

Surface relaxation of polarized Xe atoms dissolved in deuterated ethanol

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Abstract

We measured the spin relaxation of polarized xenon atoms dissolved in deuterated ethanol. Surface relaxation was suppressed by coating the cell walls with deuterated eicosane. From the dependence of the decay rate on temperature and static magnetic field, we obtained the correlation time of random fluctuations of the local field at the liquid–solid interface. By varying the cell volume, the wall coating, and the surface area of the eicosane, we measured the contribution of the spin–rotation interaction to the relaxation. The use of both deuterated molecules enables us to distinguish surface relaxation from the magnetic dipole–dipole and spin–rotation interactions in solution.

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1. Introduction

Hyperpolarized xenon (Xe) holds great promise for extremely sensitive NMR spectroscopy [1,2]. Because the initial polarization is high independent of the magnitude of the external magnetic field, the spin dynamics in solutions can be investigated in a wide range of fields. The spin relaxation is dominated by cross-relaxation between Xe atoms and solution molecules [3–7]. Since the moving magnetic dipoles transiently interact with each other, lower viscosity leads to a smaller decay rate in the fast motion limit [8]. On the other hand, wall relaxation can be dominant in low-viscosity solutions because Xe atoms collide with the cell walls within the relaxation time of the dissolved Xe [9]. If we can succeed in suppressing wall relaxation, the resonance signals could be detected many times before the atoms depolarize. In addition, we could detect weak perturbations such as the spin–rotation (SR) interaction and chemical shift anisotropy (CSA) [10–13], which would otherwise be hidden by the above relaxations in a finite-sized cell. Spin relaxation on solid surfaces has been report-

ed for cross-relaxation of gaseous and liquid ^{129}Xe nuclei with protons of coating material [14,15], relaxation of gaseous ^3He nuclei due to magnetic sites in the glass [16], and relaxation of a thin ^{129}Xe film on metal [17]. For Xe atoms in solution, we need to develop a better understanding of wall relaxation as well as the weak perturbation due to the solvent such as a straight-chain molecule.

In this paper, we study the spin relaxation of the dissolved ^{129}Xe atoms at cell walls. A Pyrex glass cell was filled with deuterated ethanol (ethanol- d_6 , $\text{C}_2\text{D}_5\text{OD}$, 99.5 ATOM% D, ISOTEC), and the inner walls were coated with deuterated paraffin (eicosane- d_{42} , $\text{CD}_3(\text{CD}_2)_{18}\text{CD}_3$, 98 ATOM% D, ISOTEC). One is an alkanol and the other is a straight-chain alkane. The coating serves to smooth out discontinuities in the xenon chemical shift and permeability at the interface. Xenon nuclear spins evolve in similar magnetic circumstances everywhere in the glass cell. The decay rate was measured as a function of the temperature, field strength, surface area of eicosane, and volume of the glass cell. In solutions, unlike in gaseous mixtures, Xe atoms are under the strong influence of dipole interactions with solvent molecules. It is the use of a deuterated solvent and coating that enables us to investigate the surface interaction in this experiment. We report on the suppression of

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wall relaxation and the SR interaction between xenon and ethanol.

2. Experiment

Xenon was polarized by spin-exchange optical pumping with a flow-type polarizer [4]. The Xe gas was of natural abundance and the partial pressure was 26 kPa. With the N₂ and He gases, the total pressure was 290 kPa. The spin polarization was approximately 4%. The spin relaxation time of gaseous atoms is longer than that of dissolved atoms, so we need to avoid the complex situation that the decay rate includes a contribution from exchange of Xe atoms between the gas and solution. As shown in Fig. 1, we used a glass cell designed to suppress the exchange of Xe atoms [9]. The inner diameter of the cell labeled $\phi 9$ was 9 mm and smaller than the $\phi 13$ and $\phi 18$ cells used as reference. The length was 21 mm and nearly equal to the others. The small cell was prepared specifically to study wall relaxation. The temperature T of the Xe-saturated solution was controlled by blowing cold N₂ gas on the glass cell. The external magnetic field B_0 was applied at 27.7, 100, and 330 mT to study the dependence of decay rate on static field. By applying RF pulses with a typical period of 60 s, we measured the Xe spin polarization by calculating the area of the NMR peak. The flip angle was less than 5° every excitation, and 25 pulses were typically applied for a single decay measurement. Since the width of the NMR spectra was not observed to change within the experimental resolution of 45 ppm, the time dependence of the peak area was taken as that of amplitude of the free-induction decay. The flip angle and spin density of the polarized Xe solution were so small that radiation dumping and maser oscillation as well as nonlinear effects to spin dynamics were negligible at our magnetic fields. The increase of the decay rate due to excitation pulses

