Temperature Dependences of the Nuclear Quadrupole Resonance Frequencies in 1,4-Dihalogenocyclohexanes

By Tadashi TOKUHIRO

(Received January 24, 1962)

By our studies of the halogen nuclear quadrupole resonance in *cis*-1, 4-dibromo- and diiodo-cyclohexanes, it has been found that the chemical inequivalence of the two halogen nuclei, which are, respectively, in the 1e and 4a positions[1] of the cyclohexane ring, leads to doublet lines. As for *trans*-1, 4-dibromo- and diiodo-cyclohexanes, it is no surprise that only one line was observed in the iodo-derivative and that two lines, separated by only 0.11 Mc./sec., were observed in the bromo-derivative, since both the halogen atoms in these compounds occupy the e-positions of the ring in the solid. From only a comparison of the frequencies of the doublet lines in the cis-compound with those in the trans-compound, the assignment of the doublet lines could not be made, however, be cause two frequencies of the doublet lines are not close to those in the trans-compound. However, as it has been found that the doublet separation varies considerably with the rising temperature, it seemed probable that this phenomenon is due to the different contribution from molecular torsional motions to the temperature dependence of the resonance frequency of each line and that a consideration of this would shed light on the assignments. In an attempt to clarify this

1) D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Nature*, **172**, 1096 (1953); *Science*, **119**, 49 (1953).

point, the following studies have been carried out.

Experimental

Preparations of 1, 4-Dibromocyclohexanes. — A mixture of quinit and a hydrobromic-sulfuric acid solution was allowed to stand overnight[2] and was then heated for 3 hr. on a steam bath. By standing at room temperature, an oily layer was separated from the solution. The product was washed with water and dried over calcium chloride. A fractional distillation of the product under reduced pressure gave two parts of the distillates, namely, *trans*-1,4-dibromocyclohexane, and a mixture of *trans*- and *cis*-1,4-dibromocyclohexanes. The trans-isomer was recrystallized from ethyl alcohol. By fractional crystallizations, in which ethyl alcohol and petroleum ether were alternately used as solvents, the cis-isomer was isolated from the mixture. The trans-isomer had a m. p. of 112°C, the cis-isomer, a m. p. of 49°C. These values agreed with those reported previously[3]. The purity for both isomers was ascertained by infrared spectra.

Preparations of 1, 4-Diiodocyclohexanes. — By using a method similar to that of Kwestroo et al.[4], *trans*- and *cis*-1,4-diiodocyclohexanes were prepared from quinit and a 52% hydroiodic acid solution. The melting point values for the isomers (trans-, 142°C; cis-, 67°C) agreed with those reported by Kwestroo. By infrared evidence it was shown that no impurity was contained in either of the isomers.

Apparatus.—The spectrometer used in this work was a frequency-modulated (50 c./sec.) super-regenerative oscillator with 955 acon tubes[5]. A push-pull oscillator with a transmission line-tuned circuit was quenched by an oscillator of a few kilocycles. By displacing the movable reflecting disk and the 955 acon tubes at points $\lambda/2$ and $\lambda/4$ of the transmission line in the plate circuit respectively, the oscillator has a workable range of from 160 to 360 Mc./sec. In this frequency range, the quenching frequencies were from 100 to 300 Kc./sec. In order to obtain the maximum sensitivity of the detector, the quenching frequency, the quenching voltage, and shorted point of the transmission line in the cathode circuit were suitably chosen. The signal was picked up through the anode resistance, amplified by four stage audio-amplifiers (12AX7×2), and displayed on a cathode-ray oscilloscope screen. For the line-width measurement, the derivative of the signal was recorded by the help of a narrow-band lock-in system, followed by a chart-recorder. The resonance frequencies were measured with a heterodyne frequency-meter calibrated within the order of 10^{-5}.

