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Spin-Probe Analysis of Graphene Oxide Membranes: Determining Orientational Order from Room-Temperature EPR Spectra with Interfering Signals

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Abstract

The internal architecture of graphene oxide membranes (GOMs) strongly influences their functional properties. We previously developed a quantitative spin-probe method for determining the orientational order of oxidized graphene layers within GOMs. So far, this method has been applied only to EPR spectra recorded at low temperatures, where the rotational mobility of the probes is effectively suppressed. Here, we present a computational approach for analyzing room-temperature EPR spectra. These spectra have narrower lines and a more pronounced angular dependence, allowing the orientational order of GOMs to be determined more accurately. A weighted least-squares procedure allows the weak spin-probe signal to be extracted in the presence of the much more intense intrinsic EPR signal of graphene oxide.

Keywords: Graphene oxide membranes, inner structure, orientational order parameters, EPR spectra angular dependence, EPR spectra simulation, intense interfering signals, weighted least-squares procedure.

1. Introduction

Graphene oxide membranes (GOMs) are of interest for both fundamental research and practical applications because of their selective permeability. Nair et al. [1] were the first to demonstrate the high permeation selectivity of these membranes toward different polar liquids. GOMs are therefore promising for separating substances of similar polarity, particularly for dehydrating organic solvents. Such solvents often form azeotropes with water, making their dehydration energy-intensive [2],[3]. Inexpensive graphene oxide membranes could provide an alternative method for separating these azeotropes. However, the mechanism of selective permeation through GOMs remains unclear. For example, it is still unclear why the water flux through GOMs exceeds that of lower alcohols by several orders of magnitude, or why membranes

prepared using identical procedures can differ markedly in their functional properties, particularly water permeability [4]. Theoretical models of GOM permeability typically assume defect-free structures formed by perfectly stacked oxidized graphene layers. Real membranes, particularly free-standing membranes tens of micrometers thick, deviate from these ideal structures. Published studies [5],[6],[7] indicate that the functional properties of GOMs depend on both the properties of graphene oxide (GO) and the internal membrane architecture. The former includes the degree of oxidation, the relative amounts and surface distribution of oxygen-containing groups, and the flake-size distribution; the latter includes the orientational ordering of the oxidized graphene layers.

Until recently, membrane ordering was assessed either visually from SEM images of membrane cross sections [5],[8],[9] or semiquantitatively from the widths of XRD reflections [6],[10]. The latter approach is generally used to compare membranes prepared by the same research group. Several years ago, we proposed a method for the quantitative analysis of GOM architecture using EPR spectroscopy with spin probes. Stable paramagnetic molecules are introduced into the membrane and are rigidly and specifically adsorbed on the surfaces of the oxidized graphene layers [11],[12]. Joint numerical analysis of EPR spectra recorded at different membrane orientations relative to the magnetic field determines the orientational ordering of the radicals within the membrane and, hence, that of the oxidized graphene layers. Because the membranes are axially symmetric, the orientation distribution function (ODF) of the layers can be expanded in a series of Legendre polynomials. The coefficients of this expansion are related to the orientational order parameters, which are a generally accepted measure of orientational order [13].

The shape of an EPR spectrum depends on three groups of parameters: the magnetic parameters of the probe molecules, their orientational ordering within the sample, and their rotational mobility. The spin Hamiltonian parameters of a radical in a given matrix can be determined independently from the spectrum of a disordered (isotropic) sample recorded at a temperature low enough to suppress radical rotation. Separating the contributions of orientational order and rotational mobility to the spectral shape is a complex and, in general, ill-posed problem with multiple solutions. At sufficiently high probe mobility (10^8–10^9 s^{-1}), these contributions can be distinguished, although the correlation between the corresponding fitted parameters remains unresolved; examples are given in [14]. At low probe mobility (10^6–10^7 s^{-1}), this separation is practically impossible because the spectral shape is less sensitive to rotational mobility in this range. The mobility ranges given here refer to X-band EPR spectroscopy.

Spin probes strongly adsorbed on oxidized graphene layers are suitable for determining membrane ordering because their orientation reflects the alignment of the layers. However, these probes have low rotational mobility. Our previous studies therefore analyzed the angular

dependences of EPR spectra recorded at 100–120 K, where probe rotation is effectively suppressed and does not affect the spectral shape [11],[15]. At these temperatures, however, anisotropy of the spin Hamiltonian parameters produces broad EPR spectra. The broad lines reduce the differences between spectra recorded at different membrane orientations and thus limit the information that can be obtained about radical ordering. In [14], the highest determinable rank of the orientation distribution function of spin probes in macroscopically ordered liquid crystals was shown to depend strongly on the measurement temperature and, consequently, on the line width. Order parameters up to rank 18 could be determined from high-temperature spectra, whereas low-temperature spectra provided parameters only up to ranks 8–10. Recording the angular dependence at a higher temperature is therefore expected to reveal finer details of orientational ordering.

Room-temperature analysis of the angular dependence of EPR spectra in GOMs can be combined with an independent determination of probe rotational mobility. This can be done using a disordered graphite oxide powder prepared from the same graphene oxide dispersion as the membranes. The rotational mobility of the probes in the powder can be determined from the EPR spectral shape. Since the powder and the membranes contain graphene oxide of the same chemical structure, we assume that the interaction energy between the probe and the oxidized graphene surface, and hence the probe rotational mobility, is the same in both materials.