was calculated from the flip angle to be less than the fitting error (typically, $\pm 3 \times 10^{-5}$ 1/s). This polarization loss was numerically compensated when single-exponential decay curves were fitted to the measured amplitudes. The temperature dependence of the polarization loss generally arises from variations in the Q factor of the probe with changing temperature. The resonance frequency of probe was insensitive to the temperature of solution because the tuning capacitors were placed at room temperature. Moreover, the change of temperature was negligible during a single decay measurement. Even in the measurement of temperature dependence of decay rate, the signal amplitude was consistent with the dependence of Xe solubility on temperature. Therefore, we conclude that systematic error due to temperature variations is not a serious problem in our experiment.

Polarized gas was flowed into the solution with a capillary tube as shown in Fig. 1A. The solution was agitated by the gas flow though no visible bubbles were left under the constriction of the glass cell. When decay rates were measured for the uncoated and coated cells, data acquisition was typically started two minutes after stopping the gas flow. In spite of this delay, we obtained different values of the diffusion coefficient every shot with the steady-gradient spin-echo diffusometry over time intervals longer than 100 ms. Therefore, we guess that the translational motion of Xe atoms and ethanol molecules was dominated by convection rather than diffusion. This convection is driven by the gas flow, the temperature gradient, and the difference of mass density between Xe and ethanol [18]. This is similar to gas experiments in that the gaseous atoms collide with the cell walls by both diffusive and convective motions in buffer gases [19]. Because of the convection, the polarized Xe atoms collide many times with the walls within the relaxation time in ethanol. The issue on the translational motion is further discussed in the section of decay measurement for uncoated cell.

As a pretreatment for coating, the glass cell was baked in air and rinsed with protonated ethanol once and then with deuterated ethanol. After the cell had dried, the eicosane- d_{42} was treated with vacuum degassing three times. No more purification of eicosane was performed. The eicosane- d_{42} was warmed to approximately 315 K in the presence of N₂ gas and then applied to the inner walls. Therefore, oxygen molecules were expected to be absent from the coating. The coated walls appeared to have a textured surface at room temperature. An average coating thickness of 0.16 mm is enough to decouple Xe atoms from any magnetic sites in/on the glass surface. Though protonated eicosane would be suitable for the study of wall relaxation, it was not used so as to prevent some protonated molecules from seeping out. The coated glass cell was filled with ethanol- d_6 . To de-oxygenate the ethanol, we flowed a mixture of Xe, He, and N₂ gas into the ethanol by varying the pressure of the flowing gas up and down. After stopping the gas flow at a pressure of 300 kPa, we left the glass cell at 290 K for a night. The surface area of the capillary is

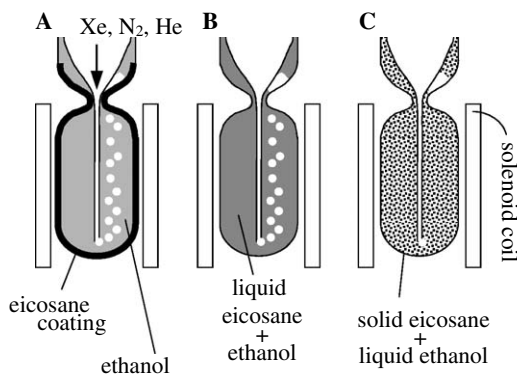


Fig. 1. Glass cells were designed with a constriction which suppresses the exchange of Xe atoms between the gas and liquid phases. A solenoid pick-up coil covers the volume below the constriction. The length and inner diameter are 21 and 9 mm, respectively. (A) The cell walls are coated with the eicosane- d_{42} at an average thickness of 0.16 mm. (B) Above the melting point, all of the eicosane molecules dissolve in the ethanol. (C) Upon rapid cooling with cold N₂ gas, the crystallites of eicosane- d_{42} distribute over the whole volume.

so small that the spin relaxation due to the uncoated tube is negligible. In fact, as discussed below, the decay rate due to the glass walls of the uncoated cell was approximately 2×10^{-4} 1/s at 260 K. The contribution of the capillary tube is estimated to be 5×10^{-6} 1/s from the ratio of its surface area to that of the glass walls.

