

PHOTOCHEMISTRY
AND MAGNETOCHEMISTRY

Photoinduced Orientational Order
of Dichloride Anion Radicals

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Abstract—The photo-orientation of dichloride anion radicals ($\text{Cl}_2^{\cdot-}$) in a glassy solution of 5 M LiCl is discussed. The quantitative characteristics of orientation of paramagnetic molecules were determined using the anisotropy of optical absorption and the angular dependence of the EPR spectrum. The orientational distribution function of ordered anion radicals was determined by joint computer modeling of the EPR spectrum recorded at different directions of the symmetry axis of a sample relative to the magnetic field of a spectrometer. It was found that the value of the order parameter (-0.1 ± 0.01), calculated from the orientational distribution function coincides with the value obtained under the measurements of the linear dichroism in the range of the detection error (-0.12 ± 0.01).

Keywords: EPR spectra, photo-orientation, dichloride anion radical, paramagnetic molecules.

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INTRODUCTION

Photo-orientation is a light-induced orientational order of molecules [1–4]. This phenomenon is observed upon the fulfillment of two conditions: (1) the probability of light being absorbed by a molecule depends on the latter's orientation relative to the vector electrical component of the light wave; (2) having absorbed a photon, the molecule changes its spatial orientation. When these conditions are met during the irradiation of an initial isotropic medium, the light-adsorbing molecules are accumulated in an orientation in which the probability of light adsorption is minimal.

At present, the phenomenon of photo-orientation is under intense scrutiny using the examples of azobenzene and other dyes, and of polymers based on them [5–11], due to the prospects for developing information recording and storage devices [12–14], and for practical use in the field of polarized holography [15].

The main characteristic of materials with a partial ordering of molecules is the orientation factor or order parameter. This characteristic is most often determined from the linear dichroism spectrum of an anisotropic sample [3, 16–21]. Earlier [22], we developed another method for determining the orientational order characteristics that is applicable only to paramagnetic molecules and is based on computer modeling of the angular dependence of the EPR spectrum. The orientational distribution function obtained is the most comprehensive and informative description of the particles' orientational order. From the orientational distribution function, we can calculate in

particular the orientation factor of the studied molecules.

The most important stage in the testing and development of the new method is comparing the results obtained with those of the standard optical method of molecular ordering investigation. It is to this task that the present work is devoted.

Dichloride anion radicals ($\text{Cl}_2^{\cdot-}$) in a glassy matrix of 5 M LiCl solution were chosen as the object of investigation, since it is known that the photo-orientation phenomenon is observed in this system [22–24], $\text{Cl}_2^{\cdot-}$ anion radicals have an optical adsorption band that is easy to measure [23], and an EPR spectrum that is described in the literature [25, 26]. It is also highly important that the simplicity of the $\text{Cl}_2^{\cdot-}$ molecule's geometry allows us to determine unambiguously the directions of a dipole moment of optical transition and those of the main axes of g- and hyperfine interactions-tensors relative to the molecular coordinate system.

EXPERIMENTAL

An aqueous solution of LiCl (5 M) containing dissolved molecular chlorine was obtained by applying the desired amount of gaseous chlorine with a gas syringe. The solution was immersed in a quartz ampoule for EPR spectroscopy. A glassy sample was obtained by rapid cooling of the ampoule to 77 K. $\text{Cl}_2^{\cdot-}$ radicals were generated by irradiation the sample with light having a wavelength of 254 nm. A BUF-4 non-

electrode mercury vapor lamp of low pressure with high-frequency excitation was used for this purpose. Upon irradiation, the ampoule was rotated with a speed of 2–3 rps around its axis. The sample was irradiated until the value of the optical absorption of Cl_2^- radicals reached a value of $D = 2$ at the maximum of the adsorption band (345 nm).

The orientational order of Cl_2^- radicals was produced by irradiation of an isotopic sample with a parallel beam of plane-polarized light having a wavelength of 365 nm. To accomplish this, a high-pressure mercury vapor lamp (500 W) equipped with a system of quartz lenses, a standard kit of glass light filters, and a Glan polarization prism was used.

