EPR Study of the Orientation Distribution Function of HO₂⁻ Radicals Ordered by Light Irradiation

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Abstract. Partial orientational alignment of HO₂⁻ 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 HO₂⁻ 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 photoselector 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 \( \rho(\alpha, \beta, \gamma) = \partial N/\partial \alpha \partial \beta \partial \gamma \) 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 $\text{HO}_2^-$ 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%.

$\text{HO}_2^-$ 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 ferrylxalate actinometry and amounted to $4.6 \cdot 10^{13}$ quant/s $\cdot$ 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 $\pm 1$ 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 $\pm 2^\circ$.

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 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 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
broadening as a result of an unresolved anisotropic HF interaction was taken into account. The line shape was given by a tensor whose principal axes in the general case do not coincide with principal axes of the g-tensor. The EPR spectra were calculated in the rigid limit.

The magnetic parameters of the radicals and the parameters of the orientation distribution function were determined by the minimization of the sum of squared deviations of the numerically modeled EPR spectra from the experimental spectra. The global minimum was obtained with the nonlinear least-squares method whose computational implementation is described in ref. 15.

3 Results and Discussion

3.1 Generation of HO₂ Radicals and Finding Their Magnetic Parameters

The quantum yield of the HO₂ radical formation \( \varphi = 0.68 \pm 0.07 \) was determined from the starting part of the kinetic curve, which shows the accumulation of the radicals during irradiation.

It is known from ref. 19–22 that the photochemical degradation of hydrogen peroxide includes the following reactions

\[
\begin{align*}
\text{H}_2\text{O}_2 & \xrightarrow{h\nu} \text{[OH'OH']}, \\
[\text{OH'OH'}] + 2\text{H}_2\text{O} & \mathrel{\longrightarrow} \text{[HO₂;HO₂⁺]} + 2\text{H}_2\text{O}, \\
\text{HO₂} + \text{H}_2\text{O} & \mathrel{\longrightarrow} \text{[HO₂;HO₂⁺]} + 2\text{H}_2\text{O}, \\
\text{HO₂} & \xrightarrow{h\nu} \text{OH}^- + \text{O}, \\
\text{OH}^- + \text{H}_2\text{O} & \mathrel{\longrightarrow} \text{HO₂} + \text{H}_2\text{O}, \\
\text{O} + \text{H}_2\text{O} & \mathrel{\longrightarrow} \text{O}_2 + \text{H}_2\text{O}.
\end{align*}
\]

One can see from the above reactions that peroxide radicals are generated in the form of radical pairs. In our experiments the existence of radical pairs was confirmed by the observation of the EPR signal in the area of \( \Delta m_s = 2 \). The dipole–dipole interaction of radicals in a pair causes sufficient broadening of the spectrum (Fig. 1a). At annealing of a sample the distance between radicals increases as a result of radical movements and recombination of closely arranged pairs. The spectrum of annealed sample is better resolved, in such spectrum the HFS becomes apparent. In the sample annealed at 124 K radical pairs are practically absent (Fig. 1b).

Using a computer modeling of the spectrum, represented in Fig. 1b, the magnetic parameters of HO₂ radicals isolated in the matrix were estimated as well as the parameters characterizing the shape of an individual resonance line. The result of modeling is represented in Fig. 2. One can see that the disagreement
between the theoretically calculated spectrum and the experimental one does not exceed errors of their registration. It should be emphasized that the quantitative coincidence of calculated and experimental spectra can be achieved only if the directions of principal axes of $g$ and HFS tensors do not coincide. When these axes coincide, the calculated spectrum noticeably differs from the experimental one at any set of magnetic parameters. The Euler angles connecting the systems of coordinates of $g$-tensor and HFS tensor are $\psi = -70^\circ \pm 1^\circ$, $\chi = 47^\circ \pm 1^\circ$, $\xi = 35^\circ \pm 1^\circ$. The substantial tilt between the axes of $g$ and HFS tensors seems to disagree with the internal symmetry of the radical which has the reflection symmetry plane. Evidently, the direction perpendicular to this plane should be one of the magnetic axes mutual for both tensors. The absence of a satisfac-

![Figure 1](image1.png)

**Fig. 1.** EPR spectra of HO$_2^*$ radicals in glassy hydrogen peroxide: a 77 K, b after annealing at 124 K. Double integrals of the spectra are normalized to unity.

