

Fundamentals and Applications of Supramolecular Chemistry

Deepak Chopra

Department of Chemistry

IISER Bhopal

Week 01

Lecture 02

W1L2_ Induced Dipole and Dispersive Interactions

So, hello everybody let us continue our discussion further from where we left in the previous lecture. So, in the last lecture we looked at ion-ion interactions which exist between the cation and anion in solids.

We looked at the ion dipole interactions, okay, which exists between anions and molecules which have got a permanent dipole moment, and this plays a very important role, particularly in stabilizing cations and anions in solvent systems.

And then we looked at the next set of chemical forces which are dipole-dipole interactions which are probably responsible, for example, the association of water molecules to form different states of matter whether it is liquid, water or ice.

Or you can have other polar molecules like alcohols, ethyl acetate, ethers. All these compounds which have got permanent dipole moment can actually associate with each other via hydrogen bonding interactions which takes place between the atoms in these polar solvent molecules and are responsible for the formation of the liquid state.

So, and we know that the energetics associated with these interactions drop drastically, when it is the highest for ion-ion, then lower for ion-dipole, and becomes weaker for dipole-dipole interaction.

Therefore, the number of such interactions also needs to go up proportionately so that we have a large number of such non-covalent interactions, supramolecular interactions which stabilize association of these molecules in a particular state of matter, and these play a very vital role.

The next class of chemical forces which we would like to discuss about is the induced dipole interactions. So, in this case, what we are going to do, for example, you may consider now a charged species, and you have got a nonpolar atom or a molecule.

For example you have got a nonpolar molecule. To start with the non-polar molecule

does not have a permanent dipole moment that is μ dipole is equal to zero. Now what is this positive charge going to do? The positive charge to start with creates an electric field.

There is an electric field which is created by this positive charge and this positive charge will now try to polarize the electron density which is associated with the non-polar molecule and this is a very fundamental happening in matter that whenever you have a charged species and you bring in its proximity an uncharged species it will try to polarize the electron density distribution in the molecule.

And we know that molecules contain atoms and atoms are composed of nuclei and electrons and electrons can be the core electrons as well as the valence electrons and now the role of this positive charge is to polarize this electron density such that the negative charges come towards the positive charge and the positive end of the dipole.

So now you see that there is an induced dipole, which is created in this non-polar molecule, and this is called the μ induced dipole. So, this is called a μ induced dipole, and this ability to polarize the electron density depends upon the polarizability of the molecule.

Ok, how susceptible the molecule is to get polarized depends upon the polarizability of the molecule, ok. That means how much will the polarization happen in this non polar molecule depends upon the polarizability of the molecule. If you have got loose electron density, then it is easy to polarize electron density distribution.

If it is associated with tightly packed electron density or electron density which is strongly held by the nuclei, for example, triple bonds or double bonds where the electron density is relatively tightly held by the nuclei, then it will be difficult to polarize these kinds of bonds.

So, the magnitude now of the dipole moment which is going to be induced will depend upon two factors. It will depend upon the polarizing power of the cation, and it will depend upon the polarizability of the molecule that means how facile it is to polarize the electron density distribution in the molecule and that depends upon the quantity which we specify by α .

Handwritten equation:
$$\frac{\text{polarizing power of the cation}}{\text{energy of such an interaction}} = \frac{\alpha}{\frac{1}{2} \frac{q^2 d^2}{r^3}}$$
 The term $\frac{1}{2} \frac{q^2 d^2}{r^3}$ is labeled as "dipole moment" with an arrow pointing to it.

So now the energy of such an interaction, is minus half $Z^2 \alpha e^2 / R^4$, where Z is the charge on the cation, it can be mono positive, di positive, tri positive and α is the polarizability of the molecule, and r is the equilibrium separation between the cation and the molecule.

In other words, it is important to keep in mind how the molecule orients itself so as to maximize the magnitude of the dipole moment which is being induced in the nonpolar molecule.

