

**Interpretative Spectroscopy**  
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**Lecture 30**  
**Introduction to IR Spectroscopy-2**

Hello everyone, it is with pleasure I welcome you all once again to MSB lecture series on interpretative spectroscopy. In my last lecture I started discussion on IR spectroscopy and I was discussing about some of the fundamentals concerned with IR spectroscopy. Let me continue from where I had stopped, I am repeating again. The energies of photon associated with the infrared region are not large enough to excite electrons from the one level to another, but the energy associated is quite adequate to induce vibrational excitations of covalently bonded atoms and groups. If you recall, the covalent bonds present in the molecules are not rigid sticks or rods holding two atoms together, they are more like stiff springs that can be rotated provided they are bonded with single bond or they can be stretched or they can be bent or they can be scissored. So, all kind of things can happen when energy is applied in the infrared region for these molecules.

So, these different types of vibrational motions are characteristic to a molecule component atoms. That means, all organic and inorganic compounds will absorb infrared radiation that corresponds in energy to these vibrations and infrared spectrometers allow chemists to obtain absorption spectra of components that are unique reflections of their molecular structure, showing all kinds of these vibrational motions. In my last lecture, I discussed in detail about triatomic bent molecules like water and also, we looked into triatomic linear molecules like carbon dioxide and also, we looked into possible vibrational motions for CH<sub>2</sub> in a molecule.

So, now let us continue. Imagine a diatomic molecule to two balls of mass **m** connected by a spring with a force constant **F** that can be calculated by the following equation. Hooke's law. If you recall that can give you vital information about what we are talking about.

So, here that can be given in the form of  $\nu$  equal to  $1$  over  $\pi$  into square root of  $F$  over  $2m$ . The vibrational motions and frequencies of a structure containing several balls of different masses connected by springs with different force constants can be studied using classical mechanics which can be correlated with the motion of a molecule. If you understand classical mechanics studied from physics, understanding and extrapolating that to chemical molecules would be rather simple.

So, that we can understand the relationship of the stretching frequency with respect to force constant and the mass of the two constituent atoms in the form of reduced mass. The simplest way to study polyatomic molecules is by treating various parts as diatomic species. That means at a given time, if several atoms are there and several bonds are there understanding, would be rather difficult. So, what we should do is, instead of making an attempt to study a polyatomic molecule, we take a component as a diatomic species, every segment, and then we can try to understand, so that the interpretation would be rather easy.

This works well when one of the two atoms is not bonded to any other atom in the molecule. We will have a terminal atom, other one is bonded to another. In that case, it helps very well. For example, if you take C-H, C may be connected to something else, but C-H is terminal. Similarly, In case of methyl amine, we can consider C-H or N-H, both have a terminal atom and, similarly we can consider C-H and O-H in case of acetone. So, something like this. So, we can always simplify for better understanding of all these facts that are governed by quantum mechanical rules.

Now using Hooke's law, the stretching frequency of a diatomic molecule can be readily calculated. So, here the equation is simplified and more useful, it is not very complicated. It is very easy to remember  $\bar{\nu}$  that is wave number equal to  $130.3$  is a constant.

It is obtained after simplifying into square root of  $f$  over  $\mu$  ( $\sqrt{\frac{f}{\mu}}$ ), where  $F$  is the force constant and  $\mu$  is the reduced mass. Of course, reduced mass, how to determine, we know if a diatomic molecule having two atoms of mass  $m_1$  and  $m_2$  then  $\mu$  will be  $m_1$  into  $m_2$  divided

by  $m_1$  plus  $m_2$  [ $\mu = \frac{m_1 m_2}{m_1 + m_2}$ ], and at the end, I would show you lot of examples, and how to determine for a given molecule either force constant or stretching frequency. So, one of those things can be conveniently measured and by simply determining the reduced mass.

