Relaxation Behavior of Laser-Polarized ^{129}Xe Gas: Size Dependency and Wall Effect of the T_1 Relaxation Time in Glass and Gelatin Bulbs

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Size dependency of the relaxation time T_1 was measured for laser-polarized ^{129}Xe gas encapsulated in different sized cavities made by glass bulbs or gelatin capsules. The use of laser-polarized gas enhances the sensitivity a great deal, making it possible to measure the longer ^{129}Xe relaxation time in quite a short time. The size dependency is analyzed on the basis of the kinetic theory of gases and a relationship is derived in which the relaxation rate is connected with the square inverse of the diameter of the cavity. Such an analysis provides a novel parameter which denotes the wall effect on the relaxation rate when a gas molecule collides with the surface once in a second. The relaxation time of ^{129}Xe gas is also dependent on the material which forms the cavity. This dependency is large and the relaxation study using polarized ^{129}Xe gas is expected to offer important information about the state of the matter of the cavity wall. © 2001 Academic Press

Key Words: laser-polarized noble gas; size dependency of relaxation time; wall effect in relaxation time; gelatin capsule; glass materials.

INTRODUCTION

Laser-polarized noble gas NMR has attracted special attention recently in material science, solid state chemistry, and clinical medicine (*1*). Under optimized conditions this method can give sensitivity enhancement of as much as 10^5 compared with the thermal equilibrium in ^{3}He and ^{129}Xe NMR. Relaxation time, especially T_1, is a very important property in handling substances with such a highly polarized state. T_1 is long in the pure gaseous state, but is shortened when O_2 is mixed with the gas (*2*). It is also shortened very much when dissolved in a liquid solution of various media, including biological samples (*2c, 3*). On the other hand, T_1 is expected to offer important information on the surroundings in which the noble gas is situated. In this respect ^{129}Xe is a very prominent nucleus since its chemical shift also changes in wide ranges of parts per million (as much as 200 ppm) depending on the state of the matter (*4*).

Hitherto, the wall effect has been discussed in relation to the mechanism of relaxation in laser-polarizing glass cells (*5–7*), and it was found that the silicone coating of the interior wall of the glass cell is very efficient in reducing the relaxation effect from the wall. In these studies the size of the gas container was kept constant and the composition or temperature of the gas mixture was changed. Also, surface relaxation of the ^{129}Xe nucleus on the silicone-coated glass cell was shown to be dipolar in origin, and such a weak interaction with protons in the coatings was concluded to be responsible for the long relaxation time on the silicone-coated wall (*8*). However, for further understanding of the wall effect it seems necessary to examine the relaxation behavior in detail by changing the size of the cavity. The laser-polarized ^{129}Xe gas has made it possible to measure the longer relaxation time T_1 in quite a short time, and it is well suited to the detailed study of relaxation behavior.

In the present study T_1 of ^{129}Xe gas is measured by changing the size of the gas container using glass bulbs and gelatin capsules, and the size dependency is analyzed quantitatively on the basis of the kinetic theory of gases. The results are useful for the quantitative discussion of the relaxation time pertinent to the wall material.

EXPERIMENTAL

Optical Pumping System

An optical pumping cell was placed at the side of a superconducting NMR magnet (vertical type) used for NMR measurement under a fringe field of about 12 mT. A Pyrex cylinder cell with a diameter of 60 mm and a length of 100 mm was used. Rb metal (about 0.2 g) was sealed into the cell under high vacuum (10^{-6} Torr) and Xe gas was supplied from a cylinder through a predrying vessel containing K–Na alloy. This alloy is a fluid with metallic luster and is very useful for rigorous drying of gases. It is also useful for removing oxygen and carbon dioxide, which are possibly included in the Xe gas and eat Rb metal. The metallic luster was checked for high sensibility of the alloy when passing the Xe gas over the metal alloy. When a small amount of the polarized Xe gas was drawn from the optical pumping cell to

