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

W1L1_Chemical Forces, Ion-Ion, Ion-Dipole and Dipole-Dipole Interactions

Hello everybody, today we are going to start discussion on the course of supramolecular chemistry, where we will be discussing about the principles and applications of supramolecular chemistry.

In the first part of the course, we will be discussing about the concepts which are relevant to supramolecular chemistry and we will be also looking at applications of this very interesting field in different areas of chemistry, biology and materials science and engineering.

And this course will also extend towards different states of matter, for example, in solution, in gas phase as well as in the liquid state. And there will be very interesting diverse array of topics which will be covered in this particular course.

And so to start with, we will now look at the essential concepts which are core towards the understanding of supramolecular chemistry. Now, to start with we are all aware about matter, we are all aware of the fact that matter is made up of atoms and molecules because atoms combine to give molecules and then molecules can actually interact with each other and give rise to different states of matter.

And depending upon the extent of aggregation, we can have, you know, the interaction between the molecules is minimal. For example, the available space is large, then it gives rise to the gaseous state. If the molecules interact appreciably well, then they give rise to the liquid state. And then if the molecules interact very strongly with each other and pack in well ordered array, it gives rise to the solid state.

And the solid state can again have a crystalline nature as well as amorphous nature depending upon the long range or the short-range nature of the interactions which form the solid state or the aggregation of molecules in the solid.

And to start with we will first look at the, so the first lecture here will try to address we will try to address chemical forces which are very important when it comes to molecular recognition in matter. And to start with we are all aware of very simple solids for example sodium chloride, potassium chloride, magnesium chloride, barium sulphate. This gives rise to the class of ionic solids. Then we have also got covalently bonded solids.

For example, we have got naphthalene, we have got anthracene and even we can form this kind of a fused hydrocarbons and these essentially are covalent in nature, these are covalent solids.

And when these molecules interact with each other, for example, we noted anthracene as as well as naphthalene, these are solids at room temperature. And these are essentially covalent in nature. And then we can also have metal organic complexes, where a metal ion in a particular oxidation state interacts covalently with the ligand molecules to form molecular complexes. And these can also exist in a solution in the liquid state as well as in the solid state.

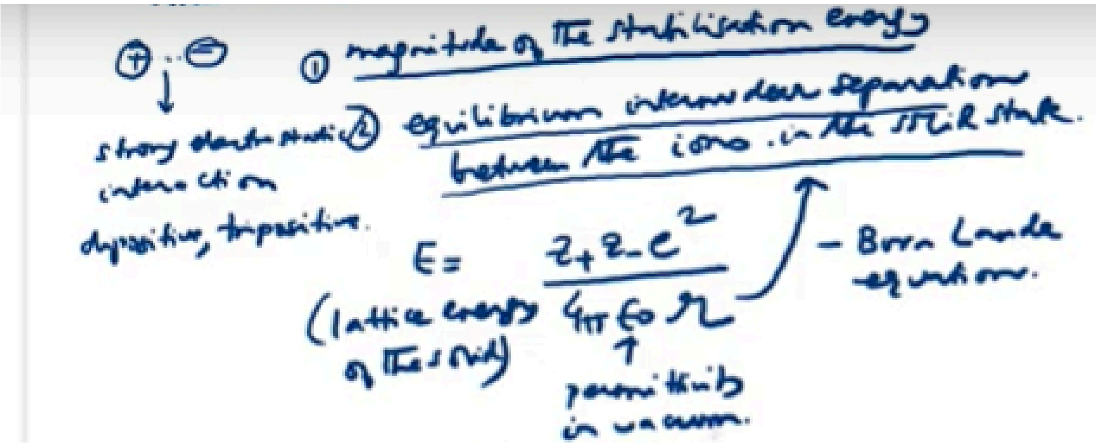
So, we also have these kind of metal organic complexes. We also have organometallic complexes, we can have proteins, we can have viruses, and many molecules of biological origin. So it is very important to understand what are the chemical forces which actually are responsible for the aggregation of matter. And to start we will first look at the strongest of chemical forces which are responsible and then we will go to the weakest of forces. So there is a spectrum, chemical forces there is a spectrum of interactions.

