EPR Study of the Orientation Distribution Function of HO$_2^\cdot$ Radicals Ordered by Light Irradiation

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Abstract. Partial orientational alignment of HO$_2^\cdot$ radicals in the matrix of glassy hydrogen peroxide was created by light irradiation. The orientation distribution function of the radicals was found by analyzing the angular dependence of electron paramagnetic resonance spectra. The direction of the dipole transition moment of HO$_2^\cdot$ in the molecular frame of reference was determined.

1 Introduction

The action of light irradiation on solids induces the partial orientational alignment of the molecules as a result of photoselection or photoorientation [1–7]. The photo-induced macroscopic anisotropy is used for recording and processing information as well as for the study of the light-absorbing properties of molecules.

Usually the photo-induced anisotropy is studied by optical methods, most often the ultraviolet–visible dichroism of a sample is recorded [2, 8–11]. It should be noted that the optical methods give only the averaged characteristics of the orientational alignment of the molecule ensemble – the extent of the orientation or ordering parameters [12]. If the sample contains ordered paramagnetic species, not only optical methods but also electron paramagnetic resonance (EPR) spectroscopy can be used. In this case a more detailed information can be obtained. Actually, the position of the resonance signal of a radical center in the EPR spectrum depends on the radical orientation in the magnetic field of a spectrometer. Hence, the information about orientation of each subensemble can be obtained separately by analyzing the spectrum [13, 14].

Earlier, a method was elaborated which allows one to find the most exact characteristic of the orientational alignment of paramagnetic species – the orientation distribution function [15]. The orientation distribution function $\rho(\alpha, \beta, \gamma) = \frac{\partial N}{\partial \alpha \partial \beta \partial \gamma}$ gives the number of particles which are oriented in the angular in-
interval $\alpha + d\alpha$, $\beta + d\beta$, $\gamma + d\gamma$, where $\alpha$, $\beta$, $\gamma$ are the Euler angles connecting the sample frame with the frame of the particle. The method is based on computer modeling EPR spectra recorded at different positions of the sample of respect to the magnetic field vector of a spectrometer. Formerly, the method was applied for the investigation of samples which have mechanically [16] or magnetically induced anisotropy [17].

The aim of this work is to apply this method [15] for the investigation of photo-induced anisotropy. Radicals HO$_2^-$ in the matrix of glassy hydrogen peroxide were chosen as a model object of the investigation.

2 Materials and Methods

78–87% hydrogen peroxide was obtained by distillation of a 30% solution of hydrogen peroxide at low pressure. Hydrogen peroxide was placed into a quartz ampoule with an inner diameter of 3 mm (the height of the samples was 10 mm) and was cooled at 77 K by immersion into liquid nitrogen. The samples obtained in that way formed a transparent glass. According to the data of ref. 18, hydrogen peroxide forms glass in the concentration interval of 45.5–87%.

HO$_2^-$ radicals were generated by irradiating glassy hydrogen peroxide with light of a low-pressure electrodeless mercury lamp with high-frequency power supply. The wavelength of irradiation was 254 nm. The light intensity was determined by ferricyanide actinometry and amounted to $4.6 \cdot 10^{13}$ quant/s·mm$^2$. The anisotropy of a sample was induced by a parallel beam of nonpolarized light.

Annealing of samples was performed with a temperature control accuracy of ±1 K.

EPR spectra were recorded at 77 K on a Varian E-3 spectrometer. It was proved by special experiments that the light-induced anisotropy was not changed at 77 K in the time scale of our experiments (i.e., several hours). During the registration of the angular dependence of EPR spectra the orientation of the sample in the magnetic field was fixed with an accuracy of ±2°.

The number of spins in the sample was determined by double integrating the EPR spectrum of the sample and by comparing this integral with double integral of the EPR spectrum of the crystal CuCl$_2$·2H$_2$O with the known number of particles.

2.1 Computer Modeling of EPR Spectra

Numerical modeling of EPR spectra was carried out by a spin Hamiltonian with second-order terms. The energy of the nuclear Zeeman interaction and forbidden transitions were taken into account. The relative orientation of the principal axes of $g$ and hyperfine structure (HFS) tensors was given by Euler angles. A convolution of Gaussian and Lorentzian functions, as the most general representation of individual line shapes, was used for modeling. The dependence of the line shape on the orientation of the species in the magnetic field reflecting line