of hydrogen plus oxygen.

So, these kinds of interesting situations, exist with respect to hydrogen bonds and in this regard, we have different classifications of hydrogen bonds. And we have got different types of hydrogen bonds, for example, we can have a donor atom which can interact with two different acceptors.

These are referred to as a bifurcated donor. You can also have three acceptors. In that case, you will say trifurcated donor. Similarly, you can have an acceptor accepting 3 hydrogen bonds this will be referred to as a trifurcated acceptor because this acceptor A accepts 3 different hydrogen bonds from 3 different from 3 molecules of the same type and forms this kind of a hydrogen bonding network.

So, you can have you can have bifurcated donor, you can have a trifurcated donor, you can have a bifurcated acceptor, you can have a trifurcated acceptor, and these kinds of species are present as well. The next thing which is very important in supramolecular chemistry about which I would like to give a brief introduction is that there are different techniques which are used to detect non-covalent interactions which are used to detect the occurrence of this hydrogen bonds and in this regard one particular technique which is very sensitive is IR spectroscopy.

IR spectroscopy which essentially looks at changes in the bond length associated with different bonds in a species. So, what happens when you have a hydrogen bond there is an electrostatic attraction of the oxygen for this hydrogen atom. So, this bond tends to get elongated.

So, there is a lengthening of the OH bond. So, if there is a lengthening of this OH bond then the bond length becomes longer, the bond becomes weaker and every bond is characterized by a force constant that is how much of force you need to stretch per unit length of the bond.

This force constant actually decreases. So, the energy which is necessary to stretch this bond also decreases. So, there is a lowering in the stretching frequency of this particular OH bond which is non covalently associated with another acceptor atom in the formation of the hydrogen bond. And such type of hydrogen bonds where there is a lowering of the stretching frequency of particular bonds associated in hydrogen bonding is referred to as red shift. So, the value was say x centimeter inverse in terms of wave number it has now decreased to y.

So, there is a lowering and we say it is red shift. On the contrary if there is an increase in the stretching frequency for that particular bond then we refer to it as blue shifted hydrogen bonds.

So, what has been observed here when you have the strong hydrogen bonds the stretching frequency for OH which is 3400 centimeter inverse in the case of benzoic acid in the gas phase, now in liquid phase it is lowered to 2500 centimeter inverse. So, there is a lowering in the stretching frequency relatively you can see of the OH group compared to the gas phase value, the value in the liquid phase is 2500 centimeter inverse.

So, this kind of changes takes place in the stretching frequency and that is a measure of the fact that the formation of hydrogen bonds results in red shifted hydrogen bonding. And towards the last part of this lecture, I will just give you some properties of hydrogen bonds.

For example, we will look at strong, medium and weak hydrogen bonds.

In case of A-H...B, let us consider this example. There is a case of strong hydrogen bond, these are mainly covalent in nature. These are electrostatic and these are both electrostatic plus dispersive. So, now you see that for weak interactions similar to van der Waals interactions we also have the dispersive component in the hydrogen bonds.

Bond dissociation energy that is for strong hydrogen bond 60 to 120 kilo joule per mole, whereas for medium it is 15 to 60 kilo joule per mole and for weak it is less than 15 kilo joule per mole. The separation between the hydrogen atom and the acceptor for strong hydrogen bonds is in the range of 1.2 to 1.5 angstrom, 1.5 to 2.2 angstrom for medium hydrogen bonds, and greater than 2.2 to 3.2 angstrom this range is there for the very weak hydrogen bonds.

The acceptor donor distance that means the distance between acceptor and the donor and the acceptor is 2.2 to 2.5 angstrom, 2.5 to 3.2 angstrom, and this is greater than 3.2 to 4 angstrom limit. And then the directionality, the directionality of hydrogen bonds, as I know that strong hydrogen bonds are highly directional, 175 to 180 degree, 130 to 180 degree and this is between 90 to 140 degree.

And the percentage change in stretching frequency, is 25 percent approximately, this is 10 to 25 percent and this is less than 10 percent. So, this table now nicely summarizes the properties of hydrogen bonds starting from the strong hydrogen bonds to the medium to the weak and the contributions like primary covalent, electrostatic, electrostatic plus dispersion and these are very important geometrical data, associated with hydrogen bonds. These are the three important attributes, the distance between the donor and the acceptor written as small d.

The distance between the A and the B that is the donor and the acceptor non-hydrogen atoms and the directionality which we specify as theta. These three are the important geometrical features of hydrogen bonds which will be very important in our course.

What is the bond dissociation energies, or the binding energies associated with strong hydrogen bonds and a technique to characterize is the changes in these distances of hydrogen bonded substances is via IR stretching frequency which is via IR spectroscopy.

And most importantly one of the very important techniques to actually characterize substances in the solid state is single crystal X-ray diffraction from where we determine the crystal structure of the substances and we can get all the geometrical characteristics in solids.

So, with this we more or less come to an end of the first module, and I hope you have been able to understand the salient features of chemical forces, the importance of chemical forces which are going to play a very important role in the next set of modules which will accompany the next set of lectures.

Thank you very much.