Field dependence of nuclear magnetic relaxation of ^{119}Sn in SnCl$_4$, SnBr$_4$, and SnI$_4$

Robert R. Sharp

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104
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Longitudinal and transverse relaxation times of ^{119}Sn have been measured as a function of temperature at several field strengths in SnCl$_4$, SnBr$_4$, and SnI$_4$. T_2 in all three liquids is field independent and is governed by scalar coupling to the halogen. T_1 is strongly field dependent in SnBr$_4$ and SnI$_4$ and exhibits a minimum with increasing temperature due to competing scalar and spin–rotation interactions. Coupling constants and correlation times previously computed for SnCl$_4$ and SnI$_4$ have been confirmed by measurements at 3.3 kg. Analysis of the data for SnBr$_4$ yield $J(^{119}$Sn$-^{81}$Br$)=920$ Hz, $T_2(^{81}$Br$)=0.748 \times 10^{-6}$ sec at 294°K, and $\tau_\theta^{(2)}=3.1 \times 10^{-12}$ sec at 294°K. Molecular reorientation in SnBr$_4$ is highly unusual in that the reduced angular correlation time $\tau_\theta{}^*$ reaches a minimum value owing to the onset of dynamically coherent reorientation at a temperature (80°C) that is not far above the melting point (30°C), and $\tau_\theta{}^*$ remains in the inertial rotation region over much of the liquid range. Various other indications of significant dissimilarity of microdynamical behavior in SnCl$_4$, SnBr$_4$, and SnI$_4$ are pointed out. Assuming the validity of the J-diffusion model, we complete the spin–rotation and magnetic shielding constants for SnBr$_4$, but these results are not consistent with the chemical shifts and shielding constants previously inferred for SnCl$_4$. The inconsistency is believed to be associated with the extremely small reduced frictional constant of SnBr$_4$ and with the possibly inappropriate use of extended diffusion theory to describe reorientation in this liquid.

I. INTRODUCTION

Two previous papers in this series have investigated magnetic relaxation of the central metal nucleus in three Group IV tetrahalides, SnCl$_4$, SnI$_4$,[1] and PbCl$_4$.[2] A novel feature of relaxation in the latter two liquids is the importance of scalar coupling as a dominant pathway for longitudinal as well as transverse relaxation. In previous studies a dominant scalar contribution to T_1 has been observed only when the coupled spins have closely similar Larmor frequencies, such as ^{13}C and ^{79}Br.[3]

Coupling constants between directly bonded heavy metal and halogen isotopes are generally quite large however, and give rise to an efficient T_1 process when the halogen relaxation time is sufficiently short. Theoretical expressions for the scalar contributions to T_1 and T_2 of a spin $\frac{1}{2}$ metal nucleus bonded to a quadrupolar halogen isotope can be written[4]

$$(T_1)^{-1}_{\text{sc}} = \frac{2}{3} A_i^2 S_i (S_i + 1)\{\tau_i/[1 + (\omega_M - \omega_i)^2 \tau_i^2]\} \qquad (1a)$$

and

$$(T_2)^{-1}_{\text{sc}} = \frac{1}{3} A_i^2 S_i (S_i + 1)\tau_i + \frac{1}{2}(T_1)^{-1}_{\text{sc}}, \qquad (1b)$$

where the halogen isotope has nuclear spin S_i, relaxation time τ_i, scalar coupling constant A_i, and angular Larmor frequency ω_i. The frequency factor in the denominator of Eq. (1a) is normally the order of 10^{14}–10^{16} sec^{-2}, so that appreciable scalar contributions to T_1 are found only when the halogen relaxation time is very short (usually less than 10^{-5} sec) and the coupling constant is large (the order of 1 kHz). When scalar contributions to both T_1 and T_2 of the metal can be identified, Eqs. (1a) and (1b) provide a useful indirect method for measuring coupling constants and relaxation times of resonances that are too broad to be observable directly by wide line NMR. In this way relaxation times have been measured for ^{127}I in SnI$_4$, ^{35}Cl in PbCl$_4$, ^{79}Br in PBr$_3$,[5] as well as ^{79,81}Br in HBr using measurements in the rotating frame.[6]

Because of the high molecular and nuclear site symmetry in MX$_4$ compounds, an analysis of the relaxation of a spin $\frac{1}{2}$ metal isotope provides, in addition to the halogen relaxation times and coupling constants, a relatively complete description of magnetic interactions and reorientational correlation times in the liquid phase. The angular correlation time $\tau_\theta^{(2)}$ for reorientation of a second rank molecular tensor is calculable directly from the halogen relaxation rates τ_i^{-1} which for all isotopes except ^{19}F are invariably dominated by the electric quadrupole interaction and are given by the expression[4]

$$\tau_1^{-1} = \tau_2^{-1} = \frac{3}{40}[(2I + 3)/I^2(2I - 1)](e^2 qQ/\hbar)^2[1 + (\eta^2/3)]\tau_\theta^{(2)}, \qquad (2)$$

where η is an asymmetry parameter that vanishes when the halogen lies on a threefold axis and $(e^2qQ/\hbar)$ is the quadrupole coupling constant. Covalently bonded ^{127}I and ^{79,81}Br isotopes are associated with large quadrupole coupling constants and short relaxation times and are likely to produce a substantial scalar component in the T_1 of a directly bonded metal nucleus. Detectable scalar contributions to T_1 are much less likely to result from coupling to the ^{35,37}Cl isotopes, which have smaller quadrupole moments than do the heavier halogens.

Aside from scalar coupling, the only other interaction that produces significant relaxation in SnCl$_4$, SnI$_4$, and PbCl$_4$ is spin–rotation. Chemical shift anisotropy vanishes in tetrahedral symmetry and is not a relaxation mechanism, while nuclear dipole–dipole coupling can be neglected because of typically large internuclear separations and small gyromagnetic ratios of heavy isotopes. The spin–rotation contribution depends on the angular momentum correlation time τ_J and is given, for a nucleus in cubic site symmetry, by the expression

$$(T_1)^{-1}_{\text{SR}} = (T_2)^{-1}_{\text{SR}} = 2IkT\hbar^{-2}C_0^2\tau_J, \qquad (3)$$

where C_0 is the (scalar) spin–rotation constant in radians per second. An independent determination of the

factors C_0 and τ_J provides particularly valuable information in tetrahedral MX$_4$ molecules. The spin–rotation constant and the paramagnetic part of the shielding constant are both scalar and are rigorously related by the fact that they both depend on the same second order sum over excited states[7]:

$$\sigma = \sigma_d' + \sigma_p'$$

$$\sigma_d' = \left(\frac{e^2}{3mc^2}\right)\left(\left\langle 0 \left| \sum_i r_i^{-1} \right| 0 \right\rangle - \sum_K' \frac{Z_k}{r_{ik}}\right) \qquad (4)$$

$$\sigma_p' = \frac{M_p}{m\hbar g_K} C_0 I,$$

where symbols in the expression for σ_d' are defined in Refs. 8 and 9. M_p and m are proton and electron masses, g_k is the nuclear g factor, and I is the moment of inertia. The diamagnetic part of the shielding constant, σ_d', is approximately constant in most molecular environments and can, according to Flygare and Goodisman[8] and Deverell,[9] approximately be set equal to the Lamb shielding of the free atom. Thus measurement of C_0 determines an independent point on the absolute shielding scale of the metal nucleus. Two previous points on the absolute shielding scale of ^{119}Sn have been inferred from relaxation data obtained at 11.74 kG for SnCl$_4$ and SnI$_4$. Further data at a lower field are reported here for these liquids in order to confirm the quantitative mechanistic assignments proposed earlier for T_1 and T_2. Relaxation times of ^{119}Sn in SnBr$_4$ are also reported at three field strengths and are used to compute a third point on the absolute shielding scale. Internal consistency of these points can be checked by comparing their differences with measured chemical shifts of the compounds. (In Ref. 1 positive, rather than negative, signs should be chosen for computed $|C_0|$ values. The choice of negative signs resulted from neglect of the negative sign of the g-value for ^{119}Sn when using Eq. (4).)

The separation of C_0 and τ_J using measured values of $(T_1)_{SR}^{-1}$ is not straightforward (unless external experimental information, such as a molecular beam determination of C_0, is available) but must be based on theoretical diffusion models that relate τ_J to the experimentally determined value of τ_θ. Although this dependence on highly simplified physical assumptions underlying the diffusion models lessens the reliability of the shielding scale, the temperature dependence of $(T_1)_{SR}^{-1}$ and $(T_{1,2})_{sc}^{-1}$ provide direct experimental information about the relationship of τ_θ and τ_J. SnCl$_4$, SnBr$_4$, and SnI$_4$ comprise a very interesting homologous series for a study of diffusive reorientation because of their high molecular symmetry, their large moments of inertia, and their nearly spherical intermolecular potential energy functions.

II. EXPERIMENTAL

Samples of SnCl$_4$ and SnI$_4$ were prepared from commercial material of the highest available purity and were degassed but not further purified. Tin tetrabromide (mp 30 ± 1 °C) was purchased commercially and was received in a glass ampoule under nitrogen atmosphere. Degassed samples were prepared in 7 and 10 mm tubes using the commercial product without further purifica-
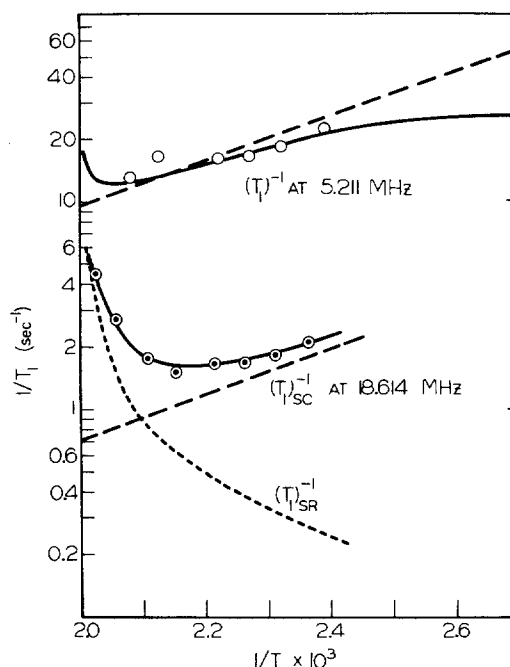

FIG. 1. $(T_1)^{-1}$ of ^{119}Sn in neat SnI$_4$ as a function of temperature at 11.75 and 3.29 kG.

tion. Two sample sizes were required for measurements above and below 16 MHz. Tin tetrabromide decomposes slowly in the presence of dissolved oxygen to form a yellow precipitate. For this reason the commercial sample was distilled under vacuum and used to prepare a second set of samples. Relaxation data from the two sets were consistent, and the second set showed no evidence of decomposition after several months of storage.

Relaxation measurements were made using an externally locked, variable frequency pulsed NMR spectrometer that has been described previously.[1,2,10] T_1 was obtained from a $180°-\tau-90°$-F.I.D. sequence by plotting the height of the F.I.D. against τ. 64 accumulations were obtained at each value of τ, and at least 10 τ values were used to define each exponential. T_2 was measured using the phase shifted Carr–Purcell sequence with pulse spacings of 600 μsec and 1 msec.

III. RESULTS

Nuclear relaxation rates of ^{119}Sn have been measured as a function of temperature at several field strengths in the neat liquids SnCl$_4$, SnBr$_4$, and SnI$_4$.

A. SnCl$_4$

Results for SnCl$_4$ at 18.644 MHz are reported in Ref. 1. A few values of T_1 and T_2 have more recently been measured at 5.22 MHz and these values agreed with those at the higher field strength. The fact that T_1 and T_2 are field independent confirms a previous conclusion that T_1 is dominated by spin–rotation and has no appreciable contribution from scalar coupling or chemical shift anisotropy.
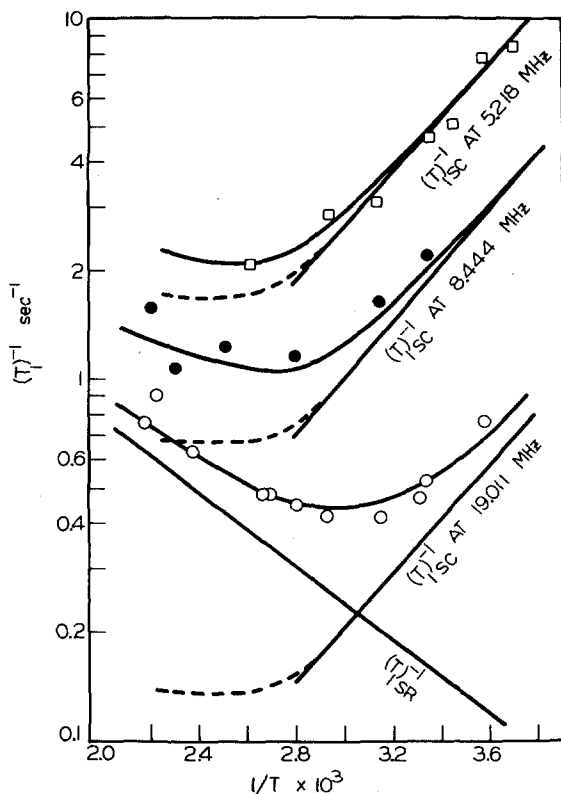
FIG. 2. $(T_1)^{-1}$ of ^{119}Sn in neat SnBr$_4$ as a function of temperature at 3.29 kG, 5.33 kG, and 12.0 kG.

