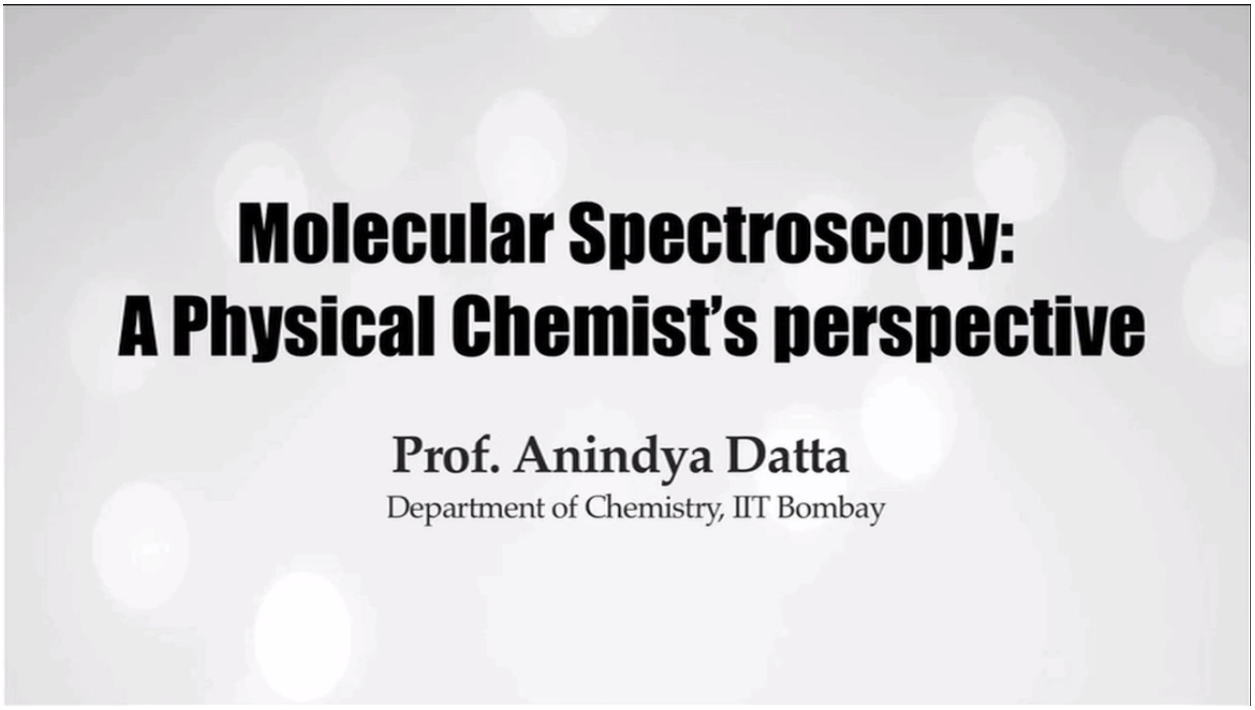

Molecular Spectroscopy: A Physical Chemist's perspective

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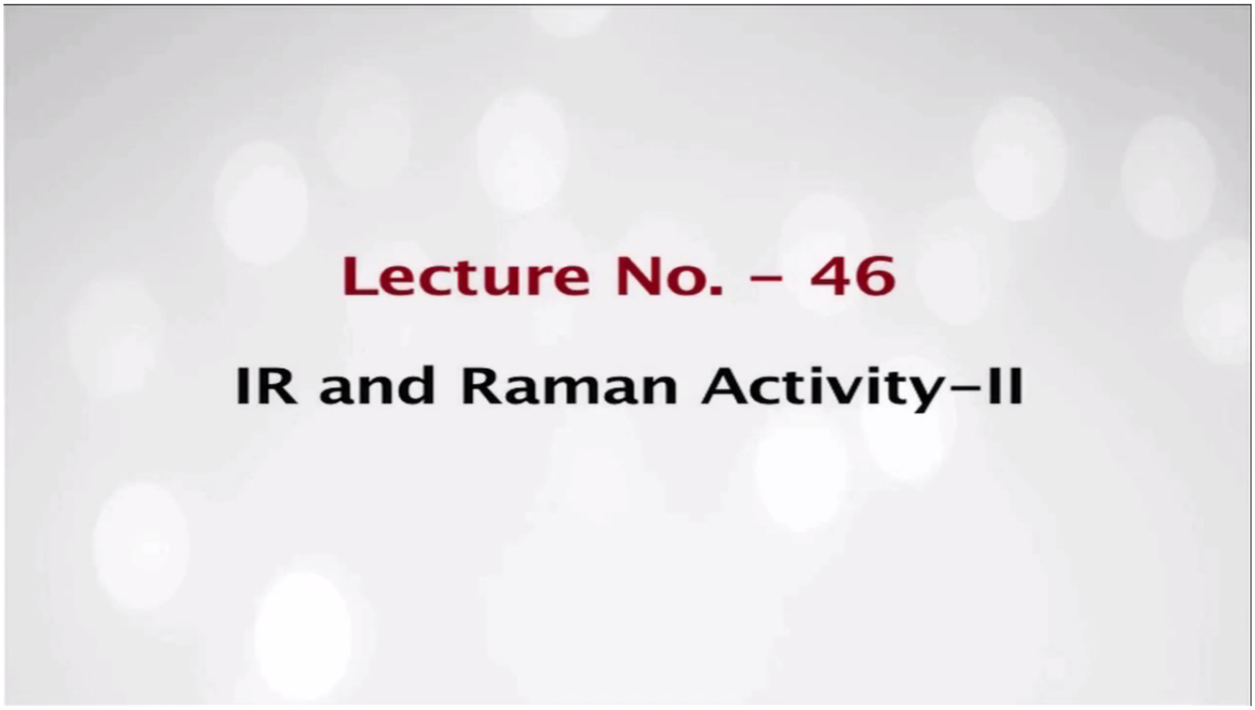

Lecture No. – 46

IR and Raman Activity–II

Knowledge is supreme.

IR and Raman activity part two. So so far we have established that the condition for IR activity is that the normal mode of vibration must have – must belong to the same symmetry species as either X or Y or Z. We can go back to D3h and discuss it. Before that since we already have this C2v open in front of us do we remember what are the normal modes of vibration of water? What are the symmetries of normal mode of vibration of water? Symmetric stretch where does it belong? A1. What about bend? This bend where does that belong? Yeah. E? Where is E? We are talking about water. Bend, where does bend belong? This is plus. This is minus. So apply E it remains the same. Theta d minus theta doesn't become minus theta. Apply C2 it turns but whatever was going again was keeps going in so it is plus one. Apply Sigma V same. See remember this is plus this is minus. It remains the same. Apply sigma v this is sigma v. I am sorry. This is sigma v it remains same. Apply sigma v dash then also it remains same. So what are the characters? 111 so bend also belongs to a1. And what about the asymmetric stretch? Character of e is one but if you apply C2 it becomes minus one. Apply sigma v it remains the same. Apply sigma v dash what is it plus one or minus one. Minus one. So one minus one one minus one. What is it? b1. So asymmetric stretch is b1. So now let us see rest of it is very simple. A1 is the symmetric species to which z belongs. So my condition for IR activity is satisfied. Right or wrong? What is the condition for IR activity that the normal mode must have the same symmetric as one of the cartesian coordinates. So if you look at symmetric stretch or if you look at bend then they belong to the same symmetric species as Z so are they IR active or are they IR inactive. Active. So it is IR active and we say it is z polarized. What is the meaning of z polarization? Of course I think you are not strangers. Polarization is not new to you as far as light is concerned. You know what polarize light means. So what we are saying is that if unpolarized is incident on your sample then only the z component of the light should be absorbed. X component, y component should not be absorbed as far as these symmetric stretch and bend are concerned. That is the meaning of z polarization. It only absorbs the z component of the light.