The spectra of optical absorption were registered in polarized light on a SPECORD M40 spectrophotometer; EPR spectra were registered using a Varian E3 EPR-spectrometer. The spectra were registered at 77 K in quartz Dewar vessels. The angular dependences of the EPR spectra were registered by turning a sample in the spectrometer's resonator with an increment of 20° using a goniometer; the accuracy of the angle arrangement was $\pm 2^\circ\text{C}$.

Method for the Computational Modeling of EPR Spectra

The EPR spectra were modeled in an approximation of a weak external field accurate to within the second-order terms with allowance for the energy of nuclear Zeeman interaction and the contributions of forbidden transitions. The program for calculating the spectra allows the use of the most general form of an individual line's shape, a convolution of the Gaussian and Lorentz functions. Upon modeling, however, it was found that the shape of the individual line of Cl_2^- anion radicals is described by a Gaussian function. Modeling also showed that the width of an individual line in the studied spectra depends on the projection of the magnetic moment of the nuclei, m_I , and on a radical's orientation relative to the magnetic field.

It is known [27] that in the spectra of paramagnetic particles registered in the solid phase, the dependence of the width of a spectral line on the projection of a nucleus's magnetic moment can be expressed as:

$$\sigma_k = a_k + b_k m_I + c_k m_I^2,$$

where $k = x, y, z$. The width of a Gaussian line of Cl_2^- binucleate particles is therefore described in the present work with a second order tensor whose main values were calculated as follows:

$$\begin{aligned} \sigma_x = \sigma_y = \sigma_\perp &= \left((a_\perp + b_\perp m_1 + c_\perp m_1^2)^2 \right. \\ &\left. + (a_\perp + b_\perp m_2 + c_\perp m_2^2)^2 \right)^{1/2}, \\ \sigma_z = \sigma_\parallel &= \left((a_\parallel + b_\parallel m_1 + c_\parallel m_1^2)^2 \right. \\ &\left. + (a_\parallel + b_\parallel m_2 + c_\parallel m_2^2)^2 \right)^{1/2}, \end{aligned}$$

where m_1 and m_2 are projections of the nuclear spin of two nuclei of Cl_2^- anion radicals.

To consider the natural isotopic composition of chlorine atom nuclei, the EPR spectrum of Cl_2^- anion radicals was calculated as a sum of the spectra of three particles, $^{35}\text{Cl}^{35}\text{Cl}$, $^{35}\text{Cl}^{37}\text{Cl}$, and $^{37}\text{Cl}^{37}\text{Cl}$. The natural content of ^{35}Cl and ^{37}Cl atoms is approximately 75.78 and 24.22%, and the ratio of summation coefficients of the three spectra was therefore 9.75 : 6.32 : 1. The constants of the hyperfine interaction of an unpaired electron with nuclei of ^{35}Cl and ^{37}Cl are proportional to the magnetic moments of the nuclei, which are 0.8219 and 0.6841 units of nuclear magneton, respectively [28]. In accordance with the geometry of dichloride anion radicals, all anisotropic characteristics such as g-tensor, the tensor of hyperfine interaction, and the characteristics of the half-width of a line are described using axial tensors.

The computational modeling of experimental EPR spectra of an isotropic sample was performed in order to determine the magnetic resonance parameters of the Cl_2^- radicals. In the course of modeling, the determined parameters (the characteristics of the individual line width, g-tensor and hyperfine interaction tensor components) were varied in order to find the minimum of the sum of squares of deviations of the spectrum calculated from the experimental spectrum. Minimization was performed using the nonlinear least squares method [29, 30]. The experimental and calculated spectra of Cl_2^- anion radicals in an isotropic sample are shown in Fig. 1. The magnetic resonance parameters obtained by modeling are shown in the table. The main values determined by the authors of [25] for the g- and hyperfine interaction tensors are also shown in the table. We can see that the values obtained as a result of spectrum modeling are in reasonable agreement with the literature data.

