

electronic state because of the relatively large number of other states of He_2 lying within kT of the $3p\ ^3\Pi_g$.

It is interesting to note that the collection of statistically significant data is limited at both high and low pumping intensities. In the former case, the use of an excessively intense correlated source appears to cause progressively shorter lifetimes of the enhanced population as the intensity is increased beyond some threshold value. Conversely, the use of a source of insufficient intensity does not produce statistically significant fluorescent signals in a reasonable number of laser pulses. The relatively short operational lifetime of the flashlamp pumped dye laser systems places a limit of about 1000 pulses on the duration of an experimental measurement. It appears that as nitrogen pumped dye

laser systems⁶ are beginning to achieve radiancies comparable to those quoted here for the flashlamp system, those devices may eventually offer considerable improvement to such fast reaction studies since their mean time to instability is substantially greater.

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Rotational Diffusion and Magnetic Relaxation of ^{119}Sn in Liquid SnCl_4 and SnI_4

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Longitudinal and transverse relaxation times of ^{119}Sn have been measured as a function of temperature in liquid SnCl_4 and SnI_4 . For SnCl_4 , T_1 is a monotonically decreasing function of temperature and is dominated mechanistically by spin-rotation over the entire liquid range. In SnI_4 , T_1 passes through a maximum near 190°C. Spin-rotation and scalar coupling to ^{127}I , respectively govern the relaxation above and below this temperature. $T_2 \ll T_1$ in both liquids; scalar coupling, modulated by relaxation of the halogen isotopes, dominates the transverse relaxation. Dipolar coupling does not contribute appreciably to relaxation in either compound. Knowledge of the scalar contributions to T_1 and T_2 in SnI_4 permit calculation of the ^{127}I relaxation time [$\tau_{127} = 1.5(10^{-7})$ sec at 150°C] and the angular correlation time [$\tau_\theta = 3.67(10^{-12})$ sec at 150°C]. These values, and the published τ_{35} for SnCl_4 , give the tin-halogen scalar coupling constants: $J(^{119}\text{Sn}-^{35}\text{Cl}) = 470$ Hz and $J(^{119}\text{Sn}-^{127}\text{I}) = 940$ Hz. Spin-rotation constants are obtained using Steele's rotational diffusion theory and are used to calculate an absolute shielding scale for ^{119}Sn . From the shielding constants and the relative resonance frequencies of ^{119}Sn and ^1H , the ^{119}Sn magnetic moment is calculated to be $(-1.04347 \pm 0.00036\mu_N)$. Rotational correlation times in SnCl_4 and SnI_4 have been compared with theoretical predictions of the J diffusion and damped diffusion models. SnCl_4 shows significant deviations from Hubbard's relation although the motion is diffusive according to both theories. Inertial effects are important for reorientation in SnI_4 ($\tau_J^* \sim 2$ at 220°C), and damped diffusion appears to describe reorientation more accurately at these temperatures than does J diffusion. The relative roles of spin-rotation, scalar coupling, and dipolar coupling as relaxation pathways in other tin-containing systems are considered. It is concluded that the first two interactions usually dominate dipolar coupling for tin and for other heavy metals.

I. INTRODUCTION

The recent development of carbon-13 NMR as a research tool of wide application in chemistry has spurred exploratory research on the resonances of other less sensitive nuclei. Relatively few magnetic nuclei have resonances suitable for high-resolution NMR. This is due in part to experimental difficulties which accompany low isotopic abundance and poor intrinsic sensitivity. High resolution nuclei are further restricted to elements with diamagnetic oxidation states and isotopes with nuclear spins of $\frac{1}{2}$. When the nuclear spin is greater than $\frac{1}{2}$, electric quadrupole

relaxation broadens the resonance, usually obscuring multiplet structure and small chemical shift differences. For this reason, the chemical information that can be obtained from chlorine, bromine, and iodine resonances, as well as from ^{17}O and ^{33}S , is rather limited.

Several metals in Groups II and IV possess naturally abundant spin-1/2 isotopes which are potentially useful high resolution nuclei. Among these are ^{113}Cd , ^{199}Hg , ^{119}Sn , and ^{207}Pb , all of which ordinarily occur with diamagnetic oxidation states. NMR data for these resonances are very scanty, although chemical shifts of ^{119}Sn and ^{207}Pb have been surveyed in a variety of pure compounds and simple solutions.¹⁻³ The

resonances have sensitivities that are poor relative to protons but by no means prohibitively low. The range of chemical shifts is extraordinarily large ($\sim 17\,000$ ppm for ^{207}Pb and 2000 ppm for ^{119}Sn), and consequently NMR spectra should provide an extremely sensitive probe of chemical environment. Relaxation times have been reported only in the pure metals,⁴⁻⁶ where relaxation is governed by interactions with the conduction electrons. An elucidation of relaxation mechanisms in diamagnetic systems has not previously been attempted, although such studies yield valuable information about many parameters in the nuclear spin Hamiltonian.

The present investigation concerns a study of ^{119}Sn relaxation in two tetrahalides, SnCl_4 and SnI_4 . Measured relaxation rates in these liquids have been separated by means of temperature variation into contributions arising from dipolar coupling, scalar coupling, and nuclear spin-internal rotation coupling. Separation of the contributions permits calculation of the respective coupling constants and dynamic correlation times. Scalar and spin-rotation coupling constants provide particularly valuable information for understanding magnetic interactions and relaxation of heavy spin- $\frac{1}{2}$ nuclei. In contrast to magnetic dipole relaxation rates, which can be estimated reasonably accurately for systems with known molecular geometry, there is at present little experimental or theoretical basis for predicting quantitatively spin-spin or spin-rotation coupling constants for these nuclei. The relative contributions of various relaxation mechanisms are probably different in general for the ^{119}Sn resonance than for lighter nuclei (such as ^1H , ^{13}C , and ^{19}F) since several parameters that appear in relaxation theory have strong, and possibly periodic, dependence upon atomic number. The most extensively verified of these trends is that for chemical shifts. Similar trends probably exist for spin-rotation and scalar coupling, although experimental data for heavier nuclei are largely confined to metal-proton coupling constants.

The liquids SnX_4 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) comprise the simplest tin-containing systems for studying the latter two interactions. Dipolar relaxation in these liquids is minimal (relative to proton-rich systems), and the resonant tin nucleus lies at a site of tetrahedral symmetry. In this symmetry the spin-rotation and the magnetic shielding tensors both reduce to scalars and chemical shift anisotropy is not a relaxation mechanism.

