Rotational Excitations and Tunneling of Nonequivalent Methyl Groups in Tetramethylstibonium Iodide as Studied by Nuclear Magnetic Resonance and Inelastic Neutron Scattering

Günter Burbach* and Alarich Weiss

Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Darmstadt, FRG

Z. Naturforsch. **46a**, 759–769 (1991); received June 4, 1991

Nuclear magnetic resonance (NMR) and inelastic neutron scattering techniques (INS) have been applied to study the rotational motions and methyl group tunneling in tetramethylstibonium iodide, $[Sb(CH_3)_4]I$, over a wide temperature range. Parameters describing the $[Sb(CH_3)_4]^{\oplus}$ cation tumbling and the methyl group reorientation at high temperatures and quantum mechanical tunneling of the methyl groups at low temperatures were determined.

The results for INS and NMR experiments at low temperatures can be explained in terms of two crystallographically inequivalent methyl groups $CH_3(1)$ and $CH_3(2)$, which were established earlier by the crystal structure determination. In the INS spectra two tunneling lines at 22.0 μeV for $CH_3(1)$ and 1.05 μeV for $CH_3(2)$ with inelastic intensities in the ratio 3:1 were observed at $T = 4$ K.

The activation energies derived from proton NMR spin-lattice relaxation time measurements for the thermally activated methyl group rotation are 1.50 kJ/mol for $CH_3(1)$ and 3.81 kJ/mol for $CH_3(2)$. They are in accordance with the activation energies obtained from neutron fixed-window measurements.

The activation energy for $[Sb(CH_3)_4]^{\oplus}$ cation tumbling is 50.9 kJ/mol as determined from the high temperature spin-lattice relaxation behaviour.

Rotational potentials for the methyl groups are derived. For both kinds of inequivalent methyl groups the threefold potential terms dominate; three- and sixfold potential contributions are shifted by 180°.

Introduction

Rotational excitations of a methyl group provide a simple example of motional processes in the solid state. They have been studied both at higher temperatures as thermally activated random reorientation and in the quantum mechanical regime at low temperatures. At very low temperatures the methyl group rotation can be described via quantum mechanical tunneling between the splitted torsional state [1]. Increasing the temperature, rotation of the methyl group becomes thermally activated and can be treated classically. In the high temperature limit, additionally tumbling of the whole molecular framework can be activated in case of highly symmetric quasi spherical molecules or ions. Using nuclear magnetic resonance (NMR) methods, the activation energies of the thermally activated processes of the methyl group and the molecule as a whole as well as the reorientation rates can be determined [2].

High resolution inelastic neutron spectroscopy (INS) has provided as suitable tool to determine the tunneling splitting in the quantum mechanical regime. The determination of this splitting is a good probe of the height and shape of the hindering potential barriers [3].

Investigations of tetramethyl metal compounds with an element of the main group IV of the periodic system as central atom (e.g. tetramethyl lead, tetramethyl tin) have demonstrated that the interpretation of the NMR and INS data can not be described quantitatively without taking into account crystal structure data [4, 5].

The present investigation was undertaken to study the rotational behaviour of charged $X(CH_3)_4$ systems. $[Sb(CH_3)_4]^{\oplus}$ is isoelectronic to $Sn(CH_3)_4$, where two tunneling lines in the INS spectrum have been found [5]. Thus, rotational tunneling in the tetramethylstibonium cation was expected [6]. Tetramethylstibonium iodide, $[Sb(CH_3)_4]I$, was chosen, since the crystal structure at room temperature has recently been determined [7].

* Part of Dr.-Ing. thesis of Günter Burbach, TH Darmstadt (D 17).

Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, W-6100 Darmstadt, FRG.

0932-0784 / 91 / 0900-0759 $ 01.30/0. – Please order a reprint rather than making your own copy.

The states of motion of tetramethylstibonium iodide are known: ^{1}H NMR wide line measurements have shown that $[Sb(CH_3)_4]^{\oplus}$ undergoes isotropical cation reorientation at $T > 326$ K involving all the four threefold or pseudo threefold axes of the ion. In the temperature range $77 \leq T/K \leq 256$ rotation of the methyl groups about the threefold axes occurs [7].

Experimental

Tetramethylstibonium iodide (sublimation point: 528 K) was prepared as described previously [7].

Neutron scattering investigations were carried out using the time-of-flight spectrometer IN 5 and the backscattering spectrometer IN 10 at the ILL, Grenoble.

In a first experiment the tunneling transitions of tetramethylstibonium iodide were investigated at the IN 5 spectrometer in an energy window $|E| \leq 100$ μeV and an energy resolution $\delta E_{res} = 6$ μeV. The tunnel spectrum in an energy range $|E| \leq 5.88$ μeV was studied with a higher energy resolution $\delta E_{res} = 0.5$ μeV by the backscattering spectrometer IN 10; the tunneling transitions were measured at two different momentum transfers $Q = 1.48$ Å^{-1} and $Q = 1.94$ Å^{-1}. The spectra recorded at $T = 4$ K are shown in Figs. 1 and 2.

The intensity of the elastic line was measured in a so-called "fixed-window scan" at three different detector angles by setting the spectrometer IN 10 to the elastic position (zero energy transfer). The energy window is determined by the resolution of the spectrometer. A temperature range $2.5 \leq T/K \leq 157$ K was covered. The temperature dependence of the elastic intensity I_{el} measured at a momentum transfer $Q = 1.94$ Å^{-1} and an energy resolution $\delta E_{res} = 0.5$ μeV is given in Figure 3.

For the NMR experiments the polycrystalline sample was sealed in a 7 mm external diameter glass ampoule under helium as heat exchange gas. Identical material as in the INS measurements was used.

The proton spin-lattice relaxation times T_1 were measured at two different Larmor frequencies $\omega_0/2\pi = 21.05$ MHz and 36.55 MHz, respectively, and over a temperature range $7.2 \leq T/K \leq 417$. All relaxation measurements were carried out applying $180° - \tau - 90°$ pulse sequences. T_1 was determined using an exponential fitting procedure [8]. The accuracy of the measured T_1-values is estimated to be $\pm 5\%$.

Temperatures above $T = 73$ K were produced by use of a cold nitrogen gas flow cryostat and measured with a copper-constantan thermocouple near the sample site. For $T < 73$ K the temperature was controlled by a continuous flow liquid helium cryostat (Oxford Instr.). It was independently measured near the probe by a NiCr–Au (0.02 atom% Fe) thermocouple. The measurement of the temperature was accurate to ± 0.2 K. Figures 4 and 5 show the observed temperature dependences of the ^{1}H NMR spin-lattice relaxation rates $1/T_1$.