Modeling of the Angular Dependence of the EPR Spectrum

The method for modeling the angular dependence of EPR spectra is described in [22]. To determine the orientational distribution function of paramagnetic particles, six spectra of an anisotropic sample, registered at different angles between the axis of anisotropy of the sample and the direction of the spectrometer's magnetic field, were modeled jointly at fixed magnetic

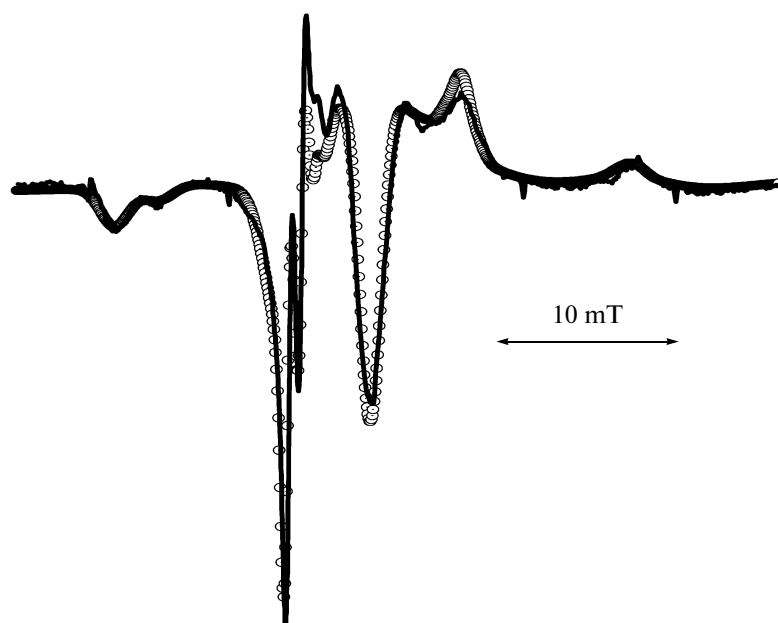


Fig. 1. EPR spectrum of statistically oriented Cl_2^- anion radicals in 5 M LiCl at 77 K (line) and the results from their computational modeling (circles).

resonance parameters upon variation of the A_k coefficients of the series expansion of the orientational distribution function by a Legendre polynomial:

$$\rho(\beta) = \sum_{k=0}^{\infty} A_k P_k(\cos\beta), \quad (1)$$

where β is the angle between the sample's axis of symmetry and the direction of the Cl–Cl bond of a paramagnetic molecule (the direction of the z axis of a g -tensor).

In the course of modeling, it was found that using coefficients of expansion of the fourth order and higher does not lead to an improvement in the quality of the EPR spectra's description. Modeling was therefore performed using coefficients of the second order.

RESULTS AND DISCUSSION

Photo-Orientation: The Value of a Sample's Optical Dichroism

The photo-orientation of Cl_2^- radicals in a glassy media has been studied quite extensively [22, 24, 31]. Photo-orientation is specified by the probability of the light absorbance by a molecule being proportional to the square of the cosine of an angle between the vector of a molecule's dipole transition moment and the electrical component of the light. A Cl_2^- anion radical oriented properly for light absorbance reacts with a neighboring chlorine anion of a matrix ($\text{Cl}_2^- + \text{Cl}^- \rightarrow \text{Cl}^- + \text{Cl}_2^-$), and a similar anion radical with other spatial orientation is formed as a result. Through the

Magnetic resonance parameters and half-width of the Cl_2^- anion radicals spectra in 5 M LiCl

Direction relative to the Cl–Cl bond	$a \times 10^4$	$-b \times 10^4$	$c \times 10^4$	γ	$A_{\text{SFI}}(^{35}\text{Cl}) \times 10^4, \text{T}$	$A_{\text{SFI}}(^{37}\text{Cl}) \times 10^4, \text{T}$
Perpendicular	13.30 ± 0.26	2.83 ± 0.56	3.64 ± 0.33	2.03865 ± 0.00006	14.00 ± 0.29	11.77 ± 0.24
				2.050 [25]		
Parallel	3.98 ± 0.36	10.03 ± 0.79	14.00 ± 0.30	2.00791 ± 0.00015	100.9 ± 0.24	84.06 ± 0.20
				2.004 [25]		

Note: A_{SFI} is a constant of hyperfine interaction; a , b , and c are components of the Gaussian width of an individual line, T.

