

## ESR Study of Photoselection and Photo-orientation

Andrey Kh. Vorobiev

Department of Chemistry, Moscow State University, Leninskie Gory, Moscow, 119899, Russia

Received: February 3, 1994; In Final Form: August 5, 1994<sup>⊗</sup>

Evolution of ESR spectra upon irradiation in the course of photoselection and photo-orientation has been investigated experimentally and by numerical simulation. Light-induced angular dependence of spectra has been considered. The quantitative characteristics of the light-induced orientation degree for paramagnetic species are suggested. The alignment of paramagnetic species was shown to depend on light absorption anisotropy, a maximal alignment being achieved upon irradiation with both polarized and unpolarized light. The values of orientation degree, which can be experimentally achieved, are determined, and the reasons for their decrease in comparison with those theoretically predicted are discussed. The possibilities of the method suggested for estimation of the transition dipole moment by ESR investigation of photoselected samples are demonstrated.

Photoselection and photo-orientation are known to be the processes in which the sample anisotropy appears due to the irradiation by light. As the molecules absorb light to a variable degree depending on orientation of their electric vector with respect to the molecular frame, the molecules in the rigid medium absorb light and react with different probabilities. Selection of the molecules with the favorable orientation creates the light-induced anisotropy of the initially isotropic disorder sample.<sup>1,2</sup> Long-lived anisotropy obtained by photoselection or photo-orientation of solids was originally observed as an orientational dependence of optical properties of a sample, for example, as the induced linear dichroism. Induced alignment of the paramagnetic molecules is observable by ESR. It may be viewed as the angle dependence of the ESR spectrum shape.

ESR study of the transient alignment of the excited triplet states induced by polarized light is well-known as the magnetophotoselection method.<sup>3</sup> This technique has been used for determination of optical transition direction in aromatic molecules<sup>3,4</sup> as well as in biradicals.<sup>5</sup>

ESR measurements of the alignments of stabilized radicals and radical pairs have been used for the study of rotational mobility of paramagnetic molecules<sup>6,7</sup> and the mobility of holes in glasses.<sup>8</sup> Registration of photoselection and photo-orientation by ESR is shown to be highly sensitive. However, until the present the following questions remain obscure: what are the characteristic magnitudes of light-induced angle dependence of ESR spectra for the photoselected samples; what values must be extracted from ESR spectra to describe the molecular alignment; and what experimental conditions are favorable for the ESR observations of the induced anisotropy?

In the present work we answer these questions by means of numerical calculations of the spectra of photoselected samples and compare the calculated results with the experiments.

### Model

We consider the rigid isotropic matrix containing the paramagnetic guest molecules with a sufficiently long one-to-one distance. For simplification suppose that light-absorbed paramagnetic centers have the cylindrical extinction tensor ( $\epsilon_x = \epsilon_y \neq \epsilon_z$ ) and the cylindrical  $g$ -tensor ( $g_x = g_y \neq g_z$ ). The unique principal axes of the  $g$ - and  $\epsilon$ -tensors do not necessarily coincide.

The extinction tensor describes the total probability of the light absorption with a given wavelength in contrast to the dipole transition moment, which describes the absorption probability in a transition. We shall treat the photoselection as a monomolecular photochemical reaction of paramagnetic centers and suppose that the ESR spectrum of the product does not overlap with the initial one. Photo-orientation of paramagnetic centers is considered to be the process of light-induced reorientation resulting from radical photomigration or photorotation without variation of their concentrations.<sup>9</sup> Among three possible mechanisms of light-induced reorientation—(i) photo-induced rotational diffusion, (ii) photo-induced rotational jump on a designated angle, and (iii) photo-induced rotational jump on an arbitrary angle—the latter mechanism will be considered in the present investigation as it occurs in experiments more frequently.

### Computational Methods

Kinetics of photochemical reactions in course of photoselection and photo-orientation have been previously considered.<sup>2,10–12</sup> Appropriate equations allow characterization of the time evolution of the orientation distribution functions. It should be emphasized that in all cases photoinduced anisotropy of initially isotropic samples has uniaxial symmetry. The sample's unique axis coincides with the propagation direction of the unpolarized light or the electric vector direction of plane-polarized light. Thus, the orientation distribution function becomes the function of an angle between the unique axis of the molecular  $\epsilon$ -tensor and the unique axis of the sample.