Another difficulty in analyzing spin-probe EPR spectra in GOMs is the intrinsic paramagnetism of graphene oxide: its EPR signal is much more intense than the probe signal. Increasing the radical concentration increases the probe signal intensity but also broadens the lines through dipole–dipole spin interactions. Fitting a weak probe signal in the presence of an intense GO signal gives poor results because the GO signal dominates the loss function (LF). In this study, we addressed this problem by using a weighted least-squares loss function.

Here, we show that room-temperature EPR spectra of orientation-sensitive spin probes in GOMs allow membrane orientational order to be determined more accurately. In particular, the highest determinable rank in the spherical-harmonic expansion of the orientation distribution function increases from 4–6 for the broad spectra recorded at 120 K to 6–8 for room-temperature spectra. The software implementing this weighted analysis can also be used to extract weak target signals in the presence of strong interfering signals in both orientationally ordered and isotropic systems.

2. Materials and Methods

2.1. Graphene Oxide Materials

We studied four GOMs prepared from the same GO dispersion at different concentrations using vacuum filtration and pressure-assisted filtration. Graphene oxide was synthesized by the Hummers method [16].

The stable nitroxide radical H2 was used as the spin probe (Fig. 1). Its sensitivity to GOM ordering was established in our earlier work [12].

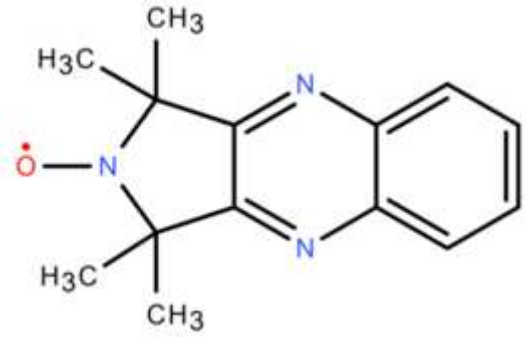


Figure 1. Structure of the nitroxide spin probe H2.

The spin probe was introduced into membrane fragments (~4 × 10 mm) by immersing them in a 3.5 mM radical solution in a 1:1 water/acetonitrile mixture. The fragments were then removed from the solution and dried in air at 333 K until the EPR signal of rapidly tumbling radicals in the liquid phase disappeared. Each sample contained approximately 3×10^{16} paramagnetic molecules. At this probe loading, dipole–dipole interactions between spins are negligible and do not broaden the EPR lines.

To prepare the graphite oxide powder, the same graphene oxide dispersion used to prepare the membranes was evaporated in air at room temperature under vigorous stirring. An air stream from a fine capillary was directed onto the dispersion surface to accelerate drying. The dried powder was mechanically ground to obtain a homogeneous sample. The spin probe was introduced from an acetonitrile solution, and the solvent was evaporated in air until the EPR signal of highly mobile radicals was no longer detected. The powder sample contained 3×10^{16} spins/mg.

2.2. EPR Spectroscopy

EPR spectra were recorded on an X-band ADANI spectrometer (Belarus) equipped with an ADANI nitrogen-flow temperature controller. The angular dependences of the spectra were recorded using a manually operated ADANI goniometer with a rotation accuracy of ±2°. The

microwave power was 1 mW, and the magnetic-field modulation amplitude was 0.1 mT. These settings did not distort the spectra.

Graphite oxide powder was placed in a glass capillary with an internal diameter of 1 mm.

For measurements at 120 K, membrane samples containing the spin probe were fixed in a quartz holder as described in [11]. The holder consisted of a quartz tube, thin quartz plates, and a Teflon seal and protected the membrane from the nitrogen vapor flow. For measurements at room temperature, the membrane fragments were mounted on a quartz rod. The temperature was maintained at 298 K by water-cooling the spectrometer resonator using a LAUDA ECO RE630 thermostat (Germany). The holder or rod was rotated about its axis to vary the angle between the membrane normal and the magnetic field. EPR spectra were recorded at the angles from 0° to 90° in 10° steps and at 125°, 145°, 165°, and 180°; a total of 14 spectra. Because of the orthorhombic symmetry of the magnetic resonance parameters of H2, the spectra recorded at 0° and 180° should be identical. Agreement between these spectra within experimental error was used as a criterion for a successful experiment.

Figure 2 compares the angular dependences of EPR spectra recorded at 120 and 298 K for the same membrane. The room-temperature spectra are much narrower and show a more pronounced angular dependence. The ratio of the GO signal intensity to the probe signal intensity is also much higher at room temperature. This is because the intrinsic GO signal is strongly saturated by microwave power, and its degree of saturation depends on the spin relaxation rate and therefore on temperature [17],[18]. Thus, the room-temperature spectra contain more information about radical orientational ordering, but their simulation is complicated by the intense GO signal, which strongly overlaps the spin-probe signal.

