

**Coexistence of two molecular environments in liquid *cis*-decalin
revealed by spin probe**

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Abstract

We used a nitroxide radical as a spin probe in electron paramagnetic resonance (EPR) to study the highly fragile glass-forming molecular liquid *cis*-decalin and the similar liquid *cis*-perfluorodecalin. EPR spectra of the radical dissolved in *cis*-decalin were measured upon cooling from its equilibrium liquid state at 373 K to its supercooled state below 229 K. Analysis of the EPR spectra revealed the anomalous temperature behavior of the EPR parameters and rotational diffusivity of the radical in *cis*-decalin, which was not found in *cis*-perfluorodecalin. The anomalous behavior in *cis*-decalin led us to conclude that a distinct slow environment appears around the radical upon cooling through the equilibrium state, and that the exchange rate between fast and slow radical environments decreases upon cooling into the supercooled state. Because of the slowing down of exchange, we were able to simulate the radical's low-temperature EPR spectra by two spectral components corresponding to the two radicals' environments. By using the theory of environment exchange in EPR, we performed the fitting of EPR parameters to determine temperature dependences of environment-exchange quantities and rotational radical diffusivities in each environment. The fraction of the slow environment was found to continuously grow on cooling, implying that *cis*-decalin does not exhibit liquid-liquid transition and fluid polyamorphism. However, the coexistence of two local liquid environments in *cis*-decalin deserves further examination as it may be closely related to very high fragility and other properties of this material. We broadly discuss our spin-probe results and their relations with the literature data for *cis*-decalin.

I. INTRODUCTION

There is both theoretical and practical interest in studying the rotational and translational diffusion of solvent molecules (self-diffusion) and diluted solute molecules (tracer diffusion) in water¹⁻⁴ and other molecular liquids with ionic⁵⁻⁸ and neutral⁹⁻¹³ constituents. Translational molecular diffusion is a fundamental process in solution chemistry, and tracer diffusion studies provide information about interactions between solute and solvent molecules. When the solute molecule is a long-lived free radical, its rotational and translational diffusion can be studied by electron paramagnetic resonance (EPR).¹⁴⁻¹⁶ Rotational diffusion of solvated radical modulates anisotropies of the g -tensor and hyperfine interactions of its unpaired electron spin. This affects the EPR spectrum of the radical and enables one to determine the radical's rotational diffusion coefficient (or diffusivity) from EPR spectral shape.^{14,17-19} Similarly, the relative translational diffusion of solvated radicals modulates their electron spin interactions and affects their EPR spectrum. This enables one to determine translational radical diffusivity by measuring the shape change of the EPR spectrum with radical concentration.^{14-16,20-23}

It is particularly interesting to study diffusion in glass-forming liquids,^{11-13,22,24} where translational diffusion exhibits crossover phenomena above the glass transition temperature T_g . The Stokes-Einstein violation appears below the crossover temperature $T_c \approx 1.2T_g$, which lies in the supercooled state below the melting temperature T_m . This phenomenon denotes a strong enhancement of translational tracer and self-diffusivity relative to the Stokes-Einstein law predictions below T_c , which is widely associated with the onset of spatially correlated and heterogeneous dynamics at T_c .¹¹⁻¹³ Rotational tracer and self-diffusivity studies revealed that the Stokes-Einstein violation below T_c is accompanied by the translation-rotation decoupling, or a

strong violation of the ratio of translational and rotational diffusivities that is expected from both the Stokes-Einstein law and the Stokes-Einstein-Debye law for rotational diffusivity.^{12,13}

The Arrhenius crossover occurs below the higher temperature T_A , which lies around or above T_m .^{12,13,22,24} In this phenomenon, the Arrhenius temperature dependence of translational self-diffusivity above T_A changes into a stronger non-Arrhenius one below T_A .²⁴ The Arrhenius crossover was also detected in the temperature dependence of the relaxation time and viscosity,²⁵ which is attributed to the onset of correlated and cooperative diffusive motion of molecules at T_A . This attribution was strengthened by the EPR study of translational radical diffusivity in glass-forming solvents.²² The radical diffusivities, being lower than the self-diffusivities at high temperatures, were found to approach the self-diffusivities by cooling below the onset temperature T_{on} . This crossover was explained by envisioning that radical diffusion, as a mostly single-molecule process above T_{on} , becomes more collective and cooperative below T_{on} . A general agreement between T_{on} and the temperature T_A estimated from viscosity indicates the same origin of both radical diffusion and Arrhenius crossovers.²²

The fragility of a glass former is a measure of the temperature sensitivity of its transport properties, such as viscosity η near T_g , which is usually quantified by the kinetic fragility index:

$$m = \frac{d \log \eta}{d(T_g/T)} \bigg|_{T=T_g} . \quad (1)$$

Network liquids such as silica belong to the group of strong glass formers, which exhibit low values of fragility indices and small deviations from the Arrhenius temperature dependence of transport properties near T_g . Molecular liquids belong to the opposite group of fragile glass formers, which exhibit high fragility index values and strong non-Arrhenius temperature

dependence of transport properties near T_g . Metallic liquids cover the intermediate fragility range between strong and fragile glass-forming liquids. The interesting finding was that more fragile groups of glass formers exhibit lower values of the relative Arrhenius crossover temperature, T_A/T_g .^{24,25} Network liquids, having a low fragility index in the range $m=20-30$, exhibit high values of relative Arrhenius temperatures ($T_A/T_g > 2$), which depend on material. Metallic liquids covering the intermediate fragility range $m=30-90$ exhibit rather universal value $T_A/T_g \approx 2$. Finally, the most fragile group of molecular liquids, with fragility index in the range $m=50-130$, also exhibits a relatively universal but lower value $T_A/T_g \approx 1.4$, which implies that T_A is close to T_m .

In this context, it is interesting to consider glass-forming liquid *cis*-decalin (*cis*-decahydronaphthalene), which is a bicyclic-saturated hydrocarbon (Fig. 1). The mixture of *cis*- and *trans*-isomers of decalin (Fig. 1) was reported to have fragility index $m=147$, which makes it one of the most fragile glass formers of all.²⁶ This property stimulated several studies on decalin.^{22,26-28} In our EPR study of translational radical diffusivity,²² we found that the onset temperature of radical diffusion crossover, T_{on} , in *cis*-decalin is close to its Arrhenius crossover temperature, T_A , estimated from viscosity. However, the obtained values of these temperatures, $T_{on} \approx T_A \approx 335$ K, are significantly higher than the melting temperature $T_m=229$ K. Additionally, we obtain the high value of relative Arrhenius temperature $T_A/T_g \approx 2.3$, when relating T_A to the reported glass transition temperature $T_g=145$ K.²⁷ Neither of the above results is expected for a highly fragile molecular glass former. The results of neutron scattering measurements and molecular dynamics simulations at ambient conditions indicate that the degree of definition of neighbor shells in *cis*-decalin is as high as in metallic glass formers,²⁷ which generally exhibit lower values of fragility. Moreover, it was found that molecular neighbor shells in *cis*-decalin are much better

defined than in the typical molecular glass former cumene (isopropylbenzene) with a lower fragility of $m \approx 90$.²⁷ Such short-range ordering in *cis*-decalin could be responsible for its high values of T_A/T_g , but it seems unexpected from the point of view of its very high fragility.

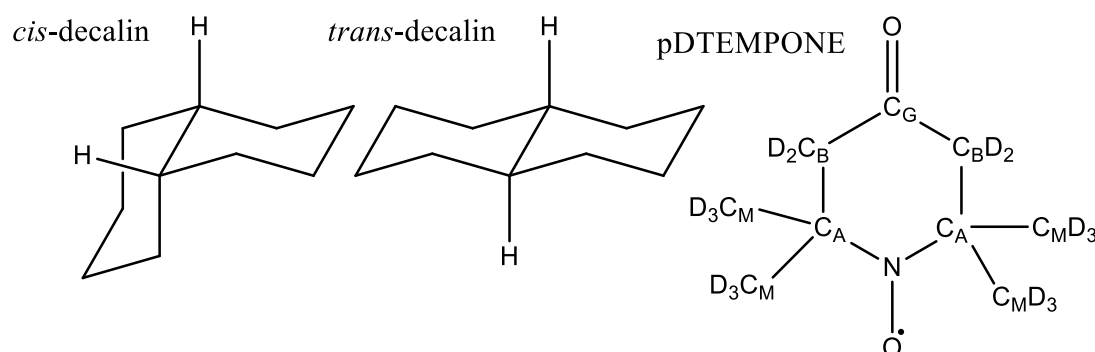


FIG. 1. Chemical structures of *cis*-decalin, *trans*-decalin, and pDTEMPONE radical. C atoms of pDTEMPONE are labeled according to their positions (M-methyl, A-alpha, B-beta, G-gamma).

In the present study, EPR measurements of nitroxide radical pDTEMPONE (Fig. 1), or perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl ($C_9D_{16}NO_2$), were performed in *cis*-decalin and *cis*-perfluorodecalin over broad temperature ranges. We studied pDTEMPONE radicals labeled with ^{15}N and ^{14}N isotopes (^{15}N - and ^{14}N -pDTEMPONE), which exhibit different ESR spectra but practically equal rotational and translational diffusivities. We applied detailed fitting analysis of the measured EPR spectra to determine the temperature dependence of the rotational diffusivity of the radical. Unexpectedly, the analysis revealed the anomalous temperature behavior of the EPR parameters and rotational diffusivity of the radical in *cis*-decalin, which was not found in *cis*-perfluorodecalin. In order to explain the anomalous behavior, we assumed that upon cooling through the equilibrium state of *cis*-decalin, the radical begins to sense an additional high-density liquid environment, which does not occur in *cis*-perfluorodecalin. We

additionally assumed that the exchange of high- and low-density radical environments slows down upon cooling into the supercooled state of *cis*-decalin. Following the second assumption, we successfully simulated low-temperature EPR spectra using two spectral components that correspond to the low- and high-density radical's environments. By using the theory of environment exchange in EPR, we performed a global fit of simulated EPR parameters to find the temperature dependence of the high-density environment fraction and the exchange rate between the two environments.

II. THE RADICAL EPR SPECTRA IN *CIS*-DECALIN AND *CIS*-PERFLUORODECALIN

The EPR study was performed for the radical ^{14}N -pDTEMPONE (98.2%-d16) and its ^{15}N -labeled isotopologue ^{15}N -pDTEMPONE (99%-d16, 99%-% ^{15}N), which were purchased from CDN Isotopes and used as received. EPR spectra of both isotopologues were measured in *cis*-decalin and *cis*-perfluorodecalin, which were bought from TCI and Manchester Organics, respectively. The *cis*-perfluorodecalin has the chemical structure of *cis*-decalin (Fig. 1), but with all hydrogens replaced by fluorine. The 0.5 mM solutions of ^{14}N - and ^{15}N -pDTEMPONE in both solvents were prepared by weighing. The *cis*-perfluorodecalin samples of about 50 μL were drawn into open-ended polytetrafluoroethylene (PTFE) tubing,¹⁹ which was then folded and squeezed with flat-nose pliers at the ends. PTFE tubing, which is permeable to oxygen and nitrogen but not to liquids, was used for the sample deoxygenation at 373 K, prior to recording EPR spectra. The nitrogen gas that controls sample temperature deoxygenates the sample in PTFE tubing, which sharpens the EPR lines, improves the signal-to-noise ratio, and makes the resulting EPR spectrum more sensitive to radical reorientation.¹⁹ The *cis*-decalin samples of about 50 μL were drawn into glass

capillaries, which were then flame-sealed at both ends. Deoxygenation in sealed glass capillaries was produced by annealing the *cis*-decalin samples at 373 K for about 15 minutes. We found that this deoxygenation of *cis*-decalin appears above 353 K, most likely as part of the same chemical reaction that causes the anomaly of viscosity at 383 K.²⁹

EPR spectra were recorded with an EMX X-band spectrometer equipped with a Bruker microwave bridge and a Bruker high-Q cavity, using a microwave frequency of about 9.3 GHz and a microwave power of 0.5 mW. The precise microwave frequency was measured by an HP microwave frequency counter. Since the deoxygenation of samples produces narrow EPR lines (Fig. 2), we used small modulation amplitude of 0.1×10^{-4} T. Scans of applied magnetic field during acquiring EPR spectra were taken for the central magnetic field in the range 331.1-331.4 mT and the sweep width of 50×10^{-4} T for ^{14}N - and 40×10^{-4} T for ^{15}N -pDTEMPONE (Fig. 2). In order to further improve EPR signal, we recorded 2048 points for each spectrum using the scan time of 129 seconds. The sample temperature was controlled with a Bruker variable temperature unit and measured with a thermocouple using an Omega temperature indicator. The thermocouple tip was positioned at the top of the active region of the EPR cavity to avoid reducing its quality factor. After deoxygenation of the sample at an initial temperature of 373 K, the temperature was decreased in small steps of 1 or 2 K between recording EPR spectra. The samples of *cis*-perfluorodecalin were cooled down to 265 K, which corresponds to the melting point. The samples of *cis*-decalin were cooled down to 211 K, which lies below its melting point, $T_m=229$ K, and above its crystallization temperature of about 190 K.²⁸

The experimental EPR spectrum $P(B)=dR(B)/dB$ [Figs. 2(a,b)] is the first derivative of the absorption EPR signal $R(B)$ with respect to the applied magnetic field B .^{16,21-23} Since the spin of

the nitrogen nucleus is $I=1$ for ^{14}N and $I=1/2$ for ^{15}N , while the number of corresponding hyperfine lines is $2I+1$, the EPR spectra of ^{14}N - and ^{15}N -labeled pDTEMPONE radicals exhibit three and two strong hyperfine lines, respectively [Figs. 2(a,b)]. These main hyperfine lines can be assigned according to their position in the spectrum as high- (h), low- (l), and central- (c) field lines [Figs. 2(a,b)]. The field positions of main hyperfine lines for ^{14}N -pDTEMPONE can be written as:

$$B_h = B_0 + A + C; B_l = B_0 - A + C; B_c = B_0, \quad (2a)$$

where A is the ^{14}N hyperfine coupling constant, C is a small shift of the outer lines due to the second-order hyperfine effect, and B_0 is the central-line position. The positions for ^{15}N -pDTEMPONE are:

$$B_h = B_0 + A/2; B_l = B_0 - A/2, \quad (2b)$$

where A is the ^{15}N hyperfine coupling constant, and B_0 is the central-field position of the spectrum.

Additionally, there are pairs of weak satellite hyperfine lines, symmetrically positioned around the main lines [Figs. 2(c,d)]. They originate from the radicals possessing the ^{13}C nucleus ($I=1/2$) of carbon at the X site C_X , where $X=\text{M, A, B, G}$ (Fig. 1). The positions of the high- (+) and low- (−) field satellite lines of C_X around the main line at B_f ($f=h,l,c$) are:

$$B_{f,\pm}(\text{C}_X) = B_f \pm A_{\text{C},X}/2. \quad (3a)$$

Here, $A_{\text{C},X}$ is the absolute ^{13}C hyperfine coupling constant, whose values are about 5.7, 5.1, 2.3, and 0.38 in 10^{-4} T (or Gausses) for M, A, B, and G sites, respectively.¹⁴ We also expect weak satellite lines from protons or ^1H ($I=1/2$) at radicals that are not fully deuterated. The high- (+) and low- (−) field ^1H satellite lines of single-proton radicals $\text{C}_9\text{HD}_{15}\text{NO}_2$ are positioned at:

$$B_{f,\pm}(\text{H}_X) = B_f \pm A_{\text{H},X}/2 \quad (3b)$$

around the main line at B_f . The absolute ^1H hyperfine coupling constant $A_{\text{H,X}}$ is about 0.12×10^{-4} T and 0.02×10^{-4} T for the sites M and B, respectively.¹⁴ Finally, there is a weak signal of naturally abundant ^{15}N ($\sim 0.36\%$) in the ^{14}N -pDTEMPONE spectra and a weak signal of ^{14}N in the ^{15}N -pDTEMPONE spectra due to the imperfect ^{15}N -labeling of 99% [Figs. 2(c,d)].

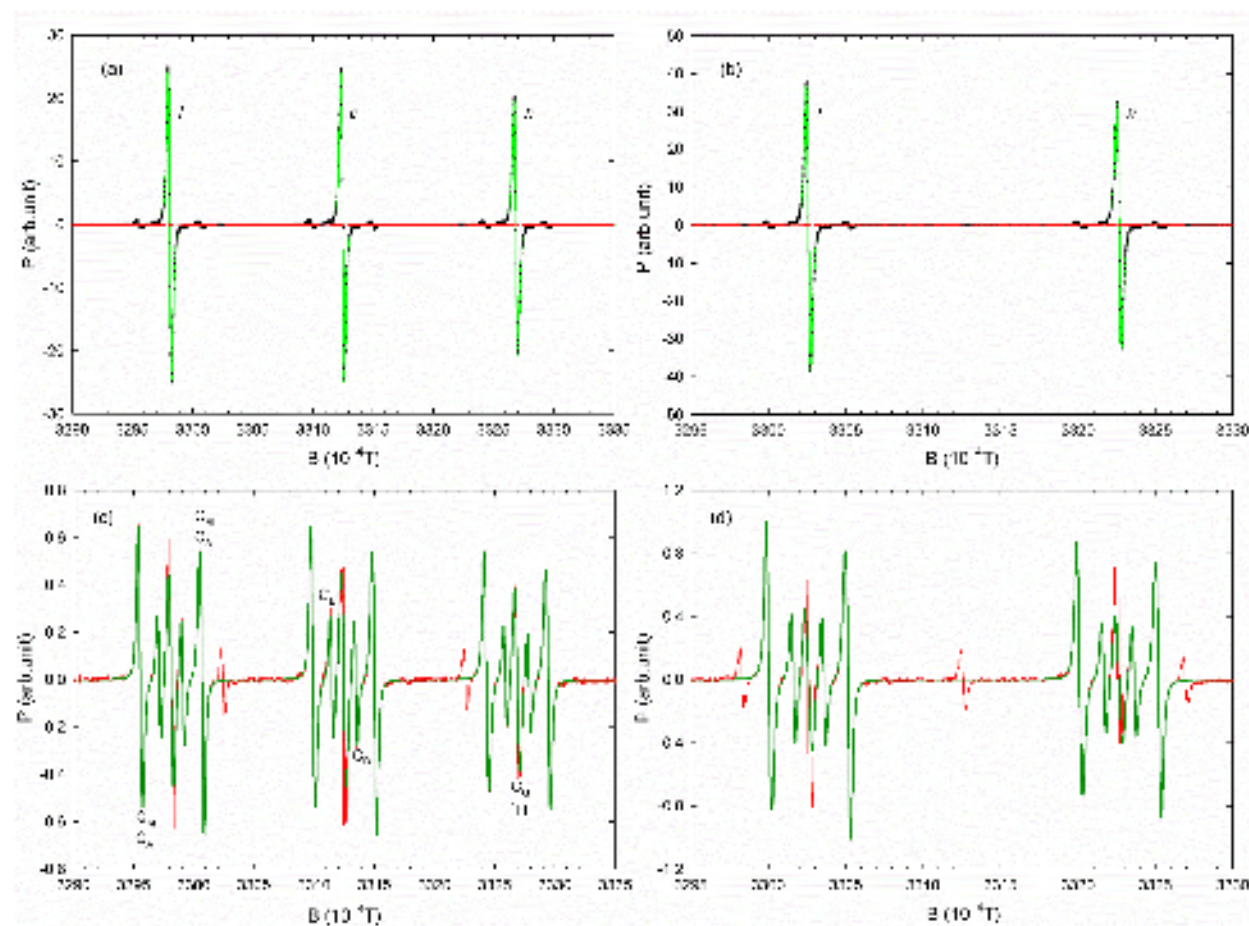


FIG. 2. (a,b) Experimental EPR spectra (black crosses), fits (thick green line) and residuals (thin red line) of (a) ^{14}N - and (b) ^{15}N -pDTEMPONE in *cis*-perfluorodecalin at 273 K. Main hyperfine lines at high (h), low (l) and central (c) field are denoted. (c,d) Reduced EPR spectra upon subtracting the fits of main hyperfine lines from the experimental spectra (thin red line) and the fits of satellite hyperfine lines (thick dark green line) of (c) ^{14}N - and (d) ^{15}N -pDTEMPONE. ^1H satellite lines and ^{13}C satellite lines of C_M , C_A , C_B , and C_G carbons are assigned.

