Spectroscopy

Spectroscopy is basically an experimental subject concerned with absorption, Emission and Scattering of electromagnetic radiation by atoms or molecules.

Reference: Modern Spectroscopy – J M Hollas

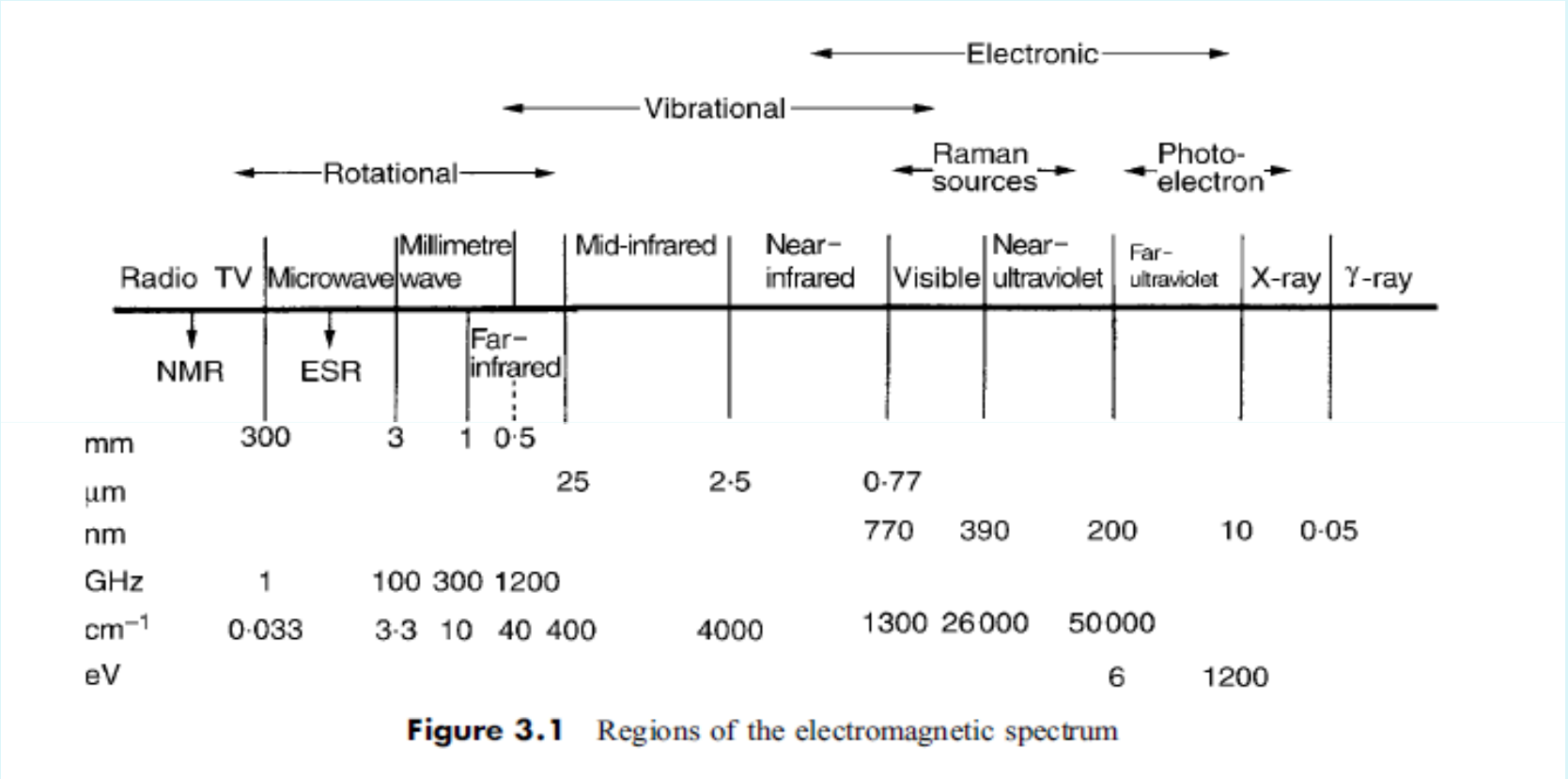


Figure 3.1 Regions of the electromagnetic spectrum

Regions of electromagnetic spectrum. Indications of region boundaries are given in Wavelength, frequency and wave numbers. High energy regions are indicated in electron volts.

