Interpretative Spectroscopy

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Lecture 46

Introduction to EPR Spectroscopy-2

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. I started discussion on EPR spectroscopy from my previous lecture. Let me continue from where I had stopped. ESR or EPR measures the transition between the electron spin energy levels. Transition induced by the appropriate frequency of radiation and required frequency of radiation depends upon the strength of the magnetic field. As we increase the magnetic field strength, what happens the energy gap between the nuclear spin states steadily increases and if you go for higher field strength magnetic field then higher microwave radiation is required to achieve the transition. Common field strengths are anywhere in the range of 0.34 to 1.24 tesla this about magnetic field B and then 9.5 and 35 gigahertz is the microwave region between 9.5 to 35 gigahertz is the microwave region that is applied in a direction perpendicular to the applied magnetic field to perform transition of electron spins.

This is how a typical EPR instrument looks like. This is the magnetic field and the sample is kept here and the signals will go to the detector and then that goes to the plotter for plotting the spectrum. How does the spectrometer work? can be seen here. This is the source and this is the detector and sample cavity is here, and this is the electromagnet and phase sensitive detector is here and modulation input comes from this part here. That means the radiation source used is called klystron. Klystron are vacuum tubes known to be stable high-power microwave sources which have low noise characteristics and thus give high intensity, that is the reason we use this source of microwave radiation called klystron. The sample is placed in a resonant cavity in between the magnets, which admits microwaves

through an iris. The cavity is located in the middle of the electromagnet and helps to amplify the weak signals from the sample.

Most of the external components such as the source detector is contained within the microwave bridge control. Additionally, the other components such as attenuator, field modulator, amplifier also included to enhance the performance of the instrument. EPR spectrometers typically use electromagnets and the microwave absorption is monitored as the field is varied. When an electron is placed within an applied magnetic field B_o, the two possible spin states of the electron would have different energies. In the absence of magnetic field, the spin states would have the same energy, but the moment an electron is placed in a magnetic field, they possess two different energies. The lower energy state occurs when the magnetic moment of the electron is aligned with the magnetic field and a higher energy state where M is aligned against the magnetic field.

So, that means when the spin is aligned against the magnetic field will be having here plus half (+1/2). In case of NMR the one that is aligned with the magnetic field would have lowest energy that is to be plus half (+1/2), whereas here opposite of that one comes here. The lowest energy in case of NMR is plus half (+1/2) and higher energy is minus half (-1/2) in case of NMR. Here it is opposite, the two states are labeled by the projection of the electron spin m_s and the direction of the magnetic field where m_s equal to minus half (-1/2) is the parallel state and m_s half (1/2) is the anti parallel state. This is actually aligned in this direction, where this one is aligned in this direction, whereas here this is aligned in this direction and this is aligned in a direction opposite to the applied magnetic field. That is shown here and of course, plus half, you can see in this direction, and minus half is in this direction and again it is always convenient to compare these two methodologies NMR and EPR. Similar to NMR, EPR can be used to identify the geometry of a molecule through its magnetic moment and the difference in electron and nuclear mass and EPR is mainly used for the detection and study of free radical species either in testing or analytical experiments.

Spin labeling species of chemicals can be a powerful technique for both quantification

and investigation of otherwise invisible factors that you cannot really detect using other methods. The EPR spectrum of a free electron shows only one line, single peak, whereas that of the hydrogen displays two lines, two peaks, due to the interaction between the nucleus and the unpaired electron. This is called hyperfine splitting so that means, the electrons with spin half and minus half can also interact with nuclear spin and the lines can be further split and this we call it as hyperfine splitting. In NMR we call it as coupling, spin-spin coupling. The distance between two lines is called hyperfine splitting constant A; we call it as a coupling constant in case of NMR spectroscopy.

By using this simple 2nI plus 1 (2nI +1) rule, number of hyperfine lines of a multiplet of an EPR transition can be calculated, where n is number of spin, and I is the number of equivalent nuclei. For example, for nitroxide radicals, the nuclear spin of ^{14}N is 1 so n equal to 1 and I equal to 1 therefore, 2nI plus 1 = 3 (2nI + 1 = 3). Three lines here that means EPR transition for a nuclear spin equal to 1 consists of a triplet. To absorb microwave, there must be unpaired electrons in the system. That means of course, only when we have an unpaired electron or a radical species that we subject for EPR study. In a diamagnetic system or having no unpaired electrons, no EPR signals will be observed as there will be no resonant absorption of microwave energy. That means EPR cannot be used for diamagnetic species and molecules such as NO, NO_2, O_2 do have unpaired electrons in ground state and EPR can also be performed on proteins with paramagnetic ions such as Mn2 plus (Mn^{2+}) Fe3 plus (Fe^{3+}) and copper 2 plus (Cu^{2+}) and other relevant a transition metal ions.