The orientation distribution function of the remaining molecules in the course of photoselection is<sup>10</sup>

$$Q(\beta) = \frac{\sin(\beta)}{2} \exp(-\tau\epsilon_\beta) \quad (1)$$

where  $\epsilon_\beta$  is the effective extinction coefficient for axial molecules with a given orientation; for polarized irradiation  $\epsilon_\beta = \epsilon_1 \sin^2 \beta + \epsilon_3 \cos^2 \beta$ , and for unpolarized irradiation  $\epsilon_\beta = \epsilon_1(1 + \cos^2 \beta)/2 + \epsilon_3(\sin^2 \beta)/2$

$$\epsilon_1 = \epsilon_x/\bar{\epsilon} = \epsilon_y/\bar{\epsilon}, \quad \epsilon_3 = \epsilon_z/\bar{\epsilon}, \quad \bar{\epsilon} = (\epsilon_x + \epsilon_y + \epsilon_z)/3$$

(that is,  $2\epsilon_1 + \epsilon_3 = 3$ ) where  $\epsilon_x$ ,  $\epsilon_y$ , and  $\epsilon_z$  are principal values of the extinction tensor,  $\tau$  is the dimensionless irradiation time,  $\tau = \bar{\epsilon}\phi I_0 t$ ,  $\phi$  is the quantum yield,  $I_0$  is the light intensity, and  $t$  is the irradiation time.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, September 15, 1994.

The orientation distribution function upon photo-orientation can be presented by a function series. For our purpose the most useful presentation is the expansion in a Fourier series:

$$\rho(\beta) = \sum b_k(\tau) \sin(k\beta) \quad (2)$$

Coefficients of the series can be obtained by resolving the appropriate set of equations as in ref 12. ESR spectra were simulated in accordance with

$$F(H) = \int_0^\pi f(H, \theta) \rho(\theta) d\theta \quad (3)$$

where  $\theta$  is the angle between the unique axis of the  $g$ -tensor and the magnetic field direction.

Gaussian and Lorentzian line shapes ( $f(H, \theta)$ ) were used for simulation. Simulation shows that the variations in line shapes cause the variations in resolution of spectra, but they do not influence qualitative results and will not be specially discussed.

The most convenient method of eq 3 integration in the course of the simulation of the spectrum orientational dependence is the integration over angles relative to the unique axis of the sample. Let  $\eta$  be the angle between the symmetry axis of the sample and the magnetic field direction;  $\theta$  is the angle between the unique axis of the  $g$ -tensor in a molecule and the magnetic field direction. If the axes of the  $g$ - and  $\epsilon$ -tensors in molecules coincide,  $\theta$  is evaluated by

$$\cos(\theta) = \sin \beta \sin \gamma \sin \eta + \cos \beta \cos \eta \quad (4)$$

where  $\beta$  and  $\gamma$  are Euler angles. The line shape in (3) is

$$f(H, \theta) = f[H - H_\perp / (1 - a \cos^2 \theta)^{1/2}]$$

where  $a = (H_\perp^2 - H_{||}^2) / H_{||}^2$ .  $\rho$  is given by (1) or (2). Expression 3 is integrated with respect to  $\beta$  and  $\gamma$ .

Simulation of the spectra with the fine and hyperfine structure can be performed in the same manner if the corresponding tensors are used instead of the  $g$ -tensor.