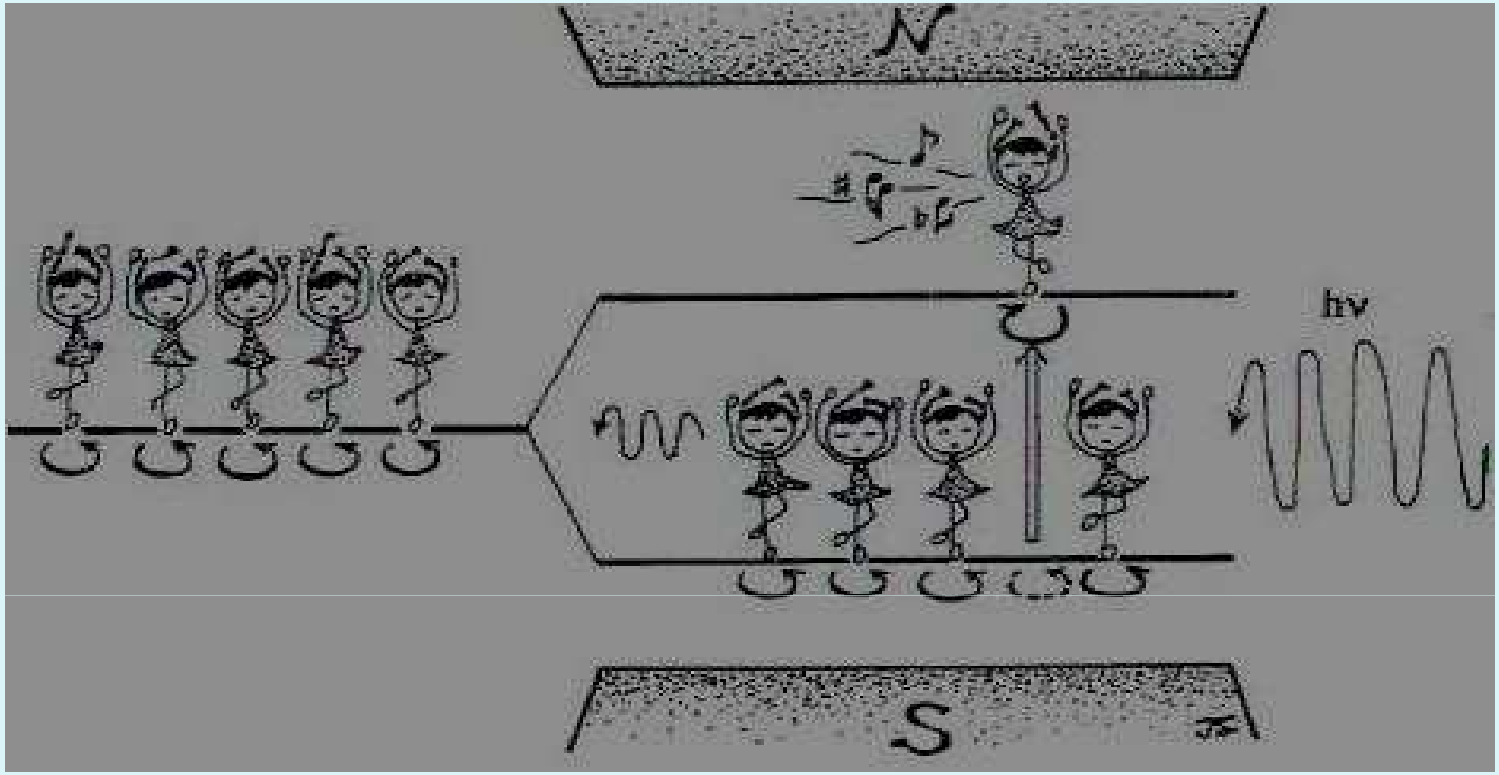
- **ESR spectroscopy (Frequently Microwave region)**
- **NMR spectroscopy (usually in Radiowave region)**

1. **Electron Spin Resonance (ESR)**
2. **Nuclear Magnetic Resonance (NMR)**

The major difference between electron spin resonance and nuclear magnetic resonance is that the nuclear properties are hardly affected by the surroundings whereas the electronic properties strongly dependent on the surroundings due to its much greater physical size and much smaller energy to excited states.