III. ANOMALOUS EPR SPECTRAL PARAMETERS IN *CIS*-DECALIN

The EPR absorption signal of the main hyperfine lines for the deuterated nitroxide radical in solution can be written as the following sum:²¹

$$R_{ML}(B) = \text{Re} \sum_f J_f \mu_f(B), \quad (4)$$

where the hyperfine line f is defined by the intensity of its absorptive component J_f and the lineshape function $\mu_f(B)$. Neglecting the inhomogeneous broadening due to unresolved deuteron hyperfine structure, the line f has the following lineshape function:

$$\mu_f(B) = (1 + i\theta_f) / Z_f; \quad Z_f = \Gamma_f + i(B - B_f), \quad (5a)$$

where θ_f is the relative intensity of its dispersive component, Γ_f is its width, and B_f is its field position. This lineshape function implies that the absorption EPR signal of the line f in Eq. (4) has the Lorentzian form:

$$R_{ML,f}(B) = J_f \frac{\Gamma_f + \theta_f(B - B_f)}{\Gamma_f^2 + (B - B_f)^2}. \quad (5b)$$

Here, the second term is the dispersive component of the signal, induced by instrumental dispersion,¹⁹ spin interactions between radicals,^{14-16,21-23} or rotational radical diffusion.^{21,30} In order to determine EPR spectral parameters of ¹⁴N- and ¹⁵N-pDTEMPONE in deoxygenated *cis*-perfluorodecalin and *cis*-decalin, we initially fitted the main hyperfine lines of experimental EPR spectrum $P_{ML}(B) = dR_{ML}(B)/dB$ by using $R_{ML}(B)$ from Eq. (4), the Lorentzian lineshape functions from Eq. (5a), and the field positions of lines from Eq. (2). However, we found large differences between the experimental and fitted EPR lines (residuals), which indicate a need to introduce the

inhomogeneous broadening of deuteron hyperfine structure in the fitting function. Hence, the inhomogeneous broadening was approximated by the Gaussian distribution of Lorentzian lines,¹⁴ which results in the Voigt lineshape function:

$$\mu_f(B) = (1 + i\theta_f)/V_\sigma(Z_f); V_\sigma(Z_f) = \left[\frac{1}{\sigma} \sqrt{\frac{\pi}{2}} e^{\frac{Z_f^2}{2\sigma^2}} \operatorname{erfc}\left(\frac{Z_f}{\sqrt{2}\sigma}\right) \right]^{-1}, \quad (6)$$

where σ is the standard deviation of the Gaussian distribution. By using the Voigt lineshape functions in the fitting function Eq. (4), we achieved much smaller residuals at line positions than in the initial fit. Hence, we also used the Voigt lineshape functions to fit the ^{13}C and ^1H satellite hyperfine lines. The EPR spectrum was fitted using the absorption signal of the main and satellite lines:

$$R(B) = R_{ML}(B) + R_{SL}(B); R_{SL}(B) = \sum_{X=M,A,B,G} R_{C,X}(B) + \sum_{X=M,B} R_{H,X}(B), \quad (7a)$$

where the signal of satellite lines R_{SL} contains the sums of ^{13}C and ^1H satellite hyperfine lines over different isotope positions. The used forms of ^{13}C and ^1H signals are:

$$\begin{aligned} R_{C,X}(B) &= \rho_{C,X} \operatorname{Re} \sum_f J_f \sum_{p=\pm 1/2} \mu_{C,X,f,p}(B); \rho_{C,X} = \frac{N_X u_C}{1 - u_C} \\ R_{H,X}(B) &= \rho_{H,X} \operatorname{Re} \sum_f J_f \sum_{p=\pm 1/2} \mu_{H,X,f,p}(B); \rho_{H,X} = \frac{n_X u_{d15}}{1 - u_{d15}} \end{aligned} \quad (7b)$$

Here, u_C is the ^{13}C abundance in the radicals and N_X is the number of C_X at radical, being $N_M=4$, $N_A=N_B=2$, and $N_G=1$ (Fig. 1). Also, u_{d15} is the abundance of $\text{C}_9\text{HD}_{15}\text{NO}_2$ -radicals in samples and n_X is the fraction of H_X at radical, being $n_M=3/4$ and $n_B=1/4$ (Fig. 1). The spectral functions $\mu_{Y,X,f,p}(B)$ in Eq. (7b), where Y is C or H , are the Voigt functions Eq. (6) having Z_f replaced with:

$$Z_{Y,X,f,p=\pm 1/2} = Z_f + ipA_{Y,X}, \quad (7c)$$

where $A_{Y,X}$ are the hyperfine constants from Eq. (3). It was implied in Eqs. (7b) and (7c) that the satellite lines have equal dispersive components and linewidths as the corresponding main lines.

We did some preliminary fits in *cis*-perfluorodecalin to decide which parameters of the final fitting function Eq. (7) to set fixed. First, we fixed the parameters of the proton satellite lines as they couldn't be reliably fitted. The parameter u_{d15} was set to the difference between the perfect and declared purity of d16-radicals (98.2% for ^{14}N - and 99% for ^{15}N -pDTEMPONE), while the literature values¹⁴ were taken for the hyperfine constants of H_M and H_B (Table I). We also fixed the parameters $A_{C,G}$ and u_C to the values obtained from the fit of ^{14}N -pDTEMPONE in *cis*-perfluorodecalin at 273 K (Table I). The parameter $A_{C,G}$ could not be reliably fitted at high temperatures, and its fixed value is close to the literature value,¹⁴ while the fixed value of u_C agrees with the natural ^{13}C abundance $u_C=(1.06\pm0.10)\%$. Finally, the intensities of absorptive components J_f were found to vary slightly between the hyperfine lines, and the common value J was set as a free fitting parameter in the final fitting function (Table I). Thus, the final fitting function can be written in the form:

$$R(B) = J \times \text{Re} \sum_f (1 + i\theta_f) \left[\frac{1}{V_\sigma(Z_f)} + \sum_{Y,X} \sum_{p=\pm 1/2} \frac{\rho_{Y,X}}{V_\sigma(Z_f + ipA_{Y,X})} \right], \quad (7d)$$

where V_σ , Z_f , and $\rho_{Y,X}$ are defined by Eqs. (6), (5a), and (7b), respectively.

The fitted and fixed EPR parameters of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-perfluorodecalin at 273 K are presented in Table I, while the corresponding spectra are shown in Fig. 2. The Gaussian linewidth σ , being about half of the Lorentzian linewidths Γ_f (Table I), significantly contributes to the overall linewidths, which illustrates the importance of accounting for inhomogeneous broadening of deuterons. EPR spectra from experiment and fit cannot be

distinguished, while the difference between these spectra, or the residual line, is a flat line with almost zero value [Figs. 2(a,b)]. This confirms the Voigt function as an appropriate approximation for the effect of inhomogeneous broadening of deuterons. The differences between the experimental and fitted spectra can be seen around the resonant positions of the main hyperfine lines in Figs. 2(c,d), where the fits of satellite hyperfine lines are compared with the reduced EPR spectra, which are obtained by subtracting the fits of main hyperfine lines from the experimental spectra. Also, there are weak ^{15}N - and ^{14}N -signals in the ^{14}N - and ^{15}N -spectra, respectively [Figs. 2(c,d)], which were not considered in the fitting functions. Expectedly, the fitted ^{13}C hyperfine coupling constants at M, A, and B sites hardly differ for ^{14}N - and ^{15}N -pDTEMPONE (Table I).

TABLE I. Fitted and fixed values of EPR spectral parameters for ^{14}N - and ^{15}N -labeled pDTEMPONE in *cis*-perfluorodecalin at 273 K.

Label	J arb. unit	Γ_h 10^{-4}T	Γ_c 10^{-4}T	Γ_l 10^{-4}T	θ_h %	θ_c %	θ_l %
^{14}N	1.396	0.1772	0.1542	0.1534	-1.186	-1.189	-0.689
^{15}N	1.957	0.1610	-	0.1438	-0.486	-	-1.242
Label	A 10^{-4}T	B_0 10^{-4}T	C 10^{-4}T	σ 10^{-4}T	u_C^a %	$A_{C,M}$ 10^{-4}T	$A_{C,A}$ 10^{-4}T
^{14}N	14.3782	3312.4654	0.0316	0.0833	1.08	5.23	4.85
^{15}N	20.0576	3312.6268	-	0.0824	1.08	5.21	4.84
Label	$A_{C,B}$ 10^{-4}T	$A_{C,G}^a$ 10^{-4}T	u_{d15}^a %	$A_{H,M}^a$ 10^{-4}T	$A_{H,B}^a$ 10^{-4}T		
^{14}N	1.97	0.34	1.8	0.12	0.02		
^{15}N	1.96	0.34	1.0	0.12	0.02		

^aFixed values.

The fitted values of most EPR parameters of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin and *cis*-perfluorodecalin are presented versus temperature in Fig. 3. The intensity of the absorptive component of hyperfine lines J for a weak microwave field is proportional to the equilibrium longitudinal magnetization M_0 , which is parallel to the applied magnetic field and decreases with

temperature according to the Curie law, $M_0 \propto 1/T$.^{14,15,31} Therefore, the intensity J is expected to increase on cooling, which is observed for both pDTEMPONE radicals in *cis*-perfluorodecalin [Fig. 3(a)]. However, the intensity J in *cis*-decalin exhibits anomalous behavior, saturating on cooling at about 250 K and decreasing below this temperature [Fig. 3(a)].

The hyperfine lines in *cis*-perfluorodecalin exhibit small dispersive components, whose relative intensities to the absorptive component θ_f do not depend much on temperature and have absolute values less than a few percent [Table I and Figs. 3(b,c)]. This is the expected result for the dilute solution of rapidly tumbling radicals, where small instrumental dispersion¹⁹ dominates over dispersions induced by spin interactions between radicals^{14-16,21-23} and rotational radical diffusion.^{21,30} The relative dispersion intensities θ_f in *cis*-decalin follow this behavior above 270 K, but exhibit large temperature- and field-dependent departures from this behavior below 270 K [Figs. 3(b,c)]. The fact that the high- and low-field hyperfine lines exhibit dispersive components of opposite sign below 270 K agrees with the dispersion induced by spin interactions and rotational diffusion via a coherence transfer mechanism.^{14,21} However, the surprising fact that the central field hyperfine line of ¹⁴N-pDTEMPONE also exhibits a large dispersive component points to another mechanism that produces dispersion of hyperfine lines.

When considering the temperature behavior of hyperfine line positions, one can see that the nitrogen hyperfine coupling constants A exhibit maxima for *cis*-decalin, which are not visible for *cis*-perfluorodecalin [Fig. 3(d)]. The maximum or positive shoulder is also visible in *cis*-decalin for the averaged ¹³C hyperfine coupling constants of ¹⁴N- and ¹⁵N-pDTEMPONE at different sites $A_{C,X}$ [Fig. 3(e)]. These features appear below the temperature of about 320 K, which is higher than the onset temperature of the anomalous dispersion signal (~270 K).

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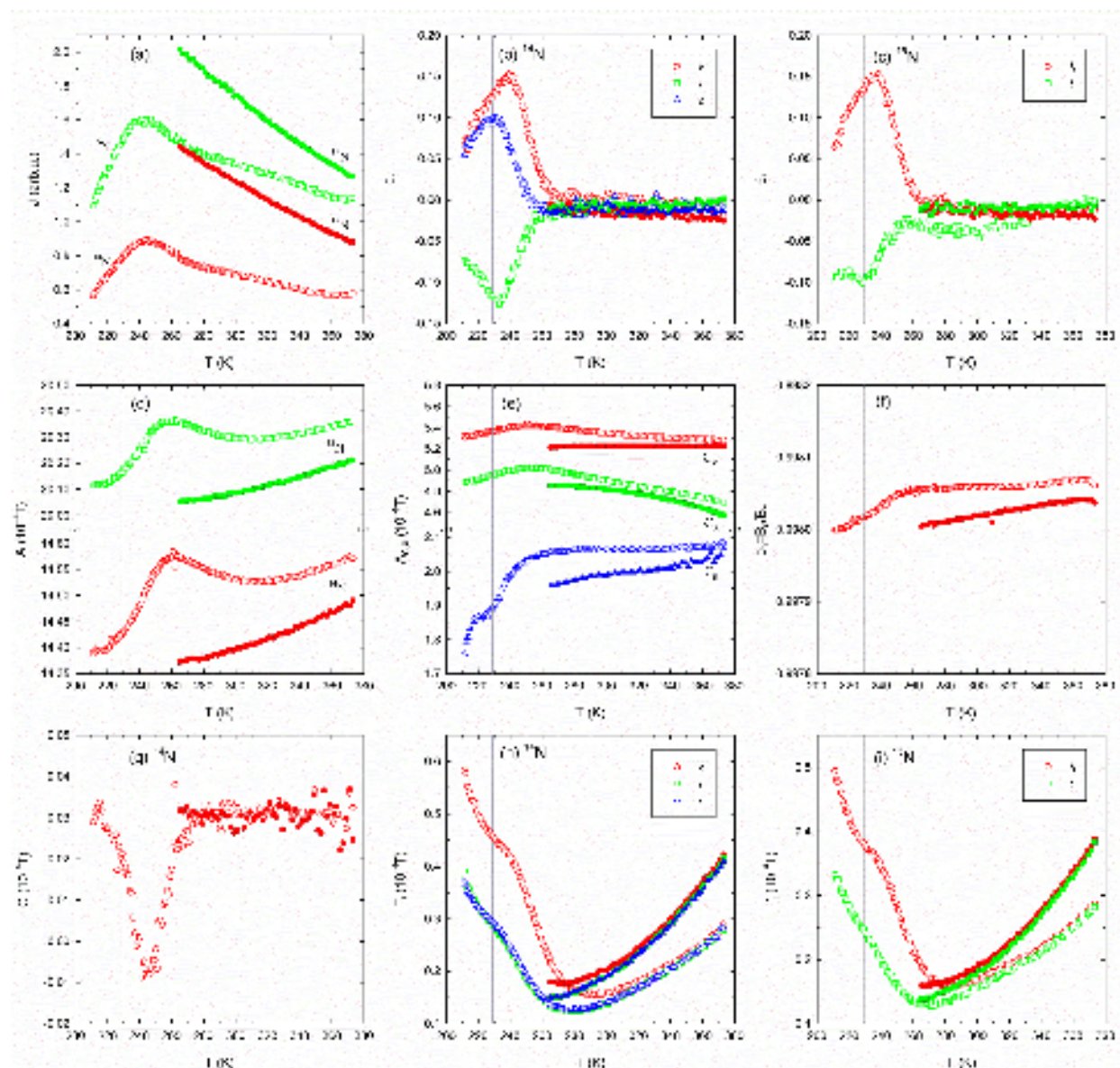


FIG. 3. Fitted EPR parameters of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin (empty symbols) and *cis*-perfluorodecalin (full symbols): intensities of absorptive component (a), relative intensities of dispersive component (b,c), nitrogen hyperfine coupling constants (d), averaged ^{13}C hyperfine coupling constants of ^{14}N - and ^{15}N -pDTEMPONE at C_M , C_A , and C_B carbons (e), averaged relative central fields of ^{14}N - and ^{15}N -pDTEMPONE (f), second-order hyperfine shift (g), and linewidths (h,i). Parameters of high-, low- and central-field lines are denoted by h , l and c , respectively. Vertical lines denote the melting point in *cis*-decalin.

The fitted central-field parameter B_0 is determined very precisely by the resonance condition for Zeeman interaction between electron spin and applied magnetic field $B_0 = \hbar \omega_e / (g \beta_e)$, where β_e is the Bohr magneton, ω_e is the measured angular microwave frequency, and g is the isotropic g -value of the radical.¹⁴ The corresponding resonant field of a free electron is $B_e = \hbar \omega_e / (g_e \beta_e) = \omega_e / \gamma_e$, where $\gamma_e = 1.761 \times 10^{11} \text{ s}^{-1} \text{ T}^{-1}$ is the electron gyromagnetic ratio. In order to eliminate the temperature dependence of microwave frequency, we calculated the relative central field $b_0 = B_0 / B_e$, which should correspond to the ratio of the free electron and radical g -values, g_e / g . The averaged values of the relative central field b_0 for ^{14}N - and ^{15}N -pDTEMPONE also show a positive shoulder in *cis*-decalin, which is not visible in *cis*-perfluorodecalin [Fig. 3(f)].

Finally, the second-order shift C of ^{14}N -pDTEMPONE exhibits a strong minimum below 270 K in *cis*-decalin [Fig. 3(g)], which is a particularly peculiar effect. Namely, this relative shift between the outer and central lines is given by $C \approx A^2 / (2B_0)$ in the second-order theory of nitrogen hyperfine interaction,^{31,32} and it is not expected to show any significant temperature dependence. The shift C exhibits expected temperature independence in *cis*-decalin above 270 K and *cis*-perfluorodecalin [Fig. 3(g)], where its value agrees with the expected value $A^2 / (2B_0) \approx 0.03 \times 10^{-4} \text{ T}$ that is calculated from the values of A and B_0 in Table I.

The fitted widths of hyperfine lines Γ_f in magnetic-field units [Figs. 3(h,i)] and the corresponding transverse relaxation times T_{2f} are related by $\Gamma_f = \hbar / (g \beta_e T_{2f})$,³¹ which can be approximated by $\Gamma_f = 1 / (\gamma_e T_{2f})$ as the g -value ratio of free electron and radical $g_e / g = b_0$ is almost one [Fig. 3(f)]. Since the rotational diffusion of the radical modulates the g -tensor and nitrogen hyperfine tensor, it also affects the transverse relaxation rates and consequently the widths of hyperfine lines.¹⁴ The effect of slowing down of rotational diffusion on the fitted linewidths Γ_f is

the separation of high-field linewidth Γ_h from the others below some temperature [Figs. 3(h,i)]. The separation occurs at a higher temperature in *cis*-decalin than in *cis*-perfluorodecalin, and the separation at the same temperature is higher in *cis*-decalin [Figs. 3(h,i)], which both indicate slower rotational diffusion in *cis*-decalin. However, this is not the expected result because *cis*-perfluorodecalin contains heavier and larger molecules and exhibits higher viscosity at the same temperature.³³ Also, the linewidths in *cis*-decalin exhibit small bumps below 270 K, where the previous EPR parameters exhibit maxima and minima.

We conclude that fitted EPR parameters of ^{14}N - and ^{15}N -pDTEMPONE exhibit anomalous behavior in *cis*-decalin, which is absent in *cis*-perfluorodecalin. Since the anomalous behavior appears in the equilibrium state above T_m (Fig. 3), it is certainly not connected with possible crystallization, which was found to affect the EPR spectra below 211 K. Also, anomalous temperature behavior of EPR parameters was found for fresh *cis*-decalin solutions of ^{14}N -pDTEMPONE in PTFE tubing, measured during cooling from 353 K with and without deoxygenation. This shows that the anomalous behavior of *cis*-decalin is not connected with the sample deoxygenation, the sample container, or the chemical reaction that causes deoxygenation above 353 K.