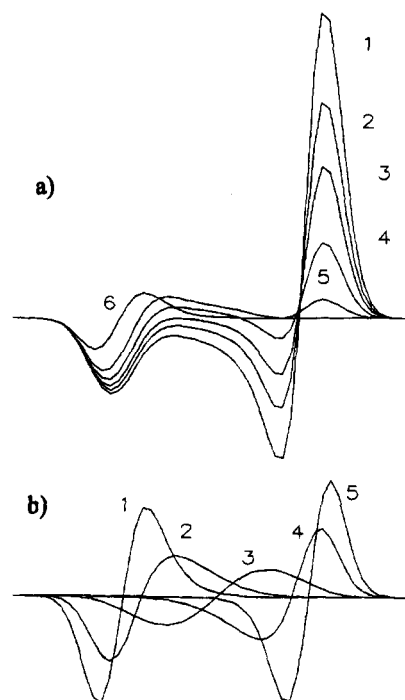
In a more complicated case,  $\xi$  is the angle between the unique axis of the  $g$ -tensor and the unique axis of the  $\epsilon$ -tensor. In that case the orientation distribution function of the molecular  $\epsilon$ -axis ( $\rho'(\beta')$ ) described in (1) or (2) must be transformed into the distribution function of the  $g$ -tensor axis ( $\rho(\beta)$ ):

$$\rho(\beta) = \frac{\sin \beta}{\pi} \int_{\beta-\xi}^{\beta+\xi} \frac{\rho'(\beta') d\beta'}{[\sin^2 \beta \sin^2 \xi - (\cos \beta - \cos \beta' \cos \xi)^2]^{1/2}}$$

To illustrate the simulated spectra, the following parameters approximately corresponding to an organic radical with  $g$ -tensor anisotropy are used:  $H_\perp = 3250$  G,  $H_{||} = 3300$  G, and  $\delta H$  of an individual line is 10 G.

## Results

Simulated ESR spectra of the photoselected sample in the case of the coinciding  $g$ - and  $\epsilon$ -tensor axes are shown Figure 1a,b. Irradiation with a collimated beam of both polarized and unpolarized light produces the angular dependence of the spectrum. In the course of irradiation, the shape of a spectrum gradually approaches that characteristic of a single crystal. Induced anisotropy of the sample depends on anisotropy of molecular optical properties ( $\epsilon$ -tensor) as well as the light polarization and the irradiation time. To specify the induced angular dependence of an experimental ESR spectrum, the empirical parameters containing the amplitudes of the different lines are commonly used.<sup>13</sup> These empirical parameters have the uncertainty limits of variation and do not allow a comparison of the alignment of the different particles. In our opinion, the



**Figure 1.** Simulated ESR spectra of the samples photoselected with unpolarized light. The molecules absorb light as a vector ( $\epsilon_3 = 3$ ,  $\epsilon_1 = \epsilon_2 = 0$ ). (a) Parallel orientation of the sample axis and magnetic field direction; irradiation times are  $\tau = 0$  (1), 0.25 (2), 0.5 (3), 1 (4), 2 (5), and 8 (6). (b) Dependence of spectrum shape ( $\tau = 8$ ) on the angle  $\eta$  between the sample axis and the magnetic field direction  $\eta = 0$  (1),  $\pi/8$  (2),  $\pi/4$  (3),  $3\pi/8$  (4), and  $\pi/2$  (5).

most physically adequate value reflecting the orientational anisotropy which can be easily extracted from experimental spectra is that calculated similarly to the optical linear dichroism, when it is measured in the  $g_{||}$  region of the ESR spectrum:

$$A = \frac{h_{||} - h_{\perp}}{h_{||} + 2h_{\perp}} \quad (5)$$

where  $h_{||}$  and  $h_{\perp}$  are measured at parallel and perpendicular orientation of the sample axis to the magnetic field, respectively. The quantity  $A$  is equal to 0 for a disordered sample and is equal to 1 for the perfectly oriented molecules. The disadvantage of (5) is the necessity of recording ESR spectra at two mutually orthogonal orientations of the sample. Experimentally, the use of absolute amplitudes of ESR lines measured for different spectra results in additional errors. Thus, a more appropriate evaluation of  $A$  may be achieved by the unique recording of the spectrum with a parallel orientation and by using the following expression:

$$A = \frac{h_1/h_1^0 - h_2/h_2^0}{h_1/h_1^0 + 2h_2/h_2^0} \quad (6)$$

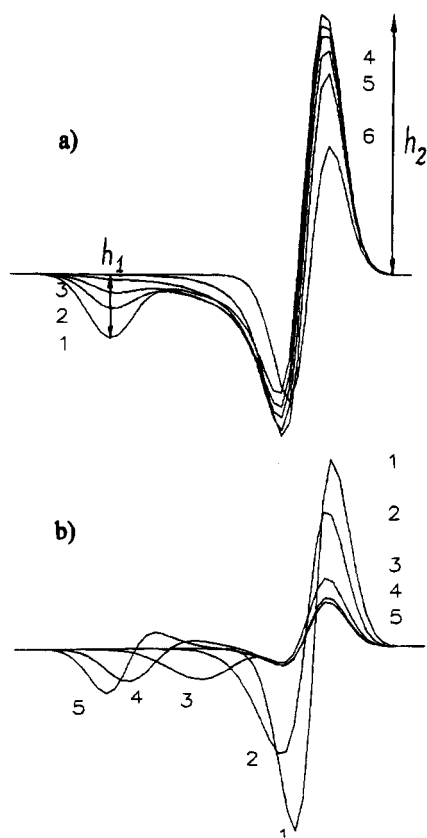
where  $h_1$  and  $h_2$  are amplitudes of the  $g_{||}$  and  $g_{\perp}$  components of the ESR spectrum (Figure 2a);  $h_1^0$  and  $h_2^0$  are the same amplitudes for the isotropic sample before irradiation.

One can transform (6) to

$$A = \frac{(h_1/h_2)(h_2^0/h_1^0) - 1}{(h_1/h_2)(h_2^0/h_1^0) + 2} \quad (7)$$

which contains only the ratios of amplitudes. By the numerical simulation, expression 5 has been verified to be equivalent to (7), when the resolved spectra are treated.

The quantity  $A$  characterizes the orientational alignment of paramagnetic centers. It can be used in the case of  $g$ -tensor



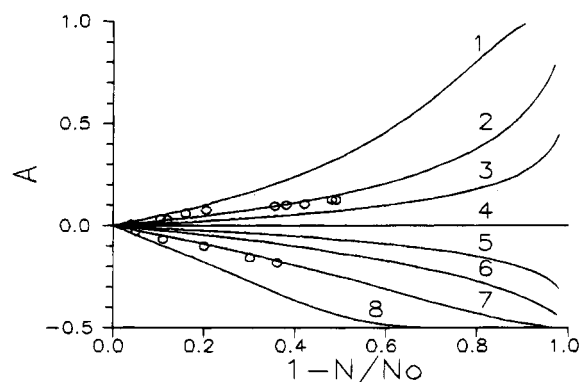
**Figure 2.** Simulated ESR spectra of the samples photoselected with polarized light. The molecules absorb light as a vector ( $\epsilon_3 = 3$ ,  $\epsilon_1 = \epsilon_2 = 0$ ). (a) Parallel orientation of the sample axis and the magnetic field direction; irradiation times are  $\tau = 0$  (1), 0.25 (2), 0.5 (3), 1 (4), 2 (5), and 8 (6). (b) Dependence of the spectrum shape ( $\tau = 8$ ) on the angle  $\eta$  between the sample axis and the magnetic field direction  $\eta = 0$  (1),  $\pi/8$  (2),  $\pi/4$  (3),  $3\pi/8$  (4), and  $\pi/2$  (5).

anisotropy as well as in the case of hyperfine interaction anisotropy. One of the essential demands is the sufficient resolution of parallel and perpendicular components in the ESR spectra. The limits of variation and the qualitative behavior of  $A$  are similar to the known characteristic, Saupe's matrix elements.<sup>2</sup> However, the quantity  $A$  is not a value integrated over the orientation distribution. It is the reason for a quantitative disagreement between  $A$  and Saupe's factors.