We have the strongest, for example, the ionic bonding and we can go to the weakest, which is the non-covalent bonding. So, let us start by looking at these chemical forces one by one. So, to start with we will look at, we will look at first the strongest forces, we look at ion-ion interactions and in this regard we have all looked at ionic bonding, which essentially exists between for example, say a cationic species and an anionic species.

So, there is a strong electrostatic interaction, which exist between the cation and the anion. And this can be a monopositive cation, monopositive anion.

This can be a dipositive. This can be a tripositive cation and correspondingly you can have the negative, di negative and the tri negative anions as well and you can have metals in even higher oxidation states which can interact with anions as well.

So, the primary force which holds the ions in place is strongly electrostatic in origin and what is important to understand is when you consider two ionic species interacting with each other, what is the magnitude of the stabilization energy and what is the equilibrium inter nuclear separation between the ions in the solid state.



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① magnitude of the stabilization energy

② equilibrium internuclear separation between the ions in the solid state.

strong electrostatic interaction

dipositive, tripositive.

$$E = \frac{Z_+ Z_- e^2}{4\pi\epsilon_0 r}$$

(lattice energy of the solid)

permittivity in vacuum.

— Born Lande equation.

Because ionic bonding primarily leads to the formation of solids, so it is important to see what is the equilibrium internuclear separation between the ions in the solid state. And this particular theory of ionic bonding has been well established in the literature, where it has been shown that the energy of stabilization which we also refer to as the lattice energy of the solid is actually given by the product of the magnitude of the charges Z plus or Z minus on the cation and the anion square the electronic charge.

This is divided by 4 pai epsilon 0 into R and epsilon 0 here is the permittivity in vacuum, r is the equilibrium inter nucleus separation and Z plus Z minus is the magnitude of the charge on the cation and the anion respectively. So, this is also referred to as the Born-Lande equation and in this particular expression we are actually neglecting the repulsive forces and the zero point energy as well.

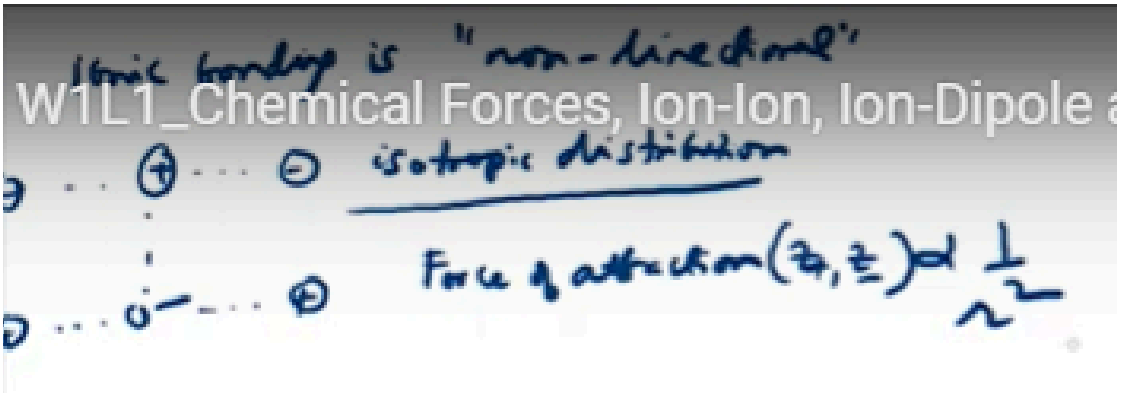
So we also need to keep in mind that when two oppositely charged nuclei come close to each other or two oppositely charged hands come close to each other, there is also a repulsion between the nuclei as well as the electrons of the inner shell. So that as of now has been neglected. We are only considering the electrostatic contribution towards the overall stabilization.