IV. ANOMALOUS ROTATIONAL CORRELATION TIME IN *CIS*-DECALIN

The isotropic (g , A) and anisotropic components (Δg , δg , ΔA , δA) of the g -tensor and nitrogen hyperfine tensor are defined as:¹⁴

$$\begin{aligned} g &= (g_{xx} + g_{yy} + g_{zz})/3; \Delta g = g_{zz} - (g_{xx} + g_{yy})/2; \delta g = (g_{xx} - g_{yy})/2 \\ A &= (A_{xx} + A_{yy} + A_{zz})/3; \Delta A = A_{zz} - (A_{xx} + A_{yy})/2; \delta A = (A_{xx} - A_{yy})/2 \end{aligned} \quad (8a)$$

where g_{ii} and A_{ii} ($i=x,y,z$) are the principal values of tensors. The aforementioned rotational modulation (r) of the g -tensor and nitrogen hyperfine tensor contributes to the widths of hyperfine lines in magnetic-field units according to the following relation:

$$\Gamma_r(m_I) = \Gamma_{Ar} - \Gamma_{Br}m_I + \Gamma_{Cr}m_I^2, \quad (8b)$$

where m_I is the magnetic quantum number of the nitrogen nucleus. The coefficients in Eq. (8b) can be written as:

$$\Gamma_{Ar} = \frac{\omega_e^2(\Delta g^2 + 3\delta g^2)}{45\gamma_e} \left(j_0 + \frac{3j_{\omega_e}}{4} \right) + \frac{I(I+1)\gamma_e(\Delta A^2 + 3\delta A^2)}{30} \left[\frac{j_{\omega_N} + j_{-\omega_N}}{2} + \frac{7j_{\omega_e}}{3} \right], \quad (8c)$$

$$\Gamma_{Br} = -\frac{4\omega_e(\Delta g\Delta A + 3\delta g\delta A)}{45} \left(j_0 + \frac{3j_{\omega_e}}{4} \right) - \frac{\gamma_e(\Delta A^2 + 3\delta A^2)}{30} \frac{j_{\omega_N} - j_{-\omega_N}}{2}, \quad (8d)$$

$$\Gamma_{Cr} = \frac{4\gamma_e(\Delta A^2 + 3\delta A^2)}{45} \left(j_0 - \frac{3}{8} \frac{j_{\omega_N} + j_{-\omega_N}}{2} - \frac{j_{\omega_e}}{8} \right). \quad (8e)$$

Here, the real part of the spectral density for rotational diffusion at the frequency ω is given by:

$$j_\omega = \tau_R / (1 + \omega^2 \tau_R^2), \quad (8f)$$

while the nuclear spin transition frequency is $\omega_N = \gamma_e A/2$. The coefficients in Eq. (8b) are obtained from Redfield theory presented in Appendix O.6 of Ref. 14 by keeping the signs of the energy level differences and taking $g = g_e = 2$ in the final result. The spectral density is determined by the rotational correlation time $\tau_R = 1/(6D_R)$, where D_R is the rotational diffusivity. ^{14}N -pDTEMPONE is described in Eq. (8) by $I=1$ and the values $m_I = -1, 0, 1$, which correspond to the high-, central-, and low-field hyperfine lines, respectively. Also, ^{15}N -pDTEMPONE is described by $I=1/2$ and the values $m_I = -1/2, 1/2$, which correspond to the high- and low-field hyperfine lines, respectively.

In order to determine tensor components in Eq. (8a), we recorded EPR spectra of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin for the samples that were rapidly cooled to 153 K. We used rigid-limit fitting in EasySpin software package³⁴ to obtain the principal values of tensors in Eq. (8a). Then, the isotropic and anisotropic components of ^{14}N - and ^{15}N -pDTEMPONE were averaged, taking into account that the g -tensor components should be the same for both radicals, while the nitrogen hyperfine tensor components of ^{15}N -pDTEMPONE should be higher by factor of $q=1.403$ than those of ^{14}N -pDTEMPONE.¹⁴ The obtained values of g -tensor components are $g=2.0061$, $\Delta g=-0.0054$, and $\delta g=0.0015$. The obtained values of hyperfine tensor components for ^{14}N -pDTEMPONE are $A=14.9\times 10^{-4}$ T, $\Delta A=26.4\times 10^{-4}$ T, and $\delta A=-0.2\times 10^{-4}$ T, while those of ^{15}N -pDTEMPONE are q times larger. These values of the tensor components were used to calculate the rotational correlation times τ_R from Eq. (8d) for both *cis*-decalin and *cis*-perfluorodecalin. The coefficient Γ_{Br} in Eq. (8d) was solved for τ_R at each temperature to reproduce the experimental Γ_B . It was calculated as $\Gamma_B=(\Gamma_h-\Gamma_l)/2$ for ^{14}N -pDTEMPONE and $\Gamma_B=\Gamma_h-\Gamma_l$ for ^{15}N -pDTEMPONE from the fitted linewidths Γ_h and Γ_l [Figs. 3(h,i)]. The obtained values of τ_R below 350 K are presented in Fig. 4, while those above 350 K are excluded due to a large uncertainty. The values of τ_R are similar for ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin above 250 K, as expected, and they exhibit a strong increase on cooling below 290 K [Fig. 4(a)]. The anomalous behavior appears below 250 K, where the values of τ_R are different for ^{14}N - and ^{15}N -pDTEMPONE, and their temperature dependences exhibit maxima.

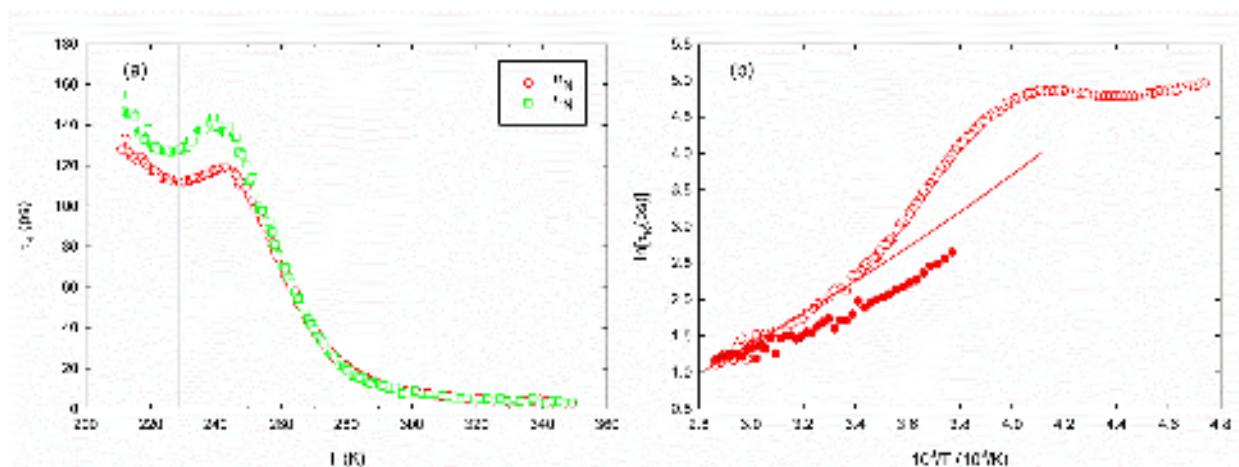


FIG. 4. (a) Rotational correlation time vs. temperature for ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin. Vertical line marks the melting point. (b) Arrhenius plot for the averaged rotational correlation time of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin (empty circles) and *cis*-perfluorodecalin (full circles). Predicted rotational correlation time in *cis*-decalin from the Stokes-Einstein-Debye law with slip coefficient $\kappa=0.065$ (line).

The averaged τ_R of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin and *cis*-perfluorodecalin are presented as the Arrhenius plot ($\ln \tau_R$ vs. $10^3/T$) in Fig. 4(b). We can see that the strong increase in τ_R upon cooling in *cis*-decalin is absent in *cis*-perfluorodecalin. Also, the increase of τ_R in *cis*-decalin doesn't follow the Arrhenius behavior ($\ln \tau_R \propto 10^3/T$), as it can't be described by a straight line in Fig. 4(b). The rotational correlation time τ_R of solute with the van der Waals radius r is usually related to the viscosity of solvent η by the Stokes-Einstein-Debye (SED) law:^{14,19}

$$\tau_R = 4\pi r^3 \kappa \eta / (3k_B T), \quad (9)$$

where k_B is the Boltzmann constant and κ is the slip coefficient. Measured viscosity of *cis*-decalin between 243 and 353 K²⁹ was fitted to the Vogel-Fulcher-Tamman (VFT) law $\ln \eta = \ln \eta_0 + \Theta_\eta / (T - T_\eta)$, where η_0 , Θ_η , and T_η are fitting parameters.^{2,7,12,18} The expected τ_R of pDTEMPONE in *cis*-decalin was calculated from Eq. (9) by using the fitted viscosity parameters,

$r=0.35$ nm for the van der Waals radius of pDTEMPONE,^{16,17} and $\kappa=0.065$ for its slip coefficient. Such a low slip coefficient, chosen here to reproduce experimental high-temperature values of τ_R [Fig. 4(b)] using the SED law from Eq. (9), is common in EPR studies of radical rotation.¹⁹ It follows that the predicted rotational correlation time from the SED law can't reproduce the strong increase of τ_R on cooling in *cis*-decalin [Fig. 4(b)]. Hence, we conclude that in addition to the EPR parameters of pDTEMPONE, its rotational correlation time τ_R also exhibits the anomalous temperature behavior in *cis*-decalin, which was not found in *cis*-perfluorodecalin. This anomalous behavior of τ_R includes its strong increase on cooling to 250 K, the maximum at about 240 K, and the differences in its values for ¹⁴N- and ¹⁵N-pDTEMPONE below 250 K. Any existing theory of rotational diffusion in homogeneous liquid, such as the SED law, can't explain these phenomena in *cis*-decalin above T_m .

V. COEXISTENCE OF TWO RADICALS' ENVIRONMENTS IN *CIS*-DECALIN

The anomalous behavior of EPR parameters and rotational diffusivity of pDTEMPONE in *cis*-decalin is attempted to be explained by the theory of environment exchange in EPR, as presented in Appendix A.^{14,15,31,32,35} We consider the theoretical EPR signal of solution of ¹⁴N- or ¹⁵N-labeled nitroxide radicals, and we assume that *cis*-decalin is a dynamically heterogeneous solvent showing locally two types of domains with different structures. One is the low-density liquid domain, characterized by fast molecular motion and denoted as the fast (*F*) domain, while the other is the high-density domain, characterized by slow molecular motion and denoted as the slow (*S*) domain. The radical environment can be a part of the *F* or *S* domain, with probabilities $1-\phi$ and ϕ , respectively. The probabilities correspond to the fractions of *cis*-decalin molecules

participating in F and S domains in bulk liquid. The exchange of F and S environments around the radical is described by the exchange rate in magnetic field units $W=w/\gamma_e$, where $w=w_{FS}+w_{SF}$ is the exchange rate, w_{FS} is the transition rate from F to S environment, and w_{SF} is the transition rate from S to F environment.

In Appendix A, we consider the EPR signal of the hyperfine line f , whose width Γ_{fE} and position B_{fE} differ between the environments $E=F$ and $E=S$. In the case of very slow exchange of radical environments ($W \rightarrow 0$), the EPR signal consists of two Lorentzian lines, whose widths and positions correspond to those in the F and S environments, while their intensities are proportional to the probabilities of each environment. In the general case $W > 0$, the EPR signal of the hyperfine line can also be represented as the sum of two Lorentzian lines, but the intensities, positions, and widths of these lines depend on ϕ and W according to Eq. (A4). Since the intensities of Lorentzian lines are proportional to the complex parameters $1-\Phi_f$ and $\Phi_f=\phi_f-i\theta_f$, where Φ_f tends to zero for $W \rightarrow \infty$, it follows that the first of these lines persists in the spectrum for a very fast exchange rate, while the other one disappears. The persistent line is named the primary line, whereas the disappearing line is named the secondary line. The primary line in the fast-exchange regime becomes the Lorentzian line with environmentally averaged width and position [Eq. (A4a)].

It follows that the absorptive component $1-\phi_f$ of the primary-line intensity parameter $1-\Phi_f$ decreases due to the slowing down of exchange, which is illustrated by the example in Appendix A [Fig. 10(a)]. This loss of the primary-line intensity is similar to the experimental absorption decrease of pDTEMPONE hyperfine lines in *cis*-decalin on cooling down below 250 K [Fig. 3(a)]. It was also shown that the dispersion component θ_f of the primary-line intensity parameter is low in the slow and fast exchange regimes, while θ_f shows up in the intermediate exchange regime

[Fig. 10(b)], where its exchange-rate dependence develops the maximum or minimum, depending on the sign of the line-position shift between environments. Again, this behavior agrees with the maxima and minima observed in dispersion intensities of hyperfine lines of pDTEMPONE radicals in *cis*-decalin below 270 K [Figs. 3(b,c)]. Finally, pDTEMPONE radicals in *cis*-decalin below 270 K exhibit maxima or minima in line position parameters [Figs. 3(d-g)], the small bumps in linewidths [Figs. 3(h,i)], and the maxima in rotational correlation times [Fig. 4(a)]. These maxima, minima, and bumps are anomalous features whose low-temperature behavior can be ascribed to the transition of the primary line from the average line at high W to the narrower one of two environment lines at low W [Figs. 10(c,d)]. However, the high-temperature behavior of these anomalous features has to be attributed to the anomalous temperature behavior of the average lines, which is beyond the scope of the simple example in Appendix A. We can guess that the anomalous behavior of average lines may result from the appearance and rise of a second environment during cooling, which would affect the average parameters in Eq. (A4a).

According to the above analysis, the EPR absorption signal under environment exchange is the sum of primary and secondary signals, $R(B)=R_I(B)+R_{II}(B)$. Since only the primary signal exists in the fast-exchange regime, which is assumed to be realized at high temperatures, we used the previous fitting function Eq. (7d) and the complex intensity parameter of the primary line in Eq. (A4c), $1-\Phi_f=1-\varphi_f+i\theta_f$, to construct the following fitting function for the primary signal:

$$R_I(B) = J \times \text{Re} \sum_f (1 - \varphi_f + i\theta_f) \left[\frac{1}{V_\sigma(Z_f)} + \sum_{Y,X} \sum_{p=\pm 1/2} \frac{\rho_{Y,X}}{V_\sigma(Z_f + ipA_{Y,X})} \right], \quad (10a)$$

where $Z_f = \Gamma_f + i(B - B_f)$. Hence, we can still use our previous fitting results (Table I and Fig. 3) at high temperatures where the exchange is very fast, and the absorption intensities of secondary lines

φ_f are negligible [Fig 10(a)]. The fitting function for the secondary signal was constructed from Eq. (10a) using the intensity parameter $\Phi_f = \varphi_f - i\theta_f$ and the difference parameter $\Delta_f = \Delta\Gamma_f - i\Delta B_f$ of the secondary line in Eq. (A4c). The resulting secondary-signal fitting function has the form:

$$R_{II}(B) = J \times \text{Re} \sum_f (\varphi_f - i\theta_f) \left[\frac{1}{V_\sigma(Z_f + \Delta_f)} + \sum_{Y,X} \sum_{p=\pm 1/2} \frac{\rho_{Y,X}}{V_\sigma(Z_f + \Delta_f + ipA_{Y,X})} \right]. \quad (10b)$$

The quantities in Eq. (10) are already defined: V_σ is the function in Eq. (6), B_f are the field positions of hyperfine lines in Eq. (2), and $\rho_{Y,X}$ are relative intensities of satellites in Eq. (7b). It was assumed in Eq. (10b) that the secondary signal has the equal width of inhomogeneous deuteron broadening σ and the equal hyperfine constants of satellite lines $A_{Y,X}$ as the primary signal. This assumption can be justified if ^2H -, ^1H -, and ^{13}C -hyperfine constants differ slightly between two environments, which is assumed to be the case. Using fixed EPR parameters in Table I and the two-signal function $R(B) = R_I(B) + R_{II}(B)$ defined by Eq. (10), we fitted the experimental spectra $P(B) = dR(B)/dB$ of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin at low temperatures. The fitted parameters at 223 K are written in Table II, while the corresponding experimental spectra and fits are shown in Fig. 5.

TABLE II. Fitted EPR parameters for ^{14}N - and ^{15}N -labeled pDTEMPONE in *cis*-decalin at 223 K.

Label	J a.u.	Γ_h 10^{-4}T	Γ_c 10^{-4}T	Γ_l 10^{-4}T	θ_h %	θ_c %	θ_l %	A 10^{-4}T
^{14}N	1.00	0.399	0.272	0.271	6.4	4.0	-4.1	14.409
^{15}N	1.87	0.344	-	0.253	7.2	-	-3.7	20.142
Label	B_0 10^{-4}T	C 10^{-4}T	σ 10^{-4}T	$A_{C,M}$ 10^{-4}T	$A_{C,A}$ 10^{-4}T	$A_{C,B}$ 10^{-4}T	φ_h %	φ_c %
^{14}N	3314.541	0.021	0.070	5.34	4.91	1.96	47.1	38.7
^{15}N	3314.934	-	0.060	5.33	4.93	1.98	44.1	-
Label	φ_l %	$\Delta\Gamma_h$ 10^{-4}T	$\Delta\Gamma_c$ 10^{-4}T	$\Delta\Gamma_l$ 10^{-4}T	ΔB_h 10^{-4}T	ΔB_c 10^{-4}T	ΔB_l 10^{-4}T	
^{14}N	37.4	1.76	0.87	0.86	0.33	0.24	-0.23	
^{15}N	30.3	1.50	-	0.78	0.38	-	-0.37	

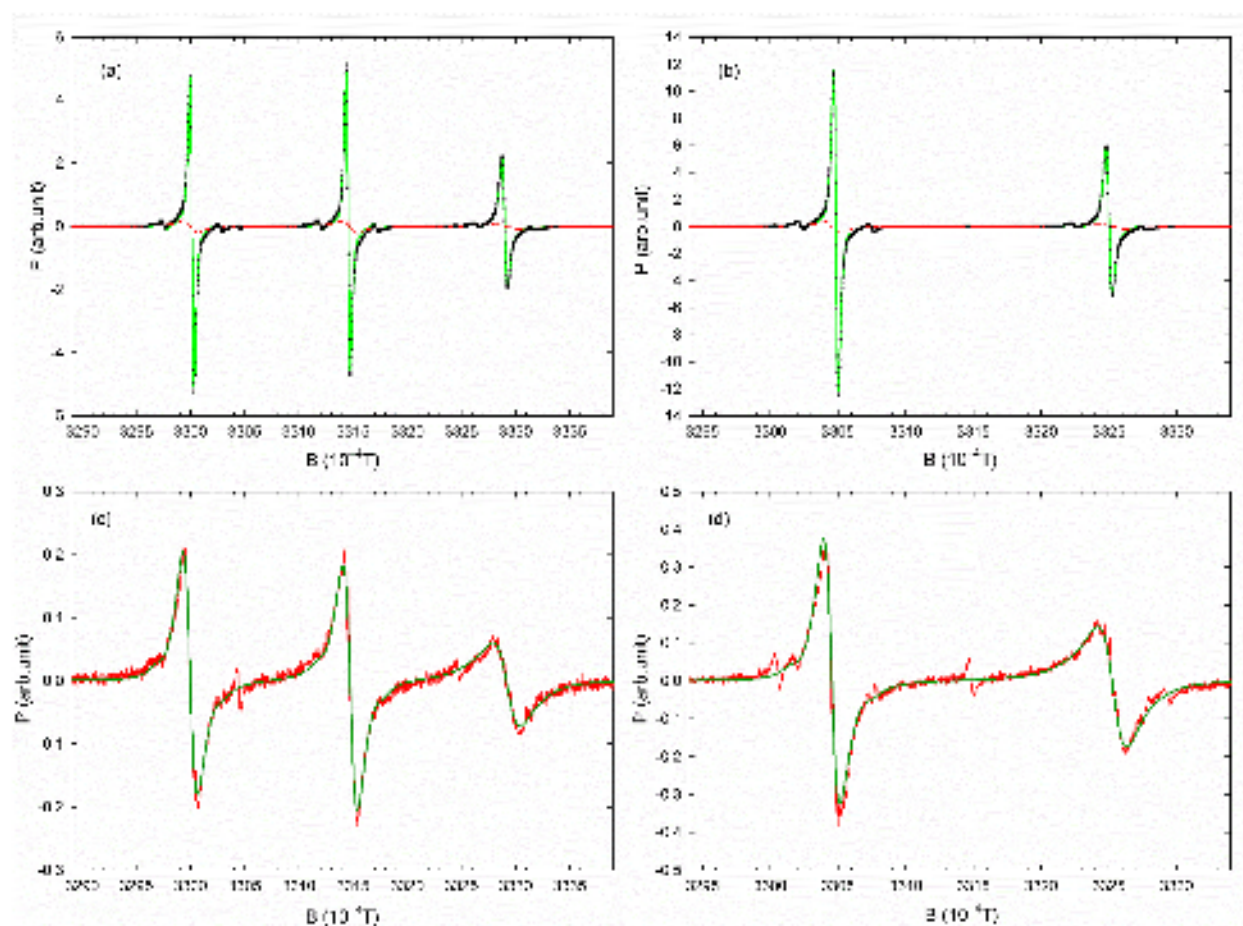


FIG. 5. (a,b) Experimental EPR spectra (black crosses), primary-spectrum fits (thick green line) and residuals after subtracting primary-spectrum fits from experimental spectra (thin red line) of (a) ^{14}N - and (b) ^{15}N -pDTEMPONE in *cis*-decalin at 223 K. (c,d) Residuals after subtracting primary-spectrum fits (thin red line) compared to secondary-spectrum fits (thick dark green line) of (c) ^{14}N - and (d) ^{15}N -pDTEMPONE.