The decay rates were measured from 230 K up to the melting point of eicosane, approximately 309 K. A small amount of eicosane dissolves in ethanol even below the melting point. This dissolved eicosane was moved and deposited above the constriction of glass cell by convection during gas flow. This dissolution affects the decay rate less at lower temperatures. Twenty decay measurements were typically performed for a whole day without loss of the coating. Because the mole fraction solubility of Xe is 3.24×10^{-2} in liquid eicosane at 313 K [20], which is of the same order as the solubility in ethanol [9,21,22], we need to take into account the dissolved eicosane above the melting point. The possibility of micelles in the solution could not be eliminated at present. This issue could be investigated with high-resolution Xe NMR in the presence of both ethanol and eicosane.

We also measured the decay rate for a mixture of solid eicosane and liquid ethanol as shown in Fig. 1C in order to study its dependence on the eicosane surface area. The mixture obtained by rapid cooling consisted of an assembly of eicosane crystallites suspended in liquid ethanol, which is a kind of slurry. Polarized gas flow, however, breaks up the structure of the mixture. We needed an experimental procedure specific to this mixture. As shown in Fig. 1B, polarized xenon was flowed into the liquid mixture above the eicosane melting point. The amount of eicosane was measured such that all of it was dissolved in the ethanol, resulting in a homogeneous liquid. We monitored the NMR signal amplitude by small-angle pulses during the gas flow. After the amplitude reached equilibrium, the flow was shut off and the mixture was rapidly cooled to the target temperature. It typically took five minutes to stabilize the temperature at the constriction, where the sensor was located. We started the acquisition of free-induction signals after that. Because cold gas was blown on the bottom of glass cell, some temperature gradient seemed to remain, but it went away gradually. Once the melted eicosane was cooled below the melting point, recrystallized eicosane was distributed over the whole volume of the cell. The solubility of Xe gas in the crystal is generally lower than that in the liquid. The phase-relaxation time of Xe atoms in solid eicosane is also much shorter than that in a liquid phase. Since we detected the free-induction signals with a narrow bandwidth optimized for solution, most of the signal can be attributed to polarized Xe dissolved in the ethanol- d_6 . We assumed that the exchange between Xe atoms inside the crystallized eicosane and the ethanol solution is much slower than the spin relaxation time in the solution and thus negligible.

3. Uncoated cell

Here, we outline the spin relaxation in the uncoated cell, which will be compared to the coated cell in the following sections. The decay rates in the uncoated glass cell are shown in Fig. 2 (○). The temperature dependence arises mostly from the decay rate ρ_{dd}^{et} due to the magnetic dipole–dipole interaction with the deuterons of the ethanol molecules. The rate ρ_{dd}^{et} is proportional to $1/D$, where D is the diffusion coefficient of Xe atoms. It is consistent with decay rates measured for Xe atoms and protons in ethanol- h_6 , considering that decay rate scales properly according to the dipole moment [9]. The dipolar relaxation caused by deuterated ethanol is so small that the flat offset of the dashed curve in Fig. 2 dominates at room temperature. The possible causes of offset are: the magnetic dipole interaction on the glass walls, the SR interaction, CSA in the ethanol solution, and other interactions of electron origin. There are many protons chemically bonded to the glass walls and many ethanol molecules adsorbing onto them. In addition to these nuclear magnetic dipoles, paramagnetic impurities are also suspected of causing wall relaxation. The SR relaxation ρ_{SR}^{et} due to ethanol molecules depends on temperature, but the dependence is unclear for solutions because it is introduced through the rotation energy and the correlation time of magnetic field fluctuations. Therefore, we will approximate it as a linear function of T in following sections. We note that relaxation due to CSA depends on the magnetic field ($\propto B_0^2$), though it also depends on temperature. In our previous work [9], however, we assumed that unknown relaxation was independent of temperature and came from interactions on the glass wall. In this work, we first assign the kind of interaction