The tin tetrahalides are also of interest as model liquids for the investigation of diffusive reorientation. They provide a homologous series of molecules with cubic symmetry, roughly spherical molecular potential energy functions, and wide variation in the moments of inertia. Due to tetrahedral molecular geometry, the rotational diffusion tensor reduces to a scalar and reorientation can be described rigorously in terms of an angular correlation time and an angular momentum correlation time. Diffusional motion in simple liquids

has received considerable theoretical and experimental attention in recent years.⁷⁻¹³ At least three detailed models of molecular reorientation have been formulated.^{7,10,13} Tests of these models have involved rather complex chemical systems in as much as both the nuclear spin parameters and rotational diffusion require several tensor components for their rigorous description. The tin tetrahalides were chosen largely because they circumvent these difficulties and provide truly primitive systems for examining rotational diffusion.

II. EXPERIMENTAL

Anhydrous tin tetrachloride was obtained commercially as a reagent grade chemical with minimum purity of 99.6%. The liquid was transferred under nitrogen to the sample tube, degassed by the freeze-pump-thaw method, and sealed under its vapor pressure. Tin tetraiodide (mp $143\text{--}144^\circ\text{C}$) was purchased from Alpha Inorganics. The sample was degassed thoroughly but not further purified.

Relaxation times for ^{119}Sn were measured using a Bruker B-KR 322s variable frequency (4-60 MHz) pulsed spectrometer at a field of 11.74 kg. The field value was maintained within about $1:10^6$ over the long term by means of an external proton NMR field lock. The locking system is home built and utilizes the "time-shared"¹⁴ technique. Temperature at the sample was controlled within $\pm 0.5^\circ\text{C}$ by a Bruker B-ST 100/700 variable temperature accessory, which was calibrated frequently by means of a thermometer in a dummy sample. The absolute temperature uncertainty is estimated to be less than $\pm 1^\circ\text{C}$. Data were sampled using techniques described below and accumulated in a Fabri-Tek model 1064 signal averaging computer.

Transverse relaxation times were measured by the phase shifted Carr-Purcell sequence using pulse spacings that were typically one-third the measured T_2 . The T_1 's were measured using the sequence $180_0\text{--}\tau_1\text{--}(90_0\text{--}\tau_2\text{--}180_\pi\text{--}\tau_2\text{--}90_0)_n\text{--}$. The triplet of pulses repeatedly samples and restores the magnetization during the exponential decay. A triplet sequence (sometimes called DEFT) which differs in the rf phasing has been described previously^{15,16}: $180_0\text{--}\tau_1\text{--}(90_0\text{--}\tau_2\text{--}180_{\pi/2}\text{--}\tau_2\text{--}90_\pi)_n$. The first sequence appears to be preferable in that the effects of H_1 inhomogeneity and incorrectly set pulsewidths is canceled for both the 90_0° and 180_π° pulses by means of a single phase-shifted pulse.

The method of sampling was likewise modified by integrating, rather than filtering, signal between the 180_π and 90_0 pulses. Following the 180_π pulse (and the "dead" period), the receiver output is gated on and integrated until the 90_0 restoring pulse. The integral is held following the 90_0 pulse, sampled by the signal averaging computer and reset prior to the next triplet sequence. Integrating the signal in this manner gives optimum signal to noise ratios and is

particularly advantageous when the filter time constant must be very short (e.g., when T_2 is short). The Carr–Purcell sequence is sampled in a similar manner. In this case the gate is opened at echo maxima, and the signal integrated until the following pulse.

The system was calibrated at 25°C using degassed water, for which the literature value for T_1 (3.60 sec) was reproduced within 2%.

III. THEORETICAL

A. Relaxation Mechanisms

The physical interactions leading to magnetic relaxation of spin- $\frac{1}{2}$ nuclei in diamagnetic liquids are well understood. The most common relaxation mechanism for lighter nuclei is magnetic dipole coupling modulated by molecular translation or reorientation. When the coupled nuclei are on different molecules, translational diffusion modulates the interaction, and the relaxation rate is given in the extreme narrowing approximation by¹⁷

$$(T_1)_{\text{inter}}^{-1} = (T_2)_{\text{inter}}^{-1} = \left(\frac{1}{3}\pi\right) (N\gamma_I^2\gamma_S^2\hbar^2/aD).$$

N is the density of spins/cubic centimeter, γ is the gyromagnetic ratio, a is the mean molecular radius, and D , for pure liquids, is the self-diffusion coefficient. Experimental values of D are often not available, and the Stokes–Einstein expression, which relates D to the macroscopic viscosity η , is introduced

$$(T_1)_{\text{inter}}^{-1} = (6\pi^2/5)\gamma_I^2\gamma_S^2\hbar^2N\eta/kT. \quad (1a)$$

Refinements of this equation have been proposed but Eq. (1a) is sufficiently accurate for the present analysis. Intramolecular dipolar coupling between a pair of spins I and S in the same molecule produces a relaxation contribution which is inversely proportional to the sixth power of the internuclear separation b ,

$$(T_1)_{\text{intra}}^{-1} = (T_2)_{\text{intra}}^{-1} = (4/3)(\gamma_I^2\gamma_S^2\hbar^2S(S+1)/b^6)\tau_\theta. \quad (1b)$$

τ_θ is the angular correlation time, which is defined as one-half the zero frequency spectral density function for second order spherical harmonics.

Scalar coupling of spins also leads to relaxation when the coupling is time dependent due to magnetic relaxation of one of the spins or to chemical exchange. Both physical situations give rise to formally similar results when modulation of the coupling is sufficiently rapid to destroy multiplet structure. For a spin I , with Larmor frequency ω_I , coupled to a second spin S by $(A/2\pi)$ Hz, the longitudinal and transverse relaxation rates are given by

$$(T_1)_{\text{sc}}^{-1} = (2/3)A^2S(S+1)[\tau_2/1 + (\omega_I - \omega_S)^2\tau_2^2], \quad (2a)$$

$$(T_2)_{\text{sc}}^{-1} = (1/3)A^2S(S+1)$$

$$\{\tau_1 + \tau_2/[1 + (\omega_I - \omega_S)^2\tau_2^2]\}. \quad (2b)$$

τ_1 and τ_2 are correlation times for scalar coupling and are equal either to the chemical exchange time, $\tau_{\text{ex}} = \tau_{1,2}$ (if exchange occurs), or to the relaxation times, $T_{1,2}$, of the S spin, depending on which process is more rapid. The physical origin of the correlation times can usually be determined from the temperature dependence of $(T_2)_{\text{sc}}^{-1}$. Correlation times increase with increasing temperature if they are relaxation times and decrease with increasing temperature if they are exchange times. Scalar relaxation usually contributes significantly only to transverse relaxation because the denominator of Eq. (2a) is typically much greater than unity. Nevertheless, an appreciable scalar contribution to $(T_1)^{-1}$ may occur when the coupling constant is large and the correlation time is very short, or alternatively, when the coupled nuclei have nearly equal Larmor frequencies, such as ^{13}C and ^{79}Br .

