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Temperature Dependence of the NQR Frequencies in $SnBr_4$ and SnI_4

(NQR/tin compounds)

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The nuclear quadrupole resonances for ^{81}Br and ^{127}I were observed in polycrystalline $SnBr_4$ and SnI_4 at temperature between liquid nitrogen and room temperature. In $SnBr_4$ the phase transition between α-form and β-form was observed at 13.5±0.5°C. In α-$SnBr_4$ the assignment was discussed in a qualitative way in terms of the anisotropy in the thermal motions of molecule. In β-$SnBr_4$ and SnI_4 the splitting of the resonance signals was correlated with molecular oscillations and intermolecular interactions.

INTRODUCTION

The temperature dependence of the nuclear quadrupole resonance (NQR) frequencies was at first explained by Bayer1), who attributed this phenomenon to the influence of molecular librations on the electric field gradient (EFG) tensor. This theory was extended by Kushida2), who took into account the influence of all lattice vibrations on the EFG tensor. These theories were applied with isotropic vibrations and a single tortional frequency. However, they are not sufficient to be applied to molecules vibrating anisotropically. Wang3) developed the theory of Bayer in consideration of the change of the EFG with temperature and the anisotropy in the molecular librations. Applications of this theory

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to several compounds, such as $SbCl_3$[4) and LaF_3[5), were tried.

The NOR's on tin (IV) halides were observed by several groups$^{6-9)}$, and the spectra were interpreted mainly in terms of the bond character. However, few data are available for a quantitative analysis of the temperature dependence of the NQR frequencies.

In the present study, in order to analyze the temperature dependence of the NQR frequencies, the NQR's of ^{81}Br in $SnBr_4$ and of ^{127}I in SnI_4 were observed at various temperatures. Though the presence of two modifications of α- and β-forms in $SnBr_4$ has been reported$^{10)}$, the transition point between them will be determined. The assignment of the NQR signals in α-$SnBr_4$ will be discussed in terms of the anisotropy in molecular librations on the basis of the theory of Wang. In β-$SnBr_4$ and SnI_4 the origins of the splitting of the NQR signals will be discussed.

EXPERIMENTS

Tin(IV) bromide and tin(IV) iodide were obtained commercially and used without further purification. They were sealed in glass tubes.

The NQR signals in the range 140—210 MHz were detected with a frequency-modulated superregenerative spectrometer which was a modification of the design of Koi$^{11)}$, and the signals in the range 400—450 MHz were detected with a modified Shawlow-type superregenerative spectrometer$^{9)}$. The NQR frequencies were determined on an oscilloscope by use of a VHF signal generater (Nippon Musen NJM-501C) and a frequency counter (Iwatsu UC-8003C). The accuracy of the frequency measurements is approximately ±0.02 MHz. The samples were immersed in a liquid nitrogen and n-hexane bath. The temperature measurements, using a copper-constantan thermocouple, were accurate to ±1°C.

ANALYSIS

When the principal axes of the EFG, x, y and z, coincide with the inertial axes, X, Y and Z, around which the torsional motions take place, the time averaged EFG, $\langle q\rangle$, due to thermal motions can be related to the EFG in the static molecule, q, as follows ;

$$\langle q\rangle = q\{1-3/2(\langle\theta_X^2\rangle + \langle\theta_Y^2\rangle) - \eta/2(\langle\theta_X^2\rangle - \langle\theta_Y^2\rangle)\}^{3)}, \qquad (1)$$

where $\langle\theta_i^2\rangle$ is the mean sqaure amplitude around the i-th axis and η is the asymmetry parameter in the static molecules. If the torsional motions are described by an Einstein molel, $\langle\theta_i^2\rangle$ can be expressed as

$$\langle\theta_i^2\rangle = \frac{h}{4\pi^2}\,\frac{1}{I_i\nu_i}\left(\frac{1}{2} - \frac{1}{\exp(h\nu_i/\boldsymbol{k}T)-1}\right), \quad i=X,\ Y,\ Z, \qquad (2)$$

where I_i and ν_i are the moment of inertia and the torsional frequency, respectively, around the i-axis.

