5.14: Electron Paramagnetic Resonance

EPR spectroscopy is possible to come out of any sample that has transiently or statically unpaired electron spins. For instance, radicals and electronic triplet states. Electron paramagnetic resonance spectroscopy (EPR) is a powerful tool for investigating paramagnetic species, including organic radicals, inorganic radicals, and triplet states. The basic principles behind EPR are very similar to the more ubiquitous NMR, except that EPR focuses on the interaction of an external magnetic field with the **unpaired electron(s)** in a molecule, rather than the nuclei of individual atoms. EPR has been used to investigate kinetics, mechanisms, and structures of paramagnetic species and along with general chemistry and physics, has applications in biochemistry, polymer science, and geosciences.

EPR Features

Measured physical quantities

- Energy separation between different electron spin states
- Nuclear hyperfine coupling constants

Information available

- Spin state, S, of paramagnetic center
- Magnitude of hyperfine interactions
- Zero-field splitting of half-integer $S > 1/2$ states
- Possible identity of paramagnetic center (free radical; metals in metal cluster)
- Possible identity of ligating atoms

Information NOT available, limitations

- No information for diamagnetic sites
- Integer spin states often unobservable

Examples of questions that can be answered

- What are the different paramagnetic centers in the sample?
- How do these centers change with changes in redox potential and pH or during substrate binding or catalysis?

Major advantages

- Volume (300 mL) and concentration (1.0-0.01 mM) often low
- Recording spectrum can be done quickly (usually no more than 15-20 min)
- Spectrum is only of paramagnetic species
- Spectrum is often simple to interpret
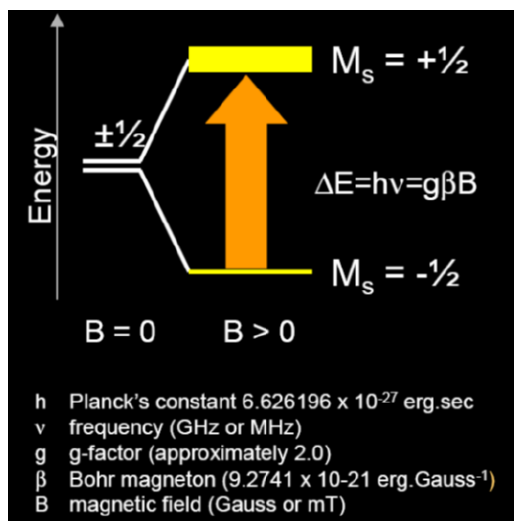- Spectrum often can be recorded *in vivo*

Major disadvantages

- Most paramagnetic metal centers require low (20 K or lower) temperatures for detection

Sample constraints

- Sample volume is ca. 0.3 mL
- Concentration can range from 0.01-1.0 mM
- Sample should be free of any paramagnetic impurities

The degeneracy of the electron spin states is lifted when an unpaired electron is placed in a magnetic field, creating two spin states, $m_s = \pm\frac{1}{2}$, where $m_s = -\frac{1}{2}$, the lower energy state, is aligned with the magnetic field.

The spin state on the electron can flip when electromagnetic radiation is applied. In the case of electron spin transitions, this corresponds to radiation in the microwave range. The energy difference between the two spin states is given by:

$$\Delta E = E_{+} - E_{-} = h v = g \beta B \tag{5.14.1}$$

where h is Planck's constant (6.626 x 10^{-34} J s-1), ν is the frequency of radiation, β is the Bohr magneton (9.274 x 10-24 J T^{-1}), B is the strength of the magnetic field in Tesla, and g is known as the **g-factor**.

The g-factor is a unitless measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023. The value of g can vary, however, and can be calculated by rearrangement of Equation 5.14.1:

$$g = \frac{h v}{\beta B}$$

using the magnetic field and the frequency of the spectrometer. Since h, ν, and ß should not change during an experiment, g values decrease as B increases. **The concept of g can be roughly equated to that of chemical shift in NMR**.

Reference

https://egpat.com/test-papers/esr?Page=1