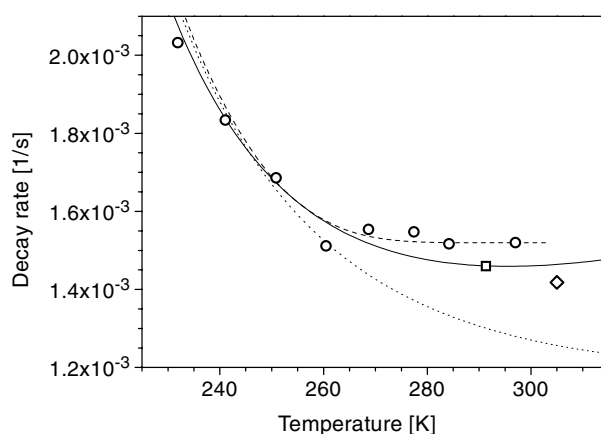


Fig. 2. Decay rates for polarized Xe atoms dissolved in the pure ethanol- d_6 in the uncoated cell. The inner diameter of the cell and the magnetic field are, respectively, 13 mm and 5.4 mT (○), 18 mm and 0.1 T (◇), and 9 mm and 0.1 T (□). The fitting error of decay rate is typically $\pm 3 \times 10^{-5}$ 1/s. The dashed curve is the interpolation of those at 5.4 mT. The decay rate ρ_{dd}^{et} can be extracted from measurements between 160 and 295 K, and is 4.7×10^{-4} 1/s at 260 K [9]. The dotted curve is $\rho_{dd}^{et} + 1.06 \times 10^{-3}$ 1/s, and the solid curve is $\rho_{dd}^{et} + 3.5 \times 10^{-6}T + 2 \times 10^{-4}$ 1/s as presented in Eq. (2).

inducing the spin-relaxation, and then obtain its magnitude.

We measured the decay rates for the uncoated cell refilled with fresh ethanol- d_6 , after it had remained filled with the other ethanol- d_6 for two months. This should be long enough to desorb a sort of molecules. Since the measured rates are identical to the ones shown in Fig. 2 (○), the flat offset is not due to impurities physically adsorbed to the glass walls. Next, in Fig. 2 we present the size dependence of the decay rate at 0.1 T in order to study wall relaxation in relation to the translational motion of Xe atoms. Because $\rho_{\text{dd}}^{\text{et}} \propto 1/D$, the local motion is dominated by diffusion in a time scale of 10 ns. Both diffusion and convection competitively contribute to the translational motion on a scale of 100 ms as observed with the spin-echo diffusometry. The typical time for Xe atoms to reach the cell walls by diffusion is proportional to R^2/D ($\approx 10^4$ s at 300 K), where R is the radius of the cell. In the case of diffusive motion and hard collisions, the relaxation time is proportional to R^2 as in the case of alkali-metal atoms in buffer gas. If the polarization of Xe atoms on the surface is the same as that in bulk solution, which is realized by agitating the solution or in the soft-collision regime, the fraction of the bound and polarized atoms is equal to the ratio of the volume of adsorption sites to the cell volume, so the relaxation time caused by wall relaxation is proportional to R as in the case of gaseous Xe atoms [23]. Therefore, we expect that the real situation is in the two extremes, $1 \leq m \leq 2$, where the decay rate due to wall relaxation is expressed as $\rho \propto 1/R^m$. The R dependence of relaxation for the $\phi 9$ (□) and $\phi 18$ (◇) cells is so weak, as shown in Fig. 2, that the wall relaxation is only a small part of the relaxation which remains after accounting for $\rho_{\text{dd}}^{\text{et}}$. The decay rate became less dependent on the cell volume since the motion of Xe atoms was not diffusional and the spin polarization relaxes through many times of collisions to walls, i.e., the soft-collision regime in the convecting solution. As suggested by previous studies of steady-gradient spin-echo diffusometry and magnetic resonance imaging of Xe atoms dissolving into ethanol [4], convection in the solution seems to slow down gradually on a timescale of thousands of seconds.

4. Paraffin coating

The temperature dependence of the decay rate was also measured for a glass cell coated with eicosane- d_{42} . The temperature was carefully kept below the melting point of eicosane. The magnetic dipole interaction between Xe atoms and ethanol molecules in solution is described by the fast motion limit at 0.1 T in the same way as at 5.4 mT. The decay rates shown in Fig. 3 (■) are less than those of the uncoated cell and an increase in the rate appears at 260 K. Though these changes are no more than 20%, a structure certainly exists in the T dependence. This is a reproducible effect because the data were taken twice by refreshing the coating and ethanol, and because the tem-