In such a molecule as SnX_4, this expression cannot be applied immediately to the analysis of the EFG at the halogen nucleus because of the absence of the coincidence between the principal axes of the EFG and inertial axes. It has been determined that at room temperature the η values are 0.0 and 0.8% for the I atoms in SnI_4[8] and $\eta < 2.5\%$ for the Br atoms in $SnBr_4$[10]. Therefore,as a first-order approximation, η can be neglected and eq. (1) can be modified as follows ;

$$\langle q\rangle = q(1-3/2\sum_i\langle\theta_i^2\rangle\sin^2\alpha_i)^{2,13)} \qquad (3)$$

where α_i is the angle between the z-axis of the EFG at the halogen nucleus and the i-th inertial axis.

If the observed frequencies are approximated by fitting eqs. (1) and (2) to the experimental data, the calculated curves can be analyzed by eq. (3). Then, if the torsional frequencies are approximated by the procedure of Brown[14], the calculated curves can reproduce the experimental data better. In α-$SnBr_4$ $\langle\theta_i^2\rangle$ can be determined by applying the least-square method to four equations, since four NQR lines were observed in this compound. In β-$SnBr_4$ and SnI_4, since these compounds exhibit only two lines, $\langle\theta_X^2\rangle=\langle\theta_Y^2\rangle$ was assumed considering the the molecular geometry. The moments of inertia were calculated from the molecular geometry, assuming that the SnX_4 molecule is rigid.

RESULTS AND DISCUSSION

The temperature dependence of the NQR frequencies of ^{81}Br

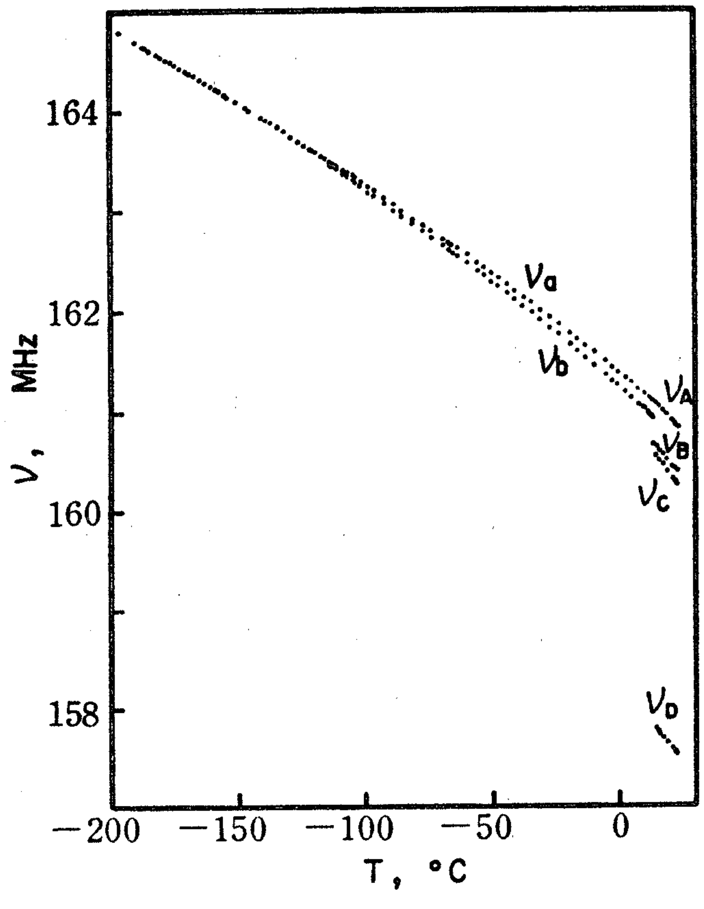


Fig. 1. Temperature dependence of ^{81}Br nuclear quadrupole resonance frequencies in $SnBr_4$.

in $SnBr_4$ are shown schematically in Figs. 1 and 2. The data which were observed with cooling slowly the sample are plotted in Fig. 1. In the vicinity of the transition point the sample was not only cooled but also warmed slowly. The resonance frequencies, 160.96 and 160.14 MHz, at 12°C, are in good agreement with the previous data[10)] within ±0.01 MHz. As can be seen in Fig. 1, the resonance lines are discontinuous at 13.5 ±0.5°C, where the phase transition occurs. Shimomura termed the high temperature phase and the low one α-form and β-form, respectively. The α-β transition between liquid nitrogen and dry-ice temperature was not found, though it was suggested previously[10)].

