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Electron paramagnetic resonance study of the radiation damage centers in menadione single crystal

Menadione tek kristalinde radyasyon hasar merkezlerinin elektron paramanyetik rezonans çalışması

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Electron Paramagnetic Resonance Study of the Radiation Damage Centers in Menadione Single Crystal

Highlights

- *Menadione single crystal was exposed to high energy radiation.*
- *The paramagnetic centers in the menadione single crystal were examined by EPR Spectroscopy.*
- *It was observed that two similar radicals formed.*
- *Hyperfine structure constants and spectroscopic splitting factors were calculated.*
- *It was observed that the EPR parameters showed an anisotropic change.*

Graphical Abstract

Gamma irradiation generated two similar radicals in the menadione single crystal.

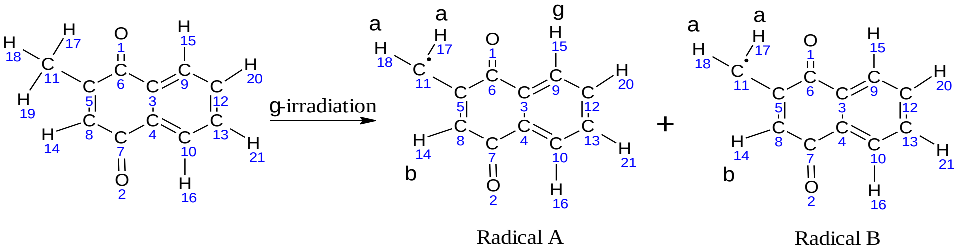

Figure. Structure of the two radicals observed in menadione single crystal

Aim

It is to examine the effect of gamma irradiation on menadione single crystal by EPR Spectroscopy.

Design & Methodology

Menadione single crystals were investigated by the EPR Spectroscopy method.

Originality

This article is a completely original work.

Findings

As a result of breaking the C(11)-H(19) bond in the gamma irradiated menadione single crystal, two radicals with similar structure were formed.

Conclusion

The two radicals formed in the menadione single crystal also have anisotropic EPR parameters.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Menadione Tek Kristalinde Radyasyon Hasar Merkezlerinin Elektron Paramanyetik Rezonans Çalışması

Araştırma Makalesi / Research Article

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ÖZ

^{60}Co-γ ışınları ile ışınlanmış menadion (2-metil-1,4-naftokinon; K_3 vitamini; $C_{11}H_8O_2$) tek kristallerindeki radyasyon hasar merkezleri, 120 K'de Elektron Paramanyetik Rezonans (EPR) spektroskopisi ile incelenmiştir. Bileşikte, iki radikalin varlığı tespit edilmiştir. Her iki radikal de karbon-merkezli radikaldir. Üç farklı eksen boyunca gama ışınlanmış menadion tek kristallerinin EPR spektrumlarının analizi, bileşiğin C(11)-H(19) bağının kırıldığını göstermiştir. Eşlenmemiş elektronun, C(11) atomu üzerinde bulunduğu belirlenmiştir. Menadion tek kristalinde gözlenen radyasyon hasar merkezlerinin g değerleri ve aşırı ince yapı sabitleri elde edilmiştir. Simülasyon çalışması ile, deneysel verilerin doğruluğu gözlenmiştir.

Anahtar Kelimeler: EPR, menadion, K_3 vitamini ($C_{11}H_8O_2$), spektroskopik yarılma faktörü, aşırı ince yapı çiftlenim sabiti, radyasyon hasar merkezi.

Electron Paramagnetic Resonance Study of the Radiation Damage Centers in Menadione Single Crystal

ABSTRACT

The radiation damage centers in the ^{60}Co-γ rays irradiated menadione (2-methyl-1,4-naphthoquinone; Vitamin K_3; $C_{11}H_8O_2$) single crystals were examined at 120 K by Electron Paramagnetic Resonance (EPR) spectroscopy. The presence of two radicals was detected in the compound. Both radicals are carbon centered radicals. Analysis of the EPR spectra of gamma-irradiated menadione single crystals along three different axes showed that the C(11)-H(19) bond of the compound was broken. It was determined that the unpaired electron located on the C(11) atom. The g values and the hyperfine structure constants of the radiation damage centers observed in menadione single crystal were obtained. Accuracy of experimental data was observed by simulation study.

Keywords: EPR, menadione, vitamin K_3 ($C_{11}H_8O_2$), spectroscopic splitting factor, hyperfine coupling constant, radiation damage center.

1. INTRODUCTION

Vitamin K plays an important role in physiological processes of many organisms [1]. It regulates blood functions, normalizes mineral metabolism and prevents cancer [2]. In mammals it is used to control blood clotting and bone formation and assists in converting glucose to glycogen in the intestines [3]. In plants and bacteria it is, for example, involved in electron transfer in photosynthesis [4-6]. In nature two types of vitamin K are found. Vitamin K_1 (VK_1), also called phylloquinone, is found in plants and cyanobacteria [4,7]. Vitamin K_2 is a collective term for a group of compounds, called menaquinones (MQs), synthesized by anoxygenic bacteria [8]. They differ from VK_1 with respect to the length and structure of the chain attached to position 3 of the quinone ring. There are also artificial forms, vitamin K_3 (VK_3), menadione, and vitamin K_4, called menadiol [1]. Menadione or vitamin K_3 is the key compound in the synthesis of all vitamins of this group [2]. Vitamin K_3 is more active than other vitamin K derivatives for blood coagulation [9].

