

Communication

Quantitative estimation of SPINOE enhancement in solid state

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ABSTRACT

A theoretical approach to quantitatively estimate the spin polarization enhancement via spin polarization-induced nuclear Overhauser effect (SPINOE) in solid state is presented. We show that theoretical estimates from the model are in good agreement with published experimental results. This method provides a straightforward way to predict the enhanced factor of nuclear magnetic resonance signals in solid state experiments.

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The nuclear spin polarizations of noble gases, like ³He and ¹²⁹Xe, can be increased by four or five orders of magnitude over thermal equilibrium via spin-exchange optical pumping (SEOP) [1–5], and such noble gases are referred to as ‘hyperpolarized’ or ‘laser-polarized’ gases. The hyperpolarized noble gases are rapidly being applied in various disciplines, such as magnetic resonance imaging (MRI) [6], biological systems [7], precision measurements [8], quantum computation [9], etc. Since the important discovery of Pines et al. [10] that polarization could be transferred from hyperpolarized ¹²⁹Xe to protons in solution via the spin polarization-induced nuclear Overhauser effect (SPINOE), the method of SPINOE has been widely utilized in other fields [11–16]. However, applications of SPINOE have almost exclusively been implemented in solution or at material surfaces, and under these conditions, the SPINOE enhancement can be readily theoretically estimated in the fast motion limit ($\omega\tau_c \ll 1$) [10]. If a SPINOE occurs in the solid state [17], which is usually found in the slow motion limit ($\omega\tau_c \gg 1$), there are currently no models to predict the signal enhancement in this regime. In this letter, we demonstrate an approach to quantitatively estimate the SPINOE enhancement in the solid state, and such theoretically predicted results are in agreement with experimental measurements.

Generally, the interactions of atoms and molecules are so complicated in the solid state. But in a SPINOE experiment, the cross-relaxation induced by the internuclear magnetic dipole interaction is the primary mechanism for a spin polarization transfer (SPINOE)

[14]. Accordingly, in this article, we will focus our discussion on the direct nuclear dipolar interaction, and the dipolar Hamiltonian can be written as:

$$H_D = \frac{\mu_0 \hbar \gamma_S \gamma_I}{4\pi r^3} \left[\hat{S} \cdot \hat{I} - \frac{3(\hat{r} \cdot \hat{S})(\hat{r} \cdot \hat{I})}{r^2} \right], \quad (1)$$

where \hat{I} and \hat{S} are the spin angular momentum operators. \hbar is the Planck constant divided by 2π . γ_I and γ_S are the gyromagnetic ratios of spin I and spin S , respectively, and μ_0 is the magnetic constant. \hat{r} denotes the directional vector, and r is the magnitude of \hat{r} , i.e., the distance between two spins. The perturbation part of Hamiltonian (H_D) induces transitions between the eigenstates of the unperturbed Hamiltonian, according to the following transition probabilities [18]:

$$\begin{aligned} w_0^S &= \frac{2\delta}{20} J(\omega_I - \omega_S) \\ w_{1I}^S &= \frac{3\delta}{20} J(\omega_I) \\ w_{1S}^S &= \frac{3\delta}{20} J(\omega_S) \\ w_2^S &= \frac{12\delta}{20} J(\omega_I + \omega_S), \end{aligned} \quad (2)$$

with

$$\delta = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_S^2 \gamma_I^2}{r^6}, \quad (3)$$

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \quad (4)$$

here, τ_c is the correlation time of spin systems.

