Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 45

Introduction to EPR Spectroscopy-1

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. Today, I shall start discussion on EPR Spectroscopy or ESR Spectroscopy, Electron Paramagnetic Resonance Spectroscopy or Electron Spin Resonance Spectroscopy both are essentially the same. EPR is fundamentally very similar to popular NMR Spectroscopy, we are very much familiar with it, with several important distinctions. While both the methods deal with the interaction of electromagnetic radiation with magnetic moments of particles. There are many differences between the two spectroscopic methods as well. Now for example, EPR focuses on the interaction between the external magnetic field and the unpaired electrons of whatever the system it is delocalized to as opposed to the nuclei of individual atoms. Of course, in NMR Spectroscopy, we look into nuclear spin transition, whereas in case of EPR, we look into electron spin transition, that is the major difference between EPR and NMR.

The electromagnetic radiation is used in NMR is in the radio frequency range of 300 to 1000 megahertz (MHz). Whatever the frequency we are applying in a direction perpendicular to the applied magnetic field to bring resonance with the Larmor frequency, so that flipping or transition of a nucleus takes place. The electromagnetic radiation comes in the radio frequency range of 300 to 1000 megahertz (MHz), whereas in case of EPR, microwaves are used in the range of 3 to 400 gigahertz (GHz). So, in EPR, the frequency is typically held constant. This is the major difference between NMR and EPR.

In EPR, frequency is typically held constant, microwave frequency whatever we are applying is held constant, while the magnetic field strength is varied. In contrast to this, in

NMR experiments, the magnetic field is held constant B_o, whatever we say and then we are tuning the radio frequency to match the Larmor frequency of the nuclei which is perturbed because of the local magnetic field generated, which can either align with the magnetic field or oppose the magnetic field. That is the major difference. Magnetic field is kept constant in case of NMR and the radio frequency is varied. These are the major difference between EPR and NMR spectroscopic methods.

Due to the short relaxation times of electron spins compared to nuclei, they have a very short relaxation time, whereas in case of nuclei this is much larger. As a result, EPR experiment must be performed at very low temperature, often below 10K and sometimes as low as 2K. This typically requires the use of liquid helium. This is a major drawback that we face in case of EPR spectroscopy. EPR spectroscopy is roughly 1000 times more sensitive than NMR due to the higher frequency of electromagnetic radiation employed here.

Advanced pulse EPR methods are also used directly to investigate specific couplings between paramagnetic spin systems and specific magnetic nuclei. That means we can also look into the interaction between paramagnetic spin systems as well as specific magnetic nuclei. So, the most widely used method is electron nuclear double resonance indoor called as. In this method of EPR spectroscopy, both microwave and radio frequencies are used to perturb the spins of electrons and nuclei simultaneously in order to determine very specific coupling between these two entities which is not attainable through traditional continuous wave methods. So, this is the major difference between EPR and indoor.

The objective of indoor is to look into the coupling between the nuclear spin as well as the electron spin. Let us look into the origin of the EPR signal. Electron, we all know is a negatively charged particle with certain mass that shows two kinds of movements. One is spinning around the nucleus in an orbital movement which brings orbital magnetic moment and also it spins around its own axis known as spin magnetic moment. This is again very similar to what we see in case of nuclear spin.

Nuclear spin besides precessing on its own axis, it also revolves around the magnetic field in an orbital fashion. So, magnetic moment of the molecule is primarily due to spin magnetic moment of unpaired electron that is given by M_s equal to square root of s into s plus 1 into h over 2 pi ($M_s = \sqrt{s(s+1)}\frac{h}{2\Pi}$) Where M_s is the total spin angular moment and s is the spin quantum number and h is Planck's constant. In the z direction, the component of the total spin angular moment can have only two values Ms equal to small m_s into h over 2 pi ($M_s = m_s\frac{h}{2\pi}$). So, Ms can have 2S plus 1 (2S +1) different values starting from plus S to minus S.