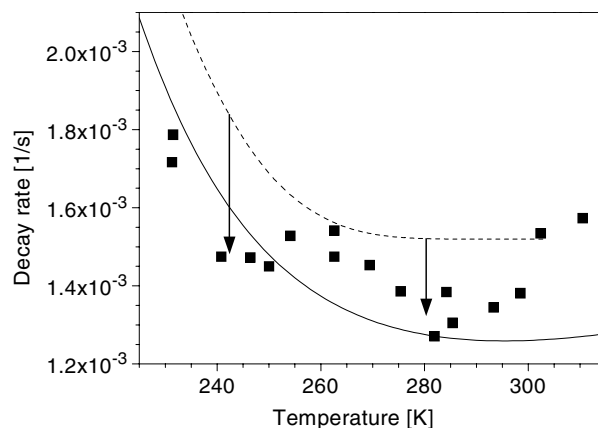


Fig. 3. Temperature dependence of the Xe decay rate of polarized Xe atoms dissolved in ethanol- d_6 at 0.1 T (■). The glass walls of the $\phi 9$ cell are coated with eicosane- d_{42} . The rate is large near the melting point of eicosane, approximately 309 K. The dashed curve is the interpolation of decay rates at 5.4 mT shown in Fig. 2 (○), and the solid curve is the calculated rate, $\rho_{\text{dd}}^{\text{et}} + 3.5 \times 10^{-6} T$ 1/s.

perature was changed not consecutively but randomly so that the data would remain unaffected by the drift of system parameters. Since relaxation due to the ethanol molecules is the same as in the uncoated cell, the decrease of the decay rate indicates that wall relaxation has been suppressed in spite of the increase of nuclear magnetic dipoles on the surface. The decrease at 240 K seems to be larger than that at 280 K.

Here, we discuss spin relaxation due to magnetic dipole interactions. One rate is the dipolar relaxation $\rho_{\text{dd}}^{\text{et}}$ by the ethanol molecules in the homogeneous solution, and the other is the relaxation $\rho_{\text{dd}}^{\text{ei}}$ by the eicosane and ethanol molecules adsorbed on the eicosane surface. The decay rate at each site i is described by the correlation time τ_c^i of field fluctuation as follows [8,14]:

$$\rho_{\text{dd}}^i = f^i \left(\frac{\mu_0}{4\pi} \right)^2 \frac{2}{15b^6} \gamma_{\text{Xe}}^2 \gamma_{\text{D}}^2 \hbar^2 S(S+1) \tau_c^i \left[J(\omega_{\text{Xe}} - \omega_{\text{D}}, \tau_c^i) + 3J(\omega_{\text{Xe}}, \tau_c^i) + 6J(\omega_{\text{Xe}} + \omega_{\text{D}}, \tau_c^i) \right], \quad (1)$$

where $J(\omega, \tau_c) = 1/(1 + \omega^2 \tau_c^2)$; γ_{Xe} (< 0) and γ_{D} (> 0) are, respectively, the gyromagnetic ratio of Xe and deuterium; $\omega_j = \gamma_j B_0$; μ_0 is the magnetic permeability in vacuum; b is the average distance between Xe nucleus and deuterium; and S is the nuclear spin of deuterium ($= 1$). We have assumed that the interaction has spherical symmetry even on the solid surface. In the case of convection and soft collisions, the coefficient f^i is equal to the fraction of site volume [14]. We can approximate that $f^{\text{et}} \approx 1$. The decay rate is independent of field within the fast motion limit ($|\omega_{\text{Xe}} \tau_c^{\text{et}}| \ll 1$), and monotonically depends on temperature through $\tau_c^{\text{et}} \propto 1/D$, as shown in Fig. 2. The relative T dependence of τ_c^{et} in solution is obtainable from the measured decay rates. On the other hand, large correlation time at the gas–solid interface has been reported to be $\tau_c = 9.3$ and $0.6 \mu\text{s}$ [15]. Therefore, in order to calculate $\rho_{\text{dd}}^{\text{ei}}$ we need to take into account that the function $\tau_c(T)J(\omega, \tau_c(T))$ for

