Fundamentals and Applications of Supramolecular Chemistry
Deepak Chopra
Department of Chemistry
IISER Bhopal
Week 01
Lecture 03

W1L3_Van der Waals Radius

So, hello everybody, today we are going to continue our discussion on chemical forces from where we left in the last lecture.

So, in the last lecture we talked about dipole-dipole interactions, we also talked about dispersive interactions and we also looked at how inert gas atoms actually interact with each other.

And towards the end of the previous lecture, we looked at the attractive work forces which primarily govern recognition between molecules which are of a non-polar nature. And, we also looked at the role of nucleus-electron attractions and electron-electron repulsions which are responsible for the origin of the dispersive interactions.

Classically, we also attributed this to the presence of an instantaneous dipole which is created by the momentary electron density imbalances in the electron density distribution, because of the circulating electron clouds, and this instantaneous dipole is then able to induce a dipole in the other non-polar molecule and this results in the origin of attractive forces existing between the molecules.

Now, the next part of this discussion looks at what happens when two atoms come close to each other.

So in dispersive interactions, we looked at the attractive forces and this happens because we talked about the presence of instantaneous dipole-induced dipole interactions.

And this happens, when you have, for example, we considered rare gas atoms say for example in a gas container that collide with each other. So, now if you reduce the available volume which is available between the rare gas atoms in a particular container, then these atoms are going to come further and further close to each other.

It is also important to realize the maximum extent to which two atoms can come close to each other.

So, when we now have two atoms, we consider the two spherical atoms, this is the nucleus, this is the inner electron shell and now when the two atoms come close to each

other and we are considering them as hard billiard balls that means essentially the atoms do not get deformed when they actually come in contact with each other during the process of colliding with each other.

At this particular point the nucleus-electron attraction and electron-electron repulsions are present. Now if the atoms try to actually come close further then what happens is that there is repulsion. So there exists a repulsion between the nucleus of the two atoms and there is also repulsion between the electrons of the inner core.

So, these are the two fundamental forces which now operate when two atoms actually come closer to each other.

You have repulsion between the nuclei and you also have repulsion between the electrons of the inner core and as a result of which this is the origin of repulsive forces, and in the real situation both the attractive and the repulsive forces coexist with each other.

So,, we have the E attractive forces plus the destabilization because of the repulsive forces. So we need to keep in mind here four important things.

Forces are attractive or repulsive and subsequently the energetic stabilization is negative that means it lowers the potential energy of the system and repulsive means it raises the potential energy of the system. So now you have the potential energy which is lowered when you have attractive forces and you have potential energy which is raised when you have got repulsive forces.

Energetics are always attractive if it is negative. So energetics are stabilizing if there is a lowering of the potential energy and the energetics are destabilizing, if you have an increase of the potential energy of the system and this overall constitutes the concept of dispersive interactions where you have an attractive component and you also have a repulsive component.

Now it is very important that in a real situation like this when you have got attractive and repulsive forces which operate between atoms it is also important to keep in mind that similar forces also operate between molecules.

So now when you have got a molecule for example, you can take a benzene ring and then you have another benzene ring these two benzene rings can actually interact with each other because both of them are essentially non-polar molecules. They can interact via the dispersive interactions.

So, there exists both attractive forces and when the two benzene rings come close to each other then they can be repulsive forces. Now, it is very important to decide what is the

limit which is allowed for the two atoms to approach or come closest to each other, what is this limiting distance?

This limiting distance such that the attractive and repulsive forces balance each other is related to the van der Waals radius of the atom. So now we would like to know about the van der Waals radius of the atom which is fundamentally different from the atomic radius of an atom of interest.

So when we have got two atoms which come close to each other they come and touch each other and if you further push them closer to each other then the repulsive force becomes more and there is a destabilizing situation. Initially it is attractive the potential energy of the system is lowered.

Now, they come to this limiting distance when the separation is actually twice the sum of the van der Waals radius. Why? Assuming that these are the same atoms, say a collection of argon atoms, krypton, xenon, radon or you have got hydrogen atoms of any chemical species when they are actually interacting with each other.

They will not be able to come close together further when the limiting distance is the sum of the van der Waals radius. So, essentially when the two atoms touch each other we can say, that if these two are carbon, then this is sigma. I refer this to as sigma, where essentially sigma refers to the van der Waals radius of that atom.

