Supplement of

Mechanical ordering of pigment crystallites in oil binder: can electron paramagnetic resonance reveal the gesture of an artist?

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1. Demonstration of Equation (7)

The Wigner matrix elements $D_{0\Omega}^{(l)}(\Omega)$ in Eq. 6 can be expressed as (Eq. 12 in Hentschel et al., J. Chem. Phys. 68, 56-66, https://doi.org/10.1063/1.435473, 1978):

$$D_{0\Omega}^{(l)}(\Omega) = \sum_{n=-l}^{l} D_{on}^{(l)}(\Omega') D_{0n}^{(l)}(\Omega_n)$$  \hspace{1cm} (S1)

Then Eq. 4 becomes:

$$S(B,\Omega_0) = \sum_{l=0}^{\infty} p_l \left\{ \sum_{n=-l}^{l} D_{on}^{(l)}(\Omega_0) \int_{\Omega'} D_{o\Omega}^{(l)}(\Omega') \omega(\Omega') f(B - B_r(\Omega')) d\Omega' \right\}$$  \hspace{1cm} (S2)

where the integration over $\Omega$ is replaced by an integration over $\Omega'$ since a set of orientations $(\Omega,\Omega_0)$ determines an orientation $\Omega'$ in a bi-univocal way. In the above equation:

$$\int_{\Omega'} D_{o\Omega}^{(l)}(\Omega') \omega(\Omega') f(B - B_r(\Omega')) d\Omega' = \int_{\varphi=0}^{2\pi} d\varphi \int_{\theta=0}^{\pi} f(B - B_r(\theta)) \sin \theta d\theta \int_{\psi=0}^{2\pi} \omega(\varphi,\theta,\psi) D_{on}^{(l)}(\varphi,\theta,\psi) d\psi$$  \hspace{1cm} (S3)

For weakly anisotropic $g$-factor as is the case here, $\omega(\varphi,\theta,\psi)$ is almost constant and will be dropped afterwards as it then appears as an irrelevant scaling factor.

From the property:

$$\int_{\varphi=0}^{2\pi} D_{o\Omega}^{(l)}(\varphi,\theta,\psi) d\psi = \begin{cases} 0 & \text{if } n \neq 0 \\ 2\pi D_{o0}^{(l)}(0,\theta,0) & \text{if } n = 0 \end{cases}$$  \hspace{1cm} (S4)

we get:

$$S(B,\Omega_0) = (2\pi)^2 \sum_{l=0}^{\infty} p_l D_{o0}^{(l)}(\Omega_0) \int_{\theta=0}^{\pi} D_{o0}^{(l)}(0,\theta,0) f(B - B_r(\theta)) \sin \theta d\theta$$  \hspace{1cm} (S5)

and since $D_{o0}^{(l)}(\Omega_0) = p_l (\cos \beta_0)$ and $D_{o0}^{(l)}(0,\theta,0) = p_l (\cos \theta)$, we finally get Eq. 7:

$$S(B,\Omega_0) = S(B,\beta_0) = \sum_{l=0}^{\infty} p_l p_l (\cos \beta_0) \int_{\theta=0}^{\pi} f(B - B_r(\theta)) p_l (\cos \theta) \sin \theta d\theta$$  \hspace{1cm} (S6)

after dropping the irrelevant $(2\pi)^2$ factor.

2. Numerical calculation of the coefficients $p_l$ from experimental EPR spectra

For practical implementation, the discrete summation over $l$ in Eq. S6 must be truncated to a finite order $l_{\text{max}}$. In addition, EPR spectra are recorded for a finite discrete set of $m$ field values $(B_i)_{i=1,\ldots,m}$. For a specific orientation $\beta_{0,k}$ ($k = 1,\ldots,n$) in a set of $n$ different orientations of the sample in the laboratory frame, we then define a matrix $G(\beta_{0,k})$ with elements:

$$G_{ij}(\beta_{0,k}) = p_{2(j-1)} (\cos \beta_{0,k}) \int_{\theta=0}^{\pi} f(B_i - B_r(\theta)) p_{2(j-1)} (\cos \theta) d\cos \theta$$  \hspace{1cm} (S7)

with $j = \frac{l}{2} + 1$, which runs from 1 to $N = \frac{l_{\text{max}}}{2} + 1$ by step of 1 when $l$ runs from 0 to $l_{\text{max}}$ by step of 2, since $l$ is even. In practice, the integral in Eq. S7 is replaced by a discrete summation and a Voigt line shape is used for $f(B_i - B_r(\theta))$. The theoretical EPR spectrum at orientation $\beta_{0,k}$ is then expressed as an $m$-line column vector:
\[ S_k^{th} = G(\beta_{0,k}) \left( \begin{array}{c} p_0 \\ \vdots \\ p_{l_{\text{max}}} \end{array} \right) \]  

