

Field-dependent relaxation and absolute nuclear shielding of ^{207}Pb in liquid PbCl_4

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(Received 27 June 1973)

Relaxation times T_1 and T_2 of ^{207}Pb in liquid PbCl_4 have been studied for the purpose of establishing an absolute nuclear shielding scale for lead. T_1 has been decomposed into scalar and spin-rotation contributions using variable temperature measurements at the two field strengths 6.59 and 16.90 kG. T_2 is much shorter than T_1 and is strongly dominated by scalar coupling to chlorine. Knowledge of the scalar contributions to T_1 and T_2 determines the halogen relaxation times ($\tau_{35} = 7.15 \mu\text{sec}$ at 25°C), the lead-chlorine coupling constant [$(J(^{207}\text{Pb} - ^{35}\text{Cl}) = 705 \text{ Hz})$], and the reorientational correlation time ($\tau_\theta = 1.72 \times 10^{-11} \text{ sec}$ at 25°C). A correlation time τ_r for the angular momentum vector has been computed using J diffusion theory, but the value obtained appears to be too short ($0.8\text{--}2.9 \times 10^{-14} \text{ sec}$) to be meaningful in terms of classical diffusion of rigid molecules. Nevertheless, the known range of ^{207}Pb chemical shifts places an absolute upper limit on τ_r of $6 \times 10^{-14} \text{ sec}$ at 263°K . The physical significance of such short correlation times is discussed, and it is concluded that τ_r probably describes collision-induced distortions in the molecular structure. Experimental values of the spin-rotation contribution to $(T_1)^{-1}$ are used in conjunction with estimated values of τ_r to compute limiting values for the spin-rotation constant that place limits on the paramagnetic part of the magnetic shielding constant. A shielding scale previously deduced from optical pumping data is discussed, and a source of possibly substantial error in this scale is pointed out.

I. INTRODUCTION

Group IV elements possess a series of isotopes for which absolute nuclear shielding scales can readily be determined by magnetic relaxation measurements. All except germanium have naturally abundant spin- $\frac{1}{2}$ isotopes. Relaxation times T_1 and T_2 of these nuclei often contain an identifiable contribution from the spin-rotation interaction, the tensor elements of which are directly proportional to corresponding elements of the magnetic shielding tensor.^{1,2} Thus, relaxation data provide a direct means of establishing absolute nuclear shielding scales when (1) the correlation time τ_r for the spin-rotation interaction is known and (2) anisotropies of the spin-rotation tensor and the reorientational self-diffusion tensor are known. The simple tetrahedral compounds of Group IV elements are particularly convenient for study since both these anisotropies vanish. The resonant nucleus lies in a site of tetrahedral symmetry, and consequently the spin-rotation and shielding constants are scalar. Molecular reorientation is likewise isotropic and is described by two correlation times τ_θ and τ_r that characterize, respectively, reorientation of a molecule-fixed tensor and reorientation of the angular momentum vector.

Magnetic relaxation of ^{119}Sn in liquid SnCl_4 and SnI_4 has previously been analyzed by one of us³ and the results used to obtain an absolute shielding scale for tin. In the present work we extend these measurements to the ^{207}Pb resonance in liquid PbCl_4 . Only two studies of ^{207}Pb relaxation in nonmetallic systems have previously been published. These include a preliminary account of the

temperature dependence of T_1 in aqueous perchlorate solution⁴ and various room temperature T_1 measurements in undegassed samples of organolead compounds.⁵ Gibbs and co-workers,^{6,7} however, have reported an absolute magnetic moment for ^{207}Pb based on their optical pumping data, which are sufficiently precise for accurate calculations of an absolute shielding scale. The shielding scale computed from this magnetic moment predicts shielding and spin-rotation constants that are extremely large compared to those of other elements (for example, $\sigma_p \approx -1.8\%$ in aqueous solution^{4,6}). In fact, computed spin-rotation constants imply that T_1 for ^{207}Pb in most liquid phase compounds is of the order of a few milliseconds and is entirely dominated by spin-rotation. T_1 of ^{207}Pb in aqueous perchlorate solution is indeed dominated by spin-rotation at higher temperatures, but the relatively long value of T_1 (7 sec at 25°C) implies an angular momentum correlation time that is difficult to rationalize in terms of any conceivable rotating molecular entity. The present measurements on PbCl_4 were undertaken to provide an independent determination of the shielding constant for lead.

II. EXPERIMENTAL

PbCl_4 was prepared from PbCl_2 and chlorine gas by the method of Baudler.⁹ In this procedure lead is oxidized to the stable yellow pyridinium hexachloroplumbate (IV) complex, which reacts with a large excess of cold (-10°C) H_2SO_4 to produce lead tetrachloride. 20 g of PbCl_2 yields 10 g (3.5 ml) of PbCl_4 , which settles out of the sulfuric acid as a clear, rather viscous yellow liquid. The melting point of freshly prepared degassed PbCl_4

is -10°C , which is substantially higher than a previous literature value of -15°C .¹⁰ Liquid PbCl_4 is unstable with respect to slow thermal decomposition to PbCl_2 and chlorine. PbCl_2 is easily removed by shaking the sample with concentrated H_2SO_4 , but chlorine gas is probably quite soluble in PbCl_4 and apparently lowers the melting point as it saturates the liquid. Approximately 2 ml of the sample were transferred to a 10 mm NMR tube and maintained under 5 ml of concentrated H_2SO_4 . Samples were degassed by ten freeze-pump-thaw cycles and sealed under vacuum. The tubes were sealed with a Teflon stopcock joined to the NMR tube by an O-ring seal in order to provide a means of relieving the buildup of chlorine gas pressure that accompanies decomposition.