B. SnI$_4$

T_1 for SnI$_4$ is strongly field dependent as is shown in Fig. 1. This behavior was anticipated from earlier data at 18.614 MHz, for which a scalar interaction was assigned as the dominant low temperature relaxation pathway. According to Eq. (1a), $(T_1)_{sc}^{-1}$ varies as the inverse square of field strength when $(\omega_M - \omega_i)^2 \tau^2 \gg 1$ and passes through a maximum when $(\omega_M - \omega_i)^2 \tau^2 = 1$. Due to the extremely short ^{127}I relaxation time, this maximum occurs just below the melting point at 5.211 MHz. The upper solid curve in Fig. 1 represents the sum of a spin–rotation contribution that was assigned from the high field data and a scalar contribution computed from Eq. (1a) using coupling constants and correlation times given in Ref. 1. The excellent agreement of computed and observed relaxation times supports the quantitative mechanistic assignments given in the figure as well as numerical values of coupling constants and correlation times reported in Ref. 1.

C. SnBr$_4$

The normal liquid range of SnBr$_4$ is 30.5–212 °C, but a very pure degassed sample is easily supercooled to –10 °C. Relaxation data were obtained for both the stable and supercooled liquid.

$(T_1)^{-1}$ is shown as a function of temperature at 3.29 kg, 5.33 kg, and 12.0 kg in Fig. 2. Relaxation at low temperature is inversely proportional to the square of the field strength, which clearly indicates that scalar coupling, modulated by ^{79,81}Br relaxation, is the domi-

nant T_1 mechanism. Spin–rotation becomes increasingly important at higher temperatures, and the data at 8.444 MHz and 19.011 MHz show distinct minima. Rather surprisingly, the scalar contribution to $(T_1)^{-1}$ also levels off at higher temperature. This behavior is confirmed by measurements of $(T_2)^{-1}$, which is entirely dominated by scalar relaxation and very clearly exhibits a maximum (or at least levels off) in the neighborhood of 370 °K (Fig. 2, lower curve). It appears at first sight that very rapid intermolecular halogen exchange provides a straightforward interpretation of the maximum. Chemical exchange modulates scalar coupling between ^{119}Sn and the two bromine isotopes and will contribute to the correlation time for scalar relaxation if the exchange rate τ_e^{-1} is comparable to the bromine relaxation rates, τ_x^{-1}. Since τ_x and τ_e have opposite temperature dependence, chemical exchange could produce a minimum in $(T_1)_{sc}^{-1}$ at sufficiently high temperature. Fairly rapid nonselective chemical exchange is known to occur in ternary solutions of SnCl$_4$, SnBr$_4$, and SnI$_4$, where individual NMR resonances[11] and Raman bands[12] can be observed for every possible species of pure and mixed tetrahalide. Exchange is rapid on the time scale of these measurements at room temperature, but is sufficiently slow that NMR resonances are fully resolved. From the latter observation an upper limit of about 10^2 sec^{-1} can be placed on the room temperature exchange rate. In order to influence the relaxation of ^{119}Sn, τ_e must be comparable to τ_x, which is 1.8×10^{-6} sec for ^{81}Br at 100 °C. This criterion requires that the reaction rate constant increase by a factor of at least 5.5×10^3 over a 75 °C temperature range, implying a minimum activation energy of 26 kcal/mole for chemical exchange. This activation energy is much too high for such rapid exchange and does not conform to the broad maximum observed in $(T_2)^{-1}$.

An alternate interpretation of the maximum involves the onset of dynamically coherent molecular reorientation. T_2 is unquestionably dominated by scalar coupling to ^{79,81}Br with a correlation time equal, at least in the absence of very rapid chemical exchange, to the halogen relaxation time. The only other mechanism that leads
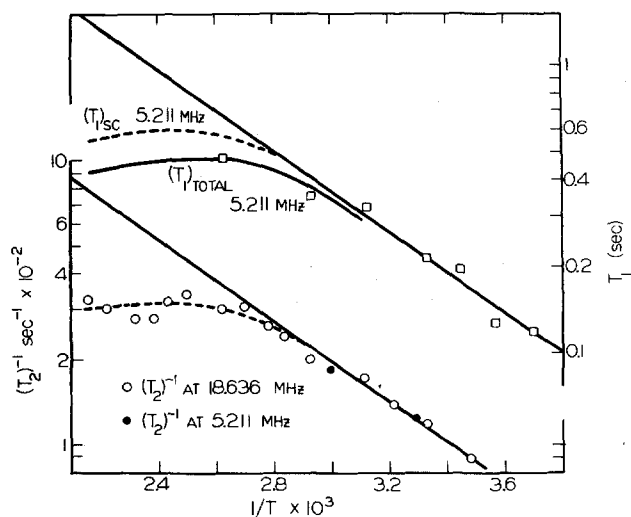

FIG. 3. Comparison of the temperature dependence of $(T_2)^{-1}$ and T_1 (5.211 MHz) in SnBr$_4$.
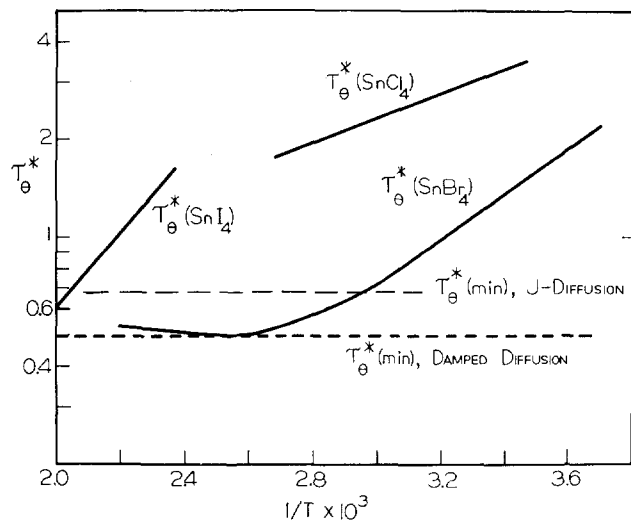
FIG. 4. Comparison of reduced angular correlation times $\tau_\theta{}^* = \tau_\theta (kT/I)^{1/2}$, in $SnBr_4$ and SnI_4. Damped diffusion refers to Steele's model based on the Langevin equation and to the classical limit of Atkin's model of interacting quantum mechanical rotors.

to values of $T_2 \ll T_1$ in diamagnetic systems is chemical exchange between chemically shifted sites, but this mechanism cannot produce significant relaxation since it varies as the square of the field strength in contrast to the observed field independence of T_2 (Fig. 3). If complications due to the presence of two bromine isotopes are for the moment neglected, Eqs. (1) and (2) state that $\tau_{sc} = \tau_x \sim \tau_\theta^{-1} \sim (T_2)^{-1}$, so that the temperature dependence of T_2 is the same as that of τ_θ. Therefore the leveling off of τ_{sc} at high temperatures may reflect identical behavior in τ_θ due to a qualitative change in molecular dynamics.

