Fundamentals of Spectroscopy

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Lecture 40
Nuclear Spin Statistics

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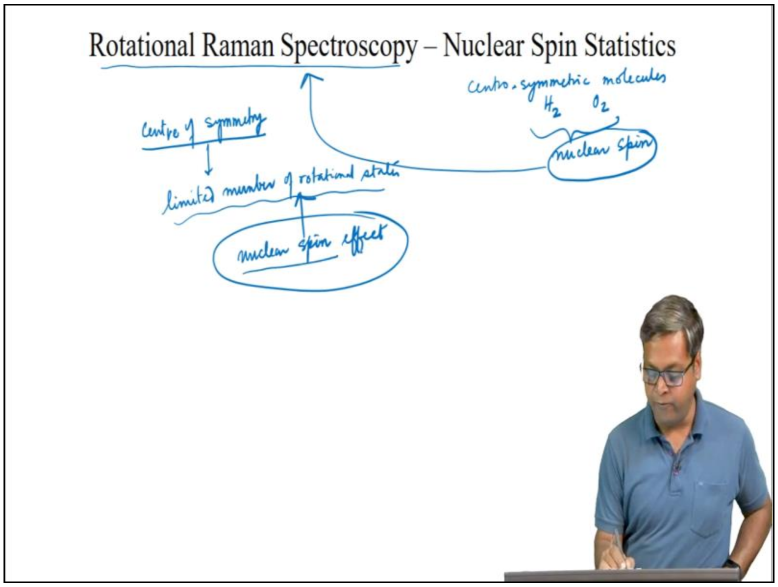

Rotational Raman Spectroscopy – Nuclear Spin Statistics

Hello all welcome to the fourth lecture on Raman spectroscopy in the last lecture we have discussed rotational Raman spectroscopy and during the end of our discussion we mentioned that Centro symmetric molecules. For example hydrogen or oxygen the effect of nuclear spins will be observed. So, for these molecules will observe the effect of nuclear spin, in today's lecture we will look into the effect of nuclear spin on the rotational Raman spectrum for molecules containing a center of symmetry.

It has been observed that limited numbers of rotational states are observed experimentally or in some cases we will see an alternation of the intensities in the rotational Raman spectrum. These observations can be explained using the nuclear spin effect. So, nuclear spin effect can explain these kind of observations in the rotational Raman spectrum. So, we have to understand how does this nuclear spin affect the rotational Raman spectrum.

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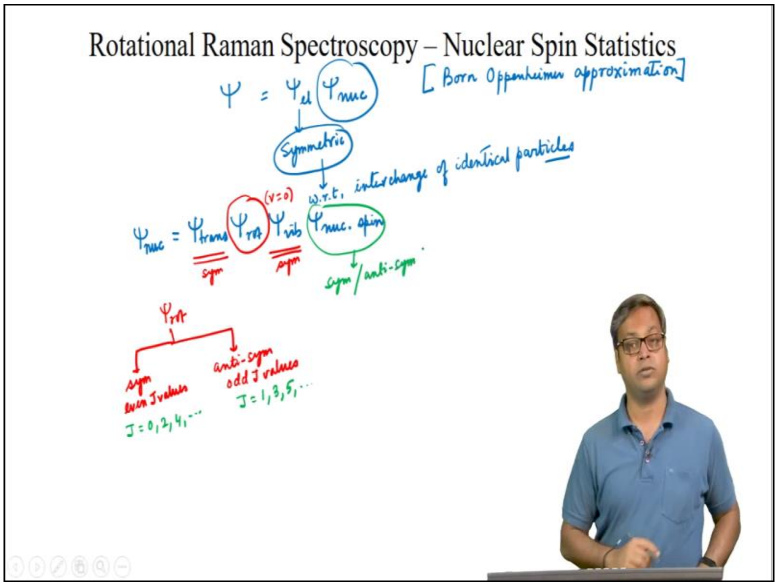

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$\Psi = \Psi_{el} \Psi_{nuc}$ [Born Oppenheimer approximation]

$\Psi_{nuc} = \Psi_{trans} \Psi_{rot} \Psi_{vib} \Psi_{nuc.\ spin}$

So, the total wave function Psi can be represented as a first approximation as psi electronic times psi nuclear and as we have discussed before this is Born Oppenheimer approximation. So, for molecules with the axial component of total electronic angular momentum equals 0 the psi electronic is symmetric with respect to the interchange of identical particles. So, it is symmetric with respect to inter change of identical particles or we can say it is symmetric with respect to the reflection at the center.