So, the limiting distance now essentially is twice sigma. So, beyond this they cannot approach each other or there will be strong repulsive forces operational. So, this twice sigma is the limiting distance when both the atoms are in a comfortable position and sigma is referred to as the Van der Waals radius of the atom of interest.

So, we can also now take this particular situation. When we can now consider, for example, a slightly more involved example where we consider for example a fluorine molecule.

So, in a fluorine molecule we have the F-F bond where a covalent bond is formed between the atoms and now I bring in its vicinity another F2 molecule, we can also consider chlorine, bromine, iodine, also the heavier halogens as well and now we allow these two atoms, two molecules containing fluorine atoms to interact with each other.

The dotted line represents the interaction that is this is the non-covalent interaction and this is the covalent one between the two fluorine atoms. So, if you were to actually draw this picture a bit more cleanly. So we can now draw, and similarly we can have so we can now look at the region.

So, this is the region of orbital overlap, where the two fluorine atoms extensively covalently bond with each other and there is some amount of electron density which is being shared between the two fluorine atoms because both the atoms are similar this region is present exactly at the center of the covalent bond.

And half of this separation, between the two fluorine atoms gives you the covalent or the atomic radius of fluorine atom. Now, this particular situation is when the 2 fluorine atoms now touch each other and this separation is now twice the van der Waals radius of fluorine.

So now if you know this particular distance which is the separation between the two fluorine nuclei you will know exactly the magnitude of twice the van der Waals radius of fluorine and half of that will give you the van der Waals radius of the fluorine atom.

So this particular picture very nicely depicts that you have extensive orbital overlap which forms a traditional covalent bond and you can also represent here the inner core of electrons as well.

And when you have this extensive overlap you also need to keep in mind that during the process of bond formation you are also going to have nucleus-electron attractions and electron-electron repulsions and that time the repulsion will exist between the inner core of electrons with that of the outer electrons or the valence electrons of fluorine atom and overall this situation gives rise to the fluorine molecule.

Whereas when you are going to have the non-covalent interaction there exist attraction between the nucleus of the fluorine with the electrons of fluorine, but also repulsion between the inner electrons as well as the nucleus-nucleus repulsion.

So a combination of all these interactions gives rise to this equilibrium situation when now the fluorine molecules non covalently interact with each other giving rise to this to this final geometrical arrangement of two fluorine molecules which essentially constitutes a square like arrangement where the four fluorine atoms are at the corners of the square and this particular distance as I told you is twice the covalent radius of the fluorine atoms.

So, this gives us a very clear picture of what is the origin of the Van der Waals radius that now you have two fluorine atoms which actually feel each other's presence. However, if you want to push them further or closely to each other, then there is going to be severe repulsion between the nucleus as well as the inner electrons, inner core electrons and that is going to be a destabilizing situation.

So, this thing was very well understood and the next thing which was important is that what are the factors that decide the Van der Waals radius of an atom.

Now we all know that atomic radii is constant, it is invariant by and large. Now to some extent it depends upon the oxidation state in case of transition metals and in case of lanthanides and actinides by and large. But in case of the main group elements or neutral atoms the atomic radii remain constant. Unlike atomic radii, van der Waals radii is actually very sensitive to the electronic environment. This is the first thing which is very important with respect to the Van der Waals radius.

So it is very sensitive to the electronic environment that is it depends upon the different substituents attached to the atom of interest and the second thing is that it also depends upon the state of aggregation of the substance.

Because if you are going to have a solid then you are going to push the atoms a bit more close because in solids the arrangement is pretty compact the density of solids is high and therefore atoms tend to get a bit closer to each other.

So there are compressive forces which are operational and that can actually modulate or change the Van der Waals radius of the atom in comparison to the same atom being in a liquid state compared to that in a gaseous state. We can look at some examples. So to start with we can look at for example.

For the first case, let us look at xenon atom. The van der Waals radius of xenon atom is 216 picometer, but now if you consider xenon in XeF_4 then the van der Waals radius drops to 170 picometer. So right away you can see that there is a contraction in the size of the xenon atom by 36 picometer.

And this is attributed to the fact that in xenon fluoride it is connected to four highly electronegative fluorine atoms which withdraw electron density towards itself and which introduce a electropositive character on xenon. Now because there is an associated intrinsic electrophilic component on the xenon atom, there is an effective increase in the nuclear charge.