The best estimates of the unknown coefficients \((p_0, \ldots, p_{l_{\text{max}}})\) are obtained by minimizing:

\[ L^2 = \sum_{k=1}^{n} \| S_k^{\text{exp}} - S_k^{th} \|^2 \]  

which represents the squared distance between all theoretical spectra \(S_k^{th}\) and experimental spectra \(S_k^{\text{exp}}\), with respect to the variations of the coefficients \(p_i\). The best estimates are then given by:

\[ \left( \begin{array}{c} p_0 \\ \vdots \\ p_{l_{\text{max}}} \end{array} \right) = \left( \sum_{k=1}^{n} G(\beta_{0,k})^T G(\beta_{0,k}) \right)^{-1} \left( \sum_{k=1}^{n} G(\beta_{0,k})^T S_k^{\text{exp}} \right) \]  

where the upper script \(T\) denotes the transposed matrix.
3. Matlab script for the calculation of the orientation probability density

clear;

[B_exp_angle,spc_exp,Params]=eprload('Experimental spectrum file name');

% B_exp_angle: cell containing the experimental magnetic field values and
% the rotation angles
% spc_exp: experimental EPR spectra at different orientations
% Params : cell containing the EPR acquisition settings
% eprload : Function in Easyspin allowing the loading of EPR spectra in
% Bruker format

B_exp_angle{1,1}=B_exp_angle{1,1}/10; % G to mT conversion of magnetic
fields

size_Bexp=size(B_exp_angle{1,1});
index_point_B250=find(B_exp_angle{1,1}>=250); % indices of all points such
as field >= 250 mT
index_point_B400=find(B_exp_angle{1,1}>=400); %indices of all points such as
field >= 400 mT

% Restriction of the experimental spectra to 250 mT < field <400 mT
Bmax=B_exp_angle{1,1}(index_point_B400(1));
Bmin=B_exp_angle{1,1}(index_point_B250(1));
B_sweep = Bmax-Bmin; % magnetic field interval width

length_spc_exp=size(spc_exp);
for i=1:length_spc_exp(2)
    spc_exp(:,i)=spc_exp(:,i)-spc_exp(index_point_B400(1),i); % base line
    set to 0
end

% PLOT THE SUPERPOSED SPECTRA SET
{%
figure;
hold on
for j=1:2:19
    plot(B_exp_angle{1,1},spc_exp(:,j))
end
hold off
%

Sys.S=1/2; % Electron spin of Cu2+
Sys.g=[2.055 2.34]; % [g_perpendicular g_parallel] g-factors for Cu2+

Param.mwFreq = Params.MWFQ/10^9; % Experimental microwave frequency
Param.Range = [Bmin Bmax]; % Magnetic field range

[phi,theta,weight]= sphgrid('Dinfh',100); % Set of orientations of the
magnetic field in the molecular frame for a magnetic system with axial
symmetry

Param.CrystalOrientation = transpose([phi; theta; weight]);
resfields = resfields(Sys, Param); % resfields : Easyspin function to compute the resonance fields (pos) and transition probabilities (amp)

% Calculation of the EPR spectra

nb_trans = size(pos); % number of calculated EPR transitions
nb_orientations = size(theta); % number of field orientations in the molecular frame
beta0 = B_exp_angle{1,2}*pi/180; % conversion of angles in radian
max_spectre = 19; % number of spectra at different sample orientations
max_order = 16; % highest order of the Legendre polynomials in the expansion of the probability density P(beta)