And in this regard, I can consider one particular example, for example, in the case of lithium fluoride, the E calculated is minus 665 kilo joule per mole, where is the experimental value of the lattice energy is 765 kilo joule per mole.

And it has also been observed that as the size of the ion increases, there is a decrease in the magnitude of the lattice energy as well. So, smaller is the size of the cation, more is the energetic stabilization, larger is the size of the cation, the energy drops substantially.

And another thing to keep in mind is that these ionic bonding, is non directional. In other words, because you have cations surrounded by anions and then anions surrounded by cations.

This is a isotropic distribution. That means a given cation is surrounded by a given set of anions and anion in turn is also surrounded by a similar environment of cations. So, this is an isotropic distribution and therefore ionic bonding is non-directional in nature. And so this is what essentially constitutes ionic bonding and it is also important to look at the force of attraction.



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Ionic bonding is "non-directional"

isotropic distribution

Force of attraction $(Z_+, Z_-) \propto \frac{1}{r^2}$

The force of attraction between the ions given a set of ions Z plus and Z minus is proportional to 1 by r square because force is essentially the first derivative of E with respect to distance. So, force of attraction is inversely proportional to 1 by r square.

So, and I have already given you the examples on ionic bonding. The next classification of chemical forces which comes after ionic bonding is the ion dipole forces. Now, this is a very interesting array of chemical forces where you have an anion. For example, you have got say a fluoride ion or you have a chloride ion or you can say magnesium 2 plus cation and this is extensively solvated, for example by the water molecules.

Say this is hydrogen and then this is oxygen and this is hydrogen. So you have this kind of a supramolecular association wherein an anion is solvated by the water molecules and this actually constitutes the first coordination shell but this coordination is primarily hydrogen bonding in nature.

You can see that there are OH...F minus hydrogen bonds and hydrogen bond is essentially a class of dipole-dipole interactions which we will discuss next in case of dipole-dipole interactions. But as of now we can see very clearly that the OH polar bond interacts with the fluoride ion and it extensively solvates the fluoride ion as you can see here and you have these ion-dipole interactions.

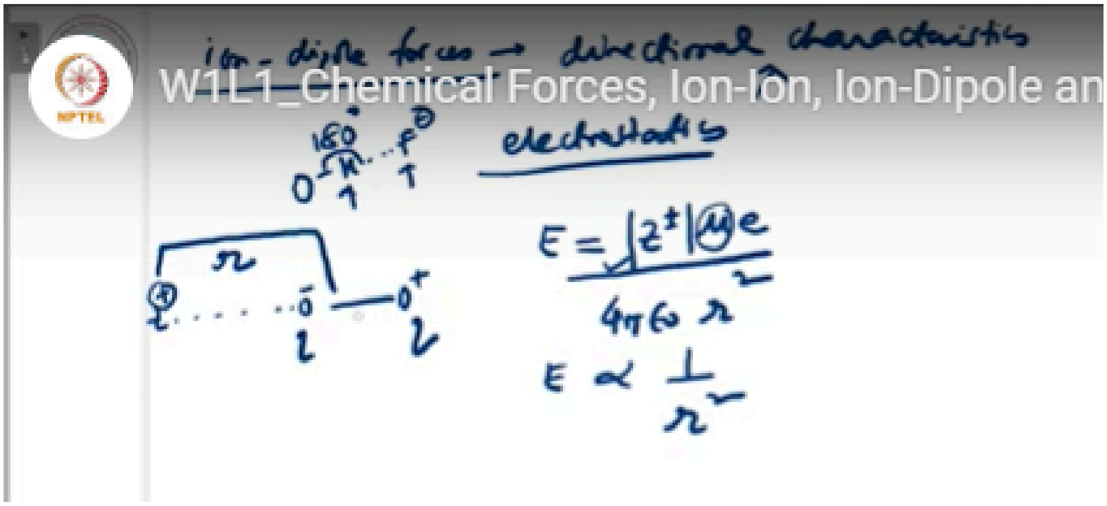
Similar thing can also happen with, for example, you can add a polar solvent like acetonitrile. And acetonitrile can also solvate, for example ionic species, depending upon the fact whether they dissolve in acetonitrile or not. Similarly you can also have cationic species like magnesium 2 plus which is solvated by the water molecules.

