Supporting Information of the paper
"Rotation of Four Small Nitroxide Probes in Supercooled Bulk Water"
by
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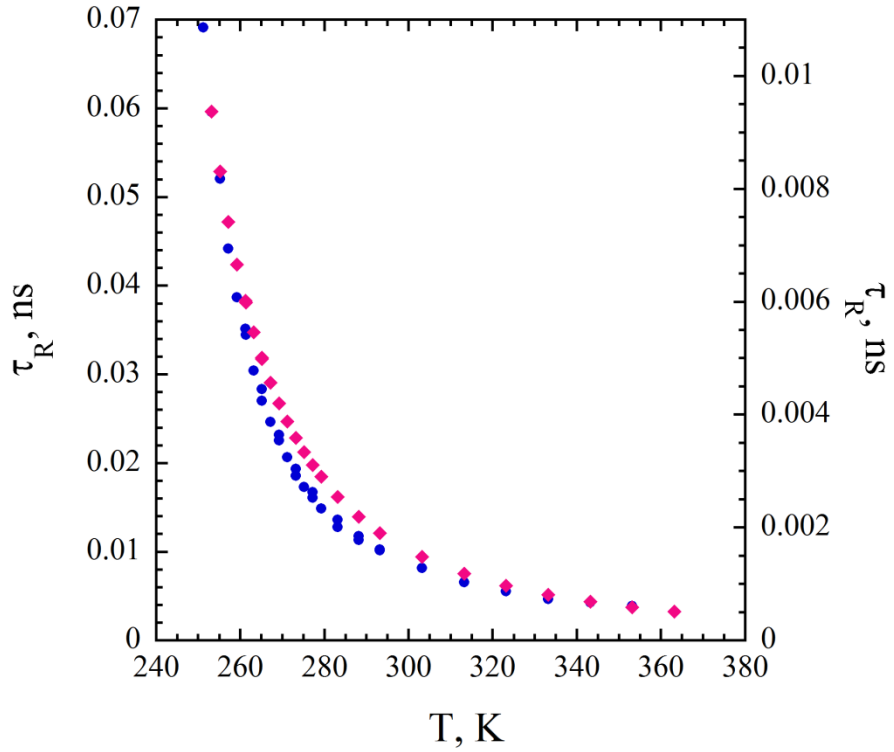

Figure S1. Rotational correlation time τ_R of pDT (circles), left ordinate, and τ_R of water (diamonds) calculated using eq 2.4 from ref [1], right ordinate, as a function of temperature.

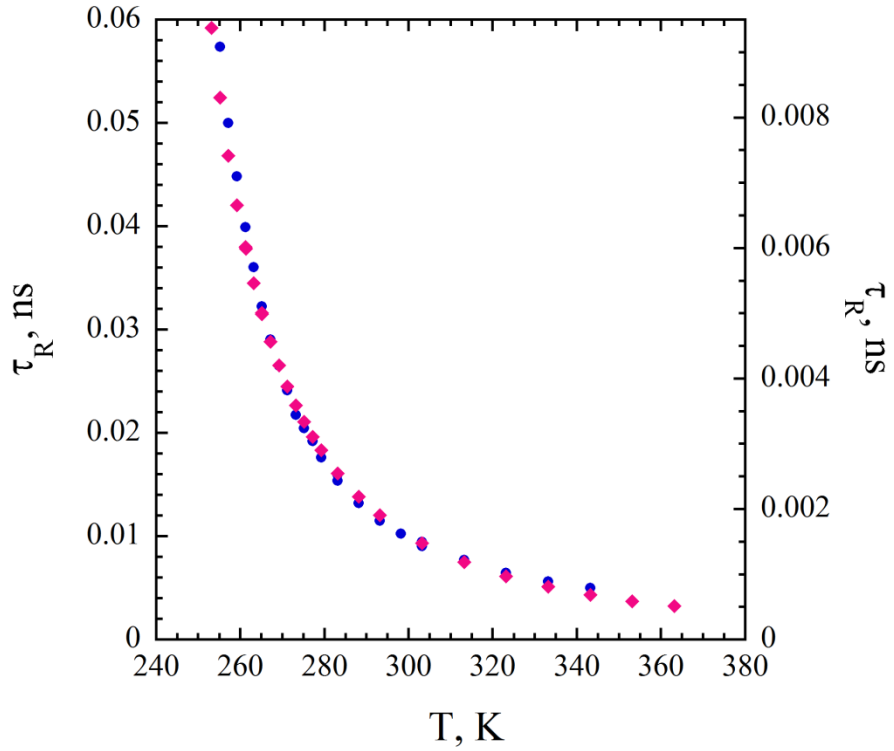

Figure S2. Rotational correlation time τ_R of pDTO (circles), left ordinate, and τ_R of water (diamonds) calculated using eq 2.4 from ref [1], right ordinate, as a function of temperature.