When the resonant nucleus is scalar coupled to two naturally abundant isotopes, as occurs in SnCl_4 , the right hand side of Eqs. (2) must be written as a sum of terms, weighted by the fractional abundances of the appropriate isotopes. The coupling constants and correlation times differ for the two isotopes but are related by the simple equations,

$$A_{35}/A_{37} = \gamma_{35}/\gamma_{37},$$

$$\tau_{35}/\tau_{37} = (Q_{37}/Q_{35})^2,$$

where Q is the nuclear quadrupole moment, τ is the halogen transverse relaxation time, and subscripts identify the isotopes. After accounting for the naturally abundant isotopes and their Larmor frequencies, we have for the scalar relaxation times

$$\text{SnCl}_4: (T_1)_{\text{sc}}^{-1} = 1.43 (10^{-16}) A_{35}^2\tau_{35}^{-1}, \quad (3a)$$

$$(T_2)_{\text{sc}}^{-1} = 4.30 A_{35}^2\tau_{35}, \quad (3b)$$

$$\text{SnI}_4: (T_1)_{\text{sc}}^{-1} = 0.80 (10^{-14}) A_{127}^2\tau_{127}^{-1}, \quad (3c)$$

$$(T_2)_{\text{sc}}^{-1} = 11.7 A_{127}^2\tau_{127}. \quad (3d)$$

Equations (3) are obtained from Eqs. (2) assuming that relaxation modulates the scalar coupling and that $(\omega_I - \omega_S)^2\tau^2 \gg 1$. Halogen relaxation times determined below show that the latter condition is easily fulfilled for SnCl_4 and SnI_4 at the magnetic field strength employed.

Relaxation for the halogen isotopes $^{35,37}\text{Cl}$ and ^{127}I is dominated by the nuclear electric quadrupole interaction and is much more efficient than relaxation of ^{119}Sn . Relaxation times are given by the expression¹⁷

$$(T_1)_q^{-1} = (T_2)_q^{-1} \\ = \frac{3}{4}\left[\frac{2I+3}{I^2(2I-1)}\right] \\ \times (e^2qQ/\hbar)^2(1 + \frac{1}{3}\eta)\tau_\theta. \quad (4)$$

Quadrupole coupling constants (e^2qQ/\hbar) have been determined for all the tin tetrahalides by NQR spec-

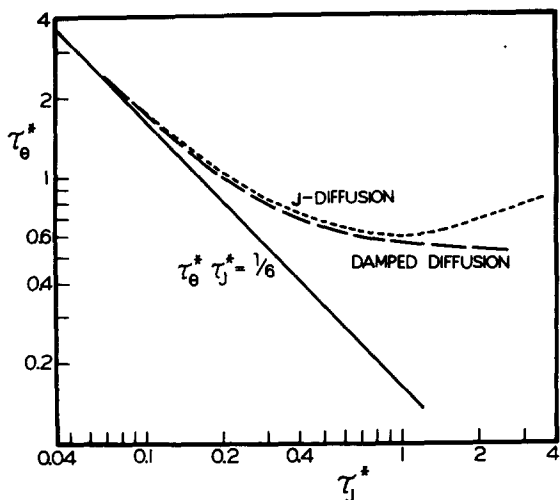


FIG. 1. Theoretical plots of reduced angular correlation time against reduced angular momentum correlation time.

trospecty.¹⁸ Neglecting the anisotropy η of the coupling constant, τ_θ can be calculated directly from measured halogen relaxation times.

The remaining modes of relaxation for ¹¹⁹Sn result from anisotropy in the shielding tensor and from the spin-rotation interaction. Shielding anisotropy does not contribute to relaxation in the tetrahalides where tin is in a site of tetrahedral symmetry. Spin-rotation may contribute substantially to T_1 , however. Hubbard⁹ and McClung¹¹ have derived identical relations for $(T_1)_{SR}^{-1}$ appropriate for the present systems in which the spin-rotation coupling constant C_0 and the moment of inertia I are scalars:

$$(T_1)_{SR}^{-1} = (T_2)_{SR}^{-1} = 2IkT\hbar^{-2}C_0\tau_J. \quad (5)$$

The correlation time τ_J , which is discussed in more detail in the following section, is that for the angular momentum vector. It is well known that τ_J increases with increasing temperature, while τ_θ has the opposite temperature dependence. This singular temperature dependence is useful for separating the spin-rotation contribution to T_1 . The spin-rotation constant can be measured for symmetrical molecules by molecular beam techniques, but unfortunately no data are available for tin tetrahalides. An indirect method for estimating the spin-rotation constant is based on a relation between C_0 and the paramagnetic part of the chemical shift. This relation is discussed further below.

B. Spectral Density Functions

Rotational motion for even the simplest polyatomic molecules in a real liquid is at present not amenable to accurate theoretical understanding. The many degrees of freedom involved and the uncertainties in intermolecular potential energy functions do not permit explicit solutions to the equations of motion, although exact relations are known between transport properties and time correlation functions.¹⁹ The time

correlation functions upon which magnetic relaxation times depend have been derived for two rather simple models of molecular interaction. The first of these is the rotational diffusion model based on an equation of motion for the angular momentum vector which is formally similar to Langevin's equation:

$$\dot{\omega} = -B\omega + \mathbf{A}(t). \quad (6)$$

This model asserts that molecular reorientation is damped by a frictional torque proportional to ω and is otherwise influenced by random torques $\mathbf{A}(t)$, characteristic of Brownian motion. The solution of Eq. (6) is formally similar to that for the rigid rotor problem and has been published in detail by Steele⁷ and Hubbard.⁹ A second model of reorientation has been formulated by Gordon.¹⁰ In the J -diffusion model Gordon assumes that reorientation results from a random succession of intermolecular collisions. Each collision randomizes both the length and direction of the angular momentum vector, and the interval between collisions is given by the Poisson distribution.

A choice of the more realistic model for a particular liquid seems to depend primarily on the shape of the intermolecular potential energy function. For molecules that are nearly spherical and highly polarizable several collisions are probably required to randomize the angular momentum vector. In these liquids rotation is damped by intermolecular forces and Eq. (6) is likely to be realistic. When the potential energy function has sufficiently large angular dependence, individual collisions will randomize the angular momentum and Gordon's model should be the more realistic. The spherical top molecules investigated here are probably best described by damped reorientation. It will however be shown below that magnetic relaxation does not depend in a sensitive manner on the choice of model. For the damped diffusion model certain changes in the frictional parameters can be predicted across a homologous series of molecules. The damping constant B should decrease (at given temperature) with increasing sphericity in the potential energy function and with increasing moment of inertia. Thus B is expected to decrease across the series $\text{SnCl}_4 > \text{SnBr}_4 > \text{SnI}_4$.