A_l = [];
for l = 0:2:max_order
    sum = 0;
    for i = 1:nb_trans(1)
        for k = 1:nb_orientations(2)
            w_i_thetak = amp(i,k);
            P_l_thetak = legendreP(l, cos(theta(k)));
            B_res_i_k = pos(i,k);
            if isnan(B_res_i_k) == 0
                fwhmGL = [0.86+sqrt(6.1^2*cos(theta(k))^2+3.4^2*sin(theta(k))^2)]; % width at half maximum for gaussian and lorentzian component of the EPR line shape
                f_B_Bres_i_k = voigtian(B_exp_angle{1,1}(index_point_B250(1):index_point_B400(1)),
                B_res_i_k, fwhmGL,1);
                sum = sum + P_l_thetak * w_i_thetak * f_B_Bres_i_k * weight(1,k);
            end
        end
    end
    A_l = [A_l, transpose(2*pi*sum)];
end

G = {};
sum_GS = 0;
sum_GG = 0;
for num_spectrum = 1:max_spectre
    G_beta = [];
    for l = 0:2:max_order
        P_l_beta = legendreP(l, cos(beta0(num_spectrum)));
        G_beta = [G_beta, P_l_beta*A_l(:,l/2+1)];
    end
    G{end+1} = G_beta;
    sum_GS = sum_GS + transpose(G_beta) * spc_exp(index_point_B250:index_point_B400,num_spectrum);
    sum_GG = sum_GG + transpose(G_beta)*G_beta;
end

p_matrix = inv(sum_GG)*sum_GS;

% Plot of experimental and calculated spectra
for num_spectrum_reconstitute=1:1:max_spectre
    spc_th = G{1,num_spectrum_reconstitute}* p_matrix; % Calculates the theoretical EPR spectrum

    figure;
    plot(B_exp_angle{1,1}(index_point_B250(1):index_point_B400(1)),transpose(spc_th), B_exp_angle{1,1}(index_point_B250(1):index_point_B400(1)),spc_exp(index_point_B250:index_point_B400,num_spectrum_reconstitute));
end

% Plot of the probability density

betas=linspace(0,pi,480);
distrib_beta_i=[];
distrib_deconv=[];
for beta=betas
    legendres=[];
    for l=0:2:max_order
        legendres = [legendres, legendreP(l,cos(beta))];
    end
    proba_beta_i = legendres*p_matrix;
    distrib_beta_i=[distrib_beta_i, proba_beta_i];
end

distrib_beta_i_norm=distrib_beta_i/trapz(betas,4*pi*pi*distrib_beta_i.*sin(betas)); % normalisation of the probability density
p_matrix=p_matrix/trapz(betas,4*pi*pi*distrib_beta_i.*sin(betas));% normalisation of the p_l coefficients

figure;
polarplot([betas,betas+pi], [distrib_beta_i_norm,distrib_beta_i_norm])% plot in polar coordinate the orientation probability density
hold on
polarplot([betas,betas+pi], 1/(8*pi*pi)*ones(2*size(betas)))% plots the isotropic probability density
3. Experimental and calculated EPR spectra

**Figure S1.** Experimental (black) and calculated (red) EPR spectra of microcrystals of cuprorivaite magnetically oriented in fluid oil for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis. The rotation axis is $Y_0$ and the sample was set with $Y \parallel Y_0$. 
Figure S2. Experimental (black) and calculated (red) EPR spectra of microcrystals of cuprorivaite in a dried oil film deposited with an applicator for different orientations of the measuring field with respect to the sample $X$-axis, upon rotation about the $Z$-axis. The rotation axis is $Y_0$ and the sample was set with $Z \parallel Y_0$. 
Figure S3. Experimental (black) and calculated (red) EPR spectra of microcrystals of cuprorivaite in a dried oil film deposited with an applicator for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis. The rotation axis is Y₀ and the sample was set with Y \parallel Y₀.
Figure S4. Experimental (black) and calculated (red) EPR spectra of microcrystals of cuprorivaite in a dried oil film deposited with paintbrush for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis. The rotation axis is Y₀ and the sample was set with Y \parallel Y₀.
Figure S5. Experimental (black) and calculated (red) EPR spectra of microcrystals of cuprorivaite in a dried oil deposited as a droplet for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis. The rotation axis is $Y_0$ and the sample was set with $Y \parallel Y_0$. 
Figure S6. Experimental (black) and calculated (red) EPR spectra of microcrystals of cuprorivaite in a dried oil deposited by dabbing for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis. The rotation axis is Y₀ and the sample was set with Y || Y₀.