![Figure 2](image2.png)

**Fig. 2.** Result of modeling the EPR spectrum of isolated HO$_2^*$ radicals. Solid line, experiment; circles, result of modeling.
tory simulation of the EPR spectrum under this condition evidences the distortion of the molecular symmetry of HO$_2$$. We suppose that the source of this distortion are hydrogen bonds of the HO$_2$ radical with molecules of media.

The optimal principal values of $g$ and HFS tensors were found to be $g_{xx} = 2.0043$, $g_{yy} = 2.0082$, $g_{zz} = 2.0356$, $a_{xx} = -5.3$, $a_{yy} = 8.7$, $a_{zz} = -20.1$. It is necessary to note that only the anisotropy of magnetic parameters was studied, therefore, the average value of the $g$-factor was not determined and was taken from ref. 23.

Noncoincidence of $g$ and HFS tensor axes is significant in the determination of the orientation distribution function of paramagnetic species. It is necessary to examine this problem in more detail. When the axes of $g$ and HFS tensors coincide, for each direction in the species reference frame other seven directions exist with identical effective magnetic parameters. Hence some orientations of the species in the magnetic field are indistinguishable. If the $g$ and HFS tensor axes do not coincide, each direction in the species reference frame is characterized by a unique set of magnetic parameters. In this case, each orientation of the paramagnetic species in the magnetic field may be registered separately in the EPR spectrum.

A nonannealed sample contains both isolated radicals HO$_2^*$ and radical pairs with different distances between radicals. The spectrum of such sample must be calculated as the sum of the spectrum of isolated radicals and the averaged spectrum of radical pairs. The generation of radicals and their photoorientation occur simultaneously in the system under consideration and the photo-induced orientational alignment complicates the exact determination of magnetic parameters of radicals and radical pairs in the nonannealed sample. To overcome this difficulty the nonannealed sample with the isotropic orientation distribution of paramagnetic species was prepared by pounding an irradiated sample immediately in liquid nitrogen. The result of modeling of the EPR spectrum of this sample is represented in Fig. 3. It was found that the magnetic parameters of isolated radicals HO$_2^*$ are quite similar to the values obtained by modeling of the spectrum of the annealed sample. Individual line widths are somewhat different as a result of the dipole–dipole interaction.

The EPR spectrum of radical pairs extracted in the course of the spectrum simulation is a very broadened doublet line that is quite similar to the theoretically predicted one [24]. By supposing that the distance between the components of this spectrum is nearly equal to the dipole–dipole splitting ($\Delta H_{\text{dip}}$), the average distance between the radicals in a pair was estimated by the formula $r = (3g_{\beta}2\Delta H_{\text{dip}})^{1/3}$ [24] as about 0.8 nm.

Special experiments were carried out to determine the angular dependence of the radical pair EPR spectrum. It was found that 313 nm light irradiation produces radical pairs only. EPR spectra do not show the angular dependence in this case. Obviously, it means that 313 nm light is not absorbed by HO$_2^*$ radicals and consequently it does not induce the photoorientation. Such samples, containing radical pairs only, were irradiated then by 254 nm light. EPR signal of isolated HO$_2^*$ radicals arose in the course of this experiment and the simultaneous appearance of the angular dependence was observed. It was concluded from these
Fig. 3. Result of modeling the EPR spectrum of the sample containing both radical pairs and isolated \( \text{HO}_2^\cdot \) radicals with the statistic orientation. Solid line, experiment; black circles, result of modeling; white circles, radical pairs component; white squares, isolated radical component.

experiments that Eq. (1) proceeds with the orientational randomization and the EPR spectrum of primary stabilized radical pairs does not depend on the orientation of the sample in the magnetic field.