Steele⁷ and McClung¹¹ have derived accurate expressions for the angular and angular momentum time correlation functions in each model. The angular correlation functions are not in general exponential, although they do reduce to an exponential form, $G_{(2)}(t) = \exp(-6kTt/IB)$ for long τ_θ . This limit is characterized by reorientation sufficiently slow that $\bar{\omega}\tau_\theta \gg 2$, where $\bar{\omega} = (kT/I)^{1/2}$ is the mean angular velocity of the free rotor. Both damped diffusion and J diffusion predict that in the "diffusion-controlled" limit, τ_θ and τ_J are related simply by

$$\tau_\theta^* \tau_J^* = 1/6, \quad (7)$$

where

$$\begin{aligned} \tau_\theta^* &= \tau_\theta (kT/I)^{1/2}, \\ \tau_J^* &= \tau_J (kT/I)^{1/2}. \end{aligned}$$

In the opposite limit, $\bar{\omega}\tau_\theta \ll 1$, the theory of dilute gases applies, and McClung has shown that $\tau_J = \tau_\theta/4$. When $\bar{\omega}\tau_\theta$ is of order unity, the exact spectral density functions which relate τ_θ and τ_J must be used. These functions have previously been evaluated numerically and the results are compared in Fig. 1. Both models give quantitatively very similar results over the entire liquid range and approach Eq. (7) in the diffusive limit. This fact practically precludes an unambiguous distinction between the two theories in most chemical systems, at least if that distinction is based on magnetic relaxation data. On the other hand, the fact that the two theories give nearly coincident results does suggest that their common result is accurate for many types of intermolecular potential energy function.

Using the theoretical results of Fig. 1 along with τ_θ^* and the spin-rotation contribution to $(T_1)^{-1}$, one can readily determine the spin-rotation constant for a spherical top molecule.

IV. RESULTS

Relaxation rates for SnCl_4 and SnI_4 are shown in Figs. 2 and 3. These data were measured at 18.644 and 18.614 MHz, respectively. Chemical shift values were found to be temperature independent within experimental error (± 6 ppm). The shifts agree with wide-line results of Burke and Lauterbur,¹ who found that SnI_4 is shifted far upfield of ^{119}Sn resonances in most other compounds. Accuracy of the relaxation times is estimated to be about $\pm 7\%$, and is governed largely by the ratio $(T_2/T_1)^{1/2}$. Each data point for

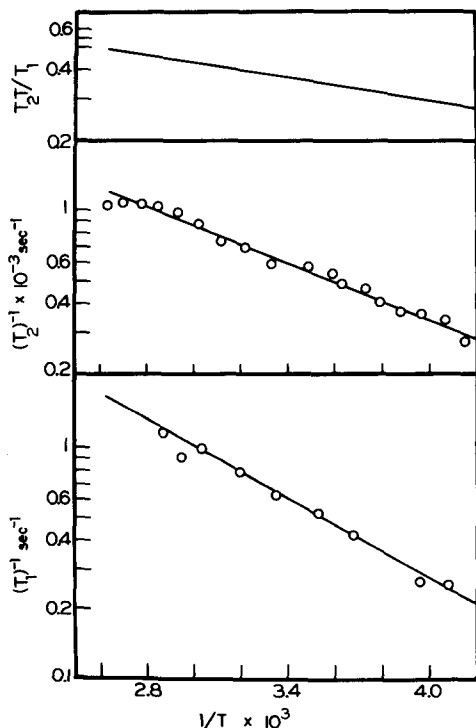


Fig. 2. Relaxation rates for $^{119}\text{SnCl}_4$ as a function of temperature. Upper curve is a test of Hubbard's relation.

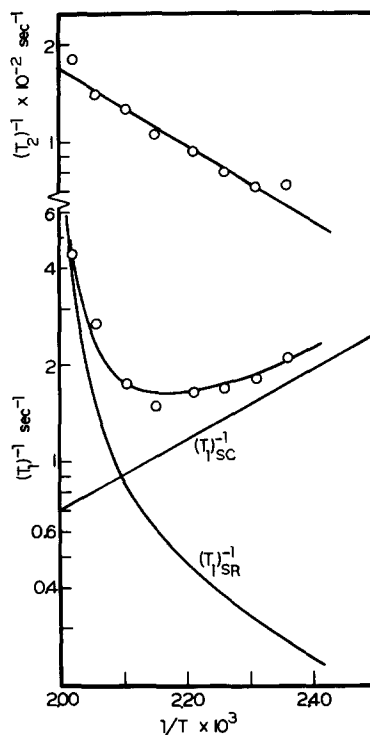


Fig. 3. Relaxation rates for $^{119}\text{SnI}_4$ as a function of temperature.

the iodide represents about 2 h of accumulation, while 3 h or longer were required for the chloride because of the short T_2 for this compound.

A. SnCl_4

Transverse relaxation in $^{119}\text{SnCl}_4$ is much more efficient than longitudinal relaxation, which indicates that scalar coupling to $^{35,37}\text{Cl}$ is the dominant T_2 mechanism. Since $(T_2)^{-1}$ increases with increasing temperature, scalar coupling is modulated by nuclear relaxation of the halogen and Eq. (3b) applies. Using Eq. (3b) and the known value for the chlorine relaxation time in neat SnCl_4 [$\tau_{35} = 2.2 \times 10^{-5}$ sec at 25°C ²⁰], the scalar coupling constant $J(^{119}\text{Sn}-^{35}\text{Cl})$ is found to be 470 Hz.

Longitudinal relaxation can in principle contain scalar, dipolar and spin-rotation contributions although the temperature dependence of T_1 clearly indicates that spin-rotation dominates over the entire liquid range. The dipolar contributions can be calculated accurately from Eqs. (1) using a bond length (2.28×10^{-8} cm) obtained from electron diffraction along with the experimental viscosity and density (see Table I), and a value of τ_θ derived from the ^{35}Cl linewidth.²⁰ This calculation shows that the dipolar contribution is entirely negligible at 25°C : $(T_1)_{\text{intra}}^{-1} = 5.9 \times 10^{-4}$ sec $^{-1}$ and $(T_1)_{\text{inter}}^{-1} = 6.8 \times 10^{-5}$ sec $^{-1}$. The scalar portion of T_1 can likewise be calculated from Eq. (3a) using τ_θ and the value of $J(^{119}\text{Sn}-^{35}\text{Cl})$ obtained above. This contribution, $(T_1)_{\text{sc}}^{-1} = 4.3 \times 10^{-4}$ sec $^{-1}$, is also negligible compared to the

TABLE I. Nuclear spin parameters and molecular constants for SnCl₄ and SnI₄. E_a° is the activation energy for τ_{θ} .