the surface relaxation has a broad resonance at $\tau_c(T) = |1/\omega|$ with respect to the temperature. The decay rate depends on the temperature through the fraction f^{ei} of adsorbed Xe atoms as well as the correlation time τ_c^{ei} . The T dependence of τ_c^{ei} will be obtained from the resonance if we measure the decay rate by varying T and B_0 . At first we examine the T dependence of the decay rate with B_0 kept constant. The increase in the decay rate at 260 K shown in Fig. 3 indicates that the correlation time on the surface is much longer than that in solution. For the resonance frequencies of ^{129}Xe and deuteron, the three terms in Eq. (1) overlap each other and a maximum is obtained at $\tau_c^{\text{ei}} \approx 1/|\omega_{\text{Xe}} + \omega_{\text{D}}|$. Assuming that the increase at 260 K is this resonance, τ_c^{ei} is approximately equal to 0.3 μs . It is reasonable that τ_c^{ei} is smaller than the correlation times at the gas–solid interface, considering that Xe atoms collide with the other molecules at higher rate at the liquid–solid interface.

Next we will discuss the field dependence. At 27.7 mT, the decay rate for the coated cell was measured to be 1.2×10^{-2} 1/s with little dependence on temperature. Because τ_c^{ei} is small, $\rho_{\text{dd}}^{\text{ei}}$ remains as small as for the uncoated cell at 5.4 and 100 mT. Therefore, most of measured rate comes from the surface relaxation. Since this is larger than what is predicted from $\tau_c^{\text{ei}} \approx 0.3 \mu\text{s}$ and Eq. (1), the surface interaction should be described by multiple correlation times as reported for the gas–solid interface [15]. In addition to eicosane, ethanol molecules are adsorbed onto the surface. Therefore, the relaxation is not necessarily described by a single correlation time. The observed field dependence indicates that the surface relaxation is a large component at 27.7 mT among the remaining offset after extracting the dipolar relaxation $\rho_{\text{dd}}^{\text{ei}}$. If the dipole interaction at the surface also predominates at 0.1 T, the spin relaxation may be more suppressed when higher magnetic fields are applied.

The T dependence of the decay rate was measured at 0.33 T for the uncoated cell as shown in Fig. 4 (Δ). The measured rates are less than those at 5.4 mT and differ

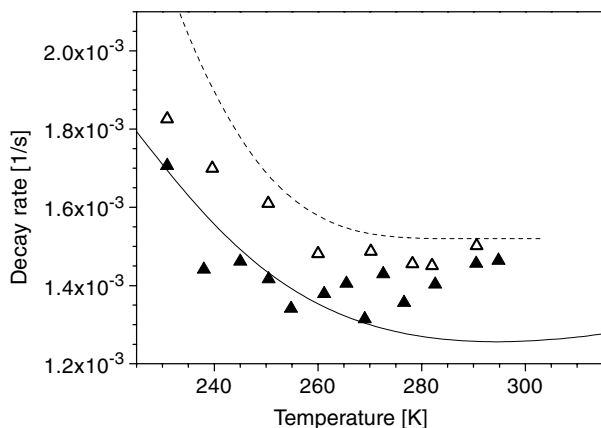


Fig. 4. Temperature dependence of the Xe decay rate in the uncoated (Δ) and eicosane-coated (\blacktriangle) $\phi 9$ cells at 0.33 T. The dashed curve is the interpolation of the decay rates at 5.4 mT shown in Fig. 2 (\circ), and the solid curve is the calculated rate, $\rho_{\text{dd}}^{\text{ei}} + 3.5 \times 10^{-6} T$ 1/s.

more at lower temperatures. The dipolar relaxation in solution at 0.33 T deviates from that of the fast motion limit. Since the T dependence of the correlation time has been obtained except for a proportionality constant by using the relation $\tau_c^{\text{ei}} \propto \rho_{\text{dd}}^{\text{ei}}$ at 5.4 mT, $\tau_c^{\text{ei}} \approx 12$ ns at 260 K is calculated from the amount of the decrease. For the coated cell shown in Fig. 4 (\blacktriangle), the minimum of the decay rate differs little from that shown in Fig. 3 (\blacksquare), and the resonance seems to shift from 260 K to higher temperatures (around 300 K). Therefore, the dipolar relaxation $\rho_{\text{dd}}^{\text{ei}}$ on the eicosane surface is only a part of relaxation at both 0.1 and 0.33 T. The magnitude of $\rho_{\text{dd}}^{\text{ei}}$ can be estimated from the height of the increase shown in Fig. 3, and is 2×10^{-4} 1/s at the resonance of 260 K. The residual part of approximately 9×10^{-4} 1/s comes from relaxation mechanisms other than the dipole interactions. Because the offset is independent of field, the relaxation caused by CSA is negligible in the ethanol solution.