3.2 Orientation Distribution of \( \text{HO}_2^\cdot \) Radicals

The photochemical reaction of the \( \text{HO}_2^\cdot \) radical is accompanied by the formation of a new \( \text{HO}_2^\cdot \) radical in another space orientation (Eqs. (2) and (3)). By repeated acts of pseudo-rotation, radicals are accumulated in the orientation with least probability of light absorption. Thus, during irradiation the orientation ordering of \( \text{HO}_2^\cdot \) radicals takes place without the change of their number. This process is known as the photoorientation phenomenon [25]. It is known that absorption of light is the least probable when the dipole transition moment of a molecule is oriented perpendicular to the vector of the electric component of light. In our experiments the samples were irradiated by a parallel beam of unpolarized light. In this case the direction perpendicular to the electric vector of light coincides with the direction of the light beam. Thus, the radicals with dipole transition moments parallel to the direction of the light beam are accumulated during irradiation.

The position of the resonance signal of each radical in the EPR spectrum depends on the orientation of this radical relative to the magnetic field vector of a spectrometer. The intensity of a signal in each point of the EPR spectrum \( H_i \) can be expressed as

\[
I(H_i, \theta, \phi) = \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} F(H_i, g_{\text{eff}}, a_{\text{eff}}, h_{1/2}) \rho(\alpha, \beta, \gamma) \sin \beta \, d\alpha d\beta d\gamma ,
\]

(4)
where \( F \) is the shape of individual resonance line, \( g_{\text{eff}} = g_{\text{eff}}(\theta, \varphi, \alpha, \beta, \gamma) \) is the effective value of the \( g \)-factor, \( a_{\text{eff}} = a_{\text{eff}}(\theta, \varphi, \alpha, \beta, \gamma) \) is the effective value of the HFS constant, \( h = h(\theta, \varphi, \alpha, \beta, \gamma) \) is the distance between the points of maximal slope of individual resonance line (line width), where angles \( \theta, \varphi \) define the direction of the magnetic field vector in the sample reference frame, \( \rho(\alpha, \beta, \gamma) \) is the orientation distribution function of paramagnetic species in the sample, where angles \( \alpha, \beta, \gamma \) define the orientation of the particle reference frame in the sample reference frame.

In our experiments the sample has an axial symmetry with the symmetry axis coinciding with the direction of light beam. But the studied paramagnetic species do not have an axial symmetry. In this case the orientation distribution function depends on the two angles \( \beta \) and \( \gamma \) which define the orientation of the symmetry axis of the sample in the molecular frame of a radical. This function can be expressed in terms of spherical harmonics as follows:

\[
\rho(\beta, \gamma) = \sum_{j=0}^{\infty} \left( \frac{1}{2} a_j^k P_j(\cos \beta) + \sum_{k=1}^{j} P^k_j(\cos \beta)(a_{jk} \cos(k\gamma) + b_{jk} \sin(k\gamma)) \right),
\]

(5)

where \( P_j \) are Legendre polynomials, \( P^k_j \) are associated Legendre functions, \( a_j^k \) and \( b_j^k \) are expansion coefficients.

The distribution function, which is determined from the analysis of EPR spectra, is always symmetric versus the origin of coordinates because effective parameters of paramagnetic species do not change with reversing of the magnetic field direction. Hence, a part of the information about species orientation is inevitably lost. The symmetry of the function imposes certain limitations on its expansion coefficients. In particular, if the function is represented as Eq. (5), all \( a_{jk} \) and \( b_{jk} \) coefficients with the odd \( j \) are equal to zero.