The pulsed NMR spectrometer, gated integrator, and signal averaging computer have been described elsewhere.³ The older 12-in. wide-gap magnet has been replaced by a 9.5 in. Varian electromagnet, which, although capable of higher fields (21 kG), is relatively inhomogeneous ($T_2^* \cong 2$ msec over a 10 mm diameter by a 2.5 cm high sample volume). The field is locked externally on the ^7Li or ^1H resonance of a doped aqueous LiCl solution. A broad-band time-shared field lock has been constructed which permits locking on resonances in the frequency range 16–32 MHz.

Longitudinal relaxation times were measured by plotting the height of the free induction decay (FID) following the $\pi/2$ pulse of a $\pi-\tau-\pi/2$ sequence as a function of pulse separation τ . 64 FID's were sampled for each value of τ , with a delay of five T_1 between successive sequences. At least ten τ values were used to define each exponential. The null technique has often been used to measure T_1 , although substantial corrections for H_1 inhomogeneity and long T_2 are required to obtain accurate data.^{11,12} Corresponding corrections are negligible in the present system, for which $\tau_{180} \ll T_2^* \ll T_1$ (τ_{180} is the width of the π pulse), as long as a full exponential plot is used to define T_1 . The estimated uncertainty for each data point is $\pm 10\%$.

T_2 was measured using the phase-shifted Carr-Purcell sequence, with pulse spacings of 400 and 600 μsec . Since T_2 is dominated by scalar coupling to chlorine, the pulse spacing must be long compared to the halogen relaxation time (2–10 μsec). The CAT samples successive echo peaks and averages 64 decays. Tuning in the probe of the Bruker spectrometer, and hence the rf phase shift, is rather temperature dependent and was readjusted carefully at each temperature. Measured T_2 values were reproducible within 10% and probably have an accuracy similar to the T_1 data.

III. RESULTS

Lead tetrachloride, like most other tetrahalide compounds of Group IV elements, is composed almost entirely of unassociated tetrahedral molecules in the liquid phase. Raman spectra of PbCl_4 show the four fundamentals characteristic of tetrahedral geometry,^{13,14} and the Raman frequencies and force constants form a regular series with those of other Group IV tetrachlorides.^{14,15} The NMR spectrum of $^{207}\text{PbCl}_4$ consists of a single resonance, shifted 850 ppm upfield from the ^{207}Pb resonance in PbEt_4 . Thus the major species in PbCl_4 is definitely a tetrahedral monomer, and the available spectral data give no indication of substantial concentrations of either polymers or ion pairs. Lead relaxation could also be affected by the presence of small concentrations of nontetrahedral species if chemical exchange between major and minor species were rapid on the NMR time scale. These effects can, however, be identified qualitatively from their specific temperature and field dependence. A detailed analysis of lead relaxation presented below indicates that chemical exchange does not contribute significantly to observed relaxation times and that T_1 and T_2 are readily understood in terms of mechanisms intrinsic to monomeric PbCl_4 .

A. Relaxation mechanisms

General features of the relaxation behavior of $^{207}\text{PbCl}_4$ are very similar to those previously observed for ^{119}Sn in SnCl_4 .³ (T_2)⁻¹ is shown as a function of temperature and field strength in Fig. 1. T_2 is more than three orders of magnitude shorter than T_1 at a given temperature, indicating that scalar coupling from ^{207}Pb to $^{35,37}\text{Cl}$ dominates the relaxation. Both chlorine isotopes possess nuclear quadrupole moments and are relaxed on a submillisecond time scale. An additional T_2 pathway could in principle be present if lead exchanged rapidly between the major molecular species PbCl_4 and various chemically shifted species present in much smaller concentration. This mechanism increases as the square of the field, however, and cannot contribute significantly to the observed T_2 , which is field independent. Thus transverse relaxation of ^{207}Pb results solely from scalar coupling to the two naturally abundant chlorine isotopes and consists of a superposition of exponentials arising from five isotopic species, $^{207}\text{Pb}^{35}\text{Cl}_n^{37}\text{Cl}_{4-n}$ ($n = 0, \dots, 4$). Each $^{207}\text{Pb}-^{35}\text{Cl}$ bond contributes an amount¹⁶

$$(T_2)_{s,c,a}^{-1} = \frac{1}{3} A_{35}^2 S(S+1) \times \left(\tau_{35} + \frac{\tau_{35}}{1 + (\omega_{207} - \omega_{35})^2 \tau_{35}^2} \right) \quad (1)$$