Electron Paramagnetic Resonance (EPR) enables one to investigate not only free radicals and atoms, but also charged paramagnetic particles formed as a result of irradiation, in particular trapped electrons. Therefore, it was possible to study more thoroughly the mechanisms involved in the radiation chemistry of condensed phases. The determination of radicals structure, conformation, reactions and other radical conversions which are indicative of radicals chemical properties are all general problems of EPR spectroscopy of free radicals [10].

Absorption of ionizing radiation in the condensed phase causes the formation of free radicals. EPR spectroscopy focuses particularly on issues related to the trapping of radicals in solid crystalline matrix [10-14]. Investigation of ionizing radiation effect on menadione, an important vitamin for human health, is extremely important not

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only for physics or chemistry but also for medicine and pharmacy. Analyzing the radiation damage centers in the menadione with EPR spectroscopy, which is one of the magnetic resonance spectroscopy methods and has an application area in medicine, is also a guiding study for various EPR studies on drug research. In this study, the radiation damage centers in gamma-irradiated menadione single crystal are examined determined by EPR method at 120 K. It has been obtained from the literature studies that the EPR study of three different axes of gamma irradiated menadione single crystals at 120 K has not been performed before. The results of the experimental study were supported by the simulation study.

2. MATERIAL and METHOD

The single crystals of menadione were grown in the laboratory by slow evaporation of concentrated benzene solution. A slow evaporation technique was used to amplify the crystals. The single crystals crystallized in the monoclinic space group $P2_1/a$, with cell dimensions of a = 11.1325(1) Å, b = 20.6726(2) Å, c = 7.44834(5) Å, β=97.985(1)$^{\circ}$, V = 1697.52(3) Å^3 and the unit cell contains eight molecules (Z=8) [15].

The single crystals were irradiated with a ^{60}Co γ-ray source at 1.66 kGyh^{-1} for 169 h at room temperature. The samples were exposed to a total absorbed dose of about 280 kGy. Gamma irradiation was carried out with SVST Co-60-1 type tote-box gamma radiation source capable of continuous and intermittent irradiation at the Turkish Atomic Energy Authority (TAEK) Sarayköy Nuclear Research and Training Center. The spectra were recorded with a Bruker EMX 081 EPR Spectrometer using 1.001 mW microwave power. The microwave frequency of the EPR spectrometer is 9.424 GHz, 9.429 GHz and 9.434 GHz for the *a*-axis, *b*-axis and *c*-axis of the laboratory axis system, respectively. The modulation frequency of the magnetic field was 100 kHz and the modulation amplitude was 1 G. The single crystals were mounted on a goniometer and the spectra were recorded in three mutually perpendicular planes (*a*b*, *a*c*, *bc* crystallographic axes) at 120 K. The EPR signals were changed gradually from 0º to 180º. Oriented single crystals were positioned inside the microwave cavity and the spectral position of the resonance lines measured as a function of the orientation of the magnetic field maintained parallel to each of the *a*b*, *a*c*, *bc* planes of the single crystal sample. The spectra were simulated by using the Win-EPR simulation program.

3. RESULTS AND DISCUSSION

Menadione single crystals were formed in the laboratory and then irradiated with ^{60}Co γ-rays. Immediately after irradiation, the EPR spectra were taken at 120 K. The damping of the radical structure is prevented by low temperature study. The EPR spectra of menadione single crystal were investigated according to both microwave power and temperature changes and no change was observed according to these parameters. By searching in detail according to three different axes of the crystal, it was tried to detect the radicals or radicals formed and it was decided that two free radicals were formed. The molecular structure of the menadione single crystal is shown in Figure 1.