And this psi nuclear can be written as psi nuclear equals psi translational times psi rotational times psi vibrational times psi nuclear spin. Now the psi translational is symmetric with respect to reflection at the center and psi vibrational is also symmetric because we should remember that for rotational transitions we mainly consider V equals 0 that is the ground vibrational state which is symmetric with respect to the reflection at the center.

But this psi rotational so we can write psi rotational is symmetric for even J values and psi rotational is anti-symmetric for odd J values so here we will write odd J values. So, in other words high rotational will be symmetric for J equals 0, 2, 4 etcetera. On the other hand psi rotational is anti-symmetric for J equals 1, 3, 5 etcetera. Similarly shiny nuclear spin can also be symmetric or anti-symmetric. So, this can be symmetric or anti symmetry for a 2 spin system with nuclear spin I equal half.

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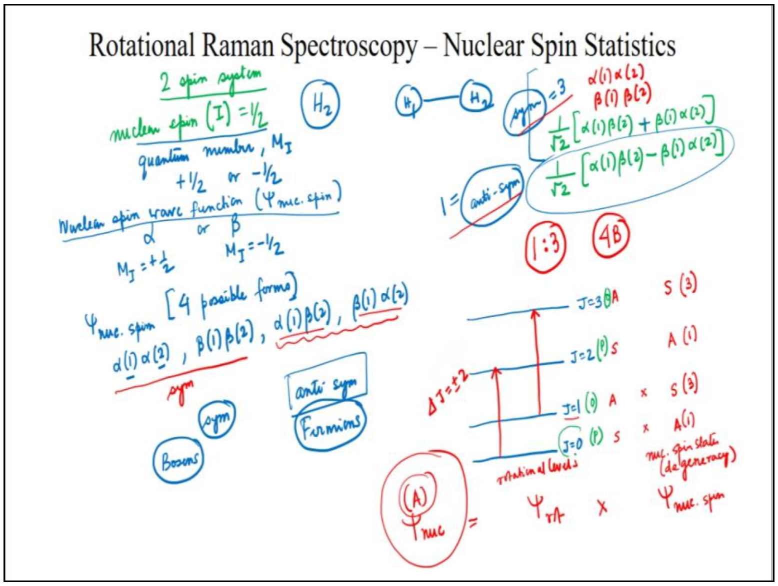

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So let us say we have a 2 spin system where the nuclear spin which is denoted by I equals 1/2 and an example of this is the hydrogen molecule. Because in hydrogen the I for each proton equals 1/2 space quantization of nuclear spin angular momentum results in the quantum number M I. So, we have a quantum number that is M I and M I can take in this case values of plus 1/2 or -1/2 the nuclear spin wave function is usually written as alpha or beta. So, this is the nuclear spin wave function or psi nuclear spin.

So this is written as either alpha or beta so alpha corresponds to M I equals + 1/2 and beta corresponds to M I equals -1/2 and so we have hydrogen molecule so there are 2 hydrogen atoms and let us say we label the nuclei as 1 and 2. So, these nuclei labeled 1 and 2 can either have an alpha or a beta spin wave function so there are 4 possible forms of psi nuclear spin. So, psi nuclear spin has 4 possible forms. So, what are these forms we can write this as alpha 1 alpha 2 so where alpha 1 and 2 are the 2 nuclei.

