

Nuclear Magnetic Resonance of Xe^{129} in Natural Xenon*†

E. R. HUNT‡ AND H. Y. CARR

Department of Physics, Rutgers University, New Brunswick, New Jersey

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Nuclear magnetic resonance studies of natural xenon have been continued using fluid samples with improved purity. The Xe^{129} spin-lattice relaxation time in the gas was found to be inversely proportional to the density: $1/T_1 = (5.0 \pm 0.5) \times 10^{-6} \rho$, where T_1 is in sec and ρ in amagats. For the liquid in equilibrium with its vapor, the relaxation time throughout the temperature range 0° to -72°C is 1000 ± 200 sec. In both the gas and the liquid the paramagnetic shift in the resonant value of the local field H at the nucleus, relative to its value for the isolated atom in the same external field, is directly proportional to the density and the external field: $\Delta H = +(4.22 \pm 0.05) \times 10^{-7} \rho H_0$, where ΔH and H_0 are in G and ρ is in amagats. The above T_1 and ΔH data agree well with a relationship derived by Torrey involving an analysis of the fluctuating magnetic field at a nucleus due to the rotation of a diatomic configuration. The derivation is based on Ramsey's theory of the chemical shift and the spin-rotational coupling which exist when two atoms are sufficiently close to interact.

I. INTRODUCTION

THE Xe^{129} relaxation rate^{1,2} and density-dependent shift² of the resonance have been studied further using purer samples of natural xenon. The previous shift data have been confirmed and additional data obtained as a function of field. The earlier low-density relaxation data have been confirmed, but different values for the relaxation times at high densities have been observed. The new data, like the earlier results,³ still cannot be accounted for by the direct nuclear dipole-dipole interaction during collisions. Using recent theoretical results obtained by Torrey,⁴ it can be shown that the rotation of the diatomic charge distributions during collisions—a mechanism suggested by Staub¹ and first discussed in detail by Adrian⁵—provides extensive coherence to the Xe^{129} relaxation and shift data.

II. EXPERIMENTAL RESULTS

Nuclear magnetic resonance free-precession techniques have been used to measure the Xe^{129} relaxation rate, resonance shift, and self-diffusion constant.

The new samples are similar to ones previously described.² In preparing the new samples, additional care was taken in removing impurities both from the sample fluid and the glass container walls. The pressure in the glass containers, both prior to the admission of the xenon and while the frozen xenon was pumped on

to remove the noncondensed oxygen impurity, was approximately 1μ . This pressure, determined by the vapor pressure of the mercury in the Toepler pump used to introduce the xenon, was more than an order of magnitude lower than that used in the preparation of the earlier samples.² The walls of one new sample were coated with General Electric Dri-Film⁶ in an effort to check wall effects. Another sample was condensed, pumped on, and evaporated three times in an effort to remove oxygen which might have been trapped in the liquid or solid xenon.

(1) These new samples were first used to measure the field and density dependence of the shift. In the present work we have observed directly the shift $\Delta\omega$ in the free precession frequency as the sample density is varied in a given external field H_0 . If H is the local field, then $\omega = \gamma H$ where γ is the gyromagnetic ratio. The shift in the local field, ΔH , is equal in magnitude but opposite in sign to the change in the external field measured in the earlier constant frequency experiments.²

As the density increases, the shift in the local field increases in the direction of the externally applied field. It can be described as a decrease in the normal diamagnetic correction appropriate to an isolated atom, or alternatively as a separate paramagnetic correction. For our dense samples, the density-dependent shift is the order of 1 G in an external field of 10 000 G. The normal diamagnetic shift for xenon in this field is approximately 50 G.

Figure 1 shows our shift data for two external fields, 12.2 and 4.58 kG. The original data of Streever and Carr² for 8.06 kG also are included. The densities are given as a ratio of the actual density of the sample to the density of the gas at standard conditions, that is, in amagats. The shift is directly proportional to the density throughout the gaseous region and very nearly so throughout the liquid region observed. All points shown above 300 amagats are for the liquid in equilibrium with its vapor. These liquid points have been

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‡ Present Address: the Department of Physics, Duke University, Durham, North Carolina.