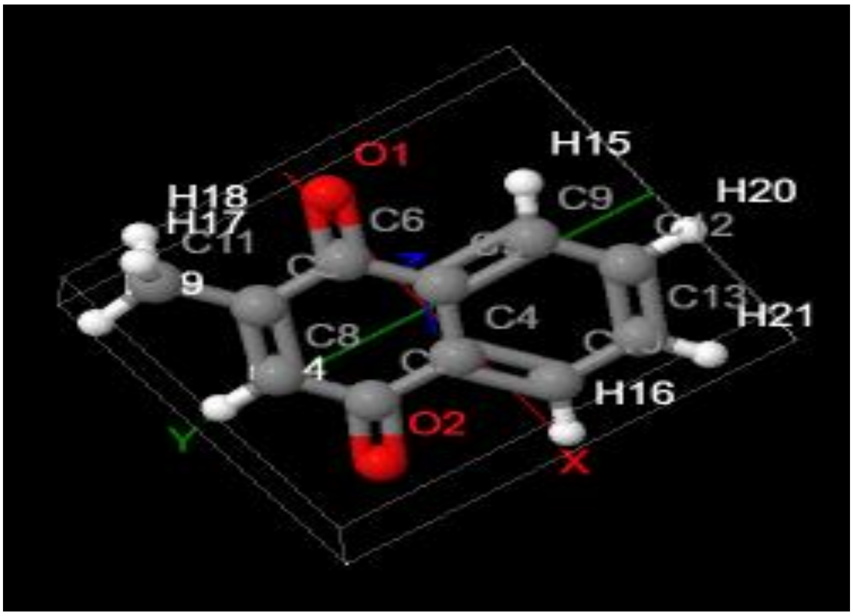

Figure 1. Molecular structure of menadione

The structure of the radiation damage centers formed in the gamma-irradiated menadione single crystal is also shown in Figure 2. EPR analysis of gamma irradiated menadione single crystals at 120 K showed that ionizing radiation generated two carbon-centered free radicals in the compound. Both radicals have formed in the same structure. These radicals are called radical A and radical B. These two radicals, which have the same structure, are different in terms of hyperfine structure splittings. Radical A shows alpha, beta and gamma splittings, while radical B shows only alpha and beta splittings. Radical A was formed by breaking the C(11)-H(19) bond. Alpha-group hyperfine splittings occur as a result of the interaction of H(17) and H(18) protons bound to the C(11) atom by an unpaired electron. The H(14) proton bound to the C(8) atom forms the beta splittings . The proton H(15) bound to the C(9) atom forms the gamma splittings. Alpha protons produce the hyperfine structure splittings with a 1: 2: 1 intensity ratio. The beta proton produces the hyperfine structure splittings with a 1:1 intensity ratio. The gamma proton produces again the hyperfine structure splittings with a 1: 1 intensity ratio. Radical B was formed by breaking the C(11)-H(19) bond. Alpha-group hyperfine splittings occur as a result of the interaction of H(17) and H(18) protons bound to the C(11) atom by an unpaired electron. The H(14) proton bound to the C(8) atom forms the beta splittings. Alpha protons produce the hyperfine structure splittings with a 1: 2: 1 intensity ratio. The beta proton produces the hyperfine structure splittings with a 1:1 intensity ratio.

The simulations of the EPR spectra were carried out using the Win-EPR software. The simulation values of the hyperfine coupling constants of the simulated spectra in Figure 3, Figure 4 and Figure 5 are given in Table 1. These parameters were slightly modified untill a reasonable agreement between simulated and experimental spectra were reached.

The EPR parameters belonging to the two radicals observed in menadione single crystals are included in Table 2 and Table 3. The angular variations of A-values and the g-value of the radical A observed in menadione single crystals at 120 K are shown in Figure 6, Figure 7, Figure 8 and Figure 9. The angular variations of A-values and the g-value of the radical B observed in menadione single crystals at 120 K are shown in Figure 10, Figure 11 and Figure 12.

The angular dependences of EPR spectra were obtained for different orientations of the static magnetic field with respect to the crystalline axes. For the radical A and radical B, the spectroscopic splitting factor and the hyperfine coupling constants are anisotropic. For the radical A, the average values of the g-factor and the hyperfine coupling constant were obtained as g_A = 2.00626 , $\left[(a_{CH_2})_\alpha\right]_A$ = 1.465 mT , $\left[(a_H)_\beta\right]_A$ = 0.570 mT and $\left[(a_H)_\gamma\right]_A$ = 0.460 mT, respectively. For the radical B, the average values of the g-factor and the hyperfine coupling constant were obtained as g_B= 2.00528 , $\left[(a_{CH_2})_\alpha\right]_B$ = 3.330 mT and $\left[(a_H)_\beta\right]_B$ = 0.622 mT, respectively. These values are also in agreement with the literature values.