To illustrate the existence of secondary spectra at 223 K, the primary-spectrum fits were subtracted from the experimental spectra, and the obtained residual spectra are presented in Figs. 5(a,b). The residual spectra exhibit weak and broad lines that correspond to secondary hyperfine lines [Figs. 5(a,b)], and these spectra are satisfactorily simulated by the secondary-spectrum fits [Figs. 5(c,d)]. Secondary hyperfine lines produce much lower signal than primary hyperfine lines

(Fig. 5), but their contributions to total line intensities have significant values $\varphi=30.3\text{-}47.1\%$ (Table II). Secondary lines give a lower signal because they are broader than primary lines by large amounts $\Delta\Gamma_f=0.78\text{-}1.76\times 10^{-4}$ T (Table II). The noteworthy fact is that secondary lines are broader than primary ones, which agrees with the environment-exchange theory in Appendix A [Fig. 10(d)].

The final result is that the experimental spectra of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin can be successfully fitted to the sum of primary and secondary spectra below the temperature $T_s=251$ K. Since this temperature is above the melting point $T_m=229$ K, this result is experimental evidence that two different local environments exist in the equilibrium state of *cis*-decalin. Following the environment-exchange theory, the previous fitting function in Eq. (7d) can now be understood as the primary-spectrum fitting function for temperatures above T_s . Hence, the previously obtained fitting parameters above T_s are used again, but we understand them as average parameters of the radical in two environments. The actual and previously fitted values of EPR parameters are combined and presented in Figs. 6 and 7.

The total absorption intensity of primary and secondary hyperfine lines J [Fig. 6(a)] does not exhibit the anomalous maximum at about 250 K as before [Fig. 3(a)], which is the result of the inclusion of secondary lines in the fitting function. The contributions of secondary lines in the total line intensity J are given by the absorption parameters φ , whose values decrease from more than 40% at low temperatures toward small values on approaching $T_s=251$ K [Figs. 6(b,c)]. The dispersion parameters of primary lines θ_f [Figs. 6(d,e), Table II] exhibit the same sign as the position differences between secondary and primary lines ΔB_f below T_s [Figs. 6(f,g), Table II], which is an additional fact in agreement with the environment-exchange theory [Figs. 10(b,c)].

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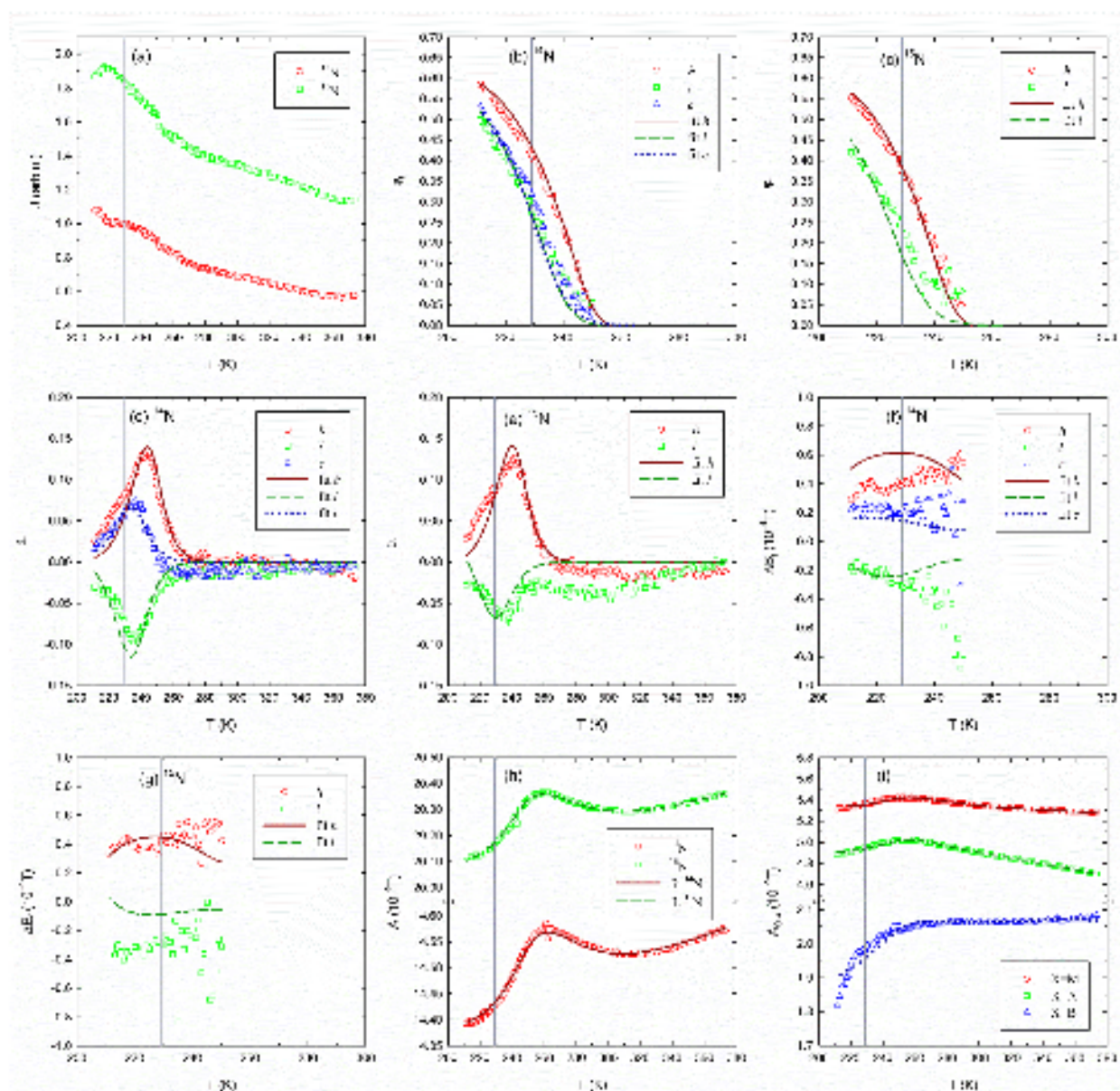


FIG. 6. Final fitted EPR parameters of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin (symbols): total absorption intensity of primary and secondary lines (a), contributions of secondary lines to total line intensities (b,c), dispersion parameters of primary lines (d,e), position differences between secondary and primary lines (f,g), nitrogen hyperfine coupling constants of primary lines (h), and averaged ^{13}C hyperfine coupling constants of primary lines of ^{14}N - and ^{15}N -pDTEMPONE at C_M , C_A , and C_B carbons (h). Lines represent the global best-fit temperature dependences from Section VI. High-, low-, and central-field lines are denoted by h , l , and c , respectively. Vertical lines mark the melting point.

According to the environment-exchange theory, T_s is not the temperature below which two environments appear, but the temperature below which two-environment exchange is slow enough that the secondary lines can be fitted. Hence, we expect that two liquid environments appear at a temperature higher than T_s , probably being the temperature below which the average parameters show anomalous behavior. Comparing the temperature behavior of the nitrogen hyperfine coupling constants A in *cis*-perfluorodecalin and *cis*-decalin [Figs. 3(d) and 6(h)], it seems that the anomalous maxima in *cis*-decalin start to develop in the region 320-340 K. Consequently, we expect that two radical environments appear in this temperature region when cooling the liquid, while only one radical's environment exists at high temperatures above this region. We named the radical's environment that persists at high temperatures as the high-temperature (HT) environment.

We speculate that the HT environment would produce a regular temperature behavior of A , similar to that in *cis*-perfluorodecalin. However, the second radical's environment is supposed to emerge below the region 320-340 K and to cause an anomalous increase of the averaged coupling constant A on cooling below this region [Fig. 6(h)]. This anomalous increase occurs because the radical in the second environment, named the low-temperature emerging (LTE) environment, has a higher value of A than in the HT environment. Besides the increase in the primary-signal constant A on cooling below 320 K, the additional point is that this increase is followed by the maximum at 260 K and a strong decrease below this temperature [Fig. 6(h)]. This additional point suggests that the primary signal in the slow-exchange regime below T_s corresponds to the HT radical's environment, while the secondary signal corresponds to the LTE radical's environment. In the opposite case, the primary-signal constant A would not show a

maximum, but instead, it would continue to increase below 260 K and approach the coupling constant of the radical in the LTE environment.

The same reasoning can be applied to the averaged ^{13}C hyperfine coupling constants of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin [Fig. 6(i)]. These coupling constants $A_{C,X}$ also show the anomalous maximum (for C_M and C_A carbons) or shoulder (for C_B carbon) at about 260 K, which looks superimposed on the regular temperature behavior that is observed in *cis*-perfluorodecalin [Figs. 3(e)]. This behavior indicates that the radical in the LTE environment also has higher ^{13}C hyperfine coupling constants than in the HT environment. It also indicates again that the HT radical's environment is the one that corresponds to the primary lines in the slow-exchange regime.

The average of the relative central field, $b_0=B_0/B_e$, for ^{14}N - and ^{15}N -pDTEMPONE also shows a positive shoulder in *cis*-decalin [Fig. 7(a)], which is not visible in *cis*-perfluorodecalin [Fig. 3(f)]. Since b_0 corresponds to the free electron and radical g -value ratio g_e/g , this result implies that the g -value of the radical is lower in the LTE than in the HT environment.

In contrast to the hyperfine coupling constants and g -value, the second-order shift of ^{14}N -pDTEMPONE C is not expected to depend on the radical's environment. This independence could be the reason why the anomalous minimum of C in *cis*-decalin develops at significantly lower temperatures below about 270 K [Fig. 7(b)], when compared with the region 320-340 K of the supposed appearance of the second radical's environment. It follows that the only reason for the minimum of C could be the effect of fast-to-slow exchange transition below 270 K. It seems possible that the positions of different primary hyperfine lines are differently affected by this transition, which can result in this anomalous minimum of C .

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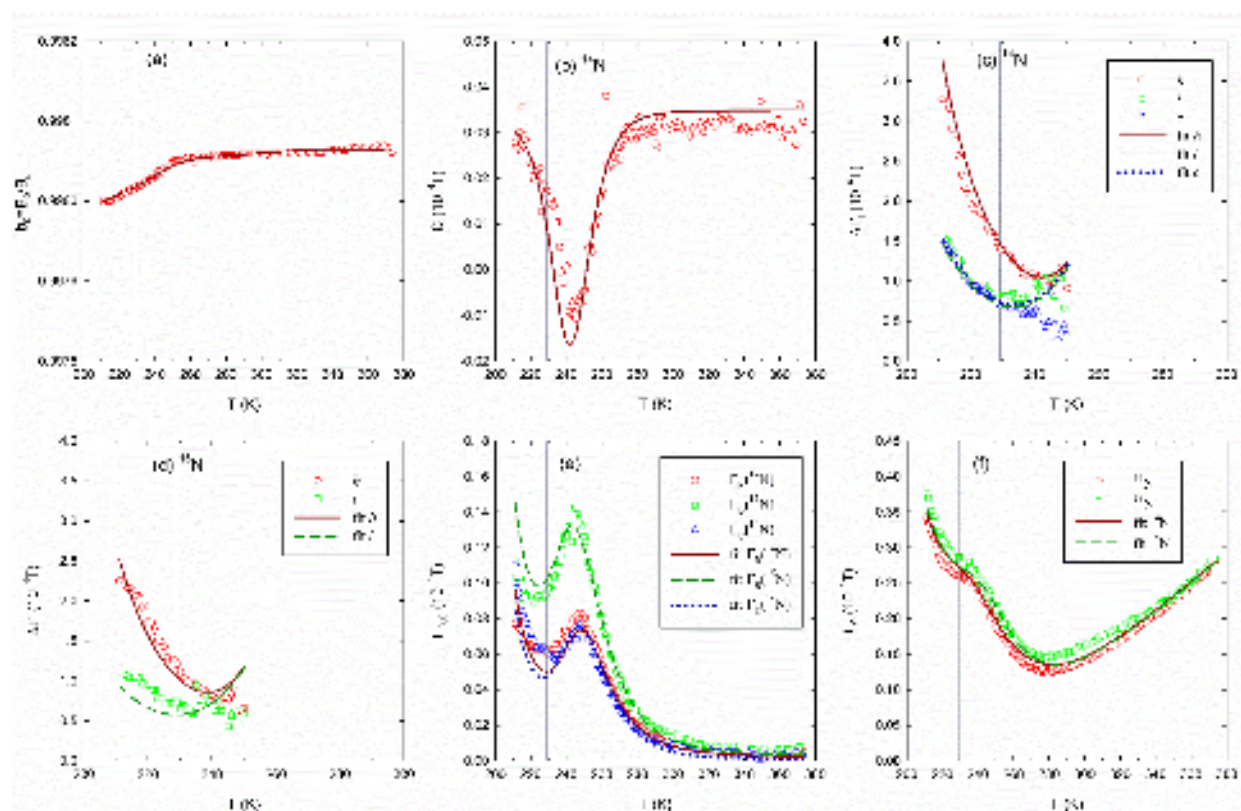


FIG. 7. Final fitted EPR parameters of ^{14}N - and ^{15}N -pDTEMPONE in *cis*-decalin (symbols): relative central fields of primary lines averaged over ^{14}N - and ^{15}N -pDTEMPONE (a), second-order hyperfine shift of primary lines (b), linewidth differences between secondary and primary lines (c,d), and linewidth coefficients of primary lines (e,f). Lines represent the global best-fit temperature dependences from Section VI. High-, low-, and central-field lines are denoted by h , l , and c , respectively. Vertical lines mark the melting point.

The positive linewidth differences between secondary and primary lines $\Delta\Gamma_f$ increase on cooling at the lowest temperatures, [see Figs. 7(c,d)]. The positive $\Delta\Gamma_f$ agrees with the environment-exchange theory for *cis*-decalin, as mentioned before. The increase of $\Delta\Gamma_f$ on cooling indicates a possibility that $\Delta\Gamma_f$ is partly caused by the higher value of radical's rotational correlation time τ_R in the LTE environment than in the HT environment. This possibility agrees with the previously obtained τ_R of ^{14}N - and ^{15}N -pDTEMPONE, which exhibits a strong increase and the

maximum on cooling below 290 K [Fig. 4(a)]. Following the aforementioned reasoning, the anomalous maxima of τ_R suggest that the LTE environment produces higher τ_R than the HT one. The question of radical's rotational mobility in two environments is intended to be clarified within the actual fitting results for the linewidths of primary lines Γ_f . Hence, the primary-signal linewidths of ^{14}N -pDTEMPONE are written as:

$$\Gamma_h = \Gamma_0 + \Gamma_B + \Gamma_C; \Gamma_l = \Gamma_0 - \Gamma_B + \Gamma_C; \Gamma_c = \Gamma_0, \quad (11a)$$

while those of ^{15}N -pDTEMPONE are written as:

$$\Gamma_h = \Gamma_0 + \Gamma_B / 2; \Gamma_l = \Gamma_0 - \Gamma_B / 2. \quad (11b)$$

The linewidth coefficients of primary lines Γ_0 , Γ_B , and Γ_C are introduced in Eq. (11) in a way that they are analogous to the line position parameters B_0 , A , and C from Eq. (2). The aim of this transformation of the linewidths into the linewidth coefficients is to better illustrate the effects of rotational radical diffusion. The coefficients Γ_0 , Γ_B , and Γ_C are obtained from the actual fitting values of Γ_f by using Eq. (11), and the resulting temperature dependences of the coefficients are presented in Figs. 7(e,f).

The coefficients $\Gamma_B = (\Gamma_h - \Gamma_l)/2$ of ^{14}N -pDTEMPONE, $\Gamma_B = \Gamma_h - \Gamma_l$ of ^{15}N -pDTEMPONE, and $\Gamma_C = (\Gamma_h + \Gamma_l)/2 - \Gamma_c$ of ^{14}N -pDTEMPONE show strong maxima in their temperature dependences presented in Fig. 7(e). In the case that the radical rotates in a homogeneous medium, the coefficients Γ_B and Γ_C will have non-zero values due to the linewidth effects of rotational modulation of the g -tensor and nitrogen hyperfine tensor. Then, Γ_B and Γ_C could be directly equated¹⁴ to the corresponding theoretical coefficients Γ_{Br} and Γ_{Cr} from Eq. (8b), which depend on the correlation time τ_R as in Eqs. 8(d,e). Since both Γ_{Br} in Eq. 8(d) and Γ_{Cr} in Eq. 8(e) are

increasing functions of τ_R , the maxima visible in Γ_B and Γ_C [Fig. 7(e)] will be visible again in the calculated τ_R , as was the case in the previously calculated τ_R [Fig. 4(a)]. Therefore, we can conclude that the anomalous maxima visible in the coefficients Γ_B and Γ_C from the actual fitting results indicate again that τ_R of the radical is higher, or that rotational radical diffusion is slower, in the LTE environment than in the HT environment.

It can be noted that the coefficients $\Gamma_0 = \Gamma_c$ of ^{14}N -pDTEMPONE and $\Gamma_0 = (\Gamma_h + \Gamma_l)/2$ of ^{15}N -pDTEMPONE show a positive shoulder at the temperatures of maxima in Γ_B and Γ_C [Fig. 7(f)]. By comparing Eqs. (8b) and (11), the coefficients Γ_0 of ^{14}N - and ^{15}N -pDTEMPONE in a homogeneous medium should contain contributions from the coefficients Γ_{Ar} and $\Gamma_{Ar} + \Gamma_{Cr}/4$, respectively, whose theoretical dependence on τ_R is given in Eqs. 8(c) and 8(e). Since Γ_{Ar} in Eq. 8(c) also increases with τ_R , the positive shoulder visible in Γ_0 should be treated as an anomalous feature, which indicates slower rotational radical diffusion in the LTE environment. Unlike the coefficients Γ_B and Γ_C , the coefficient Γ_0 in a homogeneous medium is expected to contain the spin-rotation (s) contribution that is independent of m_I and given by:¹⁴

$$\Gamma_s(m_I) = \Gamma_{As} = \frac{1}{9\gamma_e\tau_R} \sum_{i=x,y,z} (g_{ii} - g_e)^2, \quad (12)$$

as well as the contributions that are not related to rotational radical diffusion.¹⁴ Because of that, the coefficients Γ_0 don't tend to zero at high temperatures, as the coefficients Γ_B and Γ_C do [Fig. 7(e)], instead they remain finite and increase with temperature [Fig. 7(f)].

