

Quantitative determination of the orientational ordering of the graphene oxide membranes by spin probe technique

Chumakova N.A., Vorobiev A.Kh., Astvatsaturov D.A., Yankova T.S., Rebrikova A.T., Matveev M.V.

The native EPR signal of graphite oxide

The amplitude and width of the native EPR signal of graphite oxide depend on the orientation of the membrane relative to direction of magnetic field and on the concentration of paramagnetic probe in the membrane. Figure 1(a) demonstrates the angular dependence of EPR spectra of the membrane that does not contain spin probes. Figure 1(b) shows EPR spectra of the system “GOM1 – TEMPOL – H₂O” before and after partially removing the radicals from the membrane; the spectra were recorded at the parallel orientation of the membrane normal and the magnetic field lines. It is seen that after removing the nitroxide radicals the intensive GO signal appears in the spectrum.

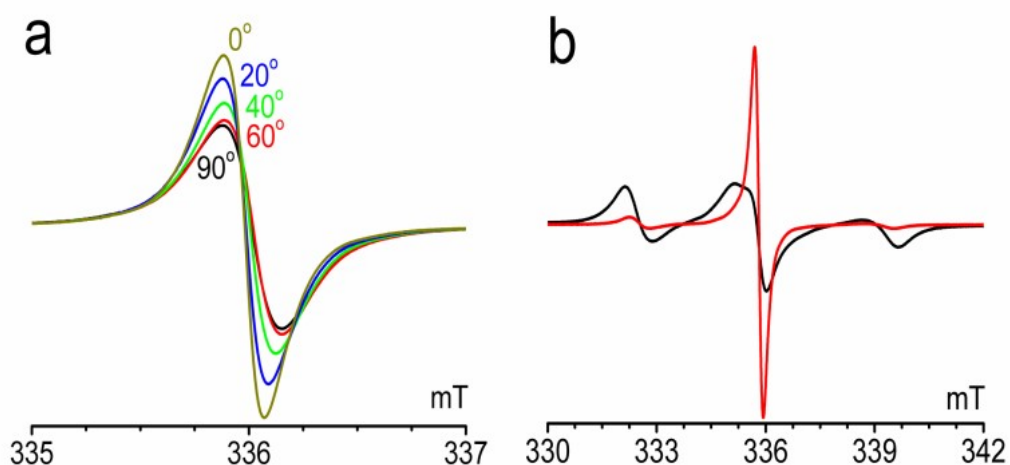


Figure 1. (a) Angular dependence of EPR spectrum of the membrane without a spin probe. The spectra were recorded at different angles between the membrane surface normal and magnetic field. (b) EPR spectra of the system “GOM1 – TEMPOL – H₂O” before (black) and after (red) partial removal of the spin probes. The spectra were recorded at the parallel orientation of the normal vector and magnetic field.

Strategy of simulation of EPR spectrum angular dependence

The main principles of the procedure of joint computer simulation of EPR spectra recorded at different orientations of an anisotropic sample relative to the magnetic field lines were described by us in [1]. In the case of the systems “nitroxide spin probe – graphite oxide” the signal of the spin probe is considerably overlapped with the native signal of GO which also demonstrates angular dependence. The shape of the GO signal depends on the experimental

conditions; therefore we cannot subtract this signal from the spectra and have to describe every spectrum as a sum of the signals of nitroxides and GO. For simulation of EPR spectra angular dependence in such a case, we worked out the following strategy. The ODF3 program used for the simulation (<http://www.chem.msu.ru/rus/lab/chemkin/ODF3>) works according to the principle of minimizing the discrepancy between the theoretically calculated spectra and the experimental ones. The discrepancy is calculated at a given number of spectrum points. Each point can be assigned with weight coefficient that changes this point contribution to the discrepancy proportionally to the value of the coefficient. We are interested in better describing the low-field and high-field components of the nitroxide radicals, so it is necessary to assign higher coefficients to the points of these components and lower coefficients to the central part of the spectrum. The main disadvantage of this approach is a poor description of the central component. However, a satisfactory description of the native GO signal should not be neglected as far as this signal makes some contributions to the low-field and high-field components of the nitroxides. To avoid this difficulty we performed the simulation procedure in several stages:

- a) Rough approximation without weight coefficients;
- b) Simulation with the weight coefficients for accurate description of the low-field and high-field components; good results were achieved using the coefficients for the low-field and high-field components that are 5-10 times greater than those for the central part of the spectrum;
- c) Simulation without weight coefficients with fixed values of the order parameters obtained at stage b);
- d) Repetition of stages b) and c) until the change in the pure discrepancy (discrepancy without taking into account the weight coefficients) becomes less than the experimental errors of the spectra recording.