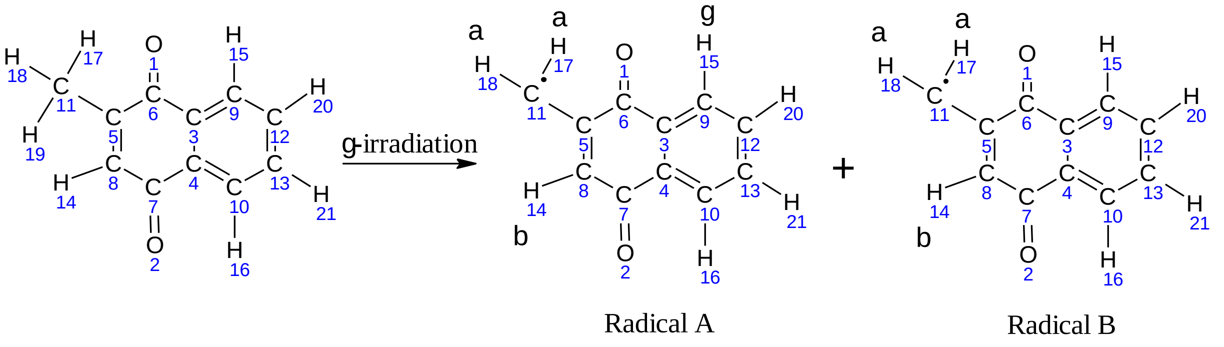

Figure 2. Structure of the two radicals observed in menadione single crystal

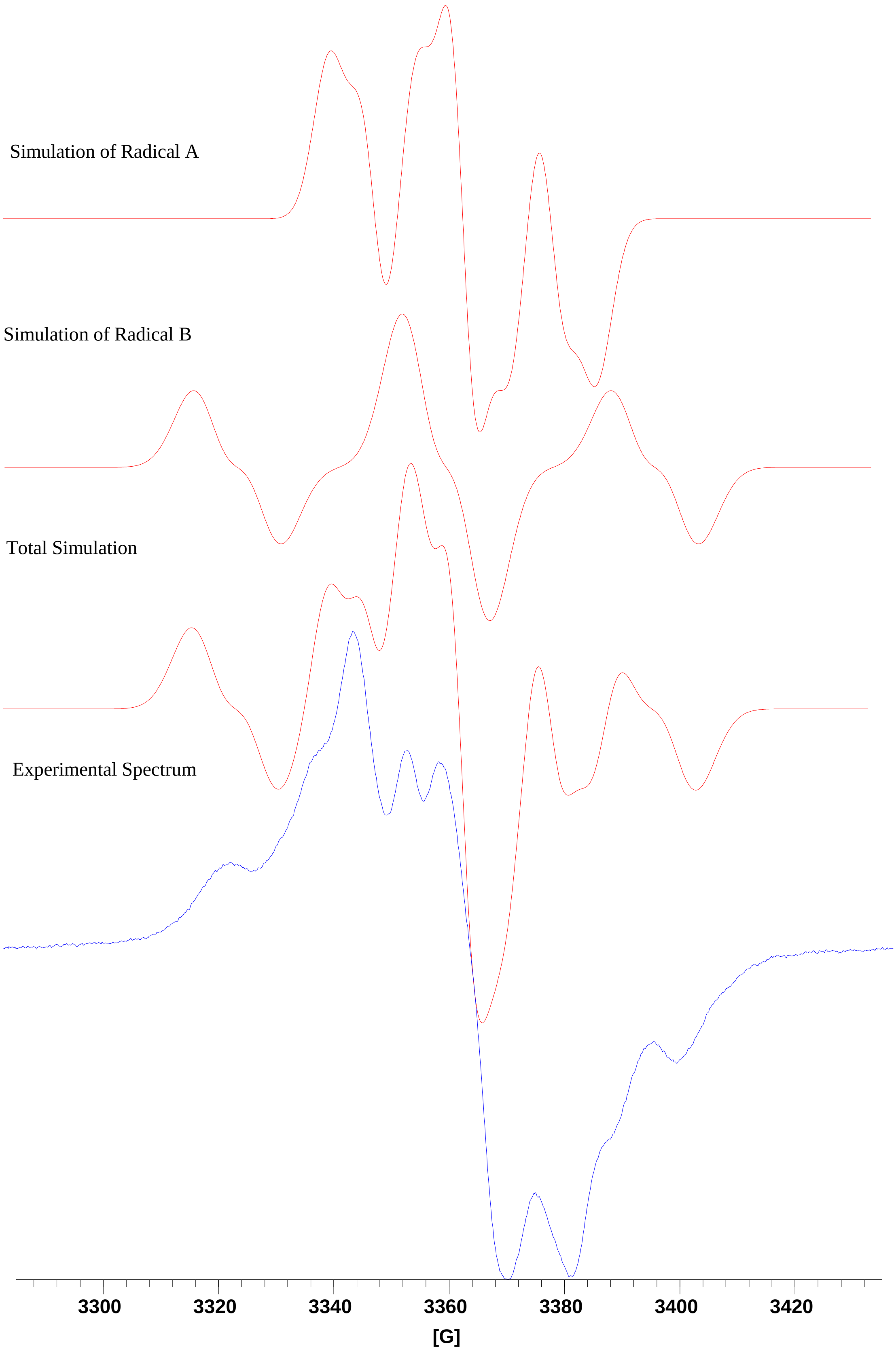

Figure 3. Experimental and simulated EPR spectra of gamma irradiated menadione single crystal at 120 K when the magnetic field is in the a*b plane at an angle 0° towards the axis