Results

The spectrum recorded at IN 5 shows a pair of tunnel peaks at $\hbar\omega_t^0 = \pm 22.0$ μeV (Fig. 1; 1 eV = 96.49 kJ/mol). Fits, using the resolution function obtained from a vanadium run, show that the measured inelastic intensity corresponds to $\approx 75\%$ of the total inelastic intensity. They reveal furthermore a peak in the shoulder of the elastic line, which is not resolved.

In the spectrum of IN 10 the shoulder in the inelastic line is resolved (Fig. 2). Fits, using the scattering function convoluted with the measured resolution function and two Lorentzians, yield a pair of tunneling lines at $\hbar\omega_t^0 = \pm 1.05$ μeV, representing 1/4 of the whole inelastic intensity.

Spin-lattice relaxation and rotation or tunneling, respectively, are coupled by dipole-dipole interactions between protons [9, 10]. Analyzing the high temperature relaxation behaviour of $[Sb(CH_3)_4]I$ at first (see Fig. 4), there are two elementary processes, whose

Table 1. Numerical values for the apparent activation energies E_H and E_T, cf. (8), relaxation constants C_{AE} and C_{EE}, cf. (7), correlation times τ_H^0 and τ_T^0, and temperature coefficient a, cf. (9), of the tunneling frequency for the two types of non-equivalent methyl groups in $[Sb(CH_3)_4]I$ as obtained from the proton spin-lattice relaxation rates at low temperatures. The tunnel frequencies ω_t^0 were taken from the INS measurements.

$[Sb(CH_3)_4]I$		$CH_3(1)$	$CH_3(2)$
Abundance		3/4	1/4
$\omega_t^0/2\pi$	[MHz]	5319.5	253.9
C_{AE}	[10^9 s^{-2}]	0.50	3.80
C_{EE}	[10^8 s^{-2}]	1.90	1.90
τ_H^0	[10^{-13} s]	0.15	2.20
τ_T^0	[10^{-12} s]	20	22
E_H	[kJ/mol]	1.50	3.81
E_T	[kJ/mol]	0.40	1.80
a	[10^{-11} K^{-6}]	100	6.73

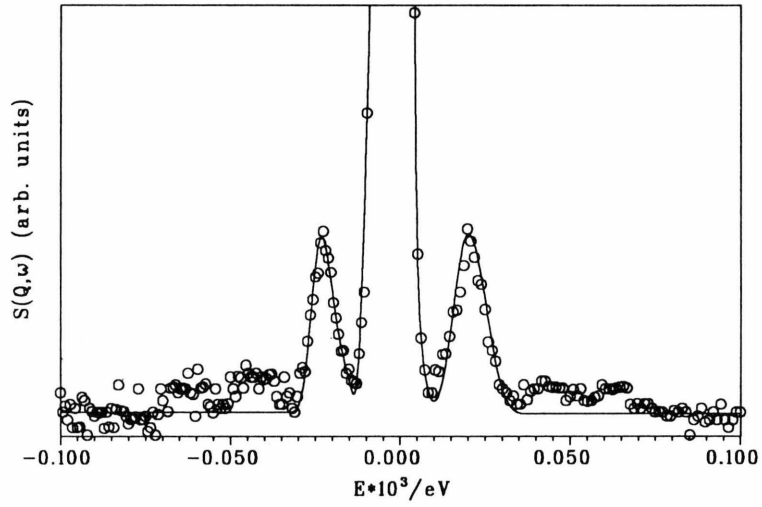

Fig. 1. Tunneling spectrum of tetramethylstibonium iodide at $T=4$ K measured on IN 5/ILL with an incident neutron energy $E_0=0.48$ meV and an energy resolution $\delta E=6$ μeV. Plotted is the scattering function $S(Q,\omega)$ as function of the energy transfer $E=\hbar\omega$ of the neutrons at a momentum transfer $Q=0.883$ Å^{-1}.

Table 2. Potential determining parameters as obtained for both inequivalent methyl groups in $M(CH_3)_4$ compounds. In brackets the values for the less preferred solution with a dominant sixfold potential term are given.

$M(CH_3)_4$	$[Sb(CH_3)_4]^{\oplus}$		$Sn(CH_3)_4$		$Pb(CH_3)_4$	
	$CH_3(1)$	$CH_3(2)$	$CH_3(1)$	$CH_3(2)$	$CH_3(1)$	$CH_3(2)$
$\hbar\omega_t^0$ [μeV]	22.0	1.05	13.2	1.72	30.7	74.0
V_3 [kJ/mol]	2.20 (1.31)	4.58 (1.96)	2.5 (1.5)	3.6 (2.0)	1.31	1.46
V_6 [kJ/mol]	0.12 (1.89)	0.45 (4.36)	0.4 (2.1)	1.1 (4.3)	0.13	1.35
k	1 (1)	1 (1)	1 (1)	1 (1)	1	0
δ	0.95 (0.41)	0.91 (0.31)	0.86 (0.42)	0.77 (0.32)	0.95	0.52
Ref.	this work		[4]		[5]	