We can also write as beta 1 beta 2 and the other 2 possibilities are alpha 1 beta 2 and beta 1 alpha 2. So, we can see that the first 2 alpha 1 alpha 2 and beta 1 beta 2 are clearly symmetric because if we interchange the labels 1and 2 then still it remains alpha 1 alpha 2 beta 1 beta 2. On the other hand the last 2 that is alpha 1 beta 2 and beta 1 alpha 2 and neither symmetric nor anti symmetry and for this we have to take linear combinations of this alpha 1 beta 2 and beta 1 alpha 2 and also normalize them.

So the 4 spin states that are possible for this nuclear spin are we can write the first were the same alpha 1 alpha 2 then we have beta 1 beta 2 and then we have these linear combinations where it is 1 by root 2 alpha 1 beta 2 +s beta 1 alpha 2 this is one linear combination. The other linear combination is by root 2 alpha 1 beta 2 - beta 1 alpha 2. So, this 1 by root 2 is the normalization constant. So, as we can see now the first 3 alpha 1 alpha 2 beta 1 beta 2 and this linear combination which is a positive combination are symmetric with respect to interchange of particles.

So, these 3 are symmetry however the last one as we can see if you change alpha and beta that means if you change 1 and 2 then it is not symmetric on the other hand it is anti symmetric with respect to interchange of particles. Thus in this case the number of symmetric states is 3 while the number of anti symmetric states equals 1. Thus for hydrogen the symmetry properties of the nuclear wave function depends on the symmetry properties of the rotational wave function and the nuclear spin wave function.

It follows from the indistinguishability of the identical particles that the total wave function is symmetric in bosons that means if bosons are particles with integral spin. So, bosons are particles with integral spin and if these bosons are interchanged then the wave function should be symmetry. On the other hand the wave function will be anti symmetric if fermions. So, fermions are particles with half integral spins.

So if fermions are interchanged the total wave function must be anti symmetry. So, as we can see the nuclear spin I for hydrogen is half in other words hydrogen is a fermions. Thus for hydrogen the nuclear wave function must be anti symmetry and we can show this schematically as follows. So let us draw the J levels, so let us say we have J equals 0 J equals 1 J equals 2 and J equals 3. So, we know that J equals 0 is symmetric equals 1 is anti-symmetric and J equals 2 again is symmetric and J equals 3 is anti-symmetric.

And so here we are talking about the rotational levels and now if we talk about the nuclear spin states on the right and if we denote the degeneracy of the spin States in bracket we will see or first of all we know that the I nuclear which is anti-symmetric in the case of hydrogen is given by psi rotational times psi nuclear spin. So, in this case we can write this; this should be anti symmetric because a symmetric time anti-symmetric gives the psi nuclear to be anti symmetry.

Similarly because the rotational level is anti-symmetric for J equals 1 we should have the nuclear spin state as symmetric this will be anti symmetric and J equals 3 will again be symmetry and the degeneracy as we found from here the degeneracy of symmetric is 3 and the degeneracy of anti-symmetric is 1. So, we will write 1 whenever we write anti-symmetric in bracket and 3 for the symmetric we should write in bracket. So, now what we see here is if we take symmetric times anti symmetric it is anti-symmetric, anti-symmetric time symmetry is also anti-symmetric.

So the psi nuclear in this way will be anti symmetric because hydrogen is a fermion. So, the rotational transition from J equals 1 to 3 because Delta J should be +- 2 or a transition from 3 to 5 will be 3 times more intense than the transitions from 0 to 2 or 2 to 4 etcetera thus there will be an alternation of intensities in the ratio 1 is to 3 in the rotational Raman spectrum of hydrogen and the gap between the successive lines in the rotational Raman spectrum will be as we know 4B.

So, we know that hydrogen can exist in ortho and para form. The para hydrogen can exist only in the even J states. So, we can write this as para and J equals 2 as para and the ortho hydrogen can exist only in odd J states so J equals 1 is ortho J equals 3 is ortho so at temperatures at which there is appreciable population up to fairly high values of J that means J equals 0 1 2 3 all are kind of populated there is roughly 3 times as much ortho as there is para hydrogen.