Additionally, molecules containing stable nitroxide radicals, nitroxide radicals such as 2,2,6,6-tetramethyl-1-pyridinyloxal, that is called TEMPO and ditertiary-butyl nitroxide radical. Now let us look into the energy levels associated with these two spins for a molecule with one unpaired electron in a magnetic field. The energy states of the electron can be defined as this one. E equal to $g\mu_B B_o M_s$ that is equal to plus or minus half $g\mu_B B_o$ ($E = gu_B B_0 M_s = \pm 1 / 2 gu_B B_0$), where g is the proportionality factor, we call it as g factor and μ_B is the Bohr magneton, B is the applied magnetic field and Ms is the electron

spin quantum number. The two spin states have the same energy when there is no applied magnetic field that means E equal to 0 in the absence of magnetic field. The energy difference between the two spin states increases linearly with increasing magnetic field strength.

The energy gap is directly proportional to the applied magnetic field strength. So, we talk about proportionality constant, what is this? This is measured from the center of the signal. For a free electron this is 2.00232, that is g. For organic radicals, typically close to free-electron value of 1.99 to 2.01. For transition metal compounds, large variations due to spin orbit coupling and zero field splitting and hence 1.4 to 3.0 is observed.

Now let us look into the techniques that are employed in EPR spectroscopy. Of course, we know the energy difference between the two states given by hν equal to $g\beta B_o$ ($h\nu = g\beta B_0$). This can be recorded either by varying hν the micro frequency or B_o. Usually B_o is varied at a constant microwave frequency. Microwave frequency is kept constant and magnetic field strength is varied in case of EPR technique and here in case of X-band EPR, typical magnetic field strength is 3000 gauss and the ν is 8398 gigahertz or hν equal to 9 gigahertz, and in case of Q-band, the magnetic field strength is 12500 gauss and hν equal to 35 gigahertz and in case of W-band EPR, hν equal to 90 gigahertz and B_o equals 3.5 tesla or 35000 gauss. You can see here; in this one E versus B_o, you can see steadily the values increasing when you go from X band to W band, because of increase in the overall magnetic field strength. Of course, if the magnetic field strength is increasing, obviously the energy required to excite the nucleus or to observe a spin transition, microwave radiation energy also increases. This gives a correlation between various bands and the corresponding microwave frequency employed in various EPR methods, where we are using X band Q band or W band. Then if you look into the spin states, energy of an electron in a magnetic field is denoted by μB_o and then of course I already referred to this equation here. μ equal to $g\beta m_s$ ($u = g\beta m_{s)}$ and β equal to eh by 4 pimc ($\beta = \frac{eh}{4\pi mc}$). e is charge of electron and negative for electron, and β is negative for electron. Atomic unit of magnetic moment is called Bohr magneton and E can be simplified as, E equal to $g\beta m_s B_o$ ($E = g\beta m_s B_0$) and then of course s can have plus and ms can have plus or minus half. When m_s

equal to minus half ($m_s = -1/2$), this the expression, and when ms equal to plus half ($m_s = 1/2$) this is the expression here.

So, this becomes something like this. As I said, in the magnetic field, they will be aligned or opposing the applied magnetic field. This is the low energy, minus half and this is the high energy, plus half. If you consider here, the corresponding energy is also m_i and m_s is also shown here. This is the energy gap between these two represented by this term, shown here. A typical EPR spectrum can look like here. The number of peaks in the absorption curve equal to number of maximum or minimum in the derivative curve. That means when you look into a typical EPR spectrum, you should observe the number of peaks in the absorption curve is equal to number of maximum or minimum in the derivative curve. You can consider the maximums or minimums, they will be essentially the same. This absorption intensity when you look into it, this is absorption curve, it looks like this and this is B_o and this is A versus B_o the first derivative of the absorption intensity is represented by this one this how you can see a derivative curve.

Again proportionality factor is measured from the center of the signal for a free electron g equal to 2.00232 for organic radicals typically close to free electron value, that is between 1.99 to 2.01, For transition metal compounds, a large variation is observed due to spin orbit coupling and zero field splitting. As a result, the range is 1.4 to 3.0. Now, let us look into few more examples here.

Even number of protons or neutrons, nuclear spin is zero. So, you do not observe any EPR signals for those which have no unpaired electrons. For example, ^{12}C, I equal to zero, ^{4}He zero, ^{16}O zero. If you have odd number of protons or neutrons, you have integral spin. For example, ^{2}H, ^{14}N, I equal to 1 and here in case of ^{10}B, I equal to 3. In case of even/odd combination, we have these things, half integral spin.