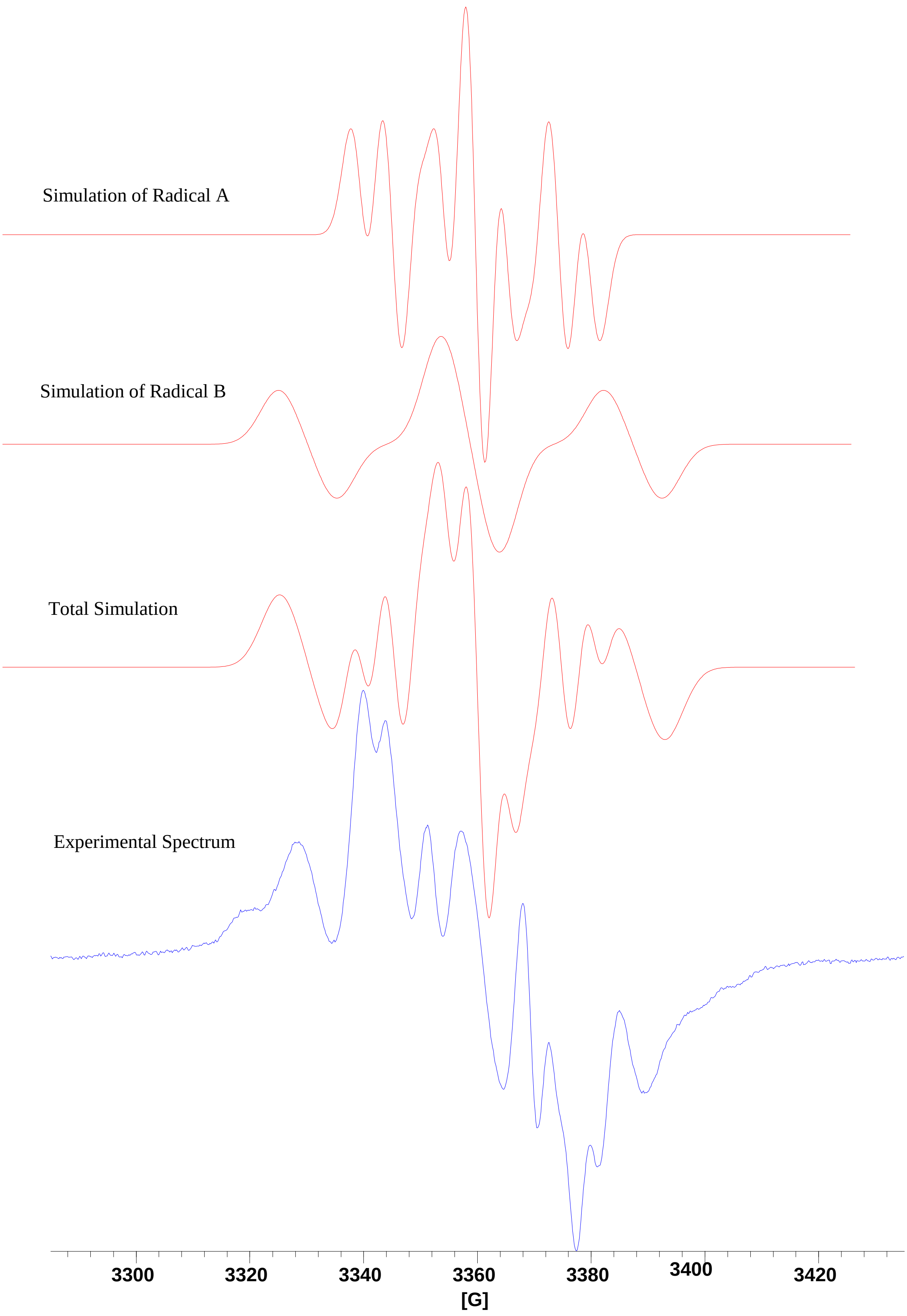

Figure 4. Experimental and simulated EPR spectra of gamma irradiated menadione single crystal at 120 K when the magnetic field is in the a*c plane at an angle 30° towards the axis

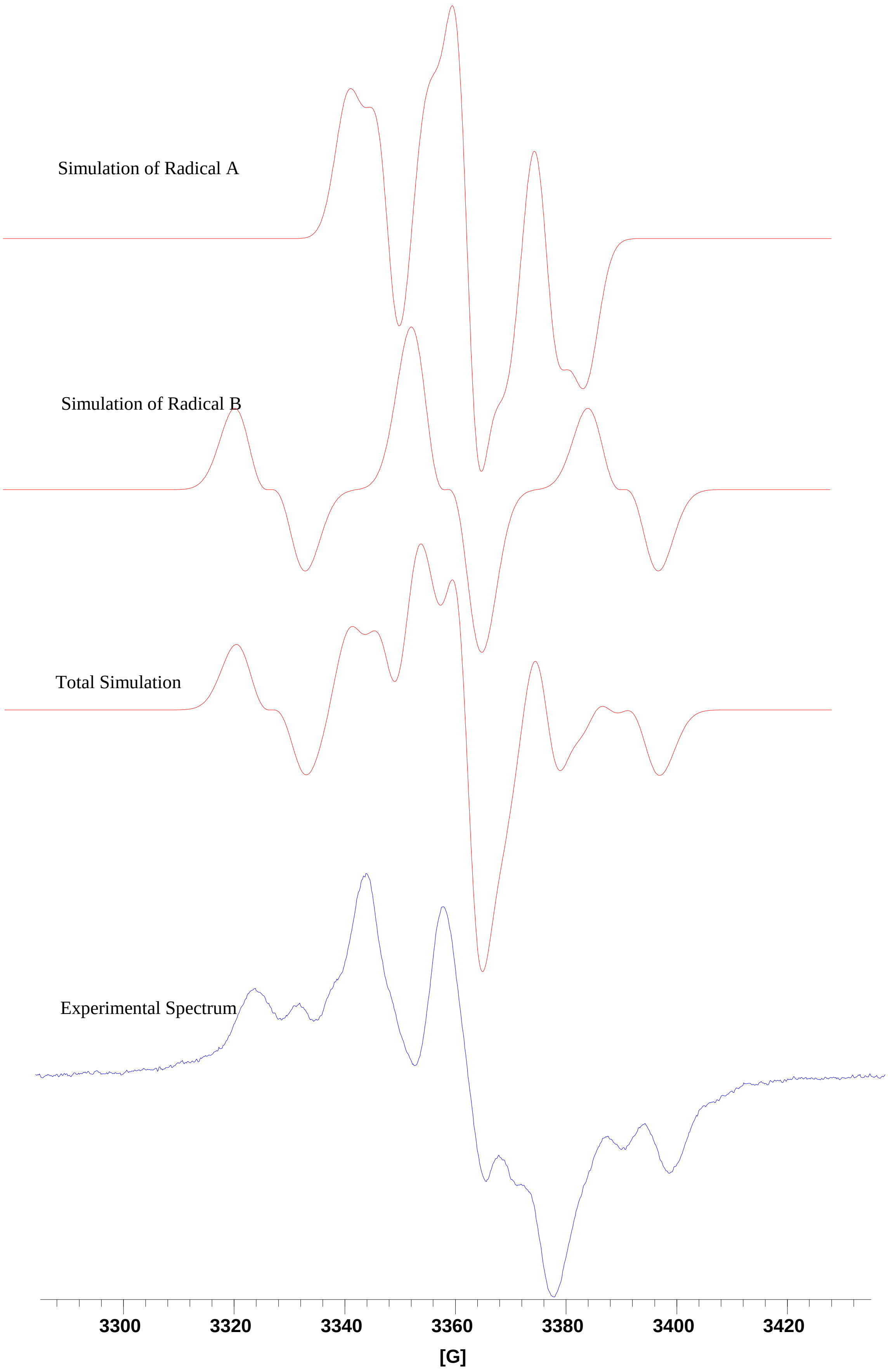

Figure 5. Experimental and simulated EPR spectra of gamma irradiated menadione single crystal at 120 K when the magnetic field is in the a*c plane at an angle 140° towards the axis