VI. FITTING THE EXPERIMENTAL RESULTS IN CIS-DECALIN

On the basis of the analysis from the previous section, we can assign two environments introduced in the environment-exchange theory (Appendix A) as follows: the slow (S) radical's environment occurring with the probability ϕ is assigned to the LTE environment, and the fast (F) radical's environment occurring with the probability $1-\phi$ is assigned to the HT environment. The probability $\phi(T)$, as the fraction of slow domains in bulk liquid, is expected to be a decreasing function of temperature, which achieves very low values in the region 320-340 K, where the LTE radical's environment is assumed to disappear. As the second of the environment-exchange parameters, the exchange rate of the radical's environments $W(T)$ is expected to be an increasing function of temperature. This speeding up of exchange with temperature could explain why the primary and secondary signals appear in the experimental spectra below $T_s=251$ K, whereas only one primary signal corresponding to the environmentally averaged signal persists above T_s . We also concluded that the radical's rotational correlation time in the S environment τ_{RS} is higher than its correlation time in the F environment τ_{RF} . This indicates that the low-temperature emerging S environment has a denser liquid structure than the high-temperature F environment.

An additional implication of the previous analysis is that the experimental EPR quantities presented in Figs. 6 and 7 are either produced or affected by environment exchange, except for the total absorption intensity of the primary and secondary lines [Fig. 6(a)]. We denote these exchange-sensitive experimental quantities as Q_j ($j=1,\dots,32$) and their values at measured temperatures T_i ($i=1,\dots,N$) as $Q_{j,i}$. Using Refs. 8, 14, 18, 32, and 36 in the analysis presented in Appendix B, we derived dependences of the quantities Q_j on the parameters Π_k ($k=1,\dots,18$). These 18 parameters Π_k include two rotational correlation times (τ_{RF} , τ_{RS}), which affect the quantities Q_j

according to the Eqs. (B1-4), (B7-8), and (B13). The parameters Π_k also include two environment-exchange parameters (W , ϕ), which affect Q_j according to Eqs. (B6), (B9) and (B11).

Except for these four parameters that are most interesting to us, the parameters Π_k include three non-rotational environmental difference parameters of main lines ($\delta\Gamma_{An}$, δb_{0n} , δA_n). These are the linewidth difference $\delta\Gamma_{An}$ for both N isotopes and every m_I , the relative central-field difference δb_{0n} for both N isotopes, and the hyperfine coupling difference δA_n for the ^{14}N isotope. These parameters enter the total environmental differences in Eq. (B8), which affect ten experimental secondary-to-primary line difference quantities $\Delta\Gamma(m_I)$ [Figs. 7(c,d)] and $\Delta B(m_I)$ [Figs. 6(f,g)] according to Eq. (B6). In addition, they affect five absorption quantities $\phi(m_I)$ [Figs. 6(b,c)] and five dispersion quantities $\theta(m_I)$ [Figs. 6(d,e)] according to Eq. (B9).

We additionally defined five non-rotational F -environment parameters (Γ_{An} , b_{0n} , A_{n2} , A_{n1} , C_n), which enter the total F -environment coefficients in Eq. (B13) and affect nine experimental quantities of the main primary lines [Figs. 6(h) and 7(a,b,e,f)] according to Eq. (B12). These parameters are the linewidth Γ_{An} , which is equal for both N isotopes and every m_I , the relative central field b_{0n} , which is equal for both N isotopes, the hyperfine couplings A_{n2} for ^{14}N and A_{n1} for ^{15}N , and the second-order shift of the ^{14}N isotope C_n .

Finally, the parameters Π_k include six satellite-line parameters: three ^{13}C coupling constants in F -environment $A_{C,X,F}$ ($X=\text{M,A,B}$), and three environmental differences of ^{13}C coupling constants $\delta A_{C,X}$. These parameters are included to reproduce the ^{13}C coupling constants $A_{C,X}$ in Fig. 6(i), which are the last three experimental quantities Q_j . The experimental constants

$A_{C,X}$ can be reproduced by averaging $A_{C,X}(m_I)$ in Eq. (B14) over different m_I and over both ^{14}N - and ^{15}N -pDTEMPONE radicals.

When defining the fitting procedure, we noted that experimental quantities Q_j depend on temperature due to the temperature dependent parameters Π_k . Hence, we introduced the set of $\nu(k)$ fitting coefficients $\boldsymbol{\pi}_k = \{\pi_{k,1}, \dots, \pi_{k,\nu(k)}\}$ for every Π_k , which defines its assumed temperature dependence $\Pi_k(T; \boldsymbol{\pi}_k)$. In order to fit the temperature dependences of all Q_j , we constructed the global weighted least-squares function:

$$\chi^2 = \sum_{i=1}^N \sum_{j=1}^{32} \left[\frac{Q_{j,i} - Q_j(T_i)}{\sigma_j} \right]^2, \quad (13a)$$

where the fitting function is:

$$Q_j(T) = Q_j[\Pi_1(T; \boldsymbol{\pi}_1), \dots, \Pi_{18}(T; \boldsymbol{\pi}_{18})] \quad (13b)$$

and the deviation from fit of each Q_j is weighted by the inverse square of its experimental error σ_j to account for the different character of quantities Q_j . By minimizing the function χ^2 in Eq. (13a) with respect to the fitting coefficients $\boldsymbol{\pi}_k$, the obtained best-fit values $\boldsymbol{\pi}_k = \mathbf{v}_k = \{v_{k,1}, \dots, v_{k,\nu(k)}\}$ determine the best-fit temperature dependences $\Pi_k(T; \mathbf{v}_k)$. After introducing $\Pi_k(T; \mathbf{v}_k)$ into Eq. (13b), we get the best-fit temperature dependences $Q_{j\nu}(T)$.

To estimate the experimental error σ_j of quantity Q_j , we performed linear temperature regression on the set of ten experimental values at consecutive temperatures $\{Q_{j,i}, Q_{j,i+1}, \dots, Q_{j,i+9}\}$, and calculated $\sigma_{j,i}$ as the standard deviation of experimental values from the linear fit. Then, we calculated σ_j as the average of $\sigma_{j,i}$ over all different consecutive sets. Finally, the errors σ_j are additionally averaged over the experimental quantities of the same character. Thus, we found that

the averaged error of absorption parameters φ_f [Figs. 6(b,c)] is $\sigma_A=8.59\times10^{-3}$, while that of the dispersion parameters θ_f [Figs. 6(d,e)] is $\sigma_A=3.99\times10^{-3}$. The secondary-to-primary line differences in position ΔB_f [Figs. 6(f,g)] and linewidth $\Delta\Gamma_f$ [Figs. 7(c,d)] exhibit similar errors and the average value is $\sigma_\Delta=56.41\times10^{-7}$ T. The error of primary-line position parameters A [Fig. 6(h)], $A_{C,X}$ [Fig. 6(i)], and C [Fig. 7(b)], is $\sigma_B=2.22\times10^{-7}$ T, while that of primary-line linewidth parameters [Fig. 7(e,f)] is $\sigma_T=1.46\times10^{-7}$ T. Finally, the error of the relative central field b_0 [Fig. 7(a)] is $\sigma_b=2.56\times10^{-6}$.

Since the experimental EPR parameters in *cis*-perfluorodecalin are regular weak functions of temperature T (Fig. 3), this was also assumed for the eight F -environment parameters (Γ_{An} , b_{0n} , A_{n2} , A_{n1} , C_n , $A_{C,X,F}$) and the six environmental difference parameters ($\delta\Gamma_{An}$, δb_{0n} , δA_n , $\delta A_{C,X}$) in *cis*-decalin. Hence, the used fitting function for these parameters was the polynomial function of T :

$$\Pi_k(T) = \Pi_{k,0} + \Pi_{k,1} \times T + \Pi_{k,2} \times T^2 + \dots, \quad (14)$$

where only the first constant term was used as the initial fitting polynomial for each of the parameters. Later, the fitting polynomials for the parameters A_{n2} and A_{n1} were extended up to the second linear term, while those for the parameters b_{0n} and $A_{C,X,F}$ were extended up to the third quadratic term. The fitting polynomial extensions were done after the improvement of agreement between the measured and fitted quantities A , b_0 , $A_{C,X}$ [Figs. 6(h,i) and 7(a)], which are directly affected by these four F -environment parameters. The best-fit temperature coefficients $\Pi_{k,l=0,1,2}$ of all fourteen weakly temperature dependent parameters are presented in Table III. These values were obtained in the final fitting procedure after defining temperature dependences $\Pi_k(T;\pi_k)$ for all parameters.

TABLE III. The best-fit coefficients of pDTEMPONE in *cis*-decalin.

$\Gamma_{An,0}$ 10^{-4}T	$b_{0n,0}$	$b_{0n,1}$ $10^{-6}/\text{K}$	$b_{0n,2}$ $10^{-9}/\text{K}^2$	$A_{n1,0}$ 10^{-4}T	$A_{n1,1}$ $10^{-7}\text{T}/\text{K}$	$A_{n2,0}$ $10^{-4}\text{T}/\text{K}^2$	$A_{n2,1}$ $10^{-7}\text{T}/\text{K}$	$C_{n,0}$ 10^{-4}T
0.03118	0.99759	2.709	-3.881	19.740	1.662	14.135	1.179	0.03484
$A_{C,M,0}$ 10^{-4}T	$A_{C,M,1}$ $10^{-7}\text{T}/\text{K}$	$A_{C,M,2}$ $10^{-10}\text{T}/\text{K}^2$	$A_{C,A,0}$ 10^{-4}T	$A_{C,A,1}$ $10^{-7}\text{T}/\text{K}$	$A_{C,A,2}$ $10^{-10}\text{T}/\text{K}^2$	$A_{C,B,0}$ 10^{-4}T	$A_{C,B,1}$ $10^{-7}\text{T}/\text{K}$	$A_{C,B,2}$ $10^{-10}\text{T}/\text{K}^2$
5.176	-1.308	-2.768	4.221	5.728	-11.91	1.081	5.485	-7.613
$\delta\Gamma_{An,0}$ 10^{-4}T	$\delta b_{0n,0}$ 10^{-5}	$\delta A_{n1,0}$ 10^{-4}T	$\delta A_{C,M,0}$ 10^{-4}T	$\delta A_{C,A,0}$ 10^{-4}T	$\delta A_{C,B,0}$ 10^{-4}T	τ_{RF0} fs	Θ_{RF} K	T_{RF} K
0.1210	5.113	0.4816	0.3488	0.4399	0.2620	201.3	519.1	130.0
τ_{RS0} fs	Θ_{RS} K	W_0 10^4T	Θ_W K	W_L 10^{-4}T	T_e K	h_1	h_2	h_3
3.899	2740	1.763	4803	0.3090	238.7	6.863	22.96	5.974

The assumed temperature dependences $\Pi_l(T; \pi_l)$ for the last four parameters (τ_{RF} , τ_{RS} , W , ϕ) were tested by another method after obtaining the global best-fit temperature dependences $\Pi_k(T; \mathbf{v}_k)$ of all parameters. In this method, the parameter of interest was considered as the fitting parameter $\Pi_l(T_i)$ at various temperatures T_i , while the global best-fit values $\Pi_{k \neq l}(T_i; \mathbf{v}_k)$ were kept for all other parameters. In other words, the local weighted least-squares function:

$$\chi_{l,i}^2 = \sum_{j=1}^{32} \left\{ \frac{Q_{j,i} - Q_j[\Pi_1(T_i; \mathbf{v}_1), \dots, \Pi_{l-1}(T_i; \mathbf{v}_{l-1}), \Pi_l(T_i), \Pi_{l+1}(T_i; \mathbf{v}_{l+1}), \dots, \Pi_{18}(T_i; \mathbf{v}_{18})]}{\sigma_j} \right\}^2 \quad (15)$$

was minimized with respect to the fitting parameter $\Pi_l(T_i)$ to obtain its best-fit value $v_l(T_i)$. The local best-fit values $v_l(T_i)$ were compared with the global best-fit values $\Pi_l(T_i; \mathbf{v}_l)$ to justify the assumed form of the fitting temperature function $\Pi_l(T; \pi_l)$. The assumed form of the fitting function was modified until a satisfactory agreement between global and local best-fit values was reached. We take into account that the sensible temperature region for comparison of the global and local fits of parameter Π_l is that where Π_l has a significant influence on the experimental quantities Q_j .

The temperature dependence of rotational correlation time is usually described by the Arrhenius and VFT laws.^{1,12,18,19,25,26} We applied the Arrhenius law as the initial fitting function for the radical's rotational correlation time in both environments. After performing the local fitting test for the *F*-environment correlation time τ_{RF} at all measured temperatures, its fitting function was modified into the VFT law $\ln \tau_{RF}(T) = \ln \tau_{RF0} + \Theta_{RF}/(T - T_{RF})$, where τ_{RF0} , Θ_{RF} , and T_{RF} are the fitting coefficients. On the other hand, the local fitting test for the *S*-environment correlation time τ_{RS} in the comparison temperature region below 282 K showed that its temperature dependence is well described by the initial Arrhenius law $\ln \tau_{RS}(T) = \ln \tau_{RS0} + \Theta_{RS}/T$, where τ_{RS0} and Θ_{RS} are the fitting coefficients. The rotational coefficients obtained in the final fitting procedure are presented in Table III, while the Arrhenius plot of the final global and local fits of τ_{RF} and τ_{RS} is presented in Fig. 8(a). Whereas some disagreement between local and global fits of τ_{RF} is visible at intermediate temperatures, the local and global fits of τ_{RF} agree quite well [Fig. 8(a)].

The Arrhenius law was also the initial fitting function for the temperature dependence of the environment exchange rate $W(T)$. Since the local best-fit values of W showed saturation at low temperatures, we introduced the constant low-temperature coefficient W_L into the fitting function, which then took the following form: $W(T) = W_L + W_0 \exp(-\Theta_W/T)$. The best-fit coefficients W_0 , Θ_W , and W_L , which are obtained in the final fitting procedure, are presented in Table III. The final results for global and local fits of W are presented in Fig. 8(b) in the form of the Arrhenius plot of environment exchange relaxation time $\tau_W = 1/W = 1/(\gamma_e W)$. The downward deviation of τ_W from the Arrhenius law at low temperatures is clearly visible, as is the agreement between global and local fits in the comparison region below 267 K. The values of τ_W exceed those of τ_{RF} and τ_{RS} , which justifies the use of rotational coefficients in Eq. (B1) and Eq. (B3) of Appendix B.

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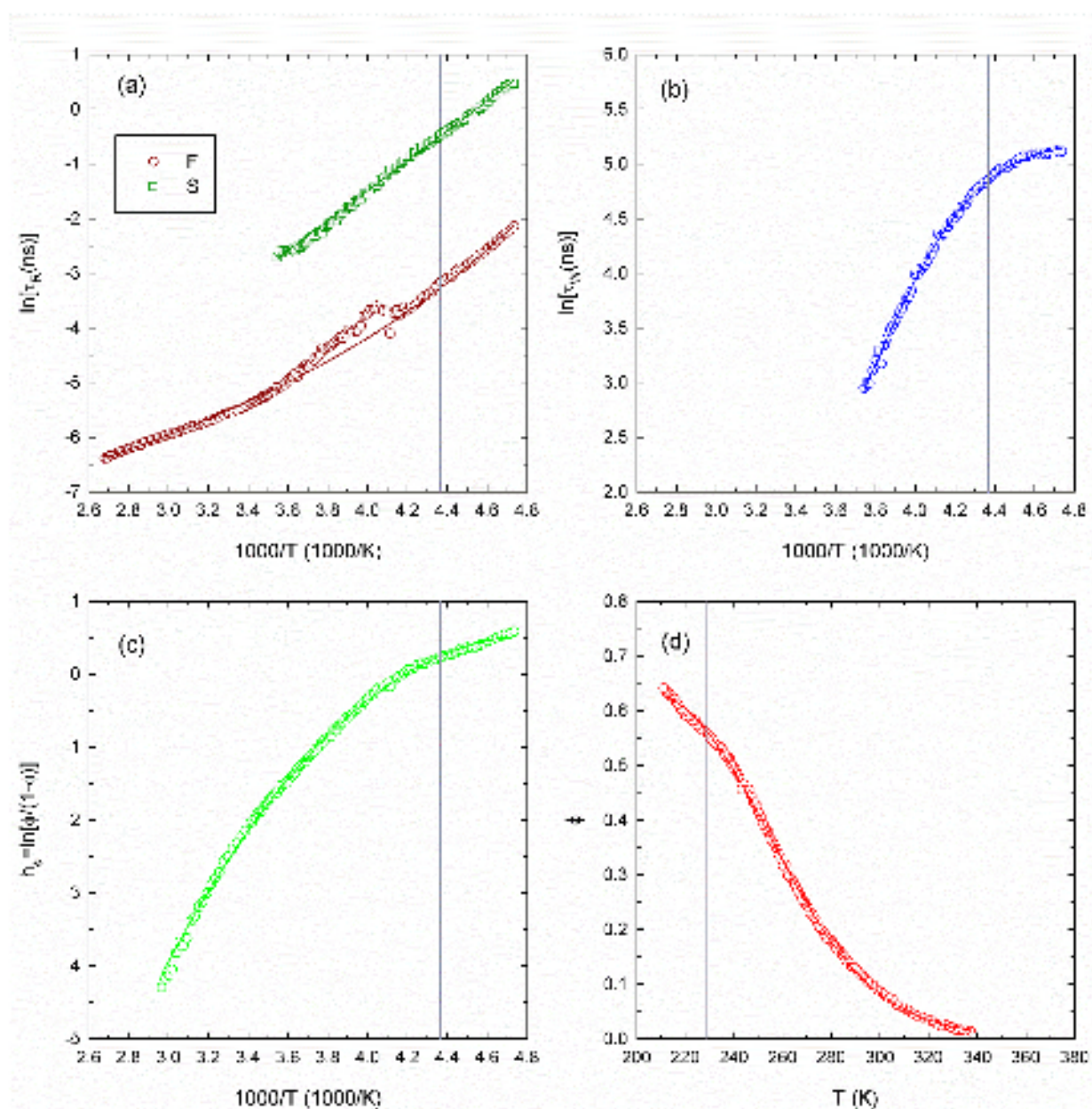


FIG. 8. Temperature dependences of global (lines) and local (symbols) best-fit values of the following parameters of pDTEMPONE radical in *cis*-decalin: radical's rotational correlation time τ_R in *F* (fast) and *S* (slow) environments (a), environment exchange relaxation time τ_W (b), reduced effective field for *S* environment h_ϕ (c), and occurring probability of *S* environment ϕ (d). Vertical lines denote the melting point.