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According to the Solomon equations, the evolution of a two-spin system could be described by [18,19]:

$$\frac{d}{dt} \begin{pmatrix} I_z \\ S_z \end{pmatrix} = - \begin{bmatrix} \rho_I & \sigma_{IS} \\ \sigma_{SI} & \rho_S \end{bmatrix} \begin{pmatrix} I_z - I_0 \\ S_z - S_0 \end{pmatrix}, \quad (5)$$

where I_z and S_z are z components of the spin I and spin S , respectively; I_0 and S_0 are their equilibrium values. ρ_I and ρ_S are the auto-relaxation rates of the spins I and S . σ_{IS} and σ_{SI} are the corresponding cross-relaxation rates. The elements of the cross-relaxation matrix can be expressed by the transition probabilities w resulting from II , SS and IS interactions [20]:

$$\begin{aligned} \rho_I &= 2(n_I - 1)(w_1^I + w_2^I) + n_S(w_0^S + 2w_{1I}^S + w_2^S) \\ \rho_S &= 2(n_S - 1)(w_1^S + w_2^S) + n_I(w_0^I + 2w_{1S}^I + w_2^I) \\ \sigma_{IS} &= n_S(w_2^S - w_0^S) \\ \sigma_{SI} &= n_I(w_2^I - w_0^I), \end{aligned} \quad (6)$$

here, n_I and n_S are magnetically equivalent spin I and spin S . A solution of Eq. (5) of particular interest in this system is the one corresponding to the initial conditions:

$$\begin{aligned} (I_z - I_0)_{t=0} &= 0, \\ (S_z - S_0)_{t=0} &= S_i. \end{aligned} \quad (7)$$

So the solution can be given by:

$$\begin{aligned} I_z(t) &= I_0 + C(\exp(\lambda_1 \cdot t) - \exp(\lambda_2 \cdot t)), \\ S_z(t) &= S_0 + C[r_1 \cdot (\exp(\lambda_1 \cdot t) - r_2 \cdot \exp(\lambda_2 \cdot t))], \end{aligned} \quad (8)$$

where λ_1 and λ_2 are given by:

$$\begin{aligned} \lambda_1 &= \frac{-(\rho_I + \rho_S) - \sqrt{(\rho_I - \rho_S)^2 + 4\sigma_{IS}\sigma_{SI}}}{2}, \\ \lambda_2 &= \frac{-(\rho_I + \rho_S) + \sqrt{(\rho_I - \rho_S)^2 + 4\sigma_{IS}\sigma_{SI}}}{2}, \end{aligned} \quad (9)$$

and

$$\begin{aligned} r_1 &= \frac{\rho_S - \sqrt{(\rho_I - \rho_S)^2 + 4\sigma_{IS}\sigma_{SI}}}{2\sigma_{IS}}, \\ r_2 &= \frac{\rho_S + \sqrt{(\rho_I - \rho_S)^2 + 4\sigma_{IS}\sigma_{SI}}}{2\sigma_{IS}}, \end{aligned} \quad (10)$$

$$C = \frac{S_i}{r_1 - r_2}. \quad (11)$$

Therefore, the dynamic evolution of the spins I and S can be described using the Eq. (8). Then the magnetization enhancement of spin I via cross-relaxation comparing with that in the thermal equilibrium is:

$$\frac{I_z(t) - I_0}{I_0} = - \frac{\sigma_{IS} \gamma_S}{\rho_I \gamma_I} \frac{S_z(t) - S_0}{S_0}. \quad (12)$$

Inserting the values (2) and (6) in (12), we obtain the SPINOE enhanced formula in solid state as follows:

$$\frac{I_z(t) - I_0}{I_0} = \frac{-\gamma_S(S_z(t) - S_0)n_S[6\delta J(\omega_I + \omega_S) - \delta J(\omega_I - \omega_S)]}{\gamma_I S_0 \{ (n_I - 1)[3\delta J(\omega_I) + 12\delta J(2\omega_I)] + n_S[\delta J(\omega_I - \omega_S) + 3\delta J(\omega_I) + 6\delta J(\omega_I + \omega_S)] \}}, \quad (13)$$