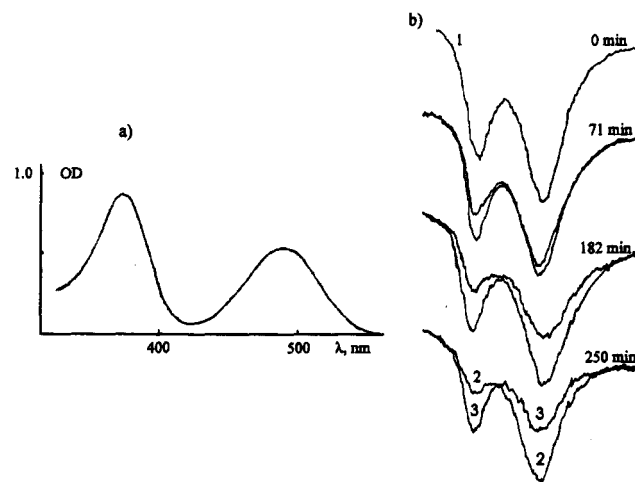
The orientation degree evaluated according to (7) for photoselected samples is shown in Figure 3 as a function of the chemical conversion degree. The lower curves in Figure 3 can be obtained only upon polarized irradiation of rod-like absorbed molecules ( $\epsilon_3 > 1.5$ ). All other curves can be obtained both upon polarized and unpolarized irradiation. For instance, a maximal orientation degree (curve 1) can be induced with unpolarized light for molecules, absorbing as a "perfect" vector ( $\epsilon_x = \epsilon_y = 0$ ,  $\epsilon_z \neq 0$ ), and by polarized irradiation for plane absorbed molecules ( $\epsilon_x = \epsilon_y \neq 0$ ,  $\epsilon_z = 0$ ).

In all cases when light absorption depends on the orientation of molecules, the limiting orientation degree at an infinite irradiation time is equal to 1 or  $-0.5$ . These values reflect two perfect alignments of the unique axes of molecules: the orientation of the axes is parallel ( $A_\infty = 1$ ), and the axes lie in a plane ( $A_\infty = -0.5$ ). Distortion of the random orientation distribution occurs even in the case of the unpolarized irradiation of the sample rotating around the axis perpendicular to the light beam direction. Experimentally, however, the limit values of orientation degree are unobtainable for the following reasons:

1. The photochemical reactions ordinarily do not result in the whole conversion necessary to achieve the limit orientation



**Figure 3.** Orientation degree of simulated spectra of the samples photoselected with polarized light and unpolarized light at the different  $\epsilon$ -tensors of molecules vs the conversion degree (p = polarized, u = unpolarized): curve 1,  $\epsilon_3 = 0$  (p),  $\epsilon_3 = 3.0$  (u); curve 2,  $\epsilon_3 = 0.5$  (p),  $\epsilon_3 = 2.0$  (u); curve 3,  $\epsilon_3 = 0.75$  (p),  $\epsilon_3 = 1.5$  (u); curve 4,  $\epsilon_3 = 1.0$ ; curve 5,  $\epsilon_3 = 1.25$  (p),  $\epsilon_3 = 0.5$  (u); curve 6,  $\epsilon_3 = 1.5$  (p),  $\epsilon_3 = 0$  (w); curve 7,  $\epsilon_3 = 2.0$  (p); curve 8,  $\epsilon_3 = 3.0$  (p). The point represents experiment; see text.



**Figure 4.** UV-vis (a) and ESR (b) spectra of  $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$  glassy solution in 5 M aqueous LiCl, recorded at 77 K: a sample before irradiation (1); a sample photoselected with 365 nm light at 128 K at the parallel (2) and perpendicular (3) orientations of the sample axis and the magnetic field direction.

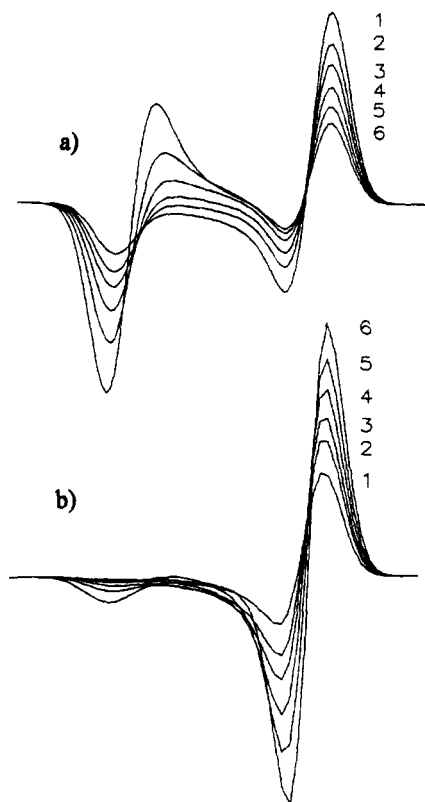
degree. Recording of the spectrum of remaining molecules at high conversion, one deals with serious experimental problems.