	¹¹⁹ Sn ³⁵ Cl ₄	¹¹⁹ Sn ¹²⁷ I ₄
Nuclear constants		
(e^2qQ/h) MHz	48 ^a	1390 ^a
$J(^{119}\text{Sn}-\text{X})$ Hz	470	940
C_0 kHz	-6.1	-0.66
σ_p' ppm	-2.76(10 ⁸)	-1.48(10 ⁸)
E_a° kcal/mole	1.86	3.5
Molecular constants		
$I \times 10^{40}$ cgs	858 ^b	4270 ^c
ρ g/cm ³	2.23 ^d	4.46 ^d
η cp	0.92 ^d	...

^a Reference 18.

^b H. Fugii and K. Masao, Bull. Chem. Soc. Japan, **43**, 1933 (1970).

^c F. Meller and I. Fankuchen, Acta Cryst. **8**, 343 (1955).

^d International Critical Tables (McGraw-Hill, New York, 1926), Vol. I.

observed relaxation rate. Therefore, only spin-rotation contributes appreciably to longitudinal relaxation. An interesting application of the relaxation data is a simple test of Hubbard's relation [Eq. (6)]. Although it is not possible to obtain direct experimental values for the angular momentum correlation time, the temperature dependence of τ_J is given directly by the temperature variation in $(T_1)^{-1}$. Since τ_{θ} is directly proportional to T_2 and τ_J is directly proportional to $(T_1)^{-1}$, Hubbard's relation can be written $(T_2T/T_1) = \text{const}$ for the specific case of SnCl₄. This product is plotted vs temperature in the upper part of Fig. 2. Hubbard's relation apparently is not strictly valid for SnCl₄, even though molecular rotation in this liquid is unquestionably "diffusive" throughout the liquid range. At the boiling point for example, $\tau_{\theta}^* \approx 1.8$, which is a sufficiently large value to be considered diffusive both in the damped diffusion and extended diffusion theories. The failure of Hubbard's relation could conceivably be traced to the inequality at $A\tau_{35} \ll 1$, which is required for the validity of Eqs. (2). This explanation seems unlikely however, since the product has a maximum value of 0.15 at 110°C, which probably does not invalidate the theory.

Although the foregoing data throw some doubt on the quantitative accuracy of Hubbard's relation, we shall assume that these deviations are minor and use the results in Fig. 1 to estimate τ_J and the spin-rotation constant. Making use once again of the angular correlation time obtained from the ³⁵Cl line-width at 25°C, we calculate $C_0 = \pm 6.1(10^8)$ Hz. The uncertainty in this value is probably about $\pm 15\%$, arising partially from the use of Hubbard's relation to estimate τ_J , and partially from the uncertainty ($\sim 5\%$) in the liquid phase quadrupole coupling constant of ³⁵Cl in SnCl₄.

B. SnI₄

Tin tetraiodide has a liquid range of 143.5–364.5°C, of which only the lower portion 143–220°C was accessible to measurement. The transmitter and receiver coils are maintained at the measuring temperature in the Bruker probe, and oxidation became apparent above 200°C. Figure 3 shows that throughout the range of measurement transverse relaxation follows a pattern similar to that observed for SnCl₄: $T_2 \ll T_1$, and T_2 decreases with increasing temperature. Therefore T_2 is dominated by scalar coupling to ¹²⁷I, modulated by nuclear relaxation. The longitudinal relaxation rate goes through a minimum, indicating that spin-rotation dominates at high temperature and that either scalar or dipolar coupling dominates at low temperature. The total dipolar contribution, calculated from Eqs. (1), is negligible for any reasonable value of τ_{θ} . Using a value of τ_{θ} derived below for 160°C, the sum of the intra- and intermolecular contributions is $5.0 \times 10^{-4} \text{ sec}^{-1}$. The small absolute value of the dipolar relaxation rate relative to typical values for ¹H and ¹⁹F results mainly from the large covalent radii of tin and the halogens (the bond lengths enter as the inverse sixth power) as well as from the decreased gyromagnetic ratios of these nuclei. Therefore scalar relaxation appears to dominate T_1 at low temperature. The scalar term is much larger for the iodide than for the chloride due to the large quadrupole moment and very short relaxation time of ¹²⁷I.

Figure 3 shows that the spin-rotation part of T_1 increases extremely rapidly with temperature above 190°C, which indicates, according to Fig. 1, that liquid SnI₄ is no longer near the diffusive limit at these temperatures. For liquids in the diffusive limit τ_{θ} and τ_J are nearly inversely proportional, and it is approximately true that $(T_1)_{sc}^{-1} = (T_1)_{sr}^{-1}$ at the minimum relaxation rate. Outside the diffusive limit this relation is not accurate and the full temperature dependence of τ_{θ}^* and τ_J^* should be used to separate the scalar and spin-rotation components. For this purpose, a trial separation of $(T_1)_{obs}^{-1}$ into $(T_1)_{sc}^{-1}$ and $(T_1)_{sr}^{-1}$ is obtained at a relatively low temperature ($T = 160^\circ\text{C}$). $(T_1)_{sc}^{-1}$ is proportional to τ_{θ} and its temperature dependence can therefore be obtained from $(T_2)_{sc}^{-1}$, which is proportional to τ_{θ}^{-1} . Using the estimated value of $(T_1)_{sc}^{-1}$ and the measured value of $(T_2)_{sc}^{-1}$ in conjunction with the predictions of Fig. 1, all the correlation times, τ_{θ} , τ_{θ}^* , and τ_J , can be calculated as a function of temperature. Then a detailed plot of $(T_1)_{sr}^{-1}$ vs temperature is drawn using τ_J^* and the original estimate of $(T_1)_{sr}^{-1}$ at 160°C. This process is repeated until the sum of $(T_1)_{sc}^{-1} + (T_1)_{sr}^{-1}$ reproduces the observed relaxation data within experimental error. The best fit obtained for SnI₄ is shown in Fig. 3 and the associated parameters are given in Table II.

TABLE II. Relaxation times and correlation times at various temperatures in stannic chloride and stannic iodide. Values for SnCl_4 at 150°C are extrapolated from lower temperature data. τ_z is the relaxation time for the specified halogen isotope.

