An EPR Study of Clinoptilolite from Bigadiç in Turkey

Recep BIYIK[a*] and Recep TAPRAMAZ[b]

[a]Çekmece Nuclear Research and Training Centre Yarımburgaz m. Nük. Arş. Merk. Yolu 34303 Küçükçekemece-İstanbul, Turkey

[b]Ondokuzmayıs University, Art and Science Faculty, Physics Dept. 55139 Samsun Turkey

Abstract

Natural and synthetic zeolites are industrial materials. They are used in many applications as food additives, molecular sieve to trap unwanted ingredients, as heavy metallic ions and groups, as shielding against radiations etc. EPR spectroscopy is a tool to characterize paramagnetic centers and radicals in the zeolite and clay type minerals. In this study natural cliptonilolite obtained from a mine in Bigadiç in western Anatolia, Turkey, was studied using electron paramagnetic resonance spectroscopy (EPR) at room temperature in natural form, following treatment of the samples: adsorbing of CO_2, H_2S, and SO_2 gases, $[Cu(H2O)6]^{2+}$ ions and exposure to gamma rays. Mn atoms become paramagnetic Mn^{2+} ions when CO_2 and H_2S gases are adsorbed to clinoptilolite and when SO_2 gas is adsorbed the system becomes unstable and the structure of the paramagnetic center changes with time. When Cu^{2+} ions are adsorbed to the Bigadiç clinoptilolite, the values of the EPR parameters are consistent with the distorted octahedral symmetry environment and after the exposure to gamma rays from a Co-60 source gives O_2^{3-} radical.

Keywords: Clinoptilolite, gas adsorption, irradiation, EPR.

1. Introduction

Zeolites are micro porous crystalline solids with well-defined structures containing silicon, aluminum and oxygen in their framework and some cations. Water and/or other smaller molecules fill their pores in its natural form. Clinoptilolite, one of the most utilized natural zeolites, is capable of either adsorbing or absorbing water and different types of gas molecules, some petrochemicals, heavy metals, low-level radioactive elements. They have large surface area. The cavities and channels between cavities occupy approximately 50% of total bulk volume. Their acidity is adjustable and they have high resistance to extreme temperatures. These properties give way to utilize them as molecular or ionic sieve in water purification plants for domestic use and separation of undesired gas molecules in slowly streaming natural gas plants. They are also used as catalyst in chemical reactions, as animal food additive in soil treatment in agriculture, in capturing radioactive byproducts in nuclear power plants and so on (e.g. see [1,2]). The environment of a natural clinoptilolite reservoir defines its characteristics: Natural temperature differences, geographic location and soil composition cause slightly different and unique composition and therefore the clinoptilolite gains a unique property [2,3].

Electron paramagnetic resonance (EPR) technique is a physical method of observing resonance absorption of microwave power by unpaired electron spins in a magnetic field. When spinning electrons are placed in an external static magnetic field the direction of the spin rotation which is initially random, becomes either the same as or opposite to that of external magnet. Energies of these two spin states are different and when this system is irradiated by microwave whose energy is equal to that of energy differences a transition takes place. This is the resonance condition given by the expression,

$$h\nu = g\beta H_0 \tag{1}$$

where v is microwave frequency, h is Planck constant, g is spectroscopic splitting factor of an electron with the value 2.002319, β is Bohr magneton and H_0 is external static magnetic filed. [4] .

EPR technique provides valuable information about the local environment of unpaired electron and therefore can be conveniently employed to detect paramagnetic centers and chemical radicals in substances, minerals, stones and zeolites in their natural states and/or after some treatments. In this work the paramagnetic species in natural clinoptilolite after exposing to gamma rays, adsorbing CO_2, H_2S, and SO_2 gases, and doping $[Cu(H_2O)_6]^{2+}$ ions have been examined.

2 Materials and Method

The clinoptilolite zeolites were obtained from the Bigadiç region of Western Anatolia where a qualitative clinoptilolite is produced from. The results of the chemical analysis of clinoptilolite are given in Table 1. The samples taken from the mine contains 88 - 95 % clinoptilolite. The samples were finely dried and grinded prior to use. Chemical reagents were purchased from Merck. The gases to adsorb zeolites were obtained in laboratory by means of related chemical reactions;

$$\begin{aligned} &CO_2 : CaCO_3 + 2HCl \rightarrow CO_2 + CaCl + H_2O \\ &SO_2 : Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O \\ &H_2S : FeS + 2HCl \rightarrow FeCl_2 + H_2S. \end{aligned} \qquad (2)$$

The moistures of gases used are removed by flowing through H_2SO_4 bath and $CaCl_2$ column. Then they were passed through clinoptilolite column for about three hours. The EPR spectra were taken at different times to observe whether any variation in paramagnetic centers occurs.

