MODULATION EFFECTS IN THE SPIN-ECHO SIGNALS OF $\dot{C}H(COOH)_2$ RADICALS

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Results are given on the angular dependence of these effects for radicals stabilized in a γ-irradiated single crystal of malonic acid. The modulation is ascribed to anisotropic hyperfine interaction with the α proton of $\dot{C}H(COOH)_2$. The results allow electron spin echo to be used in certain cases to measure small splittings in the ESR spectra of free radicals.

INTRODUCTION

The echo amplitude usually has an exponential relation to the time interval τ between the pulses, but cases are known where the exponential decay is modulated with a frequency ω_m (Fig. 4). This effect was first observed for nuclear spin echo. Hahn and Maxwell [1] examined the modulation of the echo from protons in ethanol. The frequency and depth of the modulation were determined by the difference between the Larmor frequencies of the alcohol protons, which have different chemical shifts, and by the interaction between these protons. Modulation in electron spin echo was first examined [2] for paramagnetic Ce^{3+} ions in $CaWO_4$, where it was ascribed to anisotropic interaction of the unpaired electron of Ce^{3+} with the surrounding magnetic nuclei. The effect can [2] give the same information about this interaction as the steady-state ENDOR effect.

We have observed this effect for some irradiated polycrystalline materials [3] and in irradiated single crystals of amino acids and dicarboxylic acids, as well as in frozen alcoholic solutions of DPPH. The signal envelope had a very complicated form in these cases, so it was necessary to examine the effect on a simple radical with closely known properties. The $\dot{C}H(COOH)_2$ radical in irradiated malonic acid is one of the most suitable for this purpose.

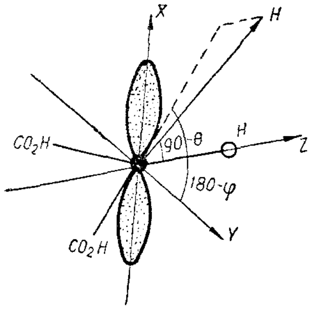

Fig. 1. Relation of structure of $\dot{C}H(COOH)_2$ radical to the XYZ coordinate system.

METHODS

We used a 3-cm instrument developed at this institute [3], with pulses of duration 40 nsec, which covers relaxation times in the range 10^{-7} to 10^{-3} sec. The limit of detection was 10^{15} paramagnetic particles in the specimen at room temperature. The two-pulse method [4] was used, in which two UHF pulses with a power ratio of 1 : 2 act at times $t = 0$ and $t = \tau$, the spin-echo signal arising at $t = 2\tau$. The frequency corresponds to the ESR condition, $h\nu = g\beta H$. The envelope of the echo signal was recorded photographically from the oscilloscope with τ swept continuously. The spectra were recorded with an RE-1301 standard ESR spectrometer.

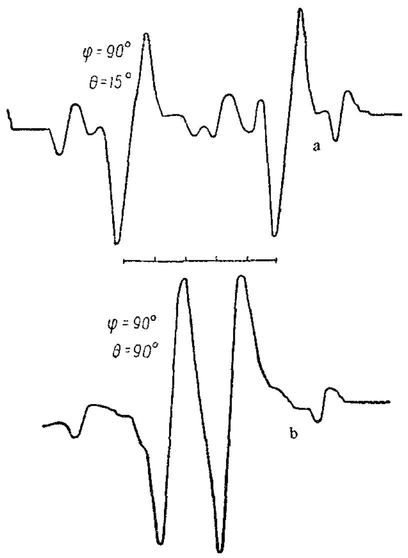

Fig. 2. First-derivative ESR spectrum of a γ-irradiated single crystal of malonic acid.

We used a single crystal of malonic acid grown by slow evaporation of an aqueous solution, which was irradiated (3 Mrad) at room temperature with a Co^{60} γ-ray source. The measurements were made at room temperature with the crystal in a holder providing rotation about one of the three orthogonal XYZ axes linked to the crystal. The echo signal and ESR spectrum were recorded at intervals of 3° about each axis. Identity of the settings in ESR and spin echo was checked by measuring the splittings in the spectra with an NMR field meter of autodyne type and a heterodyne wavemeter.