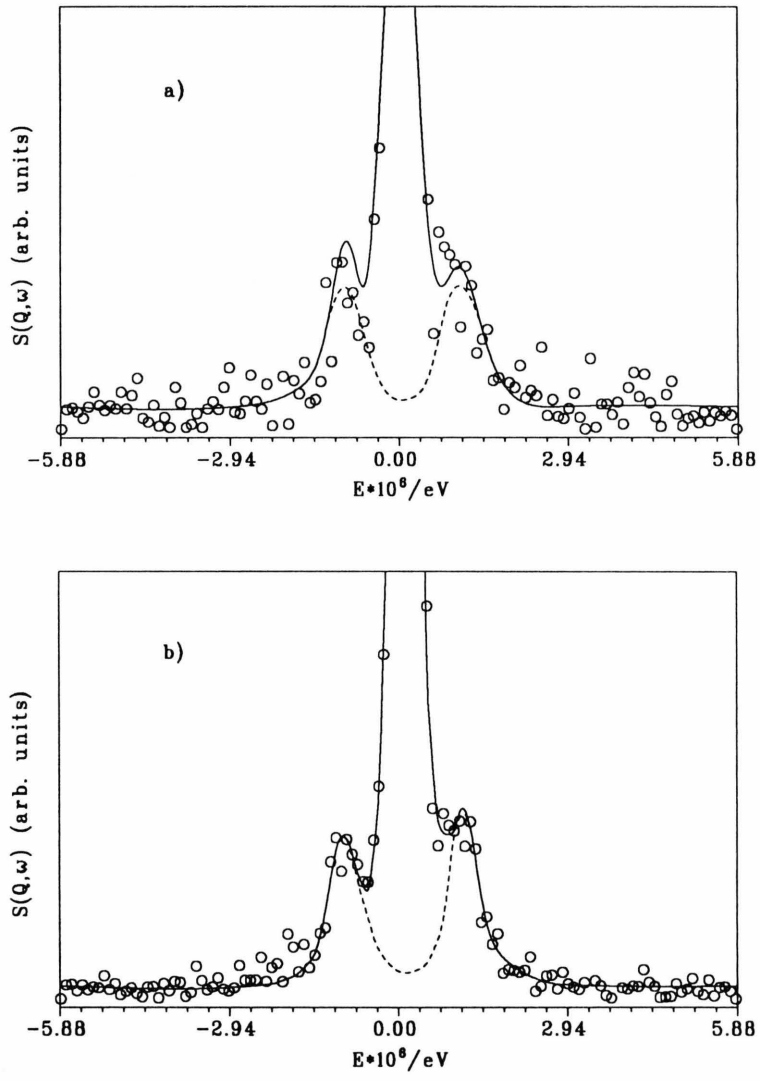

Fig. 2. Tunneling spectra of tetramethylstibonium iodide as measured by IN 10/ILL at $T=4$ K with an energy resolution $\delta E=0.5$ μeV. Plotted are the scattering functions $S(Q,\omega)$ vs. the energy transfer $E=\hbar\omega$ of the neutrons at two different momentum transfers. a) Momentum transfer $Q=1.48$ Å^{-1}, b) momentum transfer $Q=1.94$ Å^{-1}.

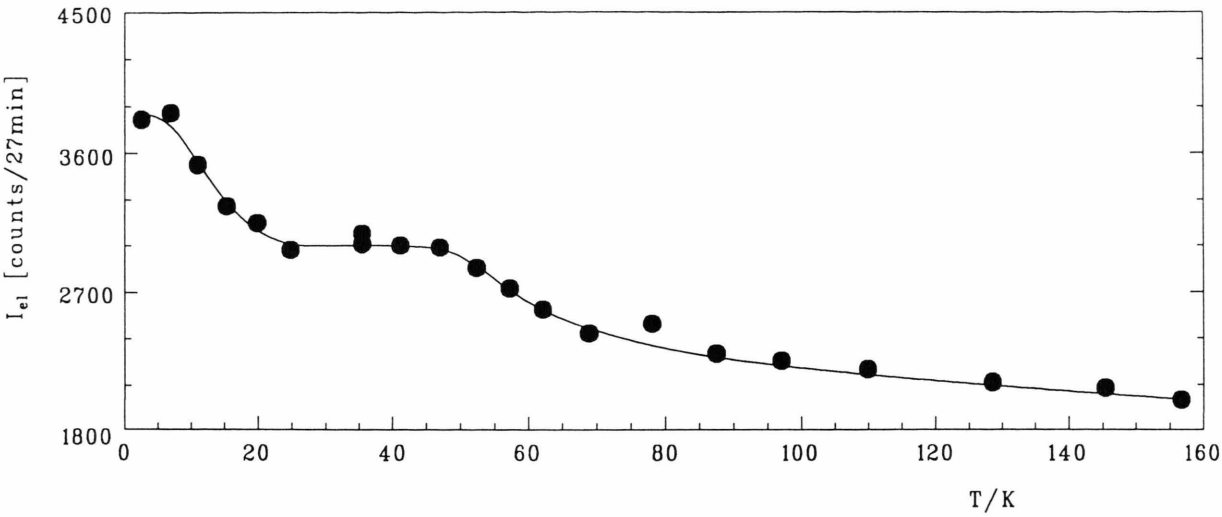

Fig. 3. Fixed window measurements of the elastic scattering from tetramethylstibonium iodide at a momentum transfer $Q = 1.94$ Å^{-1}. Two activation steps are observed and attributed to the rotational motion of the two inequivalent methyl groups $CH_3(1)$ and $CH_3(2)$.

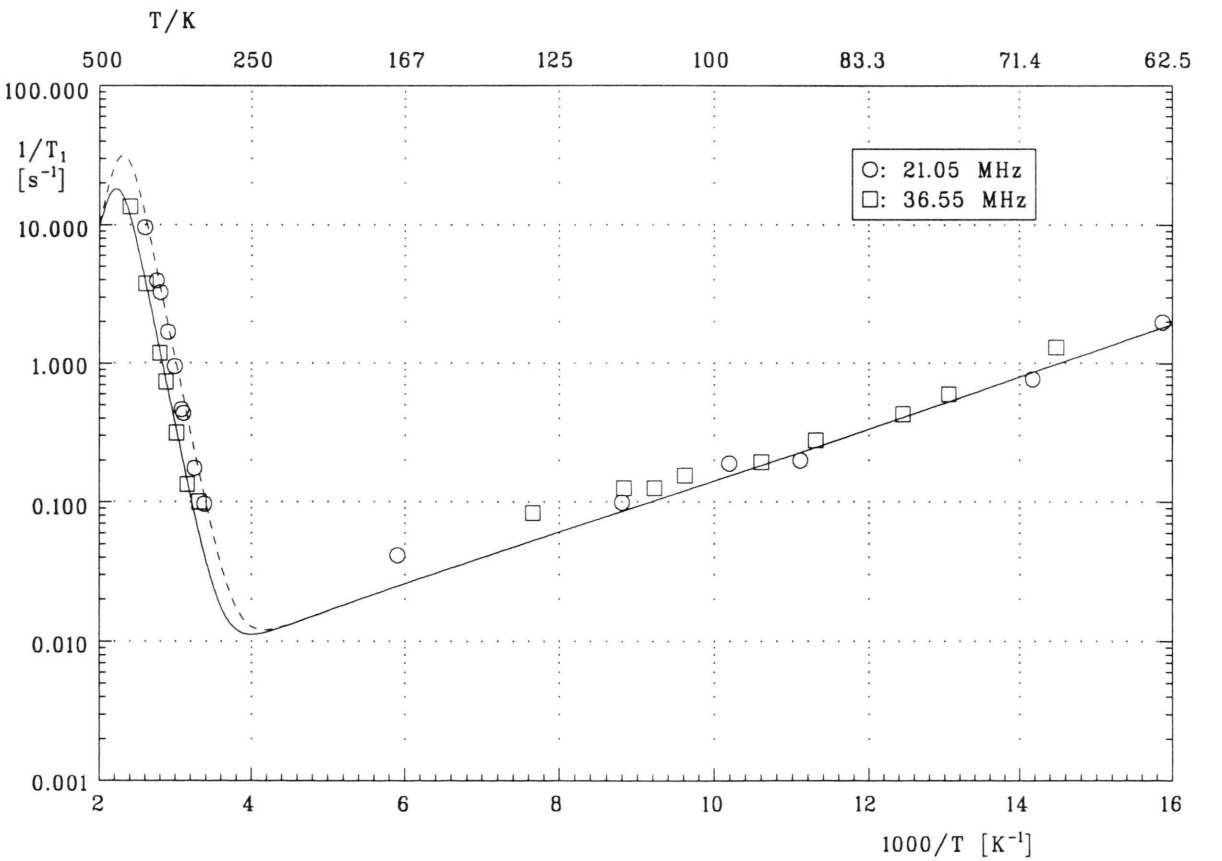

Fig. 4. Proton spin-lattice relaxation rates T_1^{-1} of $[Sb(CH_3)_4]I$ vs. inverse temperature (○ = 21.05 MHz, □ = 36.55 MHz). The lines are calculated from (3) using the parameters given in the text.