The dipolar relaxation in solution, $\rho_{\text{dd}}^{\text{ei}}$, varied from 4.3×10^{-4} to 4.7×10^{-4} 1/s at 260 K as the magnetic field was changed from 330 to 27.7 mT. On the other hand, the surface relaxation $\rho_{\text{dd}}^{\text{ei}}$ drastically varied from 2×10^{-4} to 1.2×10^{-2} 1/s. Therefore, we were able to investigate the surface relaxation of Xe polarization due to the magnetic dipole interaction by using deuterated molecules. On the other hand, the decay rates in the protonated materials ethanol- h_6 and eicosane- h_{42} can be calculated by assuming that both correlation times, τ_c^{et} and τ_c^{ei} , for protonated molecules are unchanged from those for deuterated ones. When γ_{H} is substituted for γ_{D} and $S = 1/2$ in Eq. (1), the decay rate on the eicosane- h_{42} surface is nearly equal to or less than that in ethanol- h_6 at the magnetic fields of our system. At lower fields such as 1 mT, the surface relaxation becomes larger than that in solution. It is, however, so fast that the boundary condition could change from soft to hard collisions. As a result of the complex situation of convection and hard collisions, it would be difficult to study the relaxation mechanisms. At higher fields, both relaxations are hidden by the offset, which is independent of magnetic field. Therefore, it would not be possible to study the surface relaxation by using protonated materials.

5. Paraffin–ethanol mixture

In this chapter, we investigate the origin of the relaxation offset of 9×10^{-4} 1/s. To discuss the decay rates of Xe atoms dissolved in the eicosane–ethanol mixture shown in Fig. 1C, we mention briefly a unique aspect of the mixture. It is noticeable that the total surface area of crystalline eicosane is much larger than the eicosane surface area in the coated cell shown in Fig. 1A. The Xe atoms remain in their local volume as if in small cells because long-distance diffusion and convection is restricted by the heterogeneous structure, i.e., the ethanol- d_6 liquid and the assembly of eicosane- d_{42} crystallites. Though the eicosane coat had melted into solution, the

effect of the uncoated glass walls on the spin relaxation is limited to the atoms near the walls. The structure of mixture was maintained during each decay measurement. Instead of flowing polarized gas into this mixture, as shown in Fig. 1B, a homogeneous solution of polarized Xe atoms and liquid eicosane in ethanol was cooled down to the target temperature as described in the experiment method. As shown in Fig. 5, there is an increase of the decay rate around the eicosane melting point of 309 K, and no increase at 260 K even at 0.1 T, in contrast to the decay rates shown in Fig. 3. The increase for the coated cell comes from a resonance at $\tau_c^{\text{ei}} \approx 1/|\omega_{\text{Xe}} + \omega_{\text{D}}|$. The disappearance of this resonance for the mixture means that the correlation time changes, i.e., the surface of the crystallites is microscopically different from that of the coating. The T dependence below the melting point is nearly identical to that for the uncoated cell even though the surface area of the eicosane has increased by a great extent. Though we have no indication whether the similarity of both curves (the dashed curve and the measured rates (\blacktriangledown) in Fig. 5) is accidental or not, we can conclude at least that the offset of the decay rate has little dependence on the surface area of eicosane. Most of the relaxation offset does not originate from $\rho_{\text{dd}}^{\text{ei}}$ and the electron-induced relaxation on surface, but from interactions with ethanol molecules. This is consistent with the observation of the independence of the decay rate on the volume of the uncoated cell.

Now we have a deep understanding of the spin relaxation in the coated cell. The decay rate mainly consists of $\rho_{\text{dd}}^{\text{et}}$, $\rho_{\text{dd}}^{\text{ei}}$, and other relaxation rates due to ethanol molecules in solution. The most probable residual relaxation mechanism is the SR interaction, though SR coupling between Xe atoms and straight chain molecules is expected to be weaker than that for aromatic molecules