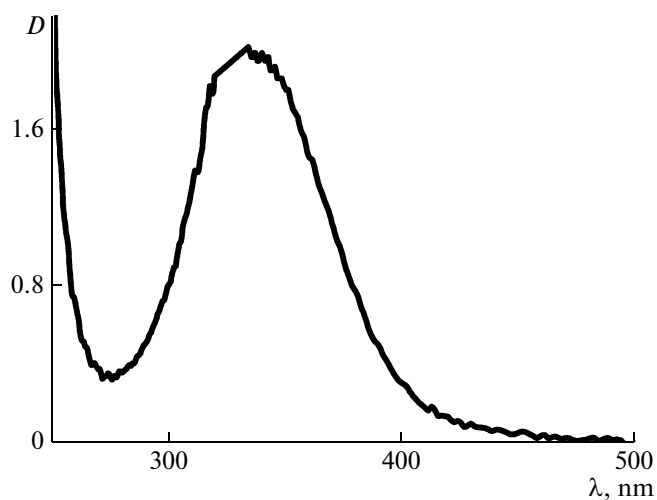


Fig. 2. Optical absorbance spectrum of Cl_2^- anion radicals in 5 M LiCl at 77 K.

multiple repetition of this process, the sample is depleted of radicals capable of absorbing light. Anisotropy of the sample results and appears in both the optical spectra and the EPR spectra.

The spectrum of the optical absorbance of Cl_2^- anion radicals in 5 M LiCl at 77 K is shown in Fig. 2. The maximum of the absorption band corresponds to a wavelength of 345 nm. In order to minimize the measurement errors in calculating the value of optical

dichroism, a region of the spectrum was chosen in which the optical density did not exceed $D = 2$. The regions of the sample's absorption spectra used for the calculations after photo-orientation are shown in Fig. 3. We can see that the intensity of the recorded spectrum upon the perpendicular polarization of the orienting and probing beams is higher than that upon parallel polarization. This means that Cl_2^- molecules are oriented so that their vectors of the dipole moment of transition are mostly directed perpendicularly to the direction of light polarization. The sample obtains an axis of anisotropy that is codirectional with the electrical component of the light. It is evident that the vector of the dipole moment of the above optical $\sigma \rightarrow \sigma^*$ transition is directed along the Cl–Cl bond. During the photo-orientation process, Cl_2^- radicals are thus oriented mainly by their Cl–Cl bond, perpendicular to the electric component of the illuminating light.

The orientational order of the vectors of dipole transition moment of molecules is characterized by the value of the sample's optical dichroism:

$$d = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}}, \quad (2)$$

where D_{\parallel} and D_{\perp} are values of the optical absorbance in spectra with mutually parallel and perpendicular polarizations of the oriented and probing beams.

The dichroism of the sample containing ordered Cl_2^- radicals was averaged over the range of wave-