The sample tube was directly immersed in liquid nitrogen and in petroleum ether cooled with dry ice for the measurements at −196 and −76°C respectively. For measurements at temperatures between −76 and 0°C, temperature regulation was achieved by using a gear pump and a wide-mouthed, 1.5 liter Dewar vessel with a cover of styrofoam as a thermal insulator. The vessel was filled with a high-boiling petroleum ether, in which the sample tube was immersed. The intermediate temperatures of petroleum ether in the vessel were reached by passing ethyl alcohol cooled with dry ice through a helicoid-type tube which was immersed in the petroleum ether of the vessel. The sample coil and the transmission line were connected through condensers to prevent heat conduction. The temperature was measured by means of a copper-constantan thermocouple placed at the surface of the sample tube. In order to avoid the temperature inhomogeneity of the sample, the measurements of the resonance frequencies were carried out after the sample tube had been placed in petroleum ether for one hour. By using the above procedure for temperature regulation, petroleum ether gave a temperature stability of about ±0.1°C.

Results and Discussion

The temperature dependences of the ^{79}Br and ^{127}I nuclear quadrupole resonance frequencies measured in 1, 4-dibromo- and diiodo-cyclohexanes are shown in Fig. 1.

At the temperature of liquid nitrogen the resonance lines of the cis-dibromo- and diiodo-derivatives showed a similar pattern of strong doublet lines, except that the latter gave rather a larger doublet separation than the former. The doublets are undoubtedly due to the fact that the two halogen atoms in

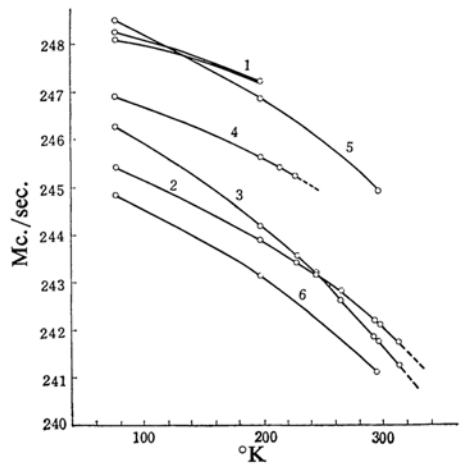

Fig. 1. Temperature dependences of ^{79}Br and ^{127}I nuclear quadrupole resonance frequencies measured in 1,4-dihalogenocyclohexanes.
1 *trans*-1,4-Dibromocyclohexane
2 (ν_1) and 3 (ν_2), *cis*-1,4-Dibromocyclohexane
4 *trans*-1,4-Diiodocyclohexane
5 (ν_1) and 6 (ν_2), *cis*-1,4-Diiodocyclohexane

2) "Organic Syntheses", Coll. Vol. 1, p. 25 (1948).
3) M. B. Rothstein, *Ann. Chim.*, **14**, 461 (1930).
4) W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. trav. chim. Pay-Bas*, **73**, 717 (1954).
5) S. Kojima, K. Tsukada, A. Shimauchi and Y. Hinaga, *J. Phys. Soc. Japan*, **9**, 795 (1954).

these molecules are in two chemically inequivalent positions, namely the 1e and 4a positions, although the crystal structures of these compounds are not known.

According to the results of X-ray analysis[6], both crystals of the trans-isomers of dibromo- and diiodo-derivatives contain two equivalent molecules in a unit cell. Therefore, it would be very natural for the resonance to give a singlet line since the two halogen atoms in the isomer are in chemically equivalent positions (1e and 4e) in the free molecule. In the case of the iodo-derivative, this is actually the case. However, the pattern of the trans-dibromo-derivative gave doublet lines near one another. The doublet separation in frequency, about 110 Kc./sec. at 77°K, may reflect the effect of the intermolecular forces which render the two bromine positions in the unit cell somewhat inequivalent.

In the case of cis-compounds, the bromine and the iodine resonance lines were observable in the solid up to their melting points. However, the bromine and the iodine resonance lines in the solid trans-compounds faded out at temperatures considerably below their melting points. In the trans-dibromo-compound, the line at −77°C was so broad that the signal could hardly be detected, and the iodine resonance of the diiodo-derivative was found to fade out at about −43°C, although it does not melt until 142°C.