The Cu^{2+} ions adsorption was made in 50 ml vials. The pH of the solution was adjusted by 0.1 M HCl and NaOH solutions and kept at the value of 5, and 0.5×10^{-4} M $CuCl_2$

was added and kept for 48 hours and then the samples were centrifuged at 100 rpm for 15 min. The samples were dried prior to spectral analyses.

The γ- irradiation were made by a ^{60}Co γ-ray source at Turkish Atomic Energy Agency (TAEK) up to dose of 10 kGy.

The X-band EPR spectra were recorded using a Varian E-109 Line Century Series spectrometer equipped with a Varian E-231 TE-102 rectangular cavity. The microwave frequency and power was kept 9.52 GHz and 2mW respectively. The sweep time optimized was 8 minutes and the modulation amplitude was 4 gauss. Quartz tube was used to record spectra. The spectrometer frequency is corrected using the DPPH (diphenylpicrylhydrazyl) sample (g =2.0036). All spectra were taken at room temperature and simulations are made using Bruker's WINEPR software.

2. Result and Discussion

2.1 Gas adsorbed clinoptilolite

The EPR spectra of the natural clinoptilolite gave only a weak line at g=2.002 which was attributed to carbonaceous radicals existed during the natural formation process [5] and no other line was observed. After CO_2 and H_2S adsorption, a manganese spectrum was observed because of that nonmagnetic permanganate ions, $(MnO_4)^-$, trapped in natural clinoptilolite lattice as an impurity, became paramagnetic $XMnSO_4$ where X stand for Na, K or equivalent ionic atom or group. Fig. 1 and Fig. 2 shows the EPR spectrums after CO_2 and H_2S adsorption, respectively.

Mn^{2+} with $3d^5$ ($^6S_{5/2}$) configuration and nuclear spin of I=5/2, exists in high spin state with S = 5/2. Therefore the EPR spectra must include five separate sextets corresponding to the spin-spin transitions expressed by the Hamiltonian [6,8] .

$$\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + g N \beta N \mathbf{B} \mathbf{I} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + D\left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2) + \frac{1}{6} a \left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1) \right] \quad (3)$$

S and **I** represents electron and nuclear spin angular momentum. Where the first, second and third terms express electron Zeeman, nuclear Zeeman and hyperfine interactions respectively; D and E are parallel and perpendicular components of spin–spin interaction and zero field splitting parameters. a is the cubic splitting parameter and because of being non measurable it is neglected in most applications.

g and A values of Mn^{2+} ions are measured to be g≈2.009 and A≈5 mT after CO_2 adsorption, Fig. 1. Because of line broadening, detailed analyses are impossible. The reason of the line broadening is mainly paramagnetic contributions of oxygen atoms surrounding paramagnetic center. After gaseous H_2S adsorption, g and A values of Mn^{2+} were measured to be g≈2.006 and A≈9 mT, which was greater than that of CO_2 adsorption. Because of H_2S does not contain oxygen atoms, paramagnetic broadening due to oxygen surrounding Mn^{2+} ions was less, therefore narrower Mn^{2+} lines were observed. It seems that no significant effect was observed on the shape and the intensity of the CO_2 gas after adsorption.

Both spectra of CO_2 and H_2S adsorbed clinoptilolites indicate distorted cubic symmetry. Approximate g and hyperfine values were measured in the spectra of powder samples. Dipolar splitting values D and E could not be measured directly from spectra, therefore spectra simulation was utilized which was one plausible way for determination. The g values of these types of complexes are relatively anisotropic and change between 1.98 and 2.02. The anisotropy in hyperfine splitting, on the other hand, is negligibly small compared to the hyperfine value itself and change around 5-10 mT [9, 10]. The zero field splitting parameters D and E for the complex under study however, must be relatively small to fit to slightly distort cubic structure of the complex [8, 11-13]. In other words the absolute value of

D parameter must be at the order of hyperfine splitting and that of E parameter must be smaller. Simulation of the Mn^{2+} spectra with the values given in Table 2 gave successful results, (Fig. 2b). The sign and magnitude of D depends on the symmetry of the metal ion. Negative value of D are related to tetragonal elongation or trigonal compression [14, 15].