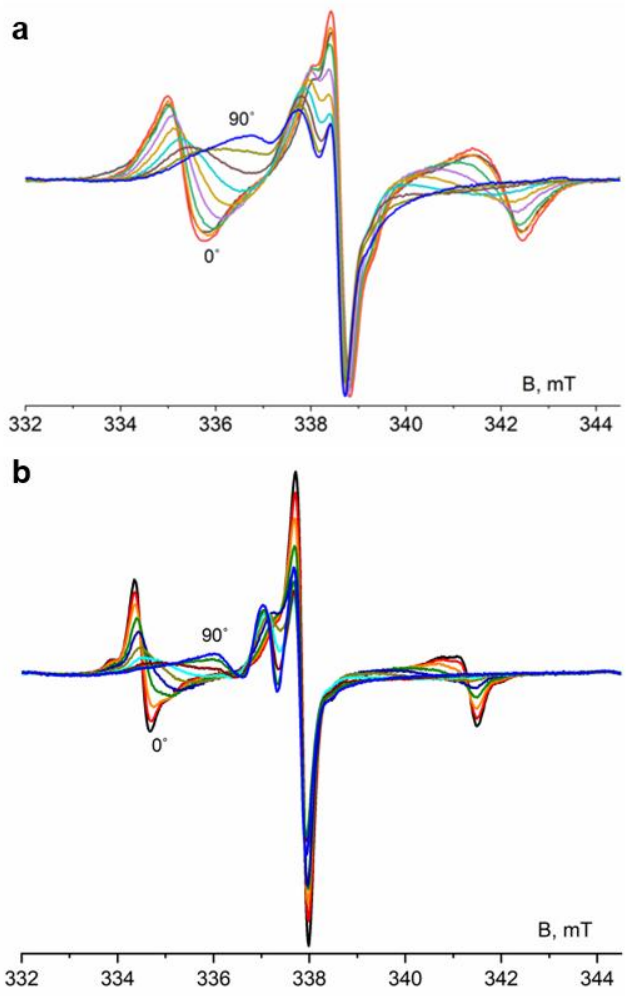


Figure 2. Angular dependences of the EPR spectra of membrane 2 containing the spin probe, recorded at 120 K (a) and 298 K (b). The angle between the membrane normal and the magnetic field was varied in 10° steps. The central singlet signals arise from graphene oxide.

2.3. EPR Spectral Simulation

EPR spectra were simulated using ODFR4, developed by A. Kh. Vorobiev (Moscow State University, Russia) and freely available at [19]. The program core calculates the EPR spectral shape from the spin Hamiltonian parameters and rotational mobility of the paramagnetic molecules. It was developed by J. Freed's group (Cornell University, USA), and its original version is described in detail in [20]. A. Kh. Vorobiev subsequently extended the program to account for radical orientational distributions without imposing a predefined system symmetry. Examples of the analysis of angular dependences of EPR spectra for spin probes in liquid crystals are given in [14]. We incorporated a weighted loss function (LF) into ODFR4 to quantify the difference between experimental and calculated EPR spectra. The weighting increases the contribution of weak target signals to the LF and reduces that of intense interfering signals. The modified version is named ODFR5 and is freely available at [21].

In the fitting procedure, the orientation distribution function (ODF) of the nitroxide radicals was represented by a series of Legendre polynomials:

$$\rho(\beta) = \sum_{l=0}^{\infty} \frac{2l+1}{2} P_l P_l(cos\beta) \quad (1)$$

The order parameter of rank l is defined as the average value of the corresponding Legendre polynomial:

$$P_l = \int_0^{\pi} P_l(cos\beta)\, \rho(\beta) sin\beta d\beta \quad (2)$$

Here, β is the angle between the membrane normal and the magnetic z axis of the nitroxide molecule. Because of the symmetry of the magnetic parameters of H2 (the g and hyperfine tensors are coaxial), the EPR spectra are sensitive only to the even-rank terms in Eq. 1.

The EPR spectra contain an intense intrinsic GO signal and a weak nitroxide signal (Fig. 2). The latter carries information about layer ordering within the membrane. The GO signal overlaps the central part of the spin-probe signal and therefore must be included in the spectral deconvolution. Its shape also depends on membrane orientation, which further complicates the analysis. To address this problem, we introduced weighting coefficients that reduce the contribution of the GO signal to the LF and increase that of the spin-probe signal. The coefficients are assigned to selected magnetic-field intervals using an interactive program available at [21] (Fig. 3). These coefficients enter the LF quadratically: the LF is calculated as half the sum, over all spectral points, of the squared weighted differences between calculated and experimental spectra.