Compound	T ($^\circ\text{C}$)	T_1 (sec)	T_2 (msec)	τ_θ^*	τ_J^*	τ_θ (10^{-12} sec)	τ_J (10^{-12} sec)	τ_z (sec)
$^{119}\text{Sn } ^{35}\text{Cl}_4$	25	1.6	1.6	3.5	0.048	5.00	0.07	$2.2(10^{-5})^a$
$^{119}\text{Sn } ^{35}\text{Cl}_4$	150	0.45	0.64	1.62	0.108	1.96	0.13	$5.6(10^{-5})$
$^{119}\text{Sn } ^{127}\text{I}_4$	150	0.49	16	1.36	0.134	3.67	0.37	$1.5(10^{-7})$
$^{119}\text{Sn } ^{127}\text{I}_4$	220	0.30	6.3	0.60	2	1.50	2	$3.8(10^{-7})$

^a Reference 20.

V. DISCUSSION

A. Absolute Shielding Constants and the Magnetic Moment of ^{119}Sn

It is well known from the work of Ramsey^{21,22} and Flygare²³ that the magnetic shielding constant is related to the spin-rotation constant through the second order paramagnetic term of Ramsey's shielding expression. Deverell²⁴ and Gillen²⁵ have recently used this relation in an approximate form to obtain absolute chemical shift scales for ^{19}F and ^{31}P . Flygare's expression for the average shielding constant of a spherical top molecule has been rewritten by Deverell as the sum

$$\begin{aligned} \sigma_{\text{Av}} &= \sigma_d' + \sigma_p' \\ &= (e^2/3mc^2) \{ \langle 0 | \sum_k r_k^{-1} | 0 \rangle - \sum_j (Z_j/r_{ij}) \} \\ &\quad + (e^2/2mc^2) (\pi C_0 I / m\mu_N \gamma_I), \quad (8) \end{aligned}$$

where Deverell's notation is used. This expression suggests that to a good approximation the effect of atoms other than that containing the resonant nucleus can be neglected in the first term. Then the only portion of the shielding constant that is sensitive to changes in chemical environment is σ_p' , which is proportional to C_0 . This expression provides a convenient basis for comparing the measured chemical shifts and spin-rotation constants in stannic chloride and iodide. Using measured spin-rotation constants from Table I, we calculate that σ_p' (SnCl_4) = $(\pm 2.76)(10^{-3})$ and σ_p' (SnI_4) = $(\pm 1.48)(10^{-3})$. The measured chemical shift for these compounds is

$$\sigma(\text{SnCl}_4) - \sigma(\text{SnI}_4) = -1.55(10^{-3}),$$

which compares quite well with the calculated shift, $\Delta\sigma_p' = -1.28(10^{-3})$, if negative signs are taken for both spin-rotation constants. The large upfield chemical shift observed for SnI_4 is consistent with a more positive spin-rotation constant in SnI_4 than in SnCl_4 . The discrepancy between computed and measured chemical shifts is about 10% of the total paramagnetic shift calculated for SnCl_4 . Ten percent is consistent

with the uncertainty estimated above for C_0 and appears to be a reasonable estimate of error.

The absolute chemical shift scale for ^{119}Sn derived above can be used along with the resonance frequencies of $^1\text{H}_2\text{O}$ and $^{119}\text{SnI}_4$ to compute a highly precise value for the magnetic moment of ^{119}Sn . Writing the ratio of tin and proton magnetic moments in terms of the resonance frequencies and shielding constants, we have

$$\mu(^{119}\text{Sn})/\mu(^1\text{H}) = \frac{[(\nu/1 - \sigma_{\text{Av}})]^{119}\text{SnI}_4}{[(\nu/1 - \sigma_{\text{Av}})]^1\text{H}_2\text{O}}. \quad (9)$$

Resonance frequencies for $^{119}\text{SnI}_4$ and $^1\text{H}_2\text{O}$ were measured several times using the external field lock. The respective values were 18.6153 ± 0.0002 MHz and 50.0048 ± 0.0002 MHz. The average total shielding constant can be calculated from Deverell's formula, $\sigma_{\text{Av}} = \sigma_d' + \sigma_p'$, where σ_d' is the diamagnetic shielding of the free atom and is tabulated as a function of atomic number by Ramsey.²¹ Adding up terms on the right hand side of (8) gives $\sigma_{\text{Av}} = 3.28(10^{-3})$ for $^{119}\text{SnI}_4$; Ramsey gives a value of $2.56(10^{-5})$ for σ_{Av} in H_2O . Thus from Eq. (9) the ratio $\mu(^{119}\text{Sn})/\mu(^1\text{H})$ is 0.373635, and the absolute magnetic moment of ^{119}Sn is $-1.04347 \pm 0.00036 \mu_N$ (based on an assumed proton moment of $-2.79274 \mu_N$). The uncertainty in the magnetic moment probably arises mainly from the estimated $\pm 15\%$ uncertainty in C_0 . Further error can arise from the "atom in a molecule" approach of Deverell, if σ_d' varies appreciably from the free atom value. The total uncertainty can be estimated conservatively by assuming a $\pm 10\%$ uncertainty in σ_{Av} , which corresponds to a $\pm 0.036\%$ error in $\mu(^{119}\text{Sn})$.

Ramsey²¹ has tabulated a magnetic moment for tin, $\mu(^{119}\text{Sn}) = -1.0461 \pm 0.0009$, which differs significantly from the value calculated above from spin-rotation constants. Ramsey's tabulated value, although obtained by magnetic resonance, was not based on a detailed assessment of the nuclear screening constant and therefore is not of comparable accuracy to the present measurement.

B. Relaxation Mechanisms

Numerous relaxation studies have indicated that in most diamagnetic liquids containing reasonably high

concentrations of magnetic nuclei, dipolar coupling provides a major, and often a dominant, relaxation pathway. Tin tetrachloride and tin tetraiodide are both rather unusual in that dipolar coupling does not contribute appreciably to either T_1 or T_2 of ^{119}Sn throughout the entire liquid range. Spin-rotation is a significant relaxation mechanism in both liquids, while for tin tetraiodide T_1 is dominated by an extremely efficient scalar contribution in the lower temperature portion of the liquid range. Although dipolar relaxation is negligible, longitudinal relaxation times are at least as short as is usually observed for many lighter nuclei (^1H , ^{19}F , ^{13}C) for which T_1 is typically dominated by dipolar coupling. From a practical standpoint, T_1 is particularly significant as a major determinant of the signal-to-noise ratio, since $S/N \sim (T_1)^{-1/2}$ for cw and many pulsed experiments. If spin-rotation and scalar coupling provide similarly efficient relaxation pathways in other tin-containing systems, reasonably good sensitivity can be expected for the ^{119}Sn resonance. In view of the present results it seems useful to estimate the relative importance of different relaxation mechanisms for tin in other compounds.