That means, if we consider a single unpaired electron, only two possible values, Ms equal to plus or minus half $\left(m_s = \pm\frac{1}{2}\right)$. The magnetic moment μ_e is directly proportional to the spin angular moment. That can be related using this equation here μ_e equal to minus g_e μ_B M_s ($u_e = -g_e u_B M_s$). We are introducing a new term called g_e. The negative sign in this expression is due to the fact that the magnetic momentum of electron is collinear with the applied magnetic field, but anti parallel to the spin itself. As a result, the expression has negative charge. The term g_e μ_B M_s is the magnetogyric ratio.

Gyromagnetic ratio, I am sure you are familiar in case of NMR. The Bohr magneton μ_B is the magnetic moment for one unit quantum mechanical angular momentum μ_B. Of course you also familiar with the expression for μ_B, Bohr magneton, that is given by μ_B equal to eh over 4pim_e ($u_B = \frac{eh}{4\pi m_e}$), where e is the electron charge, m_e is the electron mass and g_e is known as the free electron g factor which carries a most accurate value of 2.002319304386. Perhaps it is one of the most accurately known physical constant in physics or chemistry for that matter. This magnetic moment interacts with the applied magnetic field. The interaction between the magnetic moment mu and the field can be described by a simple equation e equal to μ into B ($E = -uB$). If we consider a single unpaired electron there, will be two possible energy states, this effect is called Zeeman splitting that means plus half and minus half.

So, this term can be rewritten as E plus half equal to half g μ_BB ($E_{+1/2} = \frac{1}{2} g u_B B$) and E minus half for the another one with minus half level minus half into μ_BB (($E_{-1/2} = \frac{1}{2} g u_B B$))that means both of them have different energies when they are kept in the magnetic field when the magnetic field is applied in the absence of external magnetic field E plus is equal to E minus is equal to 0 ($E_{+1/2} = E_{-1/2} = 0$). So, that we can relate them with this equation, the energy difference between the two levels is hν equal to gμ_B into B_o, where B is the applied magnetic field ($\Delta E = h\nu = g u_B B$). So, in the presence of external magnetic field, the energy difference between the two states can be represented using this diagram here. Energy versus applied magnetic field is steadily increasing, as energy of the applied magnetic field strength increases, the gap between these two levels also increases and here the gap between these two levels is given by the energy difference delta-E equal to hν equal to gμ_B x B_o ($\Delta E = h\nu = g u_B B$). From this equation, we can calculate the energy required to excite the nuclear spin from one state to another state and this comes from the microwave region. With the intensity of the applied magnetic field increasing, the energy difference between the energy levels widens until, it matches with the microwave radiation and results in absorption of photons. So, this is the fundamental basis for EPR spectroscopy.

So, in case of NMR, we talk about Larmor frequency and when the radio frequency applied in a direction perpendicular to the applied magnetic field. When that radio frequency achieves the Larmor frequency of the precessing nucleus the resonance occurs and flipping of the spin or spin transition or nuclear transition takes place. So, EPR spectrometers typically vary the magnetic field and hold the microwave frequency. This is very important. So, magnetic field is varied, whereas the microwave frequency is kept constant, whereas in case of NMR again magnetic field is kept constant and radio frequency is varied. EPR spectrometers are available in several frequency ranges and X band is currently the most commonly used and also more popular range of frequency used. Here I have given a list of different microwave bands for EPR spectroscopy and they carry different names they call S band, X band, K band, Q band and W and the corresponding frequency I have shown

here in gigahertz and also corresponding wavelength in centimeter is also given and also for corresponding particular microwave bands the magnetic field strength used is also given here in Tesla.

