Fundamentals of Spectroscopy
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Lecture 48
NMR Spectroscopy – 2

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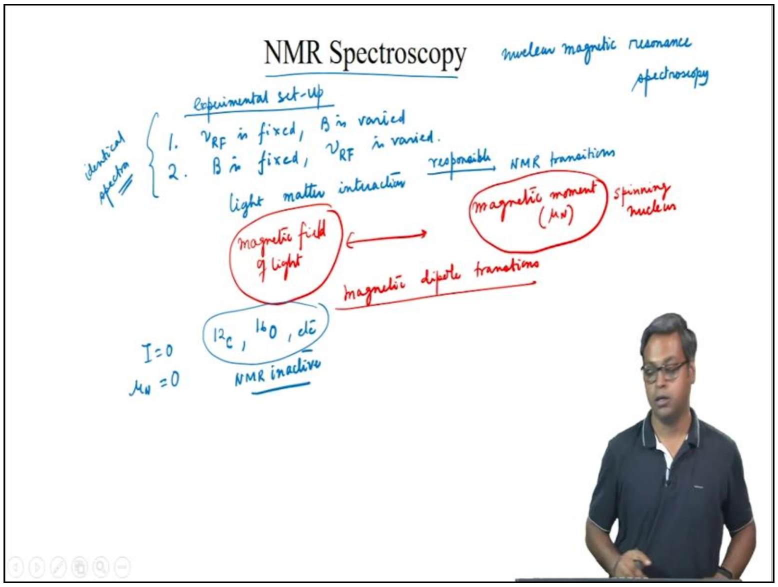

Hello all welcome to the lecture in the last lecture we started discussing nuclear magnetic resonance spectroscopy or NMR spectroscopy. We looked into the experimental setup of NMR spectroscopy and we discuss the two different ways in which the experiment can be performed so there are two different ways one is nu RF is fixed but B is varied and the other case is B is fixed and nu RF is varied.

So, both these procedures would produce identical NMR spectrum. So, let us now look into some important points related to NMR spectroscopy. So, the first important point is the light matter interaction which is responsible for this NMR transitions so this light matter interaction responsible for NMR transitions involves interaction between; the magnetic field of light. So, on one hand we have magnetic field of light which interacts with the magnetic moment.

So this magnetic field of light interacts with the magnetic moment which is represented by mu N so this magnetic moment is of the spinning nucleus. So, this magnetic moment is of the spinning nucleus. So, here therefore the transitions are magnetic dipole transitions. So, for nuclei with I equals 0 for example I equals 0 in 12 C then 16 oxygen etcetera so because I equals 0 mu N or the magnetic moment is 0 and because mu N is 0 there is no interaction with a magnetic field. So, thus this, nuclei that is 12 C or 16 O are NMR inactive.

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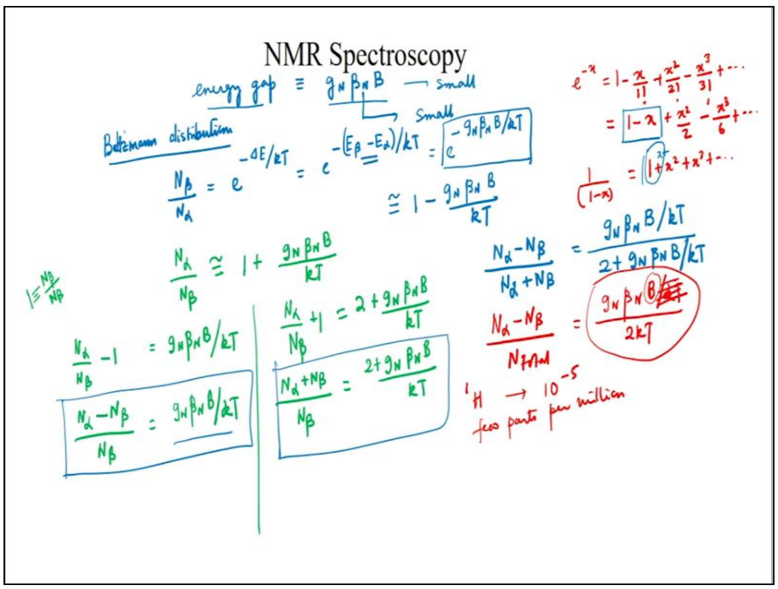