In order to determine the temperature dependence of the slow-environment probability $\phi(T)$, we used the theory for a single-component liquid that exhibits two local interconvertible supramolecular states with different structures.³⁷ The probability ϕ was understood as the fraction of *cis*-decalin molecules participating in one of such supramolecular states, and the effective thermodynamic field for this fraction was defined as $H_\phi = k_B T \cdot \ln[\phi/(1-\phi)]$. We first considered *cis*-decalin as the solution with ideal mixing of two supramolecular states, for which the field H_ϕ equals the Gibbs energy difference $G_{FS} = G_F - G_S$ between the molecules participating in *F* and *S* states.³⁷ The reduced effective field $h_\phi = \ln[\phi/(1-\phi)] = G_{FS}/(k_B T)$ can be written in the first approximation as $h_\phi(T) = h_1(T_e/T - 1)$, where $k_B h_1$ and $k_B h_1 T_e$ are, respectively, the entropy and energy differences of molecules in *F* and *S* states.³⁷ This initial function for h_ϕ , where h_1 and T_e were the fitting coefficients, was initially used to fit the *S*-environment probability given by $\phi = [1 + \exp(-h_\phi)]^{-1}$. The initial form of h_ϕ varies linearly with $1/T$, and the temperature T_e marks equal probability of two states $\phi = 1 - \phi = 1/2$. However, the local fitting of h_ϕ showed a strong nonlinear dependence on $1/T$, which is characterized by saturation at low temperatures. In order to achieve a better agreement between the global and local fits of h_ϕ , we extended the fitting function for h_ϕ to the third-order polynomial:

$$h_\phi(T) = h_1(T_e/T - 1) - h_2(T_e/T - 1)^2 + h_3(T_e/T - 1)^3, \quad (16)$$

where h_2 and h_3 are the additional fitting coefficients. This extended form of $h_\phi(T)$ shows a good agreement between the global and local fits of h_ϕ in the comparison region below 337 K [Fig. 8(c)], which is also true for the resulting global and local fits of ϕ [Fig. 8(d)]. The best-fit values of the coefficients T_e , h_1 , h_2 , and h_3 , which are obtained in the final fitting procedure, are presented in

Table III. The results of the final global fitting procedure for all 32 exchange-sensitive experimental quantities Q_j are presented by the lines in Figs. 6 and 7. We can see that the global fits do not perfectly match the experimental data, but they correctly reproduce the anomalous features in the temperature dependences of experimental quantities. Additionally, the correct reproduction of the anomalous behavior of the linewidth coefficient of primary lines Γ_B [Fig. 7(e)] explains the anomalous behavior of τ_R presented in Fig. 4(a). Using Eq. (8d) to calculate the effective correlation time τ_{Ref} from the fit of Γ_B in Fig. 7(e), it can be shown that the resulting τ_{Ref} exhibits the anomalous behavior with τ_R presented in Fig. 4(a), including the strong increase on cooling to 250 K, the maximum at about 240 K, and the differences in τ_R for ^{14}N - and ^{15}N -pDTEMPONE below 250 K. However, a direct comparison between τ_{Ref} and τ_R is not appropriate because they are calculated from Γ_B obtained using different fitting procedures below $T_s=251$ K.

VII. DISCUSSION AND CONCLUSIONS

Our EPR results support the presence of two distinguishable radical's environments in *cis*-decalin, which we interpret and discuss as corresponding to two distinct local liquid structures. Liquid polyamorphism is a property of a single-component liquid which can exist in two or more different amorphous phases, between which it can perform the so-called liquid-liquid transition.^{37,38} While liquid polyamorphism has been reported for several pure atomic systems and oxides, its existence has been suggested only for a few pure molecular liquids such as water, triphenyl phosphite (TPP), and *n*-butanol. Liquid polyamorphism requires that at least two different local structures exist in the liquid and that these local structures tend to be surrounded by the same structure, which is a property called cooperativity.^{37,38} Our results from previous sections

suggest that *cis*-decalin exhibits two different molecular environments and thus fulfills the first requirement for liquid polyamorphism. Apart from the high-temperature (HT) radical's environment in *cis*-decalin, the alternative low-temperature emerging (LTE) radical's environment was found to appear below about 340 K and to cause two distinguished EPR signals below $T_s=251$ K. However, the second requirement for liquid polyamorphism is not fulfilled in *cis*-decalin, as the occurring probability ϕ of the LTE environment doesn't show any discontinuous change upon cooling. Hence, *cis*-decalin shows polyamorphism only at the local scale, but not true polyamorphism at the global scale. However, the local-scale polyamorphism in *cis*-decalin occurs in its equilibrium state above $T_m=229$ K, while the global-scale polyamorphism in most molecular liquids is suggested to occur in their metastable supercooled state, where this phenomenon is difficult to observe and study due to crystallization effects.³⁸

In the single-component liquid with local interconvertible HT and LTE supramolecular states, the cooperativity of these states was introduced by the excess Gibbs energy G_E , which accounts for the non-ideal mixing of these states.³⁷ The proposed cooperative excess Gibbs energy from the regular solution model has the following symmetric form with respect to $\phi=1/2$:

$$G_E = 2k_B\phi(1-\phi)T_E, \quad (17a)$$

where T_E is a positive parameter promoting the separation of two supramolecular states.^{37,38} This form of G_E and the equilibrium equation for effective field $H_\phi=G_{FS}-\partial G_E/\partial\phi$ imply that the reduced effective field $h_\phi=H_\phi/(k_BT)$ in the first approximation for G_{FS} can be written as:

$$h_\phi(T) = h_1\left(\frac{T_e}{T} - 1\right) - \frac{T_e}{T}\left(\phi - \frac{1}{2}\right)h_E, \quad (17b)$$

where $h_E = 4T_E/T_e$. In the case $T_E \geq T_e$, the temperature T_e marks the liquid-liquid phase transition, while in the case $T_E < T_e$, it marks the equal fractions of both supramolecular states ($\phi = 1/2$). The temperatures T_e at various pressures define the liquid-liquid phase transition line for $T_E \geq T_e$ and the so-called Widom line for $T_E < T_e$.^{37,38} The reduced effective field in Eq. (17b) with positive T_E increases faster than $1/T$ with decreasing temperature, which is in contrast to our result in Fig. 8(c). Therefore, an attempt to simulate our local-fit results in Figs. 8(c,d) by Eq. (17b) gave a negative parameter $h_E = 4T_E/T_e$, which implies a negative parameter T_E . A negative parameter T_E promotes the mixing of HT and LTE supramolecular states, leading to the non-cooperativity of these states.

In order to properly simulate our local-fit results within the solution theory,³⁷ we applied the non-regular solution model³⁹ and extended the excess Gibbs energy in Eq. (17a) to the form:

$$G_E = -2k_B \phi(1-\phi)(T_E - T_{E1}\phi + T_{E2}\phi^2), \quad (18a)$$

where T_{E1} and T_{E2} are the non-regular solution parameters. The corresponding reduced effective field in the first approximation for G_{FS} can be written in the form:

$$h_\phi(T) = h_1 \left(\frac{T_e}{T} - 1 \right) - \frac{T_e}{T} \left[\left(\phi - \frac{1}{2} \right) h_E - \frac{3\phi}{2} \left(\phi - \frac{2}{3} \right) h_{E1} + 2\phi^2 \left(\phi - \frac{3}{4} \right) h_{E2} \right], \quad (18b)$$

where $h_{E1} = 4T_{E1}/T_e$ and $h_{E2} = 4T_{E2}/T_e$. The simulation of our local-fit results in Figs. 8(c,d) by Eq. (18b) gives the following values of parameters: $T_e = 216$ K, $h_1 = 26.0$, $h_E = 16.4$, $h_{E1} = 4.36$, and $h_{E2} = 26.0$. The simulation result for the reduced effective field from Eq. (18b) shows good agreement with local-fit results [Fig. (9a)], while the simulated excess Gibbs energy from Eq. (18a) shows negative values and an asymmetric form [Fig. (9b)]. We conclude that the reason why the reduced effective field for the LTE radical's environment grows more slowly than $1/T$ on cooling can be the non-cooperativity of the corresponding local LTE supramolecular state. The non-

cooperativity of the LTE supramolecular state can be described in the solution theory³⁷ by the negative excess Gibbs energy of mixing, which favors the miscibility of local LTE and HT supramolecular states over their separation.

One possible explanation for the enhanced miscibility of LTE and HT states is that the local order present in the LTE state is incompatible with the tiling of the whole space.⁴⁰ This feature, called geometrical frustration, can prevent the spread of the LTE state throughout the liquid and cause its localization into the so-called frustration-limited domains.⁴⁰ The enhanced miscibility of LTE and HT states may result from liquid structuring into the domains of the LTE state, which are separated by regions of the HT state.

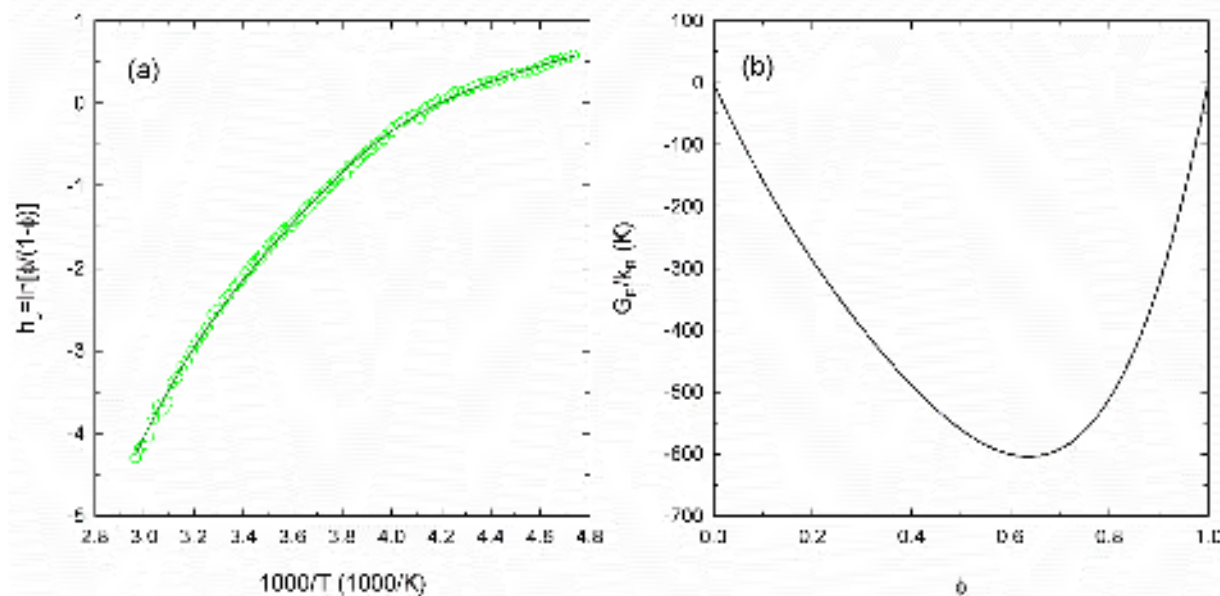


FIG. 9. (a) Local best-fit values (symbols) and simulation values obtained by Eq. (18b) (line) of reduced effective field h_ϕ versus inverse temperature. (b) Simulation values of excess Gibbs energy in temperature units G_E/k_B as a function of low-temperature emerging environment fraction ϕ .

By inspecting the literature data that could support our suggestion that the alternative LTE state exists in *cis*-decalin below about 340 K, we first mention the results of neutron scattering measurements and molecular dynamics simulations in liquid *cis*-decalin.²⁷ By cooling *cis*-decalin from room temperature into the glassy state, the intermolecular pair correlation functions from measurements and simulations show the appearance of an additional peak at about 8 Å, which is positioned between the first- and second-neighbor shell peaks. The appearance of this peak was attributed to the organization of some molecules into locally preferred structures, which were supposed to accompany the glass transition.²⁷ However, this peak can also signal the existence of an alternative LTE state in liquid.

In continuing this inspection, we should also mention the following results of temperature dependent measurements of different properties of *cis*-decalin.⁴¹⁻⁴⁴ First, the surface tension temperature dependence in *cis*-decalin exhibits an abrupt and considerable change in its slope at 323 K.⁴¹ Second, the vapor pressure of *cis*-decalin starts to deviate from its normal temperature dependence at temperatures below 333 K.^{42,43} Third, the light scattering intensity of *cis*-decalin drops markedly upon heating it from room temperature to 328 K or above, while the light scattering intensity of *trans*-decalin remains the same during such heating.^{43,44} Fourth, the heat capacity of *cis*-decalin exhibits irregular behavior in the region 323-333 K, which is not detected for the heat capacity of *trans*-decalin.⁴⁴ Finally, the temperature dependence of the Verdet constant in *cis*-decalin shows a similar change in its slope as that of surface tension, but at slightly lower temperatures.⁴³ All these results were interpreted to indicate that liquid *cis*-decalin undergoes some transformation at about 323 K, which was speculated to be some kind of coacervation.⁴³ It was proposed that *cis*-decalin is in a normal disordered liquid state above 323 K, while it undergoes

transformation into a more ordered cybotactic state below 323 K, in which islands or swarms of molecules are formed.⁴³ This interpretation surprisingly agrees with our finding that the alternative LTE radical's environment appears in *cis*-decalin below about 340 K.

We complete the inspection by reiterating our previous finding that the onset temperature of radical diffusion crossover T_{on} and the Arrhenius crossover temperature of viscosity T_A have similar values of about 335 K.²² As noted in the Introduction, these temperatures mark the onset of correlated and cooperative molecular motion on cooling, but their values in *cis*-decalin ($T_A \approx 2.3T_g \approx 1.5T_m$) are much higher than those expected for the most fragile molecular glass formers ($T_A \approx 1.4T_g \approx T_m$). In the present context, it is interesting to note that the temperatures T_{on} and T_A fall within the region where the alternative LTE radical's environment appears, suggesting that the high values of these temperatures may be related to the existence of two local supramolecular states in *cis*-decalin. It can be concluded that the mentioned experimental and theoretical results strongly indicate that our spin-probe study reveals the genuine properties of pure *cis*-decalin. More precisely, these results support our suggestion that two radicals' environments are caused by two local supramolecular states in pure *cis*-decalin, and not by some effect of the radical on the surrounding liquid. However, further diffraction measurements and molecular simulations are needed to fully confirm the coexistence of two local liquid states in *cis*-decalin.

Regarding the structural and dynamic properties of these local supramolecular states, we obtained the exchange relaxation time τ_w for two environments sensed by the dissolved radical [Fig. 8(b)]. The corresponding exchange rate $w=1/\tau_w$ is expected to have contributions from the local exchange of two supramolecular states, as well as from the radical migrations between the domains of these supramolecular states. We can speculate that different temperature dependences

of the two contributions mentioned could partly account for the unexpected downward deviation of τ_W from the Arrhenius law at low temperatures [Fig. 8(b)]. However, the low-temperature behavior of supramolecular-state relaxation in *cis*-decalin has to be elucidated through additional experimental and theoretical studies. Additional dynamical quantities obtained from our spin-probe experiment are the radical's rotational correlation times in two environments τ_{RF} and τ_{RS} [Fig. 8(a)]. Since the correlation time in the LTE environment τ_{RS} is about one order of magnitude higher than the correlation time in the HT environment τ_{RF} , we suppose that the LTE supramolecular state has a denser structure than the HT supramolecular state. Again, more detailed structural characteristics of supramolecular states in *cis*-decalin have to be provided by additional experimental and theoretical studies.

In further discussion, it is important to note that our study revealed three different relaxation times τ_{RF} , τ_{RS} , and τ_W [Figs. 8(a,b)], which clearly imply the heterogeneous relaxation dynamics in *cis*-decalin. The heterogeneity of structural relaxation dynamics in glass-forming liquids can be inferred from the distribution of relaxation times in the measured correlation function, and this distribution is associated with the non-exponential decay of the correlation function over time.^{12,13,26} The measured non-exponential decay usually follows the stretched exponential law $\exp[-(t/\tau)^\beta]$, where τ is the relaxation time and β ($0 < \beta \leq 1$) is the stretching exponent. In a given glass former, the lowness of the exponent β is not only a measure of the deviation of decay from the exponential law ($\beta=1$), but also of the wideness of its relaxation-time distribution, or the degree of its dynamical heterogeneity. The dielectric relaxation study of *cis/trans*-decalin mixture at temperatures close to T_g revealed very wide relaxation-time distributions that correspond to the low value of stretching exponent $\beta \approx 0.33$.²⁶ In addition, a

similarly low value of stretching exponent $\beta \approx 0.35$ was obtained for pure *cis*-decalin at 200 K from the time dependent relaxation results of a neutron scattering experiment.²⁷ Both results point to highly heterogeneous relaxation dynamics in *cis*-decalin, which are consistent with our results.

Another point we want to discuss in this context is the high fragility of *cis*-decalin. As we already mentioned, an extremely high fragility index $m=147$ was found for the *cis/trans*-decalin mixture by dielectric measurements.²⁶ A similarly high fragility index, $m=145$, was deduced from the calorimetric measurements for the *cis/trans*-decalin mixture with dominant *cis*-isomer.⁴⁵ Additionally, it was suggested from neutron scattering measurements that pure *cis*-decalin is as fragile as the *cis/trans*-decalin mixture.²⁷ However, it was noticed that the high fragility of *cis*-decalin is surprising given its other properties.⁴⁵ First, *cis*-decalin belongs to the group of saturated hydrocarbons, which exhibits systematically lower fragility than their aromatic analogs.⁴⁵ Second, *cis*-decalin exhibits a high ratio of its boiling point T_b and glass transition temperature T_g , which is not expected for a highly fragile glass former.⁴⁵ Third, the jump in heat capacity of *cis*-decalin at T_g seems to be too small given its high fragility.⁴⁵ The small ratio of this heat-capacity jump $\Delta C_p(T_g)$ and the fusion entropy ΔS_m is the reason why *cis*-decalin strongly deviates from the empirical formula $m=40\Delta C_p(T_g)/\Delta S_m$, which holds for many non-polymeric supercooled liquids.⁴⁶ Finally, we can again mention the high level of short-range ordering in *cis*-decalin at ambient conditions, as inferred from the neutron scattering measurements and molecular dynamics simulations.²⁷ The short-range ordering level in *cis*-decalin does not conform to its high fragility, as it is similar to that in much less fragile metallic glass formers and much higher than in the typical molecular glass former cumene.²⁷

In contrast to the above mentioned properties of *cis*-decalin, its wide relaxation-time distribution at T_g , which corresponds to the low stretching exponent $\beta \approx 0.33$, is the expected property of a highly fragile glass former.²⁶ To be more precise, *cis*-decalin satisfies the empirical expression of a positive correlation between the highness of fragility and the lowness of the stretching exponent $m = 250 - 320\beta$, which holds for a wide variety of glass formers.²⁶ Hence, the discussion presented suggests that the very high fragility of *cis*-decalin is associated with its highly heterogeneous relaxation dynamics, rather than with its other properties. This suggestion puts more significance on our spin-probe study because it revealed the coexistence of two distinct molecular environments in *cis*-decalin, which can naturally explain its highly heterogeneous relaxation.

Interestingly, our study revealed that these two environments differ not only in the values of rotational radical diffusivities but also in their temperature dependences. The radical's rotational correlation time in the slow LTE environment τ_{RS} follows the Arrhenius behavior in the comparison temperature region below 282 K. Above this region, the fraction of LTE environment becomes low ($\phi < 0.16$), and the influence of τ_{RS} on Γ_B and Γ_C becomes too weak to allow accurate determination of the temperature behavior of τ_{RS} . On the other hand, the correlation time in the fast HT environment τ_{RF} apparently changes its slope in the Arrhenius plot [Fig. 8(a)]. The slope of τ_{RF} at high temperatures is lower than that of τ_{RS} , but it increases at low temperatures, approaching the slope of τ_{RS} . Such super-Arrhenius behavior of τ_{RF} was approximated by the VFT law in the global-fit procedure [Fig. 8(a)]. These temperature behaviors are hard to relate to the very high fragility of *cis*-decalin because the glass transition temperature $T_g = 145$ K is far from the measured temperature region in our study, 211-373 K. Nevertheless, our study indicates an interesting possibility that the super-Arrhenius behavior of τ_{RF} is not the intrinsic characteristic of

the HT environment, but is induced by the appearance of LTE environment in liquid. The presence of the LTE environment near the molecule in the fast HT environment can affect its relaxation dynamics because the dynamical properties of the molecule depend not only on its immediate but also on its broader surroundings.³⁸ We can speculate that such induced fragility of the HT environment at T_g could significantly contribute to the very high fragility of *cis*-decalin.