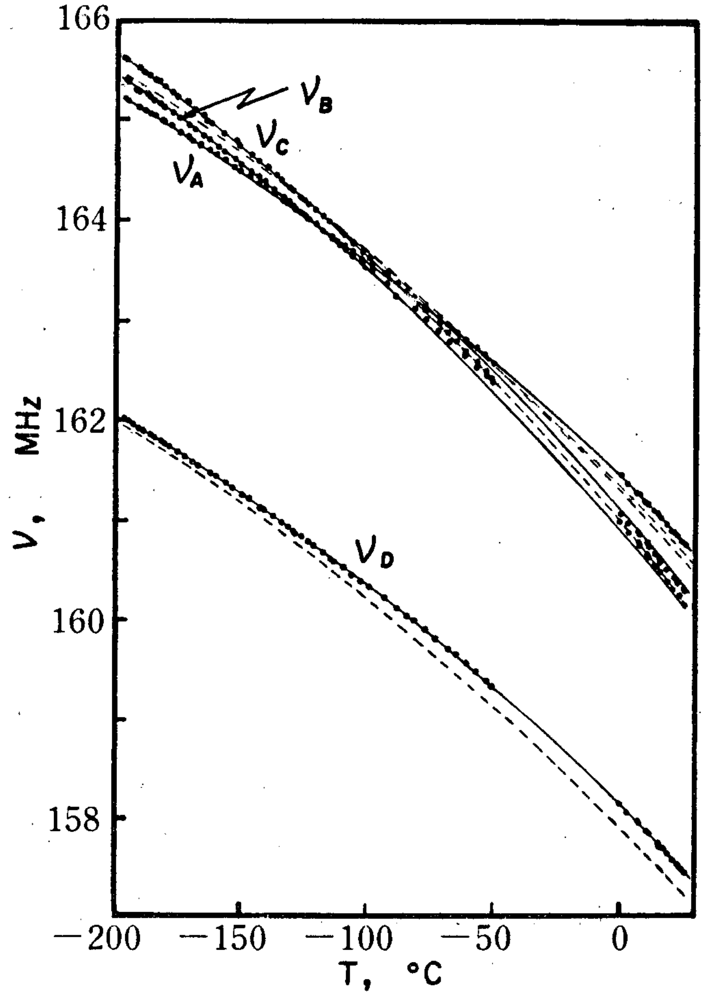


Fig. 2. Temperature deqendence of ^{81}Br nuclear quadrupole resonance frequencies in α-$SnBr_4$.

In β-SnBr$_4$ ν_a and ν_b space more closely as the temperature is lowered, and the difference in frequency between them is 0.02 MHz at −117°C. At liquid nitrogen temperature a single line was observed, the frequency of which is 164.80 MHz. Since ν_a is much broader and three times more intence than ν_b, it was difficult to determine the temperature where the two lines coalesce.

In Fig. 2 the frequencies between −196 and −50°C or those between 0 and 14°C are the values observed for the sample which was quenched rapidly from room temperature to liquid nitrogen temperature or to 0°C. The sample was allowed to warm gradually over a period of the measurement. In the range from −50 to 0°C the frequencies were not determined because of a rapid change of SnBr^4 from α-form to β-form. As compared Fig. 1 with Fig. 2, α-form which was reported to exist at liquid nitrogen temperature is presumed to be nothing but a frozen phase quenched rapidly from room temperature.

The data observed for SnI$_4$ is plotted in Fig. 3. The small dots correspond to $\nu(\pm 1/2 \leftrightarrow \pm 3/2) = \nu_1$ and the large ones, to $\nu(\pm 3/2 \leftrightarrow \pm 5/2) = \nu_2$. In contrast to β-SnBr$_4$, the difference in frequency between the higher frequency signal and the lower one is decreased with an increase in temperature, and they do not coalesce into a single line. The values of ν_2 are nearly twice as greater as those of corresponding ν_1. This suggests that the values of η's for the I atoms in SnI$_4$ are negligible.

