The electronic spectra of the other two Ni^{2+} complexes show two bonds within the ranges 15198-22963 cm^{-1} and 21032-24752 cm^{-1} assignable to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively in octahedral field. The values of magnetic moments 1.11-1.65 B.M. for these complexes are taken as additional evidence for an octahedral structure. The ligand field parameters (10 Dq and Racah parameter B) for these two complexes are calculated by solving equations 5 and 6, the values are given in Table (5), which are in the same range as reported for octahedral fields around Ni^{2+} ions[75,76].

$$\upsilon_1 ({}^3A_{2g} \rightarrow {}^3T_{2g}) = 10\,Dq \qquad (4)$$

$$\upsilon_2 ({}^3A_{2g} \rightarrow {}^3T_{1g}(F)) = 10\,Dq + \frac{15}{2}B - \frac{1}{2}[(15B - 6\,Dq)^2 + 64(Dq)^2]^{\frac{1}{2}} \qquad (5)$$

$$\upsilon_3 ({}^3A_{2g} \rightarrow {}^3T_{2g}(P)) = 15\,Dq + \frac{15}{2}B + \frac{1}{2}[(15B - 6\,Dq)^2 + 64(Dq)^2]^{\frac{1}{2}} \qquad (6)$$

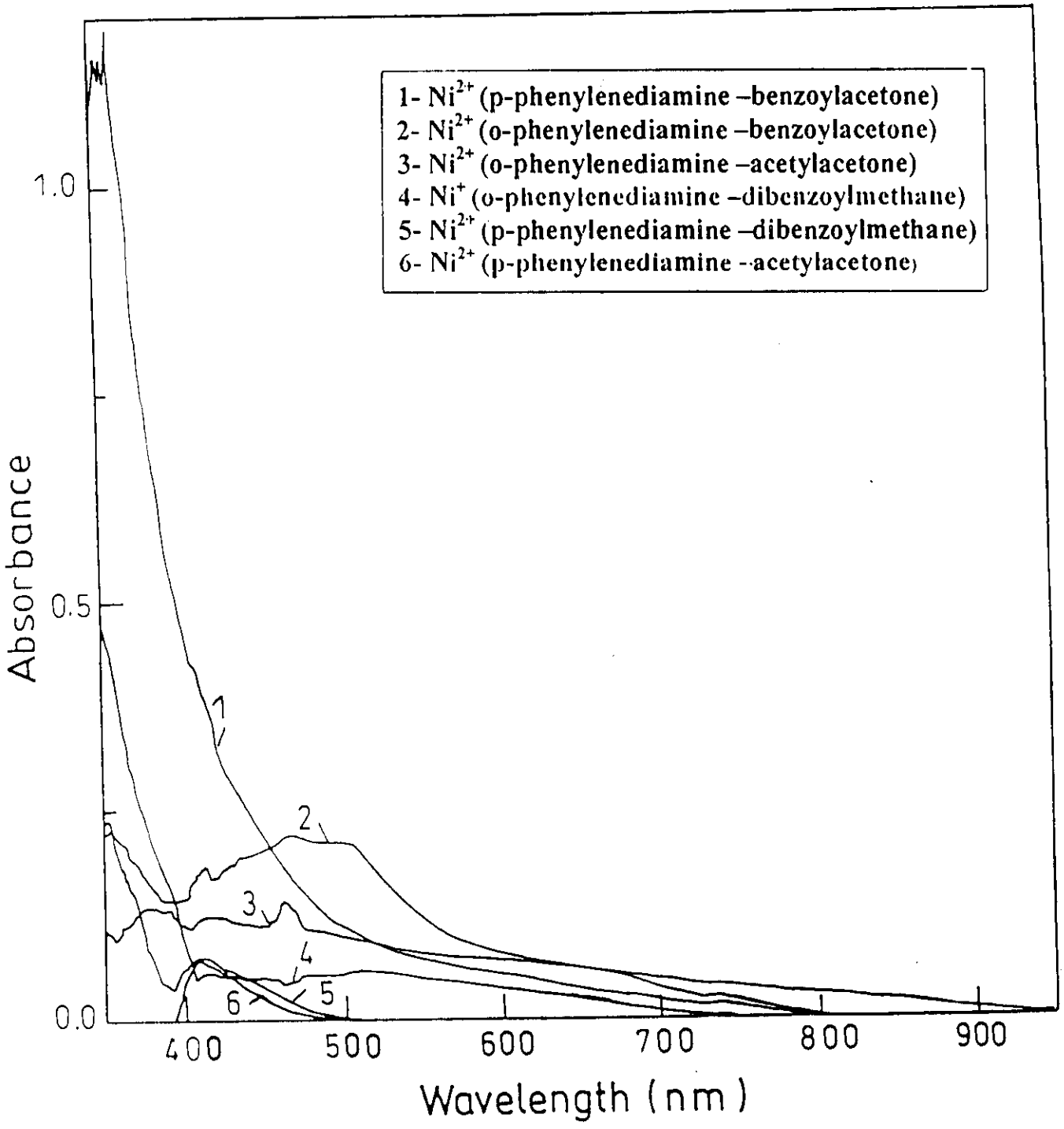

Fig. (18) Electronic absorption spectra of macrocyclic Ni^{2+} complexes in Nujul mull.