When SO_2 gas was adsorbed on clinoptilolite, a non-stable spectrum was observed. Fig. 3a shows the EPR spectra SO_2 adsorbed clinoptilolite recorded immediately after adsorption process. A broad EPR line at both sides of the transition at g≈2 and a broad line covering almost all spectral area was observed. Fig. 3b shows EPR spectrum taken after one week from SO_2 adsorption where the line at g≈2 and another broad envelope centered at lower fields with g≈4.3 took more definite shape. When spectra Fig.2a and Fig. 2b were considered together, the transition at g≈2 in Fig. 2a was attributed to Fe^{3+} complex with distorted octahedral environment and the broad envelope at both sides was attributed to some unstable paramagnetic species. In the spectrum in Fig. 2b, besides the line at g≈2, a second or more broader lines under the envelope centered at g≈4.3 was attributed to another Fe^{3+} complex surrounded with strongly distorted tetrahedral environment [1, 4, 16, 17].

Fe^{2+} ion in unprocessed clinoptilolite no line due to Fe^{3+} ion was observed because only Fe^{2+} ion existed in natural structure. After SO_2 adsorption the gas molecule oxidized non-paramagnetic Fe^{2+} to paramagnetic Fe^{3+} ion. In early stages of adsorption some SO_2 gas molecules react at the surface forming different and unstable Fe^{3+} containing structures; but as time precedes some unreacted SO_2 molecules diffuse deeper through accessible channels and form definite structures while unstable structures at the surface, too, forming definite structures [18].

2.2 Cu^{2+} ion adsorption

As molecular and ionic sieve, the zeolites in general, adsorb transition metals and hence paramagnetic Cu^{2+} ions, which are detectable by EPR spectroscopy. Paramagnetic Cu^{2+} ions

are frequently used as a probe in host materials reflecting the local symmetry and the structural properties of the host. Numerous works were made and published on Cu^{2+} adsorption by zeolites and especially by clinoptilolite [2,19]. EPR spectra is similar to those reported previously by many workers [20].

The spectrum Cu^{2+} adsorption by Bigadiç clinoptilolite zeolites (Fig. 4) belong to S=1/2 and I=3/2, and probably contain some different structures, but dominant one is assigned to square planar environment and suppresses other spectra. The measured EPR parameters ($g_{//} = 2.31$ $g_{\perp} = 2.08$ $A_{\perp} = 3$ $A_{//} = 17$) show axial structure with values given in Table 2. In generally in this type structures g and A parameters probably reflect changes in the number of surface groups bonded to Cu^{2+}. Specific Cu^{2+} adsorption on the clinoptilolite surface involves the displacement of H_2O ligands on Cu^{2+} by OH or oxygen anions [19]. The values are compatible with similar studied.

2.3 Exposing to the gamma rays

The Bigadiç clinoptilolite was irradiated by gamma radiation up to 10 kGy from ^{60}Co source. Two lines were observed (Fig. 5) in the EPR spectrum, which belong to parallel and perpendicular components of O_2^{3-} ionic radical, [5]. The EPR parameters are given in Table 2. This radical, highly active and also has long lifetime at room temperature. It is formed by irradiation of water molecules in the SiO_2 cages of the clinoptilolite and trapped there.

3 Conclusion

In this study, natural cliptonilolite obtained from Bigadiç, a town in western Anatolia where clinoptilolite is produced commercially, was studied with electron paramagnetic resonance spectroscopy (EPR) in natural form, after exposing to gamma rays, adsorbing CO_2, H_2S, and SO_2 gases, and doping Cu^{2+} ions. In natural clinoptilolite a weak line at g=2.002 due to carbonaceous radicals existed during the natural formation process. After adsorption of CO_2

and H_2S gases, nonparamagnetic $(MnO_4)^-$ ions becomes paramagnetic $XMnSO_4$ (X stand for Na, K or equivalent ionic atom or group). After SO_2 gas nonparamagnetic Fe^{2+} ion is oxidized to paramagnetic Fe^{3+} ion. Cu^{2+} ions adsorption shows that Bigadic clinoptilolite traps metal ions as most zeolites. In the last part of the experiment, clinoptilolite was exposed to gamma rays from Co-60 source and O_2^{3-} ionic radical was observed.