The angular correlation time τ_θ is expected physically to pass through a minimum when the temperature is sufficiently high that the angular momentum vector retains significant correlation over intervals required for a complete molecular rotation. τ_θ increases with temperature in the region of dynamically coherent reorientation and approaches asymptotically the dilute gas limit $\tau_\theta^{*(2)} \to \tau_J^*/4$.[13] τ_θ^* exhibits the opposite temperature dependence when $\tau_J^* < 1$ and at sufficiently low temperature approaches the limit of classical small step diffusion. Verification that the observed T_2 minimum indeed results from the onset of coherent reorientation is obtained by comparing experimental and theoretical values of τ_θ^* at the minimum. Theoretical values depend on the specific diffusional model considered, and the following values have previously been derived for spherical top molecules: $(\tau_\theta^*)_{min} = 0.51$ for both the Langevin model[14] and the classical limit of Atkins[15] model, which assumes a collection of weakly interacting quantum mechanical rotors; $(\tau_\theta^*)_{min} \cong 0.66$ for the J diffusion hypothesis[16]; $(\tau_\theta^*)_{min} \cong 0.83$ for the M diffusion hypothesis.[16] Experimental values of τ_θ^* have been computed from Eq. (2) using halogen relaxation times obtained below and are plotted in Fig. 4. Extremely good agreement between experiment and theory is found for the Langevin and quantum mechanical models. This coincidence must be considered fortuitous to some extent in view of uncer-

tainties in the relaxation data and in liquid phase quadrupole coupling constant. The J-diffusion limit is about 30% too high and probably exceeds experimental error, while the M-diffusion limit is about 60% too high and definitely exceeds experimental error. The general success of the first three diffusion models in predicting the minimum in τ_θ^* appears to demonstrate unambiguously that reorientation is dynamically coherent in the neighborhood of 100 °C.

The data in Fig. 2 have been separated mechanistically into spin–rotation and scalar contributions using the observed field and temperature dependence T_1. The scalar portion in general consists of a sum of five exponentials due to five isotopically different species of the general formula $Sn^{79}Br_{4-n}{}^{81}Br_4$ $(n = 1, \cdots, 4)$. If chemical exchange between these species is rapid compared to the relaxation time of ^{119}Sn, the decay collapses to a single exponential for which the decay constant is that of a hypothetical molecule of composition $Sn^{79}Br_{2.02}{}^{81}Br_{1.98}$. Nonexponentiality was not detected in our measurements, even at temperatures for which the chemical exchange rate is small compared to $(T_2)^{-1}$ for ^{119}Sn. Relaxation expressions corresponding to the average isotopic composition are therefore used:

$$(T_2)^{-1} = 4.025 A_{81}^2 \tau_{81} + \tfrac{1}{2}(T_1)_{sc}^{-1}, \tag{5}$$

$$(T_1)_{sc}^{-1} = 10 A_{81}^2 \tau_{81} \left[\frac{X_{81}}{1 + \Delta_{81}} + \frac{X_{79}(Q_{81}/Q_{79})^2 (\gamma_{79}/\gamma_{81})^2}{1 + \Delta_{81} f(Q_{81}/Q_{79})^2} \right]$$

$$= A_{81}^2 \tau_{81} \left(\frac{6.46 \Delta_{81} + 8.1}{6.98 \Delta_{81}^2 + 16.98 \Delta_{81} + 10} \right) \tag{6a}$$

$$\cong 9.27 A_{81}^2 \tau_{81} / \Delta_{81}, \quad \text{when } \Delta_{81} \gg 1, \tag{6b}$$

where

$$\Delta_{81} = (\omega_{119} - \omega_{81})^2 \tau_{81}^2, \quad f = [(\omega_{119} - \omega_{79})/\omega_{119} - \omega_{81})]^2,$$

$(Q_{81}/Q_{79})^2 = 0.700$,[17] and X_i is the natural abundance of the indicated isotope. Halogen relaxation times obtained below show that $\Delta_{81} > 100$ at all temperatures and field strengths investigated, so that Eq. (6b) may be used accurately in place of the more exact Eq. (6a). These equations, in conjunction with the observed temperature dependence of T_2 and a specified absolute value of $(T_1)_{sc}^{-1}$ measured at some low temperature in the scalar dominated region, completely define the behavior of $(T_1)_{sc}^{-1}$ as a function of temperature and field strength. The curves of $(T_1)_{sc}^{-1}$ shown in Fig. 2 are computed from the (graphically averaged) measured value of $(T_1)_{sc}^{-1} = 8.2$ sec^{-1} at 5.218 MHz and 273 °K. It is interesting to note that T_1 at 5.218 MHz is strongly dominated by scalar coupling and should have the same temperature dependence as $(T_2)^{-1}$, since both T_1 and $(T_2)^{-1}$ are proportional to the correlation time for the scalar interaction. This comparison is made in Fig. 3, and as expected both T_1 and $(T_2)^{-1}$ have the same functional dependence upon temperature in the scalar dominated region. Using observed values of $(T_2)^{-1}$ and $(T_1)_{sc}^{-1}$ in Eqs. (5) and (6), we compute the scalar coupling constant $J(^{119}Sn - {}^{81}Br) = 920$ Hz and the ^{81}Br relaxation time $\tau_{81} = 0.748 \times 10^{-6}$ sec at 294 °K. Angular correlation times for $SnBr_4$ have also been computed from Eq. (2), using the NQR value 330 MHz[18] for the quadrupole coupling constant. Reduced correlation times $\tau_\theta^* = (kT/I)^{1/2} \tau_\theta$ are compared with val-

TABLE I. Comparison of computed shield-
ing constants and observed chemical shifts
in tin tetrahalides.