In case of S band 0.107 in case of X band it is 0.339 Tesla, in case of K band it is 0.82, in case of Q band it is 1.25 and in case of W it is 3.3 it can go up to 4 Tesla. EPR is often used to investigate systems in which electrons have both orbital and spin angular momentum which needs the use of scaling factor to account for the coupling between the two momenta. We should look into coupling between two. This is called the g-factor. So, g-factor arrives to account for interaction between orbital and spin angular momentum and it is roughly equivalent in utility, how chemical shift is used in NMR.

The utility of this one is very similar to the utility of chemical shift in case of NMR. The g factor is associated with the quantum number J the total angular momentum, where J can take L plus S (J = L+S) value. In case of UV visible spectroscopy, J spin orbit coupling can have values of L plus or minus S and we know that it takes, L minus S when the sub shell is less than half field and it takes L plus S value, when it is when the sub shell is more than half field. For example, if you take d^4, we consider J equal to L minus S (J = L -S) and if you take d^6, we are considering J equals L plus S (J = L+S). That term is shown here this is how we can write the term here of course, the same term without these two g factors, we use for calculating μ effective in case of paramagnetic species.

In this term, g_L is the orbital g value and g_s is the spin g value. For most spin systems with angular and spin magnetic momenta, it can be approximated that g_L is exactly one and g_S is exactly two, then this equation reduces to a new expression called Lande formula and that is represented by this expression here, gJ equal to 3 by 2 minus L into L plus 1 minus S into S plus 1 over 2 J into J plus 1 ($g_J = \frac{3}{2} - \frac{L(L+1)-S(S+1)}{2J(J+1)}$). The resultant electronic magnetic dipole is μ_J equal to minus $g_J u_B J$ ($u_J = -g_J u_B J$). This is how we can represent the resultant electronic magnetic dipole.

Often these approximations do not always hold true as there are many systems in which J coupling does occur, especially in transition-metal clusters where the unpaired spin is highly delocalized over several nuclei that accounts for metal-metal bonding anyway. But for the purpose of an elementary examination of EPR theory, it is useful for the understanding of how this g-factor is derived. In general, this simply referred to as the g-factor or the Lande g-factor for a free electron with zero angular momentum, g-factor has a small quantum mechanical corrective value of g equal to 2.0023193. In addition to considering the total magnetic dipole moment of a paramagnetic species, the g-value considers the local environments of the spin system. Of course, in case of NMR also we define in a different way the net magnetic field experienced by the nucleus, when it is surrounded by electrons, would differ because of shielding or deshielding effects. Here the existence of local magnetic field produced by other magnetic species. Electric quadrupoles, magnetic nuclei, ligand fields produced by other paramagnetic species come into picture. When we talk about EPR of transition-metal complexes, which are paramagnetic in nature, all can change the effective magnetic field experienced by the electron. Similarly, the net magnetic field experienced by the electron spin is given like this B_o plus B_{local}($B_o + B_{local}$) and this is also again very similar to NMR that magnetic field experienced by the nucleus is also shown in a very similar way, that we call B_o plus B_i ($B_o + B_i$), where it is a induced magnetic field, whereas here we call it as local magnetic field. The local field can be either induced by the applied field, and as a result have magnitude dependence on B_o OR the local fields may be permanent and independent of B_o.

The local fields may be permanent and can be independent of B_o also. In the case of former, where the local field depends on the applied magnetic field, it is ideal to consider the net field experienced by the electron as a function of B_o. So, here we use the term $B_{effective}$ equal to B_o into 1 minus sigma ($B_{eff} = B_0(1 - \sigma)$) and the same terminology we use in case of NMR. Since many organic radicals and radical ions have unpaired electrons with L equals 0 and hence J becomes S, of course, it is L plus S (L+S) if L value is 0 obviously J becomes same as that of S value as a result g-value will be close to 2. However, transition metal ions or complexes due to unpaired electrons, have larger value of L and S and hence the g-value diverge from the observed value of 2 here.