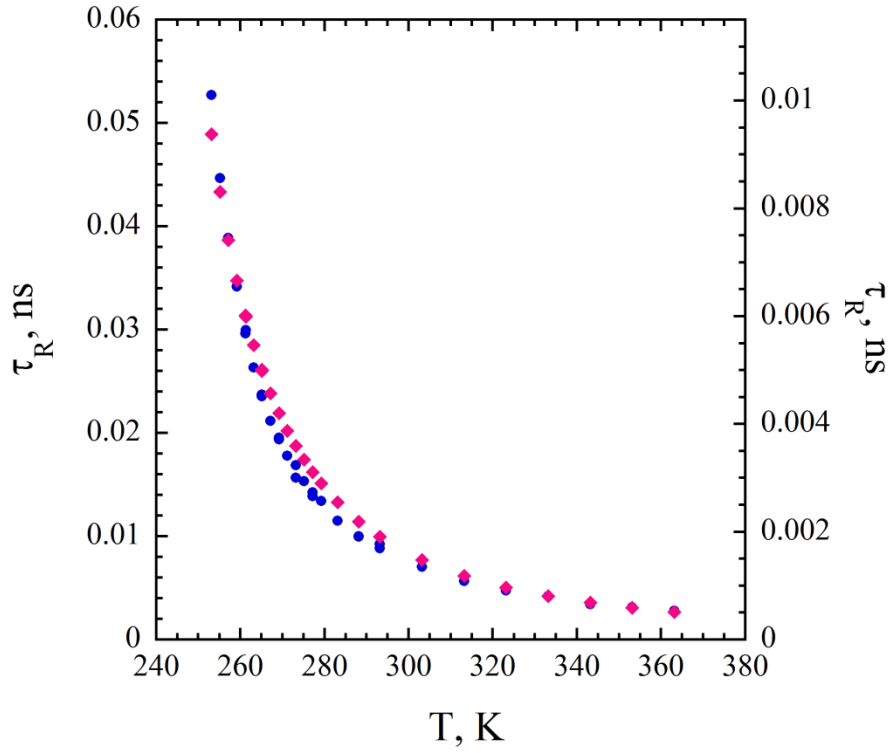

Figure S3. Rotational correlation time τ_R of DTBN (circles), left ordinate, and τ_R of water (diamonds) calculated using eq 2.4 from ref [1], right ordinate, as a function of temperature.

The EPR lines of nitroxide spin labels are usually inhomogeneously broadened due to unresolved hyperfine structure. The inhomogeneous EPR line shape can be represented with both good fidelity and good justification by the first derivative Voigt line shape: [2,3]

$$V(\upsilon) = (3\left(\frac{2}{3\pi}\right)^{\frac{3}{2}}\chi A/(\Delta B_{pp}^{G})^{2})\int_{-\infty}^{\infty}\frac{2xe^{-x^2}}{1+(\frac{2}{3})\chi^2(\upsilon-x)^2}dx, \qquad \text{(S1)}$$

where

$$\upsilon = \sqrt{2}\frac{B-B_0}{\Delta B_{pp}^{G}}, \qquad x = \sqrt{2}\frac{B'-B_0}{\Delta B_{pp}^{G}} \qquad \text{and} \qquad \chi = \frac{\Delta B_{pp}^{G}}{\Delta B_{pp}^{L}}.$$

A is equal to the doubly integrated intensity of the EPR line, *B* represents the sweeping applied magnetic field, B_0 is the center of the EPR line, and χ is the ratio of the Gaussian peak-to-peak line width component of the Voigt, ΔB_{pp}^{G}, to the Lorentzian peak-to-peak line width component

of the Voigt, ΔB_{pp}^{L}. Eq 1 can be approximated to 0.5 % by the variable weighted sum of the derivatives of the Lorentzian and Gaussian lines of equal line widths:[3]

$$V(y(B)) = -V_{pp}(\eta \frac{8y}{(3+y^2)^2} + (1-\eta)\frac{e^{\frac{1}{2}}y}{2}\exp(-\frac{y^2}{2})) \qquad \text{(S2)}$$

where V_{pp} is the peak-to-peak height, $y = 2\frac{B-B_0}{\Delta B_{pp}^{O}}$, where ΔB_{pp}^{O} is the observed peak-to-peak line width and η is a normalized variable-weight term.

Table S1. g and A principal values used in the calculations of τ_R. The values for pDTOH are adjusted to be comparable to the values in ref [4] and give the isotropic A and g values we measured experimentally.

	g_{xx}	g_{yy}	g_{zz}	g_{iso}	A_{xx}/G	A_{yy}/G	A_{zz}/G	A_{iso}/G
pDT	2.0088	2.0061	2.0023	2.0057	7.0	7.0	38.1[1]	17.37
pDTO	2.0082	2.0059	2.0025	2.0055	5.8	5.8	36.6[1]	16.07
pDTOH	2.0085	2.0058	2.0024	2.0056	7.2	7.2	36.8	17.07
DTBN[2]	2.0084	2.0056	2.0022	2.0054	8.24	6.50	36.9	17.21

1. Ref [5]
2. Ref [6]

In order to demonstrate our spectral fitting method, Table S2 shows the values of the Gaussian line widths for all probes at 298 K, extracted by spectral fitting, compared with the values from ref [2], which are calculated from the hyperfine pattern of each probe. As can be seen in Table S2, the agreement between the measured (column 2) and calculated (column 4) values is rather good.

Table S2. Gaussian line width, $\Delta H_{pp}^{G}(0)$, at zero modulation[7] at 298 K.

	$\Delta H_{pp}^{G}(0)$, G	± std, G	$\Delta H_{pp}^{G}(0)$, [3] G
pDT	0.287	0.010	0.267
pDTO	0.097	0.011	0.054
pDTOH	0.385	0.005	0.355
DTBN[2]	0.292	0.011	0.260

3. Ref [2]

References:

(1) Qvist, J.; Schober, H.; Halle, B. Structural Dynamics of Supercooled Water from Quasielastic Neutron Scattering and Molecular Simulations; *J. Chem. Phys.* **2011**, 134, 144508;144501-144520.

(2) Bales, B. L. In *Spin Labeling: Theory and Applications*; Berliner, J. L., Reuben, J., Eds.; Plenum: New York, 1989; Vol. 8, p 77-130.

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(7) Bales, B. L.; Peric, M.; Lamy-Freund, M. T. Contributions to the Gaussian Line Broadening of the Proxyl Spin Probe EPR Spectrum Due to Magnetic-Field Modulation and Unresolved Proton Hyperfine Structure; *J. Mag. Reson.* **1998**, 132, 279-286.