As shown in Fig. 1, it is easily seen that the resonance frequencies of the trans- and the cis-isomers of 1, 4-dihalogenocyclohexanes continuously decrease with the rising temperature, but the temperature dependences of the frequencies differ slightly. From this fact, it follows that no phase transitions in these solids occur within the temperature range described above and that the temperature dependence of the frequency may be ascribed to molecular torsional motions in the solids.

The theory and the extensive experimental results of the effect of temperature and pressure on nuclear quadrupole resonance frequencies have been discussed in detail by Kushida, Benedek and Bloembergen[7]. In molecular crystals, they found that the temperature dependence of the resonance frequency was due primarily to the explicit temperature dependence of the amplitudes of lattice vibrations, namely Bayer's effect[8], because of a much smaller contribution of the volume dependence of the resonance frequency. In the present article also we shall confine our attention only to Bayer's effect.

It is assumed that the direction of the maximum principal axis of the field gradient tensor at the halogen nucleus coincides with the direction of the C–X bond (X denotes halogen), and that the gradient has axial symmetry about the C–X bond (asymmetry parameter $\eta=0$). When a molecule containing the C–X bond executes torsional motions about an axis perpendicular to the C–X bond, the inclination, θ, of the C–X bond relative to its equilibrium direction in the solid gives rise to the shift of the resonance frequency $\nu(T)$ given by Eq. 1:

$$\nu(T)=\nu_0(1-3\theta^2/2) \tag{1}$$

where ν_0 is the resonance frequency when $\theta=0$. Since the frequencies of molecular vibrations and of lattice vibrations are much higher than the nuclear quadrupole resonance frequencies, the square of angular displacement, θ^2, must be averaged over all vibrational states. Therefore, we should replace θ^2 of Eq. 1 by the mean square of the angular displacement $\langle\theta^2\rangle$ of the C–X axis relative to its equilibrium direction.

When a torsional vibration can be approximated by a harmonic oscillator, $\langle\theta^2\rangle$ is expressed as follows:

$$\langle\theta^2\rangle=\frac{\boldsymbol{h}}{4\pi^2 I_t\nu_t}\left[\frac{1}{2}+\frac{1}{\exp(\boldsymbol{h}\nu_t/\boldsymbol{k}T)-1}\right] \tag{2}$$

where ν_t is the torsional frequency, I_t the corresponding moment of inertia, T the absolute temperature, $\boldsymbol{h}$ Planck's constant, and $\boldsymbol{k}$ Boltzmann's constant. From Eqs. 1 and 2 the temperature coefficient of the resonance frequency can be expressed as follows:

$$\frac{\Delta\nu}{\Delta T}=-\frac{3\boldsymbol{h}^2\nu_0}{8\pi^2\boldsymbol{k}T^2}\frac{1}{I_t}\frac{\exp(\boldsymbol{h}\nu_t/\boldsymbol{k}T)}{[\exp(\boldsymbol{h}\nu_t/\boldsymbol{k}T)-1]^2} \tag{3}$$

From Eq. 3 it can be seen that the contribution to the temperature coefficient of the resonance frequency from any other normal (intramolecular) vibrations is negligible, as compared with that of the torsional vibrations around the principal molecular axes, because the torsional frequencies, in general, are considerably lower than the frequencies of molecular vibrations.

When the torsional vibration does not take place about an axis perpendicular to the C–X bond, Eq. 3 should be modified. For this purpose a parameter, α, given by the following relation is introduced:

$$\theta=\alpha\phi$$

where θ and ϕ are the angular displacements of the C–X bond from its equilibrium direction caused by the torsional motions about an axis

6) E. Halmony and O. Hassel, *Z. physik. Chem.*, **B16**, 234 (1930).
7) T. Kushida, G. B. Benedek and N. Bloembergen, *Phys. Rev.*, **104**, 1356 (1956).
8) H. Bayer, *Z. Physik*, **130**, 227 (1951).