ESR studies involve direct transitions between electronic Zeeman levels while NMR studies involve the direct transitions between nuclear Zeeman levels.

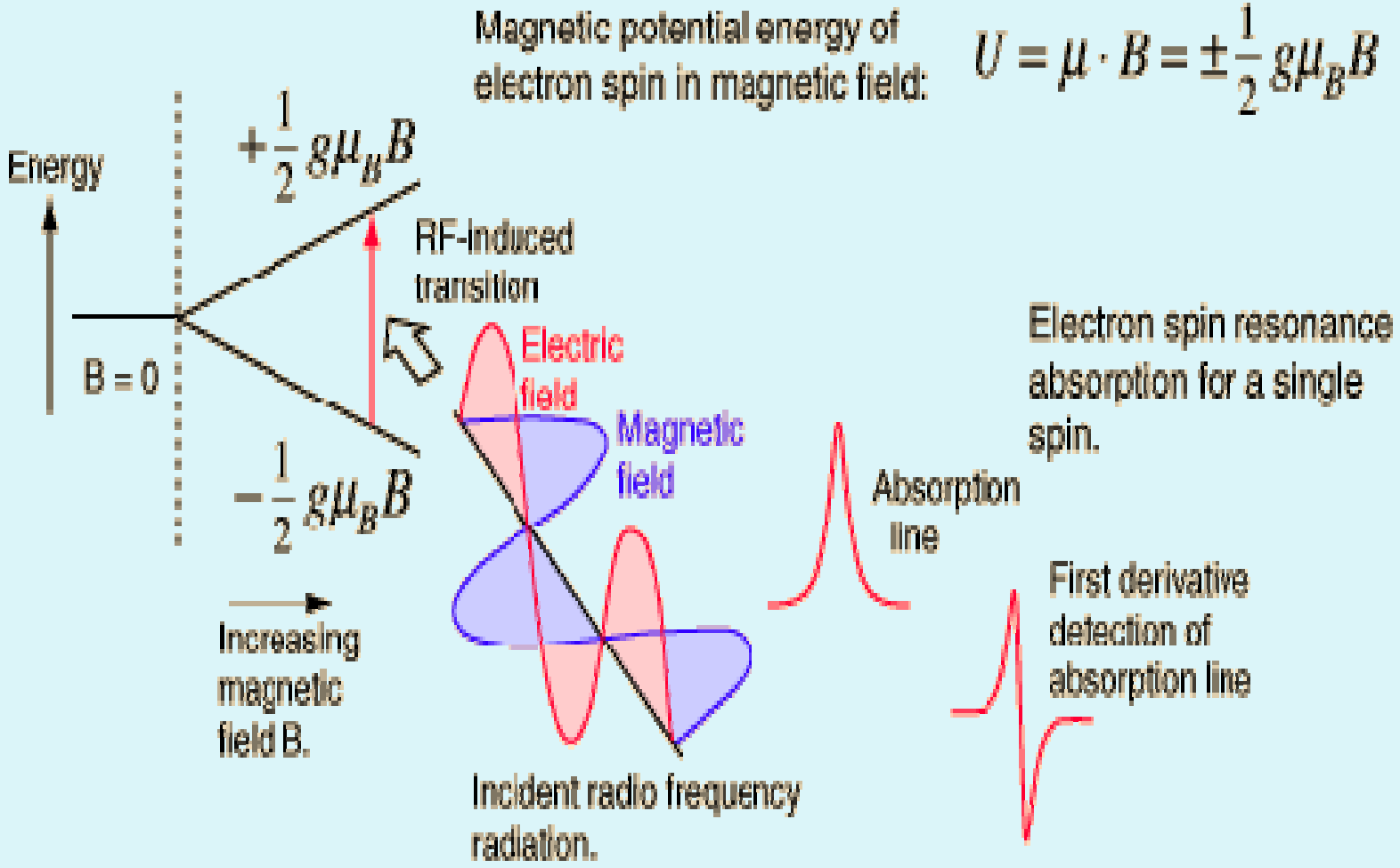
- C.P. Poole , Electron Spin Resonance, Dover(1983), p.3