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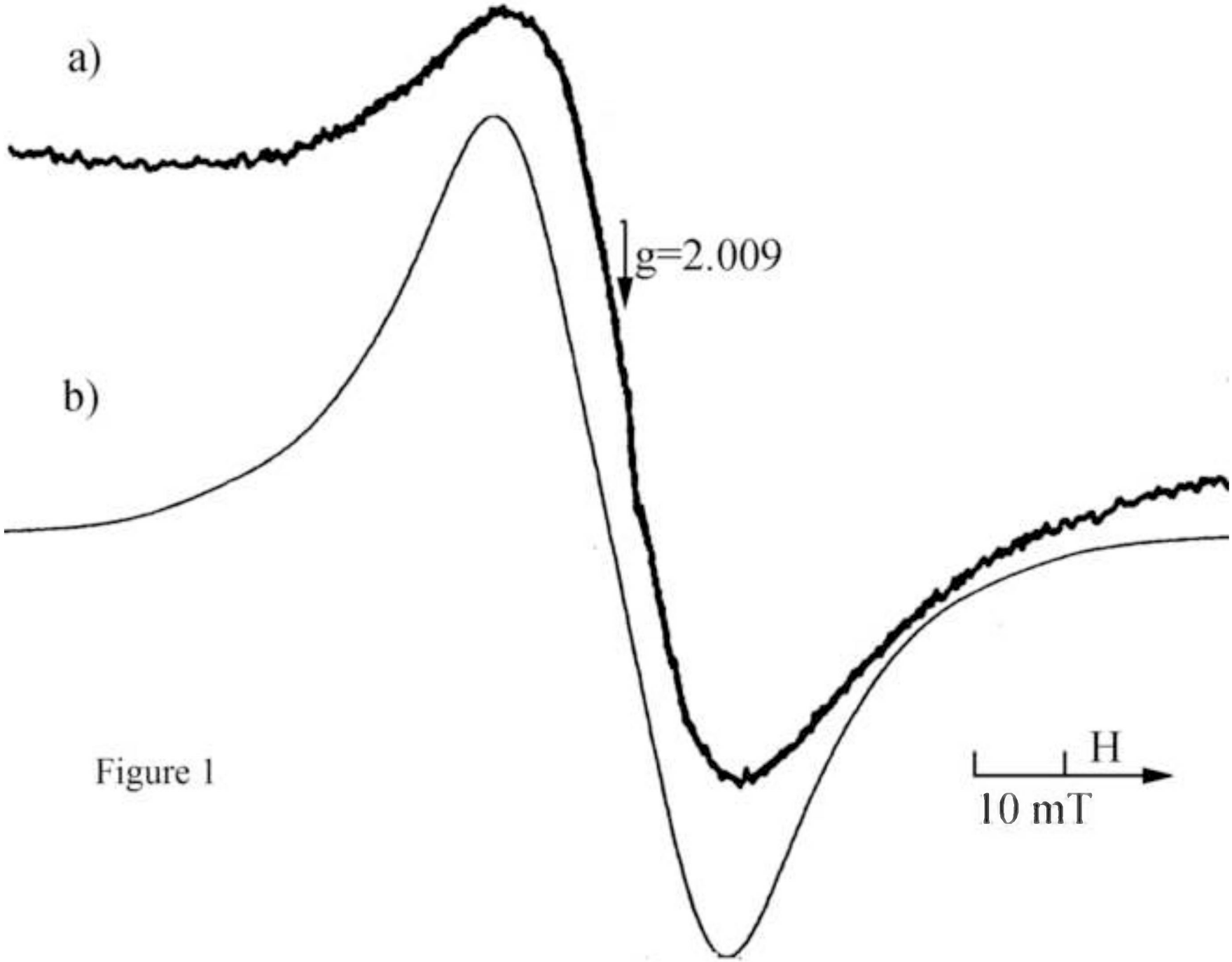