The crystal structure is known [5]. The triclinic unit cell contains two molecules, so additional lines cannot appear in the spectrum due to nonequivalent orientation of the radicals in the lattice. The orientation of the XYZ system relative to the crystallographic axes was as in [6].

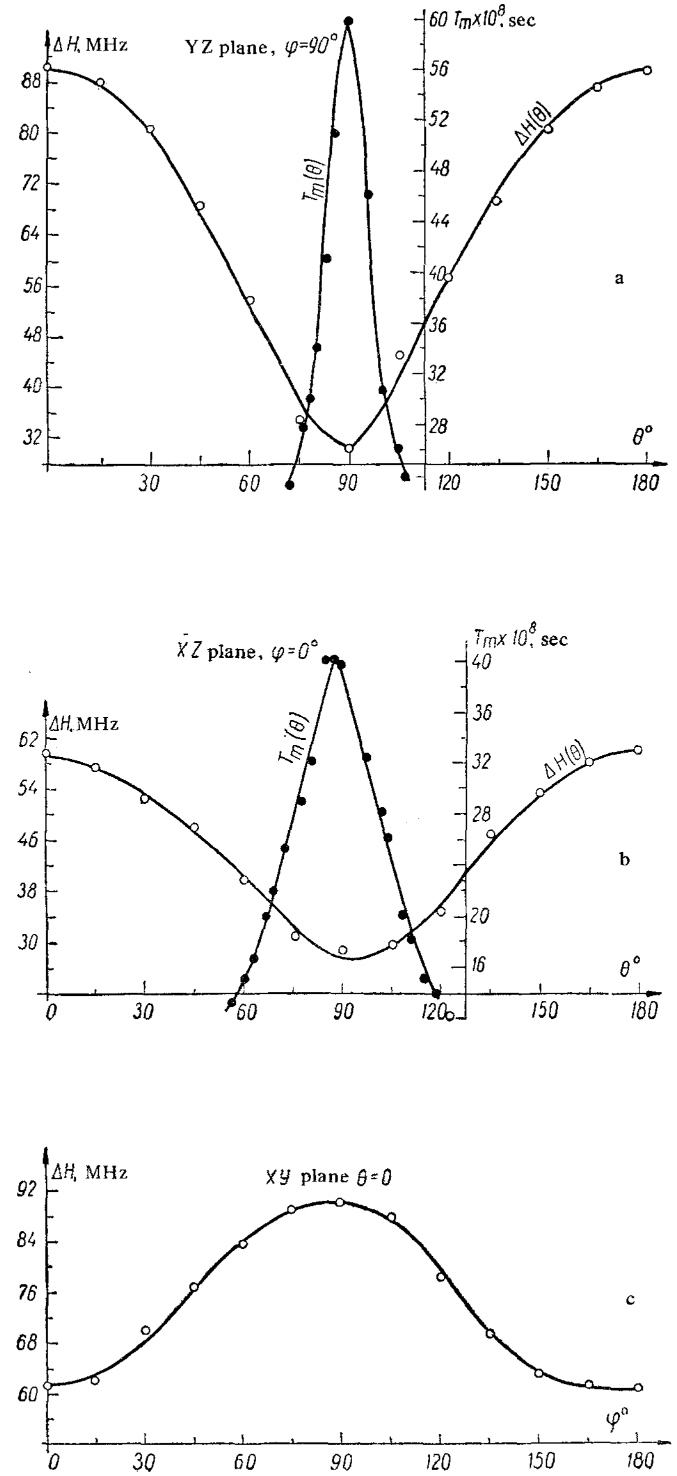

Fig. 3. Splitting of the doublet of $\dot{C}H(COOH)_2$ and modulation period T_m as functions of θ and φ.

Figure 1 shows the relation of the XYZ system to the $\dot{C}H(COOH)_2$ radical stabilized in the crystal. The unpaired electron is [6] in a $2p_x$ orbital. The external field $\mathbf{H}_0$ has a direction defined by the angles θ and φ in the XYZ system, in which θ is the angle between $\mathbf{H}_0$ and the XY plane and φ is the angle between the X axis and the projection of $\mathbf{H}_0$ on the XY plane.