However at very, very low temperature at which the population of all rotational levels other than J equals 0 is small that means mostly J equals 0 is populated then hydrogen is mostly in the para form.

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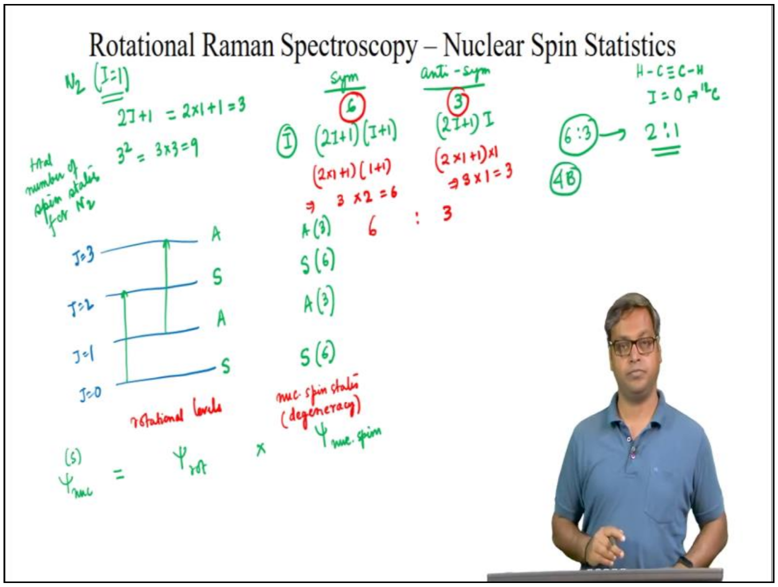

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Similarly will be a case for a symmetrical linear polyatomic molecule for example let us say we have acetylene HC triple bond C single bond H since I equals 0 for 12C. So, we should only consider the 2 hydrogen's at the 2 but the main difference is that since the rotational energy levels are much more closely spaced in acetylene as compared to hydrogen a much lower temperature is necessary to produce acetylene predominantly in the para form. So, now let us look into another homonuclear diatomic molecule that is nitrogen and for nitrogen I equals 1.

The total number of states for each nitrogen nucleus is given by 2 I + 1 so because I equals 1 this is 2 times 1 + 1 that is 3 and for nitrogen molecule the total number of spin states equals 3 squared that is 3 times 3 equals 9. So, this is total number of spin States for nitrogen so out of this 9 spin states 6 will be symmetric and three will be anti symmetry. So, the symmetric will be 6 and anti-symmetric will be 3. So, in general if the spin is I then the total number of symmetric states is given by 2 I + 1 times I + 1.

So in case of nitrogen we can see we get 2 times 1 + 1 times 1+ 1 so this becomes 3 times 2 equals 6 and that is why we wrote 6 here. On the other hand the total number of anti-symmetric states is given by 2 I + 1 times I, so in case of nitrogen this is 2 times 1 + 1 times 1 that is 3 times 1 that is 3, so we wrote 3 here. Does the symmetric and the anti-symmetric states will be in the ratio 6 is to 3 for nitrogen thus for nitrogen the rotational transitions can be shown as again we can draw this energy level diagram.

Let us say we have the rotational levels on the left and we have this nuclear spin states on the right and again we will write degeneracy in bracket. So, let us draw the energy level diagram we have J equals 0 J equals 1 J equals 2 and J equals 3 and because Delta J equals +- 2 we have transitions from J equals 0 to J equals 2 and J equals 1 to J equals 3. And as we all know so J equals 0 is symmetric J equals 2 is symmetric on the other hand J equals 1 is anti-symmetric and J equals 3 anti-symmetric.