So this is the origin of an induced dipole when you have a cation and similarly if you have got an anion then also it will polarize the nonpolar molecule, but now it will attract, it will induce a positive charge in its vicinity and the negative charges will be induced further away from the molecule, from the positive charge.

So, you now see there is a separation of these positive and negative charges and there is a μ induced dipole moment. And similarly, we can also have now a dipole, a molecule having a permanent dipole moment, when it is brought in the vicinity of another molecule which does not have a permanent dipole moment, or which is a non-polar molecule whose dipole moment is equal to 0.

That means molecules having a permanent dipole moment when they interact with non-polar molecules, they can now induce a dipole moment in the non-polar molecule also.

So, the origin of inducing a dipole moment in the non-polar molecule is because now you have got a molecule which has got a permanent dipole moment. So, you have, say, $+q$ minus q , this is a molecule which has got a permanent dipole moment, and you bring in its vicinity, say, for example, a non-polar molecule.

So, naturally it will polarize depending upon the polarizability of the molecule it will polarize the electron density distribution. This will induce a negative charge and the positive charge will be induced at the opposite end. In other words now the non polar molecule has got a induced dipole moment.

And once the dipole moment is induced, there is now going to be a favorable association between the dipole and the induced dipole in the non-polar molecule. So, you have a molecule which is called a permanent dipole moment which is approaching a non-polar molecule, it induces a dipole, and now classically we will see that there is an association between this molecule having a permanent dipole with the molecule having an induced dipole moment because of the polarization happening within the non polar molecule which is brought about by the molecule having the permanent dipole moment.

Energy of such an interaction

$$= -\frac{\mu^2 \alpha}{r^6}$$

So this is the origin of induced dipole moment and this behavior is of a classical origin that means we are trying to understand induced dipole moments based on classical electrostatics only. And in this regard what has been proposed is that the energy now of such an interaction, is proposed to be equal to minus mu square alpha by R to the power 6. So if you go to the previous examples the previous classification in case of the ion induced dipole it is R to the power of 4.

Where is when you go to the corresponding dipole induced dipole it now goes as 1 by r to the power of 6. So now you can see that it is even weaker you can see that the association is even weaker and it tends to fall off faster with slight subtle changes in the separation between the molecule having the permanent dipole moment and the non-polar molecule.

So, in this case we can have examples of solvents which are polar and which interact with non-polar solvents. For example, we can have DCM, it's a polar solvent, and we can mix it with hexane, which is a non-polar molecule. Similarly, we can have combination of ethyl acetate, which is a polar molecule having a permanent dipole moment with any non-polar solvent like hexane, heptane.

Then you can have cyclohexane, cyclopentane and you can have any of these hydrocarbons which are non-polar in nature. And which do not have a permanent dipole moment, and these are essentially miscible with the polar solvents primarily because of the dipole induced dipole interactions. And it is to be kept in mind that the nature of these interactions is extremely short that these interactions operate at extremely short distances.

So, if you slightly increase the separation between the non-polar solvent and the polar solvent then the associated interaction by the mechanism of dipole induced dipole, drops to 0, because it is operational at very very short distances and if there is a slight increase in the distance the energy of such an interaction tends to go towards 0. So, it rapidly falls off with distance and these are extremely short-ranged interactions.

So, this is the property of dipole-induced dipole interactions. Now we can now then

further go into these classifications. We can now go to the weakest of interactions. And the weakest of interactions are referred to as dispersive interactions. These are referred to as dispersive interactions and they are also called instantaneous dipole-induced dipole interactions.

And this is going to be a very interesting observation, as these dispersive interactions are present everywhere. Okay and the origin of these dispersive interactions are that they are essentially referred to in the category of instantaneous dipole-induced dipole interactions and let us look at this much more closely.

So, to start with let us consider an atom, which has got a nucleus, and which has got the electrons which are moving around the nucleus. And let us consider, for example a helium atom. Now helium atom has got electronic configuration $1s^2$.

Now when another helium atom comes in its proximity, this is the positive nucleus, and this is the electron associated with helium atom. Now what happens is that it is important to realize that we think that both the electrons classically are shown as paired up. But in reality the electrons are not particles but they are actually quantum mechanical waves.