σ_p' (SnCl$_4$) = -2.76×10^{-3}
σ_p' (SnBr$_4$) = -1.00×10^{-3}
σ_p' (SnI$_4$) = -1.48×10^{-3}
| σ(SnI$_4$) $-\sigma$(SnCl$_4$) | = 1551 ppm observed[a]
1280 ppm computed
| σ(SnBr$_4$) $-\sigma$(SnCl$_4$) | = 488 ppm observed[a]
1760 ppm computed

[a]Reference 11.

ues for SnCl$_4$ and SnBr$_4$ in Fig. 4.

The spin–rotation part of $(T_1)^{-1}$ is field independent and is represented in Fig. 2 by a curve that gives the best fit to data obtained at 19.011 MHz. $(T_1)^{-1}_{SR}$ unexpectedly exhibits Arrhenius temperature behavior with an activation energy of 2.39 kcal/mole in the dynamically coherent region. These values of $(T_1)^{-1}_{SR}$ have been used in Eq. (3) to estimate the spin–rotation constant for SnBr$_4$. The angular momentum correlation time was estimated from experimental values of τ_θ^* at 294 °K by means of the Langevin diffusional model and Gordon's J-diffusion hypothesis, using curves given in Refs. 13 and 14. Results of the two theories are essentially identical when $\tau_\theta^* > 1.1$ and $\tau_J^* < 0.15$.[1] This approach gives the following values for C_0, σ_p', and τ_J^*:

$$C_0 = 870 \text{ Hz} ,$$

$$\sigma_p' = -1.00 \times 10^{-3} ,$$

$$\tau_J^* = 0.134 \text{ at } 294 \text{ °K} .$$

The same procedure was followed previously in analyzing data for SnCl$_4$ and SnI$_4$ and provides the basis for the absolute shielding scale of tin proposed in Ref. 1. This shielding scale can be tested for internal consistency by comparing chemical shifts of SnCl$_4$, SnBr$_4$, and SnI$_4$ with differences in computed shielding constants for these compounds. Although shielding constants for SnCl$_4$ and SnI$_4$ give satisfactory agreement with chemical shift data, the shielding constant of SnBr$_4$ is not internally consistent with shielding constants of the former two compounds (Table I). The discrepancy in the case of SnBr$_4$ is obviously major and implies qualitative failure in one or more of the assumptions used to calculate the spin-rotation constant.

A portion of this failure may result from the fact that computed values of C_0 and σ_p' rely on the accuracy of $(T_1)^{-1}_{SR}$ in the low temperature region, while $(T_1)^{-1}_{SR}$ is only a minor contribution to the total relaxation rate at these temperatures and is not well defined by the data. Other sources of uncertainty in C_0 and σ_p' are discussed below. The scalar contributions, which are used to compute τ_θ, A(Sn–Br), and τ_{81}, are strongly overdetermined by the data and thus are well defined at all temperatures and field strengths. The curves of Fig. 2 that give the scalar contribution to T_1 are in no way fitted to the functional form of the T_1 data, but are completely determined as a function of field strength and temperature by the

measurements of $(T_2)^{-1}$, and a single measured value of $(T_1)^{-1}$ in the scalar dominated region (viz., $(T_1)^{-1}$ at 5.218 MHz, 0 °C). $(T_2)^{-1}$ is field independent and is between 1 and 3 orders of magnitude larger than $(T_1)^{-1}$ at all temperatures and field strengths; thus T_2 is certainly dominated by scalar interactions. Since a knowledge of the functional form of $(T_1)^{-1}_{sc}$ relies on only one T_1 value, the spin–rotation portion of T_1 is overdetermined, in the high temperature region, by the remainder of the T_1 data.

The error in $(T_1)^{-1}_{sc}$ is estimated to be $\pm 10\%$ at all temperatures and field strengths. $(T_1)^{-1}_{SR}$ is reasonably well defined by the data only at temperatures above about 90 °C, and the estimated uncertainty in this region is $\pm 15\%$. Values of the Sn–Br scalar coupling constant, the ^{79,81}Br relaxation times, and the molecular correlation time can be computed from the T_2 data and a single value of $(T_1)^{-1}_{sc}$ using Eqs. (2), (5), and (6). J(Sn–Br) is computed directly from $[(T_1)^{-1}_{sc}/(T_2)^{-1}_{sc}]^{1/2}$, and $\pm 10\%$ is probably a conservative estimate of uncertainty for this quantity. τ_{81} and τ_θ are given by the first power of $(T_1)^{-1}_{sc}/(T_2)^{-1}_{sc}$ and contain an estimated uncertainty of $\pm 20\%$.

IV. DISCUSSION

A comparison of the behavior of relaxation times and correlation times for ^{119}SnCl$_4$, ^{119}SnBr$_4$, and ^{119}SnI$_4$ reveals several unexpected features. These are summarized briefly below:

(1) Molecular reorientation can be described as dynamically coherent in SnBr$_4$ and SnI$_4$ over most of the liquid range and is significantly outside the limit of small-step diffusion even at the melting point. The onset of coherent reorientation has previously been inferred at relatively high reduced temperatures for less massive molecules, but the author is aware of no other liquid in which $\tau_\theta^* \cong 1$ at the melting point. This behavior is evidently associated with the large moments of inertia and nearly spherical potential energy functions of SnBr$_4$ and SnI$_4$.

(2) At a given temperature τ_θ^* is substantially shorter, by a factor of about three, in SnBr$_4$ than in SnCl$_4$ or SnI$_4$. This difference in molecular dynamics is emphasized by the fact that τ_θ^* is in the region of dynamically coherent reorientation at temperatures characterized by Arrhenius behavior in both SnCl$_4$ and SnI$_4$.

(3) The reduced angular momentum correlation time τ_J^* exhibits qualitatively different temperature dependence in SnBr$_4$ and SnI$_4$ as the dynamically coherent region $(\tau_J^* \gtrsim 1)$ is approached. The spin–rotation part of $(T_1)^{-1}$ rises very steeply with temperature in SnI$_4$, and the data, if approximated by Arrhenius temperature behavior in the region $\tau_J^* \sim 1$, require an activation energy of about 80 kcal/mole. This behavior is in very sharp contrast to the very gradual increase in τ_J ($E_A^J \cong 2.39$ kcal/mole) observed for SnBr$_4$. In the latter liquid no qualitative alteration in the temperature dependence of τ_J is discernible at the minimum in τ_θ.

(4) Computed shielding constants of ^{119}Sn in SnCl$_4$, SnBr$_4$, and SnI$_4$ do not comprise a shielding scale that is consistent with the observed chemical shifts of these compounds. This result is surprising in view of the fact

that the tin tetrahalides are spherical top molecules for which reorientation is described by a pair of scalar correlation times. Anisotropies that might lend ambiguity to the analysis are not present. It is worth noting that shielding constants of SnCl$_4$ and SnI$_4$ are consistent with the chemical shift between these compounds, which suggests that the analysis may be correct in these liquids but inapplicable to SnBr$_4$.