TABLE I. THE VALUES OF THE SQUARE OF PARAMETER α_i FOR THE EQUATORIAL AND THE AXIAL HALOGEN ATOMS IN 1,4-DIHALOGENOCYCLOHEXANES

	cis-1,4-Dibromocyclohexane		*cis*-1,4-Diiodocyclohexane		*trans*-1,4-Diiodocyclohexane
Positions	e	a	e	a	e
$\alpha_a^2\times10^2$	7.1	99.5	8.8	99.8	3.1
$\alpha_b^2\times10^2$	92.9	0.5	91.2	0.2	96.9
$\alpha_c^2\times10^2$	100.0	100.0	100.0	100.0	100.0

TABLE II. OBSERVED FREQUENCIES ν_1 AND ν_2 OF ^{79}Br NUCLEAR QUADRUPOLE RESONANCE IN THE *cis*-1,4-DIBROMOCYCLOHEXANE AT 77, 196 AND 295°K, AND VALUES OF TORSIONAL FREQUENCIES $\langle\nu_t\rangle$ AND ν_a CALCULATED FROM Eq. 8

Temp. °K	Resonance frequencies		Case I[1]		Case II[2]			
	ν_1 Mc./sec.	ν_2 Mc./sec.	$\langle\nu_t\rangle$ cm^{-1}	ν_a cm^{-1}	$\langle\nu_t\rangle$ cm^{-1}	g_t $\times10^3$	ν_a cm^{-1}	g_a $\times10^3$
77	245.425±0.020	246.296±0.020	44.7	39.1	35.7		77.9	
196	243.873±0.050	244.128±0.050	34.0	30.6	27.5	1.91	58.6	2.06
295	242.118±0.040	241.729±0.040	29.1	26.5	23.8	1.53	49.2	1.68

1) ν_1 and ν_2 are assigned to the equatorial and the axial bromine nucleus respectively.
2) The assignment of ν_1 and ν_2 is the reverse of case I.

perpendicular to the C–X bond and about an axis of the principal molecular axes respectively. By considering the relation between the geometrical configurations of molecules and the three principal molecular axes, the value of α can be evaluated. The method is similar to that used by Tatsuzaki and Yokozawa[9]; the values of the square of α_i for the equatorial and the axial halogen atom in 1, 4-dihalogenocyclohexanes are listed in Table I. Since molecules in the solid undergo torsional motions about the three principal molecular axes, $\langle\theta^2\rangle$ can be written by Eq. 4 as:

$$\langle\theta_i^2\rangle=\alpha_i^2\langle\phi_i^2\rangle, \qquad \langle\theta^2\rangle=\sum_i\langle\theta_i^2\rangle \tag{5}$$

where i denotes one of the principal molecular axes. Upon consideration of the first relation of Eq. 5, the following modification of Eq. 2 is obtained:

$$\langle\theta_i^2\rangle=\frac{\alpha_i^2\boldsymbol{h}}{4\pi^2I_i\nu_i}\left[\frac{1}{2}+\frac{1}{\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T)-1}\right] \tag{6}$$

where I_i is the moment of inertia around the i axis, and ν_i the corresponding torsional frequency. From the second relation of Eq. 5 and Eq. 6, Eq. 3 should be modified as follows:

$$\frac{\Delta\nu}{\Delta T}=-\frac{3\boldsymbol{h}^2\nu_0}{8\pi^2\boldsymbol{k}T^2}\sum_i\frac{\alpha_i^2}{I_i}\left[\frac{\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T)}{\{\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T)-1\}^2}\right] \tag{7}$$

where the summation runs over the three principal axes (the a, b and c axes).