Figure 2 illustrates the simulation results for the spectrum of the system “GOM1 – A5 – CH₃CN” recorded at a zero angle between the membrane surface normal and the magnetic field lines. It is seen that at stage a) the most intense GO signal was described much better than low-field and high-field components of nitroxide radicals. At stage b) because of using of the weight coefficients the low-field and high-field components were described better but the description of the central part of the spectrum got worse. At stage c) the description of the GO signal was greatly improved and the description of the low-field and high-field components almost did not change because of fixing of the probe order parameters. At stage d) the final result of the simulation was obtained.

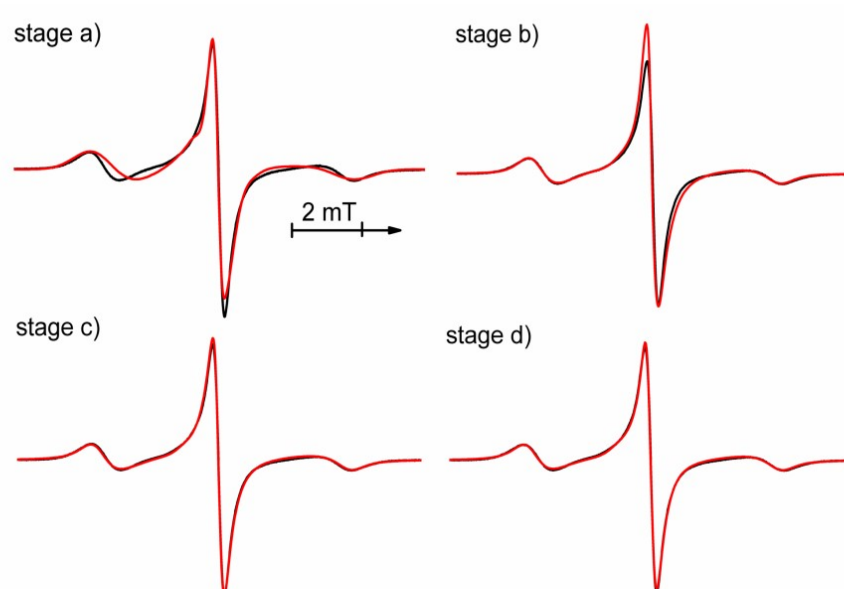


Figure 2. The simulation results of the 0° spectrum of the system “GOM1 – A5 – CH_3CN ” corresponding to the different stages of the simulation procedure; black lines are experimental spectra, red lines are the results of simulation.

Angular dependence of the low-field component of EPR spectrum of TEMPOL radical in GOM

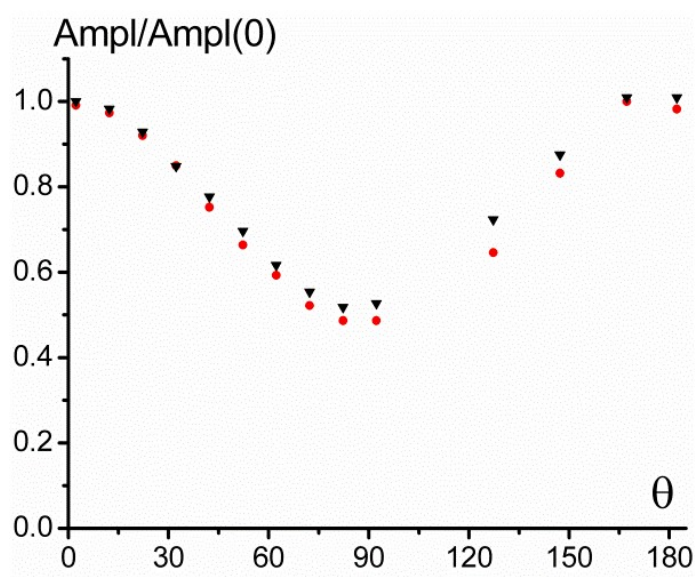


Figure 3. Angular dependence of the leftmost component amplitude of EPR spectrum of the system “GOM1-TEMPOL- CH_3CN ”. Red circles are experimental values; black triangles are the results of joint spectra simulation.