with

$$\delta' = \frac{\hbar^2 \gamma_I^4}{r^6}, \quad (14)$$

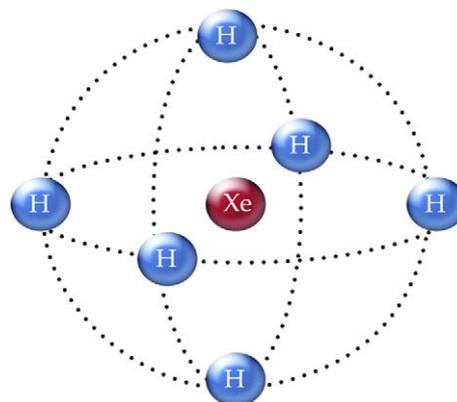


Fig. 1. Model that each one ^{129}Xe atom surrounded by six ^1H atoms on average in the solid mixture of hydrogen chloride and xenon.

here r' is the distance between spin I and I . Under the slow motion limit condition in the solid state, i.e., $\omega\tau_c \gg 1$, the spectral density function becomes $J(\omega) = 1/\omega^2\tau_c$, therefore the Eq. (13) can be derived as

$$\frac{I_z(t) - I_0}{I_0} = \frac{-\gamma_S(S_z(t) - S_0)n_S \left(\frac{6}{(\omega_I + \omega_S)^2} - \frac{1}{(\omega_I - \omega_S)^2} \right)}{\gamma_I S_0 \left\{ (n_I - 1) \left(\frac{\gamma_I}{\gamma_S} \right)^2 \left(\frac{r'}{r} \right)^6 \frac{6}{\omega_I^2} + n_S \left[\frac{1}{(\omega_I - \omega_S)^2} + \frac{3}{\omega_I^2} + \frac{6}{(\omega_I + \omega_S)^2} \right] \right\}}. \quad (15)$$

For the published SPINOE experiment of the solid state [17], the spin I is ^1H ($I = 1/2$) while the spin S is ^{129}Xe ($S = 1/2$). ω_I (^1H) and ω_S (^{129}Xe) are 80.13 MHz and 22.16 MHz multiplied by 2π on Bruker WP-80SY spectrometer (1.879 T). The enhancement of hyperpolarized solid-state ^{129}Xe , $[S_z(t) - S_0]/S_0$, is about 6000 in the experiment, which corresponds to the ^{129}Xe polarization of 2.16%. The concentrations of ^1H and ^{129}Xe are 34.6 mmol/cm³ and 5.46 mmol/cm³, respectively. If assuming that the hydrogen chloride and xenon was uniformly mixed in the solid mixture and $r = r'$, we can picture a model where each of the ^{129}Xe atoms are surrounded by six ^1H atoms on the average, as shown in Fig. 1. One can calculate the maximum solid-state proton enhancement of 7.1 using Eq. (15), which is in general agreement with the experimentally measured value of 6 ± 0.4 resulting from several measured values [5.5, 6.0, 5.8, 6.5, 5.9, 6.3] [17]. The experimental enhancement is smaller than the theoretical one, which indicates the possibility that only a fraction of the total number of ^1H interact with the hyperpolarized ^{129}Xe by direct dipole-dipole coupling. Because the condensation of mixture gas of xenon and hydrogen chloride from gas phase to solid phase takes a few minutes, the cross-relaxation between xenon and proton would be smaller at the beginning than that in the steady solid state. Our theoretical calculation is based on the two-spin system, but in our experiment there are H, Cl and Xe atoms. The couplings of H-Cl and H- ^{131}Xe also induce a leak of the proton enhancement as we previously dis-

cussed [17]. If counting all above factors, together with the polarization loss during the phase transition, all of these losses will cause the experimental enhancement to be slightly lower than that estimated from the theoretical calculation.

