Supporting Information

ESR evidence for two coexisting liquid phases in deeply supercooled bulk water

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ESR spectroscopy of spin probes: an introduction

The Electron Spin Resonance (ESR) is a spectroscopy observing a paramagnetic system situated in a static magnetic field $\boldsymbol{B}_0$ and forced by an oscillating magnetic field $\boldsymbol{B}_1(t) \perp \boldsymbol{B}_0$. Our system of interest is a single unpaired electron located in a free radical (spin probe) being dissolved as a guest molecule in a diamagnetic liquid. The mutual interactions between the spin probes are negligible owing to their low concentration and one has to consider the intramolecular interactions only. The ESR spectroscopy provides information on both the statics and the dynamics of the *orientational* degrees of freedom of the spin probe. To get to that information the quantitative description of the coupling between the magnetic properties and the orientation of the spin probe must be carried out in terms of quantum mechanics.

1 Spin hamiltonian

The electron has a magnetic dipole moment $\boldsymbol{m}$ which stems from its intrinsic angular moment (spin) $\hbar\boldsymbol{S}$ with $\hbar = h/2\pi$, h being the Planck constant. For a free electron $\boldsymbol{m} = -g_e\beta_e\boldsymbol{S}$ where $g_e = 2.0023$ and β_e are the electron Lande' g-factor and the Bohr magneton, respectively. The coupling of the magnetic moment $\boldsymbol{m}$ with $\boldsymbol{B}_0$ (Zeeman coupling) is expressed by the hamiltonian $\mathcal{H}_z \; = \; -\boldsymbol{m}\cdot\boldsymbol{B}_0 = g_e\beta_e\boldsymbol{S}\cdot\boldsymbol{B}_0$. In the nitroxide spin probes there is also a magnetic coupling (hyperfine coupling) between the unpaired electron and the close nitrogen nucleus with magnetic dipole moment $\boldsymbol{m}_n = +g_n\beta_n\boldsymbol{I}$, where g_n β_n and $\boldsymbol{I}$ are the nuclear g-factor, magneton and spin ($I = 1$), respectively (fig.S1 a).

In addition to the spin, the magnetic properties of the unpaired electron are also set by the orbital angular momentum $\boldsymbol{L}$. Even if $\boldsymbol{L}$ does not affect the electron dipole moment at first order, second-order effects are possible via the spin-orbit interaction (due to the magnetic field in the rest frame of the electron originated by its motion through the molecular electric field). Usually, one does not consider the complete hamiltonian including both the orbital and the spin degrees of freedom but, rather, an effective hamiltonian derived by averaging over all the spatial variables [1]. The resulting quantity, consisting of parameters and spin operators, is called a *spin hamiltonian.* In nitroxide free-radicals the orbital part of the unpaired electron wave function exhibits the local symmetry of the highly-directional NO bond where it is localized (fig.S1a). As a consequence, the orbital average leads to express the Zeeman and the hyperfine interactions in terms of the tensors $\boldsymbol{g}$ and $\boldsymbol{A}$, respectively and the spin hamiltonian takes the form:

$$\mathcal{H} = \beta_e \boldsymbol{B}_0 \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{A} \cdot \boldsymbol{I} \tag{1}$$

$\boldsymbol{g}$ and $\boldsymbol{A}$ have coinciding principal axis (fig.S1a). We define $g = Tr[\boldsymbol{g}]/3$ and $A = Tr[\boldsymbol{A}]/3$, where Tr denotes the trace operation. It is also convenient to consider the largest differences between the principal values of the $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors, ΔA and Δg respectively.

2 Lineshape analysis

2.1 No tumbling: powder lineshape

We first consider the spin probes as immobile in a frozen host with isotropic distribution of their orientations. In that case the energy levels of the spin hamiltonian, Eq.1, are (fig.S1 b,c) [2]:

$$E_{m_s,M}(\boldsymbol{n}) = \left[\sum_{i=x,y,z} g_i^2 n_i^2\right]^{1/2} \beta_e B_0 m_s + \left[\sum_{i=x,y,z} A_i^2 n_i^2\right]^{1/2} m_s M \tag{2}$$

with $m_s = \pm 1/2, M = \pm 1, 0$ and $\boldsymbol{B}_0 = \boldsymbol{n} B_0$, where $\boldsymbol{n} \equiv (n_x, n_y, n_z)$ denotes the direction cosines of $\boldsymbol{B}_0$ with respect to the principal axis of the magnetic tensors $\boldsymbol{g}$ and $\boldsymbol{A}$. Eq.2 assumes that the $\boldsymbol{g}$ tensor is almost spherical, i.e. $\Delta g \ll g$.