The results of the spin-probe EPR study in *cis*-perfluorodecalin are presented here to better illustrate the anomalous behavior of EPR parameters in *cis*-decalin and to justify the use of weak temperature dependences in Eq. (14) for fast-environment parameters in *cis*-decalin. However, some remarks should be made about other experimental results for *cis*-perfluorodecalin that may be relevant in the present context. Specifically, the additional Gibbs energy arising from the existence of two supramolecular states in *cis*-decalin would produce distinct features in its thermodynamic properties that should not be present in *cis*-perfluorodecalin. Two-state models for liquid polyamorphism predict that such features can appear in thermodynamic properties such as density, viscosity, heat capacity, and isothermal compressibility.^{37,38,47}

Whereas the measured density of *cis*-perfluorodecalin shows a simple linear temperature dependence in the range 288-333 K,⁴⁸ the density of *cis*-decalin measured over the wider range 243-453 K exhibits a nonlinear temperature dependence, which was described by a third-order polynomial in temperature.⁴¹ This nonlinear dependence of *cis*-decalin density could reflect the influence of two supramolecular states, but this influence can hardly be isolated by comparison with the *cis*-perfluorodecalin density, which was measured over a much narrower temperature range. It has already been mentioned that the viscosity of *cis*-decalin exhibits super-Arrhenius temperature dependence below $T_A \approx 335$ K.²² In contrast, the viscosity of *cis*-perfluorodecalin

measured in the range 278-328 K follows the standard Arrhenius law.⁴⁸ This difference again suggests that the super-Arrhenius behavior of *cis*-decalin viscosity below T_A may result from the emergence of two supramolecular states. Although the viscosity of *cis*-perfluorodecalin follows the standard Arrhenius law, the rotational correlation time of pDTEMPONE [Fig. 4(b)] appears to begin exhibiting super-Arrhenius behavior as *cis*-perfluorodecalin is cooled to its melting point $T_m=266$ K.⁴⁸ This indicates that two supramolecular states could also exist in *cis*-perfluorodecalin, but their appearance is shifted into the supercooled state. This possible shift calls for future measurements of supercooled *cis*-perfluorodecalin. Such a shift would also be analogous to the shift of a liquid-liquid transition from the equilibrium to the supercooled state, which was considered in two-state models, and which results from a decrease in both the energy difference between the two local states and the cooperative energy.^{38,47}

DSC measurements show that the glass transition of *cis*-perfluorodecalin occurs at $T_g=177$ K, while crystallization during cooling starts at $T_{cr}=256$ K, which is 10 K below T_m .⁴⁸ In contrast, DSC measurements of *cis*-decalin show that crystallization during cooling starts at $T_{cr}=191$ K, which is 38 K below $T_m=229$ K.⁴⁹ The existence of such a wide supercooling region in *cis*-decalin has been exploited in our EPR study, and this much wider supercooling region in *cis*-decalin than in *cis*-perfluorodecalin (38 K vs. 10 K) suggests that *cis*-decalin has a much higher glass-forming ability. The enhanced glass-forming ability of *cis*-decalin indicates that the LTE supramolecular states, present in *cis*-decalin and suppressed or absent in *cis*-perfluorodecalin, prevent crystallization. If so, the LTE states play a role similar to that of the so-called locally favored structures (LFSs), which were introduced in the two-order parameter (TOP) model to reproduce both the liquid-glass⁵⁰ and liquid-liquid^{47,51,52} transition phenomena.

In the TOP model, LFSs act as impurities that suppress crystallization and promote the liquid-glass transition because their symmetry is incompatible with that of the crystal.⁵⁰ It has been proposed that the number density of LFSs increases upon cooling, because LFSs are energetically more favorable than normal-liquid structures. In glass-forming liquids, LFSs are randomly distributed in a sea of normal-liquid structure,⁵⁰ whereas the cooperativity of LFSs in polyamorphic liquids produces a liquid-liquid transition from a liquid phase with a low concentration of LFSs to a liquid phase with a high concentration of LFSs.^{47,51,52} Applying the TOP model to our case, we can understand local-scale polyamorphism in *cis*-decalin as an intermediate state between the extreme cases of a typical glass-forming liquid and a polyamorphic liquid. The domains of the LTE supramolecular state can be regarded as aggregates of LFSs, whereas the regions of the HT supramolecular state can be regarded as regions of normal-liquid structure that lack LFSs. This implies that some cooperativity between LFSs exists on the local scale of the domain size, but cooperativity on larger scales is absent, so a liquid-liquid transition does not occur. According to our EPR study, the LTE domains exhibit much slower molecular motion than the HT regions, indicating a higher local density of *cis*-decalin molecules in the LTE domains. This also suggests that the LTE domains and HT regions generate simultaneous structural and dynamical heterogeneities in *cis*-decalin, which persist even in its equilibrium liquid state. This enhanced dynamical heterogeneity has already been proposed to explain the broad relaxation-time distribution at $T_g=145$ K, which is associated with the very high fragility of *cis*-decalin. However, some caution is required because the lowest measured temperature in our study, 211 K, is far from T_g .

In the context of liquid fragility, an interesting prediction of the TOP model is that a liquid with a higher concentration of LFSs is a stronger glass former.^{50,52,53} This prediction is consistent with our case because the radical's rotational correlation time follows Arrhenius behavior in the slow LTE domains with supposedly high LFS concentration, and super-Arrhenius behavior in the fast HT regions with supposedly low LFS concentration [Fig. 8(a)]. For TPP, it was reported that the liquid-liquid transition between phases I and II occurs in its supercooled state.^{51,52} An interesting point is that liquid phases I and II are respectively similar to the HT regions and LTE domains in *cis*-decalin, because the high-temperature phase I has a lower density and higher fragility than the low-temperature phase II. The TOP model ascribes the higher fragility of phase I to the lower concentration of LFSs in this phase and the liquid-liquid transition to the cooperative growth of LFSs.^{51,52} In addition to the mentioned possibility that the higher fragility of HT regions is induced by the appearance of LTE domains, the TOP model indicates that the high fragility is an intrinsic characteristic of HT regions due to the low concentration of LFSs. In the molecular simulation based on the TOP model, the supercooled glass-forming liquid was shown to contain, in addition to normal-liquid structures and LFSs that prevent crystallization, long-lived clusters of medium-range crystalline order with slow dynamics, which increase the dynamical heterogeneity and fragility of the whole system.⁵³ Since these crystal-like clusters have a stronger effect on fragility when the forming ability of LFSs is weaker,⁵³ there is a possibility that HT regions with a low concentration of LFSs exhibit high fragility due to such crystal-like clusters. The effect of crystal-like clusters in HT regions is a possible mechanism below $T_m=229$ K, which can lead to both high dynamical heterogeneity and fragility of *cis*-decalin at $T_g=145$ K. It follows that the very high fragility of *cis*-decalin and its relationship to the coexistence of two supramolecular states are

interesting subjects for future studies. Measurements of *cis*-perfluorodecalin's fragility could be a useful step in these studies, because the coexistence of two supramolecular states is absent or suppressed in *cis*-perfluorodecalin.

Since the different liquid structures of polyamorphous TPP were linked with its different crystal polymorphs,⁵⁴ we also inspected the results of experiments on crystalline *cis*-decalin.^{28,49} It was found that liquid *cis*-decalin crystallizes at about 190 K upon slow cooling, while the quenched glassy *cis*-decalin crystallizes at about 170 K upon heating.²⁸ The crystal obtained from the glass is distinctly different from the one obtained upon slow cooling, and the two crystals coincide only above 180 K. This indicates that the crystallization from the glass is a complex process, which involves more than one crystalline arrangement.²⁸ Also, the crystallization from liquid at 180 K was found to be a complex process, which involves the formation of an unstable polymorph at early times and its transformation into the stable polymorph at later times.⁴⁹ Such complex behavior of the crystallization process on cooling was also confirmed by DSC measurements.⁴⁹ Thus, it seems possible that the two local liquid environments revealed in our study are somehow connected to the different crystalline arrangements that appear during the crystallization of *cis*-decalin. It is also interesting that the crystalline *cis*-decalin exhibits strongly anharmonic vibrational spectra²⁸ and a structural phase transition at 140-150 K.⁴⁹ These results indicate a high ability of *cis*-decalin molecules to readily adopt different local configurations in the crystalline state,²⁸ which can also explain the formation of two local environments in the liquid state.

The unstable polymorph observed during the crystallization of *cis*-decalin was not observed during the crystallization of *cis*-perfluorodecalin from the liquid at 200 K,⁴⁹ which could

be the result of the absence of two different local environments in liquid *cis*-perfluorodecalin. In the *cis*-perfluorodecalin crystal, the molecules are arranged in columns and are very efficiently packed.⁴⁹ In contrast, two types of columns are formed by molecules in *cis*-decalin crystals, resulting in lower packing efficiency.⁴⁹ These differences in the crystal structures of *cis*-perfluorodecalin and *cis*-decalin can be attributed to different intermolecular interactions between these compounds. In perfluorinated compounds, the presence of strong polar covalent C-F bonds and the very low polarizability of the fluorine atom lead to strong dipolar interactions and weak van der Waals interactions between molecules.^{49,55} Although the molecules of *cis*-perfluorodecalin and *cis*-decalin have the same structures, differences in intermolecular interactions between these compounds can lead to the observed differences in their local liquid environments.

In conclusion, we can say that the spin-probe EPR technique is suitable for studying heterogeneous liquids because it is sensitive to changes in the probe's environment. Here, the nitroxide radical is used as a spin probe to study *cis*-decalin and *cis*-perfluorodecalin liquids. The EPR parameters and rotational diffusivity of the radical exhibit the anomalous temperature behavior in *cis*-decalin, but not in *cis*-perfluorodecalin. Our interpretation of this result is that *cis*-perfluorodecalin behaves as a normal homogeneous liquid, while *cis*-decalin transforms from homogeneous to heterogeneous liquid upon cooling from 373 K through its equilibrium state. It is found that in addition to the fast high-temperature (HT) environment, a distinct, slower low-temperature emerging (LTE) environment appears around the radical during this transformation of *cis*-decalin. The exchange between the two radicals' environments slows down upon cooling into the supercooled state of *cis*-decalin, which allowed us to simulate the low-temperature EPR spectra as a sum of two signals originating from these environments.

By applying the environment-exchange theory and the fitting of EPR parameters, we determined the temperature dependence of the fraction of slow LTE environment ϕ , the exchange relaxation time τ_W , and the radical's rotational correlation times in fast and slow environments, τ_{RF} and τ_{RS} . The LTE environment fraction ϕ continuously increases with cooling, and this growth doesn't show cooperativity. Since we interpret the two radicals' environments as two distinct local liquid structures, this lack of LTE environment cooperativity indicates that *cis*-decalin doesn't exhibit a liquid-liquid transition or fluid polyamorphism. Instead of true global-scale polyamorphism in *cis*-decalin, our interpretation points to its local-scale polyamorphism that produces heterogeneous liquid structure even in the equilibrium state, which would be a rather unique property among molecular liquids. Several experimental and theoretical results in the literature support our finding that two local liquid environments coexist in *cis*-decalin, which indicates that our spin-probe study revealed the intrinsic properties of pure *cis*-decalin. An interesting result is that three different relaxation times τ_{RF} , τ_{RS} , and τ_W from our study clearly imply highly heterogeneous relaxation dynamics in *cis*-decalin, which seems to be associated with its very high fragility. Our results call for further investigation into the heterogeneous liquid structure of *cis*-decalin and its relation to high fragility and other properties of this material.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors declare no competing financial interests.

Data Availability

The data that support the findings of this article are openly available.⁵⁶

Authors Contributions

Miroslava Lukešová: Conceptualization (equal); Investigation (equal); Methodology (supporting); Validation (equal); Visualization (supporting); Writing – review & editing (equal).

Jakov Slade: Conceptualization (equal); Investigation (equal); Resources (equal).

Dalibor Merunka: Conceptualization (equal); Data curation (lead); Formal analysis (lead); Funding acquisition (lead); Investigation (equal); Methodology (lead); Project administration (lead); Resources (equal); Software (lead); Supervision (lead); Validation (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal).

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APPENDIX A: THEORY OF ENVIRONMENT EXCHANGE IN EPR

In the EPR experiment, the radical solution is subjected to a static magnetic field of amplitude B along the z -axis and a circularly polarized microwave magnetic field of amplitude B_1 , which rotates at a frequency ω in the perpendicular plane. We define the partial magnetization $\mathbf{M}_f$, which produces the hyperfine EPR line f and originates from radicals with the value m_I of the magnetic quantum number of the nitrogen nucleus.¹⁵ Because of the Zeeman interaction of electron spin with static magnetic field and the hyperfine interaction of electron spin with nitrogen nucleus, the precession frequency of $\mathbf{M}_f$ about the z -axis is given by $\omega_f = \gamma B + a m_I$, where $\gamma = g\beta_e/\hbar$ and a is the hyperfine coupling constant in frequency units. It is convenient to consider the components M_{fx} , M_{fy} and M_{fz} of partial magnetization in the coordinate system rotating with microwave frequency ω about the z -axis and having the x -axis along the microwave magnetic field. The time changes of the longitudinal M_{fz} and transverse $M_{f-} = M_{fx} - iM_{fy}$ partial magnetizations are described by the Bloch equations.^{14,15,31,32} Assuming a weak, non-saturating microwave field B_1 and a negligible coupling between the transverse partial magnetizations of different hyperfine lines, the Bloch equation for transverse partial magnetization is given by:

$$\partial M_{f-} / \partial t = -(1/T_{2f} + i\omega_f - i\omega)M_{f-} + i\gamma B_1 M_0, \quad (\text{A1})$$

where M_0 is the equilibrium value of longitudinal partial magnetization. The EPR absorption signal R is proportional to $-M_{fy} = \text{Im}M_{f-}$ in the stationary case $\partial M_{f-}/\partial t = 0$. By defining the reduced transverse magnetization $\mu_f = -iM_{f-}/(B_1 M_0)$, where M_{f-} is the stationary solution of Eq. (A1), it follows that the EPR signal is proportional to $\text{Re}\mu_f$, where $\mu_f = 1/(\Gamma_f + iB - iB_f)$, $\Gamma_f = 1/(\gamma T_{2f})$, and $B - B_f = (\omega_f - \omega)/\gamma$. It can be seen that the reduced transverse magnetization μ_f corresponds to the Lorentzian lineshape function of the line f from Eq. (5a) without a dispersive component.

Now, we assume that the radical can be embedded in either the fast (F) or slow (S) liquid environment with the probabilities $1-\phi$ and ϕ , respectively. The exchange of F and S environments around the radical is defined by the transition rate from F to S environment, w_{FS} , and the transition rate from S to F environment, w_{SF} . We further assume that the hyperfine EPR line f of the radical is defined by the frequency ω_{fE} and transverse relaxation time T_{2fE} , which are both sensitive to the local environment $E=F, S$. In order to account for the environment exchange effect on the EPR spectrum, we define the transverse partial magnetizations M_{fF-} and M_{fS-} of radicals in the F and the S environments, respectively. The magnetizations obey $M_{fF-} + M_{fS-} = M_{f-}$ and the Bloch equations:^{14,31,32}

$$\begin{aligned} \partial M_{fF-} / \partial t &= -(w_{FS} + 1/T_{2pF} + i\omega_{fF} - i\omega)M_{fF-} + w_{SF}M_{fS-} + i\gamma B_1 M_0 (1-\phi) \\ \partial M_{fS-} / \partial t &= -(w_{SF} + 1/T_{2pS} + i\omega_{fS} - i\omega)M_{fS-} + w_{FS}M_{fF-} + i\gamma B_1 M_0 \phi \end{aligned} \quad (A2)$$

The transition rates obey the exchange equilibrium relations $w_{FS} = \phi w$ and $w_{SF} = (1-\phi)w$, where $w = w_{FS} + w_{SF}$ is the exchange rate. We consider Eq. (A2) in stationary case $\partial M_{fF-} / \partial t = \partial M_{fS-} / \partial t = 0$ and introduce the reduced transverse magnetization $\mu_{fF} = -iM_{fF-} / (B_1 M_0)$ and $\mu_{fS} = -iM_{fS-} / (B_1 M_0)$, which were found to satisfy the following equation:

$$\begin{bmatrix} Z_{fF} + W\phi & -W(1-\phi) \\ -W\phi & Z_{fS} + W(1-\phi) \end{bmatrix} \begin{bmatrix} \mu_{fF} \\ \mu_{fS} \end{bmatrix} = \begin{bmatrix} 1-\phi \\ \phi \end{bmatrix}. \quad (A3)$$

Here, $W = w/\gamma$ is the exchange rate in magnetic field units and $Z_{fE} = \Gamma_{fE} + i(B - B_{fE})$ are the complex functions defined by the position B_{fE} and width Γ_{fE} of the line for the environment E . By finding the solutions μ_{fF} and μ_{fS} of Eq. (A3), we can construct the EPR absorption signal $R = J \times \text{Re} \mu_f$, where J is the intensity constant and $\mu_f = \mu_{fF} + \mu_{fS}$. The Eq. (A3) has trivial solutions for $W \rightarrow 0$, and the total

magnetization is given by $\mu_f = (1-\phi)/Z_{fF} + \phi/Z_{fS}$. For a general value $W > 0$, we define the average complex function:

$$Z_{fa} = \Gamma_{fa} + i(B - B_{fa}); \Gamma_{fa} = (1-\phi)\Gamma_{fF} + \phi\Gamma_{fS}; B_{fa} = (1-\phi)B_{fF} + \phi B_{fS}, \quad (\text{A4a})$$

and the complex parameter of environmental differences in width and position:

$$\delta Z_f = \delta\Gamma_f - i\delta B_f; \delta\Gamma_f = \Gamma_{fS} - \Gamma_{fF}; \delta B_f = B_{fS} - B_{fF}. \quad (\text{A4b})$$

Using diagonalization of the square system matrix in Eq. (A3), it can be shown³⁵ that the total magnetization in this general case can also be represented as the sum of two Lorentzian lines:

$$\mu_f(B) = (1 - \Phi_f) / Z_f + \Phi_f / (Z_f + \Delta Z_f), \quad (\text{A4c})$$

where Z_f and $Z_f + \Delta Z_f$ are the eigenvalues of the system matrix. The function $Z_f = \Gamma_f + i(B - B_f)$, the intensity parameter $\Phi_f = \phi_f - i\theta_f$, and the line-difference parameter $\Delta Z_f = \Delta\Gamma_f - i\Delta B_f$ are given by:

$$Z_f = Z_{fa} + (X_f - \Delta Z_f) / 2; \Phi_f = (1 - X_f / \Delta Z_f) / 2; \Delta Z_f = \sqrt{X_f^2 + 4\phi(1-\phi)\delta Z_f^2}, \quad (\text{A4d})$$

where

$$X_f = W + (1 - 2\phi)\delta Z_f. \quad (\text{A4e})$$

For very fast exchange of radical environments ($W \rightarrow \infty$), the intensity parameter Φ_f is close to zero. Then, only the first line in Eq. (A4c) contributes to the EPR spectrum, and its complex function Z_f is close to the average function Z_{fa} . This is the expected result for fast exchange, when only a single average line exists in the EPR spectrum.^{14,31,32} The first line in Eq. (A4c), dominating in the fast-exchange regime, is named a primary line, while the other one is named a secondary line.

We present here one example of environment exchange, where the F -environment probability is $1-\phi=0.6$, while the width and field position of EPR line f are higher in the S environment by $\delta\Gamma_f=0.5 \times 10^{-4}$ T and $\delta B_f=0.2 \times 10^{-4}$ T, respectively. In this example, we used Eq.

(A4) to calculate the parameters of primary and secondary Lorentzian lines as a function of the exchange rate W (Fig. 10). The intensities of absorptive components of primary and secondary lines are proportional to the absorption parameters $1-\phi_f$ and ϕ_f , respectively, which depend on W as in Fig. 10(a). The absorption parameter of primary line $1-\phi_f$ decreases from 1 at high W to the intensity parameter of F -environment line $1-\phi=0.6$ at low W . The fact that the primary line becomes the F -environment line at low W is due to the positive value of $\delta\Gamma_f$ in our example. The intensity loss of the primary line is compensated by the intensity gain of the secondary line, whose intensity parameter ϕ_f increases from 0 at high W to that of the S -environment line $\phi=0.4$ at low W .