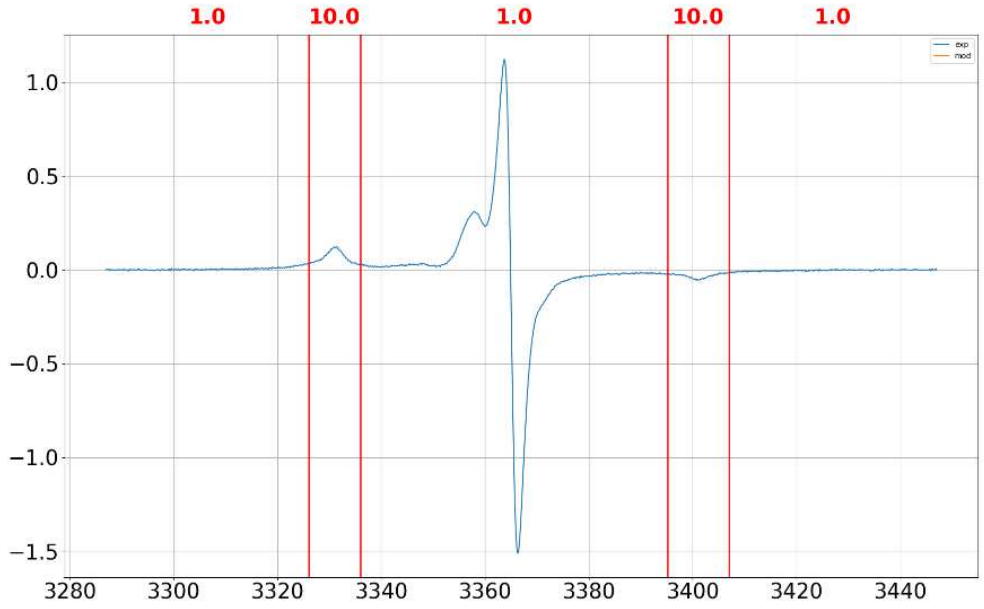


Figure 3. Interface of the program used to set the weighting coefficients. The coefficient values are shown in red.

Figure 4 compares simulations obtained using weighted and unweighted LFs for the angular dependence of the membrane EPR spectra and for the EPR spectrum of GO powder. A satisfactory fit to the weak nitroxide signal is obtained only when the contribution of the GO signal to the LF is reduced.

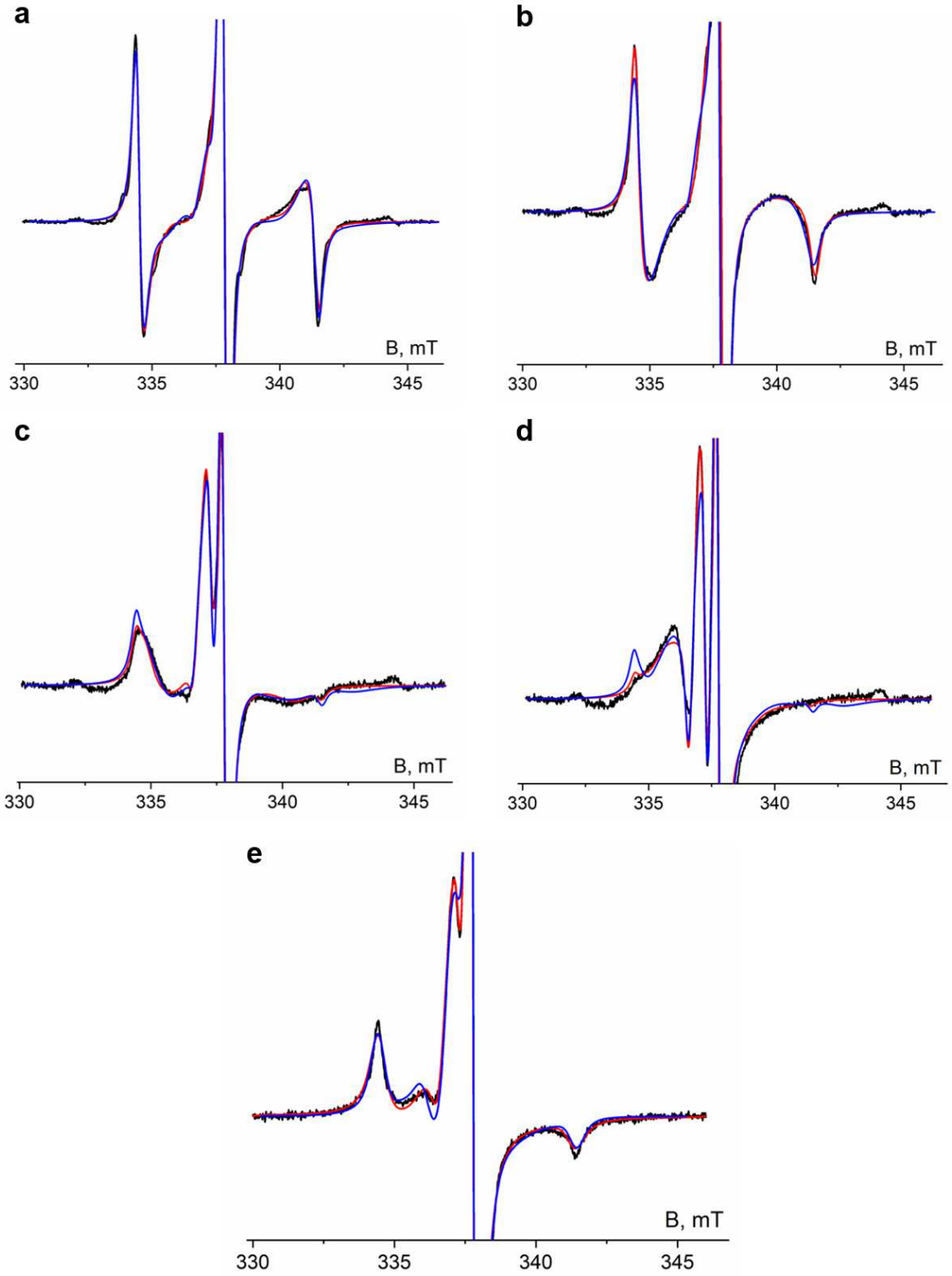


Figure 4. Simulations of EPR spectra of membrane 2 recorded at 0° (a), 30° (b), 60° (c), and 90° (d), and of the EPR spectrum of GO powder (e), obtained using weighted and unweighted LFs. Black lines: experimental spectra; red lines: simulations with the weighted LF; blue lines: simulations with the unweighted LF. The weighting coefficients were 1 for the GO signal and 10 for the spin-probe signal. The intense GO signals are truncated.