So you can look at the coordination of the oxygen lone pair with the magnesium center and this gives rise to complexes of magnesium 2 plus and you can also have similar complexes which have got different coordination number. For example, you can have nickel hexa aqua 2 plus, you can have cobalt hexa aqua 2 plus, you can have iron hexa aqua 2 plus.

So, in these particular examples you will see that essentially an ion, either a cation or an iron, interacts with the ligand environment, and is extensively solvated either by non-covalent interactions or it can also form a coordinate covalent complex constituting the ion dipole forces.

And in this regard, let us see now that the ion dipole forces unlike the ion-ion forces have got directional characteristics have got directional characteristics. In other words that the OH for example will interact with the fluoride ion such that it can maximize the interaction of the proton with the negatively charged fluoride ion.

And, more is the directionality, more is going to be the strength of the association. For example, in an idle environment, this angle at the hydrogen center should be 180 degree and that will constitute a linear and highly directional hydrogen bond. So, although the origin is electrostatics in nature, and we see that it involves an anion yet the ion dipole forces have got directional characteristics.



And we can also consider this in the following way, so you have a dipole say having charge q, charge plus q and minus q and you bring in its vicinity a cation and r is the equilibrium separation between the dipole and the cation. And then you can calculate the magnitude of the stabilization energy as z plus minus magnitude into magnitude of the dipole moment into the electronic charge divided by 4 pai epsilon 0 r square.

So, here you can see that the energy of the ion dipole interaction is proportional to the magnitude of the charge that is z plus or z minus depending upon whether it is a cation or anion.

It is also proportional to the magnitude of the dipole moment and depending upon you know, whether it is a cation or anion the corresponding negative or positive end of the dipole will interact with that species and r is the separation.

And energy falls faster, it falls as the square of the separation between the ion and the dipole. So, obviously these are much weaker in comparison compared to the ion-ion forces. Because they are weaker you need to have more association of these dipoles.

So, that the overall cluster of solvent molecules around the anion or cation stabilizes the overall association. So, now that we know that the individual magnitude of the ion dipole forces is weaker compared to ion-ion interactions, we need to overall enhance the overall energetic stabilization and that is possible by having multiple such ion dipole interactions between the cation and the dipolar ends.

So, that you can overall stabilize this association of molecules and that is what is the driving force for extensive solute-solvent interactions which stabilizes the overall supramolecular assembly. So, following the ion-dipole interactions, we now go to the next classification that is we will now look at dipole-dipole interactions where now we have got two individual dipole moments, say for example, we have got HCl molecule or HF molecule.

Or we can have lithium fluoride which has got a permanent dipole moment and the origin of the permanent dipole moment is because there is a electronegativity difference, between the hydrogen and the chlorine, the two atoms which make up the bond.

There is a difference in electronegativity and hence in the ground state there is a dipole moment associated with the molecule and HF for example is a liquid or HF is a liquid, lithium fluoride is a solid and this depends upon the association between the individual dipoles in the solid state.

So, what is important is that the arrangement of the dipoles is very important. So, when you have a dipole, it can actually arrange in two possible ways. Let us look at it. Let us consider this to be a dipole.

So, you can have a head to tail arrangement of these dipole interactions. So, this is the head to tail arrangement of dipoles. This is a parallel arrangement. And similarly, you can also have antiparallel arrangement of dipoles. So, you can have parallel arrangement, you can have antiparallel arrangement of dipoles.