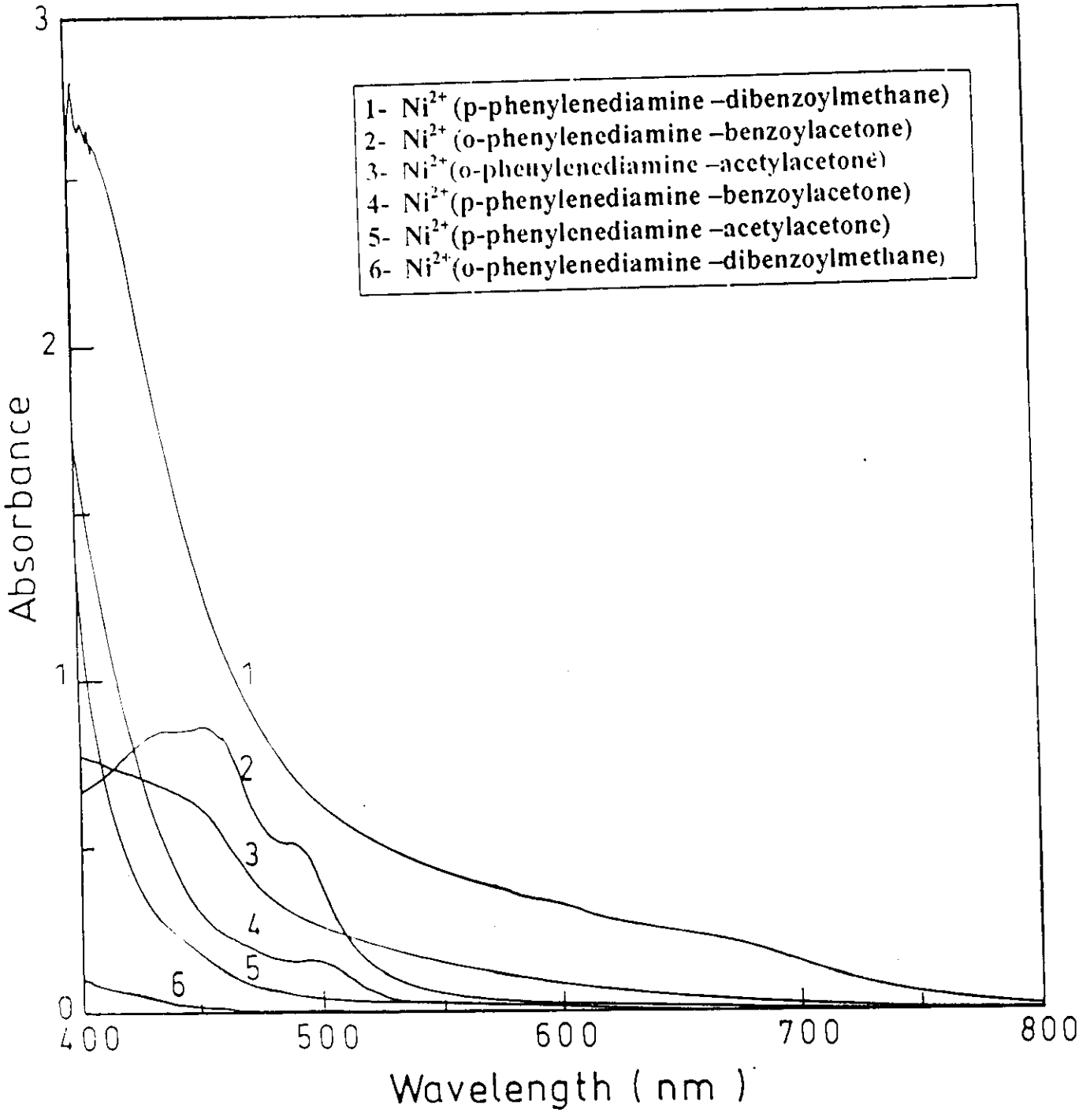

Fig. (19) : Electronic absorption spectra of macrocyclic Ni^{2+} complexes in DMF

5.4.4. Spectral and magnetic properties of Cu(II) macrocyclic complexes

The copper (II) ion ($3d^9$) has one unpaired electron in 3d-level. Its compounds are expected to show magnetic moments close to the spin only value, i.e. 1.73 B.M. based on theoretical calculation irrespective of the bond type involved. However, the observed values of the magnetic moments are 2.12 -2.38 B.M. for most copper(II) compounds with ionic or rather weak covalent bonds and 1.26-1.83 B.M. for compounds with strong covalent bonds. Also, copper (II) compounds having subnormal magnetic moments, less than 1.73 B.M. have recently been recorded. These subnormal moment values, measured at room temperature, were attributed to weak covalent bonds.

The d^9 configuration gives rise to the ^2D ground term. However, in an octahedral field the odd electron residues in an e_g orbital, and the ground term becomes ^2Eg rather than $^2T_{2g}$.

In octahedral copper (II) complexes, a single absorption band in the visible spectrum corresponding to ^2E_g -$^2T_{2g}$ is expected. In many copper(II) complexes, the Jahan-Teller distortion is so great that the coordination is almost of square planar type.