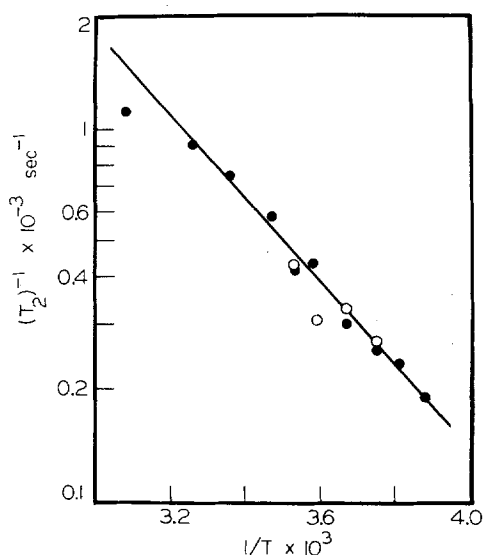


FIG. 1. $(T_2)^{-1}$ vs temperature in liquid $^{207}\text{PbCl}_4$. Data at 15.065 MHz denoted by \bullet , 5.863 MHz by \circ .

to the total relaxation with a similar contribution for the ^{37}Cl isotope. A_{35} and τ_{35} are the coupling constant and correlation time for the scalar interaction. S is the chlorine nuclear spin and ω is the angular Larmor frequency of the indicated isotope. Fortunately the T_2 's of the various isotopic species differ only slightly, and the observed relaxation rate is approximately equal to that of a molecule with the average composition $^{207}\text{Pb}^{35}\text{Cl}_{3.04}^{37}\text{Cl}_{0.96}$. Neglecting the second term in the brackets in Eq. (1) because of its large frequency denominator and using the relations $A_{35}/A_{37} = 1.202$ and $\tau_{35}/\tau_{37} = (Q_{37}/Q_{35})^2 = 0.886$,¹⁷ we find that the observed relaxation rate reduces to

$$(T_2)_{sc}^{-1} = 5.14 A_{35}^2 \tau_{35}. \quad (2)$$

[Equation (3b) of Ref. 3 is in error and should be replaced by this equation. As a result of this correction, $J(^{119}\text{Sn}-^{35}\text{Cl})$ is reduced from 410 to 375 Hz.]

The correlation time for scalar coupling is identified physically with the halogen relaxation time or, in the case of sufficiently rapid intermolecular chemical exchange, with the residence time of chlorine in a specific molecule of PbCl_4 . The temperature dependence of $(T_2)^{-1}$ unambiguously demonstrates that scalar coupling is modulated by relaxation, rather than chemical exchange, since τ_{35} becomes longer with increasing temperature. Nevertheless, chemical exchange is undoubtedly quite rapid in PbCl_4 . Even the tin tetrahalides undergo halogen exchange on a time scale of tens of milliseconds,¹⁸ and lability of Group IV tetrahalides appears generally to increase with atomic number of the central atom.¹⁹⁻²²

At sufficiently high temperature $(T_2)^{-1}$ should pass through a maximum value when exchange and relaxation rates of chlorine are equal. $(T_2)^{-1}$ does in fact fall substantially below a simple exponential dependence at the highest measured temperature (52 °C). The observed drop is larger than typical experimental uncertainty and may reflect a chemical exchange contribution to τ_{35} . Unfortunately it is difficult to obtain data at temperatures above 50 °C due to the rapid rise of chlorine gas pressure in the sealed tube.

Longitudinal relaxation rates of $^{207}\text{PbCl}_4$ are plotted as a function of temperature at two field strengths in Fig. 2. $(T_1)^{-1}$ is in general a sum of four contributions

$$(T_1)_{obs}^{-1} = (T_1)_{SR}^{-1} + (T_1)_{DD}^{-1} + (T_1)_{CSA}^{-1} + (T_1)_{sc}^{-1}, \quad (3)$$

corresponding to relaxation arising from the spin-rotation interaction, nuclear dipole-dipole coupling, chemical shift anisotropy, and scalar coupling to chlorine. The observed temperature dependence of $(T_1)_{obs}^{-1}$ is characteristic of a dominant spin-rotation interaction (T_1 decreases with increasing temperature). This contribution to the relaxation of a nucleus in tetrahedral site symmetry is given by the expression^{23,24}

$$(T_1)_{SR}^{-1} = 2IkT\hbar^{-2}(2\pi C_0)^2\tau_J, \quad (4)$$

where I is the moment of inertia, C_0 is the spin-rotation constant in Hz, and τ_J is the correlation

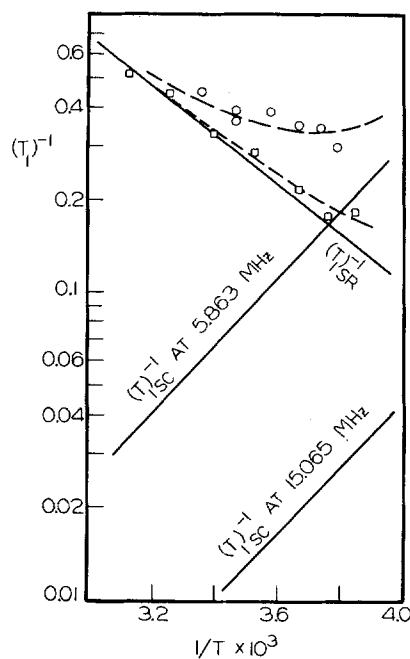


FIG. 2. $(T_1)^{-1}$ vs temperature in liquid $^{207}\text{PbCl}_4$. Data at 15.065 and 5.863 MHz denoted, respectively, by \square and \circ .