Secondly the energy gap so the energy gap which is given by gN beta NB between these Zeeman levels of the nucleus is small. So, this g N beta NB is small because the beta N itself is small. So, we have discussed this in the second lecture on resonance spectroscopy. So, according to Boltzmann's distribution so according to Boltzmann distribution we can write N beta by N alpha equals e to the power minus Delta e by k T.

And here Delta e means e to the power -e of beta -e of alpha by k T and this energy difference is the same as this energy gap so this is e to the power -g N beta N B by k T. So, we know that e to the power -X can be written as 1 - X by factorial 1 +X square by factorial 2 + X is cube by factorial 3 + dot dot dot which we can write as 1 - X + X square by 2 - X cube by 6 + dot dot dot so if we truncate or expansion the series expansion after the second term that is 1 - X we can write this e to the power - gN beta NB by k T as 1 - g N beta N B by k T.

So, we also know that 1 by 1 - X is given by 1 + X square + X cube + dot dot dot so again if we truncate the series expansion. So, 1 + X + X squared so if we truncate this series expansion after the first two terms and we invert the ratio we can write N alpha by N beta equals approximately 1 plus gN beta N B by k T. So, if you simplify this we get N alpha by N beta - 1 equals g N beta and B by k T, so we can write 1 as N beta by N beta so this means N alpha - N beta divided by N beta equals g N beta N B by k T.

Similarly if we want to write N alpha by N beta + 1 it will be 2 + g N beta N B by k T in other words what we get is in alpha plus N beta by N beta equals 2 + g N beta and B by k T. So, we have this two expressions one is N alpha - N beta by N beta is g N beta NB by k T and N alpha + N beta by N beta is 2 + gN beta N B by k T. So, if we take the ratio so these two expressions what we get is N alpha - N beta divided by N alpha + N beta equals g N beta N B by k T divided by 2 + g N beta N B by k T. So, N alpha + N beta is the total number of states because there are only two states alpha and beta.

So, we can write N alpha - N beta divided by N total and this will be we can write g N beta N B by k T and the denominator we will only write 2 K T because beta N is small. So, the second term in the denominator we will neglect. So, this is the final expression that we get. The question is why did we actually try to get this expression. So, if we do a simple calculation for let us say the proton it shows that the right-hand side that is g N beta NB by k T or g N beta N B divided by 2 kT is very small it is of the order of 10 to the power -5.

So the population of the upper and the lower levels are almost the same that means they are same to within few parts per million. So, we should note that this difference in this energy level in population is greater at higher values of B because N alpha - N beta by N total is delayed proportional to B.

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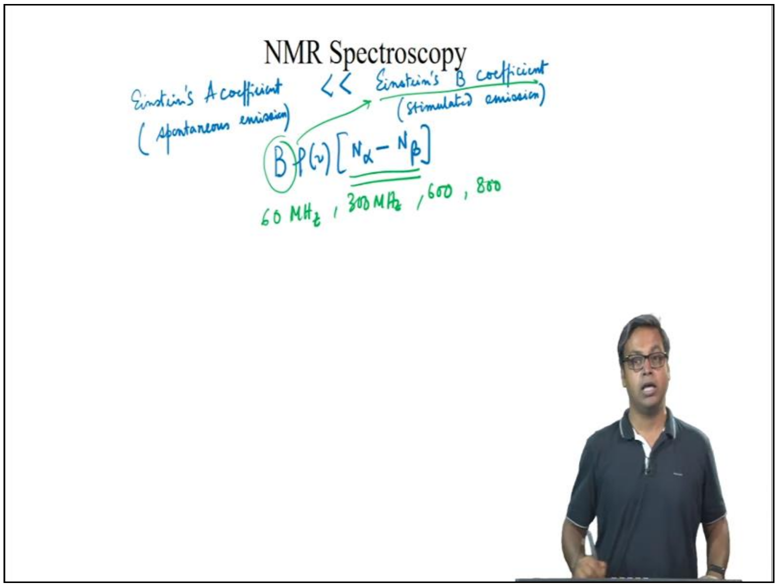