Influence of order parameter P_{60} on angular dependence of the leftmost component amplitude of EPR spectrum of the system GOM1 – $[\text{Cu}(\text{NH}_3)_4]^{2+} - \text{H}_2\text{O}$

Figure 4 shows the changes of calculated angular dependence of amplitude of the leftmost EPR component with change in the value of order parameter P_{60} . The most significant differences are observed in the range of angles (0° - 40°) and (140° - 180°). The agreement between the experimental and theoretical dependences can be expressed as a sum of squared deviations calculated for all experimental points. The dependence of this parameter on the value of order parameter P_{60} is shown in Figure 5. It is seen that the value 0.09 is optimal.

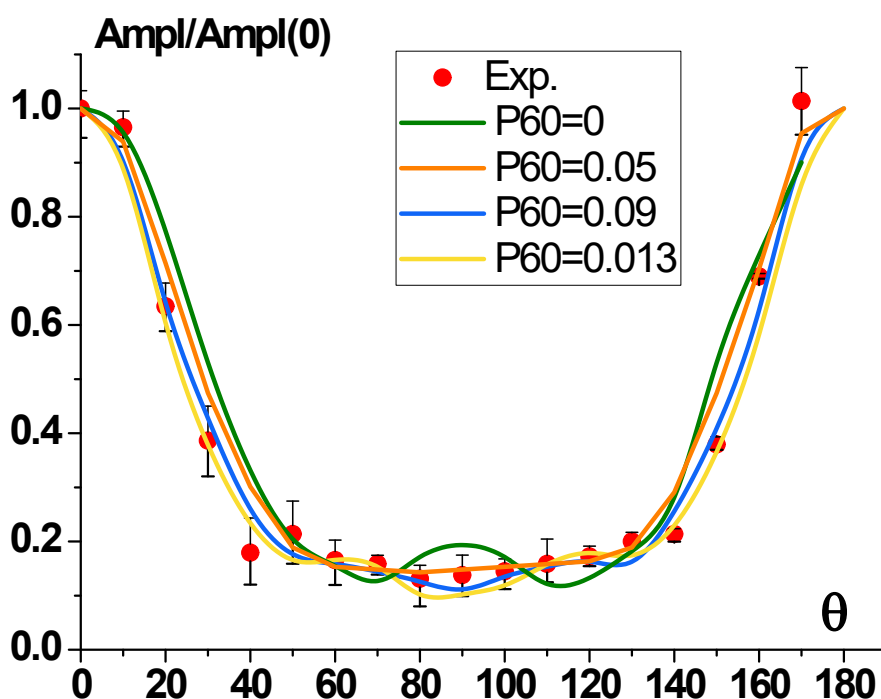


Figure 4. Angular dependences of the leftmost component amplitude of EPR spectrum of the system GOM1 – $[\text{Cu}(\text{NH}_3)_4]^{2+} - \text{H}_2\text{O}$. Red circles are experimental values; the lines correspond to different values of order parameter P_{60} : 0 (green), 0.05 (orange), 0.09 (blue), 0.13 (yellow).

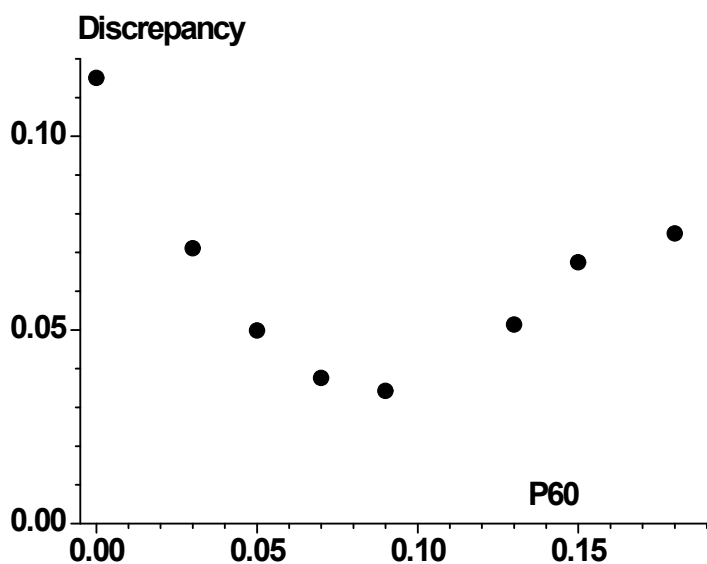


Figure 5. Dependence of the sum of squared deviations of the calculated angular dependence of the amplitude of leftmost EPR component for the system $GOM1 - [Cu(NH_3)_4]^{2+} - H_2O$ on the value of order parameter P_{60} .

- 1 A. K. Vorobiev and N. A. Chumakova, Determination of orientation distribution function of anisotropic paramagnetic species by analysis of ESR spectra angular dependence, *J. Magn. Reson.*, 2005, **175**, 146–157.