3. Results and Discussion

The rotational mobility of H2 radicals adsorbed on the oxidized graphene layers was determined by simulating the EPR spectrum of GO powder containing the spin probe, recorded at 298 K (Fig. 4e, red line). The spin Hamiltonian parameters of H2 in this GO were determined independently from the powder spectrum recorded at 120 K. The rotational diffusion coefficients along all three molecular axes were $(2 \pm 1) \times 10^6$ s^{-1}. Including rotational anisotropy did not improve the fit to the experimental spectrum; therefore, rotational anisotropy could not be determined from these data.

The low rotational mobility of H2 in GO at room temperature is consistent with its planar geometry [15] and conjugated aromatic fragments containing heteroatoms, which favor strong adsorption on oxidized graphene layers. This rigid adsorption with a well-defined orientation makes the probe sensitive to layer ordering in GOMs [12]. The high adsorption energy also restricts radical rotation on the surface, even at room temperature.

Figure 5 shows the results of joint simulations of EPR spectra recorded at different orientations of the membranes containing spin probes relative to the magnetic field. Only four spectra for each membrane are presented in the Figure 5 whereas in reality we simultaneously simulated 14 spectra (see section 2.2). The simulations reproduce the experimental spectra well despite the much greater intensity of the intrinsic GO signal. This signal also depends on membrane orientation and therefore requires a separate ODF to describe this dependence. It would be tempting to determine GOM ordering from the angular dependence of the GO signal alone, without introducing spin probes into the membranes. However, we found that the angular dependence of the GO signal does not necessarily correlate with probe ordering. The origin of the GO signal requires further study.