time for the molecular angular momentum vector. A smaller scalar contribution is also evident at lower temperatures where $(T_1)_{\text{obs}}^{-1}$ shows an inverse dependence upon field strength. $(T_1)_{\text{sc}}^{-1}$ varies as the inverse square of the field strength,¹⁶

$$(T_1)_{\text{sc}}^{-1} = \frac{2}{3} A^2 S(S+1) \left(\frac{\tau_{\text{sc}}}{1 + (\omega_I - \omega_S)^2 \tau_{\text{sc}}^2} \right) \quad (5)$$

when $(\omega_I - \omega_S)^2 \tau_{\text{sc}}^2 \gg 1$, and is therefore consistent with the observed field dependence. Of the remaining two mechanisms, $(T_1)_{\text{CSA}}^{-1}$ vanishes since the nuclear shielding tensor of lead in PbCl_4 is isotropic. A significant contribution from this term is also precluded from the experimental data since $(T_1)_{\text{CSA}}^{-1}$ increases as the square of the field strength in contrast to $(T_1)_{\text{obs}}^{-1}$, which varies in the opposite direction. Relaxation caused by dipole-dipole coupling is likewise negligible in PbCl_4 , as is readily verified using standard theoretical expressions^{3,16} and angular correlation times obtained below.

Longitudinal relaxation in $^{207}\text{PbCl}_4$ therefore results from competing scalar and spin-rotation interactions. The scalar component is computed for a molecule of the average composition $^{207}\text{Pb}^{35}\text{Cl}_{3.04}^{37}\text{Cl}_{0.96}$, using Eq. (5) and assuming that $(\omega_{207} - \omega_{35})^2 \tau_{35}^2 \gg 1$:

$$(T_1)_{\text{sc}}^{-1} = 8.32 A_{35}^2 (\omega_{207} - \omega_{35})^2 \tau_{35}^{-1}. \quad (6)$$

An expression based on the average composition is essentially exact for $(T_1)_{\text{sc}}^{-1}$ if not for $(T_2)_{\text{sc}}^{-1}$ since chemical exchange of chlorine is almost certainly rapid compared to T_1 (but not necessarily T_2) of ^{207}Pb . Equations (2) and (6) uniquely determine the scalar coupling constants and halogen relaxation times provided that $(T_1)_{\text{obs}}^{-1}$ can be separated accurately into scalar and spin-rotation components. The scalar portion of $(T_1)_{\text{obs}}^{-1}$ is readily identified by its field dependence at a specified temperature. Since scalar coupling provides the only field-dependent contribution to T_1 , we have

$$(T_1)_{\text{obs}, 5.8}^{-1} - (T_1)_{\text{obs}, 15.1}^{-1} = (T_1)_{\text{sc}, 5.8}^{-1} - (T_1)_{\text{sc}, 15.1}^{-1}$$

and from Eq. (6)

$$(T_1)_{\text{sc}, 5.8}^{-1} = 1.178 [(T_1)_{\text{obs}, 5.8}^{-1} - (T_1)_{\text{obs}, 15.1}^{-1}],$$

where resonance frequencies appear as subscripts. $(T_1)_{\text{sc}}^{-1}$ has the same temperature dependence as T_2 since they are both proportional to τ_{35}^{-1} . Thus the plots shown in Fig. (2) for the scalar relaxation component are determined within experimental accuracy ($\pm 20\%$) of the quantity $(T_1)_{\text{obs}}^{-1}$ (5.8 MHz) - $(T_1)_{\text{obs}}^{-1}$ (15 MHz).

The ratio of Eqs. (2) and (6) gives the halogen relaxation time directly, $\tau_{35} = 7.15 \times 10^{-6}$ sec at 25°C . Substituting τ_{35} back into Eq. (2) then gives the scalar coupling constant $J_{35} = 710$ Hz.

Relaxation of ^{35}Cl is considerably more rapid in PbCl_4 than in most other liquid tetrahalides including SnCl_4 , for which $\tau_{35} = 22$ μsec at 25°C .²⁵ Since the chlorine quadrupole coupling constants in PbCl_4 and SnCl_4 are nearly equal, the relaxation times indicate that PbCl_4 reorients approximately three times more slowly at 25°C than does SnCl_4 and seven times more slowly at -10°C . This difference in molecular dynamics is also apparent from the relatively large activation energy for τ_{35} in PbCl_4 , $E_A^\theta = 5.17$ kcal/mole, compared to 1.86 kcal/mole for SnCl_4 . An attempt was made to verify the computed value of τ_{35} in PbCl_4 by measuring the ^{35}Cl line width by wide-line NMR. The resonance was difficult to observe owing to its breadth, but the estimated τ_{35} (5 ± 2 μsec) is consistent with the value calculated from ^{207}Pb relaxation.

B. Correlation times

Two correlation times are required to describe reorientation in PbCl_4 . One of these $\tau_\theta^{(j,k)}$, describes reorientation of the spherical components of a molecular tensor of rank j . $\tau_\theta^{(2)}$ can be obtained experimentally from the relaxation time of ^{35}Cl , for which relaxation is dominated by interactions of molecular electric field gradients with the nuclear electric quadrupole moment:

$$\tau_{35}^{-1} = \frac{1}{10} (e^2 q Q / \hbar)^2 \tau_\theta^{(2)}.$$

The quadrupole coupling constant $e^2 q Q / \hbar$ is known from NQR measurements,²⁶ and the asymmetry parameter vanishes since chlorine lies on a three-fold axis. $\tau_\theta^{(2)}$ is an effective correlation time for the second rank coupling tensor and is given for a symmetric top molecule by the expression²⁷

$$\tau_\theta^{(2)} = \frac{3}{4} (\cos^2 \varphi - 1)^2 \tau_\theta^{(2,0)} + (3 \sin^2 \varphi \cos^2 \varphi) \tau_\theta^{(2,1)} + \left(\frac{3}{4} \sin^4 \varphi \right) \tau_\theta^{(2,2)},$$

where φ is the angle between the symmetry axis and the chlorine bond axis. In a spherical top molecule, $\tau_\theta^{(2)} = \tau_\theta^{(2,0)}$. This correlation time is plotted against temperature in Fig. 3. As mentioned above, $\tau_\theta^{(2)}$ is relatively short in PbCl_4 compared to values in other liquid tetrachlorides.