α-SnBr . The crystal and molecular structures of α-SnBr$_4$ was determined by the X-ray diffraction[15]. In the crystal, pair of SnBr$_4$ molecules exist as shown in Fig. 4(c)[11]. The base of each SnBr$_4$ tetrahedron sites opposite to that of the other one, and these bases are parallel to each other. The approximate three-fold axis of each tetrahedron is parallel to that of the other one, though

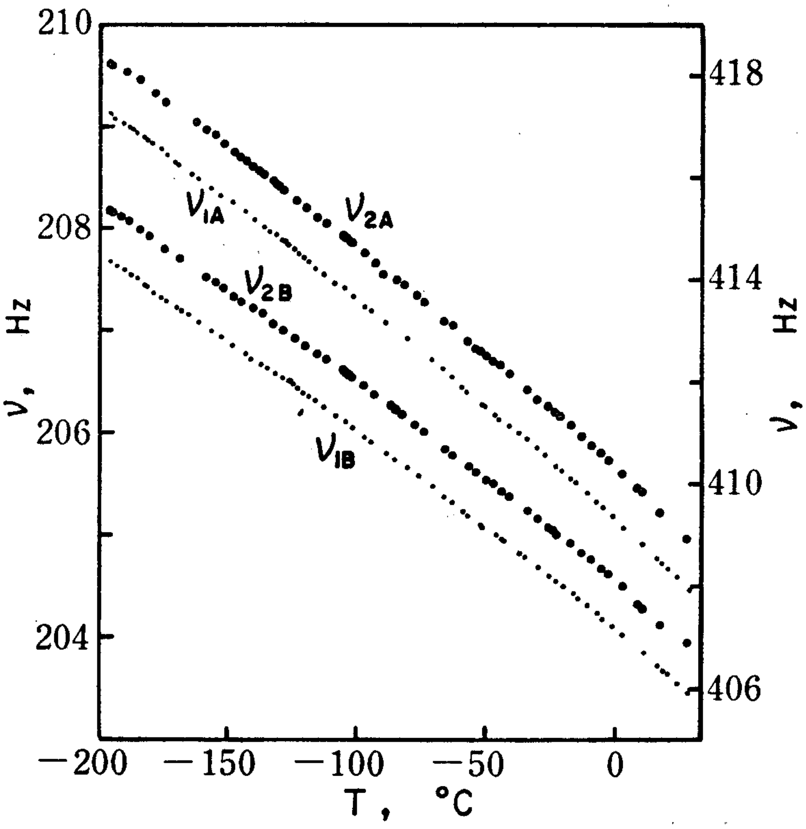
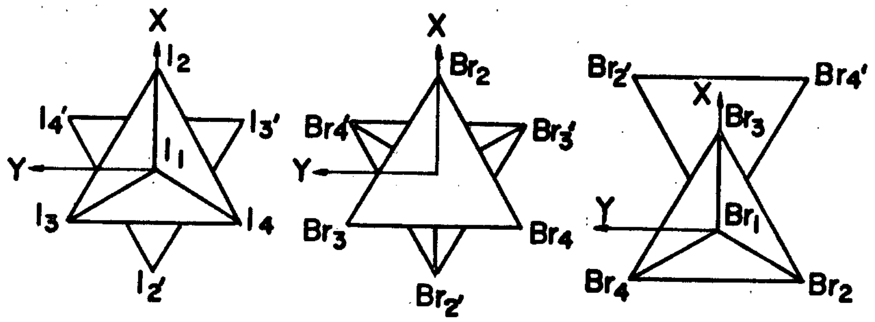


Fig. 3. Temperature dependence of ^{127}I nuclear quadrupole resonance frequencies in SnI_4.



(a) (b) (c)

Fig. 4. Pair of molecules.

the symmetry axes are not present in the pair of molecules. On the other hand, the direction of the EFG at each Br nucleus was determined by use of the results of the Zeeman effect of the NQR of ^{81}Br on a single crystal[10]. The results of the NQR are shown along with those of the X-ray diffraction in Table I. In

TABLE I. *The Relative Direction of the Principal z-axis of the Electric Field Gradient Tensors and the Bond Angles*

	NQR[a]			
	Br_B	Br_C	Br_D	b axis
Br_A	109°47′	110°18′	109°16′	90°
Br_B		109°46′	109° 7′	19°48′
Br_C			108°41′	62°20′
Br_D				61°18′