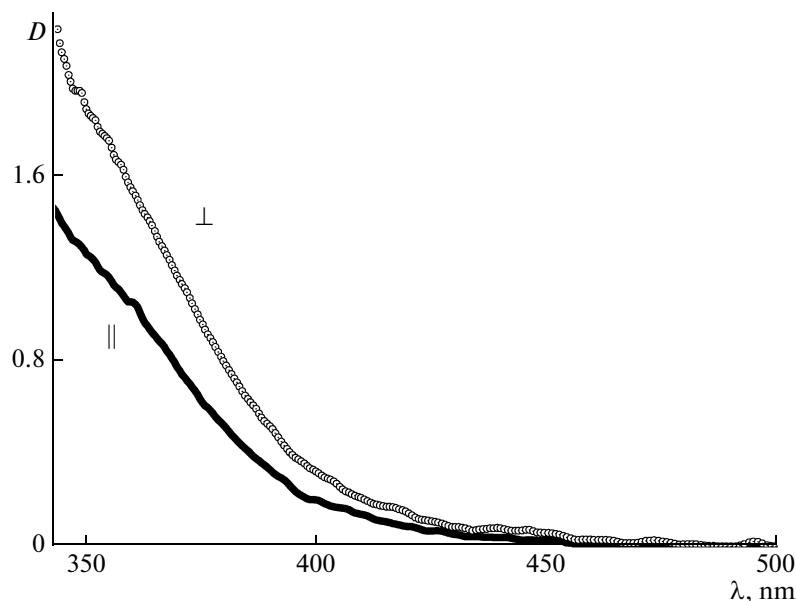


Fig. 3. Optical absorbance spectrum of Cl_2^- anion radicals in 5 M LiCl at 77 K after irradiation with linear polarized light with a wavelength of 365 nm upon parallel (line) and perpendicular (circles) mutual polarization of the probing and illuminating beams.