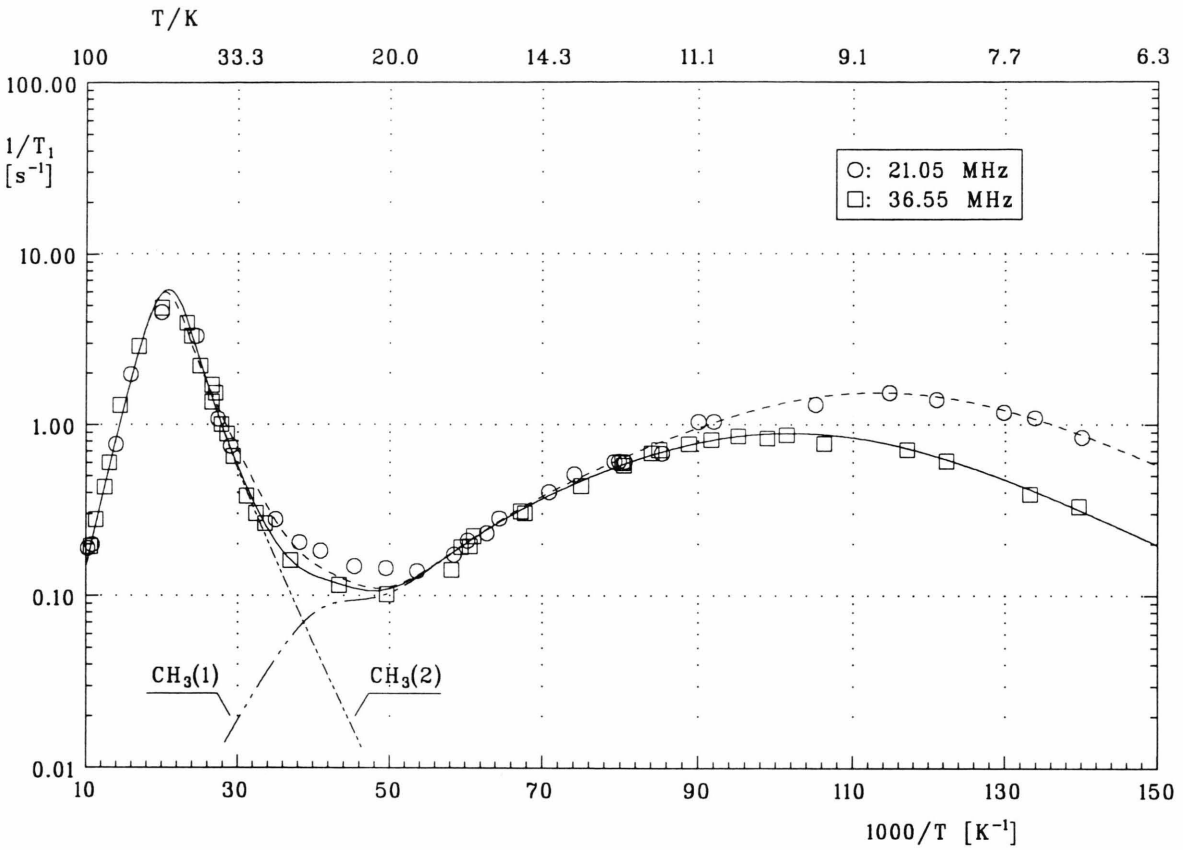

Fig. 5. Experimental proton spin-lattice relaxation rates for tetramethylstibonium iodide as functions of the inverse temperature. The solid ($\omega_0/2\pi = 36.55$ MHz) and broken ($\omega_0/2\pi = 21.05$ MHz) lines correspond to the theoretical description given in the text. The dash-dotted lines represent the $CH_3(1)$ and $CH_3(2)$ contributions to the total relaxation rate at a Larmor frequency of 36.55 MHz.

fluctuations mainly contribute to the experimental relaxation rates:

(i) reorientation of the methyl groups about their threefold symmetry axes characterized by the correlation time τ_c and
(ii) reorientation of the whole $[Sb(CH_3)_4]^{\oplus}$ cation characterized by τ_{c1}.

Neglecting the dipolar intermethyl group interactions at first, the relaxation rate produced by intramethyl proton-proton interaction is given by [11, 12]

$$\frac{1}{T_1'} = \frac{3}{20}\,\frac{\gamma^4\hbar^2}{r^6}\,[g(\omega_0, \tau_{c1}) + 3g(\omega_0, \tau_{c2})], \quad (1)$$

where

$$g(\omega_0, \tau_{ci}) = \left(\frac{\tau_{ci}}{1+(\omega_0\tau_{ci})^2} + \frac{4\tau_{ci}}{1+4(\omega_0\tau_{ci})^2}\right)$$

and

$$\frac{1}{\tau_{c2}} = \frac{1}{\tau_c} + \frac{1}{\tau_{c1}}.$$

γ denotes the gyromagnetic ratio of the proton, $\hbar$ is the reduced Planck constant and r is the proton-proton distance within one methyl group.

The interaction between different methyl groups within the same $[Sb(CH_3)_4]^{\oplus}$ unit may be considered by assuming that the protons of each CH_3 group are located at the center of the triangle of the (HHH) three spin system. This implies that $\tau_c \ll \tau_{c1}$ and gives the relaxation rate caused by the overall tumbling of the cation:

$$\frac{1}{T_1''} = \frac{27}{10}\,\frac{\gamma^4\hbar^2}{r_c^6}\,g(\omega_0, \tau_{c1}) \quad (2)$$

with r_c being the distance between the centers of the circles described by the protons in the threefold (C_3) rotation of CH_3.

Combination of (1) and (2) leads to

$$\frac{1}{T_1} = A\,g(\omega_0, \tau_{c2}) + B\,g(\omega_0, \tau_{c1}), \tag{3}$$

where A and B are the relaxation constants related to methyl group rotation and cation reorientation, respectively.

The correlation times τ_{ci} are assumed to follow an Arrhenius type temperature dependence:

$$\tau_{ci} = \tau_{ci}^0 \exp\left(\frac{E_{ai}}{RT}\right). \tag{4}$$

Thus, the slopes of the straight line portions of the semilogarithmic plot of T_1^{-1} vs. T^{-1} determine the values for the activation energies E_a and E_{a1}, and the intersections at infinite temperature establish the correlation time constants τ_c^0 and τ_{c1}^0 for methyl group C_3 rotation and overall cation tumbling, respectively.