	X-ray[b]			
	$Sn-Br_2$	$Sn-Br_3$	$Sn-Br_4$	b axis[c]
$Sn-Br_1$	109°30′	106°33′	110°33′	90°
$Sn-Br_2$		108°13′	110°44′	19°38′
$Sn-Br_3$			110°17′	62°18′
$Sn-Br_4$				62°30′

a) Ref. 10. b) Ref. 15. c) The values calculated from the data of Ref. 15.

this table, Br_A, Br_B, Br_C and Br_D are the atoms that contribute the lines, ν_A, ν_B, ν_C and ν_D, respectively, in Fig. 2. Br_1, Br_2, Br_3 and Br_4 are referred to Fig. 4(c). ν_A and ν_B can easily be assigned to Br_1 and Br_2, respectively, by comparison of the bond angles and the relative directions of the z-axes of the EFG's. The direction of the Sn-Br bond does not always coincide with the direction of the z-axis of the EFG at the corresponding Br nucleus. Unfortunately, a comparison between these directions alone is insufficient to establish the assignment of ν_C and ν_D. As can be seen in Fig. 4(c), the interation of Br_3 with the partner molecule differs considerably from that of Br_2 or Br_4. The inertial axes, X, Y and Z, are assumed in Fig. 4(c) as follows; the X-axis lies in the Br_1-Sn-Br_3 plane and is perpendicular to the Sn-Br_1 direction, whereas the Z-axis lies along the Sn-Br_1 direction. The torsional motions around these three axes are expected to be non-equivalent.

In order to examine the assignment of ν_C and ν_D, Case 1 and Case 2 are assumed ; In Case 1 Br_C and Br_D correspond Br_3 and Br_4, respectively, whereas in Case 2 the correspondence between them is inversed. The results calculated according to eqs. (2) and (3) for each case are shown in Fig. 1 and Table II. The dashed and solid lines in Fig. 1 correspond to the frequencies calculated for Case 1 and Case 2, respectively. Here, the direction of the z-axis of the EFG to the i-th axis was determined by using the results of the NQR, and the momemts of inertia were estimated at $I_X=2.04\times10^{-37}$, $I_Y=2.03\times10^{-37}$ and $I_Z=2.08\times10^{-37}$ g cm^2 from the molecular geometry. The solid curves reproduce the experimental data better than the dashed ones, though the reproducibility of ν_C and ν_D of is not sufficient. It is therefore expected that Br_3 and Br_4 contribute ν_D and ν_C, respectively.

TABLE II. *The Calculated Values of* $<\theta_i^2>$ *and* ν_i *for* β-$SnBr_4$

		77K		273K	
Case	i	$<\theta_i^2>$ $\times10^{-3}$ rad^2	ν_i cm^{-1}	$<\theta_i^2>$ $\times10^{-3}$ rad^2	ν_i cm^{-1}
1	X	1.6	31	7.8	26
	Y	2.2	26	11.4	21
	Z	2.5	24	12.4	20
2	X	2.4	25	11.5	21
	Y	1.5	32	7.5	27
	Z	2.5	24	12.7	20

The height of the potential barrier of the rotation is proportional to the square of the torsional frequency[17)]. The calculated results indicate that $\nu_X>\nu_Y>\nu_Z$ in Case 1 and $\nu_Y>\nu_X>\nu_Z$ in Case 2. The torsional motion around the Z-axis in the easiest in each case. The motion around the X-axis and that around the

Y-axis are the most difficult in Case 1 and in Case 2, respectively. According to the X-ray diffraction, the interatomic distance between Br_3 and Br_2' is 4.14 Å and that between Br_3 and Br_4', 4.13 Å. They are shorter than the mean intermolecular Br-Br distance, 4.18 Å[15]. Taking into account the isolated pair of molecules only, the molecular torsion around the Y-axis brings Br_3 close to Br_2', Br_3' and Br_4', whereas that around the X-axis brings Br_3 close to either of Br_2' or Br_4'. In addition, the distance varied by the minute rotation around the Y-axis is about 10 times longer than that around X-axis. On the other hand, either of Br_2 or Br_4 is approached to Br_3' by the rotation around the X- or Y-axis, and the distance varied by the rotation around the X axis is the same order as that around the Y-axis. It is therefore considered that the interaction between the pair of molecules which Br_2 and Br_4 take part in is not so much contributed to the anisotropy in the torsional motions in regard to the rotations around the X- and Y-axes. Accordingly, the barrier of the torsional vibrations around the Y-axis is expected to be higher than that around the X-axis. Further, Br_2 interacts with Br_2'' of another molecule, and the distance between them is 4.16 Å. However, this does not seem to influence significantly the above discussion, since this interaction hinders not only the rotation around the X-axis but that around the Y-axis. The expecutation based on the intermolecular interaction in also consistent with the results calculated for Case 2. Consequently, ν_C and ν_D are assigned to Br_4 and Br_3, respectively. Presumably, the discrepancy between the observed and calculated curves of ν_C and ν_D is responsible for an anisotropic thermal expansion of the crystal and the assumption that the molecule is rigid.