Orgel pointed out the validity of application of crystal field theory to explain the coordination in copper complexes according to the electron occupying the $d_{x^2-y^2}$ orbital. If any additional ligands are available they would take up the fifth and the sixth coordination positions. However, because the d_{z^2} always contains a lone pair of electrons, in most copper complexes the fifth and sixth ligands are in the plane and thus the complex

will have tetragonal structure. The square-planar geometry energy level diagram of one or nine d electrons is similar to that give in Fig.(5-7).

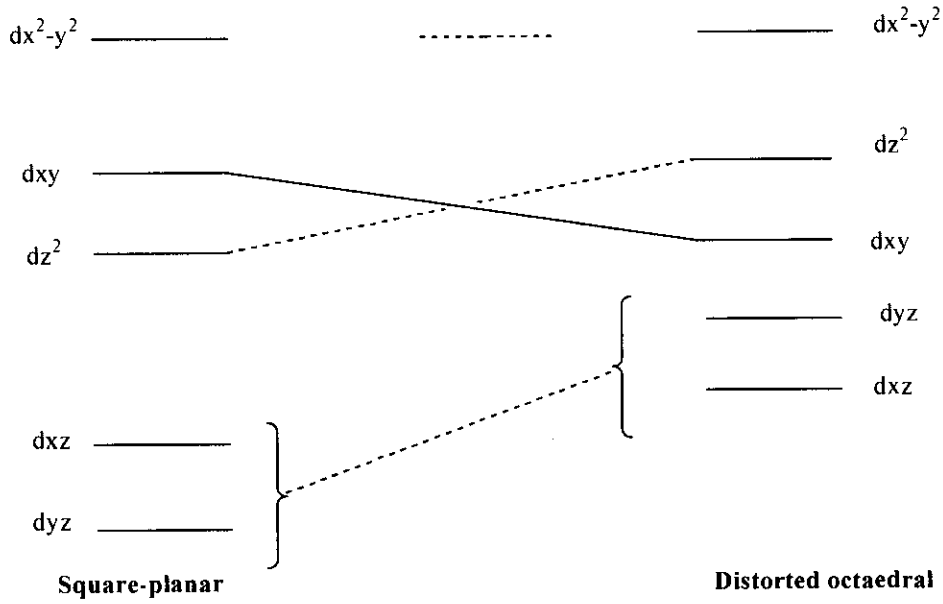

Fig.(5-7): Transition from square-planar to distorted octahedral

The isolated Cu(II) complexes have magnetic moment values (1.26-2.38 BM). No significant conclusion can be drawn from the magnetic data regarding the stereochemistry of the prepared copper(II) complexes. The electronic spectra of Cu(II) complexes show two broad band Figs. (20, 21) within 13774-20284 cm^{-1} and 16103-21459 cm^{-1} which can be assigned respectively to $^2E_{2g} \rightarrow {}^2B_{1g}$ and $^2A_{1g} \rightarrow {}^2B_{1g}$ transition in a tetragonally distorted octahedral configuration[75,76].