Figure 1

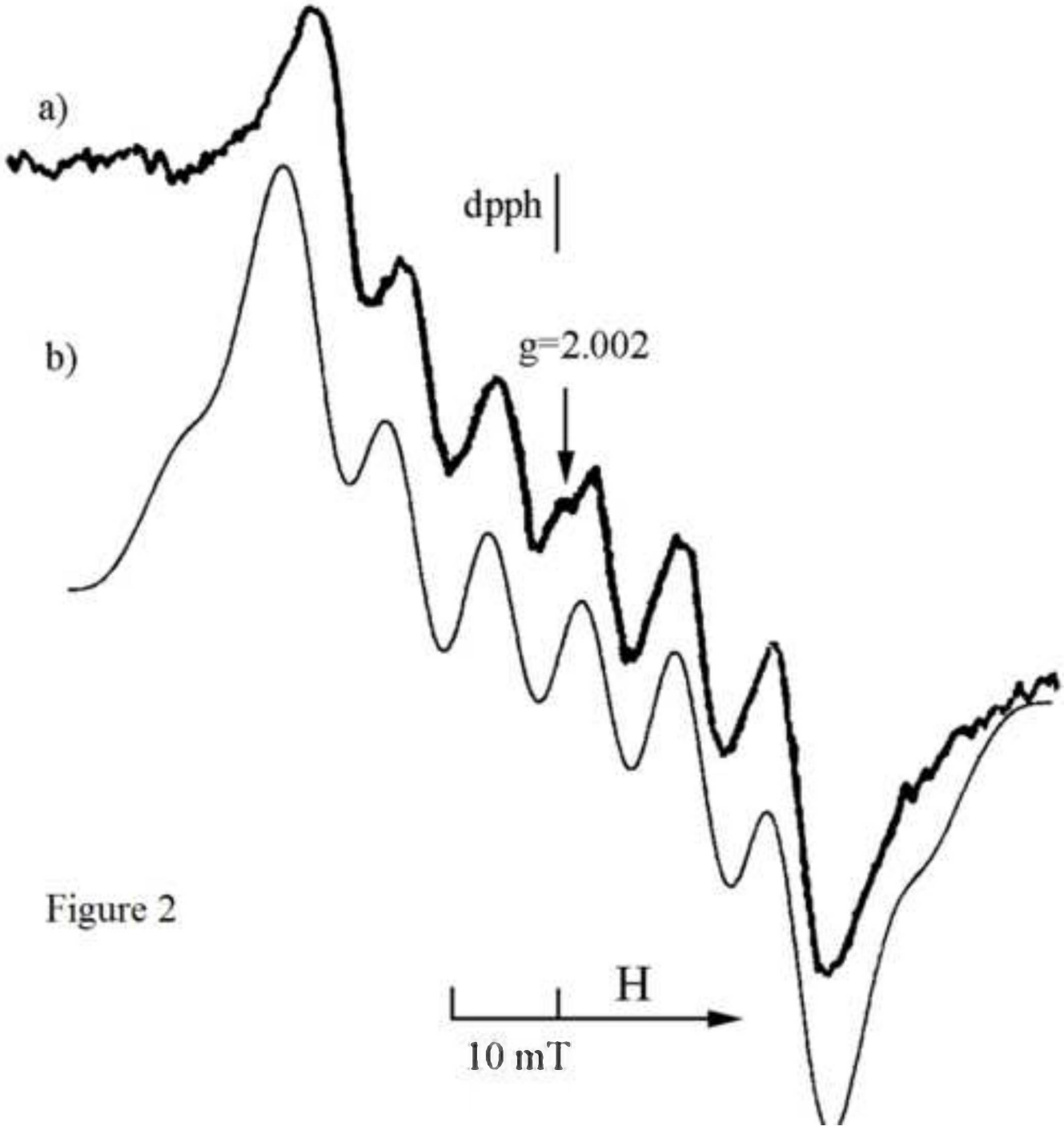

Figure 2

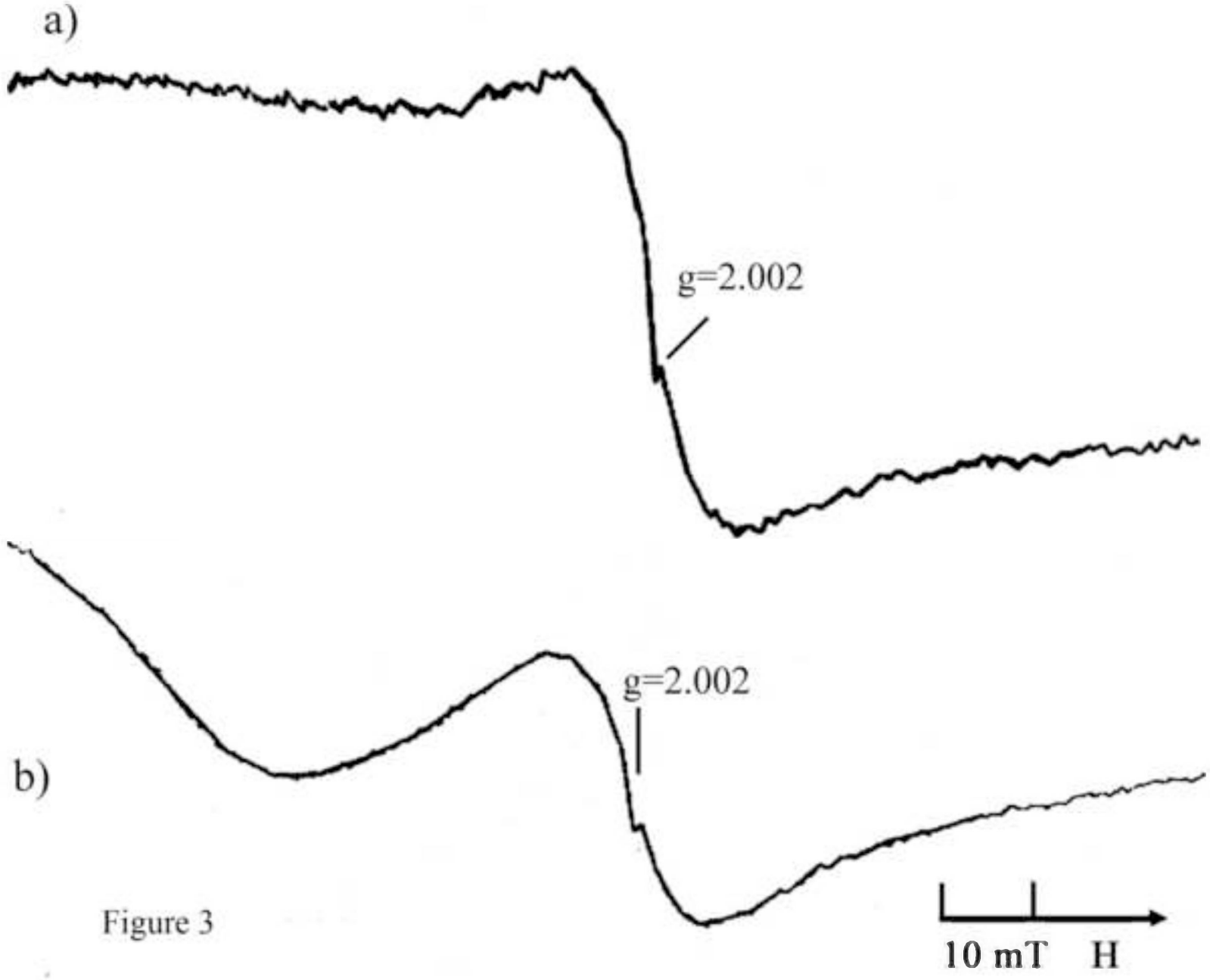

Figure 3

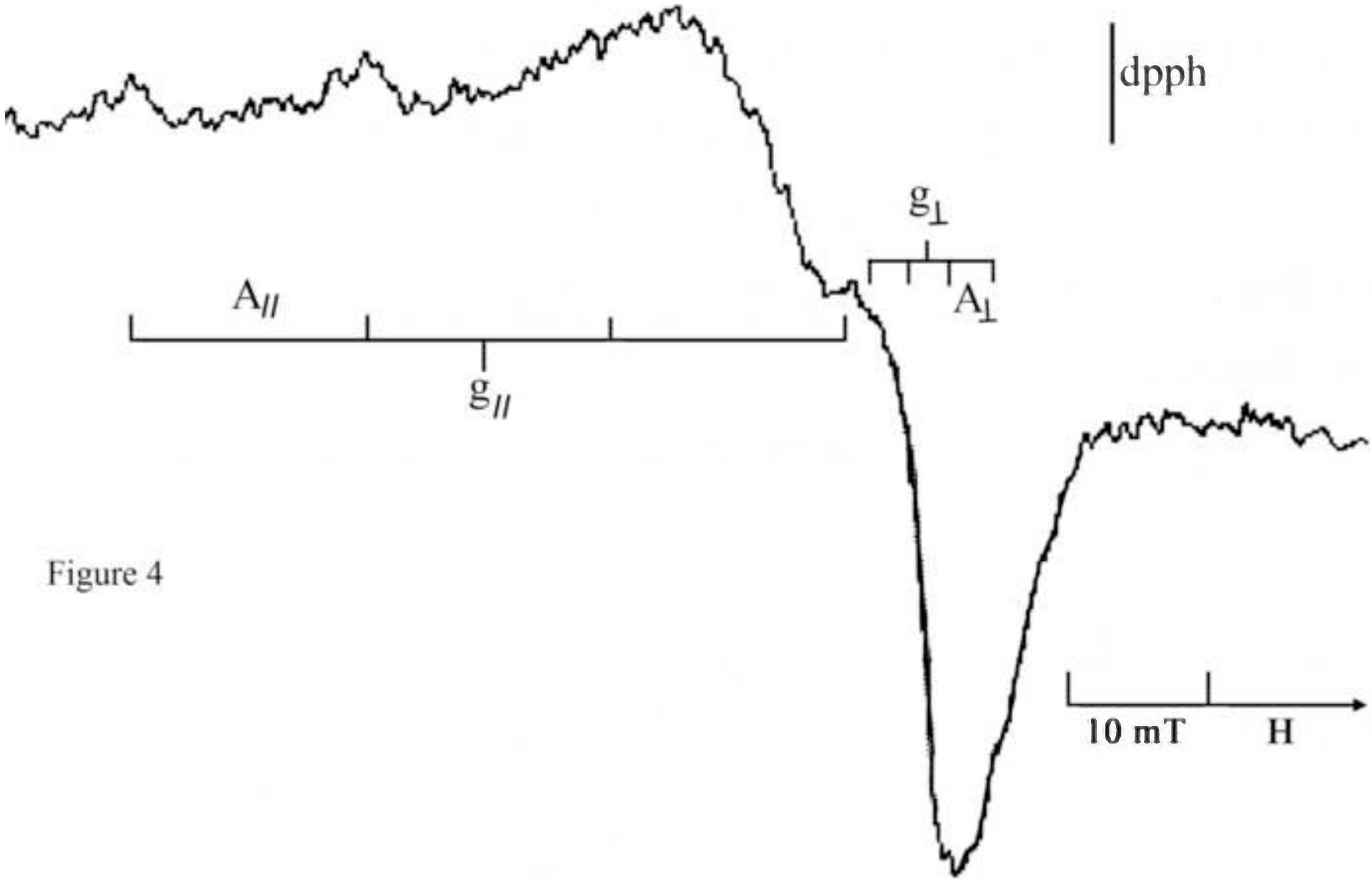

Figure 4

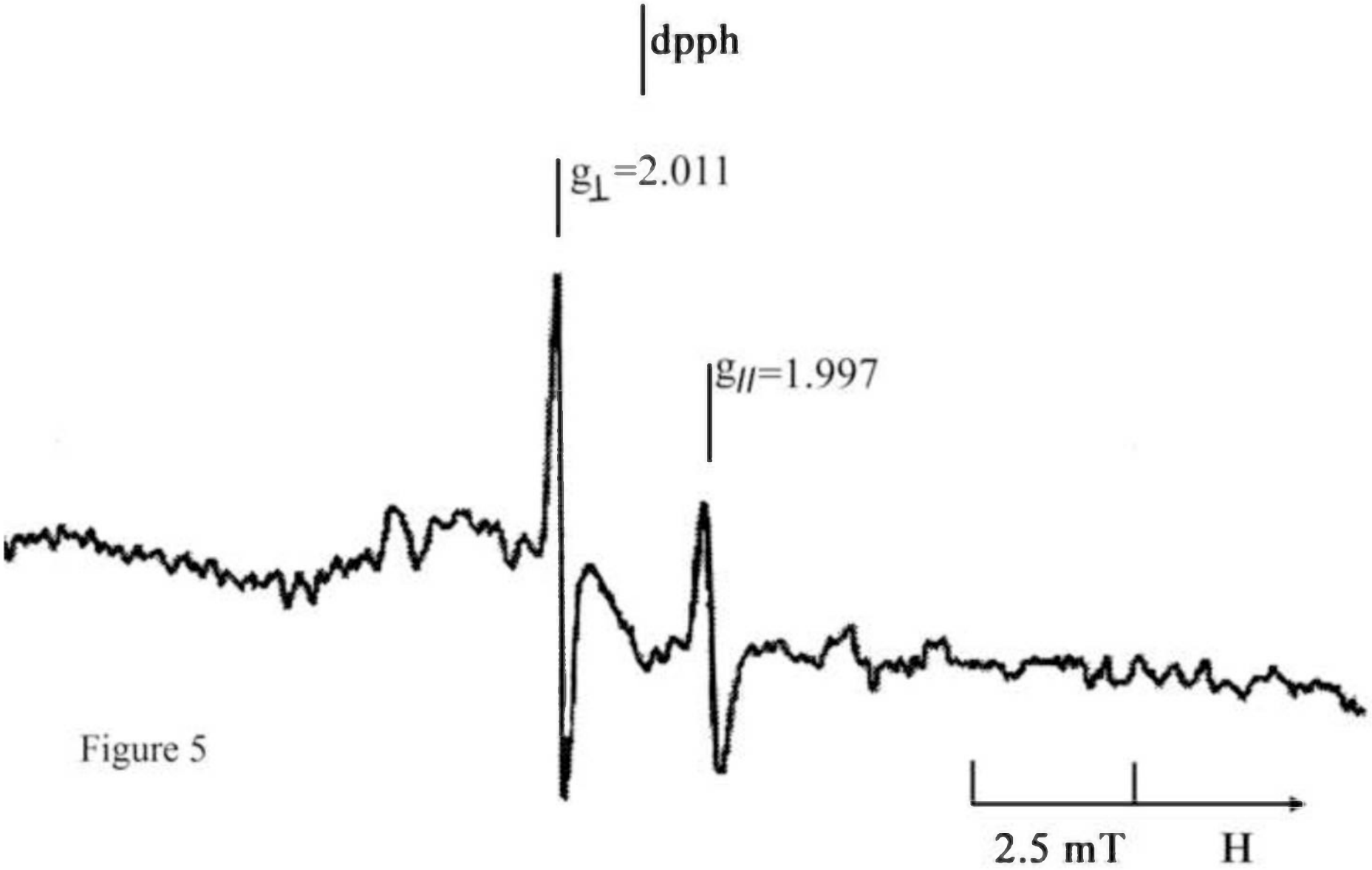

Figure 5

Figure Captions

Fig.1 The EPR Spectrum of CO_2 gas adsorption (a) and simulation (b) in Bigadiç clinoptilolite zeolite

Fig. 2 The EPR Spectrum of H_2S gas adsorption (a) and simulation (b) in Bigadiç clinoptilolite zeolite