As for *cis*-1, 4-dihalogenocyclohexanes, there is a considerable difference between the values of α_a^2 and α_b^2 for the equatorial and the axial halogen atom. Therefore, there may be expected to be some difference between the temperature coefficients of the resonance frequencies of the equatorial and the axial halogen atom. This is actually the case (Fig. 1). The theoretical value of the temperature coefficient cannot be obtained by the use of Eq. 7, since the vibrational spectra of isomers in the solid state over low frequency regions have not yet been measured. So far as the cis-isomer is concerned, it may approximately be assumed that the torsional frequencies ν_b and ν_c are nearly the same because the moments of inertia around the b and the c axis of the molecule are almost identical in magnitude. When ν_b or ν_c, and I_b or I_c, of Eq. 7 are replaced by the average value of $\langle\nu_t\rangle$ and $\langle I_t\rangle$ respectively, Eq. 7 becomes:

$$\frac{\Delta\nu_j}{\Delta T}=-\frac{3\boldsymbol{h}^2\nu_0}{8\pi^2\boldsymbol{k}T^2}\left[\frac{\alpha_b^2+\alpha_c^2}{\langle I_t\rangle}\frac{\exp(\boldsymbol{h}\langle\nu_t\rangle/\boldsymbol{k}T)}{\{\exp(\boldsymbol{h}\langle\nu_t\rangle/\boldsymbol{k}T)-1\}^2}+\frac{\alpha_a^2}{I_a}\frac{\exp(\boldsymbol{h}\nu_a/\boldsymbol{k}T)}{\{\exp(\boldsymbol{h}\nu_a/\boldsymbol{k}T)-1\}^2}\right] \tag{8}$$

where ν_j denotes one of the doublet lines. By using Eq. 8, the calculated moments of inertia, $\langle I_t\rangle$ and I_a, and the experimental values of $\Delta\nu_j/\Delta T$ at various temperatures, the torsional frequencies $\langle\nu_t\rangle$ and ν_a are calculated. The results thus obtained for the bromo-derivative are tabulated in Table II. In a similar way, $\langle\nu_t\rangle$ and ν_a for the iodo-derivative are calculated. The results thus obtained are given in Table III. Two cases are shown in Tables II and III, since a complete blank in our knowledge of the X-ray analysis of the crystal structure and of the Zeeman pattern for the nuclear quadrupole resonance of the cis-isomer

9) I. Tatsuzaki and Y. Yokozawa, *J. Phys. Soc. Japan*, **12**, 802 (1957).

TABLE III. OBSERVED FREQUENCIES ν_1 AND ν_2 OF ^{127}I NUCLEAR QUADRUPOLE RESONANCE IN THE *cis*-1,4-DIIODOCYCLOHEXANE AT 77, 196 AND 293.5°K, AND VALUES OF TORSIONAL FREQUENCIES $\langle\nu_t\rangle$ AND ν_a CALCULATED FROM Eq. 8

Temp. °K	Resonance frequencies		Case I[1]		Case II[2]			
	ν_1 Mc./sec.	ν_2 Mc./sec.	$\langle\nu_t\rangle$ cm^{-1}	ν_a cm^{-1}	$\langle\nu_t\rangle$ cm^{-1}	g_t $\times10^3$	ν_a cm^{-1}	g_a $\times10^3$
77	248.458±0.045	244.848±0.030	31.7	37.0	30.1		42.2	
196	246.837±0.035	243.133±0.035	24.5	29.3	23.5	1.83	32.4	1.95
293.5	244.874±0.02	241.082±0.040	21.2	25.6	20.4	1.49	27.9	1.56

1) ν_1 and ν_2 are assigned to the equatorial and the axial bromine nucleus respectively.
2) The assignment of ν_1 and ν_2 is the reverse of case I.

TABLE IV. OBSERVED FREQUENCIES OF ^{127}I NUCLEAR QUADRUPOLE RESONANCE IN THE *trans*-1,4-DIIODOCYCLOHEXANE AT 77, 196 AND 213.5°K, VALUES OF TORSIONAL FREQUENCIES $\langle\nu_t\rangle$ CALCULATED FROM Eq. 7 AND LINE-WIDTHS

Temp. °K	Resonance frequencies Mc./sec.	$\langle\nu_t\rangle$ cm^{-1}	g_t $\times10^3$	$\Delta\nu_{msl}$[1] kc./sec.
77	246.890±0.020	31.0		24.3±3
196	245.594±0.030	21.5	2.56	23.6±4
213.5	245.343±0.020	20.8	2.40	

1) The frequency difference between the points of maximum slope in the absorption curve.

does not permit us to determine the assignment of the doublet.