¹ E. Brun, J. Oeser, H. H. Staub, and C. G. Telschow, *Phys. Rev.* **93**, 904 (1954); *Helv. Phys. Acta* **27**, 173 (1954).

² R. L. Streever and H. Y. Carr, *Phys. Rev.* **121**, 20 (1961).

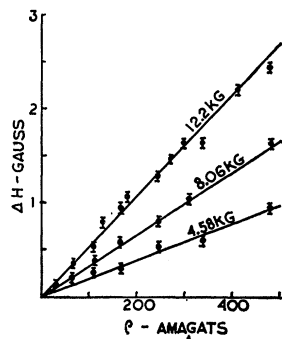
³ R. L. Streever, thesis, Rutgers, The State University, New Brunswick, New Jersey, 1959 (unpublished).

⁴ H. C. Torrey, following paper, *Phys. Rev.* **130**, 2306 (1963).

⁵ F. J. Adrian, thesis, Cornell University, Ithaca, New York, 1955 (unpublished).

⁶ M. A. Bouchiat, T. R. Carver, and C. M. Varnum, *Phys. Rev. Letters* **5**, 373 (1960).

FIG. 1. The shift ΔH in the local field at a Xe¹²⁹ nucleus as a function of density ρ . All points below 300 amagats correspond to the gas at 25°C. All points above 300 amagats correspond to the liquid in equilibrium with its vapor.



obtained by lowering the temperature of the samples below that of the critical point (17°C). To measure the relative shifts, the free precession frequencies of the samples were compared with the free precession frequency of a fast-relaxing, oxygen-doped, reference sample.

Figure 2 shows the dependence of the shift on the magnitude of the external field H_0 . It is a plot of the slope of the lines in Fig. 1 as a function of the external field. These data establish within our experimental error that this shift relative to the isolated atom in the same external field is directly proportional to H_0 and is given by $\Delta H = +(4.22 \pm 0.05) \times 10^{-7} \rho H_0$ where ρ is in amagats and ΔH and H_0 are in G.

We have made an exploratory measurement of the shift in the Xe¹³¹ resonance by observing its free precession frequencies in two samples having different densities. Within the experimental error of $\pm 15\%$, the shift was equal to that found for the Xe¹²⁹ resonance.

(2) With the new samples we observe, at low gas densities, relaxation times approximately equal to those found by Streever and Carr,² but at higher densities our values of T_1 are 3 to 4 times longer. As illustrated in Fig. 3, these longer values now reveal a linear dependence of the relaxation rate on density given by $1/T_1 = (5.0 \pm 0.5) \times 10^{-6} \rho$ where T_1 is in sec and ρ in amagats. The linear dependence has also been observed recently by Staub and his co-workers.⁷ Earlier data from less pure samples indicated that the rate varied as the square of the density.

Measurements of T_1 in fields of 5.0, 12.2, and 25 kG reveal no field dependence for T_1 .

The Xe¹²⁹ spin-lattice relaxation times observed in the liquid in equilibrium with its vapor are given in Table I. These values are approximately an order of magnitude longer than those previously reported,² again indicating a lower impurity content. In this region T_1 is constant within our experimental error. This is in contrast to the earlier results² where the relaxation rate for this range had an activation-like temperature dependence equivalent to that of the density divided by the diffusion coefficient.

All of the relaxation times in this work have been

⁷ D. Brinkmann, E. Brun, and H. H. Staub, *Helv. Phys. Acta* **35**, 431 (1962).

TABLE I. Xe¹²⁹ relaxation time T_1 for liquid.

$\rho \pm 2\%$ (amagats)	$T \pm 2^\circ$ (°C)	T_1 (min)
298	10	15.0 ± 3
339	0	17.5 ± 3
412	-30	17.5 ± 3
480	-72	16.5 ± 3

measured by using a single 90° pulse to observe the net polarization of the sample as it comes to equilibrium after having been saturated or having resided in zero field for a time long compared to T_1 .