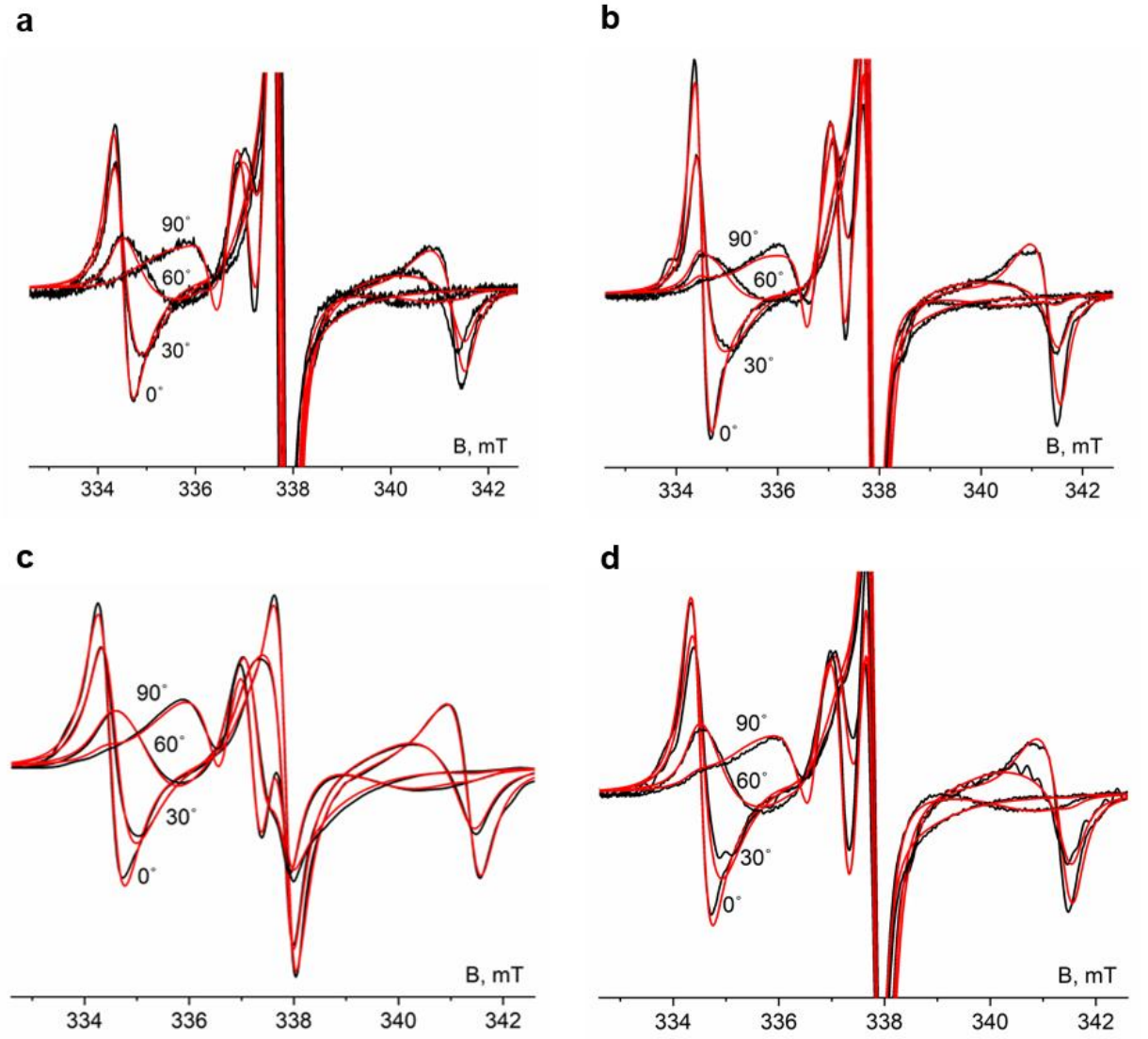


Figure 5. Joint simulations of EPR spectra of membranes containing spin probes, recorded at different membrane orientations relative to the magnetic field: (a) membrane 1; (2) membrane 2; (c) membrane 3; (d) membrane 4.

Unlike optical spectroscopy, which determines molecular ordering through second-rank order parameters or fourth-rank parameters in two-photon methods such as polarized fluorescence [22], EPR spectroscopy imposes no theoretical limit on the rank of the ODF that can be determined for paramagnetic molecules. Rotation of an anisotropic sample changes only the intensity of an optical spectrum, whereas it changes the shape of an EPR spectrum. The angular dependence of EPR spectra therefore provides more information about particles ordering. In practice, however, line broadening and partial line overlap limit the information content of the spectra and the determinable rank of the ODF expansion. To assess the reliability of the order parameters, we simulated each angular dependence repeatedly while increasing the maximum rank of the ODF expansion. We stopped when the decrease in the weighted LF upon adding the next rank was

considered insignificant. This assessment was based on the mean noise level of the experimental spectra and the relative change in the LF. Figure 6 shows the weighted LF as a function of the maximum expansion rank for each membrane; the mean noise levels are indicated by dotted lines.

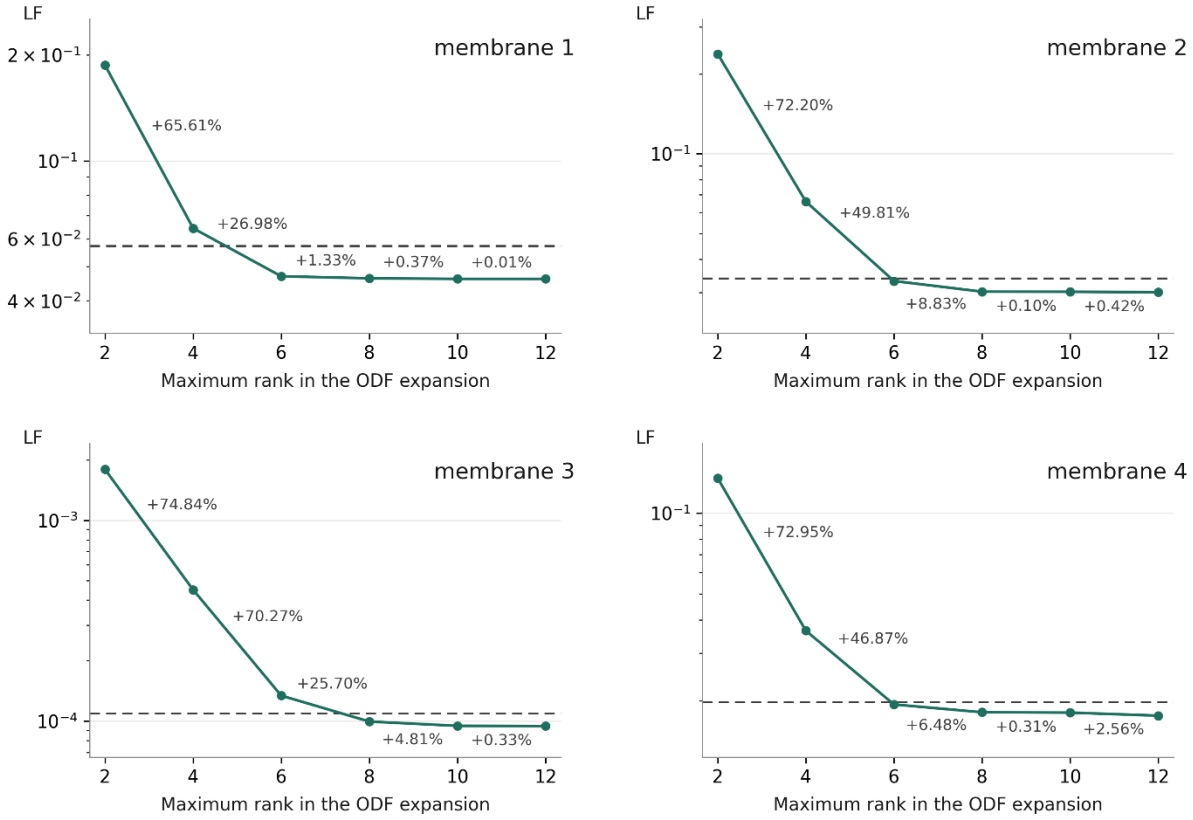


Figure 6. Weighted LF as a function of the maximum ODF expansion rank for each membrane. Dotted lines indicate the mean noise levels.