If the relaxation behaviour on the low temperature side of the minimum in Fig. 4 is caused by reorientation of methyl groups about their threefold axes, then $\tau_{c1} \to \infty$ and $\tau_{c2} \to \tau_c$. Since $\omega_0 \tau_c \ll 1$ is valid, the second term in (3) vanishes, and the parameter A is given by

$$A = \frac{9}{20} \frac{\gamma^4 \hbar^2}{r^6}. \tag{5}$$

Taking $r = 179.7$ pm as the proton-proton distance within a methyl group, $A = 7.62 \times 10^9\ s^{-2}$ is obtained.

If the high temperature relaxation behaviour on the other side of the minimum is caused by isotropic reorientation of the cation superimposed on very fast reorientation of the methyl groups, then $\tau_{c2} \to 0$; the first term in (3) can be neglected, and for $\omega_0 \tau_{c1} \gg 1$ the parameter B is given by

$$B = \gamma^4 \hbar^2 \left(\frac{3 r^{-6}}{20} + \frac{27 r_c^{-6}}{10}\right). \tag{6}$$

The second term in the brackets of (6) approximates the contribution made by the interaction between methyl groups on the same tetramethylstibonium cation (intraionic methyl-methyl interactions).

Using a mean value $r_c = 401$ pm for the distance of the centers of the CH_3 groups in $[Sb(CH_3)_4]I$ [7] and the same value for r as in (5), $B = 2.91 \times 10^9\ s^{-2}$ is obtained.

Taking A and B, (3) was least squares fitted to the experimental data. The following parameters at a Larmor frequency of 36.55 MHz are obtained:

Methyl group rotation:

$$\tau_c^0 = 5.39 \times 10^{-14}\ s, \quad E_a = 3.81\ kJ/mol,$$

Cation tumbling:

$$\tau_{c1}^0 = 3.33 \times 10^{-15}\ s, \quad E_{a1} = 50.86\ kJ/mol.$$

At very low temperatures (Fig. 5) the methyl group rotation can be described as a quantum mechanical process. According to the threefold molecular symmetry of the methyl group three rotator eigenstates describing the cyclic permutation symmetry can be distinguished: A, E_A, and E_B. Nuclear relaxation occurs via coupling of the spins with the tunneling methyl group and the lattice [10]. Again, there are two possible relaxation mechanisms:

(i) transitions between E_A and E_B, which are dependent on the Larmor frequency, and
(ii) symmetry changing transitions from A to E, which are field independent.

Thus, for low hindering barriers, which are present in this study, the classical expression for the relaxation rate of a polycrystalline sample, (3), has to be replaced by [13]

$$\frac{1}{T_1} = C_{AE} \sum_{n=-2}^{+2} \left(\frac{n^2 \tau_c}{1 + ((\omega_t + n\omega_0)\,\tau_c)^2}\right) + C_{EE} \sum_{n=1}^{2} \left(\frac{n^2 \tau_c}{1 + (n\,\omega_0\,\tau_c)^2}\right). \tag{7}$$

C_{AE} and C_{EE} account for dipole-dipole interactions which are connected with a change of symmetry of the CH_3 rotator, either from A to E (intramolecular interactions) or from E_A to E_B (intermolecular interactions).

The temperature dependences of the correlation time τ_c can be expressed by the superposition of two exponentials:

$$\frac{1}{\tau_c} = \frac{1}{\tau_H^0} \exp\left(-\frac{E_H}{RT}\right) + \frac{1}{\tau_T^0} \exp\left(-\frac{E_T}{RT}\right). \tag{8}$$

The parameters τ_H^0, τ_T^0, E_H, and E_T ($E_H > E_T$) represent the correlation time constants for infinite temperature and the activation energies in the limit of high (H) and low (T) temperature, respectively.

The temperature dependence of the tunnel frequency ω_t is given by [4]

$$\omega_t(T) = \frac{\omega_t^0}{1 + a\,T^6}\,. \tag{9}$$

As shown in the case of $Sn(CH_3)_4$, (7) is only valid, if all methyl groups are crystallographically equivalent [4]. If there are two crystallographically inequivalent methyl groups, as it is the case in $[Sb(CH_3)_4]I$, each rotor has to be treated separately by (7) and (8) with individual correlation times $\tau_c(1)$ and $\tau_c(2)$ for $CH_3(1)$ and $CH_3(2)$, respectively. The total relaxation rate is then formed by the weighted superposition of the contributions $T_1^{-1}(1)$ and $T_1^{-1}(2)$.

In Fig. 5 the fit of such a procedure is given by a solid line for the Larmor frequency $\omega_0/2\pi = 36.55$ MHz. The tunneling frequencies of the torsional ground state $\omega_t^0(1)$ and $\omega_t^0(2)$ were taken from the INS spectra. The dash-dotted lines in Fig. 5 represent the contributions of the $CH_3(1)$ and $CH_3(2)$ groups at $\omega_0/2\pi = 36.55$ MHz.

In Table 1 the parameters derived from the best fit to the experimental points are listed.

The onset of 120° jumps of methyl group protons across the rotational potential barrier has an effect upon the INS spectrum in a fixed-window measurement. It leads to a quasielastic line centered at $\hbar\omega = 0$ with a line width Γ_{qu}, which is temperature dependent. When Γ_{qu} is in the same order of magnitude as the resolution of the spectrometer δE_{res}, intensity is transferred out of the energy window and a step in the I_{el} vs. T diagram arises. At that temperature $T_{1/2}$, where half of the height of the step is lost, the condition $\Gamma_{qu} = \delta E_{res}$ is valid. The temperature dependence of the quasielastic line width can be described by an Arrhenius Ansatz [13, 14]

$$\Gamma_{qu}(T) = \frac{3}{2}\,\frac{\hbar}{\tau(T)} = \Gamma_0 \exp\left(-\frac{E_a}{RT}\right)$$
$$= \frac{3}{2}\,\hbar(\tau_H^0)^{-1} \exp\left(-\frac{E_a}{RT}\right), \tag{10}$$

where τ denotes the time between jumps, which is correlated with τ_H^0, the time constant for infinite temperature at the high temperature side of the relaxation curve, cf. (8). The barrier height E_a of the rotational potential is then obtained from

$$E_a = R \ln\left(\frac{\Gamma_0}{\delta E_{res}}\right) T_{1/2}\,. \tag{11}$$

The fixed-window measurement of tetramethylstibonium iodide yields two steps at $T_{1/2} = 14$ K and $T_{1/2} = 52$ K. They can be related with the rotational motion of $CH_3(1)$ and $CH_3(2)$, respectively.