Let us consider the simple case of no hyperfine interaction , $\boldsymbol{A} = 0$ (fig.S1b). A transition is induced by the microwave field when its angular frequency ω equals the Larmor frequency $\omega_0(\boldsymbol{n}) = (E_{1/2} - E_{-1/2})/\hbar$:

$$\omega_0(\boldsymbol{n}) = \left[\sum_{i=x,y,z} g_i^2 n_i^2\right]^{1/2} \frac{\beta_e B_0}{\hbar} \tag{3}$$

Owing to the orientation distribution of the spin probes, and then of $\boldsymbol{n}$, $\omega_0(\boldsymbol{n})$ exhibits a distribution resulting in a broad absorption line when ω is swept (fig.S2 top left). In the actual ESR experiment one sweeps $\boldsymbol{B}_0$ while keeping constant the ω frequency and the absorption is observed in derivative mode, due to the phase-sensitive signal detection. The field-swept derivative pattern of the ESR lineshape in the absence of spin-probe motion (powder lineshape) shows sharp details which allow one to measure the principal values of the Zeeman $\boldsymbol{g}$ tensor (fig.S2 top right).

If the hyperfine tensor is present as in the nitroxides spin probes, three transitions are seen when the angular frequency of the microwave field ω equals the transition frequencies $\omega_M(\boldsymbol{n}) = (E_{1/2,M} - E_{-1/2,M})/\hbar$, $M = \pm 1, 0$ (see fig.S1c):

$$\omega_M(\boldsymbol{n}) = \left[\sum_{i=x,y,z} g_i^2 n_i^2 \right]^{1/2} \frac{\beta_e B_0}{\hbar} + \frac{1}{\hbar} \left[\sum_{i=x,y,z} A_i^2 n_i^2 \right]^{1/2} M, \quad M = \pm 1, 0 \tag{4}$$

The powder lineshape is given by the sum of three components, corresponding to the three possible transitions (see fig.S 1 bottom) and each labeled by one value of the nuclear quantum number M (fig.S3 top). Also in the presence of the hyperfine interaction the principal values of both the $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors may be measured by the powder lineshape [3].

2.2 Tumbling: Motional narrowing of the ESR lineshape

To deal with the reorientation of the spin probes, it is convenient to consider the spin hamiltonian $\mathcal{H}$, Eq.1, as a sum of two contributions: an isotropic orientationally invariant part $\mathcal{H}_0$ and an orientation-dependent part $\mathcal{H}_1$. The explicit form of $\mathcal{H}_0$ is:

$$\begin{aligned} \mathcal{H}_0 &= g\beta_e \boldsymbol{B}_0 \cdot \boldsymbol{S} + A\boldsymbol{S} \cdot \boldsymbol{I} && (5) \\ &\simeq g\beta_e B_0 S_Z + A S_Z I_Z && (6) \end{aligned}$$

Eq.6 well approximates Eq.5 since $\boldsymbol{B}_0$, which defines the laboratory Z axis, is strong, namely $g\beta_e B_0 \gg A$. The energy levels of $\mathcal{H}_0$, as given by Eq.6, are:

$$E^{(0)}_{m_s,M} = g\beta_e B_0 m_s + A m_s M, \qquad m_s = \pm 1/2, M = \pm 1, 0 \tag{7}$$

They are still represented by the pattern in Fig.S1c. The explicit form of the orientation-dependent part $\mathcal{H}_1$ is:

$$\mathcal{H}_1 = \beta_e \boldsymbol{B}_0 \cdot \boldsymbol{g}' \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{A}' \cdot \boldsymbol{I} \tag{8}$$

where $\boldsymbol{g}'$ and $\boldsymbol{A}'$ are traceless tensors. When the spin probe reorients, $\mathcal{H}_1$ is a random function of time. This is made explicit by considering the time-dependent rotation matrix $\mathcal{R}$

$$\mathcal{R}(t) = \{\boldsymbol{n}_X(t), \boldsymbol{n}_Y(t), \boldsymbol{n}_Z(t)\} \tag{9}$$

transforming the electron and nuclear spins from the fixed laboratory frame $\{X, Y, Z\}$, where they are quantized, to the rotating principal axis of the magnetic tensors $\{x, y, z\}$ (Fig.S1a). The unit vector $\boldsymbol{n}_i$, with $\boldsymbol{n}_Z \equiv \boldsymbol{n}$, encloses the direction cosines of the i-th laboratory axes with respect to the magnetic principal axis. Then, Eq.8 is rewritten in the explicit time-dependent form