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the NMR tube for sample preparation, the gas was automatically refilled from the cylinder. Here a 50-ml plastic syringe was used for temporary stock space of the Xe gas from the cylinder. The pressure of Xe gas was 1 atm throughout the present experiment and no other gases were mixed. This mode of gas treatment benefits the ease of operation: the polarized Xe gas needs no solidification since the inert gas of N_2 or He-4 is not mixed and no separation is necessary. Also, this mode is safe in handling the glass apparatus: usually high-pressure gas, sometimes as high as 10 atm, is used to broaden the D_1 transition of the Rb vapor and to enhance the polarizability as much as possible. In the present study a polarizability of about 3% was attained, as judged from the enhancement in S/N ratio of the ^{129}Xe NMR signal. This value is better than a reported value of 1% for 800-Torr Xe gas in an uncoated Pyrex cell (7). Silicone coating will surely increase the Xe polarization: probably it will increase the polarization by an order (7). But it was not attempted in the present study since the signal enhancement was enough, even without such coating. A laser diode array (Opto Power Corp., Model OPC-A020-795-CSPS) was used under 15 W output power to excite the Rb vapor. The polarizing cell was situated in an oven made by a polypropylene sheet to which a constant-temperature air blower, Leister Hot Window S, was attached to maintain the oven temperature at 120°C. A schematic diagram of the apparatus is shown in Fig. 1. The polarizing system is basically made using Pyrex glass, with an optically ground plate for the window of the polarizing cell and Pyrex stop cocks with high-vacuum O-rings from Young Co. are used to manipulate the Xe gas flow.

Materials

Xe gas (natural isotope composition, ^{129}Xe $= 26.44\%$) was purchased from Osaka Sanso Co., Ltd.

Glass bulbs were all made by blowing the commercially available glass tubes: quartz was from Toshiba Co., Ltd., Iwaki TE30
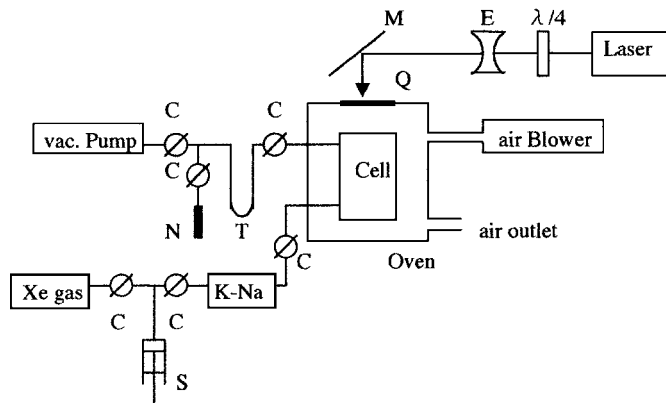

FIG. 1. Schematic view of the apparatus for supplying polarized Xe gas. E, expander of the laser beam (cylindrical concave lens); M, reflecting mirror; Q, quartz window of the oven; C, stop cock; T, trap cooled by ice; N, NMR tube (10ϕ); S, plastic syringe (50 ml).

was from Iwaki Glass Co., compatible with Pyrex 7740, hard glass (second grade) was from Akagawa Co., and Hokkai-Super glass (second grade) and Ordinary-Class glass were from Nihon Denki Glass Co. A short stem was attached to each of the glass bulbs as an inlet for the polarized Xe gas.

Empty capsules made from gelatin films, available commercially as pharmacy grade, were used for the gas container. These capsules are cylindrical in shape but the smallest diameter is used as diameter d in the analysis of T_1 data below. Also, gelatin empty bulbs specially made and supplied from Nisshin Flour Milling Co. were used for comparison. They are purely spherical in shape and a pinhole is made on the surface, which is resealed by adhesive tape after introducing the polarized Xe gas into the bulb.

NMR Experiments

NMR measurements were made on a Varian INOVA 400 WB spectrometer operating at 9.4 T and ambient temperature. A 10ϕ probe was used for ^{129}Xe (110.5 MHz) so that a wider range of sample size could be dealt with. The glass or gelatin bulbs were first put into a 10ϕ NMR tube, to be filled with polarized Xe gas (Fig. 1). The gas inlet specially made on the bulb surface was sealed by adhesive tape after the bulb was filled with polarized Xe gas. The bulbs were then put into another 10ϕ NMR tube and the ^{129}Xe NMR spectrum was measured.