As may be seen in Table II, in case I, where the two resonance lines, ν_1 and ν_2, are assigned to the equatorial and the axial bromine nucleus respectively, it is found that the difference between the two torsional frequencies, $\langle\nu_t\rangle$ and ν_a, is small and that ν_a is rather smaller than $\langle\nu_t\rangle$ at any temperature. On the other hand, in case II, where the assignment of ν_1 and ν_2 is the reverse of case I, the value of ν_a is about twice as large as that of $\langle\nu_t\rangle$.

The simple sinusoidal potential was assumed, because the form of the potential barrier for the torsional vibration in the crystal is hard to assess theoretically. Therefore, the frequency ν_i is given by:

$$\nu_i=\frac{n}{2\pi}\sqrt{\frac{V_0}{2I_i}} \quad (i=t \text{ or } a)$$

where V_0 is the height of the potential barrier with an n-fold symmetry, and I_i, the moment of inertia. If the heights of the potential barriers for different torsional axes have the same order of magnitude, the frequency, ν_i, is exclusively determined by the magnitude of the moment. From the study of the temperature dependence of the resonance frequency, of the asymmetry parameter and of the Raman spectra for the *p*-diiodobenzene, Shimauchi[10] have recently pointed out that the heights of the potential barriers for the three torsional vibrations are nearly the same.

10) A. Shimauchi, *Science of Light (Japan)*, **10**, 59 (1961).

As for 1,4-dihalogenocyclohexanes, it seems probable that the molecules execute torsional vibrations under the influence of the same heights of the potential barriers, since the molecular structures of 1,4-dihalogenocyclohexanes are not so different from those of *p*-dihalogenobenzenes. Therefore, ν_a in the cis-dibromo-compound becomes about 1.3~1.4 times as large as $\langle\nu_t\rangle$, because the moment of inertia, I_a, is about a half of $\langle I_t\rangle$ in magnitude. As is shown in Table II, case II, where ν_a is nearly twice as large as $\langle\nu_t\rangle$, seems to be more reasonable than case I. It therefore follows that the line of higher frequency at 77°K may be assigned to the equatorial bromine nucleus.

As for the cis-diiodo-derivative, the results obtained are analogous to those of the bromine-compound, but the assignment of the doublets is even more difficult, because the experimental temperature coefficients for each line do not appreciably differ when compared with those of the cis-dibromo-compound.

In the trans-compound, it may be assumed that the contribution to the temperature coefficient from the torsional motion around the a-axis is negligible, because the square of parameter α_a is very small as compared with the square of the other parameters. However, the fact that the resonance in the trans-diiodo-derivative gives a singlet line makes it impossible to determine the two torsional frequencies around the b- and the c-axes by the use of Eq. 7. Therefore, the values of the average torsional frequency, $\langle\nu_t\rangle$, at 77, 196

and 213.5°K were calculated. The average moment of inertia, $\langle I_t \rangle$, is $(I_b+I_c)/2$, and $\langle \nu_t \rangle$ denotes the corresponding frequency. The results thus obtained are listed in Table IV.

As is seen in Tables II, III and IV, all the torsional frequencies, $\langle \nu_t \rangle$ and ν_a, decrease with the increasing temperature. Such a variation of $\langle \nu_t \rangle$ and ν_a with temperature seems to imply the variations of the intermolecular potentials in the crystal caused by the thermal expansion. On the other hand, it was found, from Raman studies on various molecules, that the frequencies of lattice vibrations or torsional vibrations in molecular crystals vary with the temperature and that the experimental formula can be expressed as

$$\nu_l = \nu_l^0(1-g_l t)$$

where g_l is a constant and has a value of the range $(5\sim1.5)\times10^{-3}$ deg^{-1}, ν_l is the torsional frequency at an arbitrary temperature, ν_l^0 is the torsional frequency at some definite temperature t^0, and t is the temperature measured from t^0. By using the value of $\langle \nu_t \rangle$ or ν_a given in Tables II, III and IV, the constant, g_l, is calculated as shown in the seventh or the ninth column in Tables II and III, and in the fourth column in Table IV. As is seen in Tables II, III and IV, the agreement between the constant, g_l, obtained and those obtained by Ichishima[11] may be regarded as satisfactory.