These results indicate that ODFs can be reliably determined up to rank 6 for all four membranes. For membranes 2, 3, and 4, the inclusion of eighth-rank order parameters may also be justified. Although the change in the residual calculated over all spectra when the maximum rank is increased from 6 to 8 is below the noise level, the change is appreciable for some individual spectra. Figure 7a shows the change in the weighted residual for each spectrum of membrane 2 upon inclusion of an eighth-rank order parameter. For spectra (Figure 7b) recorded near the parallel orientation, this change substantially exceeds the noise level.

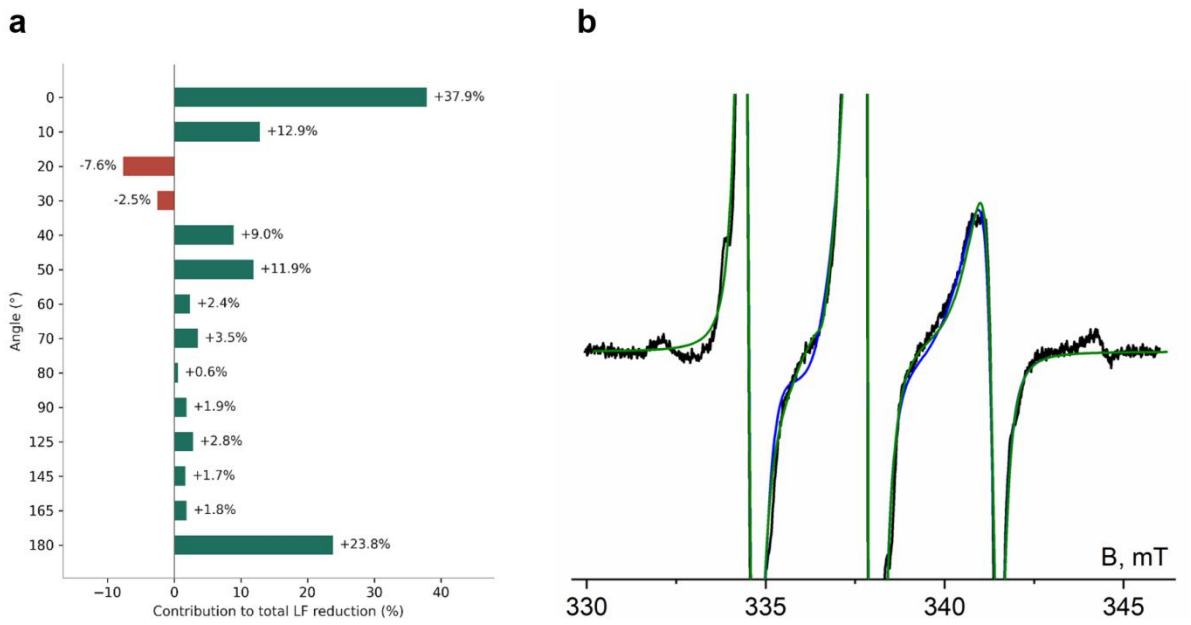


Figure 7. (a) Contribution of each spectrum of membrane 2 to the total decrease in the LF when the maximum ODF expansion rank is increased from 6 to 8; (b) comparison of the simulations for the spectrum recorded at 0°. Black line: experimental spectrum; blue line: maximum rank 6; green line: maximum rank 8.

Table 1 lists the orientational order parameters of the probes in GOMs determined from EPR spectra recorded at 120 K and 298 K. The corresponding ODFs are shown in Figure 8. To estimate the uncertainties, each order parameter was varied about its optimum value, and the spectra were refitted by varying all other parameters affecting the spectral shape. The resulting change in the weighted LF was calculated over the full angular series. The mean noise level of the experimental spectra was used as the limiting acceptable change in the LF. Because the residual changes were not evaluated for individual spectra, the reported uncertainties may be overestimated. The uncertainties were smaller for membrane 3, for which the GO signal contributed less to the spectra than for the other membranes.

Table 1. Orientational order parameters of H2 in GOMs determined from EPR spectra recorded at different temperatures.

	membrane 1		membrane 2		membrane 3		membrane 4	
	120 K	298 K	120 K	298 K	120 K	298 K	120 K	298 K
P20	0.72 ±10%	0.66 ±10%	0.64 ±10%	0.58 ±10%	0.66 ±10%	0.64 ±10%	0.54 ±10%	0.61 ±10%
P40	0.41 ±15%	0.28 ±20%	0.28 ±15%	0.25 ±20%	0.35 ±15%	0.35 ±10%	0.29 ±15%	0.28 ±20%
P60	0.12 ±50%	0.08 ±35%	0.10 ±50%	0.09 ±35%	0.13 ±40%	0.16 ±20%	0.13 ±50%	0.10 ±35%
P80	ND*	ND	ND	0.02 ±130%	ND	0.05 ±50%	ND	0.02 ±100%