The second correlation time τ_J pertains to reorientation of the molecular angular momentum vector and appears in the spin-rotation relaxation formula. Although τ_J cannot be measured directly by NMR (assuming that the spin-rotation constant is unknown), τ_J has been related theoretically to $\tau_\theta^{(2,0)}$ via the Langevin diffusional model^{28,29} and also via Gordon's extended diffusion hypothesis.^{30,31} Extended diffusion provides a convenient basis for analyzing relaxation in PbCl_4 . This theory has been tested previously on several symmetrical molecular liquids^{3,27,32-35} and simple solutions.³⁵

The results for pure liquids generally agree quantitatively with the J diffusion limit, while solutions of polyatomic molecules in noble gas solvents are described more accurately by M diffusion. In the limit of small step diffusion of a spherical top molecule, characterized by the inequality $\tau_\theta^* \equiv (kT/I)^{1/2} \tau_\theta^{(2)} \gtrsim 3$, the Langevin and J diffusion models approach the same limiting form:

$$\tau_\theta(j) \cong I/j(j+1)kT\tau_J. \quad (7a)$$

M diffusion, which assumes no transfer of rotational energy during intermolecular collisions, approaches a different limit³²:

$$\tau_\theta^{(j)}(M) = 3I/j(j+1)kT\tau_J. \quad (7b)$$

The applicability of these limiting expressions to reorientation in PbCl_4 is readily verified using data in Fig. 3a. τ_θ^* varies from 5.2 at 50°C to 33 at -10°C so that the criterion for small step diffusion is satisfied over the entire temperature range. Equations (2) and (4) also require that $\tau_\theta^{(2)}\tau_J T \sim T T_2/(T_1)_{\text{SR}}$ be independent of temperature. Figure 3b shows that this quantity is not quite constant, although the variation with temperature is much smaller than that of individual relaxation times. Similar behavior was observed for SnCl_4 , although the variation of $\tau_\theta^*\tau_J^*$ was in the opposite direction. Angular momentum correlation times for PbCl_4 have been computed from Eqs. (7a) and (7b) and are plotted in Fig. 3(c). Neither equation is entirely consistent with the observed temperature dependence of T_1 and T_2 , but results in other pure liquids containing polyatomic molecules suggest that the more accurate results are to be expected from J diffusion. Values of τ_J computed from the J diffusion model vary between 0.8×10^{-14} sec (-10°C) and 3×10^{-14} sec (50°C). This time scale is extremely short and is difficult to reconcile with the assumptions of classical diffusion. By comparison the period of a carbon-hydrogen stretching vibration is about 1×10^{-14} sec, while the period of a typical bending mode ($\sim 300 \text{ cm}^{-1}$) is approximately 10^{-13} sec. If one interprets the measured angular momentum correlation time strictly in terms extended diffusion theory, lead tetrachloride (assumed to be a rigid rotor) suffers a collision that randomizes J after an average rotation of 0.005 rad. This correlation time is unphysically short, even if the concept of binary collisions is replaced by a more sophisticated picture of random torques exerted on the rigid PbCl_4 molecule by angular variations in the intermolecular potential energy function. Diffusion theories assume that collisions are of negligible duration relative to τ_J , but the opposite inequality must apply when τ_J is much shorter than the half-period of a bending vibration. For this reason it is surprising that J diffusion

appears to describe reorientation in several liquids (ClO_3F , $^{33}\text{CCl}_3\text{F}$, $^{27,34}\text{SnCl}_4$) at temperatures for which τ_J approaches 3×10^{-14} sec. Correlation times in PbCl_4 are also qualitatively consistent with behavior expected from diffusion theory, but the extremely short values computed for τ_J emphasize the necessity of a nondiffusive interpretation of the spin-rotation correlation time.

At least two nondiffusive motional hypotheses are consistent with the relatively long measured value of τ_θ and with a relatively short value of τ_J (10^{-13} – 10^{-14} sec).