2. The longer the irradiation time, the more requirements are imposed on the optical perfection of the sample, the accuracy of sample orientations in the magnetic field and light beam, etc.

3. Rigidity of molecules in solids is believed to be absolute only theoretically. The molecular rotation mobility destroys the light-induced orientational order.

In this connection the disagreement of the experiment with the calculated orientation degree should be expected upon prolonged irradiation and at a high degree of conversion.

Let's compare calculations with experiments. Previously, we have observed photoselection in the course of the ligand photoexchange reaction in a frozen glassy solution of  $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$  in 5 M LiCl. This compound has two optical ligand field bands ( $T_{2g}^4 \leftarrow A_{2g}^4$  and  $T_{1g}^4 \leftarrow A_{2g}^4$ ) and two bands in the ESR spectrum in the region of 1200–1400 G (Figure 4). The ligand photoexchange reaction disrupts the random orientation distribution and induces the angular dependence of the line amplitudes in the ESR spectrum. The orientation degree obtained upon irradiation at the short-wave band is shown in Figure 3 (points).



**Figure 5.** Simulated ESR spectra of samples upon photo-orientation with unpolarized (a) and polarized (b) light. The molecules absorb light as a vector ( $\epsilon_3 = 3$ ,  $\epsilon_1 = \epsilon_2 = 0$ ). The main axes of the samples coincide with the magnetic field direction; irradiation times are  $\tau = 0$  (1), 0.5 (2), 1 (3), 2 (4), 4 (5), and 10 (6).

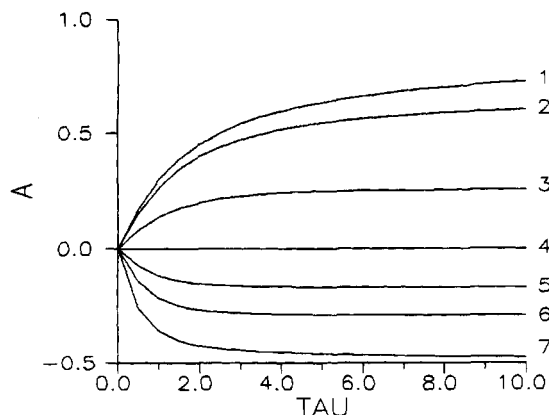
Satisfactory agreement of experimental and calculated values is observed at low degrees of conversion. The values and signs of orientation degree allow us to conclude that the dipole transition moment is close to the vector for a short-wave band ( $\epsilon_3 > 2$ ) and lies in plane for a long-wave band.

At higher degrees of conversion, the orientation degree decrease in contradiction with a calculated behavior. Besides the reasons discussed above, this discrepancy is associated with the kinetic nonequivalence of reacting molecules, when different molecules show different reactivity and some molecules are unreactive.<sup>14</sup>

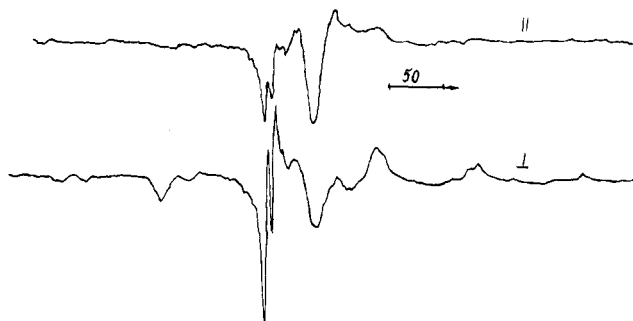
Evolution of ESR spectra in the course of photo-orientation differs from that in the course of photoselection (Figure 5a,b). The orientation degree in the process of photo-orientation increases with the irradiation time more slowly than during photoselection. Nevertheless in experiment, the induced angular dependence is easily recorded as the number of paramagnetic centers remains constant. The limiting orientation degree during photo-orientation is dictated by anisotropy of the  $\epsilon$ -tensor (Figure 6).