**ND: not determined.*

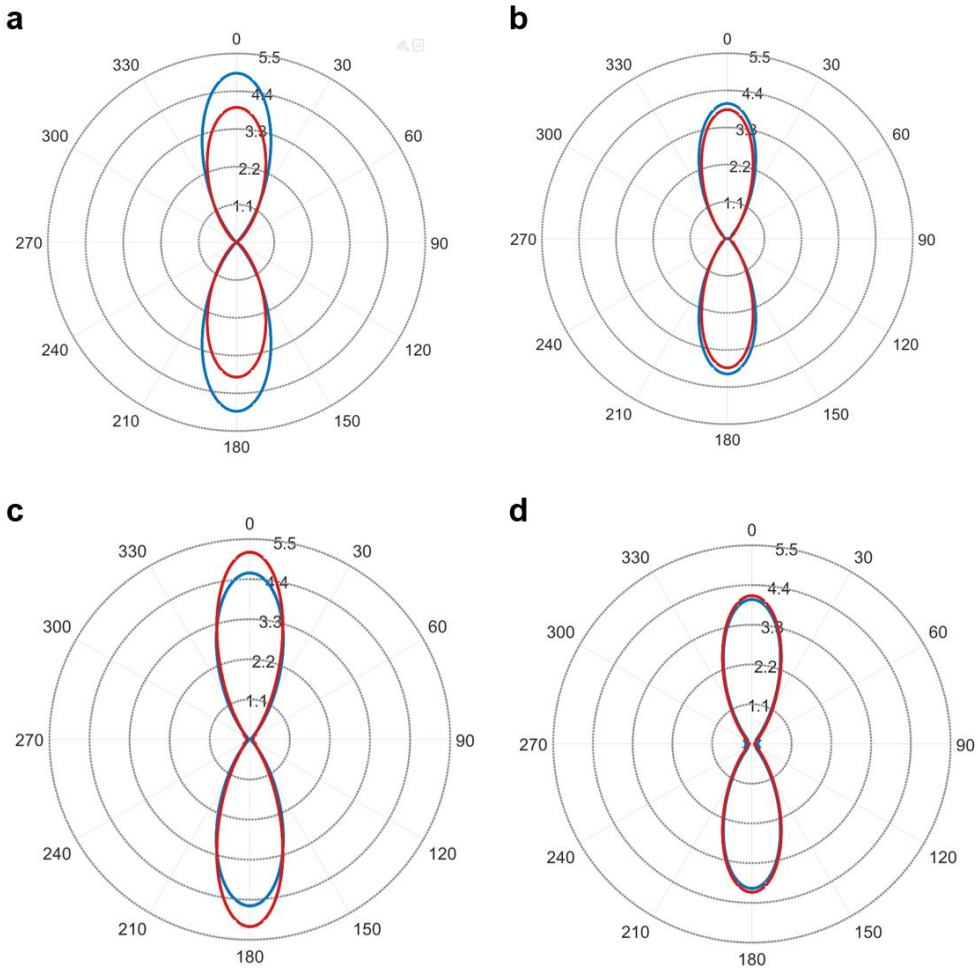


Figure 8. Polar plots for ODFs of spin probes in (a) membrane 1; (2) membrane 2; (c) membrane 3; (d) membrane 4. Blue line corresponds to ODF for experiment at 120 K, red line – at 298 K.

First, the narrower room-temperature spectra resolve finer features of the radical orientation distribution and thus provide more detailed information about the internal structure of GOMs. Higher-rank orientational order parameters can help assess the presence and size of defective membrane regions (see, for example, [15],[23]). In the present samples, however, the ODFs do not indicate significant defects.

Second, the order parameters of ranks 2, 4, and 6 determined from room-temperature spectra were close to those determined from low-temperature spectra, with deviations in both directions. These results show that probe rotational mobility does not cause a systematic underestimation of membrane ordering.

Finally, determining GOM architecture by the spin-probe method at room temperature gives reliable results while reducing the measurement time and cost compared with low-temperature experiments.

3.1. Broader Applicability

The weighted least-squares method implemented in EPR simulation software that accounts for rotational mobility and orientational ordering can be used to analyze systems in which intense interfering signals partially overlap weak signals of interest. For GOMs, this approach allows the earlier low-temperature measurements to be replaced by room-temperature experiments, which are simpler, less expensive, and more informative. The software can be used for both orientationally ordered and isotropic systems. The open-source ODFR5 program and the auxiliary programs for setting the weighting coefficients and displaying the simulation results are available at [21].

Conclusions

We implemented a weighted least-squares method in EPR simulation software that accounts for arbitrary orientational distributions of paramagnetic molecules. This allows spectra containing several paramagnetic components to be analyzed even when an intense interfering signal partially overlaps a weak signal of interest. We applied the method to determine the orientational ordering of layers in graphene oxide membranes, which are promising for separating polar liquids and dehydrating organic solvents. Accounting for probe rotational mobility allowed us to use room-temperature measurements instead of low-temperature experiments. Analysis of the narrower room-temperature spectra improved the accuracy of the determination of orientational order. The resulting method provides a detailed quantitative characterization of GOM architecture and can be used to study its relationship with membrane functional properties.

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