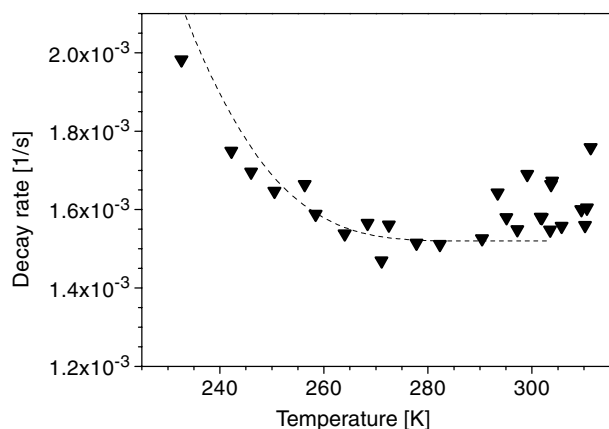


Fig. 5. Temperature dependence of the decay rate (\blacktriangledown) for polarized Xe atoms dissolved in the mixture of ethanol- d_6 and recrystallized eicosane- d_{42} in the $\phi 9$ cell at 0.1 T. The decay rate is large even around 295 K because of the presence of supercooled liquid eicosane caused by changing the temperature rapidly. The dashed curve is the interpolation of the decay rates at 5.4 mT shown in Fig. 2 (\circ).

[11]. Attributing the residual relaxation to the SR interaction, we obtained $\rho_{\text{SR}}^{\text{et}} \sim 9 \times 10^{-4}$ 1/s for the ethanol solution. The temperature dependence at 5.4 mT shown in Fig. 2 is well reproduced by the offset relaxation which increases with temperature (solid curve) rather than a constant offset (dotted curve), where $\rho_{\text{SR}}^{\text{et}}$ has been assumed to be proportional to T as the first order approximation. We summarize the above discussion as follows:

$$\rho_{\text{total}} = \rho_{\text{dd}}^{\text{et}} + \rho_{\text{SR}}^{\text{et}} + \{\rho_{\text{dd}}^{\text{ei}}(\text{coated}) \text{ or } \rho^{\text{glass}}(\text{uncoated})\}. \quad (2)$$

Roughly estimating these decay rates at 0.1 T and 260 K, $\rho_{\text{dd}}^{\text{et}} = 4.7 \times 10^{-4}$ 1/s; $\rho_{\text{SR}}^{\text{et}} \sim 3.5 \times 10^{-6}(1/\text{s} \cdot \text{K})T = 9 \times 10^{-4}$ 1/s; $\rho_{\text{dd}}^{\text{ei}} \sim 2 \times 10^{-4}$ 1/s; and the relaxation on glass walls $\rho^{\text{glass}} \sim 2 \times 10^{-4}$ 1/s. Since $\rho_{\text{dd}}^{\text{ei}} < \rho^{\text{glass}}$ at temperatures different from 260 K, ρ_{total} for the coated cell is less than that for the uncoated cell. As shown by solid curves in Figs. 3 and 4, the calculation of $\rho_{\text{dd}}^{\text{et}} + \rho_{\text{SR}}^{\text{et}}$ are qualitatively consistent with the measurements at each field for the coated cell. Some measured rates are, however, less than the solid curves, though the calculation corresponds to the decay rate for an infinitely large cell.

As long as CSA does not become a dominant mechanism, higher fields are preferable from the point of view of the spin reservoir because the spin-rotation as well as dipolar relaxations can be decreased. Since the SR interaction is inevitable and intrinsic to the ethanol solution, we need more investigations for a wide range of temperature and magnetic fields in order to evaluate it quantitatively. For this purpose, wall relaxation should be suppressed by deuterated paraffin with a higher melting point than eicosane, which may give us a purer solution of polarized Xe atoms in ethanol. For example, triacontane- d_{62} and hexacontane- d_{122} are commercially available. With further investigation, we will be able to find the optimal temperature and field strength for long-term storage of polarized Xe atoms in solutions.

6. Conclusion

We observed the spin relaxation of polarized Xe atoms dissolved in deuterated ethanol. It was found that an increase of cell volume was not directly linked to the suppression of the decay rate because of convection in the solution. On the other hand, wall relaxation was suppressed by coating the glass walls with deuterated eicosane. The correlation time of field fluctuations due to the magnetic dipolar interaction on the eicosane surface was much longer than that in the ethanol solution. The use of both deuterated molecules enable us to investigate the surface relaxation. By varying the surface area of the eicosane, we found a decay rate in ethanol solution which increases with temperature. The most probable mechanism is the spin-rotation relaxation. The chemical shift anisotropy was negligible as found from the independence of the decay rate on magnetic field within the range of our system.

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