(3) We have made direct measurements of the self-diffusion coefficient D in both the gas and liquid using the nuclear magnetic resonance free-precession technique described by Carr and Purcell.⁸ The results are shown in Table II. Until recently no xenon diffusion data for the dense gas or liquid regions were available. Naghizadeh and Rice⁹ have made measurements in the liquid as a function of temperature at two pressures using an open end capillary technique. If one extrapolates to our pressures, the discrepancy between the results obtained by the two methods is roughly 25% which is approximately the maximum value consistent with the estimated maximum errors.

(4) It is important to consider whether the above experimental data are determined by impurities. In order to study the effect of paramagnetic oxygen impurity, four xenon samples with densities of 230 amagats were intentionally doped with 2, 10, 27, and 36 amagats of oxygen, respectively. The contribution to the shift from the oxygen was found to be $\Delta H(O_2) = +(13 \pm 2) \times 10^{-7} \rho(O_2) H_0$, while the relaxation rate was given by $1/T_1 = (0.56 \pm 0.15) \rho(O_2)$. Thus, to account for the observed relaxation rates, the impurity content in our nondoped samples would presumably have to be one part in 10^5 . It is clear that even if the impurity concentration were this large, it could not affect the shift or diffusion data.

Estimates of the impurity content based on our sample preparation procedures suggest that the content is less than 1 part in 10^5 . Thus, we do not believe the relaxation rates are determined by oxygen. There is

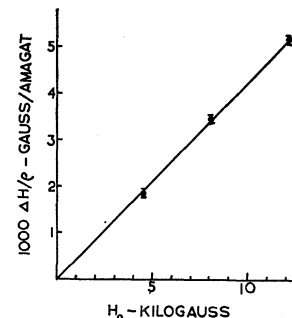


FIG. 2. The shift per unit density (from Fig. 1) as a function of the external field H_0 .

⁸ H. Y. Carr and E. M. Purcell, *Phys. Rev.* **94**, 630 (1954).

⁹ J. Naghizadeh and S. A. Rice, *J. Chem. Phys.* **36**, 2710 (1962).

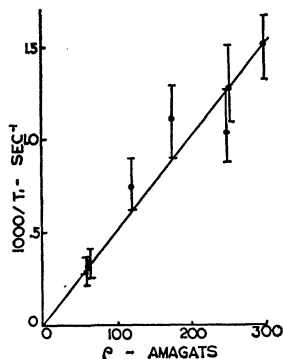


FIG. 3. The Xe^{129} relaxation rate $1/T_1$ in the gas at 25°C as a function of density ρ .

experimental evidence to support this conclusion. The earlier samples not only have larger relaxation rates but also exhibit an activation-like temperature dependence in the liquid consistent with relaxation by paramagnetic impurities. These observations suggest that the relaxation in these earlier samples is caused by an impurity, probably oxygen. If oxygen were the dominant cause of relaxation in our new samples, we might expect different values for T_1 , but the activated temperature dependence should still exist. Since our samples exhibit a very unusual absence of any temperature dependence in the liquid region observed, we conclude that oxygen cannot be the dominant cause of relaxation. Furthermore, the use of the sample which was condensed, pumped on, and evaporated three times during the sealing process revealed no change in the data. The sample with the Dri-Film coating on the walls also revealed no change. These results suggest that impurities in the bulk fluid or on the walls do not affect our data.

III. COMPARISON OF RESULTS WITH THEORY

The direct nuclear dipole-dipole interaction during collisions between xenon atoms is not capable of accounting for the order of magnitude of the observed Xe^{129} relaxation rate. In particular, the Bloembergen¹¹ theory for relaxation in monatomic systems at low densities, and the Bloembergen-Purcell-Pound¹⁰ theory for relaxation in the liquid predict relaxation rates two to three orders of magnitude slower than those given in Table I. Furthermore, an activation-like temperature dependence is predicted for the liquid. This also is quite inconsistent with our new data.

We have performed several exploratory experiments searching for evidence of other possible relaxation mechanisms. The lack of any observed dependence of the relaxation rate on external field in the range 5 to 25 kG establishes that the relaxation cannot be accounted for by an anisotropic chemical shift mechanism. Torrey¹² has noted that if the Xe^{129} relaxation were caused by an electron-coupled scalar interaction with

¹⁰ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

¹¹ N. Bloembergen, *Nuclear Magnetic Relaxation* (W. A. Benjamin, Inc., New York, 1961).

