Interpretative Spectroscopy

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Lecture-02
Introduction to ^{1}H NMR Spectroscopy

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In the last class I started discussion on NMR, and also in the beginning what I would do is I would give little bit information about all the spectroscopic methods and then start detailed discussion one at a time. In my previous lecture, I started with analytical methods and also some fundamentals about analytical methods and I started discussion on NMR, and then I started IR. So, let me continue from where I had stopped. The approximate time scale for structure determination using various techniques is very, very important. So, that gives some information about the limitations or advantage of a particular technique, when you want to use it as an analytical tool to understand the structure of a molecule. For example, if you see in case of electron diffraction, we can use up to ten to the power of minus 20 seconds (10^{-20}) or in case of X-rays it is about 10 to the power of minus 18 (10^{-18}) and in case of UV it is 10 to the power of minus 15 (10^{-15}).

That means whatever the dynamic process that happens up to 10 to the power of minus 15 (10^{-15}) can be analyzed using UV visible spectroscopy, and in case of visible, the time scale is about 10 to the power of minus 14 (10^{-14}), and in case of IR and Raman it is about 10 to the power of minus 13 (10^{-13}), and in case of ESR it can range from 10 to the power of minus 4 to 10 or to the power of minus 8 (10^{-4} to 10^{-10} or 10^{-8}) and in case of NMR it is 10 raised to minus 1 to 10 raised to minus 9 (10^{-1} to 10^{-9}). That means basically whatever the dynamic process that is happening in the time scale of 10 raised to minus 1 to 10 raised to minus 9 (10^{-1} to 10^{-9}) can be analyzed using NMR spectroscopy without any problem, but if there is any dynamic process that is much faster than 10 to the power of minus 9 (10^{-9}), let us say 10 to the power of minus 10 (10^{-10}), probably NMR would not identify. In that case, what happens probably, we have to suppress the thermal process by cooling the solution of NMR sample to much lower temperature, so that the dynamic process falls within this range so that we can study through NMR, what is happening? And similarly, if it is much slower than 10 to the power of minus 1 (10^{-1}) then probably we have to heat the sample so that dynamic process would fall in this range.

So, this is what the information we get in case of FAST kinetics; it is about 10 raised to minus 3 to 10 to the power of 2 (10^{-3} to 10^{-10}), and physical separation of isomers, if you see two isomers are formed in a reaction and then whether we can do separation after crystallization. Because if they have different morphology then at least we need 100 seconds (100 s), that means for physical separation it should be greater than 10 to the power of minus 2 (10^{-2}) time scale. That means the isomers formed should not undergo isomerization within 100 seconds (100 s). As I mentioned NMR is the most powerful tool available for organic and inorganic structure determination. It is used to study a wide variety of nuclei. I have mentioned somewhere, here it is 1-hydrogen (^{1}H), 13-carbon (^{13}C) are there, both 11 boron (^{11}B) and 10 boron (^{10}B) are there and of course 11 boron (^{11}B) has about 80 percent natural abundance and the remaining is 10 boron (^{10}B), for 10 boron (^{10}B), the nuclear spin is 3, whereas for 11 boron (^{11}B) it is 3 by 2 (3/2). Again, 14-nitrogen (^{14}N), I value is equal to 1 (I=1) and in case of 15 n I value is 1/2 and 19-fluorine (^{19}F), 31-phosphorus (^{31}P), 29-silicon (^{29}Si) and 103-rhodium (^{103}Rh), 195-platinum (^{195}Pt), 183-tungsten (^{183}W), all of them have nuclear spin value of I equal to half (I=1/2). But their natural abundance varies. I will provide you NMR periodic table in this lecture. We have some selectivity, not all elements in the periodic table you know have nuclei which can be analyzed through NMR. That means they are classified here into three different types of nuclei or into 3 categories. Even and even: what does it mean, nuclei containing even number of both protons and neutrons have I equal to 0 (I=0) and therefore they cannot undergo NMR (NMR inactive). So that means whenever we come across nuclei having even number of both protons and neutrons; they have 0 nuclear spin in that case what happens we cannot use them in NMR measurement. Examples 4-helium (^{4}He), 12-carbon (^{12}C), 16-oxygen (^{16}O), 32-Sulfur (^{32}S) etc. Next odd/odd: that means nuclei with odd number of both protons and neutrons have spin quantum numbers that are positive integers. Examples include 14-nitrogen (^{14}N), we have I equal to 1 (I=1), 2H deuterium I equal to 1 (I=1) and 10 boron I equal to 3 (I=3). The remaining nuclei odd/even or even/odd combination of protons and neutrons, all have spins that are half integral for example: 1-hydrogen (^{1}H) if you take, I equal to half (I=1/2), 17-oxygen (^{17}O) I equal to 5/2 (I=5/2), 19-fluorine (^{19}F) I equal to half (I=1/2), 23-sodium (^{23}Na) I equal to 3/2 (I=3/2), and 31-phosphorus (^{31}P) I equal to half (I=1/2).