Failure of the calculated spin–rotation constants to predict a consistent shielding scale can be traced at least partially to experimental uncertainty in high temperature values of $(T_1)_{SR}^{-1}$, and also to large theoretical uncertainty in the $\tau_\theta^* - \tau_J^*$ relation that is present when τ_θ^* passes through its minimum. The Langevin model of Steele deviates from results of extended diffusion theory in this region, and both models predict that large variations occur in τ_J^* while τ_θ^* remains essentially stationary. Thus it is difficult to relate the two correlation times accurately in SnBr$_4$ and SnI$_4$, since reorientation is definitely outside the small-step diffusion region at all temperatures for which spin–rotation is the major T_1 mechanism. Fortunately, the shielding constant σ_p' $= -2760$ ppm derived for SnCl$_4$ is not subject to similar uncertainty since reorientation is well described by the small step diffusive limit, and spin–rotation is the only significant T_1 mechanism over the entire liquid range. However, the ratio $(T_1)_{SR}^{-1}/\tau_J^*$ is not well defined from either an experimental or a theoretical standpoint for SnBr$_4$, and the computed shielding constant is much less reliable than that for SnCl$_4$. Certain other assumptions are implicit in the computation of σ_p', and three of these are examined below.

In the liquid phase $(T_1)_{SR}^{-1}$ arises from both intermolecular and intramolecular interactions although only the latter is normally taken into account. Intermolecular spin–rotation coupling can be approximated as a dipole–dipole interaction,

$$(T_1)_{SR,inter}^{-1} = (\mu^N \cdot \mu^R/r^3) - 3[(\mu^N \cdot r)(\mu^R \cdot r)/r^5] ,$$

where μ^N and μ^R are nuclear and rotational magnetic moments and r is the dipole–dipole separation. Both spin–rotation contributions exhibit the same temperature and field dependence and could cause an error in the use of Eq. (3), which describes only the intramolecular contribution. An expression for the intermolecular spin–rotation relaxation rate $(T_1)_{SR,inter}^{-1}$ is derived using the Kubo–Tomita formalism in the Appendix, and is applied specifically to the tin tetrahalides and lead tetrachloride. Rotational magnetic moments for these molecules have not been measured directly but can, in spherical top symmetry, be computed from the bulk diamagnetic susceptibility. It is shown that $(T_1)_{SR,inter}^{-1}$ is of comparable magnitude to the intermolecular dipole–dipole interaction and does not contribute significantly to the observed relaxation rate.

A second approximation that underlies the comparison of computed shielding constants is the assumed constancy of the diamagnetic term σ_d' in different molecular environments. Flygare and Goodisman[8] have discussed this question in some detail and have concluded that the approximation is valid whenever the total electronic energy is large compared to the molecular binding energy. This condition is amply met in the tin tetrahalides, and therefore the identification of σ_d' with the Lamb term for the free atom σ_d^a appears to be a reasonable approximation.

A much more questionable assumption is that the correlation times for molecular reorientation and angular momentum are adequately described by highly simplified diffusion theories of rigid molecules. Reorientation in SnBr$_4$ and SnI$_4$ is highly unusual in that inertial effects dominate frictional effects over the larger part of the liquid range. This behavior is not simply a result of the large moments of inertia, since SnBr$_4$ reorients much more freely than either SnCl$_4$ or SnI$_4$ at given temperature, but depends also on cohesive forces and on the deviation from sphericity of the molecular potential energy function. Tin tetraiodide has the largest moment of inertia and a potential energy function that must be nearly spherical owing to the large radii and high polarizabilities of the iodine atoms. Tin tetrabromide is probably not quite so spherical but reorients more freely probably because of weaker van der Waals' forces, relatively large intermolecular separation, and consequently a smaller activation volume. Tin tetrachloride has a harder, much less spherical potential energy function and is associated with a larger reduced frictional constant (by Steele's[14] definition) than is SnBr$_4$. The relatively small frictional constant of SnBr$_4$ may also be associated with the high degree of supercooling ($\sim$ 40 °C) achievable in a pure degassed sample of this liquid.

These apparent peculiarities in the microdynamical behavior of liquid SnBr$_4$ suggest that great care should be used in attempting to describe its molecular reorientation in terms of a simplified physical model. Tin tetrachloride, on the other hand, remains in the limit of small-step diffusion throughout its liquid range, and there is no obvious reason to doubt the applicability of classical diffusion theory for this liquid. Experimental values of τ_θ in SnCl$_4$ have been determined directly from observations of the ^{35}Cl resonance, and the values inferred for τ_J are similar in magnitude to those found in other simple liquids[19] for which the relaxation data agree very well with extended diffusion theory. Thus the shielding scale proposed previously is believed to be essentially correct, but further tests of its validity, perhaps using tetraalkyl tin compounds, would obviously be desirable.

ACKNOWLEDGMENTS

APPENDIX: RELAXATION DUE TO INTERMOLECULAR SPIN-ROTATION INTERACTIONS

Molecular rotation gives rise to a magnetic field which, at large distances from the molecular center of mass, can be approximated by a point dipole with magnetic moment

TABLE AI. Diamagnetic susceptibilities, rotational magnetic moments, and intermolecular spin–rotation relaxation rates of lead and tin tetrahalides.

	$\bar{\chi}_{MX_4}$ (10^{-6} cgs)	$\bar{\chi}_M$ [d] (10^{-6} cgs)	$\bar{G}_{MX_4}/\mu_N$	$\bar{g}_R$ (sec$^{-1} \cdot$ g^{-1})	I (10^{40} cgs)	r_{M-M} (10^{-8} cm)	$(T_{1 SR, inter}^{-1})$ [k] (10^{-6} sec^{-1})
SnCl$_4$	−115.3 [a]	−48.8	0.0288	138	858 [e]	6.16 [i]	0.50
SnBr$_4$	−149.0 [a]	−48.8	0.0172	83	2140 [f]	6.55 [i]	0.30
SnI$_4$	−193 [b]	−48.8	0.0124	60	4270 [g]	7.05 [g]	0.20
PbCl$_4$	−115 [c]	−56.6	0.0231	111	928 [h]	6.30 [j]	0.10

[a] Reference 24.
[b] Computed from atomic additivity constants given in Ref. 24, assuming 10% deviation from the additive value.
[c] Computed from additivity constants given in Ref. 25.
[d] Reference 26.
[e] Reference 27.
[f] Reference 28.
[g] Reference 29.
[h] Reference 30.
[i] Reference 31.
[j] Assumed value.
[k] Computed assuming 10 nearest neighbors with $\tau_J = 10^{-12}$ sec, $T = 300\,°$K.