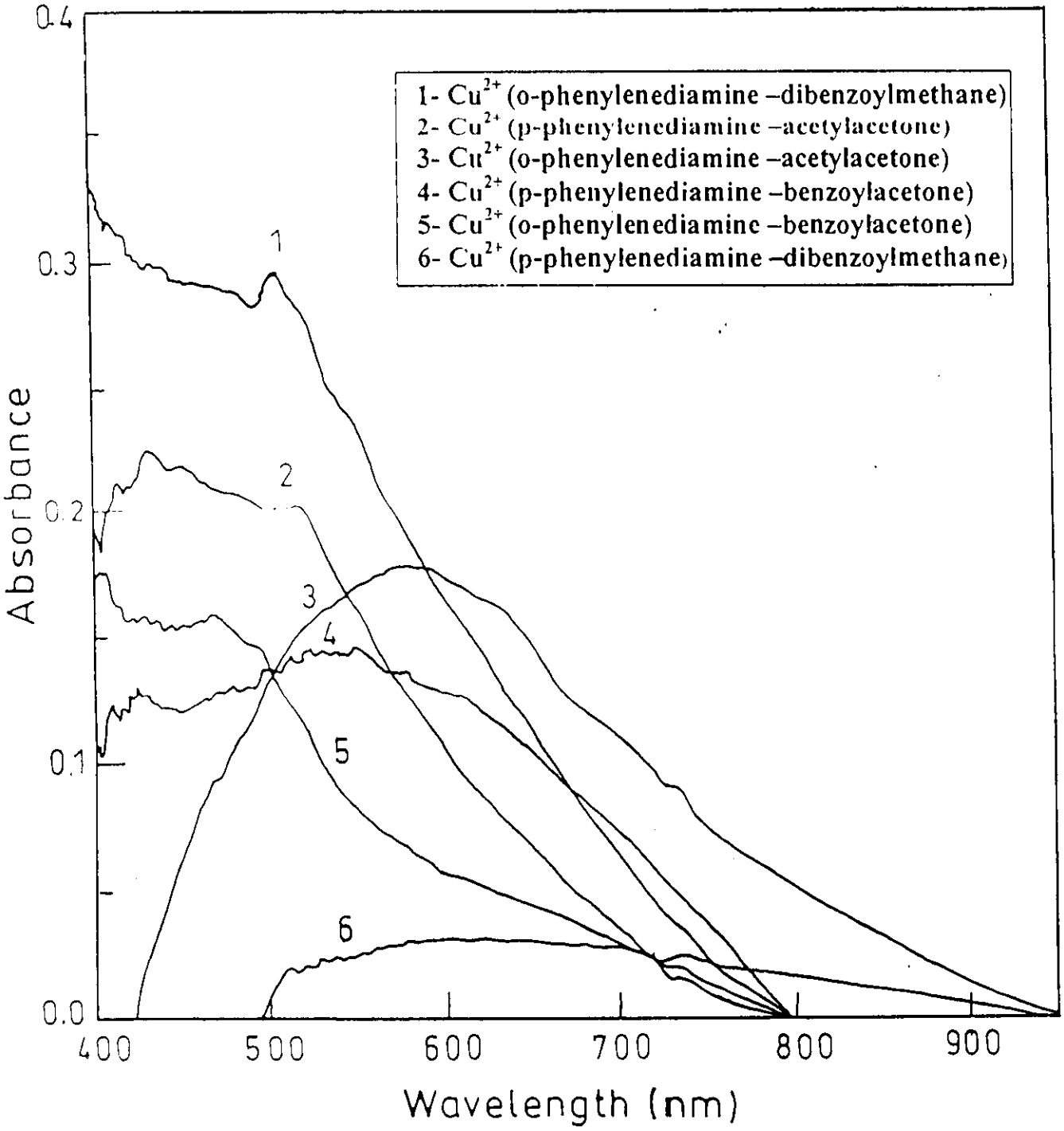

Fig. (20) : Electronic absorption spectra of macrocyclic Cu^{2+} complexes in Nujul mull.