A final point to be noticed concerns the fade-out of the resonance of the trans-compound. In the solids CCl_3CCl_3[9,12], and $CH_3 \cdot CCl_3$[12,13], it has been established that the fade-out of the resonance at a temperature far below the melting point arises from the re-orientational motion around the C–C axis. This motion leads to an exponential broadening of the line-width with the increasing temperature. In order to investigate whether or not the fade-out of the resonance of the trans-compound can be attributed to the similar motion, the line-width for the *trans*-1, 4-diiodocyclohexane was measured[14]; the results obtained are given in the fifth column of Table IV. From a comparison of the experimental value of the line-width at 77°K with those at 196°K, it is likely that the re-orientational motion responsible for the fade-out does not occur at 196°K.

In order to establish this point, the investigation of the proton magnetic resonance was carried out at room temperature and at the temperature of liquid nitrogen. Whereas it was expected that such motions would produce drastic changes in the line-width and in the line-shape of the proton magnetic resonance in solids[16], and that, for *trans*- and *cis*-1, 4-dihalogenocyclohexanes, the motion would give rise to a narrowing of the line-width of the resonance, no marked changes in the line-width or in the line-shape with the increasing temperature could be observed for either isomer. It follows that the motion cannot be responsible for the fade-out of the nuclear quadrupole resonance of the trans-isomer. To understand what causes may produce the fade-out of the nuclear quadrupole resonance of the trans-isomer, it would be necessary to measure the relaxation times at various temperatures.

Summary

The temperature dependences of the ^{79}Br and ^{127}I nuclear quadrupole resonance frequencies in 1, 4-dihalogenocyclohexanes were investigated. According to Bayer's theory (Eq. 8), the torsional frequencies were calculated by the use of the calculated moments of inertia and the experimental values of the temperature coefficients of the resonance frequencies at various temperatures. From a comparison of the torsional frequencies, the line of higher frequency at 77°K in *cis*-1, 4-dibromocyclohexane may be assigned to the equatorial bromine nucleus. All the calculated torsional frequencies decrease with the increasing temperature. Such variation in the frequencies agrees with the variation obtained by Raman studies of various molecules in crystals. The resonance lines in the trans-compounds fade out at temperatures considerably below their melting points.

The author wishes to express his deep thanks to Professor Kunio Kozima for his kind guidance and encouragement throughout this work. The author wishes also to thank Dr. Akira Shimauchi of the Institute for Optical Research, Tokyo University of Education, for his helpful advice in the development of the instrumentation. He is grateful to Professor Yoshinobu Kakiuchi and Dr. Takehiko Chiba of the Institute for Solid

11) I. Ichishima, *J. Chem. Soc. Japan. Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **71**, 607 (1950).
12) M. Bule-Bodin, *Ann. de Physique*, **10**, 533 (1955).
13) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).
14) The super-regenerative quench method is not reliable for the measurement of the true line-shape. As has been suggested by Tatsuzaki et al.[9] and Tsukada[15], however, the line-width obtained by this method provides rather useful information concerning the dynamic structure in the solid when a strong and sharp signal is detected at the temperature of liquid nitrogen or hydrogen, whereas no resonance line is observed at much higher temperatures.
15) Tsukada, *J. Phys. Soc. Japan*, **11**, 956 (1956).
16) For example, H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

State Physics, the University of Tokyo, for their interest and kind advice throughout the measurement of the proton magnetic resonance.

Research Laboratory of Spectroscopy
Tokyo Institute of Technology
Meguro-ku, Tokyo