In view of this, the energy levels correspond to the spins in an applied magnetic field can be expressed using this equation: Em_s equal to $m_s g_e \mu_B B_o$ ($E_{m_s} = m_s g_e u_B B$). Thus the energy difference associated with a transition is deltaEm$_s$=delta $m_s g_e \mu_B B_o$ ($\Delta E_{m_s} = \Delta m_s g_e u_B B$).

These two equations expressions are important in EPR. Typically, EPR is performed in a perpendicular mode where the magnetic field component of the microwave radiation is oriented perpendicular to the applied magnetic field of course, this is also very similar to the NMR where a magnetic field of frequency similar to Larmor frequency that comes from the radio frequency range, applied in a direction perpendicular to the applied magnetic field B_o. This very similar. microwave radiation is also applied or is oriented in a direction perpendicular to the applied magnetic field. The selection rule for allowed EPR transition is also similar to nuclear transition in which we are considering deltaS equals plus or minus 1 ($\Delta S = \pm 1$), and similarly in case of EPR also we are considering delta m_s equal to plus or minus 1 ($\Delta m_s = \pm 1$).

The energy of the transition can be simplified as follows like this and there is a method called parallel mode. In parallel mode what happens? Microwave radiation is applied in a direction parallel to the magnetic field in which microwaves are applied parallel to the magnetic field changing the selection rule to this one. This is the special case. In this case, the selection rule is Em_s equal to plus or minus 2 ($\Delta m_s = \pm 2$) otherwise when it is applied perpendicular to the magnetic field microwave this is very similar to what we see or what we use in case of NMR $\Delta m_s = \pm 1$. This kind of applying microwave radiation parallel to the applied magnetic field is called parallel mode EPR and I am not going to the details of parallel mode EPR theory. Let me focus only on perpendicular mode of EPR theory.

Here, I have shown a typical spectrum. EPR, electron paramagnetic resonance and ESR is electron spin resonance apply. This is applicable for species with one or more unpaired electrons. In order to use EPR to study a molecule, they should have one or more unpaired electrons or free radicals or transition metals with odd number of electrons or high spin

complexes or at least in the excited state they should have non zero S value. Again this is a non-destructive technique, very similar to NMR.

Now let us look into more points concerned with EPR spectroscopy.

EPR: what are the information we can extract from EPR spectra of a molecule which has at least one unpaired electron. It says: what types of paramagnetic species are present and what is the local structure and symmetry of this species. What is the nature of the wave function containing the unpaired electrons where are the unpaired spins delocalized all this vital information we can get from EPR spectrum. What are the major disadvantages; typically required odd integer spins. That means diamagnetic species we cannot use it and here spin should have half 3 by 2 (3/2) 5 by 2 (5/2) 7 by 2 (7/2) etcetera.

Resolution is not as good as in NMR. Broad features are observed and often require very low temperature for good resolution. There is a major drawback because of very fast relaxation. In order to slow down the relaxation in case of EPR, we have to go to much lower temperature for that one we need liquid helium this is the major disadvantage or these are the major disadvantages associated with EPR spectroscopic method. Now, let us look into the energy transition how that happens. So, ESR measures the transition between electron spin energy levels and transition induced by the appropriate frequency radiation. That means basically when we know that in the absence of magnetic field, the nucleus spin possess 0 energy and the moment field is applied, they align with plus half and minus half values.

Transition induced by the appropriate frequency. We achieve transition, electron spin transition by applying the corresponding microwave radiation. Required frequency of radiation depend on the strength of the magnetic field, you saw, the energy is associated with the energy difference between the two states, which is directly proportional to the applied magnetic field. If the field strength increases, the energy separation also increases and we need high frequency microwave radiation.

Common field strengths are 0.34 to 1.24 tesla and 9.5 to 335 gigahertz microwave region is employed here in this perpendicular mode of EPR module. So, let me stop here and continue more discussion on EPR spectroscopic methods in my next lecture. Until then have an excellent time. Thank you.