For example, let us we can take more examples as well, you can have for example, acetone. So this is an organic solvent and it has got a dipole moment associated with it. So you can have an arrangement where the two dipoles essentially arrange in an antiparallel fashion, such that in this particular dimer there exist here a center of inversion.

So, the overall dipole moment is equal to 0 because there is a cancellation of the individual dipole moments. So, the overall dipole moment is 0 and you can also have another arrangement of these dipoles.

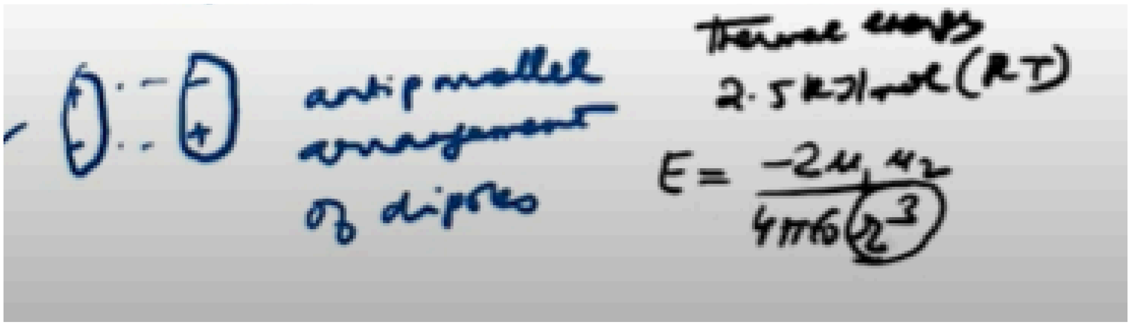
For example, you can have the carbonyl group interacting with the lone pair region, so this is the non-covalent, I can draw it in a different color this is the non-covalent region. So, this is the non-covalent region where you can see the oxygen a relatively electron rich region interacts with a relatively electron deficient region.

And there is a certain separation between these two atoms and depending upon the approach of the lone pair towards the carbon center, this we will discuss later to what extent this approach takes place.

However, in this particular arrangement, this is called a T shaped arrangement. This is a T shaped arrangement, where you can see that overall one acetone molecule interacting with another acetone molecule. And what is important is to keep these arrangements in place via dipole-dipole interactions ok.

And please keep in mind that in a liquid you also have for example, when you have HCl or HF you need to have the dipoles which are arranged in a particular way. But it is also important to keep in mind that the thermal energy which is around 2.5 kilo joule per mole, which is essentially of the magnitude of RT, around 0.5 kilocal per mole, is responsible for disrupting of the molecular arrangement because it tends to randomize the dipolar orientation because of the thermal motion associated with it and that can also minimize the dipole-dipole interactions and reduce the overall stabilization.

So, one, there are two factors which operate here, one is you would like to maximize the dipole-dipole interactions between the molecules and the other hand you have these thermal energies which are trying to randomize the dipolar orientation and the overall arrangement is a balance between these two factors.



And then what has been proposed is the magnitude of the energy E is calculated to be 2 mu 1 mu 2 by 4 pi epsilon 0 r cube, where you can see now the energy of stabilization is proportional to the magnitude of the individual dipole moments mu 1 and mu 2, if you have two different molecules.

If you have the same molecule, it is simply the product of the dipole moment square and it is inversely proportional to R cube. So, it is much more sensitive to distance and it drops off dramatically with slight changes in the equilibrium separation between the ion and the dipole. And this is what is responsible for the association of a polar liquids. For example, we looked at HCl and HF as well as acetone or acetonitrile, ethyl acetate, tetrahydrofuran, ether, alcohols.

These are the dipolar-dipolar interactions which are responsible for the aggregation of liquids. So, with this we would like to complete the current discussion. We shall continue further on chemical forces in the next lecture as well. Thank you.