1. At low temperature J may be randomized by librational motion of PbCl_4 trapped in a translationally (almost) rigid potential well. Librational motion does not contribute to efficient randomization of vectors fixed with respect to a molecular coordinate system and is therefore consistent with a

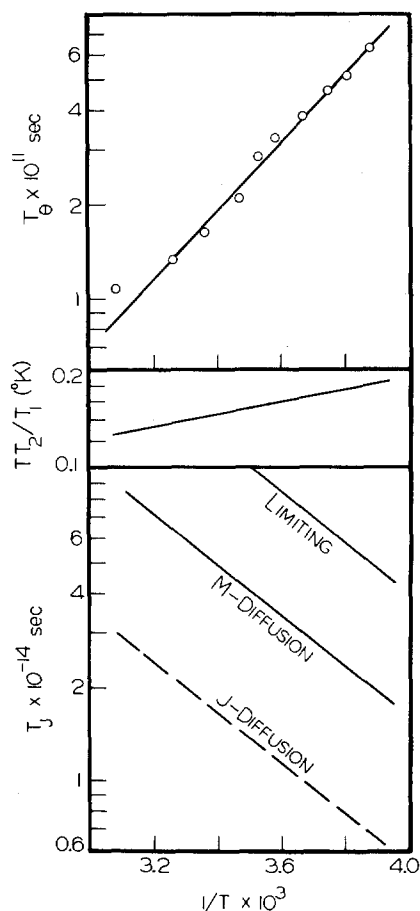


FIG. 3. Correlation times in PbCl_4 . (a) $\tau_\theta^{(2,0)}$ vs T^{-1} as derived from ^{35}Cl relaxation; (b) a test of Hubbard's relation for validity of the small step diffusion limit; (c) angular momentum correlation times derived from extended diffusion theory. "Limiting" represents absolute maximum values of τ_J permitted by the known range of chemical shifts.

relatively long value for τ_θ . On the other hand, an upper limit for a librational frequency is about 200 cm^{-1} ; J is inverted once every half-period or 0.8×10^{-13} sec. This interval is much longer than the measured value of τ_J . Furthermore, experimental evidence based on the absolute shielding scale of lead and the known range of ^{207}Pb chemical shifts places an absolute upper limit of 5.9×10^{-14} sec on τ_J at -10°C (see below).

2. τ_J may be a correlation time for collision-induced distortions. Each distortion can be decomposed into a net vibration and a net rotation with respect to the molecular center of mass. The rotational portion contributes to nuclear relaxation. If collisions with a given nearest neighbor occur every 10^{-13} sec, and if distortions arise from uncorrelated interactions with ten nearest neighbors, the time scale for changes in the angular momentum vector is 10^{-14} sec.

We believe that the latter model (collision-induced distortions) provides a qualitatively satisfactory explanation of the data. Angular reorientation is still coupled to randomization of the angular momentum vector through the frequency of intermolecular collisions. A distortional model grades conceptually into the classical diffusion picture at long τ_J and therefore may be expected to exhibit a similar τ_θ^* vs τ_J^* relation.

M diffusion predicts a range of correlation times $2.4 \times 10^{-14} < \tau_J < 9 \times 10^{-14}$ sec that are three times longer than those of J diffusion. Even these values appear to be too short to be consistent with the assumptions of extended diffusion theory.

C. Absolute shielding of ^{207}Pb

Spin-rotation constants based on both the J diffusion and M diffusion models have been calculated using Eq. (4) and are given in Table II. These scalar quantities provide an indirect means of calculating the paramagnetic shielding constant σ_p in Ramsey's shielding expression.³⁶ Of course the resulting absolute shielding scale will contain uncertainty associated with the interpretation of τ_J , but such a calculation places useful limits on σ_p and provides a very interesting comparison with an absolute shielding scale derived previously from optical pumping data.

The relation between C_0 and σ_p for a nucleus in a site of tetrahedral symmetry has been derived by Flygare¹:

$$\sigma = \sigma_d + \sigma_p \\ = \left(\frac{e^2}{3mc^2} \right) \left\langle 0 \left| \sum_i r_i^{-1} \right| 0 \right\rangle$$

$$+ \left[\left(\frac{M_p}{m\hbar} \right) \left(\frac{2\pi C_0 I}{g_l} \right) - \frac{e^2}{3mc^2} \sum_k' \frac{Z_k}{r_{lk}} \right],$$

where the sums are over i electrons and k nuclei (other than the nucleus l at resonance) in the molecule, M_p and m are proton and electron masses, I is the moment of inertia, Z is the nuclear charge, and g_l is the nuclear g factor. The magnitude of the first term in σ_p is the order of ± 5000 ppm for PbCl_4 and greatly exceeds the second term, which is only -550 ppm. The term containing C_0 is assumed to be negative in order to give σ_p a net deshielding effect. Flygare and Goodisman³⁷ have also suggested that the quantity

$$\sigma_d' = \frac{e^2}{3mc^2} \left(\left\langle 0 \left| \sum_i r_i^{-1} \right| 0 \right\rangle - \sum_k' \frac{Z_k}{r_{lk}} \right) \quad (8)$$

is approximately constant in various molecular environments and approximately equal to the free atom diamagnetic shielding constant, σ_d^a . In this approximation, σ_d' provides a fixed and calculable reference point on an absolute shielding scale, and chemical shifts reflect variations in the spin-rotation term, denoted σ_p' . The association of σ_d' and σ_d^a implies physically that the molecular binding energy is small compared to the total electronic energy.