So, this is how you can classify, so simply by looking into number of protons and neutrons in a given atom, we should be able to tell whether it is NMR active or not. If it is NMR active what is its I value. This is NMR periodic table this depicts the elements which elements have NMR active nuclei and also it has all the details one looks for to use effectively NMR. Here is another table which is pretty good because, here the color code is given for different nuclear spin. You can see here red one is I equal to half (I=1/2). We have plenty of elements which are NMR active starting from hydrogen. The elements block in red are all having I equal to half (I=1/2), and then I equal to 1 (I=1), we can see, a very few are there, one is lithium, here is nitrogen. For I equals 3/2 (I=3/2), we have quite a few all-in yellow colors. You can see beryllium, sodium, potassium, rubidium and all those, lanthanides and alkanides. We have then I equal to 5/2 (I=5/2) in green color and I equal to 7 by 2 (I=7/2) are in blue color and also 9 by 2 (I=9/2) are in purple color. So, you can see here most of the elements have some isotopes which are NMR active. Let us look into the interaction of these NMR active nucleus with a magnetic field. According to quantum mechanics the energy associated with the interaction of each different orientation of the magnetic moment with an external applied magnet will be equal to the component of μ so magnetic moment along with field B-naught (B_o) times the magnitude of B-naught (B_o) that means it can be represented using this equation here E equal to μ_z into B-naught ($E=\mu_z B_o$). Each value of μ_z is associated with a different energy level. For example, I have shown here the orientation of nucleus with I equal to 1 (I=1) and angular momentum and magnetic moment vectors in a magnetic field. So let us see, if this is the applied magnetic field and if I equal to 1 (I=1), this is how we will be having the values of minus one (-1), 0 and plus one (+1) and if the I value is half (I=1/2), again this is the one it has the same magnetic moment shown here and then these orientations will be with respect to the magnetic field. If this is magnetic field B-naught (B_o) these are the orientations of 1 and 0 and minus 1 (-1) nuclear spin. Energy levels for the interaction of nuclei I equal to 1, half, or 3 by 2 with a magnetic field B-naught (B_o) and we are using another term called gamma, gamma is nothing but the gyromagnetic ratio or magnetogyric ratio and this is positive for I equal to 1 and negative for I equal to 3 by 2 so that means at a given value of B-naught (B_o) the spacing of the energy levels are equal at a given value of B-naught (B_o). The spacing of the energy levels are equal. The difference in the energy levels increases as B increases that one should remember. The gap between the spacing of energy levels increases with increase in the magnetic field strength. This is actually a boon because many complicated spectra we get under low magnetic field can be enhanced for better refinement when we go for higher field, this is where the interest is there about making instruments having higher field strength. Thus, if the magnetic ratio is positive then μ_z equal to gamma m_I h over 2 pi ($\mu_z = m_I h/2\pi$). This implies that mu z (μ_z) and m_I will have the same sign and because of that, E equal to mu z B-naught ($E = \mu_z B_o$). The energy level with the most negative will have the highest energy. So, this is what shown here. As I said, apart from this orientation you cannot have any orientations in between. For example, here in case of I equal to 1 we have 0 plus 1, and minus 1 and in case of half we have plus half and minus half ,whereas, in case of 3 by 2: we have plus 3 by 2, half, minus half, minus 3 by 2 and similarly, if we have 5 by 2 then we will be having plus 5 by 2, plus 3 by 2, plus half, and minus half, minus 3 by 2, and minus 5 by 2.