An experimental example of the spectrum after photo-orientation is shown in Figure 7.<sup>8</sup> The spectrum of  $\text{Cl}_2^-$  radical-anion acquires a strong angular dependence after irradiation. The orientation degree calculated from the spectra presented is 0.53. From comparison of this value with the calculated one, one can conclude that the optical transition is oriented as the molecular axis. The absorption in the perpendicular plane is small:  $\epsilon_x < 0.03\epsilon_z$ . In this manner the evaluation of the extinction tensor can be achieved from limiting the orientation degree upon prolonged photo-orientation.

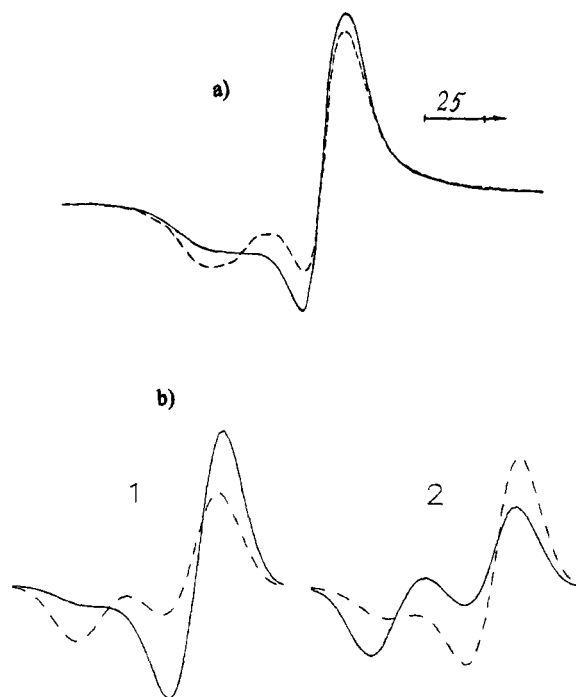
The most complicated cases are photoselection and photo-orientation when the axes of the  $g$ - and  $\epsilon$ -tensors do not coincide. In these cases, after the infinitely prolonged irradiation the ESR



**Figure 6.** Orientation degree of paramagnetic molecules upon photo-orientation with polarized light. The  $\epsilon$ -tensors of the molecules are  $\epsilon_3 = 0$  (1), 0.1 (2), 0.5 (3), 1 (4), 1.5 (5), 2 (6), and 3 (7).



**Figure 7.** ESR spectra of  $\text{Cl}_2^-$  in 5 M LiCl (77 K) irradiated with 365 nm unpolarized light and recorded at two mutually orthogonal orientations of the samples in the magnetic field.



**Figure 8.** (a) ESR spectra of the  $\text{HO}_2^*$  radical oriented with 254 nm polarized light and recorded at two mutually orthogonal orientations of the sample in the magnetic field. (b) Simulated spectra with two possible orientations of the transition moment: (1) in the molecular plane ( $\epsilon_3 = 0$ ,  $\epsilon_1 = 1.5$ ) and (2) perpendicular to the molecular plane ( $\epsilon_3 = 3$ ,  $\epsilon_1 = 0$ ).

spectrum of parallel-oriented samples must consist of one line. This line position disagrees with  $g_{\parallel}$  and  $g_{\perp}$ , but is in accord with  $g^2 = g_{\parallel}^2 \cos^2 \xi + g_{\perp}^2 \sin^2 \xi$ , where  $\xi$  is the angle between

the unique axes of the  $g$ - and  $\epsilon$ -tensors. In experiment it is difficult if not impossible to obtain such spectra. But signs and values of orientation degree allow evaluation of the angle  $\xi$ .