Recent calculations of σ_d^a using Hartree-Fock-Slater functions give a value of 10.05×10^{-3} for the lead atom.³⁸ σ_p' can be calculated for PbCl_4 from Eq. (8) using $g_{\text{Pb}} = +1.18$ and values of C_0 and I given in Tables I and II:

$$\sigma_p' = (1.109 \times 10^{31}) (C_0 I / g_k) \\ = -6.8 \times 10^{-3} \text{ (} J \text{ diffusion)} \\ = -3.9 \times 10^{-3} \text{ (} M \text{ diffusion)}.$$

An alternate method of calculating σ_p' is based on the gas phase lead atom, for which the magnetic moment has been measured in an optical pumping experiment by Gibbs *et al.*^{6,7} σ_p' for ^{207}Pb in a given compound is computed from the difference between the magnetic moment of vapor phase lead as measured by optical pumping and the effective magnetic moment of chemically bonded lead as measured by NMR. The absolute effective magnetic moment of lead in dilute aqueous solution has been reported by Lutz and Stricker⁸ using a deuterium stabilized field and by the present authors⁴ using a proton stabilized field. The shielding constant reported in Ref. 4 refers to a $3.5M$ aqueous perchlorate solution. This reference solution was chosen because the chemical shift at $3.5M$ is equal to the extrapolated shift at infinite dilution. σ_p' calculated by this method is three times as large as that calculated from relaxation data:

TABLE I. Molecular and nuclear spin parameters in PbCl_4 . E_A^0 is the activation energy of τ_0 ; η is the asymmetry parameter; $\mu(^{207}\text{Pb}, \text{corr.})$ is the magnetic moment of ^{207}Pb , corrected for diamagnetism.

$r(\text{Pb}-\text{Cl}) = 2.43 \times 10^{-8} \text{ cm}^a$
$I = 92.8 \times 10^{-39} \text{ cgs}$
$J(^{207}\text{Pb}-^{35}\text{Cl}) = 705 \text{ Hz}$
$(e^2qQ/h) = 45.4 \text{ MHz}, \eta = 0$
$E_A^0 = 4.94 \text{ kcal/mole}, \tau_0(25^\circ\text{C}) = 1.71 \times 10^{-11} \text{ sec}$
$\mu(^{207}\text{Pb}, \text{uncorr.}) = +0.582569\mu_N$
$\mu(^{207}\text{Pb}, \text{corr.}) = 0.58651\mu_N \begin{matrix} +0.00084 \text{ M diffusion} \\ -0.00084 \text{ J diffusion} \end{matrix}$

^aM. W. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941).

^bReference 26.

$$\sigma_p'(\text{Pb}, ^{+2} \text{ inf. dil. aq. sol.}) = -17800 \text{ ppm},$$

$$\sigma_p'(\text{PbCl}_4) = -19900 \text{ ppm}.$$

Shielding scales derived from both experiments are compared with the range of previously measured chemical shifts in Fig. 4. On the optical pumping scale all lead compounds for which data are available are deshielded by at least 7000 ppm with respect to the totally unshielded lead nucleus. This degree of deshielding in electronically diamagnetic compounds is unprecedented among nuclei for which shielding scales have been determined and is not readily explained by Ramsay's theory. The scale derived from relaxation data, on the other hand, places resonances of all non-metallic compounds of lead intermediate between resonances of the bare nucleus and the free atom. This behavior is expected on physical grounds and is analogous to the behavior exhibited by several lighter elements, including ^{31}P , $^{39,40}\text{F}$, ^{40}Sn , ^{41}Sn , and ^{203}Tl .⁴¹ Metallic lead and lead dioxide are electrical conductors⁴² and are Knight shifted downfield of the resonance of the bare nucleus on both scales.

The discrepancy between the two shielding scales appears to result from neglect of the coupling between electronic and nuclear magnetic moments that occurs in the ground state lead atom. This coupling increases the Zeeman splitting of nuclear spin levels in an optical pumping experiment. Atomic lead is electronically diamagnetic in the ground state of an isotope with zero nuclear spin. The magnetic moment vanishes according to the expressions.

$$\begin{aligned} \mu &= \langle J, J | \mu_{e1} \cdot \mathbf{J} | J, J \rangle / J(J+1) \\ &= \mu_0 g \sqrt{J(J+1)}, \end{aligned} \quad (9)$$

where the electronic state $|J, M_J\rangle$ is labeled by

quantum numbers of the total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, μ_0 is the Bohr magneton, and $\mu_{e1} = \mu_0(g_L \mathbf{L} + g_S \mathbf{S})$ is the electronic magnetic moment operator resulting from spin and orbital angular momentum. In a state for which $\mathbf{J} = 0$, but $\mathbf{L} = -\mathbf{S} \neq 0$, μ_{e1} does not vanish (since $g_L \neq g_S$) even though the magnetic moment defined by Eq. (8) is zero.

The presence of nuclear spin in the ^{207}Pb isotope gives rise to a total angular momentum $\mathbf{F} = \mathbf{I}$ in the nuclear Zeeman levels, $M_I = \pm \frac{1}{2}$, of the 3P_0 state. In an optical pumping experiment these levels are irradiated while resonance is detected by changes in optical absorption. The question is whether the separation of the Zeeman levels reflects shielding other than that represented by the Lamb term. This separation is given by the difference in $\langle \mu_z \rangle$ for the two levels. According to the decomposition theorem⁴³ for states of sharp angular momentum,

$$\langle \mu_z \rangle = \frac{\langle F, M_F | F_z | F, M_F \rangle \langle F, F | (\mu_n + \mu_{e1}) \cdot \mathbf{F} | F, F \rangle}{F(F+1)},$$

where μ_n is the nuclear magnetic moment operator. The first term of the sum on the right-hand side gives the usual nuclear Zeeman energy

$$M_I \langle F, F | \mu_n \cdot \mathbf{I} | F, F \rangle / F(F+1) = g_n \mu_n M_I.$$