So, similarly 7 by 2 also one can keep writing like this. Nuclei with negative magnetogyric ratio will have the highest energy for the most positive m_I value. So, I have highlighted these parts which are very important. So, nuclei with negative magnetogyric ratio will have highest energy for the most positive m_I value. So, let us look into the effect of magnetic field on nucleus in a more classical way. I will come back to that one. Since the value of mu z can never have the full value of mu z, mu and N nuclear angular momentum vector can never be collinear with B-naught (B_o). If we imagine a spinning top as a nucleus, the rotational axis cannot be aligned with B-naught (B_o). This is very very important that means when the nucleus is precessing or rotating under the influence of the magnetic field, the rotational axis can never be collinear with the direction of applied magnetic field. It is always tilted or oriented at some angle relative to B-naught (B_o), which can be visualized with the spinning tops. You can clearly visualize what I said here. You can see here. A typical top can be compared to a precessing nuclei under the influence of the magnetic field and with respect to the magnetic field. If you just try to see here, this is not really collinear. It is at an angle. Same thing is true in case of all these things. This can be compared to the rotating magnetic field generated under the influence of a magnetic field on nuclei. For example, something like this, if you see here, although under the influence of this magnetic field, they are rotating, rotational axis is not collinear with this one and it is at an angle. So, that means a tilted spinning top when subjected to a force, it precesses about the direction of the force that you saw in the previous slide. Similarly, a spinning nucleus precesses about the magnetic field B-naught (B_o) in that case, the frequency of this precessional moment is given by omega, omega is nothing but gamma into B-naught (B_o).

So, this omega is called precessional frequency or Larmor frequency, you can see here, this in the absence of the magnetic field. When the magnetic field is applied, it will be at an angle and then it will start precessing. In this one, with respect to applied magnetic field B-naught (B_o). So, this the frequency with which a nucleus precesses under the influence of the magnetic field, which is called as omega, and omega is directly proportional to the gyromagnetic ratio of that nucleus. So, this precessional frequency, omega is called Larmor frequency. Orientation of a spinning nucleus in a magnetic field is shown here. The orientation is not allowed by quantum mechanics to have this kind of things. It does not precess like this here. It is at an angle here, you can see, and precision about B-naught (B_o) in this goes like this. This is what exactly happens for a non-zero nuclear spin kept under the influence of a magnetic field with magnitude B-naught (B_o).

Again, I am repeating here a tilted spinning top when subjected to a force precesses about the direction of the force similarly a spinning nucleus precesses about the applied magnetic field B-naught (B_o) the frequency of this precessional movement is given by omega equals gamma B-naught (B_o) if you want to change the angle of rotation with respect to B-naught (B_o) we must apply a force which moves the rotation axis of the nucleus away from this. So, that means, if it is something like this, if it is precessing to increase and eventually to take it from this one away from this one what happens, we have to apply another field which is perpendicular to the applied magnetic field. If we apply another field perpendicular to the magnetic field what happens it will tilt the precessing nucleus away from the direction of applied magnetic field and eventually when the flip changes, we say resonance has occurred in NMR this force is provided by a second magnetic field Bi oriented at right angle are perpendicular to the B-naught (B_o). So, that means, here basically we have the B-naught (B_o) is there and you apply another one here this is Bi. So, this would take away the precessing the precessing frequency of this nucleus when matches the frequency of this applied magnetic field then transition occurs when B_1 that is the applied magnetic field perpendicular to the B-naught (B_o) ok.

So, that means, when B_1 rotates about B-naught (B_o) with Larmor frequency, the two rotation fields are in phase, now nucleus experiences another magnetic field about which it can precess. So, how it precesses about the new applied magnetic field can be seen here. In this diagram you can see here, earlier when B1 was not applied, under the influence of B-naught (B_o) it was precessing about B-naught (B_o) in this fashion, and the moment we applied a magnetic field (B1) perpendicular to the B-naught (B_o) and if the frequency of this one matches the Larmor frequency of this one, what happens, the nuclear transition happens ok. It will move away and then the flipping of the spin takes place and it will be flipping and going in this direction, changing the precessing angle with perpendicular rotating magnetic field.

Since B_1 is much smaller in magnitude compared to B_o, the precessional frequency of nucleus about B_1 is much lower than ω. Quantum mechanics limits the magnet moment to only certain orientations. Rotation of B_1 at Larmor frequency causes the nuclear spin from one orientation to another.