Table 1. EPR parameters of simulated spectra

Figure	Radical A	Radical B
Figure 3	$\left[(A_{CH_2})_\alpha\right]_A$ = 1.53 mT $\left[(A_H)_\beta\right]_A$ = 0.636 mT $\left[(A_H)_\gamma\right]_A$ = 0.472 mT Center Field = 336.18 mT ν = 9.424 GHz Line Width = 0.6 mT	$\left[(A_{CH_2})_\alpha\right]_B$ = 3.613 mT $\left[(A_H)_\beta\right]_B$ = 0.78 mT Center Field = 336.128 mT ν = 9.424 GHz Line Width = 0.83 mT
Figure 4	$\left[(A_{CH_2})_\alpha\right]_A$ = 1.468 mT $\left[(A_H)_\beta\right]_A$ = 0.465 mT $\left[(A_H)_\gamma\right]_A$ = 0.62 mT Center Field = 335.584 mT ν = 9.429 GHz Line Width = 0.4 mT	$\left[(A_{CH_2})_\alpha\right]_B$ =2.873 mT $\left[(A_H)_\beta\right]_B$ = 0.509 mT Center Field = 335.683 mT ν = 9.429 GHz Line Width = 0.72 mT
Figure 5	$\left[(A_{CH_2})_\alpha\right]_A$ = 1.428 mT $\left[(A_H)_\beta\right]_A$ = 0.535 mT $\left[(A_H)_\gamma\right]_A$ = 0.466 mT Center Field = 335.55 mT ν = 9.429 GHz Line Width = 0.545 mT	$\left[(A_{CH_2})_\alpha\right]_B$ = 3.201 mT $\left[(A_H)_\beta\right]_B$ = 0.668 mT Center Field = 335.906 mT ν = 9.429 GHz Line Width = 0.665 mT

Table 2. The EPR parameters of the radical A observed in menadione single crystals at 120 K (*Note*: The errors are estimated to be ±0.00005 and ±0.005 mT for all the calculated g- and A- values, respectively)

Radical Parameters (Radical A)	Principal values	Direction cosines
$\left[(A_{CH_2})_\alpha\right]_A$ (mT)	A_{xx} = 1.508 A_{yy} = 1.458 A_{zz} = 1.429 a_{av} = 1.465	0.126745 0.441334 -0.888347 -0.846244 0.515334 0.135282 0.517500 0.734612 0.438792
$\left[(A_H)_\beta\right]_A$ (mT)	A_{xx} = 0.734 A_{yy} =0.527 A_{zz} = 0.448 a_{av} = 0.570	0.229830 0.128612 -0.964695 -0.817138 -0.512919 -0.263058 -0.528643 0.848748 -0.012790
$\left[(A_H)_\gamma\right]_A$ (mT)	A_{xx} = 0.569 A_{yy} = 0.446 A_{zz} = 0.366 a_{av} = 0.460	0.839465 0.429864 -0.332441 -0.176374 0.794172 0.581535 0.513996 -0.429544 0.742496
g_A	g_{xx} = 2.00862 g_{yy} = 2.00595 g_{zz} = 2.00420 g_{av} = 2.00626	0.954854 0.269850 -0.124239 -0.275585 0.648426 -0.709646 -0.110938 0.711846 0.693518

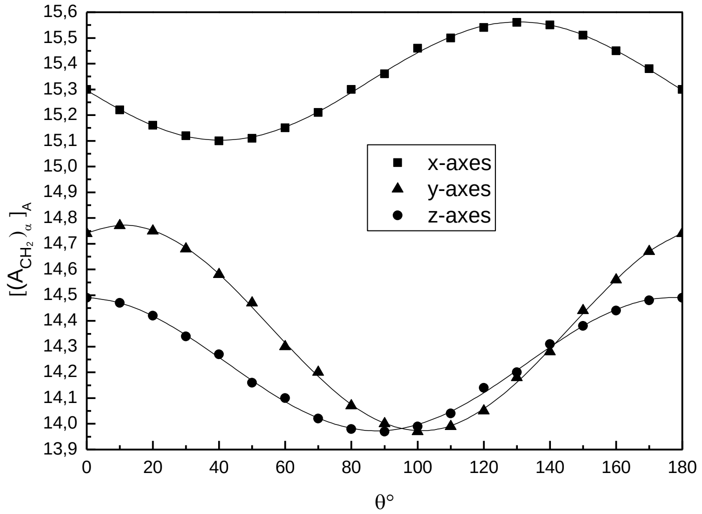

Figure 6. Angular variation of the $(A_{CH_2})_\alpha$-tensor of the radical A observed in menadione single crystals at 120 K (in Gauss)