Normally, at higher temperatures (e.g., 135 and 145 K) and magnetic fields that are not too large (<1800 G), the relaxation is almost completely dominated by the dipole–dipole interaction [21], because the correlation time of the dipole–dipole interaction is longer than that of the spin–rotation interaction [22]. The dipole–dipole interaction has a correlation time equal to the characteristic vacancy hopping time in the crystal, and this correlation time will have an Arrhenius type of dependence on temperature, $\exp(-E/kT)$ with an activation energy E given by the barrier energy for vacancy hopping. Even at temperatures close to the triple point of xenon, the hopping time is much longer than the correlation time for the spin–rotation interaction. However, the dipole–dipole interaction can be eliminated as a source of spin relaxation with magnetic fields of a few tesla, i.e., for the Larmor period to be much shorter than the hopping time [22]. Accordingly, under the conditions of our experiment (142 K and 1.879 T) with natural xenon (26.4% ^{129}Xe and 21.2% ^{131}Xe), the relaxation of ^{129}Xe is dominated by the spin–rotation interaction with Raman scattering of photons, and the cross-relaxation between ^{129}Xe and the ^{131}Xe would be negligible [23]. Then, it is unclear how such cross-relaxation could lower the experimental enhancement, and further investigations would be needed.

Based on the experimental enhancement, we can obtain $\sigma_{IS}/\rho_I = 1/280$ by using Eq. (12). Due to the accumulation effect in our experiment, the autorelaxation rate of spin I (proton) can be derived with a lower limit value ($\rho_I = 1.19 \times 10^{-2} \text{ s}^{-1}$) from the time dependence of solid proton signal [17]. Accordingly, $\sigma_{IS} = 5.05 \times 10^{-5} \text{ s}^{-1}$ provides an upper limit for cross polarization rate between xenon and proton. In terms of Eq. (6), we can estimate that the value of $r^6\tau_c$ is between $3.58 \times 10^{-64} \text{ m}^6 \text{ s}$ and $7.16 \times 10^{-64} \text{ m}^6 \text{ s}$ by using the lower limit value ρ_I and the upper limit value σ_{IS} . It was reported that the distances between xenon atoms are about 3 Å and 6.2 Å in liquid and solid xenon, respectively [24,25], and Desvaux et al. demonstrated that the distance between xenon and proton in nonspecific lipid transfer protein is less than 6 Å [26]. Fig. 2 shows the relations among the correlation time (τ_c), the distance between xenon and hydrogen nuclei (r), and the estimated $r^6\tau_c$ at a specific range determined as above. When $3 < r < 6 \text{ Å}$, the correlation time ranges from 7 to 480 ns for $r^6\tau_c = 3.58 \times 10^{-64} \text{ m}^6 \text{ s}$, and ranges from 16 to 994 ns for $r^6\tau_c = 7.16 \times 10^{-64} \text{ m}^6 \text{ s}$. Even if this means that the correlation time in few regions might just be on the border of the slow motion limit, it satisfies the slow motion limit ($\omega\tau_c \gg 1$) in most regions.

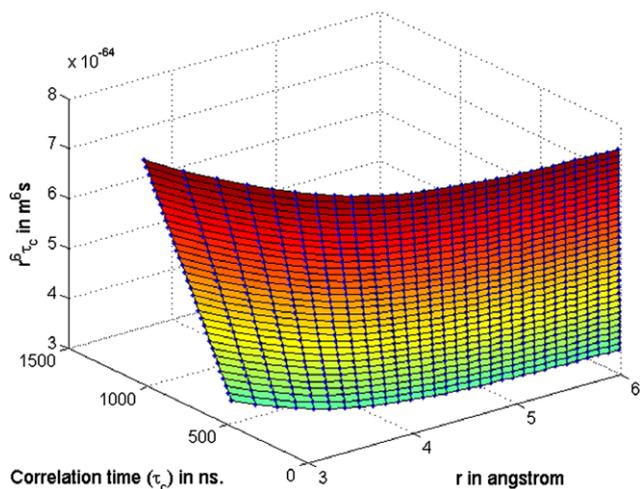


Fig. 2. 3D map of the relations among the correlation time (τ_c), the distance between xenon and hydrogen nuclei (r), and the estimated $r^6\tau_c$.