Simple calculations based on Eqs. (1) suggest that dipolar relaxation will be a relatively inefficient T_1 pathway for ^{119}Sn in most mobile liquids including those with high proton concentrations. Small dipolar contributions result in part from the fact that the gyromagnetic ratio for ^{119}Sn , which enters Eq. (1) as the square, is about one-third that for ^1H or ^{19}F . Of greater importance is the fact that the internuclear separation, which appears as the negative sixth power, is substantially larger for tin than for many lighter elements due to the difference in covalent radii ($r = 1.41 \text{ \AA}$ for tin). The upper limit of $(T_1)_{\text{intra}}^{-1}$ likely to be observed for ^{119}Sn in compounds other than stannane and its substituted derivatives can be estimated by considering the hypothetical molecular liquid SnF_4 (this compound is actually a tetragonal solid with two nonequivalent tin atoms below 705°C). For the bond length in Eq. (1b) we use the sum of covalent radii for tin and fluorine, $r_{\text{Sn-F}} = 2.1 (10^{-8} \text{ cm})$, and a rotational correlation time equal to $5 (10^{-12} \text{ sec})$. Under these assumptions, $(T_1)_{\text{intra}} = 60 \text{ sec}$. The hydrated tin ion, for which $r_{\text{Sn-H}} \cong 2.33 (10^{-8} \text{ cm})$, and tetramethyl tin [$r_{\text{Sn-H}} \cong 2.33 (10^{-8} \text{ cm})$] probably have similar values of $(T_1)_{\text{intra}}^{-1}$. Of course these estimated T_1 's are very sensitive functions of bond length, doubling for each 13% increase in internuclear separation. Fairly short relaxation times, $(T_1)_{\text{intra}}^{-1} = 0.3\text{--}10.0 \text{ sec}$ have frequently been observed for ^{13}C nuclei that are directly bonded to one or more protons.^{26,27} The difference between the carbon-hydrogen bond length of $1.09 \times 10^{-8} \text{ cm}$ and those cited above for tin underlines the decreasing significance of dipolar relaxation in the latter case.

Spin-rotation provides a highly efficient relaxation pathway for the two tin tetrahalides studied. At least

part of this efficiency results from nearly spherical potential energy functions for these molecules which are responsible for relatively long values of τ_J . Since we wish to consider the possible dependence of $(T_1)_{\text{SR}}^{-1}$ on atomic number, we shall rewrite Expression (5) for the spin-rotation relaxation rate in terms of the angular derivatives, $U'' \equiv d^2U/d\phi^2$, of the intermolecular potential-energy function. Steele⁷ has shown that $\langle U'' \rangle$ is related to the reduced frictional constant, $\xi^* = 1/\tau_J^*$, according to the expression

$$\tau_J^* = (kT/\langle U'' \rangle)^{1/2}.$$

We further use Deverell's approximation to relate the spherical parts of the spin rotation and nuclear shielding tensors, $C_0 \propto \sigma_p'/I$. Substitution of these relations in Eq. (5) gives $(T_1)_{\text{SR}}^{-1}$ in terms of the experimental chemical shifts, moment of inertia, and U : $(1/T_1)_{\text{SR}} \propto (\sigma_p')^2 I^{1/2} (\langle U'' \rangle)^{-1/2}$. The paramagnetic shielding term is a rapidly increasing function of atomic number,^{28,29} and it should largely determine the relative magnitudes of $(T_1)_{\text{SR}}^{-1}$ for different elements. Comparing molecules of even roughly similar size and shape, spin-rotation should be a much more efficient relaxation mechanism for heavy nuclei than for light nuclei. For a series of molecules that contain a given resonant nucleus, however, the relative spin-rotation contributions may be governed by τ_J , rather than by σ_p' , because the variation in σ_p' may be only a few percent of its total magnitude. This is probably the situation for most organometallic compounds of tin. Burke and Lauterbur's chemical shift data for tetramethyl tin and several organotin chlorides fall within a total range of 160 ppm, which is less than 6% of the total σ_p' calculated above. Although the chemical shift data for other heavy metals is not extensive, it appears that ^{207}Pb at least may follow a similar pattern. The range of chemical shifts in many ionic lead compounds is a small fraction of the total range of shifts observed.³

Flygare²³ has discussed the dependence of the spin-rotation constant on variations in the molecular structure and has shown that C_0 depends largely on the atomic number of elements directly bonded to the resonant nucleus. Ramsey's perturbation calculation gives C_0 as the sum of a (negative) second order perturbation term and a (positive) nuclear term. For a nucleus bonded to light elements, the inertial term is small and C_0 and σ_p' are negative. Both quantities become increasingly positive with increasing atomic number of the bonded elements. Flygare's calculations readily account for the diamagnetic shift of $^{119}\text{SnI}_4$ relative to $^{119}\text{SnCl}_4$, as well as for the small absolute magnitude of the spin-rotation constant of the former compound.

Scalar coupling dominates completely the transverse relaxation of $^{119}\text{SnCl}_4$ and $^{119}\text{SnI}_4$ as is often the case for a spin- $\frac{1}{2}$ nucleus directly bonded to a nucleus with an electric quadrupole moment. Exceptionally large

scalar coupling constants in both compounds compensate in large measure for the fairly short T_2 of chlorine and the extremely short T_2 of iodine to produce relatively efficient transverse relaxation for ^{119}Sn . Large coupling constants to nuclei directly bonded to tin are not unexpected since scalar coupling has been found in other compounds to be a strongly increasing function of atomic number. For the sake of comparison between elements it is useful to write the coupling constant as a product that specifically displays the gyromagnetic ratios of the coupled nuclei, $J_{ij} = \gamma_i \gamma_j K_{ij}$, and to consider the factor K_{ij} which describes the strength of coupling by the bonding electrons. Using data in Table I, K_{ij} for SnCl_4 and SnI_4 are, respectively, 412 and 404 [$H_z \times (\hbar/\mu_0)^2$]. Jameson and Gutowsky have tabulated experimental K_{ij} values from various sources for all the Group IV hydrides. These values increase by a factor of approximately two for each succeeding row in the periodic table:

$^{13}\text{CH}_4 < ^{29}\text{SiH}_4 < ^{73}\text{GeH}_4 < ^{119}\text{SnH}_4 < ^{207}\text{PbH}(\text{CH}_3)_3$
K_{ij} 16.0 32.7 80.5 166 365.

This series clearly shows the Z dependence of scalar coupling and indicates the correct orders of magnitude for $K(\text{Sn}-\text{Cl})$ and $K(\text{Sn}-\text{I})$.