$$\mu_R = g_R \cdot \mathbf{J} \, , \qquad (A1)$$

where $\mathbf{J}$ is the rotational angular momentum. Spherical top symmetry will be assumed at the outset so that g_R is scalar. Coupling between the rotational and nuclear spin magnetic moments is described by an interaction Hamiltonian of the form

$$H_{SR, inter} = \gamma g_R \hbar \sum_{\substack{i \\ j \neq i}} \sum_{m=-2}^{2} S_{ij}^{(m)} F_{ij}^{(m)} \, , \qquad (A2)$$

where $S^{(m)}$ comprise a set of spherical tensor components of the coupled angular momenta and are defined by the relations

$$S_{ij}^{(0)} = -I_i J_j^z + \tfrac{1}{4}(I_i^+ J_j^- + I_i^- J_j^+) \, ,$$

$$S_{ij}^{(\pm 1)} = \tfrac{3}{2}(I_i^\pm J_j^z + I_i^z J_j^\pm) \, ,$$

$$S_{ij}^{(\pm 2)} = \tfrac{3}{4}(I_i^\pm J_j^\pm) \, .$$

$F^{(m)}$ are the usual lattice functions for coupled dipoles,

$$F_{ij}^{(0)} = (\tfrac{16}{5}\pi)^{1/2} \, r_{ij}^{-3} Y_{2,0}(\theta_{ij}, \psi_{ij}) \, ,$$

$$F_{ij}^{(\pm 1)} = (\tfrac{8}{15}\pi)^{1/2} \, r_{ij}^{-3} Y_{2,\pm 1}(\theta_{ij}, \psi_{ij}) \, ,$$

$$F_{ij}^{(\pm 2)} = (\tfrac{32}{15}\pi)^{1/2} \, r_{ij}^{-3} Y_{2,\pm 2}(\theta_{ij}, \psi_{ij}) \, ,$$

where r_{ij}, θ_{ij}, and ψ_{ij} specify the vector connecting μ_j^i and μ_k^i. Components of $\mathbf{J}_{ij}$ and $\mathbf{r}_{ij}$ are random functions of time which commute with the spin variables.

Unlike the intramolecular spin–rotation interaction, which is modulated in time solely by collisional processes that transfer angular momentum, intermolecular spin–rotation is modulated both by collisions that randomize $\mathbf{J}$ and by translational self-diffusion, which alters the variables r_{ij}, θ_{ij}, and ψ_{ij}. The loss of correlation in $\mathbf{r}$ occurs over intervals that are comparable in duration to the translational step time $\tau_t = \langle r_t^2 \rangle / 6D$, where r_t is the step length and D is the self-diffusion coefficient.[20] τ_t is typically the order of 10^{-11} sec for small liquid phase molecules and is longer in more viscous liquids. Correlation times for $\mathbf{J}$ fall in the range 10^{-12}–10^{-14} sec and are virtually always short compared to τ_t. Consequently the lattice functions $F^{(m)}$ are, to a good approximation, stationary over intervals τ_J and the commutators of $S_{ij}^{(m)}$ and $F_{ij}^{(m)}$ are negligible.

In order to compute the longitudinal relaxation time resulting from the interaction (A2), we use the Kubo–Tomita relaxation formula in the form[21]:

$$(T_1)^{-1} = \frac{\int_0^\infty d\tau \, \mathrm{Tr}\{\rho[H'(0), [H'(\tau), M_z]]M_z\}}{\hbar^2 \, \mathrm{Tr}\{\rho M_z^2\}} \, . \qquad (A3)$$

The spin trace in the denominator is readily evaluated in the high temperature limit ($\hbar \omega_0 / kT \ll 1$), and gives

$$\mathrm{Tr}\{\rho_s M_z^2\} = \tfrac{1}{4}(\gamma \hbar)^2 N$$

for an ensemble of N spin $\tfrac{1}{2}$ nuclei. Substituting $H_{SR, inter}$ into (A3) we obtain

$$(T_1)_{SR, inter}^{-1} = \frac{4(\gamma g_R)^2}{N} \int_0^\infty d\tau \left(\sum_{i, i'} \sum_{\substack{j \neq i \\ j' \neq i'}} \sum_{k, k'} \sum_{m, m'=-2}^{2} \langle [S_{ij}^{(m)}(0) F_{ij}^{(m)}(0), [S_{i'j'}^{(m')}(\tau) F_{i'j'}^{(m')}(\tau), I_k^z]] I_{k'}^z \rangle_0 \right) . \qquad (A4)$$

An examination of the spin commutators and the traces over the spin operators shows that nonvanishing terms in the high temperature limit are those for which $i = i' = k = k'$, and $m' = -m$. Furthermore the ensemble averages over the lattice functions also vanish unless $j = j'$. Thus the integral in (A4) depends only on two particle correlations and reduces to

$$N \int_0^\infty d\tau \sum_{j \neq 1} \sum_{m=-2}^{2} \langle [S_{1j}^{(m)}(0) F_{1j}^{(m)}(0), [S_{1j}^{(-m)}(\tau) F_{1j}^{(-m)}(\tau), I_1^z]] I_1^z \rangle_0 \, .$$

Writing the time dependence of the spin term in $S_{ij}^{(m)}(\tau)$ explicitly in the interaction representation

$$I^{(m)}(\tau) = e^{i\omega_0 I_z \tau} I^{(m)}(0) e^{-i\omega_0 I_z \tau} \, ,$$

the commutators are readily evaluated, and the traces over spin variables are computed using the approximate density matrix

$$\rho^0 = \rho_L^0 [1/(2I+1)^N] .$$

Equation (A4) then becomes

$$(T_1)^{-1}_{SR, inter} = 4(\gamma g_R)^2 \int_0^\infty e^{i\omega_0 \tau} d\tau \sum_j \left[\tfrac{1}{32} \langle J_j^*(0) F_{1j}^{(0)}(0) J_j^-(\tau) F_{1j}^{(0)}(\tau) + J_j^-(\tau) F_{1j}^{(0)}(\tau) J_j^*(0) F_{1j}^{(0)}(0) \rangle_0 \right.$$

$$+ \tfrac{9}{8} \langle J_j^z(0) F_{1j}^{-1}(0) J_j^z(\tau) F_{1j}^{(+1)}(\tau) + J_j^z(\tau) F_{1j}^{(+1)}(\tau) J_j^z(0) F_{1j}^{(-1)}(0) \rangle_0 + \tfrac{9}{32} \langle J_j^*(0) F_{1j}^{(+2)}(0) J_j^- \rangle$$

$$\left. \times (\tau) F_{1j}^{(-2)}(\tau) + J_j^-(\tau) F_{1j}^{(-2)}(\tau) J_j^*(0) F_{1j}^{(+2)}(0) \rangle_0 \right] . \tag{A5}$$