6. Electron spin resonance spectroscopy of copper complexes:

Electron paramagnetic resonance (EPR) spectroscopy is a method to investigate the behavior of samples containing unpaired electrons (free radicals or compounds comprising an ion whose outer electronic shell is incomplete) in an applied magnetic field. It consists in recording the microwave energy absorbed by the sample as a function of the applied magnetic field. Two kinds of information may usually be obtained by this technique. The first one is a tensor characterizing the so-called Zeeman interaction, or interaction of the applied magnetic field with the unpaired electron(s). The second consists of tensors characterizing the interaction of the unpaired electron(s) with each type of nuclei possessing an intrinsic magnetic moment or spin, provided that this interaction is reflected by specific lines in the ESR spectrum.

The ESR spectra of transition metal complexes are affected mainly by spin-orbit coupling and ligand field strength. In order to obtain good information about ground and excited states in the complexes and the nature of bonding between the central metal ion and the ligand, the magnitude of "g" tensor must be calculated.

The Cu (II) ion with d^9 configuration has effective spin of $s = \frac{1}{2}$ and associated spin angular momentum, $m_s = \pm\frac{1}{2}$ giving rise to a doubly degenerate spin states in the absence of a magnetic field. In the presence of a magnetic field, the degeneracy is removed as Figure (22) and the energy difference between the two states is given by:

$$\Delta E = h\upsilon = g\,\beta\,H \qquad (6\text{-}1)$$

Where:

υ	is the frequency of microwave radiation	
H	is the strength of applied magnetic field	
β	is the Boher magneton,	and
G	is the land splitting factor	

In general, the deviation of g-value from that of the free spin "g_o" (2.0023) is mainly due to the perturbation of the ligand field, where:

$$g = g_0 - \frac{n\lambda}{\Delta} \qquad (6\text{-}2)$$

where:

n	is small integer
λ	is the spin-orbit coupling constant for the free ion ($\lambda = -829\ cm^{-1}$ for the gaseous Cu^{2+}).
Δ	is the energy separation between the ground and the excited states.

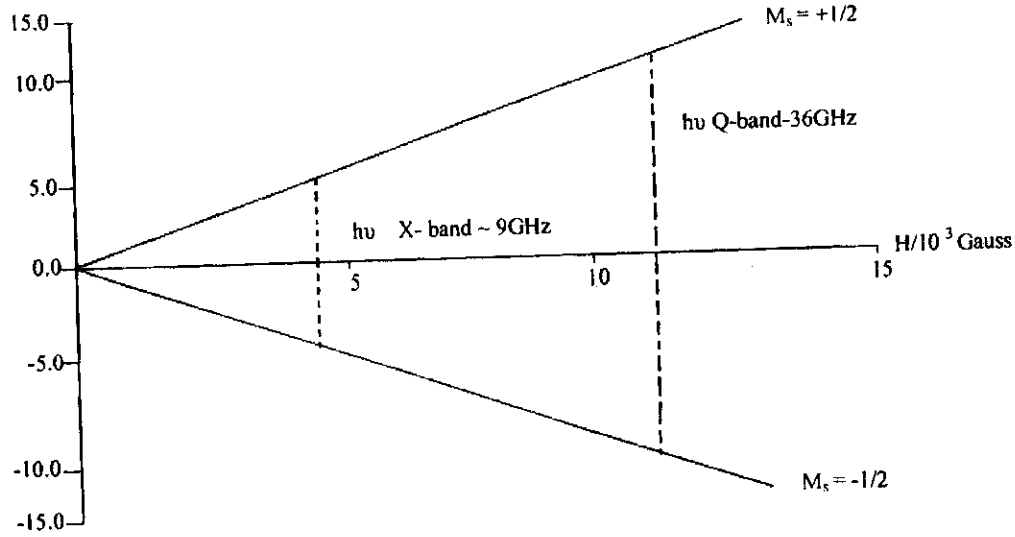

Fig.(22) : ***Effect of applied static magnetic filed (H) on an electron with "spin only" magnetism***