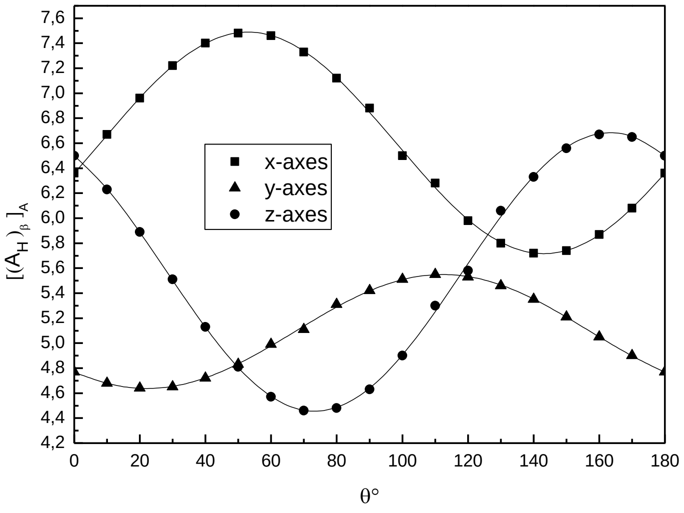

Figure 7. Angular variation of the $(A_H)_\beta$-tensor of the radical A observed in menadione single crystals at 120 K (in Gauss)

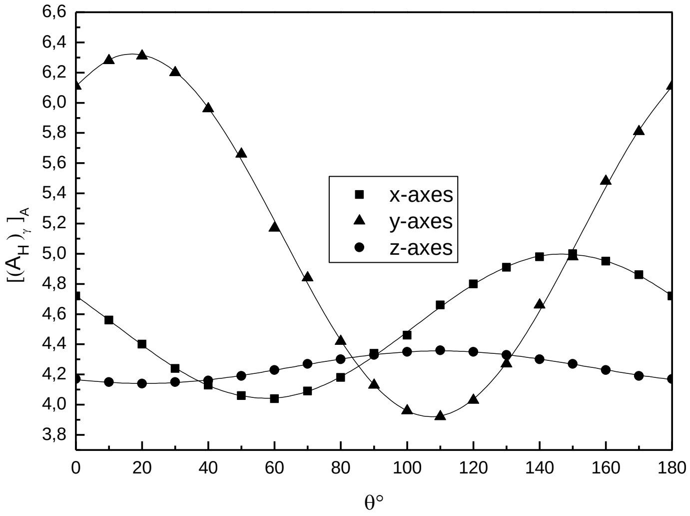

Figure 8. Angular variation of the $(A_H)_\gamma$-tensor of the radical A observed in menadione single crystals at 120 K (in Gauss)

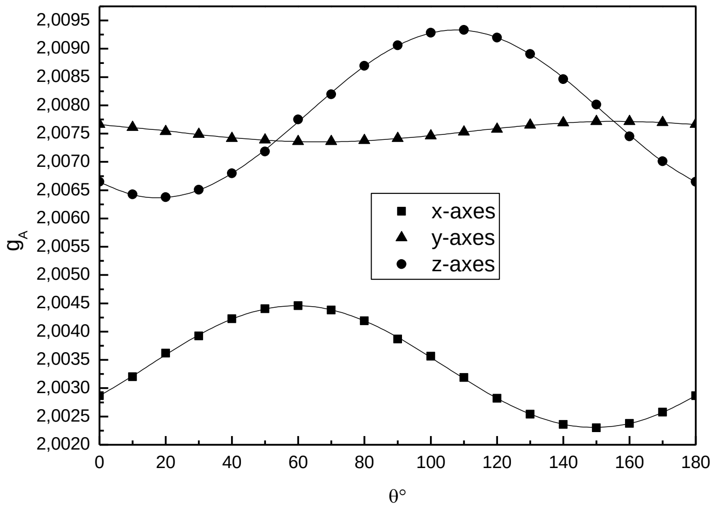

Figure 9. Angular variation of the g-tensor of the radical A observed in menadione single crystals at 120 K.

Table 3. The EPR parameters of the radical B observed in menadione single crystals at 120 K. (*Note*: The errors are estimated to be ±0.00005 and ±0.005 mT for all the calculated g- and A- values, respectively.)

Radical Parameters (Radical B)	Principal values	Direction cosines
$\left[(A_{CH_2})_\alpha\right]_B$ (mT)	A_{xx} = 3.864 A_{yy} = 3.278 A_{zz} = 2.847 a_{av} = 3.330	0.314775 0.129015 0.940357 -0.879773 0.411507 0.238037 -0.356253 -0.902229 0.243036
$\left[(A_H)_\beta\right]_B$ (mT)	A_{xx} = 0.778 A_{yy} =0.647 A_{zz} = 0.442 a_{av} = 0.622	0.664548 -0.108074 0.739389 -0.583728 0.542668 0.603964 -0.466516 -0.832965 0.297543
g_B	g_{xx} = 2.00658 g_{yy} = 2.00493 g_{zz} = 2.00432 g_{av} = 2.00528	0.940031 0.113215 -0.321751 -0.126190 0.991811 -0.019689 0.316886 0.059111 0.946620

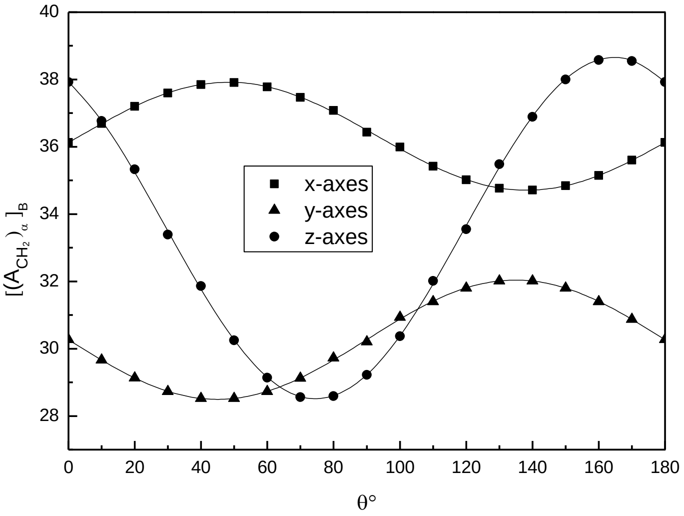

Figure 10. Angular variation of the $(A_{CH_2})_\alpha$-tensor of the radical B observed in menadione single crystals at 120 K (in Gauss)