Using the values for τ_H^0 as given in Table 1, the application of (10) and (11) yields activation energies $E_a(1) = 1.4$ kJ/mol and $E_a(2) = 3.9$ kJ/mol for jumps of the two inequivalent methyl groups over the potential barrier.

Discussion

By combining the inelastic intensities, which were measured by IN5 and IN10, all methyl groups in $[Sb(CH_3)_4]I$ have been observed. The two peaks at $|\hbar\omega_t^0| = 22.0$ μeV and $|\hbar\omega_t^0| = 1.05$ μeV with inelastic intensities in the ratio 3:1 are in accordance with the results of the crystal structure determination. The crystal structure was determined by single crystal X-ray technique at room temperature [7]. $[Sb(CH_3)_4]I$ crystallizes in the space group C_{6v}^4-$P6_3mc$ with 2 formula units in the unit cell. Two crystallographically inequivalent carbon atoms in the ratio C(1):C(2) = 3:1 were found. Thus, the tunnel splittings at 22.0 μeV and 1.05 μeV are associated with $CH_3(1)$ and $CH_3(2)$, respectively.

As can be seen in Fig. 4, a maximum of the relaxation rate at high temperatures could not be observed experimentally. The theoretical maximum relaxation rate can be calculated: (3) has a maximum for $\omega_0\,\tau_{c1,max} = 0.6158$. Insertion of $\tau_{c1,max}$ and the value for B yields a maximum relaxation rate $T_{1,max}^{-1} = 18.01\ s^{-1}$ at $\omega_0/2\pi = 36.55$ MHz. Comparison with Fig. 4 shows that this value is almost reached at the highest experimental temperature $T = 417$ K (i.e. $1000/T = 2.398\ K^{-1}$, see Figure 4). Taking the $\tau_{c1,max}$-value and (4), the corresponding temperature T_{max}, where T_1^{-1} reaches a maximum, is calculated to be $T_{max} = 451$ K (i.e. $1000/T_{max} = 2.217\ K^{-1}$).

T_{max} of $[Sb(CH_3)_4]I$ fits to the corresponding values of the homologous iodides $[M^V(CH_3)_4]I$, M^V = N, P, As, where the temperature of maximum relaxation rate could be observed experimentally at a Larmor frequency of 34 MHz (360 K, 388 K, and 400 K for M^V = N, P, and As, respectively) [15].

A ^1H NMR second moment (M_2) study of various tetramethylstibonium compounds showed a step in the M_2 vs. T diagram indicating the transition from individual methyl group rotation to cation tumbling [7]. It was assumed that at first a reorientation of the

$[Sb(CH_3)_4]^{\oplus}$ cation about the unique "long" Sb–C(2) axis (C_3' rotation) and then additionally about the three "short" Sb–C(1) axes is activated. For tetramethylstibonium iodide the activation energies of these processes were found to be 7.6 kJ/mol and 59.9 kJ/mol, respectively. They have to be compared with $E_{a1} =$ 50.9 kJ/mol found in this study.

At first sight there is a large discrepancy between the two values for cation tumbling. Since in the temperature range $285 < T/K < 417$ the slope of the curve T_1^{-1} vs. T^{-1} is very steep, the two steps are not resolved, and therefore only a mean value of 50.9 kJ/mol for both processes (cation tumbling and C_3' rotation) can be obtained. Averaging the activation energies for cation tumbling about four axes in $[Sb(CH_3)_4]^{\oplus}$ and C_3' reorientation about the unique "short" Sb–C(2) axis as derived from M_2 measurements yields 49.4 kJ/mol as a mean value. This is in good agreement with $E_{a1} =$ 50.9 kJ/mol obtained from T_1^{-1} measurements in this study.

Another indication for the assumed mechanism of the transition to cation tumbling via C_3' rotation may be the deviation of the relaxation rates from the theoretical curve in the temperature range $143 < T/K < 294$. This is the temperature intervall where the relaxation mechanism changes from methyl group rotation to $[Sb(CH_3)_4]^{\oplus}$ cation tumbling and where an anomalous behaviour of $[Sb(CH_3)_4]^{\oplus}$ was also found in T_1 studies on $[Sb(CH_3)_4]_2SiF_6$ [16].

The various values for the characteristic parameters obtained by analyzing the spin-lattice relaxation rates for $T < 77$ K (cf. Fig. 5) are listed in Table 1. They are in the same order of magnitude as those reported for tetramethyl tin and tetramethyl lead [4, 5], for which compounds also crystallographically inequivalent methyl groups have been considered.

Regarding at first $CH_3(2)$, the anomalous behaviour of the $T_1(2)^{-1}-T^{-1}$ curve is striking. The curve resembles the relaxation behaviour of methylbromide and methylisocyanate [17]. At $T \approx 48$ K there is a T_1^{-1} maximum with a small dependence on the frequency. The curves for the two Larmor frequencies intersect at $T = 38.5$ K. A level crossing peak at $\omega_1 = 2\omega_0$, as theoretically expected, is not observed. The reason might be a shift of the peak towards higher temperatures where the relaxation rates of $CH_3(2)$ at the two different Larmor frequencies match. The barrier hight $E_H(2) = 3.81$ kJ/mol is relatively large.

It is interesting to note that the relaxation constant $C_{EE}(2)$ and the apparent activation energies $E_H(2)$ and $E_T(2)$ in $[Sb(CH_3)_4]I$ are very similar to the values found for the corresponding methyl group in tetramethyl tin, $Sn(CH_3)_4$ [4]. In both substances there is one $CH_3(2)$-type methyl group in the formula unit, which is directed along the threefold molecular symmetry axis, whereas the carbons of the three remaining $CH_3(1)$-type methyl groups occupy the threefold positions. The values for the low temperature activation energy, $E_T(2) = 1.8$ kJ/mol, are the same for both compounds.

The values for $E_H(2)$ and $C_{EE}(2)$ are slightly smaller for $Sn(CH_3)_4$ (3.4 kJ/mol and 0.17×10^9 s^{-2}, respectively) than for $[Sb(CH_3)_4]I$ (3.81 kJ/mol and 0.19×10^9 s^{-2}, respectively).

The ratio $C_{AE}(2)/C_{EE}(2) \approx 20$ for tetramethylstibonium iodide indicates that the two terms of (7) coincide in one curve with a large maximum relaxation rate. The contribution of the second sum is small. This indicates a domination of the intramethyl dipole-dipole interaction in $CH_3(2)$.

The $T_1^{-1}(1) = f(T^{-1})$ curve in Fig. 5 shows two maxima. The low temperature maximum is frequency dependent and reflects the $E_A \rightarrow E_B$ transition, second sum of (7); the small high temperature maximum is frequency independent and caused by the symmetry changing $A \rightarrow E$ transition. The low temperature side of the relaxation peak occurs at so low temperatures that only the torsional ground state is populated.