Table 1 lists the ρ_I , σ_{IS} , concentration ratio of xenon to proton atoms (N_S/N_I), and proton enhancements from the representative SPINOE experiments. In Navon et al. experiment [10], because they used xenon gas dissolved in benzene, the low concentration ratio (N_S/N_I) caused a small cross-relaxation (σ_{IS}) between xenon and proton. However, if liquid xenon has been used as a solvent, i.e., a high concentration ratio (N_S/N_I), the σ_{IS} was largely increased, and the proton signal of cyclopentane dissolved in the liquid xenon has been enhanced by a factor of 45 [12]. In our solid xenon SPINOE experiment, the concentration ratio (N_S/N_I) is about 0.16, which is between gas xenon (0.0015) [10] and liquid xenon (0.42) [12] SPINOE experiments. Accordingly, the cross-relaxation rate of $< 5.05 \times 10^{-5}$ for our case is reasonable. Table 1 also shows autorelaxation rate of proton on surface is about one order of magnitude higher than other situations [13,27], which results in the disadvantage on the proton enhancement, because a smaller autorelaxation is expected for a bigger enhancement if the cross-relaxation rate is the same. The autorelaxation rate of proton can be written as $\rho_I = \rho_I^0 + \rho_I^{IS}$. ρ_I^0 is the relaxation rate from proton to proton dipole–dipole interaction, spin rotation, paramagnetism and all other interactions. ρ_I^{IS} is the contribution from the dipole–dipole coupling between proton and xenon, and should be proportional to the xenon density. On the one hand, the higher xenon density, the larger cross-relaxation rate (σ_{IS}) between xenon and proton. On the other hand, the higher xenon density results in larger ρ_I^{IS} . Therefore, the optimization of experimental conditions to achieve larger σ_{IS}/ρ_I would be helpful to obtain larger SPINOE enhancement.

In according to the Eq. (15), for further increasing the proton enhancement, one should first obtain the greatest ^{129}Xe enhancement by employing high power and narrow bandwidth lasers, and/or increasing the gas pressure of the pump cell, in which binary collisions are mainly dominated in SEOP, in order to enhance the optical-pumped absorbed power [3,28]. Alternatively, decreasing the gas pressure in the polarizer, which mainly utilizes three body collisions in SEOP at low pressure, will increase the spin-exchange rate [2,29]. A small proton number density by using partially deuterated sample and a large ^{129}Xe number density by using Xe isotopically enriched with ^{129}Xe also can boost transfer efficiency [11,27,30]. Actually, the hyperpolarized ^{129}Xe have a long lifetime in the solid state [23], which means that ^1H could keep a longer coherence time with hyperpolarized ^{129}Xe , and this offers a good system to study the spin dynamics using NMR spectroscopy.

In conclusion, we developed a theoretical method to quantitatively estimate the spin polarization enhancement via SPINOE in the solid state. The theoretical calculated enhancement factors using such approach are in agreement with previous experimental results. This approach provides a convenient way to evaluate the expected amplification of magnetic resonance signal before implementing specific experiments.

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Table 1

Comparison of autorelaxation rates, cross-relaxation rates, concentration ratios of xenon to proton atoms, and proton enhancements from the representative SPINOE experiments. For the experiment in Ref. [27], the enhancement factor of 3.3 is for ^{13}C , while other data are for proton enhancements.

	Gas Xe	Liquid Xe	Xe on surface	Xe on surface	Solid Xe
ρ_1 (s^{-1}) (^1H)	5×10^{-2} – 7×10^{-2}	1.1×10^{-1}	3×10^{-1}	$>1.19 \times 10^{-2}$	
σ_{IS} (s^{-1}) (^1H – ^{129}Xe)	1.9×10^{-6}	2×10^{-4}	7×10^{-4}	8.6×10^{-4}	$<5.05 \times 10^{-5}$
Concentration ratios (N_S/N_I)	0.0015	0.42	0.2	–	0.16
^1H enhancements	0.06	45	10.6	3.3 (for ^{13}C)	6
References	[10]	[12]	[13]	[27]	[17]

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