$$\mathcal{H}_1(t) = \beta_e \boldsymbol{B}_0 \cdot {}^T\mathcal{R}(t)\,\widetilde{\boldsymbol{g}}\,\mathcal{R}(t) \cdot \boldsymbol{S} + \boldsymbol{S} \cdot {}^T\mathcal{R}(t)\,\widetilde{\boldsymbol{A}}\,\mathcal{R}(t) \cdot \boldsymbol{I} \tag{10}$$

where ${}^T\mathcal{R}$ is the transpose of $\mathcal{R}$ and

$$\widetilde{\boldsymbol{g}} = \begin{pmatrix} g_x - g & 0 & 0 \\ 0 & g_y - g & 0 \\ 0 & 0 & g_z - g \end{pmatrix} \quad \widetilde{\boldsymbol{A}} = \begin{pmatrix} A_x - A & 0 & 0 \\ 0 & A_y - A & 0 \\ 0 & 0 & A_z - A \end{pmatrix} \tag{11}$$

2.2.1 Fast tumbling: Redfield limit

If the rotation is very fast, i.e. the rotational correlation time τ fullfills the inequalities $\Delta A, \Delta g \beta_e B_0 \ll \tau^{-1}$ (in practice $\tau \lesssim 1ns$) , $\mathcal{H}_1$ is almost averaged out and the ESR lineshape, which is quite broad if no motion is present (see Figs.S2, S3 top), experiences a strong "motional narrowing" [1]. The lineshape reduces to one peak if the hyperfine tensor $\boldsymbol{A} = 0$ (fig.S2 bottom), or, if $\boldsymbol{A} \neq 0$ as in nitroxides, to three peaks (fig.S3 bottom), corresponding to the possible transitions induced by the microwave field (fig.S1). The peak positions are set by Eq.7 and the resonance conditions $\omega = \hbar^{-1}(E^{(0)}_{1/2,M} - E^{(0)}_{-1/2,M})$, $M = \pm 1, 0$ which read:

$$\omega = \hbar^{-1}(g\beta_e B_0 + AM) \qquad M = \pm 1, 0 \tag{12}$$

If $\boldsymbol{A} = 0$ the position of the single peak is set by the condition $\omega = \hbar^{-1} g \beta_e B_0$. In the limit of fast tumbling the lineshape was expressed analytically without relying on any specific rotational model (Redfield theory) [5]. It is found that each peak is lorentzian in shape with width given by [4]:

$$T_2^{-1}(M) = \alpha + \beta\, M + \gamma\, M^2, \qquad M = \pm 1, 0 \tag{13}$$

The analytic expressions of the coefficients α, β, γ for $\boldsymbol{A} \neq 0$ were derived elsewhere (if $\boldsymbol{A} = 0$, $\beta = \gamma = 0$) [4]. They are given in terms of the principal values of both the $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors and the rotational correlation time which for a spherical molecule like TEMPOL is defined as:

$$\tau = \int_0^\infty \frac{3\cos^2\zeta(t) - 1}{2} dt \tag{14}$$

where $\zeta(t)$ is the angle spanned by one molecular axis in a time t.

2.2.2 Slow tumbling

If τ exceeds a few nanoseconds, the widths of the narrow lines increase and in the limit $\tau \to \infty$ the lineshape recovers the powder lineshape. In the "slow tumbling" regime of long, but finite, τ values the analytic lineshape theory presented in Sec.2.2.1 fails and one must resort to sophisticated approaches. In the present work the lineshape $L(B_0)$ recorded by sweeping the static magnetic field B_0 is evaluated by a stochastic memory-function approach [6] which is briefly outlined. The starting point is writing $L(B_0)$ as the Laplace transform of the correlation function of the perpendicular component of the magnetic dipole moment of the spin probe $\boldsymbol{m} = -g_e \beta_e \boldsymbol{S}$ perpendicular to $\boldsymbol{B}_0$ [1, 7] :

$$\begin{aligned} L(B_0) &= C \frac{\partial}{\partial B_0} \Re \int_0^\infty < m_x m_x(t) > e^{i \frac{g_e \beta_e B_0}{\hbar} t} dt \qquad (15) \\ &= C' \frac{\partial}{\partial B_0} \Re \int_0^\infty < S_x S_x(t) > e^{i \frac{g_e \beta_e B_0}{\hbar} t} dt \qquad (16) \end{aligned}$$