So you know that electron is associated with a particle like character as well as a wave like character. And at any moment of time, it is not necessary that these electrons are actually maintaining a spherical distribution of the electron density.

On an average you see that the atom is spherical in nature, but it is not necessary that at a given moment of time the spherical nature will be maintained. In fact, you will have momentary imbalances, or we also call it fluctuations in the electron density distribution.

It is not necessary that always you have the spherical electron density distribution because the electrons are quantum mechanical waves and they are free to move about in three dimensional space. Obviously, they are under the control of the nucleus but at any moment it is not necessary that you maintain the spherical distribution.

There is an imbalance, there are fluctuations and because of which you will see that you can have this kind of a picture where the electron is farther away and this is the nucleus.

So, this kind of creates an instantaneous dipole. This creates an instantaneous dipole within the molecule because now you see there is a momentary imbalance or fluctuation, and you can see that the nucleus is towards one end and the electron is more towards the other end and this instantaneous dipole can now induce can now induce a dipole in the neighboring helium atom with which it is interacting.

So now what it will do is that it will polarize now polarize the electron density distribution on the helium atom with which it is interacting and as a result of which you will now see that this electron and this is the nucleus, and these will now interact with each other. So there will be an interaction between the electron density distribution of one helium atom with the nucleus portion of the other atom. And there is going to be a kind of molecular association which is going to happen between two helium atoms.

So to start with we have heard that helium atoms are you know rare gas atoms, they have you know closed electronic shell configuration, they are spherical in nature but in reality when you bring in helium atoms close to each other there are instantaneous dipoles which are created and these are the fluctuations in the system which actually induce a dipole moment in the other helium atom.

And then there is a weak intermolecular association between the helium atoms, and this is more quantum mechanical in origin to start with because we are talking about the wave nature of the electrons, but this actually creates the necessary driving force for the nucleus of one helium atom to interact with the electron density of the other helium atom because it has induced a dipole in the other helium atom.

And this gives rise to the dispersive interactions which we have talked here which is a case of instantaneous dipole induced dipole interactions. Also, it is important to keep in mind this another model which is proposed here. This is one way of looking at the entire picture.

Now, another way of looking at this dispersive interaction is that when you have two helium atoms or any two rare gas atoms like krypton, xenon, radon, they come close to each other then the system always tries to lower the energy of the system. They always try to have favorable interactions, and, in this regard, they want to maximize the nucleus-electron attraction and minimize the electron-electron repulsion.

So, whenever you have two spherical atoms coming close to each other we would like to maximize the nucleus interacting with the electron and minimizing the electron-electron repulsion and this is what governs bonding phenomena.

These are the fundamental forces in nature which govern atom-atom recognition so if you talk about atomic level interactions you would like to maximize, the nucleus electron attractions, and minimize the electron-electron repulsions. This is a very very important statement here because in this regard this is how matter interacts that you will see that it will try to synchronize.

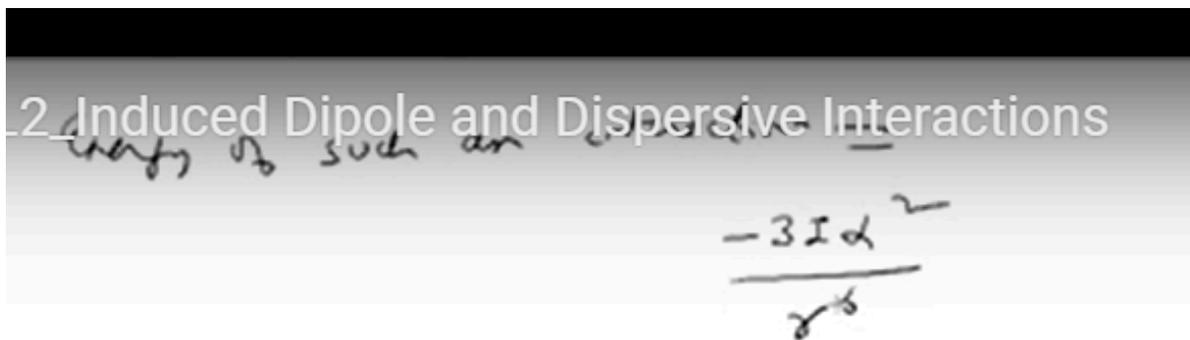
So, the system will try to synchronize the electronic motion in such a way, that you will maximize the nucleus-electron attractions and minimize the electron repulsions. And

