The Electron Paramagnetic Resonance Spectrum of γ-Irradiated Dimethyl Malonic Acid

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The electron paramagnetic resonance of γ-Irradiated single crystals of dimethyl malonic acid $[(CH_3)_2C(COOH)_2]$ has been studied for different orientations of the crystal in a magnetic field. The radicals produced by gamma irradiation have been investigated between 123 and 300 K. The spectra were found to be temperature independent, and radiation damage centres were attributed to $[(CH_3)_2C(COOH)_2]^+$ radicals. The g factor and hyperfine coupling constants were found to be almost isotropic with average values $g = 2.0036$, $a_{(COOH)_2} = 0.5$ mT, $a_{(CH_3)_2} = 2.1$ mT, respectively, and spin density $\rho = 91\%$ of the $[(CH_3)_2C(COOH)_2]^+$ radical.

Key words: Spectroscopic Splitting Factor; g;
Isotropic Hyperfine Coupling Constant a;
Spin Density ρ.

1. Introduction

EPR technique has widely been used for the identification of damage centres produced by high energy radiation. Investigations on the g tensor and hyperfine coupling constants of the spin carrying nuclei of the species give information about the structure of the centres. Although a large number of organic and inorganic species have been produced and investigated, the studies on the $[(CH_3)_2C(COOH)_2]^+$ radical carry doubts. The isotropic hyperfine coupling constants for H_α, H_β and H_γ have been analysed theoretical for the $[(CH_3)_2C(COOH)_2]^+$ radical, and experimental results are given. We have undertaken this study on dimethyl malonic acid with the hope of obtaining the $[(CH_3)_2C(COOH)_2]^+$ radical.

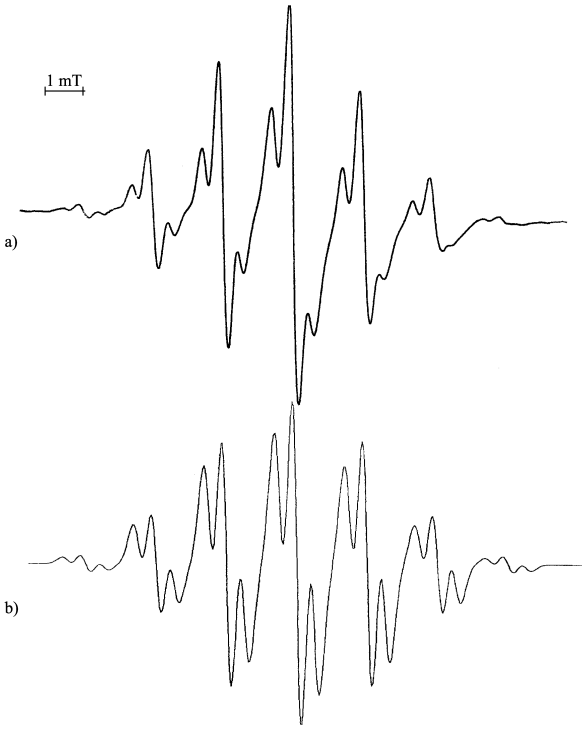

Fig. 1a) EPR spectrum of a γ-irradiated dimethyl malonic acid single crystal; b) Simulation of the spectrum. The line width is 0.4 mT.

2. Experimental

Dimethl malonic acid single crystals were grown by slow evaporation of a concentrated aqueous solution. The salt crystallises in the tetragonal system, space group $I4_1/acd$ with the lattice constants: $a = 12.662$ Å, $c = 16.234$ Å, $V = 2603$ Å, $Z = 16$ [1].

The samples were irradiated at room temperature with a Co^{60}-γ ray source of 0.3 Mrad/h. The EPR spectra were recorded using 2 mW microwave power. The measurements at 123 K and 300 K were carried out at a frequency of 9.13 Ghz using a Varian temperature controller. The crystals were rotated on a Lucite Piller about their crystallographic, axes and the angles of rotation were read on a scale in degrees.

The EPR spectra of many single crystals were reproduced several times. The g factor was found by comparison with a DPPH sample ($g = 2.0036$).

3. Results and Discussion

Free radicals produced by gamma irradiation in single crystals of dimethyl malonic acid were investigated between 123 and 300 K with EPR spectra. The spectra of the single crystals were taken at 5-degree intervals of the magnetic field H, being applied in each of the three crystallographic planes *ab*, *bc*, and *ca*.

The hyperfine splitting patterns of the experimental and simulated spectrum are shown in Figs. 1a and 1b, respectively, at all orientations of the magnetic field.

The spectrum of this radical splits into a 1:6:15:20:15:6:1 intensity pattern because of its $(CH_3)_2$-protons and, as shown in Fig. 1, into a 1:2:1:6:12:0.6:0.15:30:15:20:40:20:15:30:15:6:12:0.6:1:2:1 intensity pattern because of its $(COOH)_2$-protons. The g value of this radical is anisotropic, and $g_{av} = 2.0036$. This value agrees with literature values which were obtained by different methods [2 – 7].

The hyperfine interaction constant of the $(COOH)_2$ protons with the unpaired electron is anisotropic, its average value being $a_{(COOH)_2} = 0.5$ mT. This value supports its attribution to $[(CH_3)_2C(COOH)_2]^+$. Since no site splittings were observed, it is concluded that the 16 molecules in the unit cell of dimethyl malonic acid are magnetically equivalent. In the present work, this coupling was constant and amounted to 2.1 mT for $(CH_3)_2$-protons, and this indicates that in the $[(CH_3)_2C(COOH)_2]^+$ cation radical 91% of the spin density is on C_α carbons and 9% on C_β carbons.

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