The brackets indicate a proper thermal average, C is a constant, $\Re z$ is the real part of z, and $i^2 = -1$. The derivative takes into account that the lineshape is usually displayed in derivative mode. The correlation function $< S_x S_x(t) >$ is evaluated by the *quantum* time evolution of the electron spin under the influence of the reorientation of the spin probe according to the equation of motion [1, 7]:

$$\frac{\partial}{\partial t} S_x = \frac{1}{\hbar} [\mathcal{H}, S_x] + \Gamma S_x \qquad (17)$$

where $[A, B] = AB - BA$ and the spin hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, with $\mathcal{H}_0$ and $\mathcal{H}_1$ given by Eq.6 and 10, respectively. The Γ operator describes the rotational motion of the spin probe by considering its orientation as a *classical, stochastic* variable. For a nearly spherical molecule rotating by instantaneous random jumps of fixed size θ after a mean residence time τ_0, according to the irreducible representation of the rotation group of rank ℓ, Γ is a multiple of the identity operator I_ℓ, Γ_ℓ, which is given by [7]:

$$\Gamma_\ell = \frac{1}{\tau_0} (\gamma_\ell I_\ell - 1) \qquad \gamma_\ell = \frac{1}{2\,\ell + 1} \frac{\sin[(\ell + 1/2)\theta]}{\sin(\theta/2)} \qquad (18)$$

and the related correlation time τ (Eq.14) takes the form:

$$\tau = \tau_0 / [1 - \sin(5\theta/2) / (5 \sin(\theta/2))] \qquad (19)$$

By using a suitable memory-function approach, it is possible to derive an exact expression of the Laplace transform $< \widehat{S_x S_x(z)} >$ as a continued-fraction expansion [6]:

$$< \widehat{S_x S_x(z)} > = \cfrac{< S_x^2 >}{z - \lambda_0 + \cfrac{\Delta_1^2}{z - \lambda_1 + \cfrac{\Delta_2^2}{z - \lambda_2 + \cdot}}} \tag{20}$$

where λ_i and Δ_i^2 are (complex) constants depending on the principal values of the $\widetilde{\boldsymbol{g}}$ and $\widetilde{\boldsymbol{A}}$ tensors (Eq.11) and the parameters θ and τ_0.

The middle panels of Fig.S2 and Fig.S3 show typical patterns in the slow-tumbling regime if $\boldsymbol{A} = 0$ and $\boldsymbol{A} \neq 0$ as in nitroxides, respectively. Note that in the latter case the resulting three lines, corresponding to the three possible transitions induced by the microwave field (see fig.S 1 bottom), overlap resulting in a complex pattern.

References

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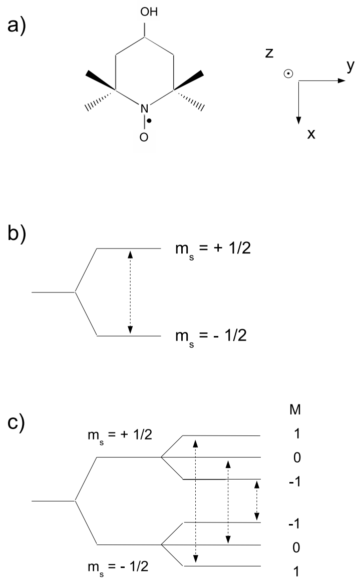

Fig. S 1: a) The structure of the spin probe free-radical TEMPOL. The unpaired electron is located in the NO bond. The magnetic principal axis are drawn. The principal values of the Zeeman $\boldsymbol{g}$ and the hyperfine $\boldsymbol{A}$ tensors of TEMPOL in water are: $g_{xx} = 2.0093, g_{yy} = 2.0064, g_{zz} = 2.00215$; $A_{xx} = 18.76\,MHz, A_{yy} = 19.88\,MHz, A_{zz} = 104.4\,MHz$, respectively. b) The energy levels of an electron with spin $S = 1/2$ in the static magnetic field $\boldsymbol{B}_0$ ($\boldsymbol{g} \neq 0, \boldsymbol{A} = 0$). c) Same as in b) including the hyperfine interaction with a nucleus with spin $I = 1$ ($\boldsymbol{g} \neq 0, \boldsymbol{A} \neq 0$). m_s and M are the projections of the electron and the nuclear spin along the direction of the static magnetic field, respectively. The dashed arrows denote the transitions induced by the oscillating microwave field applied by the ESR spectroscopy.