What about asymmetric stage b1? Is it IR active? Yes or no. And what is the polarization? Polarization X. So it is IR active and x polarized. Now what do we do? Do we talk about Raman activity or do we go to D3h? What do you want to do? Raman activity or D3h? You are out voted. We go to D3h then we come back to Raman activity. It doesn't matter. It's just the sequence. Let's go to D3h. Well the problem is I have been foolish enough to erase what I have written about D3h so I have to write again. So if I go to BF3 which is a D3h molecule please remind me what were the normal modes. We had a1, a1 dash, that was symmetric stretch we can say. Is it IR active? Should it be IR active? No because XYZ do not belong to the totally symmetric representation here. So here for the first time we encounter something that is IR inactive. What was the condition for IR activity in a diatomic molecule that the dipole moment must change. Actually it's the same condition. But we have kind of formulated it in the language of symmetry and what we say is that it must have the same symmetry as one of the cartesian coordinates that is the coordinate along which the dipole moment changes. That is what it really means. So symmetric stretch actually doesn't cause any dipole moment change. Does the dipole moment change? Bond moments do they change? Bond moments? We have bond moments. Bond moments if you look at one bond forget about the other two that should change but they are at 120 degrees to each other. So vector sum is zero. So dipole moment doesn't change. So we are not saying anything that is [Indiscernible] [00:07:08] from what we know already. We are just formulating it in the language that is convenient for us. So a1 dash symmetric stretch is IR inactive. What was the other one we have got? A2 double dash. Doming motion. A2 double dash is doming. Is it IR active? And what is the polarization? A2 double dash IR active Z polarized. IR active Z polarized. What was the other kind of vibration we had? E dash or E double dash? We have two sets of E dash. E dash right because I forgot. E dash isn't it. Two sets of E dash. What kind of motion is this. In plane bend plus stretch. IR active or IR inactive? Yeah? IR active and this time what we see is that it belongs to 2D representation. And X and Y jointly form the basis of the 2D representation. So it is now xy polarized. It will absorb X component as well as Y component of light. It will not absorb Z component of light. So let us discuss Raman activity. For Raman activity we just have to reformulate the same thing, similar line of argument. But the final expression will be little different. Why did we take xyz for IR activity? Where did xyz come from? Components of dipole moment. And dipole moment is a vector. If you remember what is the important quantity for Raman spectroscopy. Is it dipole moment? No then? No. [Indiscernible] [00:09:37] right but quantity is different. That is back calculation. He is saying dipole moment square. What is the important physical property of the molecule for Raman activity? Polarizability. So we have to get the right answer in the right way. Even if I took square of dipole moment I would have reached there. Right answer but it's a path function. You have to take the right path. Polarizability if you remember in order to specify components of polarizability we need two cartesian coordinates, isn't it? XX or XY or YZ or ZX something like that. So condition for Raman activity well dipole moment in transition moment integral will be something like psi two xy or whatever it is I can write alpha delta where alpha and delta are x, y or z. psi one. You already know what is psi one, what is psi two. Psi one is v equal to zero wave function. So totally symmetric psi two is v equal to one wave function. Same symmetry as in normal mode. So what does it boil down to? What is the condition for Raman activity? Psi must have the same symmetry we will just write same as, same symmetry as alpha delta; wher alpha and delta can be excess. So what we are saying is it must have same symmetry as some quadratic function cartesian coordinates. It can be x square, y square, z square, xy, yz, zx. So x square, y square, z square, xy, yz, zx.

Now let us go back and let us since we have the D3h character table open in front of us let us do D3h first. What was the first one? A1 dash, symmetric stretch. IR inactive. Is it Raman active? A1 dash it has x square plus y square and it has z square. So quadratic function of cartesian coordinates has the same symmetry as this normal mode. So it is Raman active.

So even though you don't see it in IR spectrum you will see it in Raman spectrum. And generally when we talk about this we don't bother about saying which component it is utilizing because in any case it is a little more complex. What about a2 double dash. It is IR active. Is it also Raman active? A2 double dash. A2 double dash is not Raman active, isn't it? You get it. A2 double dash is IR active but not Raman active because there is no quadratic function of the cartesian coordinates that has the same symmetry as that normal mode. Raman inactive. And what about the E dash vibrations. E dash vibration means in plane, bend, and stretch e dash is here, you have x square minus y square and xy. So same symmetry as some quadratic function of cartesian coordinates so that is also Raman active.