RESULTS AND DISCUSSION

^{129}Xe relaxation time was measured for various sized cavities smaller than 9 mm in outside diameter. Glass bulbs and gelatin capsules with different diameters were used to encapsulate laser-polarized ^{129}Xe gas. Gelatin capsules commercially available as Japanese Pharmacopoeia D-175 (hereafter abbreviated JP grade) were also used. Table 1 lists the T_1 data observed for these samples. The T_1 value was measured by repetitively applying small flip-angle pulses and by analyzing the intensity data according to the equation

$$\ln(S_n) = \{\ln(\cos\alpha) - T_R/T_1\}(n-1) + \ln(S_1), \qquad [1]$$

where S_1 and S_n are the signal intensities for the 1st and nth pulses, respectively, α is the pulse angle, and T_R is the pulse repetition time. This equation means that plots of $\ln(S_n)$ against $n-1$ will give a straight line with a slope of $\ln(\cos\alpha) - T_R/T_1$. Such a plot is shown in Fig. 2 for the quartz glass bulbs. Exact determination of the pulse angle α needs special consideration in laser-polarized experiments, since the ordinary determination method does not apply in this case. That is, the laser-polarized high degree of magnetization is not regained once it is tilted onto the xy plane to monitor the pulse angle in the trial and error method. In such a case, repetition of the measurement using 2α degree pulse immediately after the α degree pulse can give an estimate of the pulse angle. The difference in the

TABLE 1
Relaxation Data of the Laser-Polarized ^{129}Xe Gas Encapsulated in Glass Bulbs and Gelatin Capsules[a]

Glass bulb				Gelatin capsule			
Iwaki TE30		Hokkai-Super		JP grade		Gelatin bulb	
d	T_1	d	T_1	d	T_1	d	T_1
7.8	94.1 ± 9.8	8.1	27.6 ± 2.8	8.8(# 00)	105.4 ± 8.5	6.3	179.9 ± 15.0
6.6	66.9 ± 9.3	6.1	20.3 ± 0.1	7.8(# 0)	84.1 ± 4.7	5.7	150.0 ± 20.8
5.8	25.3 ± 4.5	5.5	17.1 ± 0.7	6.8(# 1)	78.8 ± 5.8	4.3	89.8 ± 10.3
4.2	18.7 ± 2.8	4.9	14.7 ± 0.7	6.3(# 2)	59.2 ± 3.7	4.1	79.9 ± 9.4
4.0	13.9 ± 3.4			5.8(# 3)	52.7 ± 3.8		
3.4	13.2 ± 4.6			5.1(# 4)	45.5 ± 4.0		

Glass Bulb							
Quartz		Iwaki TE30		Akagawa		Ordinary-class	
d	T_1	d	T_1	d	T_1	d	T_1
6.4	172.8 ± 16.1	6.6	65.0 ± 5.1	6.8	126.8 ± 15.3	6.4	97.2 ± 13.4

[a] d is the inside diameter of the spherical volume in millimeters and T_1 is the longitudinal relaxation time in seconds. Standard errors are estimated in the linear plots of Eq. [a-7].

slopes of the plots of Eq. [1] for the α and 2α degree pulses becomes

$$\text{slope}(2\alpha) - \text{slope}(\alpha) = \ln\{\cos(2\alpha)\} - \ln(\cos\alpha)$$
$$= \ln\{(2\cos^2\alpha - 1)/\cos\alpha\}. \quad [2]$$