The second term

$$\begin{aligned} & \frac{M_I \langle F, F | \mu_{e1} \cdot \mathbf{I} | F, F \rangle}{F(F+1)} \\ &= \frac{M_I \langle F, F | [\mu_{e1}^x I^x + \frac{1}{2}(\mu_{e1}^+ I^- + \mu_{e1}^- I^+)] | F, F \rangle}{F(F+1)} \end{aligned}$$

vanishes in the approximation that J^2 and I^2 are diagonal in the state $|F\rangle$, but in general is non-zero since the nuclear spin mixes a small paramagnetic contribution into the electronic ground state. The major contribution probably arises from the $M_F = \pm \frac{1}{2}$ Zeeman sublevels of the 3P_1 state, which lie 825 cm^{-1} above the 3P_0 ground state. We label the Zeeman components of 3P states according to the magnetic quantum numbers of \mathbf{J} and \mathbf{I} , $^3P_J(M_J, M_I)$. Mixing occurs between the following

TABLE II. Limiting values of the spin-rotation constant, the paramagnetic shielding constant, and the angular momentum correlation time consistent with extended diffusion theory and with tabulated ^{207}Pb chemical shifts.

	J diffusion	M diffusion	Lower limit permitted by chemical shift range
C_0	7.8 kHz	4.5 kHz	2.9 kHz
σ_p'	6.8×10^{-3}	3.9×10^{-3}	2.5×10^{-3}
$\tau_J(-10^\circ\text{C})$	$.81 \times 10^{-14} \text{ sec}$	$2.4 \times 10^{-14} \text{ sec}$	$5.9 \times 10^{-14} \text{ sec}$

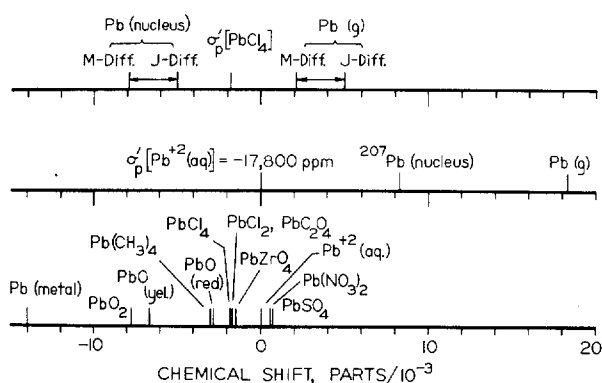


FIG. 4. Shielding scales for lead. Upper: shielding scales derived from relaxation data and extended diffusion theory. Middle: shielding scale derived from optical pumping data. Lower: typical chemical shifts for ^{207}Pb in various compounds. Data taken from Ref. 4 and L. H. Piette and H. E. Weaver, *J. Chem. Phys.* **28**, 735 (1958).

components of 3P_0 and 3P_1 :

$$^3P_0(0, +\frac{1}{2}) \rightarrow ^3P_1(+1, -\frac{1}{2}), \quad ^3P_1(0, +\frac{1}{2}),$$

$$^3P_0(0, -\frac{1}{2}) \rightarrow ^3P_1(0, -\frac{1}{2}), \quad ^3P_1(-1, +\frac{1}{2}).$$

Coupling of the electronic and nuclear angular momenta of the lead atom thus gives rise to a non-Lamb type contribution to the measured magnetic moment.

Probable limits of uncertainty on the absolute shielding scale derived from relaxation data are indicated in Fig. 4 and Table II. At the upper extreme we have the shielding constant consistent with J diffusion, for which $\tau_J = 0.81 \times 10^{-14}$ sec at -10°C . A shorter correlation time than this is difficult to rationalize in terms of any physical model. A somewhat smaller value of σ'_p is predicted by M diffusion, for which $\tau_J = 2.4 \times 10^{-14}$ sec at -10°C . It is interesting that the chemical shift data in Fig. 4 place an absolute upper limit on τ_J that appears to rule out the librational model outlined above. Assuming that lead in the ionic solids $\text{Pb}(\text{NO}_3)_2$ and PbSO_4 is deshielded relative to a spherical environment in which all shielding is due to the Lamb term, we compute an absolute upper limit of 5.9×10^{-14} for τ_J and a lower limit of 2.5×10^{-3} for σ'_p .

Spin-rotation constants, shielding constants, and correlation times obtained from these calculations are summarized in Table II. Limiting values of the absolute magnetic moment for ^{207}Pb , corrected for diamagnetism, are given in Table I. The latter values have been computed from the shielding scale in Fig. 4 and from previous measurements⁴ of the relative resonance frequencies of ^1H in H_2O and of ^{207}Pb in 3.5 molar $\text{Pb}(\text{ClO}_4)_2$. Refinement of the shielding scale can be based on relaxation measurements in other symmetrical

systems. Tetraalkyl lead compounds, in which angular correlation times can be determined directly from ^{13}C relaxation times, appear suitable for this purpose.

ACKNOWLEDGMENTS

We thank the Rackham Foundation and the Memorial Phoenix Project of the University of Michigan for partial support of this research. Financial support was also received from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. Wideline measurements were made possible through the courtesy of E. Roach and W. Burckhardt of Michigan State University.

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