Let's go back to the easier problem. Water. E dash. Okay look I pointed at the wrong symmetry species. E dash is x square minus y square and xy. Which one is e double dash? What is the question? Yeah. So it doesn't matter. There is no normal mode with e double dash symmetry. Only normal modes that are there can give you IR activity or Raman activity. Normal modes that are not there how will you see them? You have already established what are the symmetries of normal mode. So what you see is knowing the symmetry of normal modes now you see the reason why you are studying symmetry in a spectroscopy course because for a polyatomic molecule if you know the symmetry of the normal mode you can write away looking at the character table you can say what is the – whether it is IR active, Raman active or not. Shall we take C2v?

A1 is IR active. Is it Raman active? Is A1 Raman active? Are we all convinced? Convinced. Raman active. IR plus Raman active. What is the next vibration? Well there are two A1 vibrations. And the B1 vibration is IR active is it also Raman active? Yes. So in water you see for all the three normal modes are IR active as well as Raman active. In BF3 of carbonate, D3h for atomic molecule you see that there is one mode that is IR active as well as Raman active. You have something that is IR active and Raman inactive and you have third one which is is it IR active, yeah IR active as well as Raman active. Moreover the polarizations are different. So this is why IR and Raman spectroscopy are so useful for chemist. Well chemist students here have this CH531 course next semester where what you will do is you will study interpreted spectroscopy. So where you will see that looking at the spectrum you should be able to identify the compound. This is the basis.

So what you will see is by looking at IR and Raman spectra you can kind of have an idea of which molecule it is. if you build a little further upon that you reach for the concept of group frequncies but let me tell you that when you talk about group frequencies that is only an approximate picture. When you say 1750 is the carbonate stretch it is not – it may not always be only carbonate stretch other motion might have some contribution to it. It depends on what kind of normal mode is it. Fine.

That being said let me make one more point something that many of you those of you who have studied Bsc know already. We will just prove it. What have we seen in water? All normal modes are IR as well as Raman active. What have you seen in BF3? Some are only IR active not Raman active. Some are both. Some are only Raman active not IR active. And that is the general situation. It depends on which molecule whatever. Think of something which has a center of symmetry. Center of symmetry. What will I take? CO2 is we will come back to CO2 afterwards because CO2 is an infinite point group also. Let me demonstrate what I am trying to say using simpler situation we will come to CO2 after that. D6h does it have a central of inversion? It does. Now think of of course we have not worked out the symmetry is of normal mode yet but one thing you should see here is that since there is a center of inversion look at where xyz belong. Z belongs to A2u. X and y belong to E1u. It is not very difficult to understand that whenever there is a center of inversion xyz will always belong, will always have ungerade symmetry. Forget about everything else. Think of the center. Xyz will always have ungerade symmetry. Minus one character will be minus one for the inversion operation. But what about xy? What about yz? What about z square? What about x square minus y square? Will they not always have gerade symmetry? Character of ungerade A is minus one with respect to inversion so take another ungerade symmetry A and multiply minus one into minus one becomes plus one. So all quadratic functions of cartesian coordinates will necessarily have gerade symmetry. And that is manifested here. Look at this. X square plus y square z square it is A1z. Xz, yz, E1z. X square minus y square and xy jointly form the basis of E2z. Is the point made? So cartesian coordinates will always have ungerade symmetry if there is point of inversion. There quadratic function will always have gerade symmetry. Where are we leading? We are leading to that East is East and West is West and never the two end shall meet. Something that is ungerade cannot be gerade. In fact when I say it like that it sounds idiotic. Doesn't it? Of course, something that is ungerade will never be gerade that's why it's called ungerade not gerade and something that is gerade will not have ungerade symmetry. It is so obvious that it sounds stupid. But that's the fact.

So what am I trying to say a normal mode that belongs to the same symmetry species as either X or Y or Z must necessarily be ungerade if there is a point of inversion. So it will be IR active and Raman inactive. Something that belongs to the same symmetry species as x square or y square or xz or what something some such quadratic function will necessarily be gerade and therefore Raman active. And therefore IR inactive. So if you have a centro symmetric molecule then IR active normal modes are Raman active, Ramam inactive and vice versa. I think many of you would know what this principle is called. It square called as you have said rightly mutual exclusion principle this is where it comes from. So combining all these you can try to find out what is the structure of a molecule.

So what I will do is we will stop here today.