Reduced mass, if you know the atomic weight, determining or calculating reduced mass would be very easy. Now I have given some here. You can just look into it different groups, I have considered and also the corresponding mass reduced mass also in atomic mass units. I have given here and now force constant in Newton per meter is also given here for all these bonds I have shown on the left side and also the corresponding frequency also shown here stretching frequencies for these things are shown here. So, by simply using the equation. I showed you  $\nu = \frac{1}{2\pi} \sqrt{\frac{F}{\mu}}$  equals 130.3 into square root of F over mu. So, you can use that one and you can verify whether all these things are not it says you can consider as a practicing exercise and you can calculate for all.

For example, reduced mass is already given 700 is already given force constant you should be able to determine this one or you assume this is given and this is given this not given and then you can calculate. So, you practice with all those things to make yourself familiar with determining force constant. Later I will show you from force constant you can also estimate the bond distance that is very interesting before you get data from x ray bond angles and bond distances at least bond strength you can determine simply by looking into some of these parameters. F for elements in the periodic table increases from the left to right across first two rows, so as the vibration frequencies. The trends also you can see here, the stretching frequency for elements in the periodic table increase from left to right across first two rows so as the vibration frequencies.

Some of these trends are also very useful in remembering or understanding or comparing the data when we have two or three molecules having different groups on adjacent atoms. Now the knowledge of symmetry is very helpful to understand the factors influencing the intensities of IR bands symmetry and find point groups and character table comes in group theory. I am sure there are good courses and books to make yourself familiar, if you want to dig deep into understanding IR spectroscopy, but as far as interpretation is concerned, whatever I am dealing in this course is quite adequate. To observe vibrations in IR, it must

be antisymmetric with respect to the molecular center of symmetry, that is important to observe vibrations in IR spectroscopy. It must be antisymmetric with respect to the molecular center of symmetry, because this produces an oscillating dipole moment that can interact with the electric field of the radiation.

If the vibrations are symmetric with respect to the molecular symmetry, then the vibrations are IR inactive. One should remember, if the vibrations are symmetric with respect to the molecular symmetry, then the vibrations are IR inactive and you do not see any bands corresponding to that one. For example, if you consider a C-C double bond, stretching vibration is not seen in IR and only the asymmetric modes are observed at 895 and 1200 centimeter minus 1 ( $\text{cm}^{-1}$ ). For example, if you consider this example here dichloroethylene, center of symmetry is there, if you consider symmetric and asymmetric stretching, symmetric stretching is not observed on the other hand, asymmetric is observed, we see two bands at 895 and 1200 centimeter minus 1 ( $\text{cm}^{-1}$ ).

So, certain things one should remember. Now, let us consider two molecules having acetylene, alkyne groups in it. One is methyl acetylene and the other one is dimethyl acetylene. In case of methyl acetylene, C triple bond C is observed at 2150 centimeter minus 1 ( $\text{cm}^{-1}$ ), whereas this one is inactive for the same reason I said. If you consider  $\text{CH}_2$  vibrations, wagging is there and twisting is there and then the twisting mode produces no change in dipole moment, and hence IR inactive in symmetric molecules. Again, in symmetric molecules, you do not see these things because the twisting mode produces no change in the dipole moment and hence IR inactive in symmetrical molecules.

Few things one should remember. To make you familiar with what is symmetric stretching how it looks, I have put here these cartoons. Radial the symmetric in symmetric stretching you can see here it is moving in this direction and then anti symmetric you can understand very nicely simultaneous moving one is coming in one is going out and then whereas in symmetric both are projecting out and then scissoring you can clearly see the direction this is scissoring and then this is rocking in moving in the same direction. So, this is rocking and this is wagging and then this is twisting here twisting would be something like this wagging is something like this and twisting is something like this a screw action.

So, these are the fundamental stretch one can see: symmetric and antisymmetric symmetric stretching, antisymmetric in radial motion, and in latitudinal you can see scissoring and rocking, and longitudinal it is wagging and twisting. So, six types of vibrational modes we come across in most of the molecules. Now let us look into few more aspects. Let us consider coupled interactions. What is coupled interactions? Consider two independent, but identical diatomic molecules that vibrate with identical frequencies. Consider two independent, but identical diatomic molecules that vibrate with identical frequencies. So, when they are part of a molecule, they are mechanically coupled, since the vibrations of any of these groups affect the other group. For example, consider acetylene and then you consider diacetylene, I have shown here, but when they are sufficiently separated by distance little or no coupling are observed and the two frequencies will be similar if they are farther from each other.