The intensities of dispersive components of primary and secondary lines are proportional to the dispersion parameters θ_f and $-\theta_f$, respectively, which depend on the exchange rate W as in Fig. 10(b). The non-zero dispersion parameter θ_f originates from the non-zero lineshift δB_f , and since both parameters have the same signs, the positive θ_f in our example is a consequence of the positive δB_f [Fig. 10(b)]. The parameter θ_f is almost zero for very fast and very slow exchange, but it exhibits a maximum for the intermediate exchange.

We also calculated from Eq. (A4) the deviation from average position $dB_f=B_f-B_{fa}$ [Fig. 10(c)] and the deviation from average width $d\Gamma_f=\Gamma_f-\Gamma_{fa}$ [Fig. 10(d)] of primary line. As expected, the primary-line deviations are close to zero at high W , and they decrease to the corresponding deviations of F -environment line $B_{fF}-B_{fa}=-\phi\delta B_f$ and $\Gamma_{fF}-\Gamma_{fa}=-\phi\delta\Gamma_f$ at low W . The calculated position deviation $dB_f+\Delta B_f$ and width deviation $d\Gamma_f+\Delta\Gamma_f$ of secondary line are also presented in Figs. 10(c,d). These deviations at low W are close to the corresponding deviations of S -

environment line $B_{fs}-B_{fa}=(1-\phi)\delta B_f$ and $\Gamma_{fs}-\Gamma_{fa}=(1-\phi)\delta\Gamma_f$. By increasing W , the position deviation tends toward $(1-2\phi)\delta B_f$, while the linewidth deviation tends to increase proportionally to W .

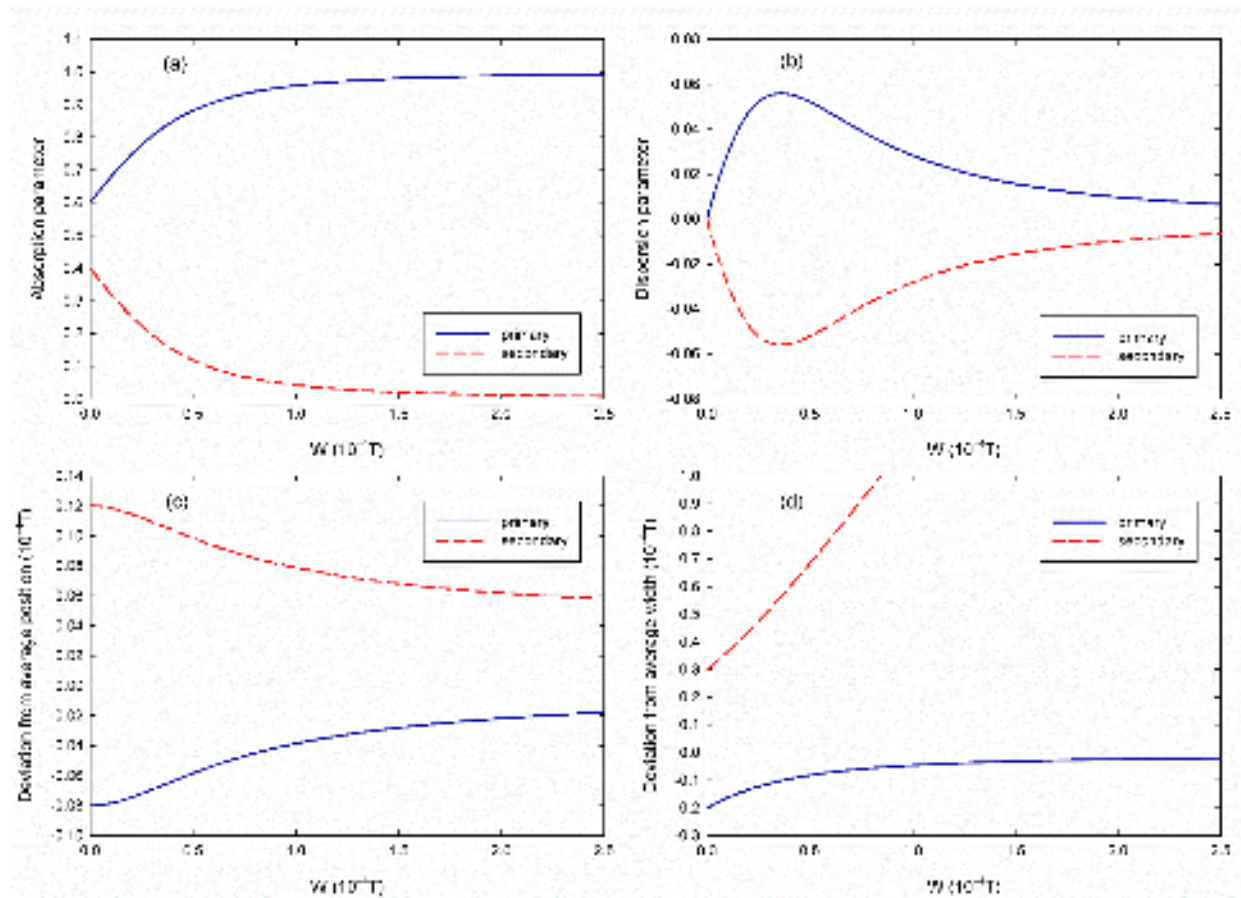


FIG. 10. Calculated parameters of the primary and secondary Lorentzian EPR lines as a function of the rate of environment exchange W : absorption parameters (a), dispersion parameters (b), deviations of line positions from the average position (c), and deviations of linewidths from the average linewidth (d). The values of exchange parameters are given in the text.

APPENDIX B: EFFECTS OF ENVIRONMENT EXCHANGE ON EPR QUANTITIES

We consider a dissolved radical surrounded either by a slow (S) environment in which its rotational correlation time is τ_{RS} , or by a fast (F) environment in which its correlation time is τ_{RF} . Then, the rotational-modulation contributions to linewidths in S and F environments can be written in the forms analogous to Eq. 8(b):

$$\begin{aligned}\Gamma_{rS}(m_I) &= \Gamma_{ArS} - \Gamma_{BrS}m_I + \Gamma_{CrS}m_I^2 \\ \Gamma_{rF}(m_I) &= \Gamma_{ArF} - \Gamma_{BrF}m_I + \Gamma_{CrF}m_I^2\end{aligned}\quad (B1)$$

Here, the coefficients Γ_{ArE} , Γ_{BrE} , and Γ_{CrE} are given by the equations 8(c), 8(d), and 8(e), respectively, while the corresponding spectral densities $j_{\omega,E}$ are given by Eq. 8(f) with τ_R replaced by τ_{RE} ($E=S,F$). The linewidths in S and F environments have additional spin-rotation contributions that are independent of m_I :

$$\Gamma_{sS}(m_I) = \Gamma_{AsS}; \Gamma_{sF}(m_I) = \Gamma_{AsF}. \quad (B2)$$

Here, the coefficients Γ_{AsE} are given by Eq. (12) with τ_R replaced by τ_{RE} . Also, the rotational-modulation mechanism produces the shifts of hyperfine lines.^{14,18,32} The resulting lineshifts in S and F environments are:

$$\begin{aligned}B_{rS}(m_I) &= B_{0rS} - A_{rS}m_I + C_{rS}m_I^2 \\ B_{rF}(m_I) &= B_{0rF} - A_{rF}m_I + C_{rF}m_I^2\end{aligned}\quad (B3)$$

Here, the coefficients B_{0rE} , A_{rE} , and C_{rE} are given again by the equations 8(c), 8(d), and 8(e), respectively, but the corresponding spectral density for environment E is given by:

$$k_{\omega,E} = \omega\tau_{RE}^2 / (1 + \omega^2\tau_{RE}^2), \quad (B4)$$

instead of the spectral density $j_{\omega,E}$. The coefficients in Eq. (B1) and Eq. (B3) are respectively defined by the real and imaginary parts of the complex spectral density $j_{\omega,E} - ik_{\omega,E}$, which is the

Fourier transform at positive times $\tau > 0$ of the autocorrelation function for rotational diffusion in E environment:

$$\Psi_{m,E}(\tau) = \langle Y_{2,m}^*[\Omega(0)]Y_{2,m}[\Omega(\tau)] \rangle / \langle |Y_{2,m}[\Omega(0)]|^2 \rangle = \exp(-\tau / \tau_{RE}) \quad (\text{B5})$$

Here, $Y_{2,m}$ are the second-rank spherical harmonics and Ω denotes polar and azimuthal angles of the radical's orientation.^{14,36} The function in Eq. (B5) can be applied if the E environment lasts longer than the corresponding rotational correlation time τ_{RE} .^{8,36} In our environment-exchange theory (Appendix A), the lifetimes of F and S environments are respectively $\tau_{FS} = 1/w_{FS} = \phi^{-1}w^{-1}$ and $\tau_{SF} = 1/w_{SF} = (1-\phi)^{-1}w^{-1}$, which means that Eqs. (B1) and (B3) hold for $\tau_{FS} \gg \tau_{RF}$ and $\tau_{SF} \gg \tau_{RS}$.

The experimental EPR quantities that we consider first are the width differences $\Delta\Gamma(m_I)$ [Figs. 7(c,d)] and the position differences $\Delta B(m_I)$ [Figs. 6(f,g)] between the secondary and primary hyperfine lines m_I . According to the environment-exchange theory in Appendix A, the secondary-to-primary line difference parameter $\Delta Z(m_I) = \Delta\Gamma(m_I) - i\Delta B(m_I)$ differs for finite exchange rate W from the environmental line difference parameter $\delta Z(m_I) = \delta\Gamma(m_I) - i\delta B(m_I)$. Here, $\delta\Gamma(m_I)$ and $\delta B(m_I)$ are defined in Eq. (A4b) as, respectively, the position and width differences between S and F environments. It follows from Eqs. (A4d) and (A4e) that $\Delta Z(m_I)$ and $\delta Z(m_I)$ are related as:

$$\Delta Z(m_I) = \sqrt{\delta Z^2(m_I) + 2(1-2\phi)W\delta Z(m_I) + W^2} \quad (\text{B6})$$

According to Eqs. (B1-B3), the environmental differences $\delta B(m_I)$ and $\delta\Gamma(m_I)$ have the following contributions from the rotational radical diffusion:

$$\begin{aligned} \Gamma_{RS}(m_I) - \Gamma_{RF}(m_I) &= \delta\Gamma_{As} + \delta\Gamma_{Ar} - \delta\Gamma_{Br}m_I + \delta\Gamma_{Cr}m_I^2 \\ B_{RS}(m_I) - B_{RF}(m_I) &= \delta B_{0r} - \delta A_r m_I + \delta C_r m_I^2 \end{aligned} \quad (\text{B7})$$

where the coefficients on the right-hand side are the differences between the S - and F -environment coefficients in Eqs. (B1-B3). However, there are contributions from the additional mechanisms that are not connected with the radical's rotation. These non-rotational (n) contributions are supposed to be the linewidth difference $\delta\Gamma_{An}$ for both N isotopes and every m_I , the relative central-field difference δb_{0n} for both N isotopes, and the hyperfine coupling difference δA_n for the ^{14}N isotope. Thus, the total environmental differences are:

$$\begin{aligned}\delta\Gamma(m_I) &= \delta\Gamma_0 - \delta\Gamma_B m_I + \delta\Gamma_C m_I^2 = (\delta\Gamma_{An} + \delta\Gamma_{As} + \delta\Gamma_{Ar}) - \delta\Gamma_{Br} m_I + \delta\Gamma_{Cr} m_I^2 \\ \delta B(m_I) &= \delta B_0 - \delta A m_I + \delta C m_I^2 = (B_e \delta b_{0n} + \delta B_{0r}) - (\delta A_n + \delta A_r) m_I + \delta C_r m_I^2\end{aligned}\quad (\text{B8a})$$

for ^{14}N -pDTEMPONE ($m_I = -1, 0, 1$) and

$$\begin{aligned}\delta\Gamma(m_I) &= \delta\Gamma_0 - \delta\Gamma_B m_I = (\delta\Gamma_{An} + \delta\Gamma_{As} + \delta\Gamma_{Ar} + \delta\Gamma_{Cr} / 4) - \delta\Gamma_{Br} m_I \\ \delta B(m_I) &= \delta B_0 - \delta A m_I = (B_e \delta b_{0n} + \delta B_{0r} + \delta C_r / 4) - (q \delta A_n + \delta A_r) m_I\end{aligned}\quad (\text{B8b})$$

for ^{15}N -pDTEMPONE ($m_I = -1/2, 1/2$).

The second group of experimental EPR quantities considered consists of the absorption parameters $\varphi(m_I)$, shown in Figs. 6(b,c) and the dispersion parameters $\theta(m_I)$ in Figs. 6(d,e). According to Eqs. (A4d) and (A4e), the experimental intensity parameter $\Phi(m_I) = \varphi(m_I) - i\theta(m_I)$ is given by:

$$\Phi(m_I) = \frac{1}{2} - \frac{W + (1 - 2\phi)\delta Z(m_I)}{2\Delta Z(m_I)}, \quad (\text{B9})$$

where $\delta Z(m_I)$ is defined by Eq. (B8), while $\Delta Z(m_I)$ is defined by Eq. (B6). Equation (B9) shows that at very low W , the intensity parameter of secondary line $\Phi(m_I)$ and that of primary line $1 - \Phi(m_I)$ tend respectively to the probability of S environment ϕ and that of F environment $1 - \phi$.

The third group of experimental EPR quantities comprises that of the main primary lines shown in Figs. 6(h) and 7(a,b,e,f). These quantities are defined by Eqs. (2) and (11), which can be written respectively for ^{14}N - and ^{15}N -pDTEMPONE as:

$$\Gamma(m_I) = \Gamma_0 - \Gamma_B m_I + \Gamma_C m_I^2; B(m_I) = B_0 - A m_I + C m_I^2, \quad (\text{B10a})$$

$$\Gamma(m_I) = \Gamma_0 - \Gamma_B m_I; B(m_I) = B_0 - A m_I. \quad (\text{B10b})$$

Here, the right-hand side coefficients are the experimental quantities, while the left-hand side quantities $B(m_I)$ and $\Gamma(m_I)$ are the primary line position and width, respectively. According to Eqs. (A4a), (A4d) and (A4e), the complex function of primary line $Z(B, m_I) = \Gamma(m_I) + i[B - B(m_I)]$ is related to the corresponding F -environment function $Z_F(B, m_I) = \Gamma_F(m_I) + i[B - B_F(m_I)]$ as:

$$Z(B, m_I) = Z_F(B, m_I) + \frac{W + \delta Z(m_I) - \Delta Z(m_I)}{2}, \quad (\text{B11})$$

where $\Delta Z(m_I)$ is given by Eq. (B6). This equation shows that the experimental primary line corresponds to the F -environment line for very low W or very low ϕ . By writing the equations analogous to Eq. (B10) for all quantities on the right-hand side of Eq. (B11), we obtain the following equations for the experimental coefficients:

$$\begin{aligned} \Gamma_0 &= \Gamma_{0F} + \frac{\delta\Gamma_0 - \Delta\Gamma_0}{2} + \frac{W}{2}; B_0 = B_{0F} + \frac{\delta B_0 - \Delta B_0}{2} \\ \Gamma_B &= \Gamma_{BF} + \frac{\delta\Gamma_B - \Delta\Gamma_B}{2}; A = A_F + \frac{\delta A - \Delta A}{2} \\ \Gamma_C &= \Gamma_{CF} + \frac{\delta\Gamma_C - \Delta\Gamma_C}{2}; C = C_F + \frac{\delta C - \Delta C}{2} \end{aligned} \quad (\text{B12})$$

where the first and second terms on the right-hand sides of equations are, respectively, the F -environment coefficients and the environmental difference coefficients from Eq. (B8). The third terms correspond to components of the complex coefficients $\Delta Z_0 = \Delta\Gamma_0 - i\Delta B_0$, $\Delta Z_B = \Delta\Gamma_B - i\Delta A$, and

$\Delta Z_C = \Delta \Gamma_C - i\Delta C$, which are the linear combinations of $\Delta Z(m_I)$ in Eq. (B6). These combinations for ^{14}N -pDTEMPONE are $\Delta Z_0 = \Delta Z(0)$, $\Delta Z_B = [\Delta Z(-1) - \Delta Z(1)]/2$, and $\Delta Z_C = [\Delta Z(-1) + \Delta Z(1)]/2 - \Delta Z(0)$, while those for ^{15}N -pDTEMPONE are $\Delta Z_0 = [\Delta Z(-1/2) + \Delta Z(1/2)]/2$ and $\Delta Z_B = \Delta Z(-1/2) - \Delta Z(1/2)$. In order to define the F -environment coefficients in Eq. (B12), we notice first that all F -environment coefficients contain the rotational-modulation and spin-rotation contributions given by Eqs. (B1-B3). We suppose that the non-rotational (n) contribution to the F -environment linewidth coefficients is only the linewidth Γ_{An} , being equal for both N isotopes and every m_I , while all F -environment line-position coefficients are supposed to contain the non-rotational contributions. The supposed non-rotational contribution to the relative central field is b_{0n} for both N isotopes, that for hyperfine coupling is A_{n2} for ^{14}N and A_{n1} for ^{15}N , while that for the second-order shift of ^{14}N isotope is C_n . The final result is that the total F -environment coefficients for ^{14}N -pDTEMPONE can be written as:

$$\begin{aligned} \Gamma_{0F} &= \Gamma_{An} + \Gamma_{AsF} + \Gamma_{ArF}; \Gamma_{BF} = \Gamma_{BrF}; \Gamma_{CF} = \Gamma_{CrF} \\ B_{0F} &= B_e b_{0n} + B_{0rF}; A_F = A_{n2} + A_{rF}; C_F = C_n + C_{rF} \end{aligned} \quad (\text{B13a})$$

while those for ^{15}N -pDTEMPONE can be written as:

$$\begin{aligned} \Gamma_{0F} &= \Gamma_{An} + \Gamma_{AsF} + \Gamma_{ArF} + \Gamma_{CrF}/4; \Gamma_{BF} = \Gamma_{BrF} \\ B_{0F} &= B_e b_{0n} + B_{0rF} + C_{rF}/4; A_F = A_{n1} + A_{rF} \end{aligned} \quad (\text{B13b})$$

The last group of experimental quantities considered includes the ^{13}C hyperfine coupling constants of satellite primary lines $A_{C,X}$ [Fig. 6(i)]. Since these coupling constants also exhibit anomalous temperature behavior, we assume that the ^{13}C coupling constant of carbon C_X has a small slow-to-fast environmental difference $\delta A_{C,X}$, which was neglected in the secondary-signal fitting function from Eq. (10b). Because of the environment exchange, the primary satellite lines

positioned around the main line m_I are displaced to each other by the field difference $A_{C,X}(m_I)$ that depends on m_I . It is easy to show from Eq. (7c), (B6), and (B11) that this field difference can be written as:

$$\begin{aligned} A_{C,X}(m_I) &= A_{C,X,F} + \frac{\delta A_{C,X} - \Delta A_{C,X,m_I}}{2} \\ \Delta A_{C,X,m_I} &= -\text{Im}(\Delta Z_{C,X,m_I,p=-1/2} - \Delta Z_{C,X,m_I,p=+1/2}) \\ \Delta Z_{C,X,m_I,p} &= \sqrt{[\delta Z(m_I) + ip\delta A_{C,X}]^2 + 2W(1-2\phi)[\delta Z(m_I) + ip\delta A_{C,X}] + W^2} \end{aligned} \quad , \quad (\text{B14})$$

where $A_{C,X,F}$ is the ^{13}C coupling constant of C_X carbon in the F -environment.

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