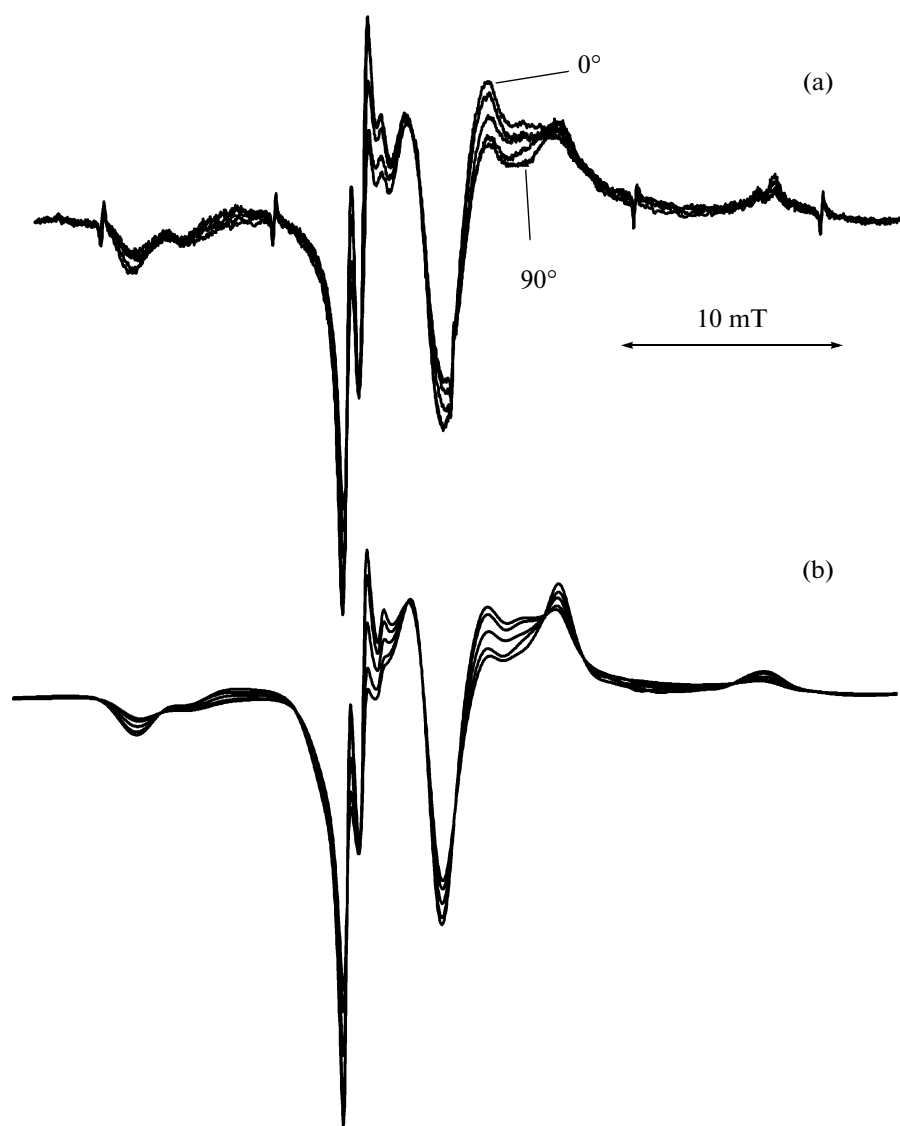


Fig. 4. Angular dependence of the EPR spectrum of Cl_2^- anion radicals (a) and the results from their computational modeling (b).

lengths from 349 to 390 nm. The value obtained is $d = -0.12 \pm 0.01$.

Orientational Distributional Function of Dichloride Anion Radicals

Figure 4 shows the experimental angular dependence of the EPR spectrum of a sample containing oriented Cl_2^- radicals and the results from their computer modeling. We can see that the values of the angular dependence (the maximum difference between the spectra registered at different angles of sample rotation) in the calculations have good reproducibility, despite the ratio of different spectrum components being reproduced inaccurately.

As was stated above, it is sufficient to use the second order of the function expansion by a Legendre polynomial (i.e., only two coefficients of expansion (1)) to describe the orientational distribution function of dichloride anion radicals. The A_0 coefficient characterizes the number of particles in a sample, while the A_2 value describes their orientational order. It was found that $A_2 = -0.25 \pm 0.02$ (at $A_0 = 1$).

The orientational distribution function obtained upon modeling is shown in Fig. 5. The function is presented in the sample's coordinate system. The z axis corresponds the direction of the electrical component of the orienting light (the sample's axis of anisotropy). The three-dimensional figure shown in Fig. 5 is the envelope of vectors coming from the coordinate origin in different directions; the length of each vector corresponds to the number of particles oriented in the

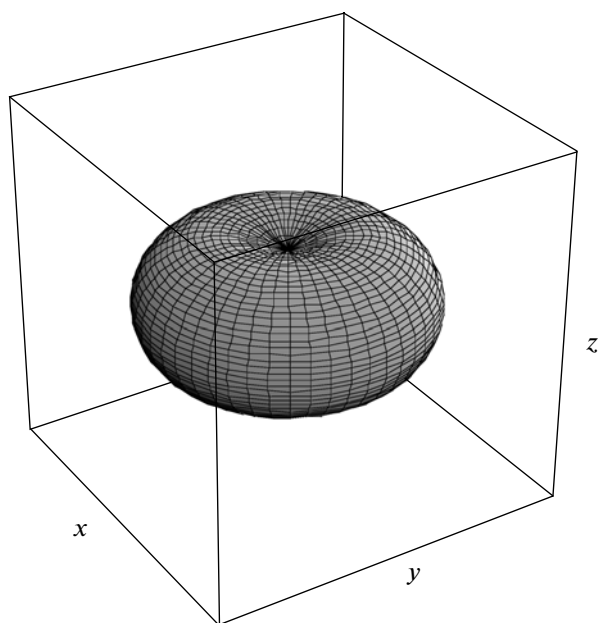


Fig. 5. Orientational distribution function of Cl_2^- anion radicals.

direction of this vector. The flattened form of the distribution function confirms that the dichloride anion radicals are mainly oriented perpendicular to the direction of light polarization as a result of irradiation by the polarized light.

The orientational order of the particles is generally characterized by the averaged value referred to as the orientation factor (the order parameter) $f = (3\langle \cos^2\beta \rangle - 1)/2$, in which the angle brackets denote averaging over all particles of the sample. It is easy to demonstrate that when the orientational distribution function of the molecules is expressed by series (1), the orientation factor is determined as $f = (2/5)A_2$. The orientation factor of Cl_2^- radicals obtained using EPR is thus $f_{\text{EPR}} = -0.10 \pm 0.01$. The negative value of the orientational factor means that particles are mainly oriented perpendicular to the sample's axis of symmetry.