¹² H. C. Torrey (private communication).

the relaxing Xe^{131} spins, there should be a 30% enhancement in the Xe^{129} polarization when the Xe^{131} spins are saturated. No enhancement, at least within the experimental error of 10%, was observed under these conditions. This suggests that such a scalar interaction also cannot be the dominant relaxation mechanism.

A promising mechanism for giving coherence to the relaxation and shift data is the rotation of the distorted charge clouds during the collisions of two xenon atoms. This was first discussed in detail by Adrian.⁵ Torrey⁴ has now related the relaxation rate to the recently discovered shift.² The distortion of the charge clouds due to the Van der Waals interaction during collisions gives rise to $\Delta\sigma$, the shift in the shielding factor relative to an isolated atom; and the rotation of the distorted charge distributions produces the time varying magnetic field H_r , necessary for relaxation. The lack of a detailed description of the charge distortion makes an accurate independent calculation of H_r very difficult. Adrian's early Xe^{129} predictions for the relaxation rate differed considerably with the experimental data not only because his calculations were of necessity very approxi-

TABLE II. Xenon self-diffusion coefficient D .

	$\rho \pm 2\%$ (amagats)	$T \pm 2^\circ$ ($^\circ\text{C}$)	$p \pm 2\%$ (atm)	$10^4 x D \pm 15\%$ (cm^2/sec)
Gas	235	25	71	1.62
	270	25	80	$1.46 \pm 20\%$
	310	25	109	1.46
Liquid	339	0	41	1.20
	380	-13	32	0.97
	412	-30	21	0.86
	480	-72	5.5	0.44

mate but also because the available data were not obtained from pure samples.

Torrey⁴ has been able to express H_r in terms of $\Delta\sigma$. His derivation is based on Ramsey's¹³ relationship between H_r and σ for a linear molecule, a relationship in which the detailed description of the charge distortion cancels out. Torrey finds that

$$H_r = (3mc/e)\omega\Delta\sigma. \quad (1)$$

Here m and e are the electronic mass and charge, c is the velocity of light, and ω is the angular velocity of the line of centers of the two colliding xenon atoms; H_r , ω , and $\Delta\sigma$ are instantaneous algebraic quantities.

Equation (1) can be used to predict correctly the sign of the shift. The electrons in the atom of the resonant nucleus provide the dominant contribution to the rotational field.¹⁴ The rotation of this negative electronic charge produces an H_r having the opposite sign to ω . Therefore, one expects negative values of $\Delta\sigma$. This corresponds to a paramagnetic shift since the local field

¹³ N. F. Ramsey, *Phys. Rev.* **78**, 699 (1950).

¹⁴ G. C. Wick, *Phys. Rev.* **73**, 51 (1948).

is given by $H = H_0(1 - \sigma)$, and the shift in the local field is $\Delta H = -H_0\Delta\sigma$.

Equation (1) can be used to obtain an expression for T_1 . Using a hard-sphere model to describe the collision trajectories, Torrey finds that for the low-density gas:

$$\frac{1}{T_1} = \frac{21}{40\pi} \left(\frac{\gamma mc}{e} \right)^2 \frac{\bar{v}_r}{R_m^4 N} \langle \Delta\sigma \rangle_t^2, \quad (2)$$

where γ is the gyromagnetic ratio of the Xe¹²⁹ nucleus, \bar{v}_r is the average relative speed, R_m is the hard-sphere diameter, and N is the total number of atoms per unit volume. The relaxation rate is expressed in terms of $\langle \Delta\sigma \rangle_t$, the observed shift which is the instantaneous shift averaged over all time. As shown by Torrey, this kinetic average is identical to the statistical average over the radial density function.