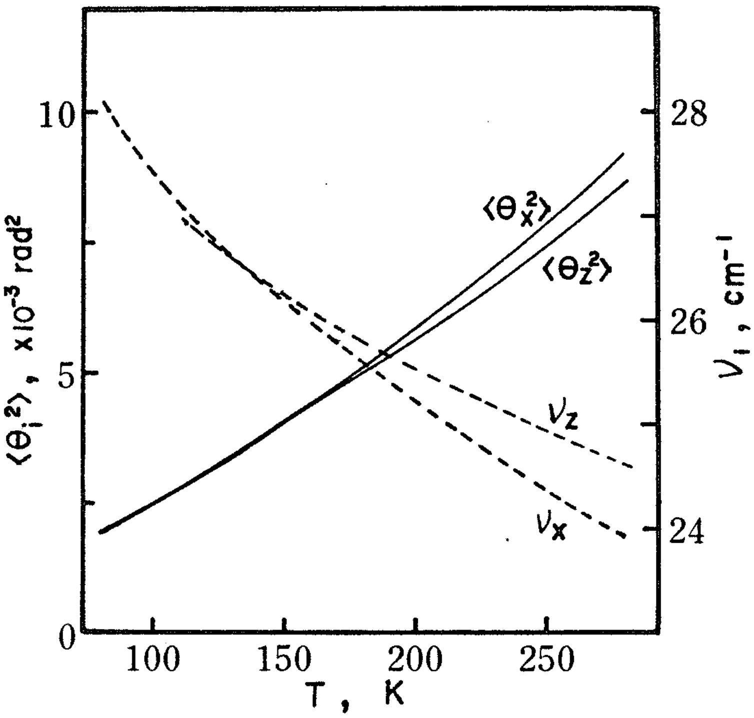
β-$SnBr_4$ and SnI_4. The molecular and crystal structures of β-$SnBr_4$ are unknown. However, the fact that a single line was

observed at liquid nitrogen temperature and the difference in frequency between ν_a and ν_b is very small even in the vicinity of 10°C suggests that β-$SnBr_4$ forms an almost regular tetrahedron in contrast to α-$SnBr_4$, and that four Sn-Br bonds are essentially equivalent. The EFG at the Br nucleus is therefore expected to be axially symmetric around the bond axis, *i. e.*, $\eta=0$. It was deduced from the spectral pattern and the intensity ratio of the two signals that the pair of tetrahedral molecules exist in the crystal and that one of the apices of each tetrahedron faces to that of the other one as shown in Fig. 4(c).

On the other hand, the X-ray diffraction on SnI_4[18,19] revealed the existence of the pair of molecules, two bases of which face and are parallel to each other, and the existence of the three-fold axis, in which two Sn and two Br atoms lie, as shown in Fig. 4(a). The three orthogonal axes, X, Y and Z, are assumed for the pair of tetrahedrons in Fig. 4(a) and (b) in the same way as the case of α-$SnBr_4$. Here, the Z-axis is coincident with the three-fold axis.

The intensity ratio of the higher frequency signal to the lower one is 3 : 1 in β-$SnBr_4$, whereas it is 1 : 3 in SnI_4. Consequently, in β-$SnBr_4$ ν_a can be assigned to the atoms, Br_2, Br_3 and Br_4, on the base and ν_b, to the Br_1 atom on the apex, whereas in SnI_4 ν_{1A} and ν_{2A} can be assigned to the atom on the apex and ν_{1B} and ν_{2B}, to the three atoms on the base. Taking into account the molecular symmetry and the molecular arragement in the crystal, $\langle\theta_X^2\rangle=\langle\theta_Y^2\rangle$ was assumed in both cases. Applications of eqs. (2) and (3) to the experimental data on these compounds lead to Figs. 5 and 6, where the mean square amplitudes and the torsional frequencies are plotted against temperature.