So, they would be looking identical in acetylene they are strongly coupled compared to diacetylene. So, for example, if you consider here  $\nu_s$  3330 centimeter minus 1 ( $\text{cm}^{-1}$ ), and  $\nu_a$  3295 centimeter minus 1 ( $\text{cm}^{-1}$ ), and  $\Delta\nu$  the separation is about 35 centimeter minus 1 ( $\text{cm}^{-1}$ ), and  $\Delta\nu$  3330 and 3295, the difference between symmetric and asymmetric stretch is 35 centimeter minus 1 ( $\text{cm}^{-1}$ ). Then when you look into here with acetylene here. Symmetric one is 3375 and asymmetric is 3280 and the difference between symmetric and asymmetric is 95 centimeter minus 1 ( $\text{cm}^{-1}$ ). Now, you can understand clearly, but when they are sufficiently separated by distance little or no coupling are observed and the two frequencies will be identical 3332, the difference is very marginal, but when they are farther what happens, they are independent, look identical, but when they are coupled, they have an influence here that can be clearly seen here. Now, let us consider another example to evaluate the coupled interaction. First, we consider acetylene and diacetylene.

Now, we consider two more molecules to have a clear idea about whatever we discussed. Again we consider here, they are coupled, but they are separated by a single C-C bond. Now, if you look into stretching frequency, symmetric stretching is 1600 centimeter minus 1 ( $\text{cm}^{-1}$ ), and asymmetric stretching is 1640. Always asymmetric will be having larger value

compared to symmetric one that you should remember and the difference between symmetric and asymmetric is 40 centimeter minus 1 in case of acetylene, besides over 35 centimeter minus 1 ( $\text{cm}^{-1}$ ). Now, if you consider this allene here, and  $\nu_s$  is 1070 centimeter minus 1 ( $\text{cm}^{-1}$ ). This is symmetric stretching and asymmetric stretching, it is 1960 centimeter minus 1 ( $\text{cm}^{-1}$ ), and the separation is larger 890 centimeter minus 1 ( $\text{cm}^{-1}$ ). This confirms what we concluded about coupled interactions with no strong coupling. The IR C=C band is expected to be around 1600 centimeter minus 1 ( $\text{cm}^{-1}$ ). Another point to remember is: asymmetric vibrational mode is higher in frequency and the symmetrical one is lower in frequency always irrespective of whether they are coupled or not. What one should remember is symmetric vibrational mode is lower in frequency compared to the asymmetric vibrational mode. The values are reflected here. Little bit more information about coupled interactions.

Vibrations of two atomic groups are not coupled unless the individual frequencies are identical. One should remember for example, we have a double bond and a triple bond they are not going to be coupled. So, vibrations of two molecules are not coupled unless the individual frequencies are identical. The coupling is stronger when the frequencies are the same. Coupling is stronger, when the frequencies are the same. Strong coupling requires a common atom between the groups. So, when the vibrations are orthogonal to each other, coupling is negligible. Even if it is observed, it is very weak and it can be neglected. So, bending and stretching vibrations can couple provided the stretching bond form one side of the changing angle there is another point.

So, bending and stretching vibrations can couple provided the stretching bond forms one side of the changing angle. Now, let us look into few more terms, that is Fermi resonance, overtone and combination. What are those? Let us look into one more term called Fermi resonance. Fermi resonance is a special case of mechanical coupling which results from a fundamental vibration with an overtone or combination. Now, I would tell you what is overtone and what is combination fundamental IR transitions or absorptions take place between the ground state vibrational level  $E_0$  and the first excited levels. For example, I can say  $E_1$  equal to  $\Delta E^*$  equal to  $E_1^* - E_0$  ( $E_1^* - E_0$ ) that is equal to  $h\nu^*$  and

here  $E_1$  equal to  $\Delta E^{**}$  equal to  $E_1^{**}$  minus  $E_0$  ( $E_1^{**}-E_0$ ) equals  $h\nu^{**}$ .  $E_1: \Delta E^* = E_1^* - E_0 = h\nu^*$ ;  
 $E_1: \Delta E^{**} = E_1^{**} - E_0 = h\nu^{**}$