Therefore, $\cos\alpha$ can be determined from the measurement using a pulse angle (and hence a pulse duration time) twice as large as the initial one. Figure 3 shows an example of the determina-
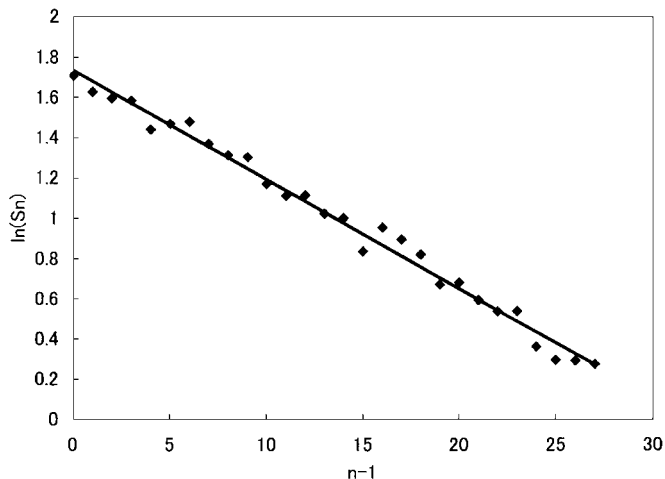

FIG. 2. Plots of $\ln(S_n)$ against $n - 1$ based upon Eq. [1] for the glass bulb made by Iwaki TE30. The bulb diameter is 6.6 mm id and a 16.5° pulse is applied repeatedly every 1.338 s (a total of 28 times). Integral intensity is taken for the S_n data on an arbitrary scale.
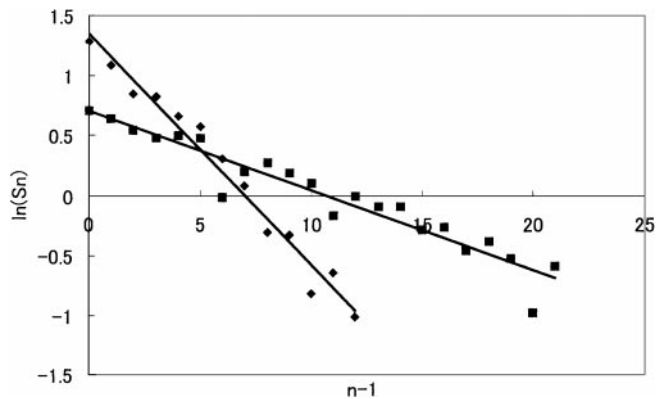

FIG. 3. The two plots of $\ln(S_n)$ against $n - 1$ to determine the pulse angle α based upon Eqs. [1] and [2]. A JP grade gelatin capsule No. 0 is used, which has a diameter of 7.8 mm id. An $\alpha°$ pulse, for which the pulse duration time is 2 μs, is applied repeatedly every 4.338 s at first (a total of 22 times), and then the $2\alpha°$ pulse, for which the pulse duration time is 4 μs, is applied in the same manner (a total of 13 times). Analysis of the plots according to Eq. [2] gives $\alpha = 16.5°$. Integral intensity is taken for the value of S_n on an arbitrary scale separately in the two cases. (■) $\alpha°$ pulse is applied. (◆) $2\alpha°$ pulse is applied.

tion of α. In the present study α thus determined was typically 16.5°.

The T_1 data measured are listed in Table 1. Error limits in Table 1 are estimated from the repeated run of the experiment.

Size Dependency of the T_1 Data

A simple treatment based on the kinetic theory of gases is given in the Appendix for the relaxation effect from the wall of the gas container. The treatment shows that the relaxation rate observed experimentally by changing the gas volume is proportional to the inverse square of the diameter for spherical samples. This type of plot is given in Fig. 4 for a typical case of gelatin capsules of JP grade, for which the regression equation
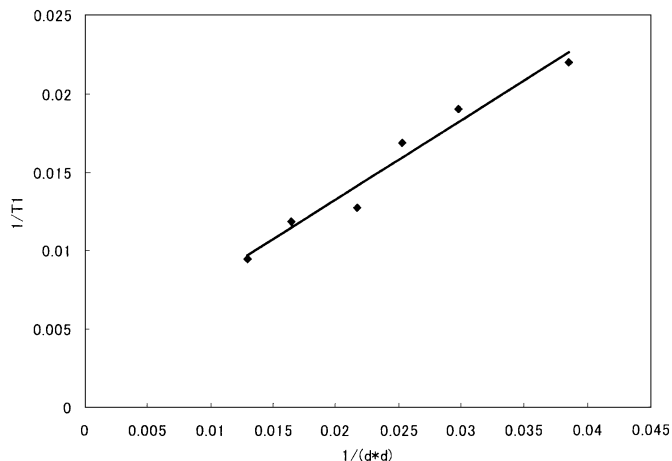