Fig. 3 The EPR Spectrum of SO_2 gas adsorption (a) and after the one week later (b)

Fig. 4. The EPR Spectrum of Cu^{2+} ions doped in the Bigadic clinoptilolite.

Fig. 5 The EPR Spectrum of irradiated the Bigadic clinoptilolite with gamma (^{60}Co) source up to 10 kGy.

Table 1.
Chemical composition (W%) of the Bigadiç Clinoptilolite material

Chemical composition	Bigadiç Clinoptilolite
SiO_2	72.12
Al_2O_3	10.48
CaO	2.49
MgO	1.2
Fe_2O_3	1.22
Na_2O	0.55
K_2O	2.20
SO_3	0.006
Mn_2O_3	0.001
TiO_2	0.07

Table 2

Measured EPR parameters from Bigadiç clinoptilolite zeolite samples after some treatments. The calculated parameters are also given.

CO_2 gas adsorption				
$g_{avg} = 2.00$	$a_{avg} = 9.4\ mT$	$D = -6\ mT$	$E = 4\ mT$	
H_2S gas adsorption				
$g_{avg} = 2.06$	$a_{avg} = 9.0 mT$	$D = -4\ mT$	$E = 2\ mT$	
SO_2 gas adsorption				
Immediately	$g_{avg} = 2.00$ Fe^{3+} (octahedral environment)			
after 1 weak	$g_{avg} = 4.30$ Fe^{3+} (strongly distorted tetrahedral environment)			
Cu^{2+} ion adsorption				
$g_{//} = 2.31$	$g_{\perp} = 2.08$	$A_{//} = 17 mT$	$A_{\perp} = 3\ mT$	
$\beta_2^2 = 0.93$	$\kappa = 0.86$			
Exposing to the gamma rays (up to 10 kGy)				
O_2^{3-} radicals	$g_{\perp} = 2.011$	$g_{//} = 1.997$		