Now so in the radio frequency range the Einstein's A coefficient, so this Einsteins A coefficient which is due to the spontaneous emission. So, we have discussed this when you are discussing the light matter interaction or a first module so this Einstein's A coefficient is much smaller than the Einstein's B coefficient. So, Einstein's B coefficient is related to stimulated or induced emission. So, because Einstein's A coefficient is much less than Einstein's B coefficient thus the induced or the stimulated emission is only important and we can neglect the spontaneous emission and the net overall absorption rate is given by B Rho of Nu times N alpha - N beta where this B is the Einstein's B coefficient.

So to get a significant NMR signal one needs larger values of this N alpha - N beta and this has several consequences any more experiments are carried out at high magnetic fields because as I just mentioned before that high magnetic field gives a larger value of N alpha - N beta because the ratio of N alpha by N beta increases. So, the NMR experiments are carried I would at high magnetic field for example 60 megahertz or it can be 300 megahertz 600 etcetera.

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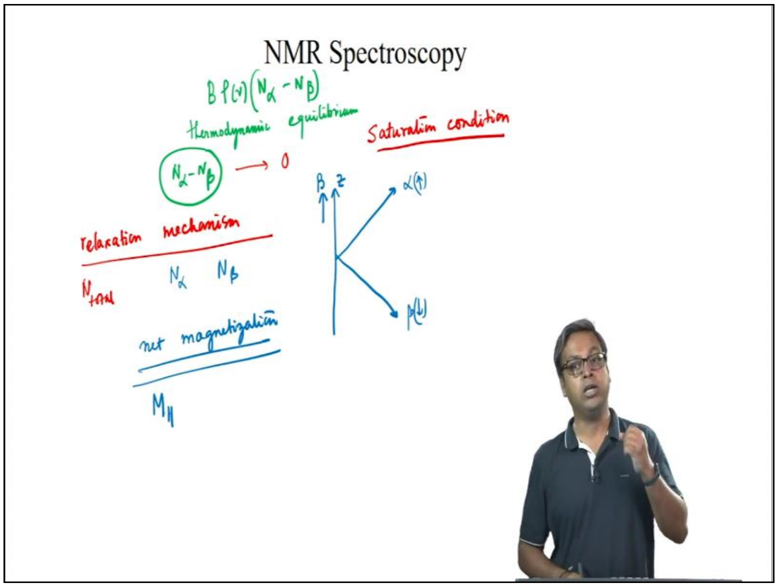

And secondly the net absorption rate which is given by B Rho nu N alpha - N beta refers to the equilibrium situation that means when the spin system is at thermodynamic equilibrium. So, this thermodynamic equilibrium is in the presence of this external magnetic field. So, when radiofrequency shines on it that means the light with radio frequency shines on it transition occurs and the equilibrium distribution is disturbed.

So the difference that is N alpha - N beta decreases and very quickly this N alpha - N beta can reach to zero and when it reaches zero because N alpha equals N beta. So, there is no net absorption or emission. So, no net absorption or emission will occur and this situation is called the saturation condition. So, we have discussed this saturation condition in the first module when we are talking about the light matter interaction in general.

So in order to avoid this saturation or in order to avoid the saturation condition there must be an efficient mechanism which will restore the equilibrium situation and this is known as the relaxation mechanism. So, in an assembly consisting of nuclear spin, so, let us say there are N total number of nuclear spins there will be populations of alpha spin which is given by N alpha and populations of beta spin which is given by N beta.