FIG. 4. Plots of $1/T_1$ against $1/d^2$ for the JP grade gelatin capsules based upon Eq. [a-7].

is obtained as

$$1/T_1 = 0.504(\pm0.049)1/d^2 + 0.00321(\pm0.00126),$$
$$= 0.981, \qquad [3]$$

where the $\pm$ values in parentheses show standard errors estimated in the regression analysis and r is the multiple correlation coefficient. The correlation coefficient is sufficiently high and the $1/d^2$ predicted in the Appendix is realized in the experiment. This also supports our Xe gas purification method, since the relaxation time data would be scattered on repeated measurements if purification is insufficient and the purity of Xe gas changes with time. From the value of the slope in this equation, $t_{1,\text{wall}} = 170 \pm 17$ is obtained according to Eq. [a-8]. This value means that the wall contribution to the relaxation time, $T_{1,\text{wall}}$, amounts to 170 s for 1 atm and room temperature Xe gas encapsulated in a gelatin capsule with an inside diameter of 9.2 mm (see the Appendix). Similar treatment of the data measured with the gelatin bulbs specially offered from Nisshin Flour Milling Co. for the present study resulted in the equation

$$1/T_1 = 0.199(\pm0.005)1/d^2 + 0.00052(\pm0.00023),$$
$$r = 0.999. \qquad [4]$$

This equation basically supports the results reached in Eq. [3], but detailed comparison shows that the slope is smaller in Eq. [4] than in Eq. [3]. This difference may come from a difference in the composition of gelatins or in the physical properties of the gelatin films, such as the hardness or permeability of gases. The shape effect may also be responsible for this small difference since the JP grade gelatin capsules are not spherical in rigorous shape. They are composed of cylinders with hemispheres at both ends, and the shortest distance is taken for the size d (diameter) of the cavity. This effect may be taken into account by calculating and averaging the distance to the wall at every point inside the gelatin capsule. Such a calculation is possible on a computer, but further detailed discussion is not attempted and another type of bulbs, i.e., glass bulbs, is tested and compared in the following paragraphs.

In the case of glass bulbs (Pyrex), similar treatment of the T_1 data has resulted in the equation

$$1/T_1 = 0.968(\pm0.163)1/d^2 + 0.00003(\pm0.00847),$$
$$r = 0.948. \qquad [5]$$

The slope in this equation gives $t_{1,\text{wall}} = 88 \pm 15$. Therefore, the glass surface is said to have a large wall effect in relaxing the laser-polarized Xe gas: it is larger by about 5 times that of the gelatin surface (Eq. [4]). The value of $t_{1,\text{wall}} = 88$ s gives an estimated value of $T_{1,\text{wall}} = 416$ s for a Pyrex cell with a 20-mm diameter. This value parallels a reported value of about

240 s in the uncoated cell (7). Hokkai-Super glass has given a similar solpe (Eq. [6]):

$$1/T_1 = 1.218(\pm0.045)1/d^2 + 0.0174(\pm0.0014),$$
$$r = 0.999. \qquad [6]$$

The intercept of the plots shown in Eqs. [3–6] is very small, indicating a large value for $T_{1,\text{inf}}$. This $T_{1,\text{inf}}$ value is estimated to be 312 s from the intercept in Eq. [3].

The T_1 value is also dependent on the glass material. Quartz is outstanding in giving a longer T_1 value when compared in a similar sized cavity (Table 1). This is probably because glasses other than quartz include metal oxides, especially paramagnetic metal ions, which effectively relax the laser-polarized Xe gas when the gas collides with the wall. Pyrex glass surely contains about 0.03% ferric oxide as an ingredient. Surface treatment by silicone compounds is reported to retard the relaxation of the encapsulated Xe gas. An extension of our studies including such a coating effect is now underway. But it is clear in the present study that the quantitative analysis of relaxation time is useful for differentiating the physical and chemical properties of the surface. Such an analysis is also expected to be useful for biomedical analysis of surfaces of tissues and organs *in vivo*.