Now the psi nuclear in this case is symmetric because I is an integer that is 1. So, in other words this is an example of a boson. So, because the shiny nuclear is symmetric from the previous example of hydrogen now we can say that the nuclear spin state here corresponding to J equals 0 should be symmetric. And as we know it has a degeneracy of 6. Now here it should be anti symmetric with degeneracy of 3 again it is symmetric with degeneracy 6 and anti-symmetric with degeneracy 3 and this is because we write psi nuclear which is symmetric as the product of psi rotational and psi nuclear spin.

So the rotational Raman transitions will show an alternation of intensities in the ratio 6 is to 3 or we can simplify this as 2 is to 1 and again because all the lines are there and no line is missing the gap between successive lines will be equal to 4B.

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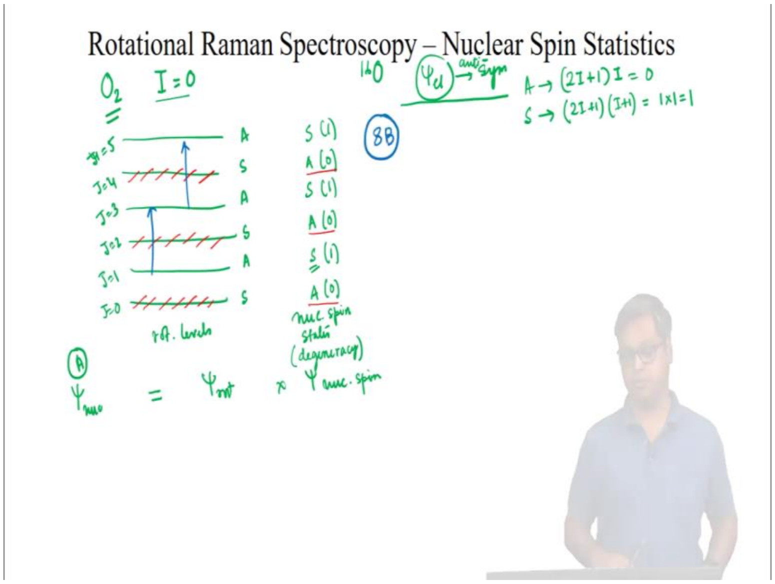

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So, now let us look into another molecule and this molecule is oxygen and for oxygen we have I equals 0. So, let me first draw the energy level diagram so let us draw the energy level diagram equals 0 J equals 1 J equals to J equals 3 J equals 4 J equals 5 and we know because these are rotational levels are additional wave functions this is symmetric, anti symmetric, symmetric, anti symmetric, symmetric, anti symmetry.

So, again here we have the rotational levels and on the right we will have the nuclear spin states and in bracket will write the degeneracy. So, since each 16 oxygen nucleus that is oxygen 16, so each of this oxygen 16 nucleus is a boson the total wave function must be symmetric to nuclear exchange. In the case of oxygen the 2 electrons with unpaired spin in the ground state so this makes the psi electronic there is a psi electronic to be symmetry.

And this is unlike the other molecules like hydrogen or nitrogen we have considered. So, the 16 oxygen will only have levels with rotational quantum numbers having odd values this is because now this total nuclear wave function has to be anti symmetric because the psi electronic is anti symmetry and so because this psi nuclear is the product of psi rotational and psi nuclear spin. So, here nuclear spin should be anti-symmetric for J equals 0 symmetric, anti symmetric, symmetric and anti symmetric and symmetry.

And as we know the number of anti symmetric states is given by 2 I + 1 times I and because I equals 0 the number of anti symmetric states equals 0. So, the degeneracy becomes 0 for even J values. And for the odd J values we have symmetric and the symmetric is given by 2 I + 1 times I + 1 so that is 1 times 1 that is 1 so the degeneracy here is 1. So, in other words in the rotational spectrum the rotational states for even J values are actually missing.

Because the degeneracy is 0 that means the number of states for the anti-symmetric is 0. So, these states will be missing from the spectrum and the only allowed transitions that we would have is from 1 to 3 or from 3 to 5. So, now because the alternate lines are missing in this case the gap between the successive lines will not be 4B but it will be double of that that is the gap between successive lines will be 8B.