This is very similar, this is about nuclear spin (I) am talking about. If we look into different main group elements and the isotopes, the spin abundance, also how many EPR lines are expected, is given in this table. For example, H if we are considering 1 as well as 2, that means hydrogen as well as deuterium, then in case of hydrogen, plus half is there in case

of deuterium plus 1 is there. This is 0.015 percent abundance. Then we can see, in case of first one, two lines and in case of the deuterium, we see three lines in EPR spectrum and in case of carbon, we have ^{12}C and ^{13}C. ^{12}C shows no signal, I mean I equal to zero, whereas in case of ^{13}C we have I equal to half this constitutes about 1.1 percent. In case of 1 we get only one line because, 2nI plus 1 =1 (2nI + 1). In case of half, we get two lines. In case of nitrogen, we have both ^{14}N and ^{15}N. ^{14}N has I equal to 1, and in case of ^{15}N we have half, that is only about 0.4 percent. We get three lines and two lines respectively in case of ^{14}N and ^{15}N and in case of oxygen we have 16 17 and 18 and ^{16}O and in case of 17 we have 5 by 2 (5/2) and 0.04 percent; 18 can be ignored.

In case of 5 by 2 (5/2) we get six lines 2 n I plus 1 (2nI +1) if you use here 2 into 1 we get six lines here and in case of zero, we get simply one line. In case of F only one isotope is there ^{19}F, I equal to half. We get two lines and similarly in case of ^{31}P also 100 percent abundant, spin is half. We get two lines in case of sulfur. We have three isotopes 32, 33 and 34. 32 has spin I equal zero, whereas 33 and 34 have 3 by 2 (3/2) that constitute about 0.8 percent. In case of 33 or 34 we get four lines in EPR spectrum. In case of chlorine, we have two isotopes 35 and 37 both have 3 by 2 (3/2) and in both the cases we get four lines. In case of arsenic, 75 is the only isotope with 3 by 2 (3/2) value, it gives four lines. In case of selenium several isotopes: 76, 77, 78, 80, 82. 76 has zero and others have half spin value and that constitute about 7.6%. We see 1 and four lines. In case of bromine, very similar to chlorine we have two isotopes 79 and 81, both have I equal to 3 by 2 (3/2). We see four lines here and in case of iodine again 127 we have 5 by 2 (5/2) spin and six lines.

Similarly, we have a table for a transient matrix also. If you consider vanadium in plus four (V^{+4}) state, isotope 51 and spin is 7 by 2 (7/2). So, we get eight lines in EPR spectrum. In case of manganese 2 plus (Mn^{2+}) 55 isotope, 5 by 2 (5/2) is the spin value and we get six lines. In case of iron 3 (Fe^{3+}), we have 54 56 57 58. 54 has zero spin, whereas 56, 57 show half and are about 2 percent. We see two lines, whereas in case of zero we get only one line. In case of cobalt, we have cobalt(II) 59 isotope 7 by 2 (7/2), we see again eight lines. In case of nickel(III) as well as nickel(I), 58 is zero. 60-62 and 64 constitute only about 1 percent and we see 3 by 2 (3/2); four lines about 0.25 percent. For copper(II) we have 63, 65 and again spin 3 by 2 (3/2), we observe four lines. In case of molybdenum in plus 5

(Mo^{+5}) state, 92, 94 to 98 and 100. 92 is zero and in case of others we see 5 by 2 (5/2) is about 25 percent.

So, what we see about one and two lines, and that is about 97 percent.

Now, let us look into hyperfine interaction like spin-spin splitting. In case of NMR that is very similar, here in addition to the applied magnetic field, unpaired electrons are also sensitive to their local environments. Frequently the nuclei of the atoms in a molecule or complex have a magnetic moment, which produces a local magnetic field at the electron. The resulting interactions between the electrons and the nuclei is called as hyperfine interaction. Here in a similar way this is the interactions between the electrons and the local magnetic field generated either independently or depending on the applied magnetic field. That results in further splitting of the lines, this we call it as hyperfine interaction. The resulting interaction between the electron and the nuclei is what decides the number of lines in the hyperfine interaction.

So, number of lines again is given by 2nI plus 1 (2nI + 1), n number of equivalent nuclei and I is spin value. The relative intensities of the lines is determined by the number of interacting nuclei. Same thing is true in case of NMR as well. For example, if you consider here, we have half and minus half, and they further interact nucleus with spin half to give four lines like this. Now, let us look into hyperfine splitting with the different nuclei having nuclear spin and also how many such nuclei are there. For example, when no interaction is there, we see single peak for one unpaired electron. In the interaction of nucleus with I equal to half, it splits into a two lines, and when this electron interacts with the nucleus spin I equal to 1 there will be three lines. In case of nuclear spin I equal to 3 by 2 (3/2), there will be four lines. Then two equivalent nuclei with I equal to half, we see again three lines and then three equivalent nuclei with i equals half we will see the four lines and then four equivalent nuclei with I equal to 1, you can see nine lines. This gives some idea about hyperfine splitting.

Let me take some specific examples in my next lecture and then continue discussion on EPR spectroscopy.

Until then have an excellent time thank you.