APPENDIX

Diameter Dependency of the Relaxation Time of ^{129}Xe Gas in a Spherical Cavity

When an atom possesses self-diffusion constant D in a cavity with diameter d, the statistical average of the time required for a collision with the surface of the cavity $\langle t \rangle$ is given by the equation

$$\langle t \rangle = d^2/(15D), \qquad [a\text{-}1]$$

where the statistical average is taken for every point inside the cavity.

This is obtained from the following relationships given in Eqs. [a-2] and [a-3]. That is, the statistical average of the distance from a point inside the cavity to the surface is given in quadratic form,

$$\langle l^2 \rangle = \int l^2 \, dv \bigg/ \int dv,$$

where dv is the volume element in the polar coordinate system, i.e., $dv = r^2 \sin\theta \, dr \, d\theta \, d\phi$. This equation leads to Eq. [a-2]:

$$\langle l^2 \rangle = (2/5)d^2. \qquad [a\text{-}2]$$

Let an atom move the averaged distance of $(\langle l^2 \rangle)^{1/2}$ within the average time $\langle t \rangle$; then Eq. [a-3] holds.

$$\langle l^2 \rangle = 6D \langle t \rangle \qquad \text{[a-3]}$$

Equations [a-2] and [a-3] give Eq. [a-1].

In the next step the relaxation rate of a Xe atom inside the cavity is considered to occur as the sum of the intrinsic relaxation rate observed under infinite size, $1/T_{1,\text{inf}}$, and the contribution from the wall, $1/T_{1,\text{wall}}$,

$$1/T_1 = 1/T_{1,\text{inf}} + 1/T_{1,\text{wall}}. \qquad \text{[a-4]}$$

The latter contribution occurs when the atom collides with the surface of cavity, and it is considered proportional to the number of collisions in a unit second,

$$1/T_{1,\text{wall}} = \langle n \rangle 1/t_{1,\text{wall}} \qquad \text{[a-5]}$$

where the number of collisions with the surface in a unit second is defined as n and averaged for every point inside the cavity leading to $\langle n \rangle$, and $t_{1,\text{wall}}$ is the contribution to the relaxation rate when one collision occurs to the atom inside the cavity. Here,

$$\langle n \rangle = 1/\langle t \rangle = 15D/d^2 \qquad \text{[a-6]}$$

holds from Eq. [a-1]. Therefore, Eq. [a-4] leads to Eq. [a-7]:

$$1/T_1 = 1/T_{1,\text{inf}} + (15D/t_{1,\text{wall}})(1/d^2). \qquad \text{[a-7]}$$

This equation demonstrates that linear plots may be obtained when the inverse T_1 observed experimentally is plotted against the inverse square of the diameter of the cavity. Furthermore, the intercept of the plot corresponds to $1/T_{1,\text{inf}}$ and the slope corresponds to $15D/t_{1,\text{wall}}$. Therefore, the value of $t_{1,\text{wall}}$ can be estimated from the slope of the plots of Eq. [a-7] using the self-diffusion coefficient of $D = 5.7$ mm^2/s for 1 atm Xe gas at room temperature (2b, 9),

$$t_{1,\text{wall}} = 85.5/\text{slope}, \qquad \text{[a-8]}$$

when the slope is given in square millimeters per second. It may be noteworthy that $t_{1,\text{wall}}$ has no dimension (or has a dimension of s/s), since its inverse indicates a contribution to the relaxation rate when a collision occurs with the wall once in a second. In other words, since the contribution to the relaxation time is described as $t_{1,\text{wall}}$ multiplied by the number of collisions per second, $t_{1,\text{wall}}$ becomes dimensionless. Finally, $t_{1,\text{wall}}$ can be said to express the wall effect in the relaxation time for 1 atm Xe gas encapsulated in a cavity of 9.2-mm diameter for which collision occurs once in a second at room temperature (Eq. [a-6]).

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