Comparison of the Value of Optical Dichroism and the Orientation Factor of Cl_2^- Anion Radicals Obtained from the Orientational Distribution Function

The coincidence of the direction of vector of dipole moment of optical transition with the direction of the Cl–Cl bond of the Cl_2^- radical allows us to compare with no additional complications the value of the optical dichroism and the radical orientation factor obtained from the orientational distribution function.

The value of optical adsorption can be calculated from the orientational distribution function as follows:

$$D = Nl \int_0^\pi \varepsilon(\beta) \rho(\beta) \sin\beta d\beta, \quad (3)$$

where N is the concentration of the light absorbing substance, l is the length of the optical path, β is the angle between the direction of the light wave's electric vector and the direction of the dipole moment of transition in a molecule, and $\varepsilon(\beta)$ is the coefficient of a molecule's optical absorbance. We can then obtain the expression for the main values of the optical absorption of a dichroic sample for the axial tensor of absorption coefficient ($\varepsilon_x = \varepsilon_y \neq \varepsilon_z$):

$$D_{\parallel} = Nl \int_0^\pi \left[\bar{\varepsilon} + 2P_2(\cos\beta) \frac{\varepsilon_z - \varepsilon_x}{3} \right] \frac{\sin\beta}{2} \times \sum_{k=0}^{\infty} A_{2k} P_{2k}(\cos\beta) d\beta, \quad (4)$$

$$D_{\perp} = Nl \int_0^\pi \left[\bar{\varepsilon} - P_2(\cos\beta) \frac{\varepsilon_z - \varepsilon_x}{3} \right] \frac{\sin\beta}{2} \times \sum_{k=0}^{\infty} A_{2k} P_{2k}(\cos\beta) d\beta,$$

where $\bar{\varepsilon}$ is the average coefficient of a molecule's optical absorbance, and $P_{2k}(\cos\beta)$ are Legendre polynomials.

It follows from (4) that the value of optical dichroism is associated with the second expansion coefficient of the orientational distribution function's expansion as follows:

$$d = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} = \frac{(\varepsilon_z - \varepsilon_x)}{15\bar{\varepsilon}} A_2.$$

For an approximation of ideal single-axis absorption ($\varepsilon_x = \varepsilon_y = 0$, $\varepsilon_z \neq 0$), we obtain $d = (2/5)A_2$, which is similar to the expression obtained for f_{EPR} .

The optical dichroism obtained according to formula (2) is the orientational factor of the dipole moment vectors of molecule transition and was found to have a value of $f_{\text{opt}} = -0.12 \pm 0.01$.

The orientational factor determined by EPR ($f_{\text{EPR}} = -0.10 \pm 0.01$) thus coincides in the range of experimental error with the orientational factor determined by optical spectroscopy ($f_{\text{opt}} = -0.12 \pm 0.01$).

CONCLUSIONS

The photoinduced orientational order of dichloride anion radicals specified by the photo-orientation phenomenon was investigated using optical and EPR spectroscopy. The value of linear dichroism for the optical absorption of an anisotropic sample was calculated. The orientational distribution function of Cl_2^- radicals was determined from an analysis of the angu-

lar dependence of the same sample's EPR spectrum. The value of the orientational factor (order parameter) of the z axis of the g -tensor of a radical that lies along the Cl–Cl bond and coincides with the direction of the dipole moment vector of the observed optical transition was obtained from the orientational distribution function. It was found that the values of the order parameter obtained from the EPR spectra coincide quantitatively. This confirms the reliability of the method developed earlier for investigating orientational order by means of EPR spectroscopy.