Basic Principle of ESR

M. Ikeya , New Appliations of Electron Spin Resonance, Word Scientific(1993),p.23

The unpaired electrons are excited to a high energy state under a magnetic field by the absorption of microwave (music). The excited electron changes its direction of spin and relaxes into the ground state by emitting phonons(song). This absorption of electromagnetic wave (Microwave) is called Electron Spin Resonance (ESR).This microwave absorption is measured as a function of the magnetic field in ESR spectroscopy.



Wertz, John E. and Bolton, James R., Electron Spin Resonance, London, Chapman and Hall, 1986.

Prob. 1
Find the ratio of Bohr magneton to Nuclear magneton.

Ans.
1836

ESR energies are generally about 2000 times as big as NMR energies.

Prob. 2

Calculate the ESR resonance frequency of an unpaired electron in a magnetic field of 0.335 T.

Ans.

9.3777GHz

Prob. 3

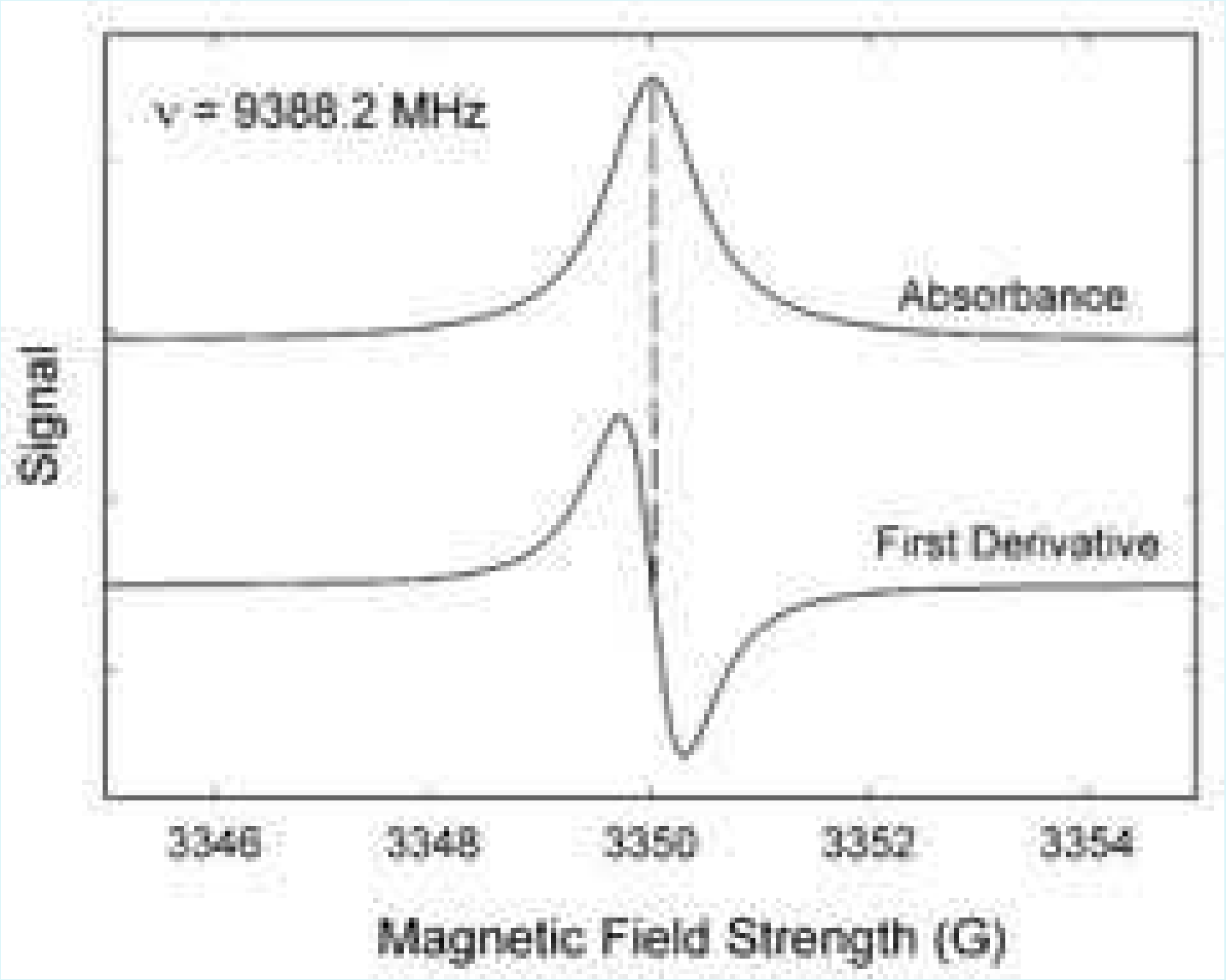
ESR spectrum of an unknown sample shows a single line at 0.335T at a frequency. DPPH (g=2.0036) show a line at 0.3375T at the same frequency. What is the g value corresponding to unknown sample?