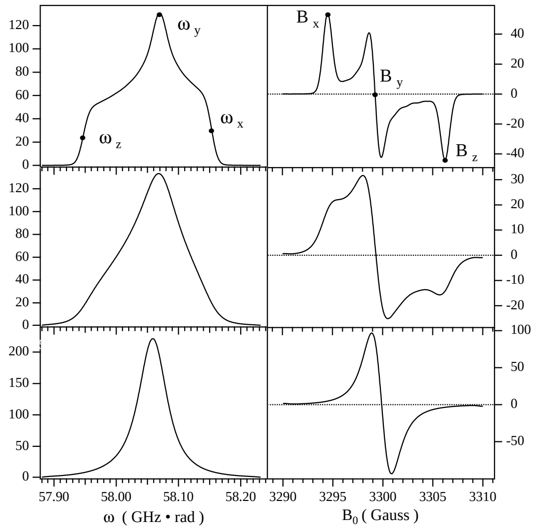

Fig. S 2: Theoretical ESR lineshapes of a spin probe ($g_x = 2.0093, g_y = 2.0064, g_z = 2.00215$, $\boldsymbol{A} = 0$) undergoing reorientation with jump angle $\theta = 80°$ and rotational correlation times $\tau = 900$ (top), 45 (middle), $9ns$ (bottom). The lineshapes are convoluted by a lorentzian with width $1/T_2^\star = 5.26\,MHz$ to account for the changes of the Larmor frequency, occurring each $T_2^\star$ on average, due to the magnetic field produced by the rotating methyl groups close to the unpaired electron. left: Absorption vs. frequency of the microwave field for constant magnetic field $B_0^\star = 3300\,Gauss$. Right: Absorption in derivative mode vs static magnetic field for constant microwave frequency $\omega^\star = 58.05\,rad \cdot GHz$. The lineshapes with $\tau = 900\,ns$ are virtually coincident with the powder lineshapes corresponding to immobile spin probes in a frozen host. Dots locate the frequencies $\omega_i = g_i \beta_e B_0^\star/\hbar$ (left) and magnetic fields $B_i = \hbar\omega^\star/g_i\beta_e$ (right) values with $i = x, y, z$. Note that the ESR lineshapes in Fig.1d correspond to $g_x = g_y = 2.0064, g_z = 2.00215$, $\boldsymbol{A} = 0$.

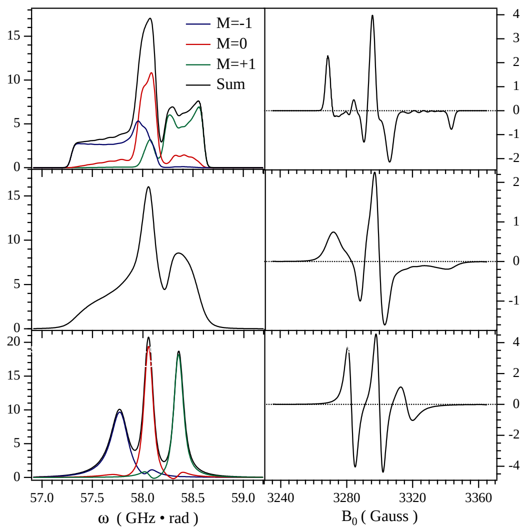

Fig. S 3: Theoretical ESR lineshapes of a nitroxide spin probe ($\boldsymbol{g}$ tensor as in Fig.S2 , $A_x = 18.76\, MHz, A_y = 19.88\, MHz, A_z = 104.4\, MHz$, $T_2^\star = 56\, ns$) undergoing reorientation with jump angle $\theta = 80°$ and rotational correlation times $\tau = 860$ (top), 9.04 (middle), $1.81\, ns$ (bottom). left: Absorption vs. frequency of the microwave field for constant magnetic field $B_0^\star = 3300\, Gauss$. Right: Absorption in derivative mode vs static magnetic field for constant microwave frequency $\omega^\star = 58.05\, rad \cdot GHz$. The lineshapes with $\tau = 860\, ns$ (top panel) are virtually coincident with the powder lineshapes corresponding to immobile spin probes in a frozen host. In that case the three hyperfine components with $M = \pm 1, 0$, corresponding to the three possible transitions (see fig.S 1 bottom), are explicitly shown. The motional narrowing reduces the three components to three distinct lines when the spin probe rotates fast (bottom panel).