What are those  $\nu^*$  and  $\nu^{**}$ ?  $\nu^*$  and  $\nu^{**}$  are different vibrational frequencies. That means a transition from ground state  $E_0$  to a higher energy level  $E_2$  is known as overtone, whereas a transition from  $E_1$  to  $E_1^{**}$  is known as combination. One should know the difference between overtone and combination. A transition from ground state  $E_0$  to a higher energy level  $E_2$  is known as overtone, whereas a transition from  $E_1^*$  to  $E_1^{**}$  is known as combination within. So, overtones and combinations are forbidden by simple harmonic oscillatory theory of molecular vibrations but they become weakly allowed when unharmonicity is taken into consideration. So, now let us look into this example. Here, I have displayed IR spectrum of benzyl chloride.

So, normally an overtone or combinations band is very weak, but when Fermi resonance occurs, sharing of intensity takes place and as a result, it can become quite strong. So, one such example I have shown here is for benzyl chloride. You focus your attention to CO stretching frequency since it has one CO one can anticipate only one single stretching frequency for CO group here, but in case of benzyl chloride, two bands are observed at 720 and 760 centimeter minus 1 ( $\text{cm}^{-1}$ ). So, they are called Fermi doublets. The spectrum may suggest the presence of two carbonate groups in the molecule is misnomer.

So, one should not confuse that they have two compounds in it. The lower frequency is due to the overtone of the CH out of plane bending mode at 865 centimeter minus 1 in Fermi resonance with the CO mode. So, the frequencies 1760 and  $1865 \times 2 = 1730$  are very close in frequency. That means basically if you multiply by this one into two you get 1730. So, that means they are very close in frequency 1720 is what we are getting and when you take the combination, we get 1730.

Sometime why that happens, because CH out of plane. Overtone of the CH out of plane, here we get two frequencies. So, now let us look into hydrogen bonding. How one can gauge hydrogen bonding using IR spectroscopy as a tool to know to what extent hydrogen bonding is there, whether weak hydrogen bonding is there, whether strong hydrogen

bonding is there, that information of course, can come very nicely from IR spectroscopy and also NMR spectroscopy, but nevertheless IR can also give you some hint about the possible hydrogen bonding in molecules. Hydrogen bonding occurs between hydrogen atom bonded to an electronegative element such as oxygen or nitrogen to another atom via its bonding or non-bonding electrons that can overlap the S orbital of hydrogen or oxygen or nitrogen lone pairs. That means basically if you consider O here consider water and if you take this can interact with.

So, this is typical hydrogen bonding, this can happen between hydrogen atom attached to an electronegative element and also it has in within the molecule or in neighboring molecules we have another electronegative atom. So, they can nicely overlap through this 1S orbital. Hydrogen bonding will be stronger when the bond formed are linear. So, it should be linear like this, 180 degree ( $180^\circ$ ) or close to 180 degree you can assume that the bonds are very stronger that can also be reflected from the stretching frequency. How to assess the presence of hydrogen bonding using IR? One thing is broadening of the band can be seen and also increase in intensity can be observed and also shift to lower wave numbers.

So, these three if you gauge you should be able to tell yes there is hydrogen bonding in the given molecule. This can be directly assessed and understood from IR data. One is broadening of the band and increase in intensity and shift to lower wave numbers. So, hydrogen bond involved OH and NH bonds show stretching bands between 2500 to 3000 centimeter minus 1 ( $\text{cm}^{-1}$ ) lower than those without hydrogen bonding. The change in the stretching frequency is a measure of the strength of the hydrogen bonding, which is in the order of 4 to 6 kilo calories per mole ( $\text{kcal}\cdot\text{mol}^{-1}$ ).

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So, let us learn more and also start looking into data and illustration or interpretation in my next lecture until then have an excellent time. Thank you