In β-$SnBr_4$, $\langle\theta_X^2\rangle$ is nearly equal to $\langle\theta_Y^2\rangle$ at the low temperature where a single line is observed, whereas $\langle\theta_Y^2\rangle$ is



Fig, 5. $<\theta_i^2>$ and ν_i for β-SnBr$_4$.

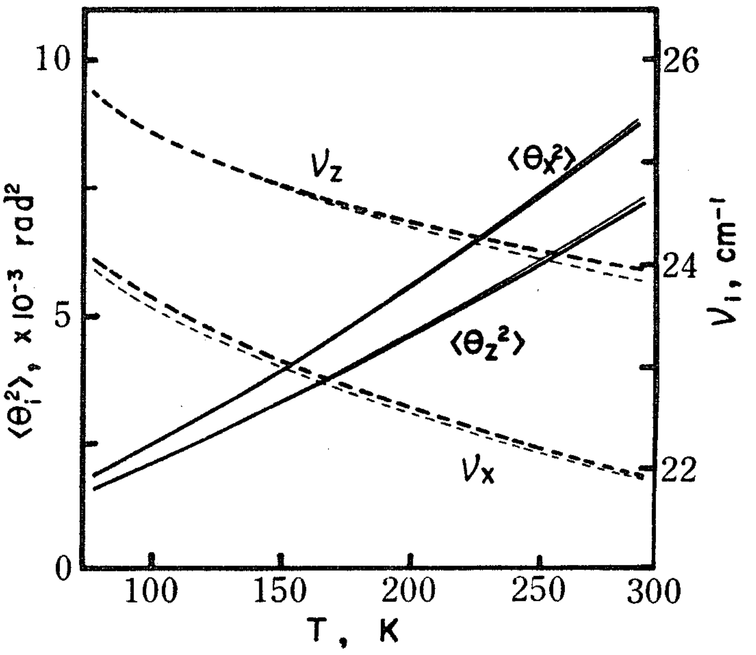


Fig. 6. $<\theta_i^2>$ and ν_i for SnI$_4$.
The bold and fine lines correspond to the values calculated from ν_1 and ν_2, respectively.

somewhat greater than $<\theta_Y{}^2>$ at the high temperature where the signal is splitted. The anisotropy in the torsional motions of molecules is very small, but it is gradually increased with an increase in temperature. In other words, the splitting of the signals becomes greater as the difference in amplitude is increased. This suggests that the anisotropic molecular motions split the NQR signal into two lines. Assuming that the lengths of the Sn-Br bonds in β-$SnBr_4$ are equal to the mean bond length in α-$SnBr_4$, *i.e.*, 2.405 Å, the torsional frequency around the X-axis and that around the Z-axis are estimated at *ca.* 24 and 25 cm^{-1}, respectively, at 0°C. The difference between them is obviously small compared with the case of α-$SnBr_4$. This indicates that the torsional motions around the three axes are isotropic rather than anisotropic. Therefore, the interaction between the partner molecules is of the same order as that between the pair and the surrounding molecules. This is consistent with the conclusion that was drawn on the basis of the quadrupole coupling constants$^{10)}$.

In SnI_4 the difference in frequency between ν_A and ν_B is increased with a decrease in temperature in contrast to β-$SnBr_4$. That is, as the influence of the molecular motions on the EFG is diminished, the splitting of the signal is increased with an increase in temperature similarly to the case of β-$SnBr_4$, though the relation of $\langle\theta_X^2\rangle > \langle\theta_Z^2\rangle$ holds regardless of temperature. This phnomenon can be interpreted as follows. One of the four Sn-I bonds is inherently somewhat non-equivalent to the other ones. This is in accordance with the known crystal structure. Since the EFG at I_1 nucleus is more vibrated than those at the other nuclei, the magnitude of the temperature coefficient of ν_A is greater than that of ν_B. This decreases the difference in frequency between them with an increase in temperature.

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