Because the correlation times for $J_j^{(m)}$ and $F_{1j}^{(m')}$ differ substantially in absolute magnitude, we assume that these variables are uncorrelated in time and that they commute. Therefore the equilibrium ensemble averages

$$\langle J_j^{(m)}(0) J_j^{(-m)}(\tau) \rangle_0 \text{ and } \langle F_{1j}^{(m')}(0) F_{1j}^{(-m')}(\tau) \rangle_0$$

can be taken separately, and the latter quantity can be set equal to

$$\langle F_{1j}^{(m')}(0) F_{1j}^{(-m')}(0) \rangle_0$$

in the integrand of (A5). Using the fact that the molecular motion is isotropic we have

$$(T_1)^{-1}_{SR, inter} = 4\gamma^2 g_R^2 \int_0^\infty d\tau \, e^{i\omega_0 \tau} \sum_j \langle \mathbf{J}_j(0) \cdot \mathbf{J}_j(\tau) \rangle_0$$

$$\times [\tfrac{1}{24} \langle F_{1j}^{(0)}(0) F_{1j}^{(0)}(0) \rangle_0 + \langle F_{1j}^{(-1)}(0) F_{1j}^{(+1)}(0) \rangle_0$$

$$+ \tfrac{3}{8} \langle F_{1j}^{(+2)}(0) F_{1j}^{(-2)}(0) \rangle_0] .$$

The integral over the correlation function $\langle \mathbf{J}(0) \cdot \mathbf{J}(\tau) \rangle_0$ is conveniently written in terms of the definition of τ_J,

$$\tau_J = \frac{\int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(\tau) \rangle_0 d\tau}{\langle \mathbf{J}(0) \cdot \mathbf{J}(0) \rangle_0} ,$$

where $\langle \mathbf{J}(0) \cdot \mathbf{J}(0) \rangle_0 = 3IkT$ in the classical limit. After averaging over the lattice functions, the final expression for the intermolecular spin-rotation relaxation rate of a spin $\tfrac{1}{2}$ nucleus reduces to

$$(T_1)^{-1}_{SR, inter} = 4(\gamma g_R)^2 IkT \tau_J \sum_j \langle r_{ij}^{-6} \rangle . \tag{A6}$$

In order to use Eq. (A6) an estimate of the rotational magnetic moment or the interaction constant in Eq. (A1) is required. Although g_R has not been determined experimentally for any of the molecules under discussion here, it can, in spherical top symmetry, be related to the liquid phase bulk diamagnetic susceptibility. The theoretical basis of this relation has been discussed by Van Vleck[22] and Davies.[23]

The diamagnetic susceptibility of a molecule with spherical top symmetry is given by perturbation theory as a sum of two terms,

$$\overline{\chi} = \overline{\chi}^L + \overline{\chi}^{HF} ,$$

where

$$\overline{\chi}^L = - \frac{Ne^2}{4mc^2} \sum_{i,j} \langle 0 \mid x_{ij}^2 + y_{ij}^2 \mid 0 \rangle ,$$

and

$$\overline{\chi}^{HF} = \frac{Ne^2 \hbar^2}{2m^2c^2} \sum_{k \neq 0} \frac{\langle 0 \mid \hat{L}_\alpha \mid k \rangle \langle k \mid \hat{L}_\alpha \mid 0 \rangle}{W_k - W_0} .$$

x_{ij} and y_{ij} are Cartesian coordinates of the projection of the radius vector of electron i in an orbital about nucleus j onto a plane perpendicular to the external magnetic field. The center of mass is taken as the origin of coordinates. The expression for $\overline{\chi}^{HF}$ contains a sum over matrix elements of the orbital angular momentum operator between the ground and excited electronic states. Physical constants have their usual meaning. The perturbation expression for the rotational constant likewise results in a sum of terms

$$\overline{G} = \overline{G}^L + \overline{G}^{HF} ,$$

where

$$\overline{G}^L = \frac{\hbar}{2cI} \sum_j Z_j (X_j^2 + Y_j^2)$$

and

$$\overline{G}^{HF} = \frac{2m\hbar}{NeI} \overline{\chi}^{HF} .$$

The high frequency terms of $\overline{G}$ and $\overline{\chi}$ are directly proportional since they both depend on the same sum over matrix elements of the orbital angular momentum operator. $\overline{G}^L$ depends on the projections X_j and Y_j of the radius vector of nucleus j with atomic number Z_j onto a perpendicular plane, and is not rigorously related to $\overline{\chi}^L$. An approximate relation can be based on the "atom in a molecule" assumption suggested previously by Flygare and Goodisman[8] and Deverell[9] with respect to the shielding constant. This approximation gives

$$\sum_{i,j} \langle 0 \mid X_{ij}^2 + Y_{ij}^2 \mid 0 \rangle$$

$$\cong \sum_j Z_j \langle 0 \mid X_j^2 + Y_j^2 \mid 0 \rangle + \frac{2}{3} \sum_i \langle r_i^2 \rangle_{central\ atom} ,$$

where the second term on the right hand side is equal, within a constant factor, to the theoretically calculable diamagnetic susceptibility, $\overline{\chi}_M$ of the central atom. Combining these equations we obtain

$$\frac{-4mc}{Ne} (\overline{\chi}_{MX_4} - \overline{\chi}_M) = \left(\frac{2I}{\hbar} \right) \overline{G}_{MX_4} ,$$

or

$$-(\overline{\chi}_{MX_4} - \overline{\chi}_M) = 2.54(10^{34}) \left(\frac{\overline{G}_{MX_4}}{\mu_N} \right) I .$$

Table AI contains a compilation of diamagnetic suscepti-

bilities, moments of inertia, and computed rotational magnetic moments for several tin and lead tetrahalides. The rotational magnetic moments fall in the range 0.01– 0.03 nuclear magnetons and compare well with experimental values for fairly massive molecules.[23] The table also contains moments of inertia and average nearest neighbor metal–metal distances in the solid. $(T_1)^{-1}_{\text{SR,inter}}$ has been computed from Eq. (A6), assuming (1) 10 nearest neighbors in the first coordination sphere, (2) $\tau_J = 10^{-12}$ sec, and (3) $T = 300\ ^\circ$K. Computed values of $(T_1)^{-1}_{\text{SR,inter}}$ are listed in the table and are obviously too small to contribute appreciably to the observed relaxation rate.

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