RESULTS

The radicals $\dot{C}H(COOH)_2$ and $\dot{C}H_2COOH$ are produced in γ-irradiated malonic acid. The ESR spectrum consists of two strong lines produced by the first and several weaker lines, some of which arise from the second. Figure 2 shows ESR spectra recorded with various orientations of the crystal. The superimposed spectrum of $\dot{C}H_2COOH$ interferes with the observation of weak lines of $\dot{C}H(COOH)_2$. The spectrum is not substantially simplified after 12 hr at 50° C.

The ESR spectrum and echo envelope of $\dot{C}H(COOH)_2$ were recorded for various orientations. Figure 3 shows the splitting ΔH of the strong doublet and the modulation period T_m as functions of θ and φ. Modulation of the echo signal is seen in the YZ plane ($\varphi = 90°$) over the range $\theta = 75°$ to $\theta = 105°$, and in the XZ plane ($\varphi = 0$) in the range $\theta = 60°$ to $\theta = 120°$. In both cases, T_m is maximal for $H_0 \| Z$. The maximum T_m in the YZ plane is 0.6 μsec, while that in the XZ plane is 0.4 μsec*. This difference arises from nonequivalence of the orientations as a result of inaccurate setting on going from one rotation axis to another. ΔH in the XY plane ($\theta = 0$) is shown as a function of φ in Fig. 3c; no modulation is seen in this plane. Figure 4 shows typical oscillograms for the change in the decay as θ is varied.

In experiments by the three-pulse method, the pulses had equal durations and a power ratio of 2 : 1 : 2, being applied at $t = 0$, $t = \tau$, and $t = \tau + T$. The stimulated echo signal then occurs at $t = 2\tau + T$. The decay curves as functions of T (τ constant) and τ (T constant) were of the same form as in the two-pulse method. The effect was not studied in detail.

DISCUSSION

Angular dependence of the modulation frequency indicates that the effect is related to an anisotropic hyperfine interaction with the α proton in $\dot{C}H(COOH)_2$. The following spin Hamiltonian ($h = 1$) describes this interaction and the interaction with the external field:

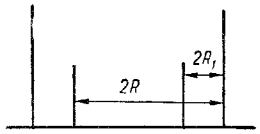

Fig. 5. Theoretical form of the ESR spectrum of $\dot{C}H(COOH)_2$.

$$\hat{H} = \nu_s \hat{S}_z + \nu_I \hat{I}_z + A\hat{S}_z\hat{I}_z + B\hat{S}_z\hat{I}_x + C\hat{S}_z I_y, \qquad (1)$$

in which A, B, and C are the constants of the hyperfine interaction in MHz and ν_S and ν_I are the Larmor frequencies of electron and proton in the field $H_0 \| Z$. The eigenvalues of this spin Hamiltonian are

$$E_1 = \frac{\nu_s}{2} + R; \qquad E_3 = -\frac{\nu_s}{2} + R_1;$$

$$E_2 = \frac{\nu_s}{2} - R; \qquad E_4 = -\frac{\nu_s}{2} - R_1, \qquad (2)$$

in which

$$R = \frac{1}{4}\sqrt{(2\nu_I + A)^2 + B^2 + C^2};$$

$$R_1 = \frac{1}{4}\sqrt{(2\nu_I - A)^2 + B^2 + C^2}.$$

The system then has four possible transitions, which should have the following frequencies:

$$\begin{aligned}
\nu_1 &= E_1 - E_4 = \nu_s + (R + R_1);\\
\nu_2 &= E_1 - E_3 = \nu_s + (R - R_1);\\
\nu_3 &= E_2 - E_4 = \nu_s - (R - R_1);\\
\nu_4 &= E_2 - E_3 = \nu_s - (R + R_1).
\end{aligned} \qquad (3)$$

The ESR spectrum of $\dot{C}H(COOH)_2$ is therefore a symmetrical quadruplet having an outer doublet of splitting $2(R + R_1)$ and an inner one of splitting $2(R - R_1)$.

It is found [6] that these two doublets never change places, the intensity of the outer one being greater than that of the inner one at 3 cm. Figure 5 shows the theoretical form of the spectrum; the actual spectrum is complicated by the lines from $\dot{C}H_2COOH$.