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REFERENCES

1. A. C. Albrecht, *J. Chem. Phys.* **27**, 1413 (1957).
2. A. C. Albrecht, *Prog. React. Kinetic* **5**, 301 (1970).
3. J. Michl and E. W. Thulstrup, *Spectroscopy with Polarized Light: Solute Alignment by Photoselection*, in *Liquid Crystals, Polymers, and Membranes* (VCH Publ., Weinheim, 1986).
4. *Experimental Methods of High Energy Chemistry: The Guide*, Ed. by M. Ya. Mel'nikov (Mosk. Gos. Univ., Moscow, 2009) [in Russian].
5. I. Zebger, M. Rutloh, U. Hoffmann, et al., *J. Phys. Chem. A* **106**, 3454 (2002).
6. A. Bobrovsky, V. Shibaev, and N. Boiko, *Prog. Polym. Sci.* **23**, 729 (2003).
7. C. Cojocariu and P. Rochon, *Pure Appl. Chem.* **76**, 1479 (2004).
8. D. Rais, S. Nešpurek, Y. Zakrevskyy, et al., *J. Optoelectron. Adv. Mater.* **7**, 1371 (2005).
9. C. C. Jung, M. Rutloh, and J. Stumpe, *J. Phys. Chem. B* **109**, 7865 (2005).
10. A. Bobrovsky and V. Shibaev, *Polymer* **47**, 4310 (2006).
11. A. Bobrovsky, A. Ryabchun, A. Medvedev, et al., *J. Photochem. Photobiol., A* **206**, 46 (2009).
12. S. Kawata and Y. Kawata, *Chem. Rev.* **100**, 1777 (2000).
13. C. C. Corredor, Z. L. Huang, and K. D. Belfield, *Chem. Mater.* **19**, 5165 (2007).
14. A. Bobrovsky, V. Shibaev, G. Elyashevich, et al., *Polym. Adv. Technol.* **21**, 100 (2010).
15. L. Nikolova and P. S. Ramanujam, *Polarization Holography* (Cambridge Univ., Cambridge, 2009), p. 88.
16. E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.* **104**, 5594 (1982).
17. J. Schellman and H. P. Jensen, *Chem. Rev.* **87**, 1359 (1987).
18. P. M. Dolan, D. Miller, R. J. Cogdell, et al., *J. Phys. Chem. B* **105**, 12134 (2001).
19. A. Rodger, J. Rajendra, R. Marrington, et al., *Phys. Chem. Chem. Phys.* **4**, 4051 (2002).
20. M. A. R. B. Castanho, S. Lopes, and M. Fernandes, *Spectroscopy* **17**, 377 (2003).
21. A. Bobrovsky, V. Shibaev, V. Hamplova, et al., *Monatsh. Chem.* **140**, 789 (2009).
22. A. Kh. Vorobiev and N. A. Chumakova, *J. Magn. Res.* **175**, 146 (2005).
23. A. Kh. Vorobiev and V. S. Gurman, *Khim. Fiz.* **6**, 1220 (1987).
24. A. Kh. Vorobiev and V. S. Gurman, *Chem. Phys.* **167**, 341 (1992).
25. E. B. Zvi, R. A. Beaudet, and W. K. Wilmarth, *J. Chem. Phys.* **51**, 4166 (1969).
26. J. E. Bennet, B. Mile, and B. Ward, *J. Chem. Phys.* **49**, 5556 (1968).
27. Yu. V. Rikitin, G. M. Larin, and V. V. Minin, *Interpretation of EPR Spectra of Coordination Compounds* (Nauka, Moscow, 1993) [in Russian].
28. P. Paghavan, *At. Data Nucl. Data Tables* **42**, 189 (1989).
29. J. E. Dennis, D. M. Gay, and R. E. Welsch, *Trans. Math. Software* **7**, 348 (1981).
30. J. E. Dennis, D. M. Gay, and R. E. Welsch, *Trans. Math. Software* **7**, 369 (1981).
31. A. Kh. Vorobiev, A. V. Polenok, and V. S. Gurman, *Khim. Fiz.* **9**, 840 (1990).