The electrons of the xenon atom are more strongly held now over this xenon-atom. There is a contraction in the size of the atomic radius and that is the reason why this value now drops to 170 picometer. Compared to fluorine if you were to have $XeCl_4$ or $XeBr_4$, the corresponding van der Waals radius is going to be different for the xenon atom. So, the van der Waals radii is very sensitive to the nature of substituents which are present on the atom of interest. Similarly, you can also consider for example, chlorobenzene.

You can take HCl and you can take chlorine gas. Or, you can take, say, for example, dichlorobenzene. So, if now say this is a solid, this is a liquid and this is a gas. Or any chlorinated compound you can consider which exists in the solid state. There you are going to have the van der Waals radius of chlorine is going to be different compared to

that in HCl compared to that in the chlorine gas and so that depends upon the state of aggregation of the substance which also affects the magnitude of the van der Waals radius.

So these are some of the important things we need to keep in mind when we look at van der Waals radius that is we need to keep in mind the effect of the substituents and the state of aggregation because that also plays a very important role in deciding the equilibrium separation between the atoms in the molecules in the state of aggregation of interest and that is going to decide the van der Waals radius of the atom in that particular electronic and steric environment.

So, both electronics and sterics influence the magnitude of the van der Waals radius of the atom of interest. So, with this background let us now go ahead and look at slightly more involved examples. So, there are some advantages of this van der Waals radius but there are also some limitations of the van der Waals radius.

Let us look at that as well. So, to start, limitations of the concept of van der Waals radius. To start with it assumes a spherical atom, it assumes a spherical atom and the fact that atoms are incompressible. Whereas in reality we must keep in mind that atoms are not spherical entities. The electron density can be deformed and the shape of the atom can be made ellipsoidal instead of it being spherical in nature. So in reality atoms can be deformed and the shape can be anisotropic for example, ellipsoidal.

And this has been found to be more realistic in nature that ellipsoidal nature of atoms more accurately describe the shape of atoms particularly in those of crystals and they also tend to get deformed in liquids as well and if you really want to look at this feature we can actually plot the third thing.

If you really want to look at the anisotropy associated with the electron density distribution you can actually plot the electron density distribution and you can see that there is not a single van der Waals radius. Every atom is associated with two different van der Waals radius and we can do that for example by plotting. So, this is essentially the electron density contours.

I will try to make it a bit more clear. So, you can see this is the electron density distribution, the contours. So here you can see that you have one particular contour, this contour in the outermost contour is 0.001 electron per angstrom cube.

So this is the limit of the electron density where essentially you see that beyond this there is no electron density available and then you can go in a perpendicular direction. So, there are two independent directions this is for the chlorine molecule I have plotted the electron density distribution and you can see here that there are two set of radii.

This particular distance from the nucleus to the outer electron density contour is 190 picometer where this is 216 picometer. So right away you can see that the electron density distribution is anisotropic it is not really spherical. Spherical is the average one.

So, there is some deformation of electron density perpendicular and there is some contraction of electron density along the bond axis. There is some contraction of electron density along the bond axis and there is some expansion of electron density perpendicular to the bond axis.

Overall this gives rise to an isotropic distribution of the electron density which again says that a given atom does not have a single van der Waals radius there are two sets of there are two values of van der Waals radii one 190 picometer another is 216 picometer. So, this talks about a non-spherical nature of atoms and this is what is the take home message for this particular lecture that we have learnt about van der Waals radii of atoms.

We have learnt about the factors which affect the magnitude of the van der Waals radii. We also have now seen that there are limitations to the concept of van der Waals radii. In reality, atoms are compressible, can be compressed, they can be deformed and the shape can be anisotropic.

For example, they can be more close to an ellipsoidal distribution and plotting the electron density contour. For example, for the Cl2 molecule tells us that there is compression along the bond axis, whereas there is expansion of the electron density perpendicular to the bond axis. This gives rise to two different values.

For the same atom, the magnitudes being different along the two different directions. The next question now we need to address is that how is the dispersive interactions modeled? So we have looked at the attractive part of the dispersive interactions, the repulsive forces.

The next thing is that we also know that it is a combination of attractive and repulsive forces. Now we need to model this Brownian motion associated with the atoms. For example, say in a gas in a container and how do we model this.

So, in the next lecture we would like to discuss how do we model dispersive interactions to better understand and quantify the energetics and the separations associated with their motion.

Thank you.