Considerable physical insight into Torrey's result, Eq. (2), and an indication of its possible extension into the dense gas or liquid region can be obtained by means of the simple random walk model.^{8,15} The conclusions drawn from such a model, however, can be considered accurate only to the order of magnitude. It is assumed that the nuclear spins interact with a fluctuating local magnetic field consisting of uncorrelated pulses of average magnitude h , random direction, average duration τ , and average frequency ν . We also can assume $\nu \gg \gamma H_0$. Such a local field provides a relaxation rate given by^{8,15,16}

$$1/T_1 \simeq \frac{1}{3} \gamma^2 h^2 \tau^2 \nu. \quad (3)$$

This is a general relationship from which the usual high-density result is obtained by setting $\tau = 1/\nu$. Averaging Eq. (1) first over one collision, and then over all collisions, one obtains

$$h = (3mc/e) \langle \omega \Delta\sigma \rangle_c. \quad (4)$$

The shift, like the Van der Waals interaction, is a rapidly decreasing function of the separation R between the colliding atoms. However, ω varies only as $1/R$ and is considered constant during a given collision. Thus,

$$h = (3mc/e) \langle \omega \rangle_c \langle \Delta\sigma \rangle_t / \tau \nu, \quad (5)$$

where $\langle \Delta\sigma \rangle_t = \langle \Delta\sigma \rangle_c \tau \nu$ is the observed shift, i.e., $\Delta\sigma$ averaged over all time. Noting that to within an order of magnitude $\langle \omega \rangle_c = \bar{v}_r / R_m$, one obtains

$$\frac{1}{T_1} \simeq 3 \left(\frac{\gamma mc}{e} \right)^2 \frac{\bar{v}_r^2}{R_m^2} \frac{\langle \Delta\sigma \rangle_t^2}{\nu}. \quad (6)$$

This result agrees with Torrey's more precise result in Eq. (2) to within an order of magnitude since in the low density gas $\nu \simeq \pi R_m^2 N \bar{v}_r$.

¹⁵ D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

¹⁶ J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959).

In terms of the diffusion constant $D = r^2 \nu / 6 \simeq \bar{v}_r^2 / 12 \nu$ where r^2 is the mean square jump distance, Eq. (6) becomes

$$1/T_1 \simeq 36 (\gamma mc/e)^2 D \langle \Delta\sigma \rangle_t^2 / R_m^2. \quad (7)$$

All three of the nonconstant quantities in Eq. (7),— T_1 , D , and $\langle \Delta\sigma \rangle_t$ —can be measured using nuclear magnetic resonance techniques.

These theoretical results give considerable coherence to the observed Xe¹²⁹ data. We have already noted that a paramagnetic shift is predicted from Eq. (1). Since $\langle \Delta\sigma \rangle_t$ is observed to be independent of field, the relaxation rates given by both Eqs. (2) and (7) are also independent of field as observed. Inasmuch as $\langle \Delta\sigma \rangle_t$ is observed to vary linearly with the density, Eq. (2) correctly predicts the observed density dependence of T_1 in the dilute gas.

Using Eq. (2), the experimental value for $\langle \Delta\sigma \rangle_t$, and 4×10^{-8} cm as a rough value for the rigid-sphere diameter, one obtains a predicted relaxation time at 60 amagats, for example, of 7×10^8 sec. The experimental value is 3×10^8 sec. These calculations based on the spin-rotational interaction provide the first Xe¹²⁹ relaxation time predictions which agree with the experimental data within the proper order of magnitude. Inasmuch as Eq. (2) is very sensitive to the precise value of the effective rigid sphere diameter, a more accurate check on the theory must involve a better determination of R_m such as that suggested by Torrey.⁴

The unusual constancy of the relaxation time throughout the observed liquid range is consistent with Eq. (7). The independently obtained experimental values of D and $\langle \Delta\sigma \rangle_t$ show that within the experimental error of approximately 20% the product $D \langle \Delta\sigma \rangle_t^2$ is constant throughout our observed liquid range. Thus, according to Eq. (7), the relaxation time should be constant as observed if one assumes any change in R_m is negligible. By contrast, the predicted relaxation based on a direct dipole-dipole mechanism would vary by a factor of 4 over this same temperature range because of the change in the factor ρ/D .

The coherence given to our data by Torrey's result, Eq. (1), suggests strongly that the charge distortion and rotation associated with two colliding xenon atoms is the dominant mechanism responsible for our observed shift and relaxation. This conclusion is supported by the failure of any other suggested mechanism to account for the data.

IV. ACKNOWLEDGMENTS

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