So the alpha spin have their Z component aligned in the direction of B so if we draw this; this is the Z component or the Z direction and the external magnetic field is aligned with the Z direction. And this alpha state and beta state for the Alpha state the Z component of the Alpha state is aligned to the direction of B whereas as we can see for the beta state which is down spin the Z component will be aligned opposite to the direction of B however it is still parallel to the external magnetic field B.

So, thus there will be something called as net magnetization so there will be a net magnetization vector representing the resultant magnetic moment in the direction parallel to B that is in the Z direction. So, in a non equilibrium situation the value of this vector which we represent by M parallel because it is along the Z direction which is parallel to the externally applied magnetic field B. So, this magnetic moment will be changed or in parallel will be changed.

So, one of the relaxation processes involves the change of the non equilibrium value of M parallel to the equilibrium value.

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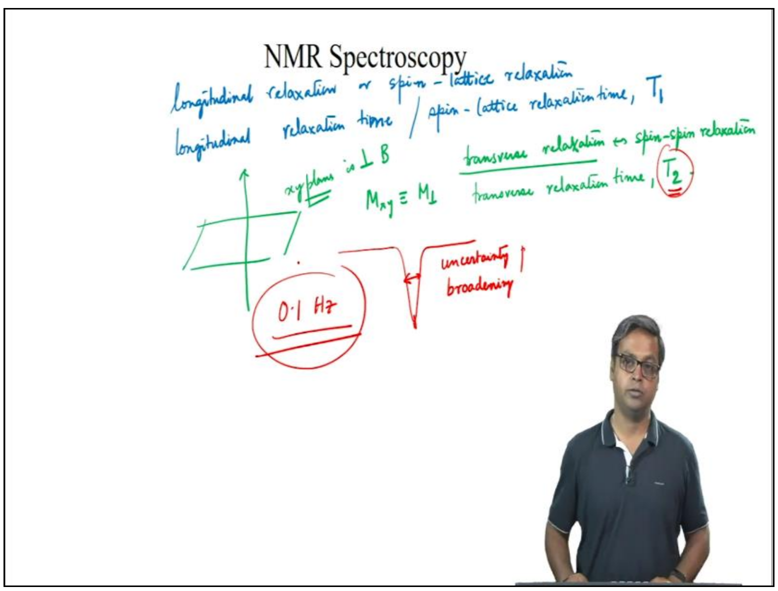

So, this is known as the longitudinal relaxation or spin lattice relaxation. So, this is known as the spin lattice relaxation because the excess of this beta spin has to be transferred to the surroundings that means it has to be transferred to the lattice. So, there is a spin that is being transferred to the lattice is the spin lattice relaxation. The characteristic time for the first order process of the spin lattice relaxation is known as the longitudinal relaxation time or it is also known as the spin lattice relaxation time and is normally denoted by T 1.

So now let us consider the situation in the plane that is perpendicular to the externally applied magnetic field. So, the field is applied in the Z direction so we are talking about a plane that is perpendicular that is the X Y plane. So, the XY plane is perpendicular to B so the relaxation of M XY or we can write this as M perpendicular will occur to a randomization of the spin vector and this is called the transverse relaxation or it is also called the spin-spin relaxation.

So this will not involve in any change in the energy but it is the entropy that only changes. So, the characteristic time for this relaxation process is known as the transverse relaxation time and this is denoted by T 2. So, in NMR experiment this T 2 is responsible for the width in the spectral signal. So, we have drawn before a spectral signal so there is a dip where this magnetic field matches with the nu RF and the width is given by T 2 and this is the uncertainty broadening.

So in solution the T 2 is long so this is true space coupling is average to 0 due to tumbling of the molecules as compared to that we have in the solid state. So, the solid state NMR experiment gives broader signal in general than in the solution state because T 2 is long in solution in the spectrum in the frequency domain the spectrum is narrower but T 2 is short in solid state so it is broader in the width. So, in general the width in solution is of the order of 0.1 hertz.

So, we will end this lecture here and in the next lecture we will talk about the selection rules and other important aspects of NMR spectroscopy.