That means, we say nuclear spin flips what is the selection rule for nuclear transition this is very important. So, for selection rule for nuclear transition is delta mi equals plus or minus 1. That means, basically when the nuclear spin should change its value from plus 1 to minus 1 or minus 1 to plus 1. So, this is against we come across spin selection rule in case of electronic transition in case of electronic transition we say equal to 0, whereas here it is plus or minus 1 we should remember that one. If we consider a nucleus with spin equals i equals half let us say simple as simple as proton have only two energy levels plus half and minus half it is placed in a magnetic field we can calculate its Larmor frequency or energy necessary for the transition.

So, whatever the Larmor frequency, that is the energy required for the nuclear transition from plus half to minus half level. If a proton is placed in a magnetic field of two Tesla (2 T), then delta E which gives a transition energy can be directly calculated using this formula. For example, transition from energy level 1 to 2 is mu z 1 B-naught minus mu z 2 B-naught that is equal to m i x gamma x h x B-naught that is equal to gamma x h x B-naught ($\mu_Z B_o - \mu_Z 2B_o = \Delta m_1 \gamma h B_o = \gamma h B_o$). Now, if the change in energy is produced by electromagnetic radiation, then we know that delta E equal to h nu that is equal to h x gamma x h x B naught ($\Delta E = h\nu = \gamma h B_o$). So, that is what is given here. If we consider Larmor frequency in place of nu then it will become $2\pi\nu$, because its angular.

So, as a result what happens omega becomes 2 pi nu then nu equal to gamma B-naught over 2 pi ($\nu = \gamma B_o/2\pi$). So, that means we can now calculate the Larmour frequency under different magnitude of B-naught (B_o). So, here, if we know the magnetic field strength and gyromagnetic ratio is constant, unique for each nucleus and then we should be able to calculate the Larmor frequency very easily. So, once we know that we can tune the NMR instrument. So, this equation is very important and this equation is nu equal to gamma x B naught over 2 pi (2π) ($\nu = \gamma B_o/2\pi$) is what you should remember that is all nothing else you should remember.

So, once you remember this, most of the problems we come across can be understood and solved as far as NMR is concerned. Now for example, let us say non-zero nuclear spin will have all possible orientations. In the absence of the magnetic field, the moment we apply magnetic field what happens. So, some of them will be aligned with the magnetic field some of them will be opposing the magnetic field, you can see here. So, for example, this is precessing with respect to B-naught (B_o) and yes when we apply another magnetic field Bi perpendicular to B-naught (B_o) what happens it flips, you can see here, how this is flipping, this is what exactly happens in case of NMR. So, here as I mentioned this equation is very very important for protons in a magnetic field of 2 Tesla (2 T). We know that gamma value (γ) is given we should calculate now mu for this proton 2 Tesla (2 T).

So, now, it is very simple you add your 226.78 into 10 raise to 7 (226.78×10^7). So, B-naught (B_o) is there. So, gamma into B-naught (γB_o) and divided by 2 into 22 by 7. If you calculate, 0.75 into 2 into 10 raise to 7 over 2 into 22/7 comes here [$26.75 \times 2 \times 10^7 \times 7)/(2 \times 22) = 90$]. If you simplify this one, it would come around 90 megahertz (MHz).

So, this how you can calculate the frequency starting from the gyromagnetic ratio and also the magnetic field strength. Similarly, one can calculate the radio frequency necessary for the transition of 11-boron (^{11}B), 31-phosphorous (^{31}P), 13-carbon (^{13}C) at magnetic field strength of 2 Tesla (2 T) and 10 Tesla (10 T). So, this is how the orientations are there in the in the absence of magnetic field the moment you apply magnetic field hey will align in such a way that some of them will be having plus half (+1/2) and some of them will be having minus half (-1/2). Nuclear spin with an odd atomic number and an odd mass number has a nuclear spin, that is what I was telling you. The spinning charged nucleus generates a magnetic field any charged species generates a magnetic field and when you apply the magnetic field, it will start rotating about the magnetic field. So, that means, here you can see here this the spinning protons under the influence of the magnetic field generate a loop of current here and loop of current. As a result, what happens, you can see, they behave like tiny magnets and aligning in this direction. I have shown here B-naught (B_o) is there. In the absence of magnetic field, they will be having all kind of rotational orientations and when you apply magnetic field, it will flip and probably it will go something like this and this is low energy more stable

So, this one we call it as plus half and this we call it as minus half. So, let me continue in the next lecture. Let me stop here and continue more discussion on NMR in my next lecture. Thank you.