again, these chemical forces which operate between the two atoms will be only operational at very very short distances and the moment you slightly increase the separation these forces cease to exist.

So again, I would like to reiterate the fact that now we are going to the spectrum of the weakest interactions. So, we started with the ion-ion chemical forces which were the strongest where the interacting entities are always close to each other and the affinity is the highest and we have gone from that situation to a very wobbly situation where electron density is kind of delocalized. There are momentary imbalances but still even for this kind of a system like rare gas atoms you will have the atoms which interact with each other.

So they actually give rise to these short range interactions. These give rise to the short range interactions and they are extremely weak. But the thing is that when you would like now you would like to actually have a state of matter say which essentially involves non-polar molecules. So, when you have non-polar molecules now you can extend this concept to non-polar molecules because they do not have any dipole moment okay. So, there can be an instantaneous dipole, which can now induce a dipole moment in another molecule.

So you have these fluctuations in the system. The electron density distribution tends to have momentary imbalances that creates a dipole moment in the nonpolar molecule which tends to now attract or interact with another nonpolar molecule. And in this way this process continues and that can lead to favorable association of molecules.



And in this regard what has been proposed is that the energy of such an interaction is minus $3I\alpha^2$ by r to the power of 6. So, we need to actually create the dipole moment in the molecule that is the instantaneous dipole is being created and the ability to create a charge separation is actually reflected by the magnitude of the ionization energy of the species.

And once this dipole is created, the instantaneous dipole, it will be able to polarize the electron density distribution in the other molecule which is a measure of the polarizability of the molecule which we call as α .

So the ionization energy of the species is I , α is the polarizability of the molecule and R is the equilibrium separation between the two molecules and this gives a magnitude of the energy of such an interaction. And we see that it is a short range because they are very sensitive to $1/r^6$ and what we also realize is that when you have an ensemble of non-polar molecules then these non-polar molecules can get associated well.

For example, you have all the non-polar molecules, like all the hydrocarbons, they do exist as liquids. Different kind of oils they exist as liquids because they do not have any permanent dipole moment.

So, the origin of this molecular association via these non-covalent interactions to give rise to this liquid state of matter is primarily aided by these dispersive interactions and the magnitude of these dispersive interactions depends upon the ionization energy, the α , polarizability of the molecule. So directly we can see that the energy is proportional to α^2 , that it is proportional to the polarizable electrons, and the number of polarizable electrons depends upon the molecular weight.

So, if it increases rapidly with increasing molecular weight and more accurately it increases with molecular volume. So now if you have got larger molecular weight or more molecular volume, that means more electron density available which can be polarized, and that essentially directly correlates with the energy of such an interaction.

So that is the reason why if you have large non-polar molecules with more molecular weight or more molecular volume, you can polarize this electron density.

First you have an instantaneous dipole because of the imbalance, and then you induce the dipole, and then there's extensive association keeping in mind that these are extremely short range interactions but they are there is a cooperativity which operates here because individual interactions are weak but collectively the entire ensemble which is formed by this collective set of interactions are sufficiently stabilizing to again stabilize this association of molecules in that cluster giving rise to that particular state of matter.

And this is something which is present everywhere and this is something which is ubiquitous and plays a very important role in different events of supramolecular recognition which will be now investigating over a period of time.

So now with this particular lecture we have an idea about the different types of chemical forces which are present now between atoms and between molecules and we will be now

taking up the more specific concepts related to these intermolecular associations between the atoms from the next lecture.

Thank you very much.