The orientation distribution function of \( \text{HO}_2 \) radicals in the sample was determined by means of joint computer modeling of ten EPR spectra which were recorded at different angles between the symmetry axis of the sample and the magnetic field vector of a spectrometer. In Fig. 4a some of these spectra are represented. In the course of the modeling the search of a global minimum of discrepancy between the spectra calculated according to Eq. (4) and the experimental ones was realized. The expansion coefficients Eq. (5) were varied. Each spectrum was modeled as the sum of the spectrum of isolated radicals \( \text{HO}_2 \) and the spectrum of radical pairs. It was taken into account that only isolated radicals make a contribution to angular dependence. The stability of this procedure is based on the following. Firstly, during the analysis of the partially oriented system a smooth function is found as a result. Secondly, orientation distribution function is the number of particles, hence it must be positive in all function domains. It was shown [15] that these assumptions make the task defined and having a single solution.

The simulation of the experimental EPR spectra was performed several times with increasing the number of expansion members Eq. (5). This process was stopped when addition of new members did not lead to a decrease of the dis-
crepancy between the calculated spectra and the experimental ones. Coefficients $a_{20}$, $a_{40}$, $b_{21}$, $a_{22}$, $b_{22}$ only were found to be significant. Their values are represented in Table 1. Coefficient $a_{00}$ is equal to 1 for the normalized function. The errors of determination of the expansion coefficients were calculated on the basis of a covariation matrix taking into account the Student distribution. The procedure of calculation of the errors is expounded in ref. 15. The result of modelling for some spectra is represented in Fig. 4b.

Fig. 4. a EPR spectra of HO$_2$ radicals recorded at various angles between the sample axis of anisotropy and the magnetic field vector; b the result of modeling of these spectra.
Table 1. Coefficients of the expansion Eq. (5) for photooriented HO$_2^\cdot$ radical in the glassy hydrogen peroxide.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{20}$</td>
<td>0.251±0.020</td>
</tr>
<tr>
<td>$a_{40}$</td>
<td>0.073±0.027</td>
</tr>
<tr>
<td>$b_{21}$</td>
<td>0.181±0.049</td>
</tr>
<tr>
<td>$a_{22}$</td>
<td>0.025±0.011</td>
</tr>
<tr>
<td>$b_{22}$</td>
<td>0.038±0.010</td>
</tr>
</tbody>
</table>

The visualization of the orientation distribution function of particles, which do not have an axial symmetry, in axial symmetric sample can be done only in the system of coordinates connected to a particle. The orientation distribution function of HO$_2^\cdot$ radicals in the sample under consideration, which is constructed according to the appointed coefficients, is represented in Fig. 5a. The three principal g-tensor axes were chosen as axes of coordinates. The orientation of these axes in HO$_2^\cdot$ radical is shown in Fig. 5b [23]. The function in Fig. 5a is an envelope figure for vectors going from the original point of coordinates in distinct direction. The length of each vector is proportional to the number of particles in the system of coordinates of which the symmetry axis of the sample is oriented in this direction.

On the basis of photoorientation model presented above, it can be shown that the direction of maximum of orientation distribution function corresponds to the orientation of dipole-transition moment (D) of radical HO$_2^\cdot$. The values of Euler angles connecting vector D with the g-tensor reference frame are $\beta = 30^\circ \pm 5^\circ$, $\gamma = 253^\circ \pm 5^\circ$. Angle $\beta$ shows the deflection of the optical axis of radical HO$_2^\cdot$ from the magnetic z-axis. According to quantum calculation this angle for radical CH$_3$O$_2^\cdot$ should be about 20° [26]. Experimentally this value was obtained for the first time. The slope of D relative to the yz-plane seems to be surprising.

![Fig. 5. a Orientation distribution function of HO$_2^\cdot$ radicals in glassy hydrogen peroxide. b Orientation of the principal axes of g-tensor in the HO$_2^\cdot$ radical.](image)
According to the theoretical conception the most probable electron transition in HO$_2^*$ radical is A$^\prime\prime$ → A$''$ (ππ$^*$); the dipole-transition moment of this transition must lie in the yz-plane. Perhaps the observed dissymmetry is a result of the hydrogen bounds between the radical HO$_2^*$ and the molecules of the matrix.

The results of the present work confirm the possibility of application of the method [15] for the investigation of photo-induced orientation order of paramagnetic species. The method allows obtaining information about mutual orientation of optical and magnetic axes of the radicals under consideration.

References


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