Jameson and Gutowsky attribute spin-spin coupling in the hydrides primarily to the Fermi contact interaction and show that the observed increase in K parallels an increase in the nuclear hyperfine interaction constants, which are used as a measure of electron density at the nucleus. Coupling constants depend in general on electron density at both coupled nuclei, so that stannic chloride and iodide should not be expected to correlate too accurately with the above series. However, a substantial increase in coupling constant from SnH_4 to SnX_4 seems reasonable, since s -electron density is greater in the halogens than in hydrogen. The near equality of $K(\text{Sn}-\text{Cl})$ and $K(\text{Sn}-\text{I})$ is probably fortuitous, since the precise value of the coupling constant depends on interactions other than the Fermi contact term. Because several interactions are involved, an accurate theory of scalar coupling for heavy atoms has not been formulated. Still it seems very likely that scalar coupling constants are generally larger, and scalar relaxation more efficient, for tin and other heavy metals than for lighter nuclei.

C. Molecular Motion in the Tin Tetrahalides

Relaxation rates for SnI_4 and SnCl_4 have been separated above into contributions due to scalar coupling and the spin-rotation interaction. Rotational correlation times, τ_θ and τ_J , derived from these separated components can be used to test theoretical predictions, summarized in Fig. 1, of the J -diffusion and damped diffusion models. As noted previously both models predict quantitatively similar relations between τ_θ^* and τ_J^* , at least throughout the region

$\tau_J^* < 1$. A critical test based on relaxation times, for the purpose of differentiating between the models must utilize a chemical system in which reorientation approaches the free rotor situation.

Reorientation in liquid SnCl_4 is unquestionably "diffusion controlled" with $\tau_\theta^* > 1.8$ below 115°C . The value of τ_θ at 25°C is known with an accuracy of about 10% from the measured ^{35}Cl quadrupole coupling constant and nuclear relaxation time; the temperature dependence of τ_θ is known from the temperature variation of $(T_2)_{\text{Sc}}^{-1}$ for ^{119}Sn . Thus the data for SnCl_4 provide a test only of the limiting relation (7), the accuracy of which has already been discussed. Relaxation of ^{127}I in SnI_4 is far too rapid to permit a similar calculation of τ_θ for this compound. Nevertheless the scalar relaxation rates for ^{119}Sn and the ^{127}I quadrupole coupling constant provide an independent means of calculating both τ_θ and the halogen relaxation time, τ_{127} . Combining Eqs. (3c), (3d), and (4) we have

$$(T_1/T_2)_{\text{Sc}} = \left(\frac{1}{2}\right) (\omega_I - \omega_S)^2 (3/125)^{-2} (eqQ/\hbar)^{-4} \tau_\theta^{-2}.$$

Values of $(T_1)_{\text{Sc}}$ depend to some degree on the separation of the total relaxation rate into scalar and spin-rotation components. The error introduced by this separation probably does not exceed ten percent, since the scalar component is strongly dominant near the melting point (143 – 145°C) and since the temperature dependence of $(T_1)_{\text{Sc}}^{-1}$ is obtained directly from $(T_2)_{\text{Sc}}$. Using the separation shown in Fig. 3, τ_θ^* is found to lie in the range $0.60 < \tau_\theta^* < 1.36$ at temperatures below 227°C . At the highest attainable temperature, τ_θ^* is equal to the minimum possible value, $\tau_\theta^* = 0.60$, predicted by J diffusion and slightly larger than the minimum value, $\tau_\theta^* = 0.51$, predicted by damped diffusion. The difference between these values is comparable to the estimated uncertainty and does not constitute a real test of the theories. A much more exacting test is supplied by the temperature dependence of τ_J^* and the computed spin-rotation constants.

Figure 3 shows that $(T_1)^{-1}$ increases very rapidly with temperature above 200°C . In fact the T_1 data can be fit accurately by two exponentials of opposite slope and apparent activation energies of 3.5 and 40 kcal/mol. The approximately exponential behavior of the spin-rotation contribution is probably fortuitous, but the very strong temperature dependence of $(T_1)_{\text{SR}}^{-1}$ near $\tau_J^* \cong 1$ is consistent with theoretical prediction. Systematic attempts have been made to fit the T_1 data as the sum of an exponential scalar component and a spin-rotation component for which the temperature dependence is given by Fig. 1. The activation energy of the scalar component is obtained from $(T_2)_{\text{Sc}}^{-1}$, which is proportional to τ_θ^{-1} . It is interesting that τ_θ is at least approximately exponential up to 220°C and shows no sign of a minimum although both theories predict that τ_θ^* is very near its minimum

value. Proceeding on the hypothesis that J diffusion correctly describes reorientation in SnI_4 , we have attempted to fit the T_1 data assuming that $\tau_J^* \leq 1$ at the highest measured temperature ($T = 220^\circ\text{C}$). The latter assumption is required by the monotonically increasing character of $(T_2)_{\text{sc}}^{-1}$. No curve computed on this basis satisfactorily reproduces the experimental data. Damped diffusion on the other hand does not require that $\tau_J^* \leq 1$, and the model does produce a satisfactory fit which is shown in Fig. 3. Only damped diffusion predicts a temperature region over which τ_J^* increases by a factor of 4 or more while τ_θ^* decreases monotonically by about 30%. Of course both theories predict an eventual increase in τ_θ^* , and for this reason data above 220°C should be highly interesting.

The chemical shift data also give strong support to the conclusion that $\tau_J^* \cong 2$ at 200°C in accord with damped diffusion, as opposed to the maximum value, $\tau_J^* = 1$, consistent with J diffusion. This shielding constant leads to a computed ^{119}Sn chemical shift between SnI_4 and SnCl_4 [$\Delta\sigma_p' = -1.28(10^{-3})$] that is in essential agreement with experiment [$\Delta\sigma = -1.55(10^{-3})$]. If $\tau_J^* = 1$, then $C_0 = -0.93$ kHz and $\sigma_p'(\text{SnI}_4) = -2.09(10^{-3})$. In this case the computed shift, $\Delta\sigma_p' = -0.67(10^{-3})$, differs substantially from the measured value.

One highly detailed test of the predictions of Fig. 1 has recently been published by Maryott *et al.*,³⁰ who measured ^{19}F and ^{35}Cl relaxation times in liquid and gaseous ClO_2F . Independently derived values for τ_θ^* and τ_J^* were obtained for this quasitrahedral molecule from the diffusive limit to $\tau_J^* \cong 1$. The results followed accurately the predictions of Fig. 1. Unfortunately, $\tau_J^* = 1$ at the critical point and it was not feasible to determine unambiguously which of the curves of Fig. 1 applies. An interesting result of this study concerns the behavior of τ_θ , which increases monotonically and exponentially with temperature to the point at which $\tau_J^* = 1$. Similar behavior of $(T_2)_{\text{sc}}^{-1}$ has been discussed above for SnI_4 . The predicted minimum value in τ_θ has not yet been verified experimentally but it is hoped that with suitable probe modifications high temperature studies on SnI_4 will be

feasible and will throw light on the nature of reorientation in this region.

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