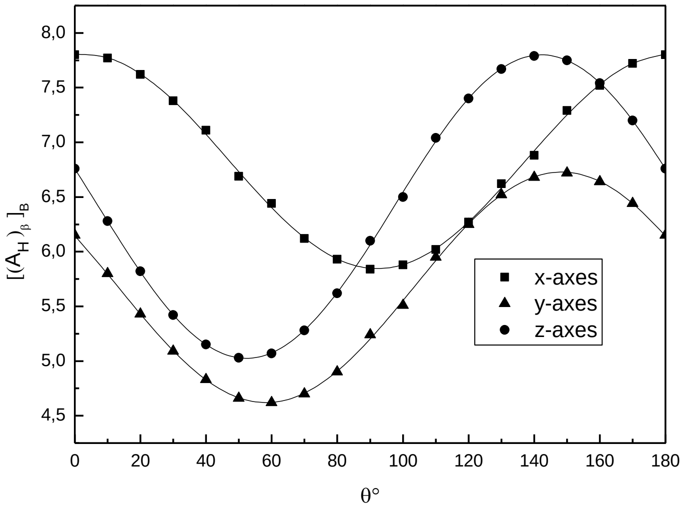

Figure 11. Angular variation of the $(A_H)_\beta$-tensor of the radical B observed in menadione single crystals at 120 K (in Gauss)

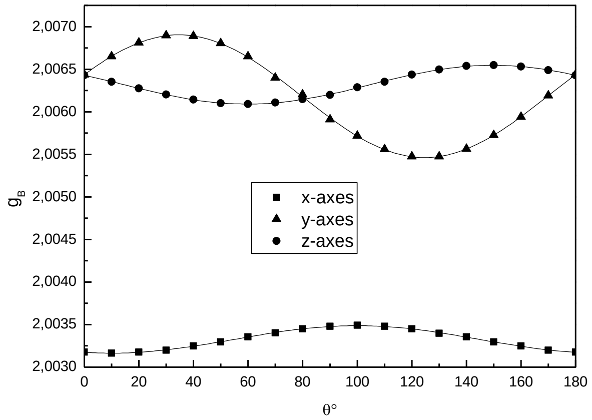

Figure 12. Angular variation of the g-tensor of the radical B observed in menadione single crystals at 120 K

The average values of the $(A_{CH_2})_\alpha$ tensors of the radical A and the radical B in the present study are close to the values of the previous studies [16-18]. The average values of the $(A_H)_\beta$ tensors of the radical A and the radical B and the average value of the $(A_H)_\gamma$ tensor of the radical A in the present study are close to the values of the previous studies [19-26].

EPR analysis of gamma irradiated menadione single crystal along three axes was performed for the first time in this study. There is no EPR study conducted under these conditions before. It is seen that some EPR studies on menadione have been done before [27-31]. Okazaki et al. found that in a sodium dodecyl sulfate (SDS) micellar solution, temporary free radicals in the magnetic field-dependent photo-reduction of menadione or anthraquinone are transformed into stable nitroxide radicals by "spin trapping" technique with or without microwave irradiation. They obtained the EPR spectrum of the radical pair (alkyl radical and semiquinone radical). Irradiation source, microwave irradiation source and the method they use is the " product yield-detected EPR " method [27,28]. Hollocher and Weber obtained the EPR spectrum of free radicals formed by alkali degradation of 2-methyl-1,4-naphthoquinone at pH 14 following reduction with $Na_2S_2O_4$ followed by partial re-oxidation with oxygen. They examined the effect of high pH effect on 2-methyl-1,4-naphthoquinone and the EPR spectrum of free radicals [29,30]. Srinivasan and Golbeck examined the semiquinone radical anion pair formed in menadione by light-induced charge separation and photosynthetic electron transfer in Photosystem I (PS I) by EPR spectroscopy [31]. In previous studies, the experimental conditions created and the method used are completely different from our study. Our study is EPR study of gamma-irradiated single crystals performed under low temperature conditions. The radical structures found in previous studies do not show consistency with the structure of the spectra obtained in our experiment.

4. CONCLUSION

The exposure of the single crystal of menadione to gamma radiation produced a change in structure. EPR analysis of menadione single crystal showed that two free radicals were formed. Radical A and radical B are broken at the same bond point. The hyperfine structure constants and spectroscopic splitting factors of two carbon centered radicals were calculated. When the EPR spectra of the compound along the three axes were examined, it was found that the hyperfine structure constants and spectroscopic splitting constants exhibited an anisotropic change. The results of the experimental study were supported by the simulation study.

ACKNOWLEDGEMENT

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DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Ali Cengiz ÇALIŞKAN: Helped conduct the experiments, analyzed the results, and did half of the writing of the manuscript.

Betül ÇALIŞKAN: Did the experiments, analyzed the results and completed half of the writing process of the manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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