Ans.

2.0185

- Put sample into experimental magnetic field
- Irradiate (microwave frequencies)
- Measure absorbance of radiation

- A 1st derivative spectrum is obtained from the unpaired electron.
- g is a characteristic of the chemical environment of the unpaired electron; for free radicals it is near 2.00 and can vary widely for transition metal centers.
- Complicated/enhanced by hyperfine interactions with nuclei with non-zero spin.


ν = 9388.2 MHz
Absorbance
First Derivative
Signal
3346
3348
3350
3352
3354
Magnetic Field Strength (G)

ESR Spectrometer

- Microwave oscillator
- Resonance cavity
- Magnet to supply d.c. magnetic field
- System for modulation of d.c. magnetic field
- Detector
- Display and Recording system

The ESR study provides various important information about the system:

1.Magnetic susceptibility of an anisotropic crystal.
2.Information about the paramagnetic ion and its diamagnetic neighbours.
3.Study of line width provides the information about spin-lattice and spin-spin interactions.
4. Study of hyperfine structure provides information about nuclear spin, nuclear magnetic moment and electric quadrupole moment.

THEORETICAL HAMILTONIAN

The total Hamiltonian with the terms written in decreasing order of magnitude is

$$\mathcal{H} = \mathcal{H}_{elect} + \mathcal{H}_{CF} + \mathcal{H}_{ls} + \mathcal{H}_{ss} + \mathcal{H}_{zee} + \mathcal{H}_{hf} + \mathcal{H}_{q} + \mathcal{H}_{N}$$

where

$\mathcal{H}_{elect}$ = electronic energy (10^4-10^5cm^{-1}) Optical Region

$\mathcal{H}_{CF}$ = crystal field energy (10^3-10^4cm^{-1}) IR and optical

$\mathcal{H}_{ls}$ = spin orbit coupling (10^2cm^{-1})

$\mathcal{H}_{ss}$ = spin spin interaction(0-1cm^{-1})

$\mathcal{H}_{zee}$ = electronic Zeeman term (0-1cm^{-1})

$\mathcal{H}_{hf}$ = hyperfine term (0-10^{-2}cm^{-1})

$\mathcal{H}_{q}$ = quadrupole interaction (0-10^{-2}cm^{-1})

$\mathcal{H}_{N}$ = nulear Zeeman term (0-10^{-3}cm^{-1})

Usually Zeeman and hyperfine terms are evaluated directly from ESR data, while the crystal field and spin-orbit energies are independently evaluated from Optical spectra, and are then correlated with the ESR data.

Main information gained from ESR spectra is an evaluation of various terms in the spin Hamiltonian. ESR spectrum of a particular paramagnetic system will be recorded at several temperatures, several frequencies and several microwave powers. ESR spectrum may be employed to identify an unknown transition –metal ion or lattice defect, or it may distinguish between several valence state of the same ion. ESR spectrum frequently identifies the lattice site and site symmetry of the paramagnetic species, particularly in case of single crystals.

Suggested reference

Atomic and Molecular Spectroscopy
V.K. Jain
Narosa

Further references:

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