Due to the error in $1/T$, which has especially a large effect at lowest temperatures, the low temperature apparent activation energy $E_T(1)$ is less accurate. The high temperature apparent activation energy $E_H(1)$ is mall (1.50 kJ/mol). It is exactly the same as the corresponding value for $CH_3(1)$ of $Pb(CH_3)_4$ [5].

In a study about rotational tunneling in methylpyridines [10] a linear relationship between $\log(C_{AE})$ and inverse temperature, where the relaxation rate is maximal, was found. For $[Sb(CH_3)_4]I$ the value of $C_{AE}(2)$ fits to this relationship.

The $T_1^{-1} = f(T^{-1})$ curve shows a deviation from the experimental points in the temperature range $20 < T/K < 25$. At $\omega_0/2\pi = 21.05$ MHz the fitted curve is shifted towards lower relaxation rates. This is due to an onset of a small non-exponentiality of the free induction decay (FID) in this temperature interval, so that the large relaxation times could not be reached. Nevertheless, the experimental rates at 21.05 MHz are higher than at 36.55 MHz, and this is in accordance with the fitted curves for both Larmor frequencies.

The results of the neutron fixed-window measurements, $E_a(1) = 1.4$ kJ/mol and $E_a(2) = 3.9$ kJ/mol, are in good agreement with the apparent activation energies $E_H(1) = 1.50$ kJ/mol and $E_H(2) = 3.81$ kJ/mol as obtained from the NMR T_1 measurements. They confirm the correct attachment of $CH_3(1)$ and $CH_3(2)$ to the respective maxima in the $T_1^{-1} - T^{-1}$ curve of Figure 5.

The observed tunneling frequencies and activation energies can be related to the rotational potential. Usually the potential is expanded into a Fourier series in the rotational angle ϑ of the CH_3 group and truncated to the first two terms [5]:

$$V(\vartheta) = \tfrac{1}{2}\{V_3(1+(-1)^k \cos 3\vartheta)\} + \tfrac{1}{2}\{V_6(1+(-1)^k \cos 6\vartheta)\}, \quad (12)$$

where V_3 and V_6 denote the three- and sixfold potential and k the phase factor indicating either no shift ($k=0$) or a phase shift of 180° ($k=1$) of the V_3 and V_6 potentials.

Using two of the three potential energies $\hbar\omega_t^0$, E_T (as the energy difference E_{01} between the torsional ground and first excited state of the potential), and E_H (as the activation energy E_a of the potential barrier), the potential determining parameters can be derived. Both inequivalent methyl groups are regarded independently from each other. The corresponding eigenvalues of the Schrödinger equation for both kinds of methyl groups were taken from the tables [18]. The solution is obtained graphically by the intersection of the curves.

In the case of $CH_3(1)$ the eigenvalues derived from $E_T(1)$ can not be considered. They yield no intersection with the curves obtained from $\hbar\omega_t^0(1)$ and $E_H(1)$; this may be due to the error in the slope in the temperature range $7.2 < T/\mathrm{K} < 10$ owing to uncertainties in temperature measurement.

Figure 6 shows the curves obtained in terms of $V_{max} = V_3 + V_6$ and $\delta = V_3/V_{max}$. The resulting potential parameters are listed in Table 2 together with the values given in literature for $Sn(CH_3)_4$ and $Pb(CH_3)_4$.

For both kinds of methyl groups in $[Sb(CH_3)_4]I$ two solutions exist. The parameter set closer to a pure $\cos 3\vartheta$ potential is preferred because experience has shown that the threefold term usually dominates. For both solutions the 3- and 6-fold potential contributions are shifted by 180°. The small sixfold contributions with a phase factor $k=1$ indicate that the threefold potential wells are narrowed, while the barriers are broadened.

Solid $Pb(CH_3)_4$, $Sn(CH_3)_4$, and $[Sb(CH_3)_4]I$ are built up from $M(CH_3)_4$ tetrahedra (M = Sn, Pb, Sb) with two inequivalent methyl groups in the ratio $CH_3(1):CH_3(2) = 3:1$. In the group-IV-tetrahedra

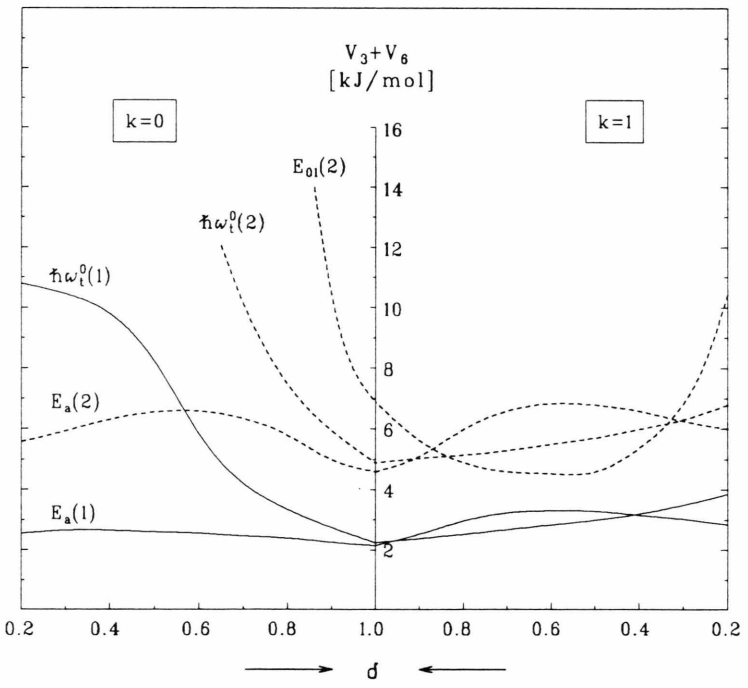

Fig. 6. Possible solutions of the Schrödinger equation for both types of inequivalent methyl groups in tetramethylstibonium iodide in the potential of (12) vs. $\delta = V_3/(V_3+V_6)$.

Table 3. Structural parameters of tetramethyl tin and tetramethylstibonium iodide.