A qualitative illustration of this possibility is presented in Figure 8, where the spectra of  $\text{HO}_2^{\bullet}$  radical after photo-orientation are shown. The  $g$ -axis of this radical is known to be directed along the O—O bond. The optical band at  $\lambda \sim 250$  nm corresponds to either  $A' \leftarrow A''$  ( $n\pi^*$ ) or  $A'' \leftarrow A''$  ( $\pi\pi^*$ ) transitions.<sup>15</sup> In the former case, the transition moment is directed perpendicular to the molecular plane, whereas in the latter case the transition moment lies in the molecular plane ( $\epsilon_x = \epsilon_y \neq 0$ ,  $\epsilon_z = 0$ ). By comparison of simulated and experimental spectra, the  $A'' \leftarrow A''$  transition is concluded to take place. The signs and values of orientation degree upon polarized and unpolarized irradiation are in agreement with the values calculated with this transition.

### Experimental Section

Samples were prepared by immersing quartz ampules containing the corresponding solution in liquid nitrogen. The optical part of the ampules had a square cross section of  $2.5 \times 2.5$  mm. The orientation degree induced in the standard cylindrical ampules was insignificantly lower. Photolysis was carried out with a high-pressure mercury lamp (500 W) provided with condensing lenses and standard glass filters and with a low-pressure resonance mercury lamp ( $\lambda = 254$  nm). Polarized photolysis was carried out with a Glan prism. The optical absorption spectra were recorded at 77 K by using a Specord M-40 spectrophotometer (Karl Zies Yena). The ESR spectra were recorded by using a Varian E-3 spectrometer.

$[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{ClO}_4$  was prepared by a standard method.<sup>16</sup>  $\text{HO}_2$  radicals were generated by 254 nm irradiation of glassy  $\text{H}_2\text{O}_2$  (>78%).  $\text{Cl}_2^-$  radical-anions were generated by 365 nm irradiation of a glassy solution of chlorine in 5 M LiCl or by 254 nm irradiation of a glassy solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_4$  in 5 M LiCl.

**Acknowledgment.** This research was supported by the Russian Fundamental Investigations Foundation, Grant 93-03-18062.

### References and Notes

- (1) Albrecht, A. C. *Prog. React. Kinet.* **1970**, *5*, 301.
- (2) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers: New York, 1986.
- (3) El-Sayed, M. A.; Siegel, S. *J. Chem. Phys.* **1966**, *44*, 1416.
- (4) Regev, A.; Berman, A.; Levanon, M.; Murai, T.; Sessler, J. L. *Chem. Phys. Lett.* **1989**, *160*, 401.
- (5) Chisholm, W. P.; Yu, H. L.; Murugesan, R.; Weissman, S. I.; Hilinski, E. F.; Berson, A. *J. Am. Chem. Soc.* **1984**, *106*, 4419.
- (6) Rachimov, R. R.; Lazarev, G. G.; Prokof'ev, A. H.; Lebedev, Ya. S. *Khim. Fiz.* **1986**, *5*, 1085.
- (7) Lazarev, G. G.; Lebedev, Ya. S. *Khim. Fiz.* **1984**, *3*, 1700.
- (8) Vorobiev, A. K.; Gurman, V. S. *Chem. Phys.* **1992**, *167*, 341.
- (9) Albrecht, A. C. *J. Chem. Phys.* **1957**, *27*, 1413.
- (10) Vorobiev, A. Kh.; Gurman, V. S. *Kinet. Katal.* **1987**, *28*, 319.
- (11) Vorobiev, A. K.; Gurman, V. S. *Kinet. Katal.* **1987**, *28*, 325.
- (12) Vorobiev, A. K.; Gurman, V. S. *Khim. Fiz.* **1987**, *6*, 1220.
- (13) Lazarev, G. G.; Lebedev, Ya. S. *Khim. Fiz.* **1988**, *7*, 1988.
- (14) Vorobiev, A. K.; Gurman, V. S. *J. Photochem.* **1982**, *20*, 123.
- (15) Landhoff, S. R.; Jaffe, R. L. *J. Chem. Phys.* **1979**, *71*, 1475.
- (16) Schlessinger, G. *Inorganic Laboratory Preparations*; Chemical Publishing Co.: New York, 1962; p 294.