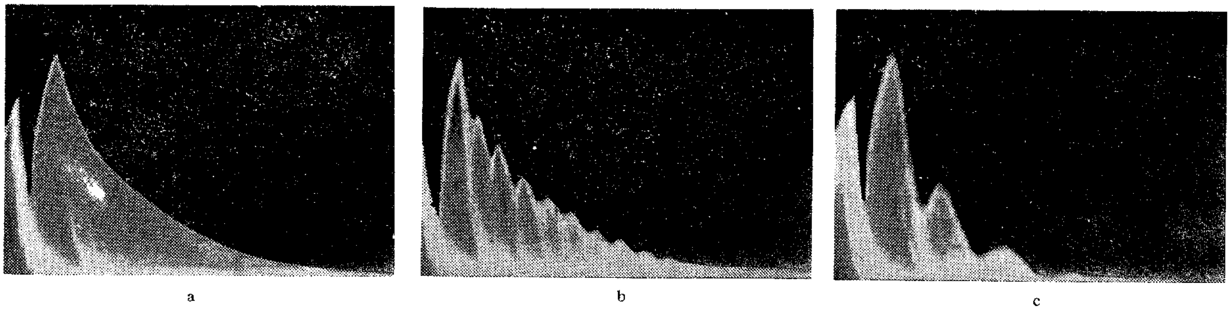

Fig. 4. Spin echo for $\varphi = 0$ at θ of: a) 30°, b) 75°, c) 90°.

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*The system allowed us to record modulation with $T_m \geq 0.07$ μsec.

It has been shown [2, 7] that the following formula describes the spin-echo decay without allowance for relaxation processes when the interaction is governed by (1), provided that all resonant transitions in the spin system are excited:

$$V(2\tau) = V(0)\left\{1 - \frac{v_l^2(B^2 + C^2)}{64R^2R_l^2} \times \right.$$
$$\times [2 - 2\cos 4\pi R\tau - 2\cos 4\pi R_1\tau +$$
$$\left. + \cos 4\pi(R + R_1)\tau + \cos 4\pi(R - R_1)\tau]\right\},$$

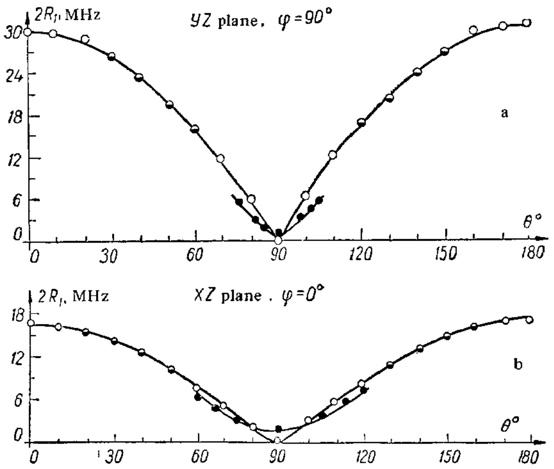

Fig. 6. Splitting $2R_l$ and modulation frequency ν_m as functions of θ: ◒ values from ESR spectrum [6], ○ theoretical $2R_l$ [6], ● ν_m from spin echo.

in which V(0) is the signal amplitude without allowance for the interaction with the nucleus.

The ESR spectrum shows that $2(R + R_l)$, 2R, and $2(R - R_l)$ are always ≥ 29 MHz, while $2R_l$ ranges from 0 to 29 MHz.

It was not practicable to measure $\nu_m > 15$ MHz, so we may assume that the sole observed frequency was $2R_l$. Figure 6 shows theoretical [6] $2R_l$ as functions of angle in the YZ and XZ planes, as well as the observed behavior of ν_m in these planes. The curves differ only within the error of measurement (±2 MHz) for the ESR hyperfine interaction constants.

Figure 6 shows that $2R_l = 0$ for $H_0 \| Z$; in fact, there was a range of ~1° near $H_0 \| Z$ in which the period of the modulation became greater than the relaxation time. The observations in the XZ plane extend over a greater angular range than those in the YZ plane, where $2R_l$ increases more rapidly.

The high line width and the interfering lines allow $2R_l$ to be deduced from the ESR spectrum only in a very restricted range of angles, whereas spin echo allows $2R_l$ to be measured when this is much less than the line width.

The results thus confirm the interpretation [2, 7] of spin-echo modulation effects as due to anisotropic hyperfine interaction. Spin echo allows one to measure small splittings in ESR spectra.

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