$M(CH_3)_4$		d(M–C) pm	d($CH_3(1)\cdots CH_3(2)$) pm	d($CH_3(1)\cdots CH_3(1)$) pm	∢C(1)–M–C(1) deg.	∢C(1)–M–C(2) deg.
$[Sb(CH_3)_4]^{\oplus}$ [7]	$CH_3(1)$ $CH_3(2)$	208.1 211.5	339.9	342.4	110.7	108.2
$Sn(CH_3)_4$ [19]	$CH_3(1)$ $CH_3(2)$	214.6 210.8	345.8	349.4	109.6	109.3

three methyl groups are located on the threefold symmetry position with a "long" X–C bond length and the fourth along the symmetry axis with a "short" X–C bond length [4, 19]. In contrast, the $[Sb(CH_3)_4]^{\oplus}$ tetrahedron is elongated along the C_3 axis, i.e. it has three "short" bonded methyl groups and one "long" bonded methyl group [7]. In Table 3 some structural parameters for $M(CH_3)_4$, M = Sn, Sb, are given. In contrast to $Sn(CH_3)_4$ and $[Sb(CH_3)_4]I$, the alkali tetramethylindates $M^I[In(CH_3)_4]$, M^I = Li, Na, crystallize in cubic primitive lattices with the $[In(CH_3)_4]^{\ominus}$ anions forming regular tetrahedra [20]. The different rotational behaviour due to different crystal structures in isoelectronic alkali tetramethylindates, tetramethyl tin, and tetramethylstibonium halides as studied by ^1H NMR is reported elsewhere [21].

It is interesting to note that the "short" bonded methyl group in $Sn(CH_3)_4$ shows a tunnel splitting (1.72 μeV) very similar to the "long" bonded methyl group in $[Sb(CH_3)_4]I$ (1.05 μeV), and, vice versa, that the tunnel transitions of the three "long" bonded methyl groups in the tin compound (13.2 μeV) are similar to three "short" bonded methyls in the isoelectronic tetramethylstibonium cation (22.0 μeV).

For an explanation the influence of the structural data (angles, distances) has to be considered (cf. Table 3). In $[Sb(CH_3)_4]I$ each $CH_3(1)$ group is surrounded by one iodine in a distance of 393.3 pm and by another two in a distance of 405.9 pm. The $CH_3(2)$ group has only one $I^{\ominus}$ neighbour at 421.2 pm and at 431.7 pm, respectively. This leads to an increase of the angle between the equivalent methyl groups to 110.7° and to a decrease of the angle between the non-equivalent methyl groups to 108.2° in relation to the ideal tetrahedral angle (109.47°). In $Sn(CH_3)_4$ the intermethyl angles (109.6° and 109.3°) have nearly the ideal tetrahedral value [19].

By the influence of the iodine the intermolecular distance between two inequivalent methyl groups is 2.5 pm shorter than the distances $CH_3(1)\cdots CH_3(1)$. In $Sn(CH_3)_4$ the respective difference is 3.6 pm. In both compounds the potential barrier is mainly determined by the interlocking of both types of methyl groups. In tetramethyl tin and in tetramethylstibonium iodide, the single $CH_3(2)$ is influenced by $3\,CH_3(1)$ in a short distance, and each of the three $CH_3(1)$ "sees" $1\,CH_3(2)$ in the same distance plus another $2\,CH_3(1)$ in a larger distance. From the intramolecular (-ionic) point of view it is thus reasonable that $CH_3(1)$ is less hindered and thus shows both a larger tunnel splitting in the INS experiments than $CH_3(2)$ and a domination of the relaxation rate at lowest temperatures in NMR T_1 measurements.

Taking into account the distances of the two types of methyl groups to the next $I^{\ominus}$ neighbours in $[Sb(CH_3)_4]I$, one would not expect that $CH_3(1)$ is less hindered than $CH_3(2)$. Since the iodine ion is soft, i.e. an easily polarisable sphere, it contributes to the high threefold potential terms for both, $CH_3(1)$ ($\delta \equiv V_3/(V_3+V_6) = 0.95$; cf. Fig. 6) and $CH_3(2)$ ($\delta = 0.91$). In tetramethyl tin such an intermolecular buffer between the methyl rotators of different molecules is absent and thus the sixfold potential contribution is higher.

The results of our work confirm the statement that a correlation of tunneling splittings with R–C bond lengths is not sufficient to describe the rotational behaviour of methyl groups and that both intra- and intermolecular interactions have to be considered [22].

Acknowledgement

The help of Dr. N. Weiden during the performance of the NMR experiments and of Dr. S. Mahling-Ennaoui and Dr. F. Rieuford at the ILL is gratefully acknowledged.

This work was supported by the Bundesministerium für Forschung und Technologie (project no. 03-WS1DAR-1).

[1] W. Press, Single Particle Rotation in Molcular Crystals, in: Springer Tracts in Modern Physics, Vol. 92 (G. Höhler, ed.), Berlin 1981.
[2] T. T. Ang and B. A. Dunell, J. Chem. Soc. Faraday Trans. 2, **75,** 169 (1979).
[3] J. Haupt and W. Müller-Warmuth, Z. Naturforsch. **23a,** 208 (1968).
[4] M. Prager, K.-H. Duprée, and W. Müller-Warmuth, Z. Phys. B **51,** 309 (1983).
[5] M. Prager and W. Müller-Warmuth, Z. Naturforsch. **39a,** 1187 (1984).
[6] Al. Weiss, Rheinisch-Westfälische Akademie der Wissenschaften, Vorträge **N 353,** 1 (1987).
[7] G. Burbach, S.-Q. Dou, and Al. Weiss, Ber. Bunsenges. Phys. Chem. **93,** 1302 (1989).
[8] M. Sass and D. Ziessow, J. Magn. Reson. **25,** 263 (1977).
[9] J. Haupt, Z. Naturforsch. **26a,** 1578 (1971).
[10] W. Müller-Warmuth, R. Schüler, M. Prager, and A. Kollmar, J. Chem. Phys. **69,** 2382 (1978).
[11] D. E. O'Reilly and T. Tsang, Phys. Rev. **157,** 417 (1967).
[12] S. Albert and J. A. Ripmeester, J. Chem. Phys. **57,** 2641 (1972).
[13] D. Cavagnat, J. Chim. Phys. **82,** 239 (1985).
[14] S. F. Trevino and W. H. Rymes, J. Chem. Phys. **73,** 3001 (1980).
[15] H. Rager and Al. Weiss, Ber. Bunsenges. Phys. Chem. **80,** 138 (1976).
[16] H. Rager and Al. Weiss, Ber. Bunsenges. Phys. Chem. **82,** 535 (1978).
[17] H. Langen, A.-S. Montjoie, and W. Müller-Warmuth, Z. Naturforsch. **42a,** 1266 (1987).
[18] R. F. Gloden, Euratom rep. EUR 4349f and EUR 4358f (1970).
[19] B. Krebs, G. Henkel, and M. Dartmann, Acta Cryst. **C 45,** 1010 (1989).
[20] K. Hoffmann and E. Weiss, J. Organometal. Chem. **37,** 1 (1972).
[21] G. Burbach and Al. Weiss, to be published.
[22] D. Zhang, M. Prager, and Al. Weiss, J. Chem. Phys. **94,** 1765 (1991).